

THE UNIVERSITY OF MANITOBA

CERTAIN PHYSICAL PROPERTIES OF MONO, DI AND
TRIETHYLAMINE IN AQUEOUS SOLUTIONS
AT ROOM TEMPERATURES

A Thesis

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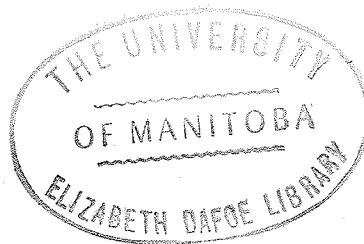
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ABSTRACT

Certain physical properties, viz., densities, relative viscosities, vapor pressures, liquid-vapor equilibrium compositions, conductances and diffusion coefficients of the binary systems, monoethylamine-water, diethylamine-water, both at 25°C, and triethylamine-water at 17°C, slightly below its lower critical solution temperature, were investigated experimentally.

Densities were determined with Ostwald-Sprengel type pycnometers. Relative viscosities were obtained by means of a Cannon-Fenske viscometer. Total vapor pressures were measured by a differential manometer using mercury as the manometer fluid and water as the reference liquid. Liquid-vapor equilibrium compositions were found by isothermal air-saturation method. On the basis of Dalton's law of partial pressure, which assumes ideal behaviour in the vapor phase, the partial pressures, activities and activity coefficients were calculated; they were shown to be thermodynamically consistent. All systems exhibit non-ideal behaviour. Negative deviation from the ideal vapor pressure curve exists at low concentrations of monoethylamine; at high concentrations, there is evidence of positive deviation. Both diethylamine-water and triethylamine-water show positive deviation. The much more pronounced nonideality of triethylamine-water was interpreted in terms of the characteristics of systems having lower critical solution temperatures. The positive excess free energies of mixing augment the heats of mixing to give large negative values of excess entropy of mixing in both cases; and this suggests that the amines are hydrated to a considerable extent, or that at least strong molecular interaction takes place as revealed by the large relative viscosities of amine solutions with respect to either component.

The conductances of the amines in aqueous solutions were measured, and corrected for the formation of carbonates. The conductances of the hydrochlorides were found experimentally, and corrected for the effect of hydrolysis by employing the method of Campbell and Bock. By the Kohlrausch principle, values of equivalent conductance of the "aminium hydroxides" were calculated. The dissociation constants for these bases were evaluated according to the method of Shedlovsky and Kay. The base strength of this series of amines in aqueous solutions increases in going from ammonia, monoethylamine to diethylamine, but a decrease in strength for triethylamine is observed. The same trend of base strength appears to be common for other series of aliphatic amines.

The diffusion coefficients of the amines in aqueous solutions were obtained experimentally by Stokes' diaphragm cell method. On account of the molecular size difference, monoethylamine has the highest diffusion rate. In less dilute solutions where electrolytic dissociation can be neglected, treatment of the diffusion coefficients at moderately low concentrations by the extended method of Hartley and Crank gave the hypothetical diffusion coefficients for the amines and showed that triethylamine has the largest hydration number. The inclusion of the viscosity factor into the same treatment led to the same hypothetical diffusion coefficients, but to negative hydration numbers, and this has no physical meaning. The hypothetical diffusion coefficients at infinite dilution decrease in going from mono- to triethylamine, and are lower than the corresponding Nernst limiting values, calculated on the basis of aminium cation and hydroxyl anion as a whole, for the diffusing entity.

TABLE OF SYMBOLS

- A Debye-Hückel constant defined by Equation (79).
- A effective cross-sectional area of diffusion cell diaphragm.
- A special function of $\frac{0}{a}$ in Equation (143).
- A empirical constant in Kohlrausch equation.
- A' empirical constant in Lattey conductance equation.
- a_A, a_B, a_i activity of water, amine and component i respectively.
- a_1, a_2 cationic activity and anionic activity respectively.
- $a_1(c), a_2(c)$ cationic activity and anionic activity associated with molarity scale.
- $a_1(m), a_2(m)$ cationic activity and anionic activity associated with molality scale.
- $a_1(x), a_2(x)$ cationic activity and anionic activity associated with mole fraction scale.
- a_{\pm} stoichiometric mean ionic activity of electrolyte defined by Equation (27).
- $a_{\pm}(c), a_{\pm}(m), a_{\pm}(x)$ stoichiometric mean ionic activities associated with molarity, molality and mole fraction scale respectively.
- a'_1, a'_2, a'_B activity of free aminium cation, hydroxyl anion and free amine respectively.
- $\frac{0}{a}$ distance of closest approach of two oppositely charged ions in Angstrom units.
- B Debye-Hückel constant defined by Equation (80).
- B special function of $\frac{0}{a}$ in Equation (150).
- B_1 constant in Onsager equation, defined by Equation (117).
- B_2 constant in Onsager equation, defined by Equation (118).
- B' empirical constant in Equations (119) and (120).

- b empirical constant in Equations (85) and (88).
- b special constant defined by Equation (146).
- c empirical constant in Equation (86).
- c, c_B stoichiometric molarity and of solute B respectively.
- c_{\pm} stoichiometric mean ionic molarity.
- c_1, c_2, c_j molarities of cation, anion and ion j respectively.
- c_1, c_2 initial concentrations in a diffusion run.
- c_3, c_4 final concentrations in a diffusion run.
- c', c'' concentrations of the more concentrated solution and less concentrated solution respectively, at any time during diffusion experiment.
- \tilde{c} molarity of "aminium hydroxide" or "Amine+H₂O", identical with c.
- c_m', c_m'' arithmetic mean concentration of the more concentrated solutions, and of the less concentrated solutions respectively, in a diffusion experiment.
- c_{corr} molarity of amine corrected for the formation of carbonate.
- D dielectric constant.
- D diffusion coefficient.
- D Empirical constant in Equations (121) and (125).
- D_1, D_2, D_3 empirical constants in Equation (126).
- D° limiting value of diffusion coefficient.
- D_{12}° hypothetical diffusion coefficient of ion pair at infinite dilution.
- $D_{AA}^{\circ}, D_{BB}^{\circ}$ self diffusion coefficients of A in pure A and B in pure B respectively.
- $D_{H_2O}^*$ tracer diffusion coefficient of water.
- D_{AB}° diffusion coefficient of A at infinite dilution in pure liquid B.
- D^V, D_A^V, D_B^V mutual diffusion coefficients of A and B. in Hartley-Crank theory.

- D'_A, D'_B intrinsic diffusion coefficient of A and B in Hartley-Crank theory
- \bar{D} integral diffusion coefficient.
- $\bar{D}(t)$ Average value of diffusion coefficient with respect to concentration over concentration range c' to c'' prevailing in experiment.
- $\bar{D}^0(c)$ integral diffusion coefficient obtained in a run of vanishingly short duration with initial concentrations c and zero on opposite sides of diaphragm.
- d, d_0 densities of solution and solvent respectively.
- E electrical field strength.
- E pre-log c constant in conductance equation, identical with $(E_1 \wedge + E_2)$.
- E_1, E_2 special functions defined by Equations (140) and (141) respectively.
- E', E'_1 special constants in Equation (148) similar to E and E_1 respectively.
- $Ei(t)$ special integral defined by Equation (154).
- F conductance function defined by Equation (131).
- \mathcal{F} Faraday.
- $F(\mathcal{z})$ Fuoss function defined by Equation (170).
- F_1, F_2 force exerted on cation and anion respectively.
- f_A rational activity coefficient of water.
- f_A^*, f_B^* activity coefficient of water and amine respectively, in the convention for binary mixtures.
- f_{\pm} stoichiometric mean ionic rational activity coefficient.
- f_{\pm}^{\dagger} true mean ionic rational activity coefficient.
- f_B^{Δ} activity coefficient of solvated B in the extended Hartley-Crank theory.

- \tilde{f}_A activity coefficient of solvent water in liquid mixtures of water and "aminium hydroxide".
- $\tilde{f}_{\pm B}$ mean ionic activity coefficient of "aminium hydroxide" associated with mole fraction scale .
- f_1, f_2 rational cationic and anionic activity coefficients respectively.
- G, G^E Gibbs free energy, and excess Gibbs free energy of mixing respectively.
- $\Delta G, \Delta G_{ideal}$ free energy of mixing, and free energy of mixing for ideal solutions respectively.
- g rational osmotic coefficient of water.
- H, H^E enthalpy, and excess heat of mixing respectively.
- $\Delta H, \Delta H_{ideal}$ enthalpy of mixing and enthalpy of mixing for ideal solution respectively.
- h hydration number
- $h(b)$ special function of b defined by Equation (145).
- I molar ionic strength, $\frac{1}{2} \sum c_i Z_i^2$
- I_m molal ionic strength, $\frac{1}{2} \sum m_i Z_i^2$
- J identical with $(\sigma_1 \Lambda^\circ + \sigma_2)$ in Equation (142).
- J function of \bar{a} in Equations (132) and (149).
- $J, J(t), J_A, J_B$ flux, time-dependent flux, flux of A and B per unit area respectively.
- K dissociation constant.
- K_A association constant.
- K_F dissociation constant obtained by using Fuoss method.
- K_S dissociation constant obtained by using Shedlovsky method.
- K_h hydrolysis constant.
- K_w ion product of water.

k Boltzmann constant.
 k constant defined by Equation (75).
 k_{\pm} constant defined by Equation (66).
 L, L_0 specific conductance and specific conductance of solvent respectively.
 L function of \bar{a} in Equation (148).
 L_{corr} specific conductance of solute corrected for the specific conductance of solvent.
 l effective average length of diffusion cell pores.
 $M_{\nu_1} X_{\nu_2}, M_{n_1} X_{n_2}$ formulae for the original solute and aggregate respectively.
 m, m_B, m_i molality, molality of B and of solute i respectively.
 m_1, m_2 cationic molality and anionic molality respectively.
 m_{12} concentration of aggregate in molality scale.
 m_1^i, m_2^i true cationic molality and anionic molality.
 m_{\pm} stoichiometric mean ionic molality.
 \tilde{m} molality of "aminium hydroxide" or "Amine+H₂O" defined by Equation (54).
 N normality.
 N_a Avogadro number.
 n number of ions per ml of solution.
 n_A, n_B, n_i numbers of moles of solvent A, solute B and component i respectively.
 $O(c^{3/2})$ special function appeared in Equation (133).
 P_A, P_B partial vapor pressures of A and B respectively.
 P_A^0, P_B^0 vapor pressures of pure A and B respectively.
 $Q = \nu_1^{\nu_1} \nu_2^{\nu_2}$

- q special constant defined by Equation (115).
 R gas constant.
 r ratio of hard spherical volume of hydrated electrolyte to that of solvent water in Glueckauf's equation.
 r_+ crystallographic radius of anion.
 S, S^E entropy, and excess entropy of mixing respectively.
 $\Delta S, \Delta S_{\text{ideal}}$ entropy of mixing and entropy of mixing for ideal solution respectively.
 S theoretical limiting slope in Fuoss-Onsager conductance equation.
 S_1 special function defined by Equation (156).
 S_η Falkenhagen coefficient.
 $S(z)$ Shedlovsky function defined by Equation (176).
 T absolute temperature.
 T_1 special function defined by Equation (153).
 t time.
 t_1^0, t_2^0 cationic and anionic transference numbers at infinite dilution respectively.
 u_+, u_-, u_{12} absolute mobilities of cation, anion and ion pair or neutral molecule respectively.
 V, V^E volume, and excess volume of mixing respectively.
 $\Delta V, \Delta V_{\text{ideal}}$ change in volume on mixing and change in volume on mixing for ideal solution respectively.
 V' volume swept by moving plane Q of unit area in Figure 1.
 \bar{V}_A, \bar{V}_B partial molal volumes of A and B respectively.
 V_1, V_2 volume of diffusion cell compartments associated with the more concentrated solution and the less concentrated solution respectively.

- V_+ apparent ionic volume of cation.
- v ionic velocity in diffusion.
- \bar{v} velocity of light in Equation (127).
- W_B molecular weight of B.
- x coordinate.
- x_A, x_B mole fraction of water and mole fraction of electrolyte defined by Equations (8) and (29) respectively.
- x_A^*, x_B^* mole fraction of water and mole fraction of amine in the convention for binary liquid mixtures.
- \tilde{x}_A, \tilde{x}_B mole fraction of water and mole fraction of "Amine+H₂O" defined by Equation (56) respectively.
- x_1, x_2 mole fractions of cation and anion respectively.
- x_{\pm} stoichiometric mean ionic mole fraction.
- x_1', x_2' true cationic and anionic concentrations in mole fraction scale.
- x_A^{*v}, x_B^{*v} vapor compositions of water and amine respectively.
- x_A^A, x_B^A mole fractions of solvent and solvated solute in extended Hartley-Crank theory.
- $y = \kappa a^0$
- y_1, y_2 cationic and anionic activity coefficients associated with molarity scale respectively.
- y_B' activity coefficient of free amine associated with molarity scale.
- y_{\pm} stoichiometric mean ionic activity coefficient associated with molarity scale.
- y_{\pm}' true mean ionic activity coefficient associated with molarity scale.
- y_{\pm}'' mean ionic activity coefficient of free "aminium hydroxide" associated with molarity scale.
- Z charge on cation or anion for symmetric electrolytes.

- Z_1, Z_2, Z_j charges on cation, anion and ion j respectively.
- z special function defined by Equation (171).
- α, α_0 degrees of dissociation, and at infinite dilution respectively.
- α_1, α_2 degrees of dissociation obtained by first approximation, second approximation, respectively.
- β diffusion cell constant.
- β identical with $\frac{1}{\sqrt{2}}$ appeared in Equation (153).
- γ_1, γ_2 cationic and anionic activity coefficients associated with molality scale.
- γ_{\pm} mean ionic activity coefficient associated with molality scale.
- γ_{\pm}^{\dagger} true mean ionic activity coefficient associated with molality scale.
- Δ penetration distance of two oppositely charged ions.
- Δ_1, Δ_2 electrophoretic terms defined by Equations (206) and (207) respectively.
- E unit charge quantity.
- η, η_0, η_{0B} viscosities of solution, solvent and pure B respectively.
- relative viscosity,
- κ Reciprocal of Debye-thickness of ionic atmosphere in \AA^{-1} ,
- Λ, Λ° equivalent conductance and limiting equivalent conductance respectively.
- $\Lambda_{\text{cal}}, \Lambda_{\text{obs}}$ calculated value and observed value of equivalent conductance respectively.
- Λ^* equivalent conductance without solvent correction defined by Equation (182).
- Λ_{η} identical with $\Lambda (1 + Fc)$.

- Λ_1^0, Λ_2^0 limiting equivalent conductance for cation and anion respectively.
- Λ_{corr} true equivalent conductance, corrected for hydrolysis effect.
- Λ_{uncorr} equivalent conductance, uncorrected for hydrolysis effect.
- μ_A, μ_B, μ_i chemical potentials of solvent A, solute B and component i respectively.
- μ_i^0 chemical potential of component i in standard state.
- μ_{Aideal}^0 chemical potential of water in ideal solution defined by Equation 9.
- $\mu^0(x^*), \mu_B^0(x^*)$ chemical potentials of pure liquid and pure amine respectively.
- $\mu_A^0, \mu_A^0(x), \mu_A^0(x^*), \mu_A^0(x)$ chemical potentials of pure water.
- μ_A'' chemical potential of water vapor at unit fugacity.
- μ_A^E, μ_B^E excess chemical potentials of water and amine respectively.
- μ_{ideal}^* chemical potential in ideal liquid mixtures.
- $\tilde{\mu}_{\text{Aideal}}^0$ chemical potential of water in ideal liquid mixtures of water and "aminium hydroxide".
- $\tilde{\mu}_B$ chemical potential of "aminium hydroxide".
- $\mu_{\pm B}^0, \mu_{\pm i}^0$ chemical potentials of electrolyte solutes B and i in the standard state respectively.
- $\mu_{\pm B}^0(\tilde{x})$ chemical potential of "aminium hydroxide" associated with mole fraction scale \tilde{x} in the standard state.
- $\mu_B^{0'}$ (c) chemical potential of free amine associated with molarity scale in the standard state.
- μ_1, μ_2 chemical potentials of cation and anion respectively.
- μ_1^0, μ_2^0 chemical potentials of cation and anion in the standard state respectively.

$\mu_1^0(c), \mu_2^0(c)$ chemical potentials of aminium cation and hydroxyl anion associated with molarity c in the standard state respectively.

ν identical with $(\nu_1 + \nu_2)$.

ν_1, ν_2 numbers of cations and anions produced by dissociation of one molecule of electrolyte.

ν_i number of ions produced by dissociation of one molecule of electrolyte i .

σ_1, σ_2 special functions defined by Equations (143) and (144) respectively.

ϕ practical or molal osmotic coefficient.

ϕ_{ideal} practical or molal osmotic coefficient for an ideal solution.

$\phi_2(\kappa a)$ special function defined by Equation (209).

φ volume fraction of ions in solution.

ω degree of hydrolysis.

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I INTRODUCTION

I.A General Significance

The study of reversible as well as irreversible thermodynamic properties of electrolyte solutions is of great importance. The results not only expand and broaden the understanding of both the microscopic and macroscopic behaviour of the component species that constitute a given system, but also stimulate and encourage the growth and development of the general theories, and in turn, the improvement of the methods by which the free energy functions and mass transports of electrolyte solutions may be studied.

In this work the methods by which electrolyte solutions have been studied consist on the one hand of measurements of free energy functions or specifically the activity coefficients which are the most important properties of reversible thermodynamics, and on the other comprise conductivity and diffusion measurements which are directly related to mass transfer and rate processes. These enable us to understand more fully the nature of the forces operating among the constituents of the system and to deduce the special features of ionic equilibria.

In the subsequent sections of this introduction, some principles and theories about free energy functions, conductances and diffusion coefficients are given. They are closely related to this work and of general interest.

I.B Fundamental Definitions and Relations in Free Energy Functions

1. Basic Definitions

The total free energy of a system is conveniently expressed in terms of the individual contributions from all its components. Let subscript A, B and . . . denote the quantities associated with the solvent water

and solute species respectively; the total free energy G of the system at constant temperature and pressure is given by

$$\begin{aligned} G &= n_A \mu_A + n_B \mu_B + \dots \\ &= \sum_i n_i \mu_i \end{aligned} \quad (1)$$

where μ_i is the chemical potential or partial molal free energy of component i , and

n_i is the number of moles of component i .

The chemical potential is made up of contributions from two terms, one of which is μ_i^0 , the same quantity in the standard state, signifying from what arbitrary level μ_i is to be measured; another term is $RT \ln a_i$ in which a_i is the activity of the component, R is the gas constant and T is the absolute temperature. Thus, μ_i may be defined as

$$\mu_i = \mu_i^0 + RT \ln a_i \quad (2)$$

It is difficult to assess the absolute values of μ_i^0 's, however, it is not of interest to do so. We are contented that by adopting certain conventions it is possible to assign numerical values to the μ_i^0 's which are consistent among themselves. Since $RT \ln a_i$ is an experimental quantity, it is evident that numerical values of μ_i can also be evaluated.

a. Water Activity

Water is a major component in dilute aqueous electrolyte solutions and its mole fraction is seldom much less than unity. It is a matter of convention that water in its pure state is taken to be the standard state having unit activity and unit activity coefficient. According to the Gibbs' criterion, when pure liquid water exists in equilibrium with its vapor at pressure p_A^0 , the chemical potentials of pure liquid water and

its vapor are equal. Water in solution can also exist in equilibrium with its vapor at pressure p_A , and the chemical potential of the solvent in solution is identical with that of its vapor at partial pressure p_A .

Thus we have

$$\mu_A^\circ = \mu_A'' + RT \ln p_A^\circ \quad (3)$$

and

$$\mu_A = \mu_A'' + RT \ln p_A \quad (4)$$

where μ_A'' is the chemical potential of water vapor at unit fugacity.

Accordingly we obtain

$$\mu_A = \mu_A^\circ + RT \ln a_A \quad (5)$$

with

$$a_A = \frac{p_A}{p_A^\circ} \quad (6)$$

We have substituted the ratio of partial pressures for that of fugacities. This is legitimate because the vapor pressures of solvent and solution are of the same order of magnitude such that the correction factors for gas imperfection are practically the same for both solvent and solution.

In an ideal aqueous electrolyte solution obeying Raoult's law

$$p_A = x_A p_A^\circ \quad (7)$$

where x_A is defined by the expression

$$x_A = \frac{55.51}{55.51 + \sum_i \nu_i m_i} \quad (8)$$

m_i is the concentration of electrolyte i in stoichiometric molality units,

ν_i is the number of ions that the i^{th} electrolyte solute gives upon ionization, and

the summation extends over all the electrolyte solutes.

The chemical potential of water in an ideal solution is then

$$\mu_{A \text{ ideal}} = \mu_A^\circ + RT \ln x_A \quad (9)$$

For non-ideal solutions, the rational activity coefficient of water, f_A is introduced as a measure of the departure of the actual chemical potential from ideality, such that

$$\mu_A = \mu_A^\circ + RT \ln f_A x_A \quad (10)$$

and

$$f_A = \frac{a_A}{x_A} = \frac{p_A}{x_A p_A^\circ} \quad (11)$$

The excess of chemical potential, i.e. the difference between the actual chemical potential and that calculated from Equation (9) is often defined as

$$\mu_A^E = RT \ln f_A \quad (12)$$

At infinite dilution, as the mole fraction of water approaches unity and the vapor pressure of water approaches p_A° , the rational activity coefficient of water also approaches unity. Thus for an ideal solution, the condition $f_A = 1$ is valid at any concentration, while for a non-ideal solution the stated condition is valid only at infinite dilution.

b. Osmotic Coefficients

In an ordinary aqueous electrolyte solution, water is present to such a large extent that its rational activity coefficient is not much different from unity. Obviously f_A is insufficient to emphasize the departure of real solution from ideality. Bjerrum⁽¹⁾ was the first to

introduce the osmotic coefficient as a more sensitive measure of the deviation from ideal behavior.

The rational osmotic coefficient g may be defined by the expression,

$$\mu_A = \mu_A^\circ + g RT \ln x_A \quad (13)$$

For an ideal solution $g = 1$ throughout the entire concentration range.

A relation between osmotic coefficient g and activity coefficient f_A is given by

$$g = 1 + \frac{\ln f_A}{\ln x_A} \quad (14)$$

g is also related to the water activity by the equation

$$\ln a_A = -g \ln \frac{1}{x_A} = -g \ln (1 + 0.018 \sum_i \nu_i m_i) \quad (15)$$

Series expansion of the logarithm gives

$$\ln a_A = -g \left[0.018 \sum \nu_i m_i - \frac{1}{2} (0.018 \sum \nu_i m_i)^2 + \frac{1}{3} (0.018 \sum \nu_i m_i)^3 - \dots \right] \quad (16)$$

We see that for a non-ideal solution, the limiting value of g approaches 1 by virtue of Equation (14).

The osmotic coefficient has been defined in several ways. The practical or molal osmotic coefficient in which we are most interested is defined by the equation

$$\ln a_A = -\frac{\sum \nu_i m_i}{55.51} \phi = -0.018 (\sum \nu_i m_i) \phi \quad (17)$$

For an ideal solution which obeys Raoult's law strictly, we have

$$\ln \frac{1}{x_A} = 0.018 (\sum \nu_i m_i) \phi_{ideal} \quad (18)$$

By expanding the left side into a series,

$$0.018 \sum \nu_i m_i - \frac{1}{2} (0.018 \sum \nu_i m_i)^2 + \frac{1}{3} (0.018 \sum \nu_i m_i)^3 - \dots = 0.018 (\sum \nu_i m_i) \phi_{ideal} \quad (19)$$

we obtain ϕ for the ideal solution as

$$\phi_{ideal} = 1 - \frac{1}{2} (0.018 \sum \nu_i m_i) + \frac{1}{3} (0.018 \sum \nu_i m_i)^2 - \dots \quad (20)$$

We see therefore ϕ_{ideal} is not equal to unity for solution of non-zero concentration, but it does approach 1 at infinite dilution.

A combination of Equations (16) and (17) gives a relation between ϕ and g , viz.,

$$\phi = g \left[1 - \frac{1}{2} (0.018 \sum \nu_i m_i) + \frac{1}{3} (0.018 \sum \nu_i m_i)^2 - \dots \right] \quad (21)$$

For small concentrations of electrolytes, ϕ and g are almost identical and at infinite dilution ϕ approaches unity as g does.

c. Activity Coefficients

The activity of an electrolyte, say B, in aqueous solution is defined in a similar manner by

$$\mu_B = \mu_{\pm B}^{\circ} + RT \ln a_B \quad (22)$$

Since electrolyte dissociates into ν_1 cations and ν_2 anions, the chemical potential of the electrolyte as a whole may be given by the sum of the chemical potentials of the ions, each of which may be described as

$$\mu_1 = \mu_1^{\circ} + RT \ln a_1 \quad (23)$$

$$\mu_2 = \mu_2^{\circ} + RT \ln a_2 \quad (24)$$

where μ_1 and μ_2 are the cationic and anionic chemical potentials respectively,

μ_1^0 and μ_2^0 are the same quantities in the standard states, and a_1 and a_2 are the corresponding ionic activities.

The chemical potential of B therefore is

$$\mu_B = \nu_1 (\mu_1^0 + RT \ln a_1) + \nu_2 (\mu_2^0 + RT \ln a_2) \quad (25)$$

A comparison of Equations (22) and (25) leads immediately to

$$\mu_{\pm B}^0 = \nu_1 \mu_1^0 + \nu_2 \mu_2^0 \quad (26)$$

and
$$a_B = a_1^{\nu_1} a_2^{\nu_2} = a_{\pm}^{\nu} \quad (27)$$

with
$$\nu = \nu_1 + \nu_2 \quad (28)$$

where a_{\pm} , defined by Equation (27) is the mean ionic activity of the electrolyte.

It is a_{\pm} that can be measured by experimental methods and has real significance. Nevertheless, the concept of individual ionic activity is useful and practically indispensable in the theoretical development, although it cannot be evaluated experimentally.

Activity may be expressed in different concentration units. Therefore activity coefficients are distinguished from one another by the scale used to express the concentration of an electrolyte, say B. It is convenient to use the stoichiometric molality scale m_B where the number of moles of solvent water is fixed, for its value is unaltered by changes in temperature and pressure. The "mole fraction" scale x_B and stoichiometric molarity scale c_B are also useful in solution theories. These quantities are related as follows:

$$x_B = \frac{m_B}{55.51 + \sum \nu_i m_i} \quad (29)$$

$$c_B = \frac{m_B d}{1 + 0.001 m_B W_B} \quad (30)$$

where d is density of solution and

W_B is molecular weight of B.

For the ionic activity coefficient, e.g., that of the cation of electrolyte B, the rational ionic activity coefficient f_1 , molal ionic activity coefficient γ_1 and molar ionic activity coefficient y_1 are defined respectively as

$$f_1 = \frac{a_1(x)}{x_1} ; \quad \gamma_1 = \frac{a_1(m)}{m_1} ; \quad y_1 = \frac{a_1(c)}{c_1} \quad (31)$$

$$\text{with } x_1 = \nu_1 x_B ; \quad m_1 = \nu_1 m_B ; \quad c_1 = \nu_1 c_B \quad (32)$$

The corresponding stoichiometric mean activity coefficients, having significance similar to the water activity coefficient, are

$$\begin{aligned} f_{\pm} &= \frac{a_{\pm}(x)}{x_{\pm}} = (f_1^{\nu_1} f_2^{\nu_2}) \\ \gamma_{\pm} &= \frac{a_{\pm}(m)}{m_{\pm}} = (\gamma_1^{\nu_1} \gamma_2^{\nu_2}) \\ \text{and } y_{\pm} &= \frac{a_{\pm}(c)}{c_{\pm}} = (y_1^{\nu_1} y_2^{\nu_2}) \end{aligned} \quad (33)$$

$$\text{with } x_{\pm} = (x_1^{\nu_1} x_2^{\nu_2})^{1/\nu} = [(\nu_1 x_B)^{\nu_1} (\nu_2 x_B)^{\nu_2}]^{1/\nu} = (\nu_1^{\nu_1} \nu_2^{\nu_2})^{1/\nu} x_B = Q^{1/\nu} x_B$$

$$m_{\pm} = (m_1^{\nu_1} m_2^{\nu_2})^{1/\nu} = Q^{1/\nu} m_B$$

$$\text{and } c_{\pm} = Q^{1/\nu} c_B \quad (34)$$

At infinite dilution of real electrolyte solutions f_{\pm} , γ_{\pm} and y_{\pm} must approach unity.

In the case of mixed electrolyte solutions with a common ion, say the cation, both electrolytes contribute to the total concentration of

the ion, and the contribution of another electrolyte C to x_1 , m_1 or c_1 of the solute B should be taken into account.

In summary, for the chemical potentials of electrolyte solutes, μ_i , we have

$$\begin{aligned}\mu_i &= \mu_{\pm i}^{\circ}(x) + \nu_i RT \ln x_{\pm i} f_{\pm i} \\ &= \mu_{\pm i}^{\circ}(m) + \nu_i RT \ln m_{\pm i} \gamma_{\pm i} \\ &= \mu_{\pm i}^{\circ}(c) + \nu_i RT \ln c_{\pm i} y_{\pm i}\end{aligned}\quad (35)$$

in which

$$\mu_{\pm i}^{\circ}(x) = \lim_{\text{all } x_i \rightarrow 0} (\mu_i - \nu_i RT \ln x_{\pm i})$$

$$\mu_{\pm i}^{\circ}(m) = \lim_{\text{all } m_i \rightarrow 0} (\mu_i - \nu_i RT \ln m_{\pm i})$$

and

$$\mu_{\pm i}^{\circ}(c) = \lim_{\text{all } c_i \rightarrow 0} (\mu_i - \nu_i RT \ln c_{\pm i}) \quad (36)$$

The condition that μ_i is the same for a given solution irrespective of the choice in concentration scale, and that $f_{\pm i}$, $\gamma_{\pm i}$ and $y_{\pm i}$ all approach unity at infinite dilution, suffice to establish relations between $f_{\pm i}$, $\gamma_{\pm i}$ and $y_{\pm i}$ and $\mu_{\pm i}^{\circ}(x)$, $\mu_{\pm i}^{\circ}(m)$ and $\mu_{\pm i}^{\circ}(c)$, viz.,

$$f_{\pm} = \gamma_{\pm} \left(1 + 0.018 \sum \nu_i m_i \right) \quad (37)$$

$$\gamma_{\pm} = \frac{c y_{\pm}}{m d_0} \quad (38)$$

$$\mu_{\pm i}^{\circ}(x) = \mu_{\pm i}^{\circ}(m) + \nu_i RT \ln 55.51 \quad (39)$$

and

$$\mu_{\pm i}^{\circ}(m) = \mu_{\pm i}^{\circ}(c) + RT \ln d_0 \quad (40)$$

The above mentioned treatment of activity coefficients is based on

the assumption that the electrolytes dissociate completely at finite concentrations. In the case of weak electrolytes and even strong electrolytes which do not ionize completely and/or form aggregates of ion pairs, the measured solute activity coefficients based on the view of complete dissociation, do not reveal directly the intrinsic nature of the free ions, for the values reflect not only the influence due to charge interaction but also the influence due to the reduction in the concentrations of the ions⁽³⁾. In order to separate the two effects, the concept of true ionic concentration has to be considered. A relation between the activity coefficient calculated on the assumption of complete dissociation and another activity coefficient computed on the basis of partial ionization has been derived⁽⁴⁾. Let $M_{\nu_1} X_{\nu_2}$ and $M_{n_1} X_{n_2}$ denote the formula of the original solute and the aggregate, and if α is the degree of dissociation of the solute, then the general relations exist,

$$m'_1 = \alpha \nu_1 m ; \quad x'_1 = \alpha \nu_1 x = \alpha \nu_1 \frac{m}{55.51 + \nu m} \quad (41)$$

$$m'_2 = \left[\nu_2 - (1-\alpha) \frac{n_2 \nu_1}{n_1} \right] m \quad (42)$$

$$m_{12} \text{ (concentration of aggregate)} = (1-\alpha) \frac{\nu_1}{n_1} m \quad (43)$$

$$f_{\pm}^{\nu} = \alpha^{\nu_1} \left[1 - (1-\alpha) \frac{n_2 \nu_1}{n_1 \nu_2} \right]^{\nu_2} f_{\pm}^{\prime \nu} \quad (44)$$

$$\gamma_{\pm}^{\nu} = \alpha^{\nu_1} \left[1 - (1-\alpha) \frac{n_2 \nu_1}{n_1 \nu_2} \right]^{\nu_2} \gamma_{\pm}^{\prime \nu} \quad (45)$$

and
$$y_{\pm}^{\nu} = \alpha^{\nu_1} \left[1 - (1-\alpha) \frac{n_2 \nu_1}{n_1 \nu_2} \right]^{\nu_2} y_{\pm}^{\nu_1 \nu_2} \quad (46)$$

here γ_{\pm} , y_{\pm} and f_{\pm} have their usual meanings and

γ_{\pm}^{\dagger} , y_{\pm}^{\dagger} and f_{\pm}^{\dagger} are the true mean ionic activity coefficients of the association theory.

Thus the relation between the two sets of activity coefficients varies according to the type of solute and type of aggregate. In particular if the aggregate is just that of the undissociated solute molecule, we have for example

$$\gamma_{\pm} = \alpha \gamma_{\pm}^{\dagger} \quad ; \quad y_{\pm} = \alpha y_{\pm}^{\dagger} \quad (47)$$

The amines which are the objects of this work are miscible with water in all proportions below 18.3°C and have appreciable vapor pressures. Their partial vapor pressures can be conveniently used as a measure of their chemical potentials. Thus their activities and activity coefficients can be defined in a way similar to water activity and activity coefficient. By adopting this convention for binary mixtures one has the following equations for solvent A and solute B

$$\mu = \mu^{\circ}(x^*) + RT \ln a \quad (48)$$

with
$$a = \frac{p}{p^{\circ}} \quad (49)$$

$$\mu_{ideal}^* = \mu^{\circ}(x^*) + RT \ln x^* \quad (50)$$

and
$$f^* = \frac{a}{x^*} = \frac{p}{x^* p^{\circ}} \quad (51)$$

where

$$x_A^* = \frac{55.51}{55.51 + m} \quad (52)$$

$$\text{or } x_B^* = \frac{m}{55.51 + m} \quad (53)$$

depending on which species one refers to.

In aqueous solutions since one amine molecule and one water molecule give rise to a substituted ammonium ion and a hydroxyl ion, the chemical potential and formula weight of the ionic species as a whole can be regarded as the sum of those of amine and water. Let \tilde{m} be the molality of "amine + H₂O",

$$\text{then } \tilde{m} = \frac{m}{1 - 0.018m} \quad (54)$$

$$\tilde{c} = c \quad (55)$$

$$\tilde{x}_B = \frac{\tilde{m}}{55.51 + 2\tilde{m}} = x_B^* ; \tilde{x}_A = \frac{55.51}{55.51 + 2\tilde{m}} \quad (56)$$

By using the convention for electrolyte solutions we have

$$\mu_A = \mu_A^{\circ}(\tilde{x}) + RT \ln a_A \quad (57)$$

$$\text{with } a_A = \frac{p_A}{p_A^{\circ}} \quad (58)$$

$$\tilde{\mu}_{A,\text{ideal}} = \mu_A^{\circ}(\tilde{x}) + RT \ln \tilde{x}_A \quad (59)$$

$$\text{and } \tilde{f}_A = \frac{a_A}{\tilde{x}_A} = \frac{p_A}{\tilde{x}_A p_A^{\circ}} \quad (60)$$

$\mu_A^{\circ}(\tilde{x})$ is identical with $\mu_A^{\circ}(x)$. \tilde{f}_A here and f_A^* mentioned previously are related by

$$\tilde{f}_A = \frac{55.51 + 2\tilde{m}}{55.51 + m} f_A^* \quad (61)$$

For the solute, "substituted ammonium ion+hydroxyl ion" as a whole or "amine+water" as a whole

$$\tilde{\mu}_B = \mu_{\pm B}^{\circ}(\tilde{x}) + 2RT \ln \tilde{x}_B \tilde{f}_{\pm B} \quad (62)$$

A relation can be obtained for the conversion from f_B^* to $\tilde{f}_{\pm B}$ by considering the following. At equilibrium, it is true that

$$\tilde{\mu}_B = \mu_A + \mu_B \quad (63)$$

or

$$\mu_{\pm B}^{\circ}(\tilde{x}) - \mu_A^{\circ}(x^*) - \mu_B^{\circ}(x^*) = RT \ln \frac{p_A p_B}{p_A^{\circ} p_B^{\circ}} \cdot \frac{1}{(\tilde{x}_B \tilde{f}_{\pm B})^2} \quad (64)$$

The quantity on the left hand side is constant at constant temperature and pressure, therefore

$$\frac{p_A}{p_A^{\circ}} \cdot \frac{p_B}{p_B^{\circ}} = k_{\pm} \tilde{x}_B^2 \tilde{f}_{\pm B}^2 \quad (65)$$

At infinite dilution $\frac{p_A}{p_A^{\circ}}$ and $\tilde{f}_{\pm B}$ approach unity, and the constant k_{\pm} is identical with the limiting value of $\frac{p_B}{p_B^{\circ} \tilde{x}_B^2}$, i.e.

$$k_{\pm} = \lim_{\tilde{x}_B \rightarrow 0} \frac{p_B}{p_B^{\circ} \tilde{x}_B^2} \quad (66)$$

Replacing $\frac{p_A}{p_A^{\circ}} \cdot \frac{p_B}{p_B^{\circ}}$ by $x_A^* f_A^* x_B^* f_B^*$ in Equation (65), the mean ionic activity coefficient in "mole fraction" scale is thus

$$\tilde{f}_{\pm B} = \frac{1}{\tilde{x}_B} \left(\frac{x_A^* f_A^* x_B^* f_B^*}{k_{\pm}} \right)^{\frac{1}{2}} \quad (67)$$

for which $x_A^* > \frac{1}{2}$, $x_B^* \leq \frac{1}{2}$ and $\tilde{x} \leq 1$ if water is the solvent. We also have

$$\mu_{\pm B}^{\circ}(\tilde{x}) = \mu_A^{\circ}(x^*) + \mu_B^{\circ}(x^*) + RT \ln k_{\pm} \quad (68)$$

By using Equations (37), (38) and (47) for the true ionic activity coefficients with α , the degree of conversion of amine into substituted

ammonium ion, or the degree of basic dissociation, we obtain

$$\tilde{Y}_{\pm} = \left(\frac{x_A^* f_A^* x_B^* f_B^*}{k_{\pm}} \right)^{\frac{1}{2}} \cdot \frac{1}{x_B^* (1 + 0.036 \tilde{m}_B)} = \alpha \tilde{Y}'_{\pm} \quad (69)$$

$$\tilde{f}_{\pm} = \left(\frac{x_A^* f_A^* x_B^* f_B^*}{k_{\pm}} \right)^{\frac{1}{2}} \cdot \frac{d_0 \tilde{m}_B}{c x_B^* (1 + 0.036 \tilde{m}_B)} = \alpha \tilde{f}'_{\pm} \quad (70)$$

Equation (70) will be useful in the calculation of basic dissociation constants for amines.

2. Basic Dissociation Constant

Reconsidering the equilibrium processes in solutions, the condition for equilibrium of a reaction is that the sum of the free energies of reactants must be equal to that of the products. When the reaction of amine and water to form substituted ammonium ion and hydroxyl ion is in equilibrium, it follows that

$$\mu_1^{\circ} + \mu_2^{\circ} - \mu_A^{\circ} - \mu_B^{\circ} = 0 \quad (71)$$

where the numerical subscripts refer to the ionic species and the alphabetic subscripts refer to the solvent and the amine as before. Introducing the definition of μ' 's,

$$\mu_1^{\circ} + \mu_2^{\circ} - \mu_A^{\circ} - \mu_B^{\circ} = -RT \ln \frac{a_1' a_2'}{a_A' a_B'} \quad (72)$$

in which a' refers to the activity of the free species. At constant temperature and pressure the activity quotient is a constant, i.e., the basic dissociation constant. It is commonly expressed in terms of the molarity scale. By so doing

$$\begin{aligned} \mu_1^{\circ}(c) + \mu_2^{\circ}(c) - \mu_A^{\circ}(x^*) - \mu_B^{\circ}(c) &= -RT \ln \frac{\tilde{y}_{\pm}^{\prime 2} d^2 c}{(1-\alpha) \tilde{y}'_B} \cdot \frac{k_A^{\circ}}{P_A} \\ &= -RT \ln K \end{aligned} \quad (73)$$

Using a method similar to that given previously, it can be shown that the activity coefficient of free amine on the molarity scale, y_B^I is related to the partial vapor pressure of amine by the expression,

$$y_B^I = \frac{k p_B}{c(1-\alpha) p_B^0} \quad (74)$$

where

$$k = \lim_{c \rightarrow 0} \frac{c(1-\alpha) p_B^0}{p_B} \quad (75)$$

If the values of α from conductance work which will be described in a later section are known, along with values of y_{\pm}^I and y' from Equations (70) and (74), the basic dissociation constant K may be calculated by means of Equation (73).

Unlike μ_1^0 and μ_2^0 , for the ionic species, these are identical with $\mu_1^{0'}$ and $\mu_2^{0'}$, but $\mu_B^0(c)$, the standard chemical potential of the free amine in solution is not equal to $\mu_B^0(c)$, the stoichiometric standard chemical potential of amine in molarity scale. However, they are related by

$$\mu_B^0(c) = \mu_B^{0'}(c) + RT \ln(1-\alpha_0) \quad (76)$$

$$\alpha_0 = \frac{K}{K_w^{1/2} + K} \quad (77)$$

α_0 is the degree of basic dissociation at infinite dilution, and K_w is the ion product of water.

3. Theoretical Calculation of Activity Coefficients

It has long been recognized that the complete dissociation of a strong electrolyte in dilute solution cannot entirely account for the deviation of the observed relative lowering of vapor pressure of water from that expected for an ideal solution obeying Raoult's law. In 1923 Debye and Hückel⁽⁵⁾ developed a theory for the quantitative calculation of activity coefficients in electrolyte solution. Their assumptions

are

1. Strong electrolytes are completely dissociated into ions in dilute aqueous solutions.
2. All deviations of dilute electrolyte solutions from ideal behaviour are attributed to the electrostatic interactions between ions. A solution of discharged ions is assumed to be ideal.
3. The solvent is a structureless dielectric continuum having a uniform dielectric constant.
4. Each ion can be regarded as a spherical cavity of radius $\overset{\circ}{a}$ inside which there is no space charge. The constant $\overset{\circ}{a}$ is called the distance of closest approach of the two ionic species in solution.

Upon solving Poisson's equation with an approximated charge density, the Debye-Hückel equation is found to be

$$\ln f_{\pm i} = -2.303 \frac{A |Z_1 Z_2|_i \sqrt{I}}{1 + B \overset{\circ}{a} \sqrt{I}} \quad (78)$$

where $f_{\pm i}$ has its usual significance for an electrolyte i ,

Z_1 and Z_2 are respectively the charges of cation and anion of solute i ,

I is the molar ionic strength defined as $I = \frac{1}{2} \sum c_j Z_j^2$

C_j is the molarity of the j ion,

Z_j is the charge of the j ion,

$\overset{\circ}{a}$ is the distance of closest approach of two oppositely charged ions and is expressed in Angstrom units, and

A and B are constants characteristic of the solvent at constant temperature,

$$A' = \frac{1}{2.303} \frac{\epsilon^2}{2DkT} \left(\frac{8\pi N_a \epsilon^2}{1000 DkT} \right)^{1/2} \quad (79)$$

$$= \frac{1.8246 \times 10^6}{(DT)^{3/2}}$$

$$B = 10^{-8} \left(\frac{8\pi N_a \epsilon^2}{1000 k} \right)^{1/2} \frac{1}{(DT)^{1/2}} = \frac{50.29}{(DT)^{1/2}} \quad (80)$$

At 25°C, values of A and B for water⁽⁶⁾ obtained by using the appropriate values of physical constants are

$$A = 0.5115 \quad ; \quad B = 0.3291$$

The numerator of the Debye-Hückel expression accounts for the effect of the long range Coulombic forces, while the denominator, in which the distance of closest approach is incorporated, shows how the former effect is modified by the short range interaction between assumed hard sphere ions.

An alternative form of the Debye-Hückel expression may be obtained by introducing Equation (37) into Equation (78) and using the molal ionic strength I_m defined as

$$I_m = \frac{1}{2} \sum m_j Z_j^2 \quad (81)$$

$$\text{Since } \frac{I_m}{I} = \frac{\sum m_j Z_j^2}{\sum c_j Z_j^2} = \frac{m}{c} = \frac{1}{d - 0.018 W_B c} \quad (82)$$

in which d is the density of the solution and W_B is the formula weight of the electrolyte; at low concentrations $d \sim 1$ and \sqrt{I} may be approximated as $\sqrt{I_m}$. The Debye-Hückel equation may then be written as

$$\ln \gamma_{\pm} = -2.303 \frac{A |Z_1 Z_2| \sqrt{I_m}}{1 + B a \sqrt{I_m}} - \ln(1 + 0.018 v m) \quad (83)$$

Further simplification of the above equation leads to the Debye-Hückel

limiting law for electrolyte solution, viz.,

$$\begin{aligned} \ln \gamma_{\pm} &= -2.303 A |z_1 z_2| \sqrt{I_m} \\ &= -\frac{2.303}{\sqrt{2}} A |z_1 z_2|^{3/2} v^{1/2} m^{1/2} \end{aligned} \quad (84)$$

Activity coefficients calculated from the Debye-Hückel expression have been extensively verified by measurements in very dilute solutions of strong electrolytes where ion association can be neglected. Although the theory is applicable only in very dilute solutions of ionic strength at most not greater than 0.1, with appropriate choices of a° 's, the theory or even the limiting law itself is exceedingly useful in providing us with a reliable method of extrapolating the thermodynamic properties of electrolyte solutions to infinite dilution.

Attempts have been made to extend the Debye-Hückel theory to higher concentrations. Equations involving semi-empirical constants have been proposed. They may be applied over a wider concentration range, but an exact treatment of electrolyte solutions at higher concentrations has not been developed. The thermodynamic properties of concentrated electrolyte solutions are influenced by many inter-related factors. These are (7)

1. The electrostatic forces of the Debye-Hückel type which have a predominant influence at low concentrations;
2. the effect of ionic hydration;
3. ion association;
4. change in dielectric constant of solvent in the immediate neighbourhood of an ion;
5. the effect of ionic sizes, not only on the Debye-Hückel term, but also on the co-volume entropy effect.

Equation (78) represents the activity coefficients as a decreasing

function of the concentration, while the experimental values often show a minimum, after which the activity coefficient is an increasing function of concentration. In order to fit the experimental data better, many modified Debye-Hückel equations which take more factors into consideration have been put forward.

Hückel⁽⁸⁾ considered that owing to the attraction between ions and the dipolar molecules of solvent, there is a tendency for the solvent molecules to orient themselves about the central ion. This causes a change in dielectric constant in the immediate vicinity of the ion and leads to the addition of a "salt-out" term in Equation (78),

$$\log f_{\pm} = - \frac{A |z_1 z_2| \sqrt{I}}{1 + B a \sqrt{I}} + b I \quad (85)$$

where a and b are empirical constants. For non-associated 1:1 electrolytes, the Hückel equation is capable of fitting the experimental data up to about $I = 1$.

For some purposes, Equation (78) is approximately equivalent to a more convenient form

$$\log f_{\pm} = - A |z_1 z_2| \sqrt{I} + c I \quad (86)$$

where c is an empirical constant. Equation (86) has the same form as an empirical equation proposed by Brönsted⁽⁹⁾, and hence it has been called the Brönsted equation.

Güntelberg⁽¹⁰⁾ proposed a simpler form for aqueous electrolyte solutions,

$$\log f_{\pm} = - \frac{A |z_1 z_2| \sqrt{I}}{1 + \sqrt{I}} \quad (87)$$

which is equivalent to putting $a = 3.04 \text{ \AA}$ in Equation (78) for all electro-

lytes at 25°C. Although there is no adjustable parameter in this equation, it gives adequate representation for a number of electrolytes up to $I = 0.1$. However, for the study of the size of hydrated ions, the equation is good only for 1:1 electrolytes; it should be modified for poly-valent inorganic ions as well as organic ions⁽¹¹⁾.

Equation (87) has been greatly improved by Guggenheim⁽¹²⁾ by adding a linear term, giving a different one-parameter equation,

$$\log f_{\pm} = -\frac{A |z_1 z_2| \sqrt{I}}{1 + \sqrt{I}} + bI \quad (88)$$

here again b is an adjustable parameter. The term bI , in fact, includes the contributions due to lowering of dielectric constant, to ion-pair formation, to effects of ion size, polarizability, and so forth. Guggenheim applied this equation to the computation of osmotic and activity coefficients from freezing point and electromotive force data at concentration less than 0.1 m. The agreement with the freezing point data is within ± 0.0002 to $\pm 0.0005^\circ\text{C}$.

From an examination of the values of b in Equation (88) for a number of 1:1 and 2:1 electrolytes, for which the degree of association is less than 5%, Davies⁽¹²⁾ proposed in 1938 an equation, at 25°C

$$\log \gamma'_{\pm} = -0.50 |z_1 z_2| \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.20 I \right) \quad (89)$$

This equation is useful to obtain an estimation of the activity coefficients when experimental data are not available. The disagreement between calculated values and experimental values at that time did not greatly exceed 2%, at concentration of 0.1 m. As the volume of data increased since then, Davies⁽¹³⁾ revised his equation for 1:1 electrolytes as follows:

$$\log \gamma_{\pm}' = -0.50 |z_1 z_2| \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.30 I \right) \quad (90)$$

This equation fits the experimental data compiled by Robinson and Stokes⁽¹⁴⁾, and Harned and Owen⁽¹⁵⁾ better. It shows an average deviation of 0.013 in γ_{\pm}' or 1.6% for some fifty 1:1 electrolytes at 0.1 m and 25°C. Guggenheim⁽¹⁶⁾ suggested that it would be an improvement to replace the 0.20I in Equation (88) by 2.0I when dealing with the 2:2 electrolytes.

Stokes and Robinson⁽¹⁷⁾ used an empirical approach based on Bjerrum's idea⁽¹⁸⁾ of ion solvation. They assumed that in aqueous solution there were solvent molecules bound to each mole of electrolyte. Thus the free water content in the solution was decreased. However, the condition that the total chemical potentials of the system remained the same enabled them to obtain a two-parameter expression to calculate single electrolyte activity coefficients. They used mole fraction statistics and a hard sphere ionic model with constant hydration number. By taking the Debye-Hückel expression to represent the mean activity coefficient of the hydrated ions, the pertinent equation is

$$\log \gamma_{\pm} = - \frac{A |z_1 z_2| \sqrt{I}}{1 + B a \sqrt{I}} - \frac{h}{\nu} \log a_A - \log [1 - 0.018(h - \nu)m] \quad (91)$$

where h is the hydration number parameter of the electrolyte, and

a represents the distance of closest approach of solvated cation and anion for a certain thickness of hydration shell.

By suitable selection of the parameters h and a^0 , the experimental values of strong electrolytes can be reproduced^(17,19) within ± 0.001 , up to molalities of 0.7 m for hydroiodic acid, zinc perchlorate and calcium iodide, and up to 4 m for alkaline halides. In general, the lower the value of h, the higher is the concentration limit up to which

the equation can be applied.

Stokes and Robinson⁽¹⁷⁾ went further to reduce their equation to a one-parameter equation. Following Bernal and Fowler⁽¹⁹⁾, they assumed that anions were only slightly hydrated and that their hydration could be neglected. From the concept of the anion penetrating into the hydration sheath of the cation, they set

$$\bar{a} = \left[\frac{3}{4\pi} (30h + V_+) \right]^{1/3} + r_- - \Delta \quad (92)$$

The value 30 (in \AA^3) is the volume occupied by a water molecule in liquid water at 25°C, V_+ is the apparent ionic volume of the cation (in \AA^3).

Thus $(30h + V_+)$ represents the volume of hydrated cation. r_- is the crystallographic radius of the anion (in \AA). Δ , the "penetration distance", is a correction factor which is constant for each valency type of salt, 0.7 \AA for 1:1 electrolytes and 1.3 \AA for 2:1 electrolytes.

From the relationship of \bar{a} and h in Equation (92), the two-parameter equation can be reduced to the one-parameter equation. The limit of validity for the latter equation is about $hm = 12$, i.e. when about one-fifth to one-quarter of the water molecules are bound to ions. When the concentration is still higher, the experimental value of h will decrease. This is due to the effects of competition between neighbouring cations. It seems unlikely that h should be independent of concentration, even at lower molalities.

Glueckauf⁽⁷⁾ was aware of the importance of the co-volume entropy contribution to the free energy of a solution. On the basis of volume fraction statistics and on the assumption that the entropy of mixing of hydrated ions and free water molecules was analogous to that of athermal solution formulated by Flory⁽²⁰⁾ and Huggins⁽²¹⁾, he⁽⁷⁾ was able to

derive his equation for the activity coefficients of strong electrolytes, viz.,

$$\ln \gamma_{\pm} = - \frac{2.303 A |Z_1 Z_2| \sqrt{I}}{1 + B a \sqrt{I}} - \frac{h}{v} \ln(1 - 0.018 m h) \quad (93)$$

$$+ \frac{0.018 m r (r + h - v)}{v (1 + 0.018 m r)} + \frac{h - v}{v} \ln(1 + 0.018 m r)$$

In this equation the quantity r is the ratio of the hard sphere volume of hydrated electrolyte to that of solvent water. It can be evaluated from the apparent molal volume of the solute at one moderately high concentration and applied to the whole concentration range. Using h and a as parameters this equation fits the experimental data as well as Equation (91), and gives hydration numbers nearly additive for separated ions.

4. Consistency and the Gibbs-Duhem Equation

The activity coefficients of the volatile solute and solvent f_B^* and f_A^* , as mentioned before, can be determined directly by vapor pressure measurements, but the two activity coefficients are not independent of each other. They are related by the Gibbs-Duhem equation. Since the free energy G of a system of two components at constant temperature and pressure is a first degree homogeneous function of the number of moles of components n_A and n_B , Euler's theorem is applicable,

$$G = n_A \left(\frac{\partial G}{\partial n_A} \right)_{n_B} + n_B \left(\frac{\partial G}{\partial n_B} \right)_{n_A}$$

$$= n_A \mu_A + n_B \mu_B \quad (94)$$

Differentiation of this equation leads to

$$dG = n_A d\mu_A + \mu_A dn_A + n_B d\mu_B + \mu_B dn_B \quad (95)$$

However, the complete differential of $G(n_A, n_B)$ is

$$dG = \mu_A dn_A + \mu_B dn_B \quad (96)$$

A comparison of the two equations above enables us to write

$$n_A d\mu_A + n_B d\mu_B = 0 \quad (97)$$

or

$$x_A^* d\mu_A + x_B^* d\mu_B = 0 \quad (98)$$

and this is the Gibbs-Duhem equation.

If sufficient data are available for the activity coefficient of the solvent, the activity coefficients of the solute can be obtained by appropriate integration of the Gibbs-Duhem equation and vice-versa. By formally substituting μ_A and μ_B of Equation (48) into this equation, and integrating in between limits, we have

$$\ln f_B^* = - \int_{x_A^*=0}^{x_A^*} \frac{x_A^*}{x_B^*} d \ln f_A^* \quad (99)$$

Values of $\ln f_B^*$ thus calculated from this equation should be identical with those derived from the solute vapor pressures if the experimental measurements are thermodynamically consistent; otherwise there must be errors in the experimental works.

The same Gibbs-Duhem equation can also be employed in calculating the mean ionic activity coefficient of electrolyte if the vapor pressure of water or the osmotic coefficient as a function of the molality is known. For this purpose, the equation takes the form

$$55.51 d\mu_A + m_B d\mu_B = 0 \quad (100)$$

Using the definitions of chemical potentials, osmotic coefficient and stoichiometric molality m for the solute, Bjerrum⁽¹⁾, and later Randall and White⁽²²⁾ obtained the equation

$$\ln \gamma_{\pm} = (\phi - 1) + 2 \int_0^m \frac{\phi - 1}{\sqrt{m}} d\sqrt{m} \quad (101)$$

An equivalent relation between ϕ and γ_{\pm} is

$$(\phi - 1) = \frac{1}{m} \int_0^m m d \ln \gamma_{\pm} \quad (102)$$

In order to calculate γ_{\pm} , the integral in Equation (101) must be evaluated by graphical integration from zero concentration up to any higher concentration for which γ_{\pm} is determined. The limiting value of $\frac{\phi - 1}{\sqrt{m}}$ may be readily established by using the Debye-Hückel limiting law and Equation (102). By substituting Equation (84) into Equation (102), one obtains after integration

$$(\phi - 1) = - \frac{2.303 A}{3\sqrt{2}} |z_1 z_2|^{3/2} \nu^{1/2} \sqrt{m} \quad (103)$$

Therefore at infinite dilution, the integrand of Equation (101) is

$$\frac{\phi - 1}{\sqrt{m}} = - \frac{2.303 A}{3\sqrt{2}} |z_1 z_2|^{3/2} \nu^{1/2} \quad (104)$$

which is universal for a given type of electrolyte at given temperature.

For all 1:1 solutes with $\nu = 2$, the limiting value of $\frac{\phi - 1}{\sqrt{m}}$ is equal to -0.3927 at 25°C.

This method has been commonly used to compute stoichiometric mean ionic activity coefficients of non-volatile electrolytes from solvent vapor pressure measurements or isopiestic measurements for which the water activity of the reference solution is known as a function of the entire workable concentration.

On the basis of the Gibbs-Duhem equation, another way to test the internal consistency is the method of Redlich and Kister⁽²³⁾, which consists of plotting χ_A^* vs. $\ln f_A^*$ and χ_B^* vs. $\ln f_B^*$. The areas under smooth curves, drawn separately through the points, should be equal if concordance of results has been achieved.

5. Thermodynamic Functions of Mixing

There are several consequences for an ideal solution which obeys Raoult's law. With reference to one mole of solution, there is no change in volume ΔV , and also no change in enthalpy ΔH upon mixing. The free energy and entropy of the mixing take the forms

$$\Delta G_{ideal} = RT (x_A^* \ln x_A^* + x_B^* \ln x_B^*) \quad (105)$$

and
$$\Delta S_{ideal} = -R (x_A^* \ln x_A^* + x_B^* \ln x_B^*) \quad (106)$$

For a non-ideal solution, ΔV and ΔH do not vanish; ΔG and ΔS are respectively,

$$\Delta G = RT (x_A^* \ln x_A^* f_A^* + x_B^* \ln x_B^* f_B^*) \quad (107)$$

and
$$\Delta S = \frac{\Delta H}{T} - R (x_A^* \ln x_A^* f_A^* + x_B^* \ln x_B^* f_B^*) \quad (108)$$

The excess molar thermodynamic functions are defined as the corresponding differences between the real and the ideal values. They are

$$V^E = \Delta V \quad (109)$$

$$H^E = \Delta H \quad (110)$$

$$G^E = RT (x_A^* \ln f_A^* + x_B^* \ln f_B^*) \quad (111)$$

$$S^E = \frac{H^E}{T} - R (x_A^* \ln f_A^* + x_B^* \ln f_B^*) \quad (112)$$

The thermodynamic functions of mixing are of considerable interest to the study of miscibility behaviour. The system of triethylamine and water, for example, shows a lower critical solution temperature below which the components are miscible in all proportions in the liquid state. Lower consolute temperature or upper consolute temperature of binary

solutions may be interpreted thermodynamically in terms of the behaviour of the excess functions.

I.C Conductance of Electrolyte Solutions

1. Theories of Conductance of Strong Electrolytes

Kohlrausch⁽²⁴⁾ observed that the equivalent conductances of strong electrolytes at low concentrations varied linearly with the square root of their concentrations, decreasing as their concentrations increased. Extrapolation of the resulting straight lines gave values of the limiting conductance Λ° , i.e., the sum of the ionic conductances by Kohlrausch law of the independent migration of ions⁽²⁵⁾. Thus the equivalent conductance could be represented by the Kohlrausch equation in very dilute solutions

$$\Lambda = \Lambda^\circ - A\sqrt{c} \quad (113)$$

where A is an empirical constant.

Debye and Hückel^(26,5) were the first to give a theoretical approach to interpreting the dependence of equivalent conductance on concentration. They supposed that the ions were under the influence of an external field, and that there were two effects which caused changes in the ionic atmosphere and gave rise to a decrease in the velocities of the ions. These are the electrophoretic effect and the relaxation effect.

In an applied field when a central ion in an ionic atmosphere travels through a viscous medium made up of solvent molecules, the neighbouring solvent molecules under the influence of the electric field of the central ion tend to drag along with them the moving ion as a result of solvation. At the same time, the oppositely charged ions in the vicinity of the central ion move in an opposite direction and experience an upstream of the solvent molecules. Such an effect, causing a decrease

in velocity and hence the conductance of an ion, is called the electrophoretic effect. It is dependent on the concentration, the nature of the ions, the viscosity of the solvent, its dielectric constant and temperature.

In the absence of the external field, the ionic atmosphere on the time average is spherically symmetrical about the central ion. If the latter is suddenly moved by an applied field, the ionic atmosphere tends to move with it, but the readjustment of the ionic atmosphere to the new condition is not instantaneous. Therefore there is a certain time called the relaxation time during which the central ion is off-centered, and is subject to a restoring force. Such an effect of retardation of ionic mobility due to unsymmetrical ionic atmosphere is called the relaxation effect. This purely electrostatic effect is independent of the viscosity of the medium, but is influenced by the concentration of electrolyte, its valence type, ionic mobilities, dielectric constant of the solvent and the temperature.

Assuming a model of point charge for the ion, that the solvent is a dielectric continuum, that the ionic atmosphere satisfied the Maxwell-Boltzmann distribution law and that the viscosity of the solution is equal to that of the solvent, Debye and Hückel⁽²⁶⁾ were able to give a first approximation formula for the ionic conductance of strong electrolyte solutions, and to demonstrate theoretically that the equivalent conductance should be a linear function of the square root of the concentration, in agreement with the empirical relation of Kohlrausch.

Debye and Hückel in their formulation of the conductance problem did not consider the thermal motion of the ions, furthermore, when calculating the electrophoretic effect, they had to use Stokes' law⁽²⁷⁾ for

the motion of the ions. The classical theory of Stokes is applicable to the motion of large sphere through a continuous medium. It is doubtful if the same law is still valid for the microscopic ions of sizes comparable to that of the solvent molecules, but, since there was no other satisfactory formula to replace Stokes' law, the same classical theory had to be incorporated into other theories of conductance.

An improved quantitative treatment of the electrostatic theory of electrolytes is due to Onsager^(28,29). By taking the Brownian motion of the ions into account and by calculating the electrophoretic effect for point charged ions, Onsager obtained the following equations for dilute strong electrolyte solutions

$$\Lambda = \Lambda^{\circ} - \left[\frac{2.801 \times 10^6 |z_1 z_2| q \Lambda^{\circ}}{(DT)^{3/2} (1 + \sqrt{q})} + \frac{41.25 (|z_1| + |z_2|)}{\eta_0 (DT)^{1/2}} \right] \sqrt{I} \quad (114)$$

$$q = \frac{|z_1 z_2|}{|z_1| + |z_2|} \frac{\Lambda_1^{\circ} + \Lambda_2^{\circ}}{|z_1| \Lambda_1^{\circ} + |z_2| \Lambda_2^{\circ}} \quad (115)$$

where η_0 is the viscosity of the solvent in poises; Λ_1° and Λ_2° are the limiting cationic and anionic conductances, the numerical values are derived from the combinations of the universal constants, i.e. Faraday, Avogadro number, Boltzmann constant and unit ionic charge quantity. Other symbols have their usual significance.

The first term in the parentheses is the contribution from the relaxation effect, and the remaining one arises from the electrophoretic effect.

For 1:1 electrolytes, $q = \frac{1}{2}$, the above expression can be written as

$$\Lambda = \Lambda^{\circ} - (B_1 \Lambda^{\circ} + B_2) \sqrt{c} \quad (116)$$

with

$$B_1 = \frac{8.204 \times 10^5}{(DT)^{3/2}} \quad (117)$$

and

$$B_2 = \frac{82.49}{\eta_0 (DT)^{1/2}} \quad (118)$$

Validity of the Onsager's equation has been extensively tested by precise experimental studies. For 1:1 electrolytes in aqueous solutions, the calculated values generally agree with the experimental values within 0.1% below about 0.001 molar. For salts of other valence type, the theory is applicable to solutions of concentrations much below $c = 0.001$. Moreover, in solvents of low dielectric constants, the predicted equivalent conductances fall off with concentrations more rapidly than in water, as confirmed by experimental results. That Onsager's equation does not hold for higher concentrations is to be expected, because in the derivation of the equation simplifications were made, higher terms in mathematical series were truncated, and such complications as interaction between electrophoretic and relaxation effects were not considered. However, it suffices to say that the theory is able to represent the limiting slopes of conductance curves for strong electrolytes in vanishingly low concentrations.

Empirical and theoretical extensions of the Onsager equation have been made by others. An early empirical formula proposed by Walden⁽³⁰⁾

$$\Lambda = \frac{\Lambda^\circ}{1 + B'\sqrt{c}} \quad (119)$$

was intended solely for the convenience of presentation of data in dilute solutions up to $c = 0.01$. The Lattey equation⁽³¹⁾ of the form

$$\Lambda = \Lambda^\circ - \frac{A'\sqrt{c}}{1 + B'\sqrt{c}} \quad (120)$$

with adjustable parameters including Λ° was fairly successful at concen-

trations below 0.1N. An added term, Dc in the above expression, added by Jones and Dole⁽³²⁾, was adequate to describe their data for Barium chloride up to 2N, within small error. However, for a given electrolyte all the empirical relations⁽³²⁾ gave different values of Λ° , and the limiting slopes were different in general from each other and from the limiting slope of Onsager. Onsager⁽²⁸⁾ found that his limiting law could be extended to somewhat higher concentration of 1:1 electrolytes by the use of the formula

$$\Lambda = \Lambda^\circ - (B_1 \Lambda^\circ + B_2) \sqrt{c} + Dc \quad (121)$$

Shedlovsky⁽³³⁾ also proposed another formula which avoided the empirical parameter D . He found that the conductance of 1:1 strong electrolytes in water up to $c = 0.01$ might be accurately represented by

$$\Lambda = \Lambda^\circ - \frac{\Lambda}{\Lambda^\circ} (B_1 \Lambda^\circ + B_2) \sqrt{c} \quad (122)$$

His equation can be written in the form of power series in $c^{1/2}$ with coefficients readily obtainable from B_1 , B_2 and Λ° . Another more useful expression was proposed by Shedlovsky⁽³⁴⁾. On rearranging the Onsager limiting law into

$$\Lambda^\circ = \frac{\Lambda + B_2 \sqrt{c}}{1 - B_1 \sqrt{c}} \quad (123)$$

he observed the quantity on the right hand side was linear with respect to the concentration c up to about 0.1 for 1:1 strong electrolytes. By adding a term Dc into the above equation, the extended form is

$$\frac{\Lambda + B_2 \sqrt{c}}{1 - B_1 \sqrt{c}} = \Lambda^\circ + Dc \quad (124)$$

or

$$\Lambda = \Lambda^\circ - (B_1 \Lambda^\circ + B_2) \sqrt{c} + Dc - DB_1 c^{3/2} \quad (125)$$

where D is an empirical constant, incidentally having a value not far

from the factor $(B_1 \Lambda^{\circ} + B_2)$. Later he found⁽³⁵⁾ that the equivalent form of the above equation for strong electrolytes of other charge types was not adequate, and proposed the following form

$$\frac{\Lambda + B_2 \sqrt{c}}{1 - B_1 \sqrt{c}} = \Lambda^{\circ} + D_1 c + D_2 c \log c - D_3 c^2 \quad (126)$$

where D's are empirical constants. When this equation was applied to sodium chloride, the agreement between the calculated and experimental values was within 0.04% up to $c = 0.2$.

It was not until the 1950's that other versions of conductance theory with ionic size parameter $\overset{\circ}{a}$ were taken up. Falkenhagen, Leist and Kelbg⁽³⁶⁾ used the Eigen-Wicke distribution function⁽³⁷⁾ and derived their relaxation effect for hard sphere ions. A later version of Falkenhagen and Leist conductance equation⁽³⁸⁾ with viscosity correction is

$$\Lambda = \left(\Lambda^{\circ} - \frac{\varepsilon^2}{3DkT} \frac{\kappa \Lambda^{\circ}}{1 + \kappa \overset{\circ}{a}} \frac{q}{(1 + \sqrt{q})(1 + \kappa \overset{\circ}{a} \sqrt{q})} - \frac{n \varepsilon^2}{3\pi \eta_0} \frac{1000}{9 \times 10^{11} c} \frac{\kappa}{1 + \kappa \overset{\circ}{a}} \right) \frac{\eta_0}{\eta} \quad (127)$$

In this equation $\frac{\eta}{\eta_0}$ is the relative bulk viscosity of the solution; ε is the charge on the proton in electrostatic unit; k is the Boltzmann constant; $\frac{1}{\kappa}$ is the Debye-thickness of the ionic atmosphere; $q = \frac{1}{2}$ for 1:1 electrolyte, and n is the number of ions per ml of solution. The agreement of the formula with measured values for alkali halides is good up to several moles per litre. A final version given by Falkenhagen⁽³⁹⁾ for 1:1 electrolytes is

$$\Lambda = \Lambda^{\circ} - \frac{\varepsilon^2 \Lambda^{\circ}}{3DkT} \frac{0.2929 \kappa}{(1 + \kappa \overset{\circ}{a}) \left(1 + \frac{\sqrt{2}}{2} \kappa \overset{\circ}{a} + \frac{1}{6} \kappa^2 \overset{\circ}{a}^2\right)} - \frac{\varepsilon^2 N_a}{27\pi \times 10^{11} \eta_0} \frac{\kappa}{(1 + \kappa \overset{\circ}{a})} \quad (128)$$

Falkenhagen contended that this expression was on sound theoretical ground as long as $\kappa \overset{\circ}{a} \ll 1$, and for solutions of high concentrations a viscosity correction $\frac{\eta_0}{\eta}$ must be introduced.

Robinson and Stokes⁽⁴⁰⁾ took the Onsager limiting expression and divided it by $(1 + \kappa \overset{\circ}{a})$ to allow for the finite ion size. The expression

$$\Lambda = \Lambda^{\circ} - \frac{B_1 \Lambda^{\circ} + B_2}{1 + \kappa \overset{\circ}{a}} \sqrt{c} \quad (129)$$

gives a fair account of conductance data for 1:1 electrolytes up to about 0.1N with $\overset{\circ}{a}$ in the range 3 to 5.5 Å.

By adopting Falkenhagen's expression for the relaxation effect⁽³⁶⁾ and the conventional Boltzmann distribution function instead of Eigen and Wicke, Wishaw and Stokes⁽⁴¹⁾ obtained the following equation for 1:1 electrolytes

$$\Lambda = \frac{\eta_0}{\eta} \left(\Lambda^{\circ} - \frac{B_2 \sqrt{c}}{1 + B_2 \overset{\circ}{a} \sqrt{c}} \right) \left(1 - \frac{B_1 \sqrt{c}}{1 + B_2 \overset{\circ}{a} \sqrt{c}} F \right) \quad (130)$$

with

$$F = \frac{e^{0.2929 B_2 \overset{\circ}{a} \sqrt{c}} - 1}{0.2929 B_2 \overset{\circ}{a} \sqrt{c}} \quad (131)$$

The equation is found to fit experimental data, such as for ammonium chloride⁽⁴¹⁾ up to $c = 5$ at 25° using $\overset{\circ}{a} = 4.35$ Å.

Pitts⁽⁴²⁾, upon using a fuller solution of the Debye-Hückel equation by Gronwell, La Mer and Sandved⁽⁴³⁾, a different mathematical method of approximation and a different boundary condition but the same continuity equations of Onsager, derived an elaborated conductance equation incorporating the ion size parameter $\overset{\circ}{a}$. It was capable of representing the experimental conductances of some 1:1 electrolytes up to about 0.1 molar.

On the basis of a hard sphere model Fuoss^(44,45) in 1957 derived conductance equation for 1:1 electrolytes having the form

$$\Lambda = \Lambda^{\circ} - S c^{1/2} + E c \log c + J c \quad (132)$$

where S is the limiting slope given previously, E is a constant and only J involves an additional parameter $\overset{\circ}{a}$. Later, Fuoss and Onsager⁽⁴⁶⁻⁴⁸⁾

revised their theories by including effects which had not been considered in the previous theories. As mentioned before, the external field causes an asymmetry in the distribution of oppositely charged ions with respect to the central ion. If the central ion is a cation, there will be a slight excess of anions behind it. Because of the coulombic interaction between the cation and anions, there are more anions striking the cation from behind it than from before it. These collisions will give to the cation a slight component of velocity in the direction of motion. A similar effect applied to a reference anion. The effect which stems from the asymmetry of osmotic pressure depends on the concentration and the parameter Λ^0 , and contributes in part to the coefficient J. Using the Einstein formula⁽⁴⁹⁾ for the effect of the ionic volume on viscosity, Fuoss gave the following results for unassociated symmetrical electrolytes with coefficients more convenient for practical computation,

$$\Lambda = [\Lambda^0 - S c^{1/2} + E c \log c + J c + O(c^{3/2})] / (1 + F c) \quad (133)$$

or
$$\Lambda = \Lambda^0 - S c^{1/2} + E c \log c + J c - \Lambda^0 F c \quad (134)$$

when the solution is dilute and $O(c^{3/2})$ originated from higher order term of the osmosis effect can be neglected. In Equation (133), which justifies the presence of $c \log c$ term in the Shedlovsky's empirical relation the following quantities occur:

$$S = B_1 \Lambda^0 + B_2 \quad (135)$$

$$B_1 = \frac{\epsilon^2 \kappa}{6 D k T (1 + q) c^{1/2}} \quad (136)$$

$$B_2 = \frac{\mathcal{F} \epsilon \kappa}{3 \pi \eta_0 c^{1/2} \times 10^{-8} \bar{v}} \quad (137)$$

$$\bar{v} = \text{velocity of light} \quad (138)$$

$$E = E_1 \Lambda^\circ + E_2 \quad (139)$$

$$0.4343 E_1 = \frac{\kappa^2 a^2 b^2}{24 c} \quad (140)$$

$$0.4343 E_2 = \frac{\kappa a b B_2}{16 c^{1/2}} \quad (141)$$

$$J = \sigma_1 \Lambda^\circ + \sigma_2 \quad (142)$$

$$\sigma_1 = \frac{\kappa^2 a^2 b^2}{12 c} \left[h(b) + 0.9074 + \ln \left(\frac{\kappa a}{c^{1/2}} \right) \right] \quad (143)$$

$$\sigma_2 = B_1 B_2 + \frac{11 B_2 \kappa a}{12 c^{1/2}} - \left(\frac{\kappa a b B_2}{8 c^{1/2}} \right) \left[1.0170 + \ln \left(\frac{\kappa a}{c^{1/2}} \right) \right] \quad (144)$$

$$h(b) = \frac{2b^2 + 2b - 1}{b^3} \quad (145)$$

$$b = \frac{|z_1 z_2| \epsilon^2}{a D k T \times 10^8} = \frac{\epsilon^2}{a D k T \times 10^8} \quad \text{for 1:1 salts} \quad (146)$$

Fc is identical with the Einstein volume term $\frac{5}{2} \varphi$ where φ is the volume fraction of the ions in solution. The factor F can be calculated from viscosity data of solutions by employing the equation

$$\eta = \eta_0 (1 + S_\eta c^{1/2} + Fc) \quad (147)$$

where S_η is the Falkenhagen coefficient. ⁽⁵⁰⁾

If the ion size is small, the term $\Lambda^\circ Fc$ can be ignored. The 1957 conduc-

tance equation with the omission of $F\Lambda^{\circ}c$ term and a claimed range of validity $\kappa a^{\circ} < 0.2$ reproduces experimental data for dilute solutions of 1:1 electrolytes⁽⁵¹⁻⁵⁵⁾ in solvents of high dielectric constants where ion association is slight. If the value of J is derived from experimental data, a° can be evaluated and is comparable to the sum of crystallographic radii.

It should be noted that two kinds of mathematical approximations were made in arriving at the above conductance equation. All terms in the development which would lead to terms of the order $c^{3/2}$ were truncated, and the Boltzmann factor was approximated in the equation of continuity by the first three terms of its power series.

During the early 1960's Fuoss and Onsager⁽⁵⁶⁻⁶⁰⁾ rederived a conductance equation using a more realistic model especially one which included the short-range ion-solvent interaction. Having obtained a new form of equation of continuity which could be integrated with retention of the Boltzmann factor explicitly in its exponential form, they derived the equation for 1:1 electrolytes

$$\Lambda = \Lambda^{\circ} - Sc^{1/2} + E'c \log(6E'_1c) + (L - A\Lambda^{\circ}y_{\pm}^2)c \quad (148)$$

where E' and E'_1 have similar significance to E and E_1 in the previous version; L and A are constants and are functions of a° . For solutions of high dielectric constants, this 1965 equation reduces to the previous one with

$$J = E' \ln(6E'_1) + L - A\Lambda^{\circ} \quad (149)$$

and demonstrates that the 1957 theory is mathematically sound.

In 1967 Fuoss and Hsia⁽⁶¹⁾ accurately reproduced a large number of data for alkali halides of high precision in water up to 0.1 molar by

using a new conductance equation resulting from a recalculated relaxation field with the last term accounting for ion association,

$$\Lambda = \Lambda^{\circ} - S c^{1/2} + E c \log c + A c - B c^{3/2} \quad (150)$$

where S and E are given by the previous theory and Λ° , A and B are constant derived from a least square method. Because A and B are functions of \bar{a} by theory, values of \bar{a} can be calculated. They are all considerably larger than the sums of lattice radii of ions for the salts investigated and clearly must include the diameter of several water molecules. The same \bar{a} predicts the conductance of salt over a wider range of dielectric constant from that of water down to about 12, in contrast to the fact that values of \bar{a} obtainable from the 1965 equation increase with a decrease in dielectric constant⁽⁶⁰⁾. For solutions of high concentration, an empirical term in c^2 is required to extend the fit to about 0.1N.

In 1968 Hsia and Fuoss⁽⁶²⁾ made a revision on the term $c^{3/2}$ of their previous 1967 equation. The resulting equation of Hsia and Fuoss, Pitts equation and the Fuoss-Onsager 1957 equation were reduced to a form similar to Equation (150) by Fernandez-Prini^(63,64) using the same mathematical approximation. The performances of the resulting equations were analyzed and compared on the basis of the same experimental data. The difference of Λ° values between Pitts and Fuoss-Hsia equation was less than 0.04% which was a great improvement when compared with a difference of 0.1% existed between the Pitts and Fuoss-Onsager equations. The curvature of the plot of $(\Lambda_{obs} - \Lambda_{cal} + \Lambda^{\circ})$ vs. concentration became smaller on going from the Fuoss-Onsager equation to Fuoss-Hsia equation. The curvature for Pitts equation was the smallest. The \bar{a} values calculated from the B coefficients in Equation (150) corresponding to Pitts theory, were smaller than those of the Fuoss-Hsia equation. Because Pitts

boundary condition implies a smaller interionic effect for a given ionic size than that in Fuoss and Onsager, in order to account for a given decrease in Λ a smaller ionic size is required by Pitts theory. This is in agreement with the observed Λ^0 values when the two theories are applied to the same electrolyte solution.

Pitts⁽⁶⁵⁾ in 1969 gave a revision of his equation for symmetric electrolytes. The new equation which incorporates minor changes is,

$$\Lambda = \left[\Lambda^0 - \frac{Z^2 \epsilon^2 \kappa}{(1+y)} \left(\frac{N_a 10^9}{3\pi \eta_0 \bar{v}^2} \right) \right] \left[1 - \frac{Z^2 \epsilon^2 \kappa}{3D kT (1+\sqrt{2})(1+y)(\sqrt{2}+y)} \right] - \frac{Z^4 \epsilon^2 \kappa^2}{3D^2 k^2 T^2} \left[\Lambda^0 S_1 - \frac{T_1}{(1+y)} \left(\frac{N_a D kT 10^9}{3\pi \eta_0 \bar{v}^2} \right) \right] \quad (151)$$

$$\eta = \kappa a \quad (152)$$

$$T_1 = T_1(\kappa a) = \frac{3}{4(\sqrt{2}+y)} + \frac{3}{8} \left[\frac{3\sqrt{2} e^{(\beta+1)y}}{(\sqrt{2}+y)} Ei[(\beta+1)y] - 2 e^y Ei(y) \right] \quad (153)$$

$$Ei(t) = \int_t^\infty \frac{e^{-u}}{u} du \quad (154)$$

$$\beta = \frac{1}{\sqrt{2}} \quad (155)$$

$$S_1 = \frac{9\sqrt{2} - 10 + y(3\sqrt{2} + 1) + 2y^2}{8(1+y)^2(\sqrt{2}+y)^2} - \frac{e^y}{4(1+y)} Ei(y) + \frac{7\sqrt{2}}{16} \frac{e^{(2+\beta)y}}{(1+y)^2(\sqrt{2}+y)} Ei[(\beta+2)y] + \frac{\sqrt{2}}{16} \frac{e^{(1+\beta)y}}{(1+y)\sqrt{2}+y} Ei[(\beta+1)y] \quad (156)$$

A comparison of the theories of Fuoss-Onsager and of Pitts was given by Pitts⁽⁶⁵⁾ with respect to the differences in mathematical details, basic equations, hydrodynamic models, boundary conditions, physical effects

and mathematical completeness of the solution of the equations.

Murphy and Cohen^(66,77) improved the results of the Fuoss theories for the coefficients of the terms $c \log c$ and c by including a contribution which had not previously been given. They⁽⁶⁷⁾ also used a higher-order expression for the equilibrium pair distribution function to extend the applicability of the theory to asymmetric electrolytes. All the previous theories of Fuoss are restricted to the case of symmetric electrolytes for the purpose of simplification. The results for the coefficients are complicated. The conductivity formula contains two adjustable parameters Λ° and $b = \frac{|z_1 z_2| \epsilon^2}{\bar{a} D k T \times 10^{-8}}$. Calculation of the b and hence \bar{a} from conductance data seems to be hopeless, judging from the extremely complicated functional form of the coefficient in c . b and Λ° are so chosen as to obtain the best possible agreement between the theoretical expression and experimental results.

Owing to the fact that the two leading theories, i.e., Fuoss et al. and Pitts were derived from different points of views which were possibly complementary to each other, Carman⁽⁶⁸⁾ most recently in a short note proposed a future synthesis of the two theories along the line of the $E c \log c$ term⁽⁶⁸⁾, where E should be given by $(E_1 \Lambda^\circ - 2E_2)$ instead of $(E_1 \Lambda^\circ - E_2)$. If such a complete synthesis is successful, it will be a great reconciliation between the two theories which seem to be mutually exclusive of each other according to subjective view points.

2. Calculation of Dissociation Constants from Conductance Measurements

In the last section the variation of conductance of 1:1 strong electrolyte solutions with concentration, where ion association is insignificant, is given by the general form⁽⁴⁶⁻⁴⁸⁾

$$\Lambda(1 + Fc) = \Lambda_\eta = \Lambda_0 - (B_1 \Lambda^\circ + B_2) \sqrt{c} + E c \log c + Jc \quad (157)$$

for which $ka \ll 0.2$. If ion association exists, especially in solvents of low dielectric constants, where ion pairs can be stabilized through electrostatic effect, or if the solute is a weak electrolyte which ionizes partially, the above expression needs modifications. Although the modification by Fuoss is primarily for ion pair formation, the same are applicable to solutions of weak electrolytes. Since conductance is made possible by free ions in solutions, irrespective of whether the neutral species are actually neutral molecules or ion pairs, the right hand side of Equation (157) should be multiplied by α , the degree of dissociation, and everywhere c replaced by αc , except in the viscosity factor, because neutral molecules or ion pairs also contribute to the Einstein viscosity if the molecule or a member of the pair is large. Hence

$$\Lambda_{\eta} = \alpha \left[\Lambda^{\circ} - (B_1 \Lambda^{\circ} + B_2) \sqrt{\alpha c} + E \alpha c \log \alpha c + J \alpha c \right] \quad (158)$$

In dealing with ion association, it is convenient to speak of the degree of association and association constant, but when dealing with weak electrolytes, it is more appropriate to refer to the degree of dissociation and dissociation constant. However, the two constants, mathematically, are reciprocals of one another. As long as one keeps in mind that they are interconvertible, it is understood that the conductance expression derived for an ion pair is also valid for a weak electrolyte. The degree of dissociation, α , is related to the association constant K_A and the dissociation constant K by

$$\frac{1}{K} = K_A = \frac{(1-\alpha)y'}{\alpha^2 c y_{\pm}^2} \quad (159)$$

or

$$\alpha = \frac{\sqrt{y'^2 + 4K_A c y_{\pm}^2 y'} - y'}{2K_A c y_{\pm}^2} \quad (160)$$

When y' , the activity coefficient of the ion pair or of the neutral molecule is approximated to unity and the square root term is expanded in a series, α becomes (69)

$$\alpha = 1 - K_A c y_{\pm}'^2 + 2 K_A^2 c^2 y_{\pm}'^4 - 5 K_A^3 c^3 y_{\pm}'^6 + \dots \quad (161)$$

On substituting this relation into Equation (158), the product on the right hand side can be given by a sum of series. In the working range usually considered, Λ_{η} can be written (70) as

$$\begin{aligned} \Lambda_{\eta} &= \Lambda^{\circ} - (B_1 \Lambda^{\circ} + B_2) \sqrt{\alpha c} + E \alpha c \log \alpha c + J \alpha c - K_A \Lambda_{\eta} c y_{\pm}'^2 \\ &= \Lambda^{\circ} - (B_1 \Lambda^{\circ} + B_2) \sqrt{\alpha c} + E \alpha c \log \alpha c + J \alpha c - \frac{1}{K} \Lambda_{\eta} c y_{\pm}'^2 \end{aligned} \quad (162)$$

This is the expression for conductance of electrolytes where ion pair formation or incomplete dissociation exists.

Although the theoretical values of the ion association constant are related to the charges of the ions, their sizes and solvent properties, by the Bjerrum theory (71) or, more correctly, the Fuoss theory (72), these theories are not applicable to weak electrolytes, such as organic acids and bases. A neutral acid molecule in solution is an aggregate of atoms held together by covalent bonds, and this defies the capability of the electrostatic theory. In a solution of a weak base, such as ammonia, the neutral species are NH_3 in majority and NH_4OH in minority (73), and the charge carriers are ammonium and hydroxyl ions. The real mechanism of formation of NH_4OH in aqueous solution is still open to question. Even if a fraction of NH_4OH molecules does arise from ion association, the association theories are unable to account for all the effects of equilibria that give rise to NH_4OH . Therefore it is futile to apply the theory of ion association to the calculation of dissociation constants

for weak electrolytes. Since the conductance method only gives the fraction of charge conducting particles expressed in the form of stoichiometric concentration c , the dissociation constant derived from it is an overall constant in terms of the activities of the starting materials, e.g., amine and water in this work, irrespective of whether there is any equilibrium leading to the formation of an intermediate compound Amine- H_2O or not.

The experimental values of dissociation constants based on conductance measurement may be obtained in many ways, depending on the magnitude of K and the mathematical methods employed. They all stem from the Ostwald dilution law with modification of the Arrhenius theory. According to the Arrhenius theory⁽⁷⁴⁾, the degree of dissociation of a weak electrolyte at concentration c is

$$\alpha = \frac{\Lambda}{\Lambda^0} \quad (163)$$

on the assumption that the ionic mobilities do not change with the concentration. If the above relation is substituted into the mass action expression

$$K = \frac{\alpha^2 c \gamma_{\pm}^2}{(1-\alpha) \gamma'} \quad (164)$$

one obtains the Ostwald dilution law in the form of Kraus and Bray⁽⁷⁵⁾, who neglect the activity coefficients,

$$\frac{1}{\Lambda} = \frac{1}{\Lambda^0} + \frac{c\Lambda}{K\Lambda^0{}^2} \quad (165)$$

According to this equation, a plot of $\frac{1}{\Lambda}$ against $c\Lambda$ gives $\frac{1}{\Lambda^0}$ as the intercept and $\frac{1}{K\Lambda^0{}^2}$ as the slope, and hence K . Such a plot is linear only at extreme dilution, because of the neglect of long range interaction upon the conductance and of the activity coefficient.

Fuoss⁽⁷⁶⁾ made use of the reduced form of Equation (158), i.e.

$$\Lambda = \alpha \left[\Lambda^\circ - (B_1 \Lambda^\circ + B_2) \sqrt{\alpha c} \right] \quad (166)$$

to calculate Λ° and K . This expression is in third power of $\alpha^{1/2}$ and is difficult to solve explicitly for Λ° and K simultaneously. Fuoss⁽⁷⁶⁾ used the method of successive approximation. For a first approximation, the Arrhenius value for α is substituted into the square root term of Equation (166) to give

$$\alpha_1 = \frac{\Lambda}{\Lambda^\circ - \frac{(B_1 \Lambda^\circ + B_2) \Lambda^{1/2}}{\Lambda^{\circ 1/2}}} \quad (167)$$

A second approximation α_2 is then obtained by substituting α_1 for α in the Onsager term of Equation (166),

$$\alpha_2 = \frac{\Lambda}{\Lambda^\circ \left[1 - \frac{(B_1 \Lambda^\circ + B_2) c^{1/2} \alpha_1^{1/2}}{\Lambda^\circ} \right]} \quad (168)$$

Repeating this process gives a convergence to the correct value of α .

The final result for α is

$$\alpha = \frac{\Lambda}{\Lambda^\circ F(\zeta)} \quad (169)$$

where $F(\zeta)$ is the continued fraction

$$\begin{aligned} F(\zeta) &= 1 - \zeta (1 - \zeta (1 - \zeta (1 - \dots)^{-1/2})^{-1/2})^{-1/2} \\ &= \frac{4}{3} \cos^2 \left[\frac{1}{3} \cos^{-1} \left(-\frac{3}{2} \zeta \right) \right] \end{aligned} \quad (170)$$

with

$$\zeta = \frac{(B_1 \Lambda^\circ + B_2) c^{1/2} \Lambda^{1/2}}{\Lambda^{\circ 3/2}} \quad (171)$$

Fuoss has tabulated numerical values of $F(\zeta)$ ⁽⁷⁶⁾ in the range $0 \leq \zeta \leq 0.209$ so that once $F(\zeta)$ is found, α can be calculated by means of Equation

(169). Substituting Equation (169) in Equation (164) and rearranging gives

$$\frac{F(\zeta)}{\Lambda} = \frac{1}{\Lambda^{\circ}} + \frac{c \Lambda y_{\pm}^{\prime 2}}{K \Lambda^{\circ 2} F(\zeta) y'} \quad (172)$$

in which y_{\pm}^{\prime} can be estimated from the Debye-Hückel expression or its extended equation, if there are no available data, and y' , the activity coefficient of the neutral molecule is approximated as unity. The above expression shows that a plot of $\frac{F(\zeta)}{\Lambda}$ vs. $\frac{c \Lambda y_{\pm}^{\prime 2}}{F(\zeta)}$ determines $\frac{1}{\Lambda^{\circ}}$ and $\frac{1}{K \Lambda^{\circ 2} y'}$ as the intercept and slope respectively, and hence Λ° and K .

In order to proceed with this method, it is necessary to know the value of Λ° first for the calculation of ζ . A starting value of Λ° may be obtained by free hand extrapolation of the conductance data. An improved value of Λ° can be obtained from the above mentioned plot. This process is repeated until a final value of Λ° is found satisfying Equations (169) and (171), and then K is derived from the plot on the basis of the last obtained Λ° .

An alternate but better method for values of Λ° and K was proposed by Shedlovsky⁽³³⁾. By writing his empirical equation, i.e. Equation (122) in the form

$$\frac{1}{\Lambda} = \frac{1}{\Lambda^{\circ}} + \frac{(B_1 \Lambda^{\circ} + B_2)}{\Lambda^{\circ 2}} \sqrt{c} \quad (173)$$

he defined α as

$$\alpha = \frac{\Lambda}{\Lambda^{\circ}} + \frac{(B_1 \Lambda^{\circ} + B_2) \Lambda}{\Lambda^{\circ 2}} \sqrt{\alpha c} \quad (174)$$

This equation is a quadratic function in $\alpha^{\frac{1}{2}}$ and is much simpler to solve than Equation (165). The solution of the Shedlovsky equation for α in terms of the variable ζ is

$$\alpha = \frac{\Lambda}{\Lambda^0} \left[\frac{z}{2} + \sqrt{1 + \left(\frac{z}{2}\right)^2} \right]^2 = \frac{\Lambda}{\Lambda^0} S(z) \quad (175)$$

with

$$S(z) = 1 + z + \frac{z^2}{2} + \frac{z^3}{8} - \frac{z^5}{128} + \dots \quad (176)$$

Values of $S(z)$ in the range $0 \leq z \leq 0.209$ are tabulated by Daggett⁽⁷⁷⁾.

Combination of Equation (175) and the mass action expression gives

$$\frac{1}{\Lambda S(z)} = \frac{1}{\Lambda^0} + \frac{c \Lambda y_{\pm}^2 S(z)}{K (\Lambda^0)^2} \quad (177)$$

By the repeated procedure described in the method of Fuoss, values of Λ^0 and K can be derived from this Shedlovsky method.

Fuoss and Shedlovsky⁽⁷⁸⁾ have shown that values of Λ^0 obtained from both methods are the same, because in the limit, the Shedlovsky equation can be reduced to the Onsager expression. However, K_S and K_F , the dissociation constants obtained from the Shedlovsky and Fuoss methods, differ and are related by

$$\frac{1}{K_S} = \frac{1}{K_F} + \frac{(\beta_1 \Lambda^0 + \beta_2)}{\Lambda^0{}^2} \quad (178)$$

In the range $10^{-3} \leq K \leq 1$, the value of K obtained through the Shedlovsky function is preferable. For $K \leq 10^{-3}$, both procedures give practically the same dissociation constant.

If the Shedlovsky plot involves too far an extrapolation for obtaining Λ^0 , it can be found more accurately by means of the Kohlrausch law.

For example, in the case of amine

$$\Lambda^0 = \Lambda_{\text{Aminium}}^0 + \Lambda_{\text{OH}^-}^0 = \Lambda_{\text{Amine}\cdot\text{HCl}}^0 - \Lambda_{\text{Cl}^-}^0 + \Lambda_{\text{OH}^-}^0 \quad (179)$$

and this is the method I have used.

In dealing with weak acids and bases, experimenters face an important problem as to the solvent correction. The most common way is to subtract the specific conductance of the solvent from that of the solution. This is applicable when the solute is an unhydrolyzed salt which does not change the original specific conductance of the solvent which may contain traces of impurities. If water contains a trace but unknown amount of weak acid impurity and is used as the solvent for a weak base, the amount of salt thus formed is a trace, yet may contribute a considerable portion to the total specific conductance of the solution. If much difficulty arises, it is convenient to handle the appropriate solvent correction in an empirical way developed and used by Shedlovsky and Kay⁽⁷⁹⁾ in their evaluation of the dissociation constant of acetic acid. Their treatment can be generalized to other weak acids and bases.

If L and L_0 are specific conductances of the solution and solvent respectively, Λ is then given by

$$\Lambda = \frac{1000 (L - L_0)}{c} \quad (180)$$

By substituting this expression and the square root of the mass action equation into Equation (175), they obtained⁽⁷⁹⁾

$$1000 L = 1000 L_0 + \frac{\Lambda^0 K^{1/2} c^{1/2}}{S_{(z)} y_{\pm}'} \left[1 - \frac{\Lambda^* S_{(z)}}{\Lambda^0} \left(1 - \frac{L_0}{L} \right) \right]^{1/2} \quad (181)$$

where

$$\Lambda^* = \frac{1000 L}{c} \quad (182)$$

The factor in brackets is not far from unity in most cases. It is a good approximation to use the expression

$$1000 L = 1000 L_0 + \frac{\Lambda^0 K^{1/2} c^{1/2}}{S_{(z)} y_{\pm}'} \left[1 - \frac{\Lambda^* S_{(z)}}{\Lambda^0} \right]^{1/2} \quad (183)$$

A graph of $1000L$ vs $\frac{c^{1/2}}{S(z) \gamma_{\pm}} \left[1 - \frac{\Lambda^* S(z)}{\Lambda^{\circ}} \right]^{1/2}$ gives the solvent correction $1000L_0$ as the intercept and $\Lambda^{\circ} K^{1/2}$ as the slope. If necessary, the resulting L_0 can be used in the calculation of the bracketed term in Equation (181). A subsequent plot of Equation (181) suffices to yield satisfactory value of $\Lambda^{\circ} K^{1/2}$. Therefore K can be computed once Λ° is known.

Λ° can be calculated from using the Kohlrausch law for the relevant limiting conductance data. Often it is required to measure the conductance of a hydrolyzed salt, e.g., NaAc, the pH of the medium being controlled to suppress hydrolysis and derive from it the limiting conductance of the salt in the unhydrolyzed form as illustrated by MacInnes and Shedlovsky⁽⁸⁰⁾.

Another method was devised by Campbell and Bock⁽⁸¹⁾. Their treatment requires the calculation of the degree of hydrolysis ω , from the known value of hydrolysis constant $K_h = \frac{K_w}{K}$ and the stoichiometric concentration of the salt of weak base, viz.,

$$\omega = -\frac{K_h}{2c} + \left[\frac{K_h^2}{4c^2} + \frac{K_h}{c} \right]^{1/2} \quad (184)$$

From ω , the "true" conductance Λ_{corr} may be calculated by means of the relation

$$\Lambda = (1-\omega) \Lambda_{\text{corr}} + \omega \Lambda_{\text{HA}} \quad (185)$$

where Λ is the observed equivalent conductance, Λ_{HA} is the equivalent conductance of the free acid in salt solution. Since $\omega \Lambda_{\text{HA}}$ is necessarily small compared with Λ , Λ_{HA} can be assumed equal to $\Lambda_{\text{HA}}^{\circ}$. Therefore

$$\Lambda_{\text{corr}} = \frac{\Lambda - \omega \Lambda_{\text{HA}}^{\circ}}{1 - \omega} \quad (186)$$

A plot of the values of Λ_{corr} vs. \sqrt{c} gives the corrected limiting con-

ductance of the salt. A similar treatment can also be applied to salts of weak acids.

In the present work to calculate the dissociation constants for amines, at first only the experimental data for the weak base and its hydrochloride salt are known. In order to use the method of Campbell and Bock for the hydrolysis of the salt, it is necessary to have a starting value of K_h from an approximated value of dissociation constant from the data of the base by a free hand extrapolation. Approximated values of Λ_{corr} for the salt are obtained. The resulting values can then be used to calculate the limiting conductance of the salt, and hence the limiting conductance of the base by Kohlrausch principle. This limiting conductance is employed to calculate the dissociation constant for the base by the Shedlovsky and Kay method. Now the dissociation constant is fed back to the procedure of calculating a better hydrolysis correction using Equations (184) and (186). Eventually as the processes of Shedlovsky and of Campbell are repeated, K , K_h and Λ° will converge to the best values.

I.D Theoretical Treatment of Diffusion

Diffusion in solution is an irreversible process by which a difference in concentration is reduced by the spontaneous flow of solute or solvent. In a single electrolyte solution, the solute moves from a higher concentration region to a lower one, and the solvent moves in the opposite direction. From the point of view of molecular kinetics, there is no preference as to the direction in which an individual solute particle moves in the suspending medium. For two adjacent volume elements containing the same number of solute molecules, if a certain number of molecules move along the x direction from one volume element into its adjacent one, the same number of molecules will leave the latter and enter into the

former along the $-x$ direction. If, however, the concentration of the first volume element is greater than that of the second one, then there are more particles leaving the first element and entering the second than there are particles from the second entering the first one. Hence, there is a net transfer of solute in the direction of lower concentration, and a similar process occurs for the solvent molecules, simultaneously, until there is only one concentration throughout the solution. The rate of flow is expected to be approximately proportional to the concentration difference existing between the two volume elements.

The first successful formulation of the diffusion rate was due to Fick(82) who deduced that the force in the diffusion process was analogous to that in heat flow. He observed that the rate of transfer was proportional to the concentration gradient at a given temperature and pressure. For a unidimensional diffusion flow, his first law may be written as

$$J = -D \left(\frac{\partial c}{\partial x} \right) \quad (187)$$

where D is the diffusion coefficient, J is the flux or the rate of material transfer per unit area, and $\frac{\partial c}{\partial x}$ is the rate of increase of concentration with distance x measured in the direction of flow. Usually the direction of flow is taken to be the positive direction of the distance x , the concentration c is expressed in the same units as used in defining the flux, and the volume unit for the concentration c is the cube of the unit of distance x . If J is expressed in moles $\text{cm}^{-2}\text{sec}^{-1}$, and x in cm , then c is expressed in mole cm^{-3} , and D the diffusion coefficient is in units of $\text{cm}^2\text{sec}^{-1}$; it is independent of the mass units used provided that the same units are used in defining J and c . The negative sign in the

first law of Fick makes D a positive quantity, since $\frac{\partial c}{\partial x}$ is negative by virtue of the choice of sign for x which increases as the concentration decreases. Although D appears in the first law as a proportionality constant, experimental measurements show that it is a function of concentration. The main objective for the study of diffusion is to explain such a variation of diffusion coefficient with concentration.

Fick's first law is important in the study of diffusion by steady-state methods in which the concentration gradient $\frac{\partial c}{\partial x}$ does not change with time. For mathematical analysis of diffusion experiments, it is convenient to transform Equation (187) into a form known as Fick's second law. By combining the said equation with the requirement of a continuity of mass over a differential volume element of unit cross-section, the following expression for Fick's second law is obtained

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial c}{\partial x} \right) \quad (188)$$

There is a relation between the diffusion coefficient of an electrolyte and its equivalent conductance, because diffusion and conductivity involve the migration of ions. When Nernst⁽⁸³⁾ originally derived the relation between these two effects for dilute solution, osmotic pressure was regarded as the driving force for diffusion. The modern view regards the gradient of chemical potential, having the dimensions of a force per unit quantity of solute, as the virtual force causing diffusion⁽⁸⁴⁾. For electrolyte solutions, each ion of the diffusing electrolyte is under the influence by two forces, (a) the gradient of chemical potential for the solute and (b) the electrical field produced by the motion of the oppositely charged ions. The more mobile ions tend to diffuse faster than the less mobile ones. They create on a microscopic scale a charge sepa-

ration or a gradient of electrical potential in the solution. This has the effect of increasing the speed of the slower ions and decreasing that of the faster, until finally they have the same speed, since a macroscopic charge separation does not occur.

Let ν_1 and ν_2 be the number of cations and anions respectively resulting from dissociation of a solute molecule, if μ_B is the chemical potential of the solute

$$\mu_B = \nu_1 \mu_1 + \nu_2 \mu_2 \quad (189)$$

where μ_1 and μ_2 are the cationic and anionic chemical potentials. The forces on a cation and an anion due to the gradient of chemical potential are

$$-\frac{1}{N_a} \frac{\partial \mu_1}{\partial x} \quad \text{and} \quad -\frac{1}{N_a} \frac{\partial \mu_2}{\partial x} \quad (190)$$

where N_a is the Avogadro Number. The negative signs are used since the ionic motion is in the direction of decreasing chemical potential. The effect arising from the unequal mobilities of the ions may be represented as an electrical field of intensity E which exerts on each ion an additional force. The total forces are

$$F_1 = -\frac{1}{N_a} \frac{\partial \mu_1}{\partial x} + Z_1 \epsilon E \quad (191)$$

$$F_2 = -\frac{1}{N_a} \frac{\partial \mu_2}{\partial x} + Z_2 \epsilon E \quad (192)$$

where Z_1 and Z_2 are cationic and anionic charges, and ϵ is the unit electronic charge quantity. If u_1 and u_2 are the absolute mobilities of the ions which produce an equal ionic velocity v , then

$$v = u_1 \left(-\frac{1}{N_a} \frac{\partial \mu_1}{\partial x} + Z_1 \epsilon E \right) = u_2 \left(-\frac{1}{N_a} \frac{\partial \mu_2}{\partial x} + Z_2 \epsilon E \right) \quad (193)$$

$$\text{or } \frac{1}{Z_1} \left(\frac{v}{u_1} + \frac{1}{N_a} \frac{\partial \mu_1}{\partial x} \right) = \frac{1}{Z_2} \left(\frac{v}{u_2} + \frac{1}{N_a} \frac{\partial \mu_2}{\partial x} \right) \quad (194)$$

By using the condition for electrical neutrality, $\nu_1 Z_1 + \nu_2 Z_2 = 0$, one obtains

$$\begin{aligned} v &= - \frac{1}{N_a} \frac{u_1 u_2}{\nu_1 u_2 + \nu_2 u_1} \left(\nu_1 \frac{\partial \mu_1}{\partial x} + \nu_2 \frac{\partial \mu_2}{\partial x} \right) \\ &= - \frac{1}{N_a} \frac{u_1 u_2}{\nu_1 u_2 + \nu_2 u_1} \left(\frac{\partial \mu_B}{\partial x} \right) \end{aligned} \quad (195)$$

If c is the concentration of solute in moles per unit volume, then the flux of the solute is

$$J = cv = - \frac{u_1 u_2}{\nu_1 u_2 + \nu_2 u_1} \cdot \frac{c}{N_a} \frac{\partial \mu_B}{\partial c} \frac{\partial c}{\partial x} \quad (196)$$

By comparison of Equation (196) with Equation (187), D results as

$$D = \frac{u_1 u_2}{\nu_1 u_2 + \nu_2 u_1} \frac{1}{N_a} \frac{\partial \mu_B}{\partial \ln c} \quad (197)$$

From the definition of mean molar activity coefficient,

$$\mu_B = \mu_B^\circ + \nu RT \ln c y_{\pm} \quad (198)$$

and the absolute ionic mobilities in units of $\text{cm sec}^{-1} \text{dyne}^{-1}$ expressed in terms of the limiting equivalent conductances, viz.,

$$u_1 = \frac{N_a \lambda_1^\circ}{|Z_1| \mathcal{F}^2} \quad \text{and} \quad u_2 = \frac{N_a \lambda_2^\circ}{|Z_2| \mathcal{F}^2} \quad (199)$$

Equation (197) takes the form

$$D = \frac{\nu \lambda_1^\circ \lambda_2^\circ}{\nu_1 |Z_1| (\lambda_1^\circ + \lambda_2^\circ)} \cdot \frac{RT}{\mathcal{F}^2} \left(1 + \frac{d \ln y_{\pm}}{d \ln c} \right) \quad (200)$$

This is the Nernst-Hartley equation. At infinite dilution, where

$\frac{d \ln y_{\pm}}{d \ln c} = 0$, one obtains the Nernst equation for the limiting value

of the diffusion coefficient,

$$D^{\circ} = \frac{\nu RT}{\nu_1 |z_1| f^2} \frac{\Lambda_1^{\circ} \Lambda_2^{\circ}}{\Lambda_1^{\circ} + \Lambda_2^{\circ}} = 8.9298 \times 10^{-10} T \frac{\nu \Lambda_1^{\circ} \Lambda_2^{\circ}}{\nu_1 |z_1| (\Lambda_1^{\circ} + \Lambda_2^{\circ})} \quad (201)$$

By using the condition for electrical neutrality, alternate equations for the diffusion coefficient are

$$D = \frac{RT}{f^2} \frac{|z_1| + |z_2|}{|z_1 z_2|} \frac{\Lambda_1^{\circ} \Lambda_2^{\circ}}{\Lambda_1^{\circ} + \Lambda_2^{\circ}} \left(1 + \frac{d \ln y_{\pm}}{d \ln c} \right) \quad (202)$$

and

$$D = \frac{RT}{f^2} \frac{|z_1| + |z_2|}{|z_1 z_2|} \Lambda^{\circ} t_1^{\circ} t_2^{\circ} \left(1 + \frac{d \ln y_{\pm}}{d \ln c} \right) \quad (203)$$

where t_1° and t_2° are the transference numbers,

or simply

$$D = D^{\circ} \left(1 + \frac{d \ln y_{\pm}}{d \ln c} \right) \quad (204)$$

The values of $\frac{d \ln y_{\pm}}{d \ln c}$ are obtained by taking the slopes from the plots of experimental values of $\ln y_{\pm}$ against values of $\ln c$.

Since deviation of the theoretical values from the experimental values were observed at low concentrations. Onsager and Fuoss⁽²⁹⁾, and Stokes⁽⁸⁵⁾ added electrophoretic terms Δ_1 and Δ_2 to the above equation. For symmetric electrolytes, the equation is

$$D = \left(1 + \frac{d \ln y_{\pm}}{d \ln c} \right) (D^{\circ} + \Delta_1 + \Delta_2) \quad (205)$$

where

$$\Delta_1 = -\frac{kT}{6\pi\eta} (t_2^{\circ} - t_1^{\circ})^2 \frac{\kappa}{1 + \kappa a} \quad (206)$$

$$\Delta_2 = \frac{kT}{12\pi\eta} \frac{\epsilon^2}{DkT} (\kappa a)^2 \left(\frac{e^{\kappa a}}{1 + \kappa a} \right)^2 \text{Ei}(2\kappa a) \left(\frac{|z|}{a} \right)^2 \quad (207)$$

For 1:1 electrolytes Δ_1 and Δ_2 at 25°C become

$$\Delta_1 = -8.07 \times 10^{-6} (t_2^0 - t_1^0)^2 \frac{\sqrt{c}}{1 + 0.3291 \text{ \AA} \sqrt{c}} \quad (208)$$

$$\begin{aligned} \Delta_2 &= 8.77 \times 10^{-21} (\kappa \text{ \AA})^2 \left(\frac{e^{\kappa \text{ \AA}}}{1 + \kappa \text{ \AA}} \right) \text{Ei}(2\kappa \text{ \AA}) \\ &= 8.77 \times 10^{-21} \phi_2(\kappa \text{ \AA}) \end{aligned} \quad (209)$$

The value of $\phi_2(\kappa \text{ \AA})$ has been tabulated in the range $0 \leq \kappa \text{ \AA} \leq 6$ by Stokes⁽⁸⁵⁾. The theory has been tested on various electrolytes and found that it is obeyed up to $c = 0.01$ with suitably chosen values of \AA .

The above equation for diffusion coefficient can be adopted to 1:1 weak electrolytes with some modifications. If α is the degree of dissociation and u_{12} is the absolute mobility of the neutral molecule, Equation (197) becomes

$$D = \left[\alpha \left(\frac{u_1 u_2}{u_1 + u_2} \right) + (1 - \alpha) u_{12} \right] 2kT \left(1 + \frac{d \ln \gamma_{\pm}}{d \ln c} \right) \quad (210)$$

which leads to

$$D = \left[\alpha (D^0 + \Delta_1 + \Delta_2) + 2(1 - \alpha) D_{12}^0 \right] \left(1 + c \frac{d \ln \gamma_{\pm}}{dc} \right) \quad (211)$$

where D_{12}^0 represents the hypothetical diffusion coefficient of a molecule or ion pair at infinite dilution and is defined by

$$D_{12}^0 = kT u_{12} \quad (212)$$

An equation equivalent to Equation (211) for zinc sulfate was first derived by Harned and Hudson⁽⁸⁶⁾. Their values of α were obtained from conductivity data. The diffusion coefficient D_{12}^0 was calculated from the experimental values of D and α in the concentration range 0.001-0.005 molar. A reasonably constant value of D_{12}^0 was obtained. D_{12}^0 for citric acid⁽⁸⁷⁾ and acetic acid⁽⁸⁸⁾ were also obtained in similar ways.

The previous theories are applicable to dilute solutions where the effects of volume restraint and diffusion of solvent are negligible. For concentrated solutions, the solvent molecules in general move in the opposite direction to that of the solute. Ions may carry with them a permanently attached shell of solvent molecules which become a part of the diffusion solute entity. The viscous force may be considerably modified by the presence of a large number of ions. A quantitative theory for concentrated solutions incorporating the effect of mass-flow was proposed by Hartley and Crank⁽⁸⁹⁾, assuming that there was no volume change upon mixing. For the inter-diffusion of two liquids A and B in a closed vessel of unit cross-section, the diffusion coefficients D_A^V and D_B^V for each species may be defined as

$$J_A = -D_A^V \frac{\partial c_A}{\partial x} \quad ; \quad J_B = -D_B^V \frac{\partial c_B}{\partial x} \quad (213)$$

If \bar{V}_A and \bar{V}_B are the constant volumes in the unit used in defining the concentrations of A and B, then the volume transfers of A and B per unit time across unit area of a fixed plane, say P in the closed vessel are

$$-D_A^V \bar{V}_A \frac{\partial c_A}{\partial x} \quad ; \quad -D_B^V \bar{V}_B \frac{\partial c_B}{\partial x} \quad (214)$$

By defining the cross-section as one across which there is no net transfer of volume, it follows that

$$D_A^V \bar{V}_A \frac{\partial c_A}{\partial x} + D_B^V \bar{V}_B \frac{\partial c_B}{\partial x} = 0 \quad (215)$$

Since c_A and c_B are the number of moles of A and B in unit volume of solute, it follows therefore that

$$\bar{V}_A c_A + \bar{V}_B c_B = 1 \quad (216)$$

and
$$\bar{V}_A \frac{\partial c_A}{\partial x} + \bar{V}_B \frac{\partial c_B}{\partial x} = 0 \quad (217)$$

In order to satisfy Equations (216) and (217) for non-zero volumes, it is necessary that

$$D_A^V = D_B^V = D^V \quad (218)$$

and this defines the mutual diffusion coefficient D^V .

Hartley and Crank further introduced the concept of intrinsic diffusion coefficients D'_A and D'_B for the two components. With reference to Figure 1,

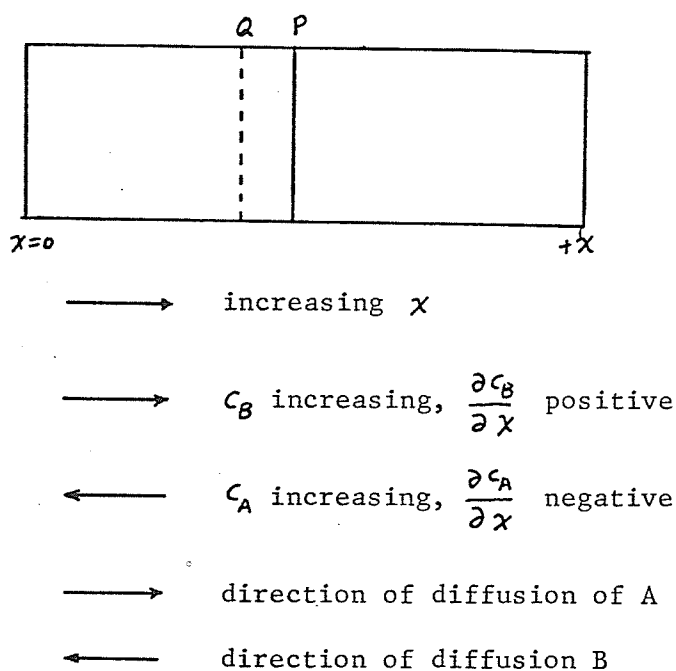


Figure 1. Intrinsic Diffusion

passage of component A through the volume-fixed plane P must necessitate the passage of an equal volume of material in the opposite direction, in order to preserve the fixed volumes on each side of the plane. Thus there is induced a bulk flow of solution across the fixed plane if the vessel is closed. A plane Q moving initially from P may be conceived so that no bulk flow occurs through Q when pure diffusion takes place. The

intrinsic diffusion coefficient is defined in terms of the flux across unit area of such a plane. The flux of A due to intrinsic diffusion of A is given by

$$J_A \left(\begin{array}{l} \text{pure diffusion} \\ \text{in } x \text{ direction} \end{array} \right) = -D'_A \frac{\partial c_A}{\partial x} \quad (219)$$

and similarly for B

$$J_B \left(\begin{array}{l} \text{pure diffusion} \\ \text{in } -x \text{ direction} \end{array} \right) = +D'_B \frac{\partial c_B}{\partial x} \quad (220)$$

The rate of volume swept towards the $-x$ direction by the moving plane Q of unit area is given by

$$\begin{aligned} \frac{\partial v'}{\partial t} &= (J_A \bar{V}_A - J_B \bar{V}_B) \\ &= -\left(\bar{V}_A D'_A \frac{\partial c_A}{\partial x} + \bar{V}_B D'_B \frac{\partial c_B}{\partial x} \right) \end{aligned} \quad (221)$$

The same quantity also represents the bulk flow rate of solution across the plane P per unit area. Then the flux of A due to bulk flow is

$$\begin{aligned} J_A \left(\text{bulk flow in } -x \text{ direction} \right) &= c_A \frac{\partial v'}{\partial t} \\ &= -c_A \left(\bar{V}_A D'_A \frac{\partial c_A}{\partial x} + \bar{V}_B D'_B \frac{\partial c_B}{\partial x} \right) \end{aligned} \quad (222)$$

The net flux of A across unit area of P in x direction therefore is

$$\begin{aligned} \bar{J}_A \text{ (net)} &= J_A \left(\begin{array}{l} \text{pure diffusion} \\ \text{in } x \text{ direction} \end{array} \right) - J_A \left(\begin{array}{l} \text{bulk flow in} \\ -x \text{ direction} \end{array} \right) \\ &= -D'_A \frac{\partial c_A}{\partial x} + c_A \left(\bar{V}_A D'_A \frac{\partial c_A}{\partial x} + \bar{V}_B D'_B \frac{\partial c_B}{\partial x} \right) \end{aligned} \quad (223)$$

Since this flux also defines the mutual coefficient D^V , so one has

$$-D_A^y \frac{\partial c_A}{\partial x} = -D_A' \frac{\partial c_A}{\partial x} + c_A \left(\bar{V}_A D_A' \frac{\partial c_A}{\partial x} + \bar{V}_B D_B' \frac{\partial c_B}{\partial x} \right) \quad (224)$$

By using Equation (215), the above equation is simplified to

$$D^y = D_A' + \bar{V}_A c_A (D_B' - D_A') \quad (225)$$

The intrinsic diffusion coefficient D_A' at finite concentration c_A is then related to its value at infinite dilution $c_A = 0$ by the factor $\frac{d \ln a_A}{d \ln c_A}$ which express the effect of the deviation of the solute from ideal behaviour. The activity in the thermodynamic factor may be expressed in any concentration scale, since the logarithmic differentiation eliminates any constant conversion factor. It is possible that the relative viscosity $\frac{\eta}{\eta_{0B}}$ should be introduced. If A is the solute and B is the solvent, then

$$D_A' = D_{AB}^0 \frac{d \ln x_A f_A}{d \ln c_A} \frac{\eta_{0B}}{\eta} \quad (226)$$

and

$$D_B' = D_{BB}^0 \frac{d \ln x_B f_B}{d \ln c_B} \frac{\eta_{0B}}{\eta} \quad (227)$$

where D_{AB}^0 is the diffusion coefficient of A at infinite dilution in solvent B, and D_{BB}^0 is the self diffusion coefficient or tracer diffusion coefficient of B in pure B. By using the relations

$$c_A = \frac{x_A}{x_A \bar{V}_A + x_B \bar{V}_B} \quad (128)$$

$$x_A + x_B = 1 \quad (229)$$

$$\frac{d \ln c_A}{d \ln x_A} = 1 - \frac{x_A (\bar{V}_A - \bar{V}_B)}{x_A \bar{V}_A + x_B \bar{V}_B} = \frac{\bar{V}_B c_A}{x_A} \quad (230)$$

and
$$\frac{d \ln c_B}{d \ln x_B} = \frac{\bar{V} c_B}{x_B} \quad (231)$$

Equations (226) and (227) can be written as

$$D'_A = D_{AB}^{\circ} \frac{x_A}{\bar{V}_B c_A} \frac{d \ln x_A f_A}{d \ln x_A} \frac{\eta_{oB}}{\eta} \quad (232)$$

and
$$D'_B = D_{BB}^{\circ} \frac{x_B}{\bar{V}_A c_B} \frac{d \ln x_B f_B}{d \ln x_B} \frac{\eta_{oB}}{\eta} \quad (233)$$

Introducing Equations (232), (233) and the Gibbs-Duhem equation, viz.,

$$\frac{d \ln x_A f_A}{d \ln x_A} = \frac{d \ln x_B f_B}{d \ln x_B} \quad (234)$$

into Equation (225), then the mutual diffusion coefficient D^V is

$$D^V = \frac{d \ln x_A f_A}{d \ln x_A} \cdot \frac{\eta_{oB}}{\eta} \left[D_{AB}^{\circ} x_A \left(\frac{1}{\bar{V}_B c_A} - \frac{\bar{V}_A}{\bar{V}_B} \right) + D_{BB}^{\circ} x_B \frac{c_A}{c_B} \right] \quad (235)$$

By using Equation (216) and the relation $\frac{x_A}{x_B} = \frac{c_A}{c_B}$, Equation (235) is simplified to the Hartley-Crank equation,

$$D^V = \frac{d \ln x_A f_A}{d \ln x_A} \frac{\eta_{oB}}{\eta} \left[x_B D_{AB}^{\circ} + x_A D_{BB}^{\circ} \right] \quad (236)$$

By symmetry D^V is also given by

$$D^V = \frac{d \ln x_B f_B}{d \ln x_B} \frac{\eta_{oA}}{\eta} \left[x_A D_{BA}^{\circ} + x_B D_{AA}^{\circ} \right] \quad (237)$$

for which A is the solvent and B is the solute.

The Hartley-Crank theory was further elaborated^(41,90) to account for the possible effect of solvation of the solute B. If B denotes the solvated electrolyte, and A free water, the above equation becomes

$$D^V = \frac{d \ln x_B^{\Delta} f_B^{\Delta}}{d \ln x_B^{\Delta}} \frac{\eta_{oA}^{\Delta}}{\eta} \left[x_A^{\Delta} D_{BA}^{\circ} + x_B^{\Delta} D_{AA}^{\circ} \right] \quad (238)$$

where x_B^Δ and x_A^Δ are mole fractions of solvated solute and free solvent respectively, i.e., the ratio of the diffusing entity to the total number of diffusing entities of both species. Since the diffusion of the ions is restricted by the condition of electrical neutrality, it is permissible to treat the concentration, partial volume, etc., as those of the hydrated electrolyte as a whole, without considering the separate ionic quantities. The only place in Equation (238) where consideration must be given to the fact of ionization is in the expression $d \ln x_B^\Delta f_B^\Delta$. This can be written as $d \ln a_B^\Delta$. Because of the hydration, and for an aqueous solution, $d \ln a_B^\Delta$ is given by

$$d \ln a_B^\Delta = d \ln a_B + h d \ln a_A \quad (239)$$

with $a_B = a_\pm^\nu$, the conventional activity as computed for the unhydrated solute. By the use of the Gibbs-Duhem equation, viz.,

$$d \ln a_A = - \frac{m}{55.51} d \ln a_B \quad (240)$$

Equation (239) becomes

$$d \ln a_B^\Delta = (1 - 0.018hm) d \ln a_B = (1 - 0.018hm)\nu d \ln a_\pm \quad (241)$$

In order that Equation (238) may reduce to the Nernst limiting value as $x_B^\Delta \rightarrow 0$, it is necessary to put $D_{BA}^\circ = \frac{D^\circ}{\nu}$ where the factor ν arises from Equation (241), or more completely $D_{BA}^\circ = (D^\circ + \Delta_1 + \Delta_2)/\nu$; and D_{AA}° becomes the self-diffusion coefficient of water $D_{H_2O}^*$. Therefore, Equation (238) can be written as

$$D^\nu = \frac{D^\circ}{\nu} \frac{d \ln a_B^\Delta}{d \ln m} \frac{d \ln m}{d \ln x_B^\Delta} \left(x_A^\Delta + x_B^\Delta \frac{\nu D_{H_2O}^*}{D^\circ} \right) \frac{\eta_0}{\eta} \quad (242)$$

Substituting the following quantities into the above equation

$$x_B^\Delta = \frac{m}{55.51 - hm + m} = \frac{0.018m}{1 + 0.018m(1-h)} \quad (243)$$

$$\bar{x}_A^0 = \frac{55.51 - hm}{55.51 - hm + m} = \frac{1 - 0.018hm}{1 + 0.018m(1-h)} \quad (244)$$

$$\frac{d \ln a_B^0}{d \ln m} = (1 - 0.018hm) \nu \frac{d \ln a_{\pm}}{d \ln m} \quad (245)$$

$$\frac{d \ln m}{d \ln \bar{x}_B^0} = 1 + 0.018(1-h)m \quad (246)$$

one obtains

$$D^V = D^0 \left(\frac{d \ln a_{\pm}}{d \ln m} \right) (1 - 0.018hm) \left[1 + 0.018m \left(\nu \frac{D_{H_2O}^*}{D^0} - h \right) \right] \frac{\eta_0}{\eta} \quad (247)$$

The diffusion coefficient D^V given by Equation (247) is that which would be obtained if the volume-concentration and flux in the diffusion experiment were computed on the basis of the hydrated solute. However, since the volume-concentration of the electrolyte is unaffected by any consideration of hydration of the ions, it is the same as the diffusion coefficient D obtained by the ordinary computation, with the concentration in moles of anhydrous solute per unit volume, and the flux also is in moles of anhydrous solute per unit cross-sectional area per second.

For 1:1 electrolytes at values of m small enough to justify the omission of the square of $(0.018hm)$, and by including the electrophoretic corrections in the main D^0 factor only, the above equation takes the form,

$$D = (D^0 + \Delta_1 + \Delta_2) \left(1 + m \frac{d \ln \gamma}{d m} \right) \left[1 + 0.036m \left(\frac{D_{H_2O}^*}{D^0} - h \right) \right] \frac{\eta_0}{\eta} \quad (248)$$

Robinson and Stokes⁽⁹¹⁾ have tested Equation (248) using the mean value of the self-diffusion coefficient of water, $2.44 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$,

taken from the work of Partington, Hudson and Bagnall⁽⁹²⁾ and of Wang, Robinson and Edelmann⁽⁹³⁾. From the experimental diffusion coefficients, limiting mobilities, thermodynamic data and assumed values of \bar{a} and hence Δ_1 and Δ_2 , they calculated values of h , the hydration number for a number of 1:1 strong electrolytes. Another set of h values was also obtained by omitting the viscosity factor. It was found that both sets of h values fitted the experimental diffusion data within 0.5% up to 1 molal, using equations with and without viscosity correction respectively. The fact that the values of the first set are about twice those of the second set shows that h is very sensitive to the viscosity factor. Aside from the possibility of an over-correction by the relative viscosity, there are uncertainties inherent in the application of the diffusion equation from a theoretical point of view. The electrophoretic corrections applicable to dilute solutions may be far from valid in concentrated solutions. The self-diffusion coefficient of water varies considerably with salt concentration and this is also a factor neglected in calculating the hydration number. All the inadequacies may be absorbed in the value of h . Thus the real meaning of h is more of a parameter than of a true hydration number.

For 1:1 weak electrolytes or strong electrolytes for which ion-association cannot be neglected in high concentration, the expression for the diffusion coefficient is

$$D = \left(1 + m \frac{d \ln \gamma}{dm}\right) \left[1 + 0.018 m \left(\frac{2 D_{H_2O}^y}{D^0} - h\right)\right] \\ \times \left[\alpha (D^0 + \Delta_1 + \Delta_2) + 2(1-\alpha) D_{12}^0\right] \frac{\eta_0}{\eta} \quad (249)$$

which is the equation used by Wishaw and Stokes⁽⁴¹⁾ to study the diffusion of ammonium nitrate in concentrated solutions. The degree of dissociation was roughly estimated from the conductivity. The value of D_{12}° for the ion pair was taken to be $1.5 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$, from the mobilities of the separate ions, by considering them to merge into an ellipsoid. Assuming that the ammonium nitrate was unhydrated, the diffusion coefficients of the salt calculated from the above expression agreed within 2% with the experimental values, up to 6 molar.

To develop a diffusion equation with hydration effect suitable for this work on the concentrated solutions of amines, it is convenient to regard the degree of ionic dissociation as zero, and the diffusing entity as the predominating hydrated amine molecule. If one starts from Equation (238) and proceeds through the necessary steps for the hydrated amine molecule, one eventually obtains

$$D = D_{BA}^{\circ} \frac{d \ln a_B}{d \ln m} (1 - 0.018 h m) \left[1 + 0.018 m \left(\frac{D_{H_2O}^*}{D^{\circ}} - h \right) \right] \frac{\eta_0}{\gamma} \quad (250)$$

where D_{BA}° is the hypothetical limiting diffusion coefficient of hydrated amine molecule in solvent water, and a_B is the activity, as computed from the unhydrated solute on the convention of binary mixtures. Multiplying out the product in the above expression and neglecting the square term in $(.018 m)$ for not too concentrated solutions, the equation simplifies to

$$D = \frac{\eta_0}{\gamma} \frac{d \ln a_B}{d \ln m} \left[D_{BA}^{\circ} + 0.036 m \left(\frac{D_{H_2O}^*}{2} - h D_{BA}^{\circ} \right) \right] \quad (251)$$

If the theory fits the experimental values of D , according to this equation, a plot of the quantity $D \left(\frac{\gamma}{\eta_0} \right) \left(\frac{d \ln m}{d \ln a_B} \right)$ vs. m will give a straight line with intercept D_{BA}° and slope $0.036 \left(\frac{D_{H_2O}^*}{2} - h D_{BA}^{\circ} \right)$.

From the known values of D_{BA}° and $D_{H_2O}^*$, the hydration parameter h can be calculated.

II NATURE OF THE PROBLEM

This work consisted of measurements of the physical properties of aqueous solutions of mono-, di-, and tri-ethylamine, specifically comprising the investigation of reversible thermodynamic properties by total vapor pressure measurements, liquid-vapor equilibrium composition experiments, and the irreversible thermodynamic properties by the diaphragm cell technique and conductance measurement. Conductivities of dilute solutions of the amine hydrochlorides were also determined to supplement those of amine solutions, so that the degrees of dissociation and the ionization constants of the weak bases might be determined. The viscosities of the mixtures were measured since viscosity was an indispensable factor in the studies of diffusion and conductance. My research was directed to obtaining a comparison of the physical properties among these systems and to correlating them, in order to establish the degree of hydration of the amines. The experimental temperature chosen for the completely miscible systems monoethylamine-water and diethylamine-water was 25°C. Since mixtures of monoethylamine and water containing more than about 70 mole % of amine, boiled at 25°C, as established by this work, measurements were not extended beyond this upper limit; also the extent of liquid-vapor equilibrium experiment at 25°C was confined to the range for which the compositions of the condensed distillates did not exceed the same limit. For the system triethylamine and water, the experimental temperature was 17°C, where they were miscible in all proportions. These liquid systems, notably triethylamine-water and diethylamine-water exhibit lower critical solution temperatures, or in other words, the solubility of one liquid in the other decreases with increasing temperature. They show a common thermodynamic behaviour and this is presumably deter-

mined by the same pattern of molecular interaction in solution. These amines contain nitrogen atoms which can interact with hydroxyl groups of water molecules through hydrogen bonding. Examination of many binary systems in the literature reveals in general that the effect of peculiarities in the behaviour of a compound at the critical region extends into the homogeneous region for large intervals of composition and temperature. The horizontal portion of the vapor pressure-composition isotherm remains practically unchanged at a considerable distance from the critical solution temperature. A study of the total vapor pressure over a binary mixture below its miscibility gap was desired in this research. It was also of interest to investigate to what extent such reversible thermodynamic property influenced the nature of the irreversible processes, especially diffusion, below the lower critical temperature.

III EXPERIMENTAL

III.A Materials1. Conductivity Water

Water of specific conductance in the order of $1 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$ was obtained by passing ordinary distilled water through a Bantam demineralizer model BD-1 with a mixed bed of ion-exchange resins.

2. Amines

The amines were the best commercial products. Triethylamine, monoethylamine and 70 wt.% of monoethylamine in aqueous solutions were obtained from Eastman Organic Chemicals, and diethylamine from the Fisher Co. Triethylamine and diethylamine were refluxed with sodium and sodium hydroxide pellets and were finally distilled. The fractions used distilled at temperatures $83.8^{\circ} \pm 0.5^{\circ} \text{C}$ and $55.7^{\circ} \pm 0.5^{\circ} \text{C}$ for triethylamine and diethylamine respectively. Weighed samples of the distilled amines neutralized the theoretical amount of hydrochloric acid within $\pm 0.2\%$, using methyl red as the indicator. Monoethylamine was used without further purification, because of its volatile nature.

3. Amine Hydrochlorides

The hydrochlorides were prepared from the resulting amines by neutralizing chemically pure hydrochloric acid solutions with slight excess of amines. The excess quantities were expelled by gently boiling off the solution until the condensate did not turn red litmus paper blue. The hydrochlorides were twice recrystallized from conductivity water and dried at 110°C before they were pulverized and kept in desiccator with phosphorus pentachloride as the desiccant.

4. Potassium Chloride

Fisher certified A.C.S. potassium chloride was used without further

purification in calibration of the conductance cells and the diffusion cell. It was dried at 115°C overnight and cooled in a desiccator.

III.B. Preparation and Analysis of Solutions

1. Amine Solutions

Aqueous stock solutions of known concentrations of triethylamine and diethylamine were prepared by mixing conductivity water and amines in known masses. The concentrations in wt.%, mole % and molality were calculated. From the measured densities of the solutions at the experimental temperatures, the molarities were also computed. A stock solution of monoethylamine about 70 mole % in amine was prepared by dissolving the amine in conductivity water. Dilute solutions of monoethylamine were prepared by diluting the stock solution. Their concentrations were determined by volumetric analysis, by neutralizing known weights of amine solutions with standardized hydrochloric acid solutions, the excess of which was back titrated, using standardized sodium hydroxide solutions and methyl red as the indicator. The results of duplicate samples were reproducible within 0.1%. From the densities of the solutions at the experimental temperature, the concentrations in any unit could be obtained. Using methyl orange as the indicator and the analytical procedure given by Welcher⁽⁹⁴⁾ hydrochloric acid solutions of various concentrations from 0.1N to 2N were standardized against reagent grade sodium carbonate which had been heated in an electric furnace at 290°C. Sodium hydroxide solutions of 0.05N and 0.1N were standardized by titration against hydrochloric acid of known concentration using bromothymol blue as the indicator. Very dilute solutions of the amines were made up by diluting dilute solutions of known concentrations on a weight basis.

Weighed samples of solutions of amines after experimental runs of vapor pressure measurements, diffusion measurements, liquid-vapor equilibrium composition determinations and the distillate thereof, were analyzed volumetrically as described above. With the aid of preconstructed graphs of density vs. composition, the concentrations of the solutions in molarity could also be found.

2. Amine Hydrochloride and Potassium Chloride Solutions

Amine hydrochloride solutions for use in conductivity measurements were prepared by dissolving weighed quantities of the salts in conductivity water of known specific conductance. The weighings of the hydrochlorides were made with a microgramatic Mettler balance. Because the hydrochlorides were hygroscopic, especially that of monoethylamine, it was necessary to take a series of readings in weighing against time and extrapolate to zero time when the desiccator was opened, to compensate for the gain in weight, due to adsorption of moisture and the possible drift of the mechanical zero of the balance. Solutions of mass up to about 3 kg. could be weighed by using a solution balance of sensitivity of 10 mg. The densities of the solutions were determined at the experimental temperature and the concentrations in molarity were computed.

Standard potassium chloride solutions for calibration of the conductance cells were prepared by dissolving weighed quantities of the salt in known amounts of conductivity water. For diaphragm cell calibrations, the solutions were made up in a similar manner. The concentrations of the solutions at the end of a diaphragm cell calibration run were calculated from the weights of the potassium chloride residues left in platinum dishes after evaporating the solvent from the weighed quantities of the solutions, and from the density data of the solutions given

by the International Critical Tables.

III.C Thermostats and Baths

Several water baths were used in this research. The vapor pressure measurements were made in a three feet tall cylindrical stainless steel bath with long vertical glass window. This bath permitted the manometer to be immersed completely. A $\frac{1}{2}$ horse power stirrer in series with a powerstat stirred the water very well. The temperature could be controlled at all heights to $\pm 0.005^{\circ}\text{C}$ using a mercury-toluene thermoregulator, a solid state relay, a 125-watt heating source and a cooling coil.

The thermostat for diffusion experiments was a well insulated container of about ten gallon capacity. The temperature control was effected by the use of a Sargent thermonitor of model ST incorporated with an auxiliary relay, a 100-watt heating source and a cooling coil in which water of temperature 2°C below the experimental temperature was circulated intermittently by a low power pump. Stirring was achieved by using a $1/100$ horse power stirrer.

Two water baths side by side were used by liquid-vapor equilibrium composition measurements. The bath in which vapor saturation took place was regulated at the required temperature. Another bath in which pre-saturation was under way was maintained at a slightly higher temperature from 1° to 5°C . Both were controlled effectively by mercury-toluene regulators with solid state relays, stirrers, heating and cooling elements.

For conductance work "Marcol" oil was used as the thermostatic fluid to eliminate extraneous capacity effect⁽⁹⁵⁾. A low wattage heating element and a cooling unit were operated alternately by a relay with a mercury-toluene regulator.

The temperatures of all the baths were determined by Beckmann ther-

mometers which had been calibrated against a standard platinum resistance thermometer using a Mueller bridge. The fluctuation of temperature in all cases was within 0.005°C.

III.D Density Measurements

The densities of the test solutions were determined with Ostwald-Sprengel type pycnometers of approximately 25 ml capacities, calibrated at the required experimental temperatures. Pre-cooled and homogeneous solution was fed into the pycnometer by using a filling bottle and application of a slow stream of compressed air. After the solution was in thermal equilibrium with the bath, the menisci in the capillaries were brought to marks, and the two ends of the capillaries were capped. Water adhering to the wall was removed with acetone. The pycnometer was transferred to the balance case and brought to equilibrium whenever it was possible without spilling due to thermal expansion. In the case of triethylamine-water, weighing was done before the pycnometer was warmed up to room temperature to avoid spilling. Since the calibration of the pycnometer had been done in a closely similar condition, it was believed that there was no significant error introduced in this respect.

III.E Viscosity Measurements

Viscosities of the solutions were measured by means of a Cannon and Fenske type viscometer⁽⁹⁶⁾ with run time for water of about 400 seconds. This type of viscometer is a modification of the Ostwald viscometer in that the upper and lower bulbs lie on the same vertical axis to reduce the error in the mean head caused by deviation of the viscometer from the vertical position. The exact position of the viscometer in the bath was fixed by using a clamp holder. It was calibrated at 17°C and 25°C with run time reproducible within 0.05%.

III.F Vapor Pressure Measurements

The vapor pressure of the solution was measured by a static differential method in which the difference between the vapor pressures of the solution and that of pure water was determined with a differential manometer. This method had been devised by Gibson and Adams⁽⁹⁷⁾, and its technique improved by Shankman and Gordon⁽⁹⁸⁾.

The apparatus used in this work is shown in Figure 2. In this apparatus the original auxiliary flasks containing water, as used by Gibson and Adams to approach equilibrium by condensation of water vapor on the solution, were dispensed with. This was because volatile liquid mixtures, rather than salt solutions, were dealt with in this experiment. It seems appropriate for the auxiliary flask to contain the same test solution as the main flask but, this arrangement had no advantage over the use of one main flask, with extra amount of solution. As long as the solution was in equilibrium with its vapor, and the solution was analyzed after completion of the experiment, there was no need for the subsidiary flasks. The internal diameter of the manometer tubing was 20 mm to avoid capillary effect. Since vacuum pump oil, diethyl phthalate, n-butyl phthalate and other manometer liquids were soluble in the amines, it was necessary to use mercury as the manometer fluid. The heights of the manometer liquid were measured with a cathetometer which could be read to ± 0.05 mm.

At the beginning of the experiment, the solution must be degassed. 30 ml of the solution were placed in the flask of 80 ml capacity. The outgassing was accomplished by freezing the solution in liquid nitrogen, then evacuating until the residual pressure was less than 0.001 mm Hg or 1.0 micron as determined by a McLeod gauge in the vacuum line shown in

Figure 2. Differential Manometer

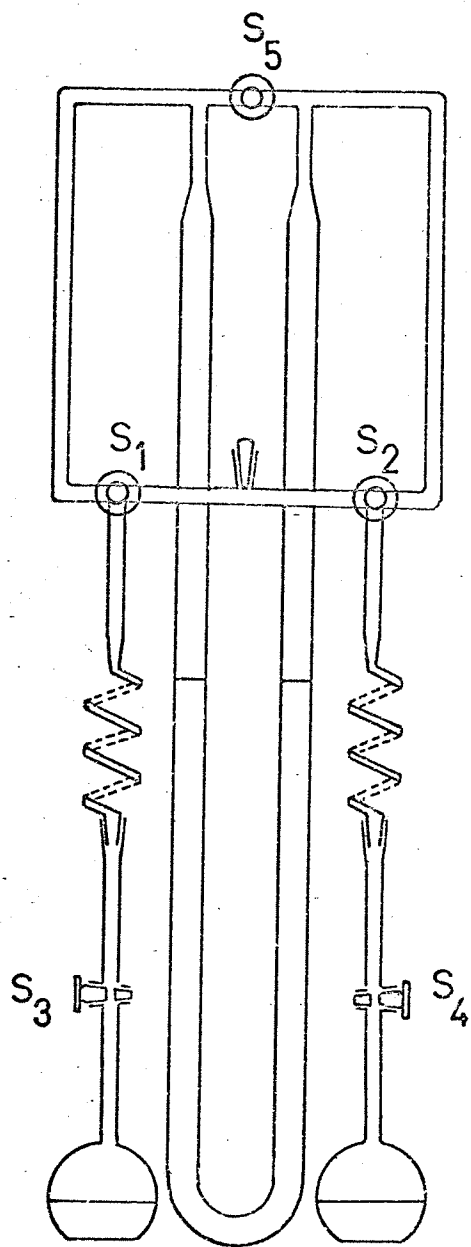


Figure 3. Then the solid was melted, the freezing and evacuating procedure were repeated five times before the flask was detached and mounted to the differential manometer. The same treatment was applied to pure water as the reference liquid in another flask. Having evacuated the manometer to about 1 micron, it was placed in the thermostat. The liquids in the flasks were agitated by magnetic stirring. The stopcock to the solvent, S_4 in Figure 2 was opened. After an hour of equilibration, manometer readings were taken until a steady value was obtained. Finally the stopcock to the solution, S_3 was opened, and the constant difference in pressure after 30 minutes was measured. Stopcocks S_3 and S_4 were closed before the manometer was removed from the bath. Samples of the solution were analyzed and the concentration of the solution in equilibrium with its vapor was determined.

All the vapor pressure measurements in mm Hg were reduced to 0°C by the use of standard formulae. The precision in the measured vapor pressure was within ± 0.1 mm Hg.

III.G Determination of Vapor Compositions

The compositions of the vapors in equilibrium with the liquids of known compositions were determined by an isothermal distillation followed by condensation and analysis of the distillates. The apparatus shown in Figure 4 was essentially that used by Bichowsky and Storch⁽⁹⁹⁾, and Pearce and Snow⁽¹⁰⁰⁾, with slight modifications. It consisted of a series of eight units in the saturator part and eight units in the pre-saturator part. Each unit in the saturator was constructed and used as follows. Nitrogen was fed into the unit through a short central tube "a", tapered down to 2 mm capillary. At the tip of the capillary the stream of nitrogen broke into bubbles which passed up a slightly inclined tube 5 mm in

Figure 3. Vacuum Line

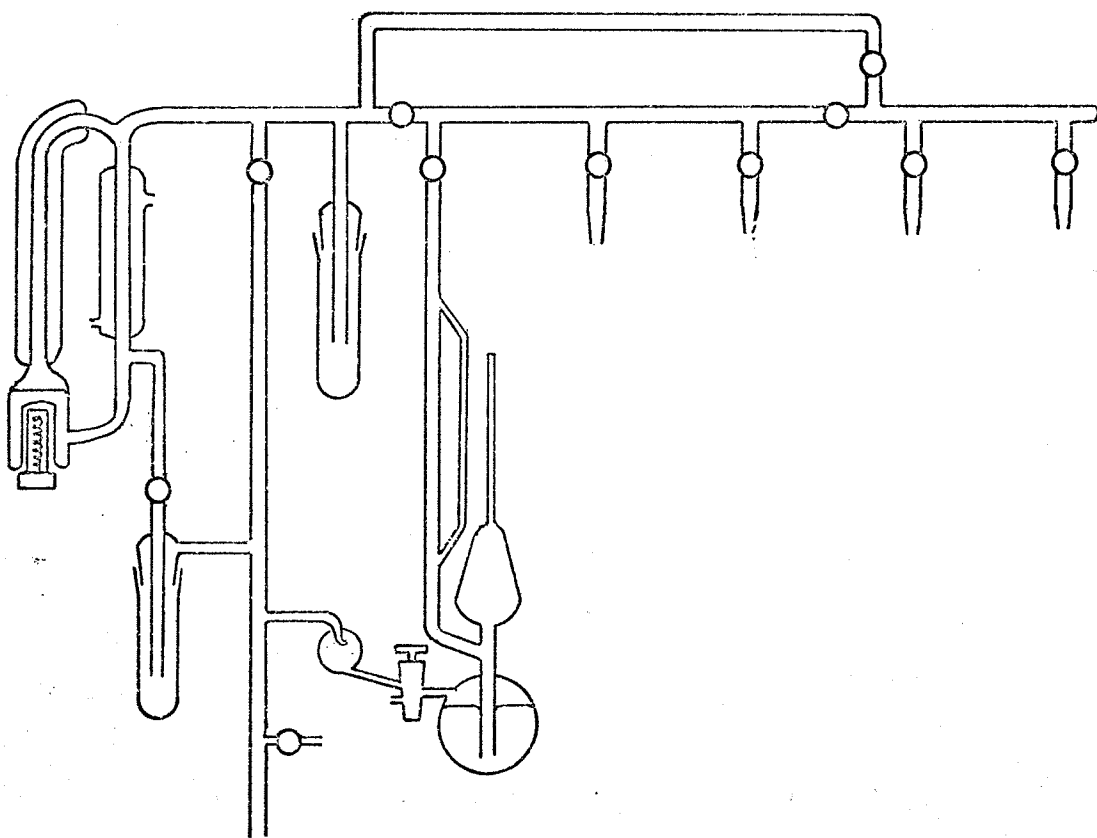
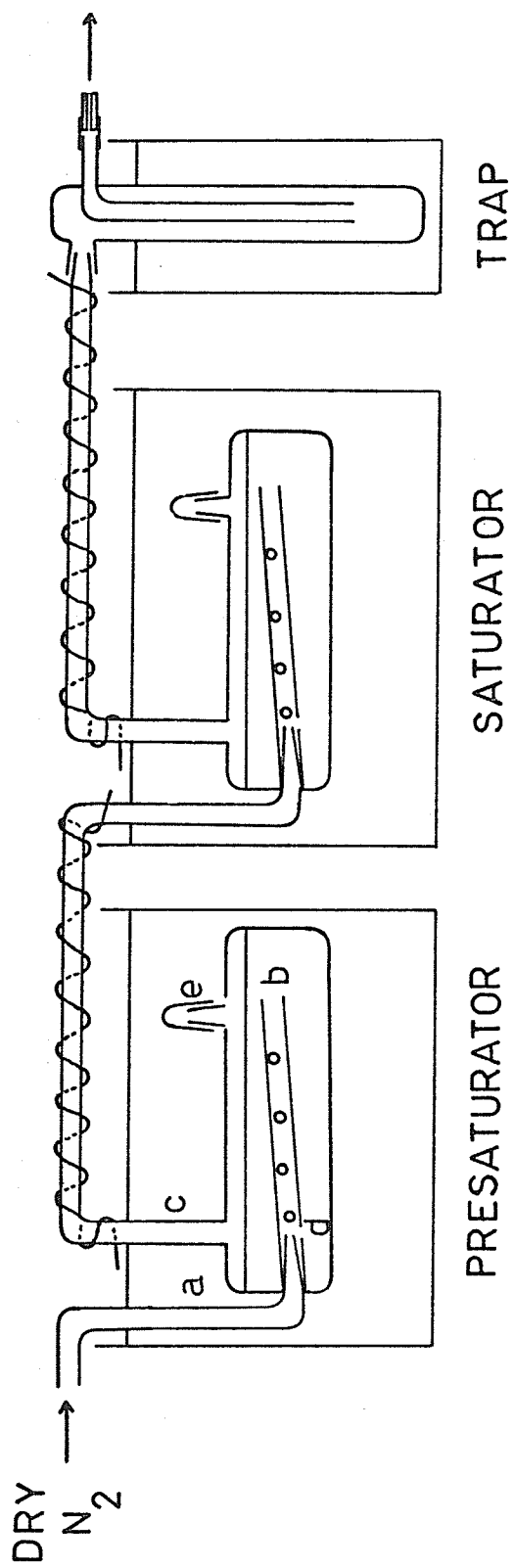


Figure 4. Apparatus for Isothermal Distillation



diameter and 80 mm in length. There was an opening through the lower side of this inclined tube just behind the tip of the capillary. Through the opening liquid was drawn from the bottom of the saturator and carried by the nitrogen bubbles up the slanting tube to the surface of the liquid. This kept the solution circulating and ensured that the nitrogen that came out of the capillary made contact with fresh solution. The gas liberated from the bubbles as they burst then passed back over the surface of the liquid to the tube "c", leading either to the next saturating unit or finally to the trap. This type of saturator had the advantage that the bubbles had to travel in the solution and keep contact with the liquid for a comparatively long duration, so that equilibrium could be approached more effectively. Each tube in the saturator was provided with a vertical tube "e" for filling and emptying. This had a water-tight ground glass cap. The capacity of each saturating unit was 40 ml when filled.

In a typical experiment, nitrogen, having been passed through a dry ice-acetone cold trap to remove moisture, was let into the presaturator at a rate of 3 litres per hour. The presaturator was kept at a temperature from 1 to 5°C above that of the saturator. The choice of the bath temperature for the presaturator was such that there was negligible net accumulation or deficiency of amine in the saturator as found out from analysis of the solution after the experiment was over. The vapor then passed through each unit of the saturator and finally into the trap. Connecting tubes outside the thermostats between two saturators and that leading to the trap were warmed by coils of Nichrome resistance wire heated by a six volt copper oxide rectifier to avoid condensation of the vapor. The trap shown in Figure 4 consisted of a glass tube 200 mm in

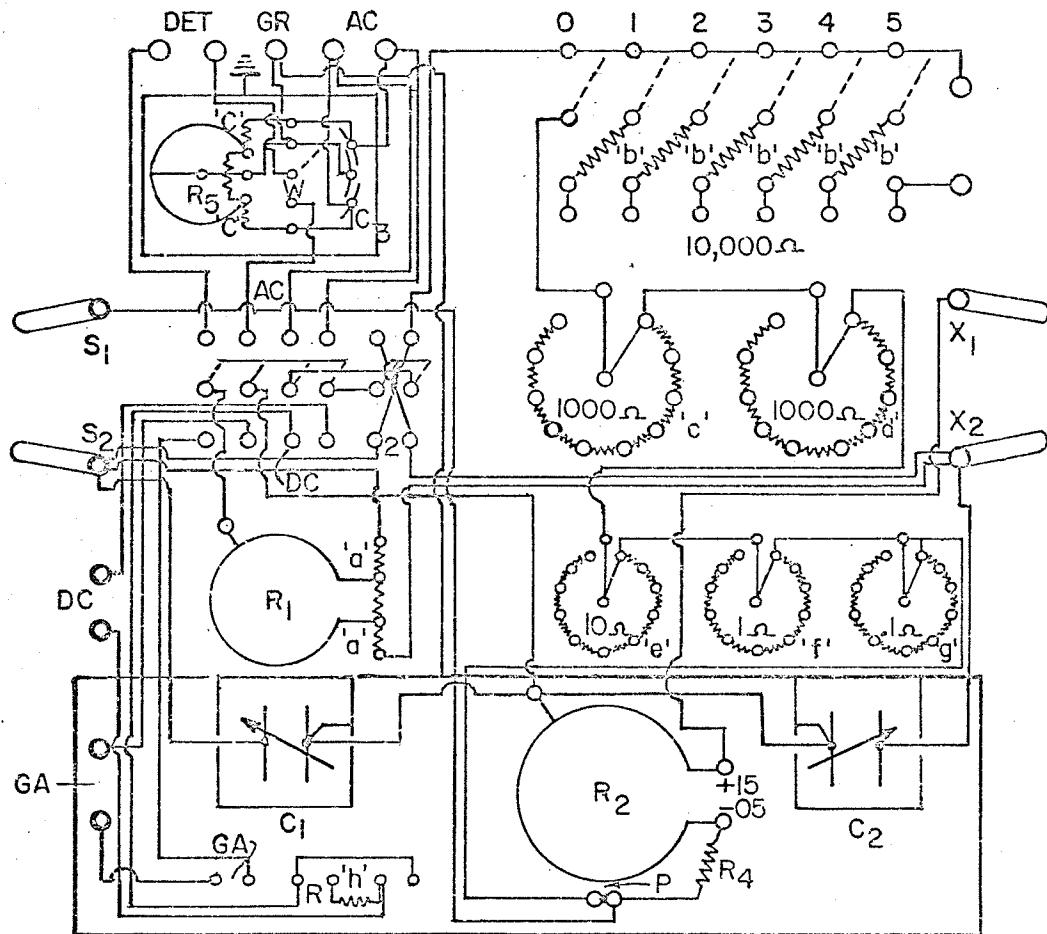
length and 25 mm in diameter with an internal tube 6 mm in diameter. It was fitted with a ground glass joint to permit attachment to, and removal from, the saturator, and was maintained at suitable temperatures in a dry ice-acetone bath for triethylamine-water and liquid nitrogen-ethanol bath for other systems. After about 5 ml of distillate were collected, the distillate and the liquid in the saturator were analyzed. If the concentration of the amine in the saturator did not change by 3% of its original value, the mean value of the initial and final values was taken to be the concentration in equilibrium with the condensed vapor, otherwise a new temperature of the presaturating bath was re-set and the experiment was repeated.

III.H Conductance Measurements

A Leeds and Northrup conductivity bridge shown in Figure 5 was used to measure the resistance of the solution. It was a modified version of the familiar Wheatstone bridge, adapted to alternating current measurement, with inclusion of the "Wagner ground", a device which eliminated the current leakage at the detector terminals. Signals of 1 kilo-cycles per second were generated by an audio oscillator. An oscilloscope in series with a tune amplifier and a frequency filter served as the detector. Measurements of resistance could be made well within one ohm in ten thousands.

Conductance cells of the type recommended by Jones and Bollinger⁽¹⁰¹⁾ were used. They were made of Pyrex glass with the leads and filling tubes sufficiently far apart to eliminate errors due to the Parker effect. A Shedlovsky quartz cell of the original design⁽¹⁰²⁾ was employed for very dilute salt solutions. Polarization errors were reduced by platinization.

Figure 5. Leeds and Northrup Conductivity Bridge



The cell constants were determined by measuring the conductance of solutions of potassium chloride made up to the standards of Jones and Bradshaw⁽¹⁰³⁾.

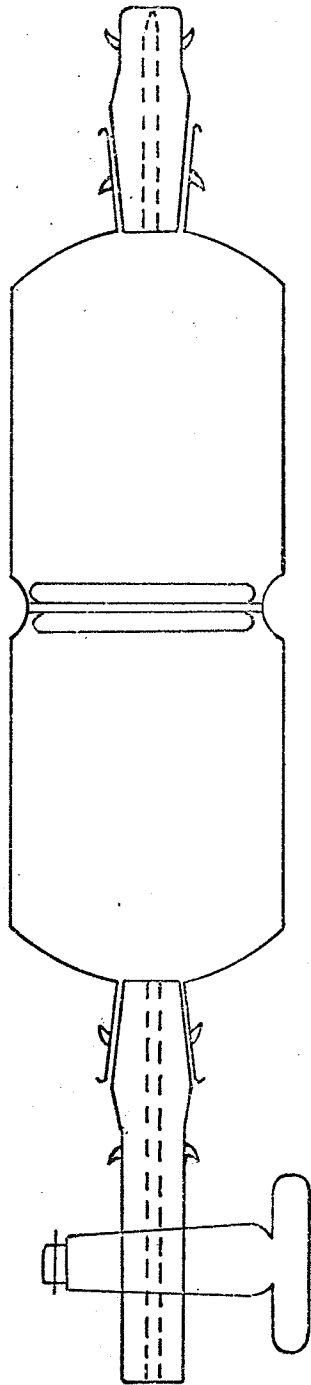
Since the amine solutions had high vapor pressures even when chilled, rinsing the cells with amine solutions would result in changing the original concentrations of the solutions. To minimize this, dry conductance cells were used without being rinsed by the solutions of known concentrations. The errors due to adsorption of amine on platinum electrodes and the possible attack on glass were compensated by plotting the measured resistance against time for two hours and extrapolating the later portion which appeared to be linear back to zero time when the cell was filled.

III.I Diffusion Measurements

The diffusion coefficients were measured by Stokes' magnetically stirred diaphragm cell method⁽¹⁰⁴⁾. The cell is shown in Figure 6. It was made of Pyrex glass and had two compartments each having about 50 ml capacity. The sintered glass diaphragm was of No. 4 porosity, 40 mm in diameter and 2 mm thick. Each compartment contained a stirrer of thin wall glass tubing, 3 mm in diameter and of length slightly less than the diameter of the diaphragm. Inside each stirrer fine iron wires of equal length were sealed. The number of wires sealed were so adjusted that the stirrer in the upper compartment sank and that the lower floated. They made contact only gently with the diaphragm to avoid excessive mechanical wear of the diaphragm. The solutions in the compartments were stirred by the rotating motion of the stirrers driven by a permanent horse shoe magnet outside the cell, to ensure homogeneity and to prevent the formation of stagnant layers on the diaphragm.

A slight modification of Stokes' cell was made. Instead of the

Figure 6. Stokes' Diaphragm Cell



rubber stoppers, the necks of the cell were closed with capillary bore stopcock at the bottom and with a fine-capillary plug at the top. They were provided with teflon sleeves slightly lubricated with high vacuum silicone grease. The evaporation of solvent or solution was negligible.

Removal of all air from the pores of the diaphragm was necessary for all diffusion measurements. In order to effect this removal of air, it was necessary to degas both solvent and solution. In this research the solvent water was degassed by evacuating the flask containing the solvent for a period of half an hour while it was being warmed. Since the compositions of the solutions might change very much from the anticipated values by such a procedure, these solutions were degassed by freezing them in liquid nitrogen, then evacuating for half an hour. The stopcock to the vacuum line was then closed, the contents of the flask melted, and the same procedure of freezing and evacuating repeated. The degassed solvent was then placed in the diffusion cell and about 500 ml of solvent sucked through the diaphragm. The cell was inverted and another 500 ml of degassed solvent was then passed through the diaphragm. After this procedure, the lower compartment was filled with solvent and was stoppered, making sure that there were no bubbles trapped. The upper compartment was half filled with solvent and then evacuated through the neck until the solvent boiled. The vacuum was released abruptly and atmospheric pressure then forced the solvent into the diaphragm pores. This procedure was repeated several times, after which the cell was completely filled with solvent and stoppered.

In order to keep the diaphragm in the degassed condition in all subsequent transfers of solution or solvent to and from the cell compartments, special side-hole pipettes recommended by Janz and Mayer⁽¹⁰⁵⁾ were

employed. In a side-hole pipette, a hole about 1.5 mm in diameter was made approximately 3 mm above the sealed tip. Thus the delivery of liquid was horizontal, not only minimizing the possibility of air bubbles being forced into the diaphragm in rapid solution transfer, but also preventing the disturbance of any linear concentration gradient across the fritted disc in such solution transfer steps.

The diffusion cell was cleaned with hot nitric acid and the volumes of the compartments were measured prior to the diffusion experiment. The total volume of the degassed cell was obtained by weight calibration with water. The volumes of the compartments excluding the diaphragm pores were calibrated with mercury since it did not wet the diaphragm and did not penetrate into the pores due to surface tension. The volume of the diaphragm pores was evaluated from these calibrations. Then the effective volumes of the compartments were calculated.

Before starting the experiment, the solvent and solutions were brought to the experimental temperature. Since the amine solutions had a smaller density than that of water, the former was placed in the upper compartment. First the solvent-filled cell with stirrers was put in an upright position in the thermostat, leaving the neck above the water. After thermal equilibration the capillary plug was removed, and the solvent in the upper compartment removed. Having rinsed this compartment four times each with 25 ml amine solution, it was completely filled and stoppered. The filled cell was aligned between the poles of the horse shoe magnet and the stirring started. At this moment the initial time was noted. The duration of the prediffusion run was determined by the Gordon criterion⁽¹⁰⁶⁾, $\tau \approx \frac{1.2 l^2}{\bar{D}}$, depending on the magnitude of the diffusion coefficient \bar{D} and the thickness of the frit l . The diffusion

data of previous runs gave rough but safe projections of the choice of prediffusion time for subsequent runs, ranging from the order of 2 hours to 15 hours. After the prediffusion period was over, the cell was raised until the upper neck was above the water level. The exposed capillary plug was removed and dried. The solution in the upper compartment was withdrawn. After rinsing it four times, the compartment was filled up with the solution. Again this solution was transferred totally from the compartment and preserved for later analysis. Its concentration found was taken as the initial concentration of the diffusing solution. A final filling with the stock solution followed, and the neck was temporarily stoppered with a short ground glass stopper having a capillary bored stopcock. The cell was then inverted for a short time, the stopper unit of the originally lower compartment was removed and the half cell rinsed and re-filled with fresh solvent. After this half cell was plugged, the entire cell was restored to its original position, with the appropriate compartment up. The temporary stopper was replaced by the fine-capillary plug. The cell was now installed under the magnet. When stirring was started, the diffusion experiment was under way. The time at which the final rinsing with solvent was completed was taken as the zero for timing the diffusion experiment.

When the diffusion experiment was completed, the cell was positioned to expose partially the upper compartment. The solution in this was withdrawn for analysis. The cell was then removed from the bath and inverted. The stopcock on the lower plug was opened, prior to the removal of the plug to avoid sucking back of the liquid from the other side of the diaphragm. Finally, the bottom stopper was removed and the solution withdrawn for analysis. The moment at which the latter compartment was

opened was the end of the diffusion experiment.

The stirring rate within the cell was 60 r.p.m., sufficiently rapid to prevent the formation of stagnant solution layers in the vicinity of the cell diaphragm, since Stokes⁽¹⁰⁴⁾ reported that any rate between 25 to 80 r.p.m. was sufficient. The alignment of the diaphragm cell was such that the diaphragm was in a horizontal plane. According to Stokes⁽¹⁰⁴⁾, deviations of one or two degrees from the horizontal would result in a bulk flow error of less than 0.2% of the total transport, and hence sufficiently accurate alignment of the cell was made by eye.

The diaphragm cell constant β in Equation (260) appearing in the next chapter was calibrated at 25°C by using approximately 1 molar potassium chloride solutions in the lower compartment and pure water in the upper one. The diffusion coefficients of potassium chloride for cell calibration at 25°C have been tabulated by Stokes⁽¹⁰⁷⁾ from the data of Harned and Nuttall⁽¹⁰⁸⁾ and of Gosting⁽¹⁰⁹⁾. Cell constants obtained by diffusing KCl counter-gravitationally to the upper compartment with the cell in normal position and inverted were found to be identical. This indicated that the diaphragm was isotropic with respect to the opposite directions of diffusion. Unfortunately, since the existing diffusion data for potassium chloride and other salts at lower temperature were insufficient, the calibration of the cell at 17°C could not be carried out. I was compelled to use the cell constant at 25°C in the diffusion measurements of triethylamine at 17°C. Considering the formal dependence of the cell constant on the dimensions of the frit and the cell, it was likely that a change in temperature by 8°C would not produce any significant change in the cell constant.

The attrition of the diaphragm due to action of the stirrers, and

the enlargement of the pores from the flow of the liquid in washing and alkaline attack by the amines during experiments caused the cell constant to change with time. Therefore the cell was calibrated once after every three runs, and the cell constant was interpolated for each experimental run.

When all the previously mentioned precautions were applied and the error in analysis was kept below 0.2%, a precision of about $\pm 0.5\%$ in the integral diffusion coefficient defined by Equation (260) could be expected. The concentrations of the test solutions were kept above 0.05 molar because surface transport in the diaphragm would lead to considerable errors below this concentration, as pointed out by Stokes⁽¹⁰⁴⁾.

IV TREATMENT OF EXPERIMENTAL DATA AND RESULTS

IV.A Densities and Relative Viscosities

The densities and relative viscosities, that is, the ratios of viscosities of solutions to those of pure water at the experimental temperatures are given in Tables 1, 2 and 3 as functions of mole fraction, molality and molarity. The relations between the densities and mole fractions of the three systems are presented in Figure 7. The relative viscosities are plotted against molalities in Figure 8 below $m = 12$, and against molarities in Figure 9.

TABLE 1

Densities and Relative Viscosities for the System
Monoethylamine-Water at 25°C

x_B^*	m	c	d	η_{rel}
Mole Fraction Amine	Molality	Molarity	Density	Relative Viscosity
0.0000	0.0000	0.0000	0.9771	1.000
0.0000899	0.00499	0.00497	0.9971	-
0.0001535	0.00852	0.00849	0.9970	1.002
0.003075	0.01707	0.01701	0.9970	1.005
0.0007403	0.04112	0.04091	0.9967	1.011
0.001721	0.0957	0.0949	0.9961	1.020
0.003688	0.2055	0.2025	0.9948	1.043
0.00938	0.5255	0.5064	0.9910	1.111
0.01878	1.062	0.999	0.9855	1.221
0.03965	2.292	2.024	0.9745	1.498
0.06486	3.850	3.159	0.9631	1.445
0.0994	6.12	4.55	0.9488	2.265
0.1319	8.43	5.71	0.9350	2.510
0.1761	11.87	7.08	0.9156	2.595
0.2270	16.30	8.40	0.8936	2.477
0.2934	23.05	9.80	0.8669	2.186
0.3866	34.98	11.32	0.8337	1.708
0.4998	55.47	12.64	0.7986	1.197
0.6639	109.7	13.97	0.7570	0.718

TABLE 2

Densities and Relative Viscosities for the System
Diethylamine-Water at 25°C

x_B^*	m	c	d	η_{rel}
Mole Fraction Amine	Molality	Molarity	Density	Relative Viscosity
0.0000	0.0000	0.0000	0.9971	1.000
0.0001435	0.00796	0.00795	0.9971	1.001
0.0004283	0.02378	0.02366	0.9967	1.005
0.000888	0.04933	0.04897	0.9963	1.016
0.001187	0.0659	0.0654	0.9960	1.030
0.001645	0.0914	0.0904	0.9956	1.033
0.002107	0.1171	0.1157	0.9952	1.050
0.003720	0.2072	0.2029	0.9937	1.080
0.006131	0.3424	0.3313	0.9917	1.134
0.009597	0.5378	0.5117	0.9888	1.225
0.01290	0.7251	0.6791	0.9863	1.309
0.01757	0.9930	0.9099	0.9828	1.439
0.02905	1.661	1.444	0.9752	1.782
0.04580	2.664	2.151	0.9646	2.293
0.06127	3.585	2.733	0.9544	2.696
0.1014	6.264	3.985	0.9276	3.364
0.1442	9.349	5.009	0.9022	3.589
0.2019	14.04	6.052	0.8735	3.424
0.2795	21.54	7.046	0.8426	2.819
0.4050	37.77	8.075	0.8044	1.822
0.5014	55.81	8.576	0.7809	1.274
0.5888	79.49	8.899	0.7629	0.935
0.7023	131.0	9.188	0.7422	0.648
0.8019	224.6	9.361	0.7263	0.493
0.9057	532.8	9.484	0.7115	0.388
0.9504	1062	9.52	0.7054	0.354
1.0000	∞	9.56	0.6989	0.323

TABLE 3

Densities and Relative Viscosities for the System
Triethylamine-Water at 17°C

x_B^*	m	c	d	η_{rel}
Mole Fraction Amine	Molality	Molarity	Density	Relative Viscosity
0.0000	0.0000	0.0000	0.9988	1.000
0.00004694	0.002605	0.002602	0.9898	1.000
0.00007498	0.004162	0.004156	0.9987	1.001
0.0001797	0.00998	0.00995	0.9987	1.001
0.0004150	0.02304	0.02295	0.9985	1.008
0.001238	0.0683	0.0688	0.9978	1.023
0.002134	0.1210	0.1192	0.9969	1.062
0.004069	0.2268	0.2207	0.9953	1.128
0.007294	0.4034	0.3847	0.9926	1.245
0.01542	0.8692	0.7878	0.9861	1.583
0.02346	1.334	1.150	0.9788	1.921
0.03146	1.803	1.480	0.9702	2.257
0.05177	3.031	2.204	0.9502	3.049
0.07935	4.784	2.989	0.9272	3.764
0.1146	7.181	3.757	0.9034	4.031
0.1620	10.73	4.518	0.8782	3.876
0.2313	16.70	5.279	0.8502	3.235
0.3372	28.29	5.999	0.8191	2.142
0.5381	64.66	6.694	0.7809	0.989
0.7107	136.3	6.992	0.7588	0.601
0.7975	218.7	7.087	0.7496	-
1.0000	∞	7.213	0.7299	0.346

Figure 7. Densities of Amine Solutions

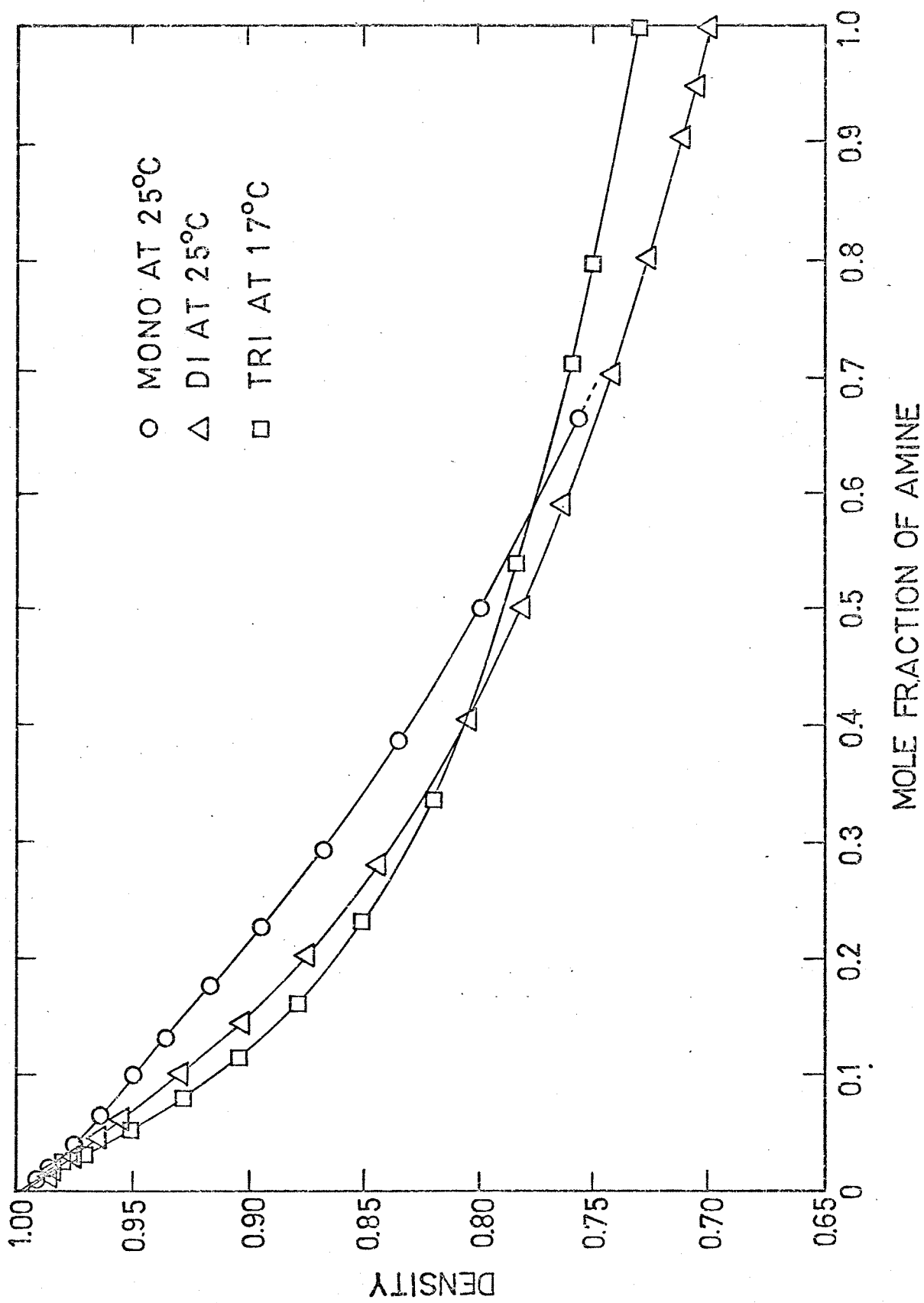


Figure 8. Relative Viscosities of Amine
Solutions vs. Molalities.

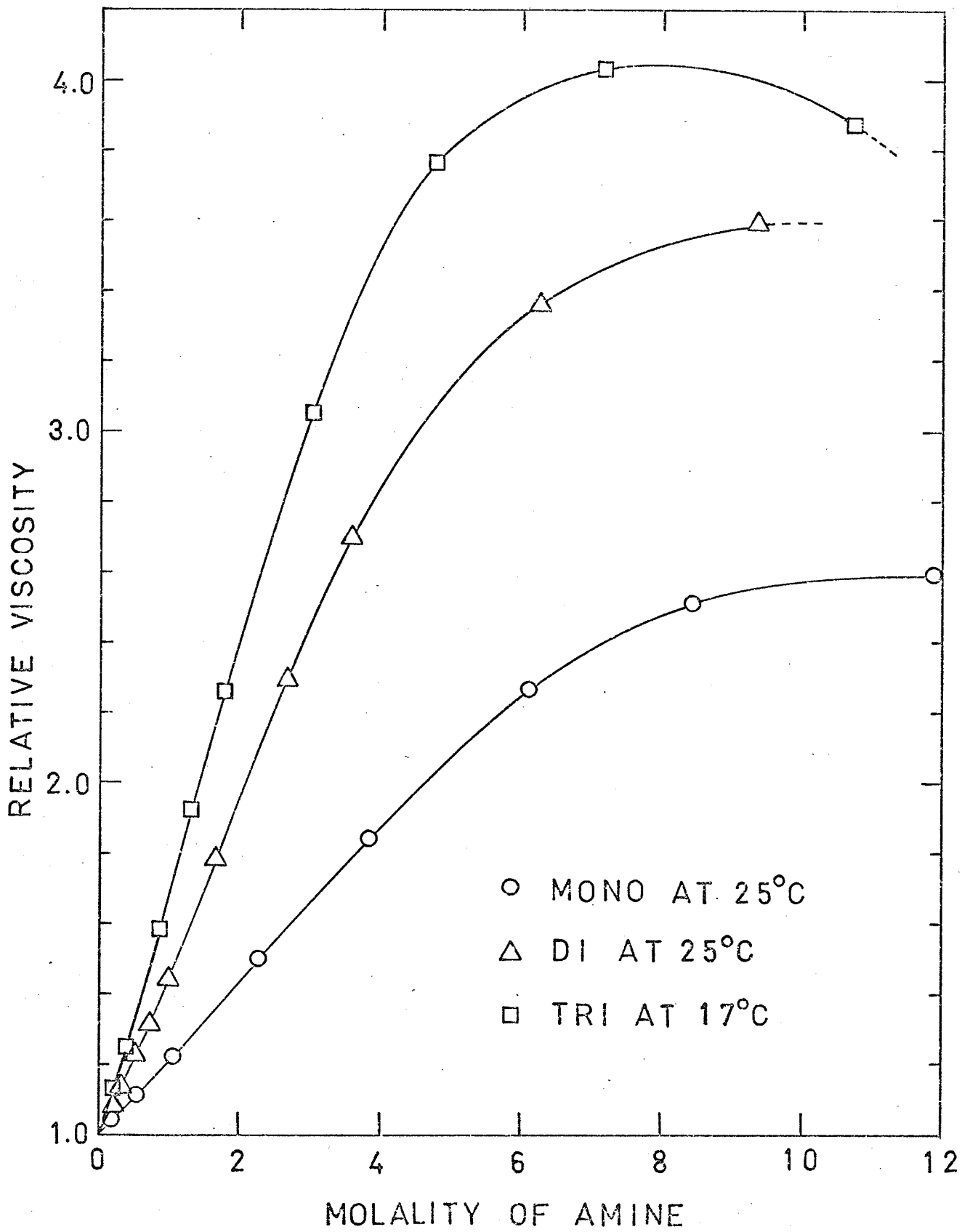
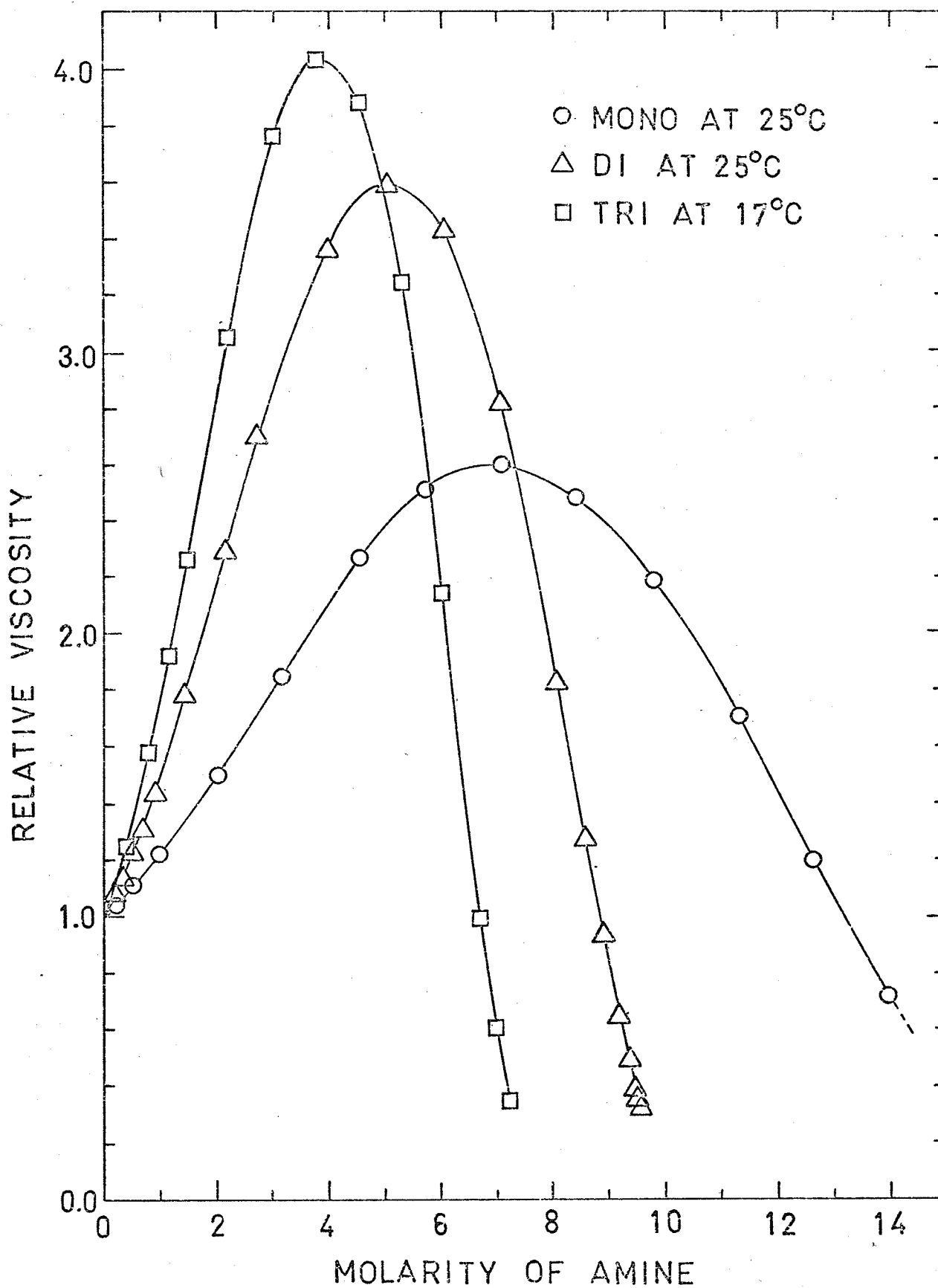


Figure 9. Relative Viscosities of Amine
Solutions vs. Molarities.



IV.B Total Vapor Pressures and Partial Vapor Pressures

The total vapor pressures for the three systems at their experimental temperatures are given in Tables 4-6 and presented graphically in Figures 10, 11 and 12 respectively. The liquid-vapor equilibrium compositions are listed in Tables 7, 8 and 9, and shown graphically in Figures 13, 14 and 15. From large scale versions of these figures, values of total vapor pressures and liquid-vapor equilibrium compositions at rounded concentrations of the liquid phase were obtained. From these values, the partial vapor pressures of amines and water were calculated on the basis of Dalton's law, viz., for amines

$$p_B = \chi_B^{*v} p \quad (252)$$

where χ_B^{*v} is the mole fraction of amine in vapor phase, and

p is the total vapor pressure.

The results are tabulated in Tables 10, 11 and 12, and plotted in Figures 10, 11 and 12.

TABLE 4

Total Vapor Pressures of the System
Monoethylamine-Water at 25°C

x_B^* Mole Fraction Monoethylamine	P Total Vapor Pressure in mm Hg
0.00000	23.75 (110)
0.00971	27.7
0.01878	31.6
0.03960	40.8
0.0648	53.5
0.0993	74.1
0.1316	95.6
0.1756	126.8
0.2260	166.7
0.2914	228.5
0.3461	287.9
0.3853	339.5
0.4465	426.5
0.4966	502.0
0.577	610.5
0.656	717.6
1.000	1066 (111)

Figure 10. Vapor Pressures of Monoethylamine Solutions
vs. Mole Fractions of Monoethylamine at 25°C.

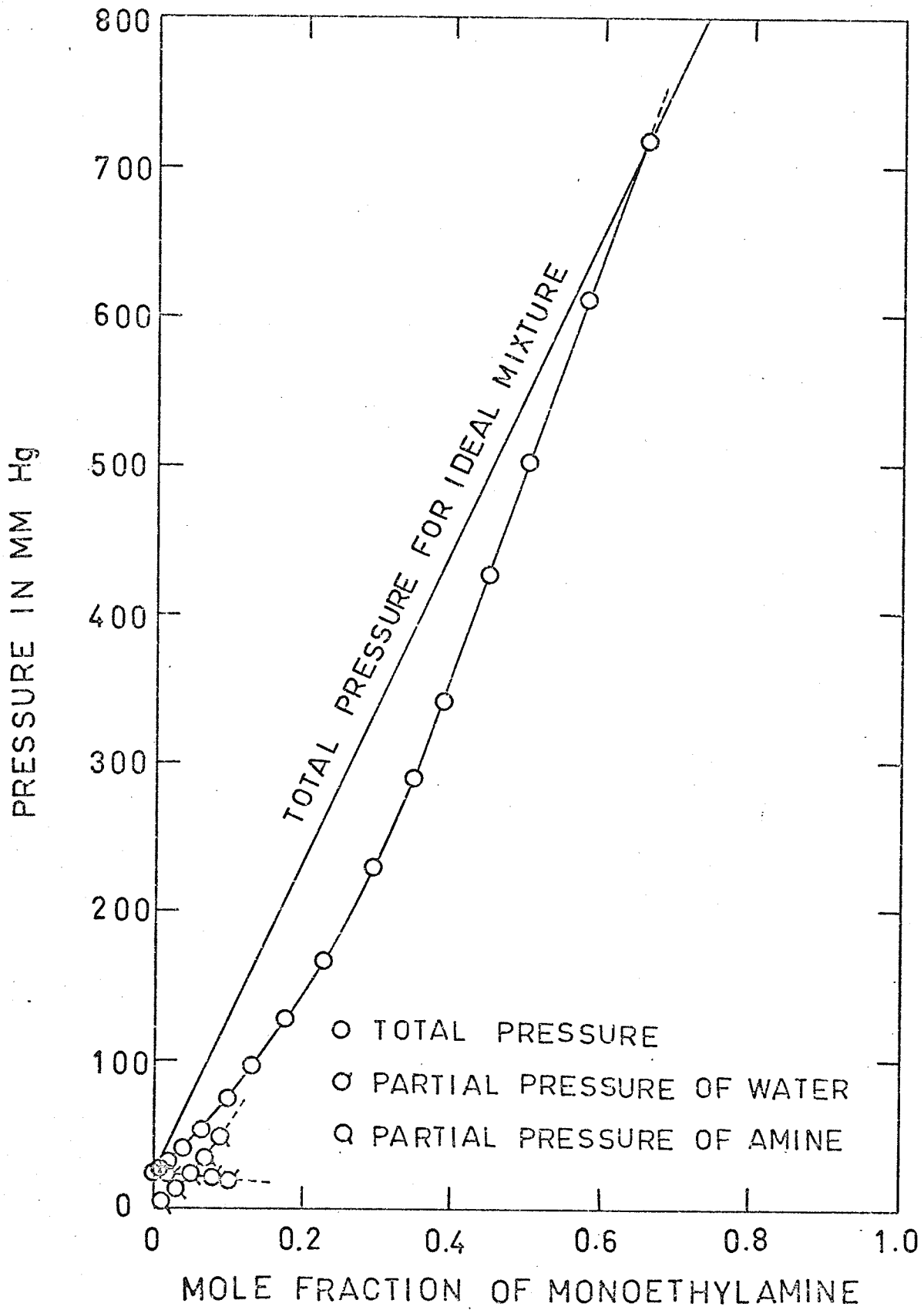


TABLE 5

Total Vapor Pressures of the System
Diethylamine-Water at 25°C

x_g^* Mole Fraction Diethylamine	p Total Vapor Pressure in mm Hg
0.00000	23.75 ⁽¹¹⁰⁾
0.01196	34.2
0.02514	45.3
0.04001	56.3
0.0548	65.3
0.0816	74.9
0.1347	86.4
0.1960	97.1
0.2546	107.1
0.3330	121.4
0.3877	131.9
0.4544	145.1
0.542	162.6
0.630	179.5
0.698	191.2
0.769	202.9
0.850	215.4
0.923	226.7
0.965	233.4
1.000	238.8

Figure 11. Vapor Pressures of Diethylamine Solutions
vs. Mole Fractions of Diethylamine at 25°C.

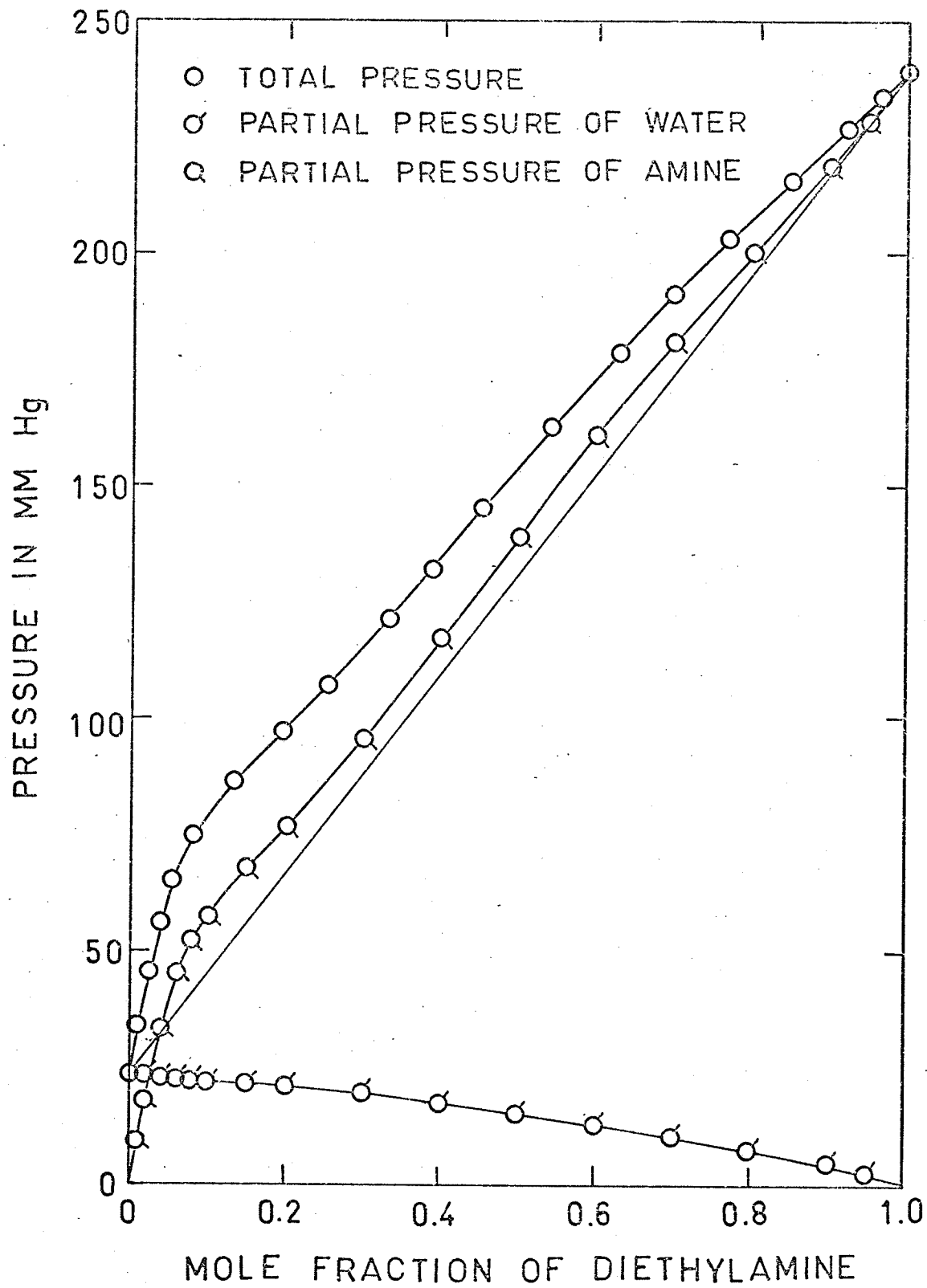


TABLE 6

Total Vapor Pressures of the System
Triethylamine-Water at 17°C

χ_B^* Mole Fraction Triethylamine	P Total Vapor Pressure in mm Hg
0.00000	14.51 (110)
0.00489	26.1
0.00994	36.7
0.01531	45.9
0.01850	49.1
0.02470	51.9
0.03423	52.5
0.0706	52.7
0.1421	52.9
0.2185	53.2
0.2958	53.5
0.3779	53.8
0.4644	54.0
0.531	54.1
0.609	54.4
0.691	54.6
0.774	54.9
0.847	54.9
0.905	54.0
0.956	52.0
0.988	48.6
1.000	46.7

Figure 12. Vapor Pressures of Triethylamine Solutions
vs. Mole Fractions of Triethylamine at 17°C.

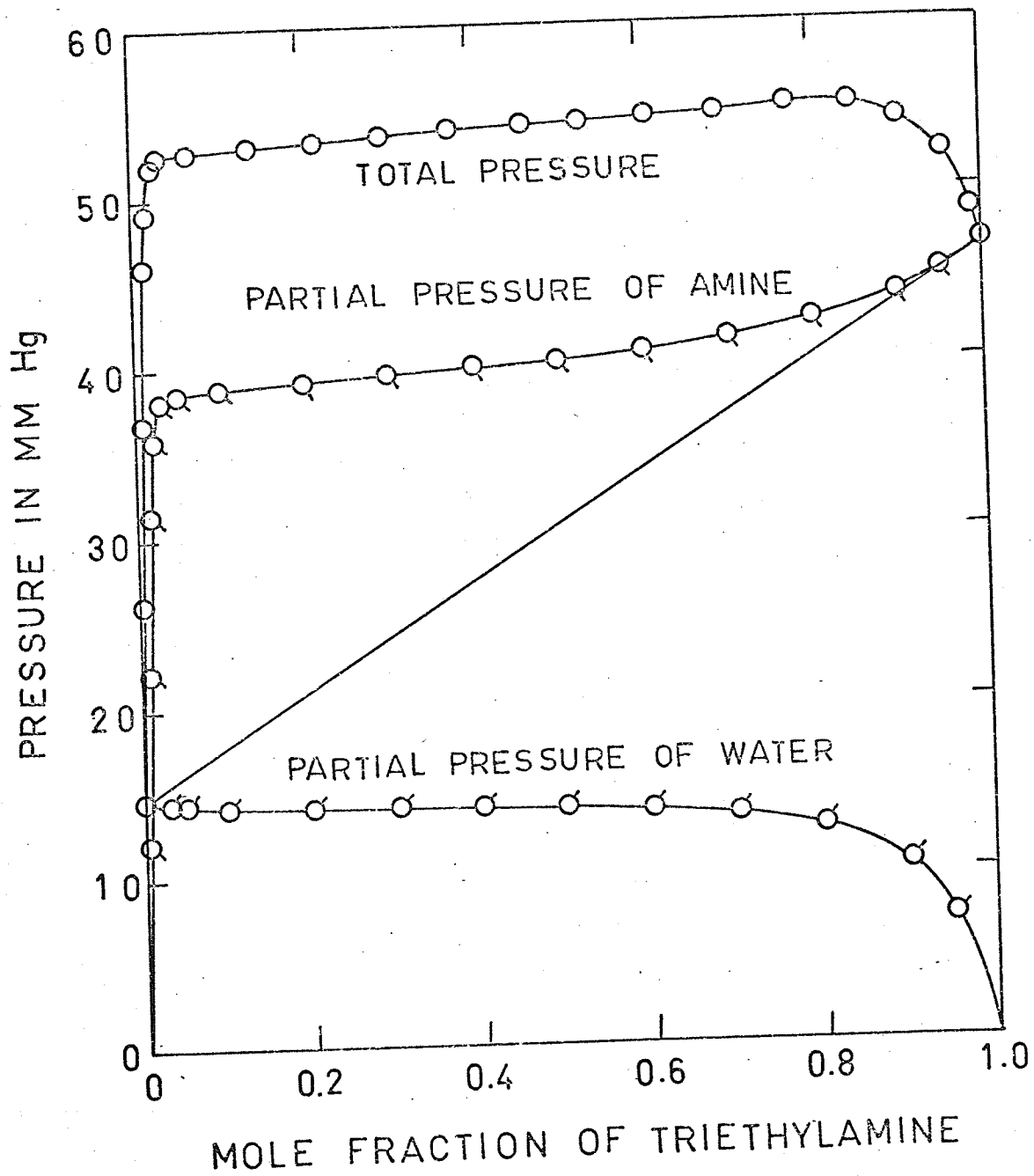


TABLE 7

Liquid-Vapor Equilibrium Compositions for the System
Monoethylamine-Water at 25°C

x_B^*	x_B^{*v}
Liquid Composition in Mole Fraction Amine	Vapor Composition in Mole Fraction Amine
0.0000	0.000
0.0084	0.152
0.0199	0.276
0.0331	0.388
0.0458	0.481
0.0560	0.535
0.0650	0.584
0.0758	0.635
0.0913	0.793
0.1020	0.725

Figure 13. Liquid-Vapor Equilibrium Compositions for
the System Monoethylamine-Water at 25°C.

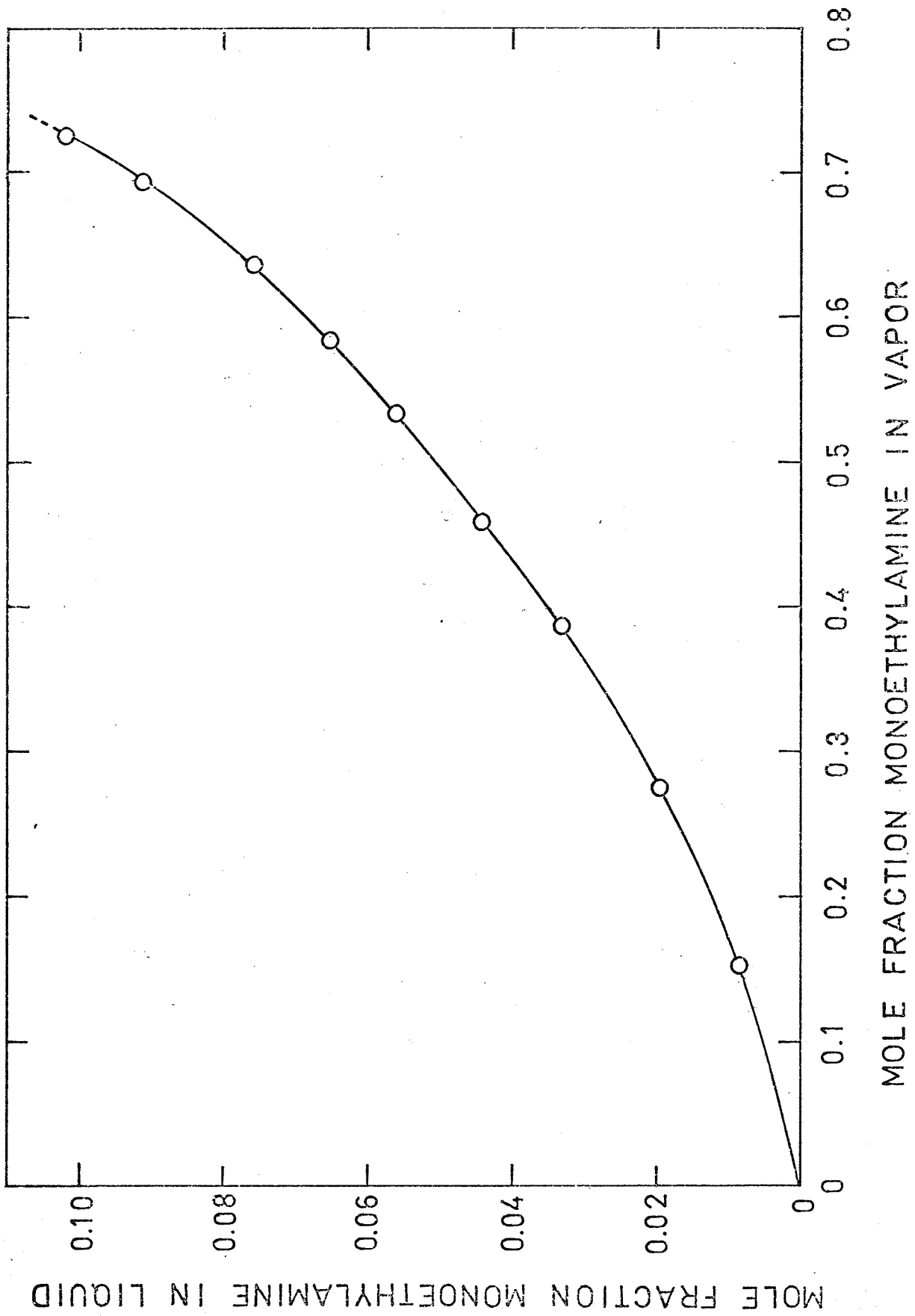


TABLE 8

Liquid-Vapor Equilibrium Compositions for the System
Diethylamine-Water at 25°C

x_B^*	x_B^{*v}
Liquid Composition in Mole Fraction Amine	Vapor Composition in Mole Fraction Amine
0.0000	0.000
0.0093	0.250
0.0248	0.487
0.0490	0.635
0.0893	0.712
0.169	0.770
0.250	0.813
0.334	0.845
0.412	0.876
0.497	0.902
0.596	0.937
0.696	0.947
0.788	0.962
0.897	0.980
0.950	0.990
1.000	1.000

Figure 14. Liquid-Vapor Equilibrium Compositions for
the System Diethylamine-Water at 25°C.

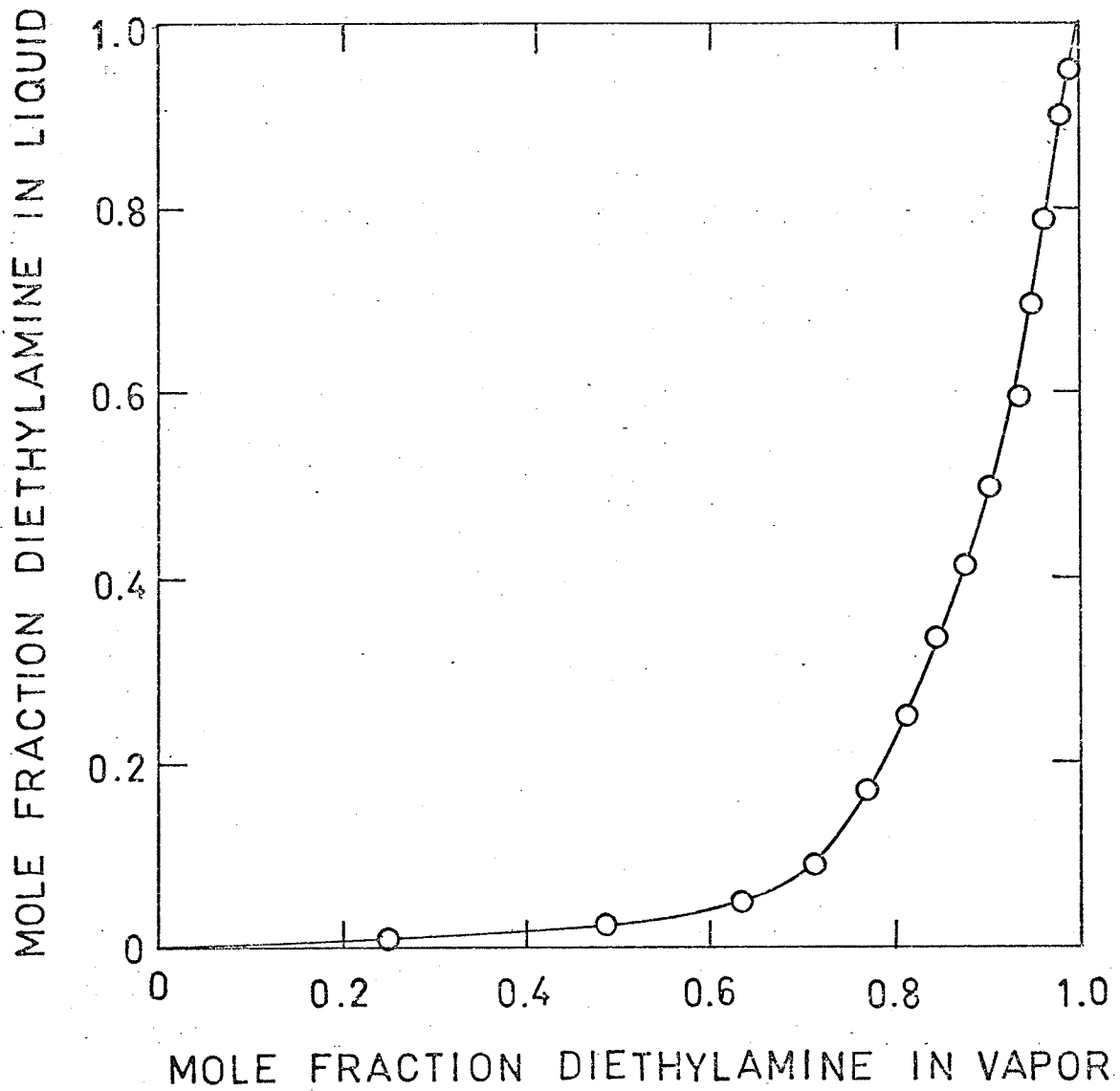


TABLE 9

Liquid-Vapor Equilibrium Compositions for the System
Triethylamine-Water at 17°C

x_B^* Liquid Composition in Mole Fraction Amine	x_B^{*v} Vapor Composition in Mole Fraction Amine
0.0000	0.000
0.0048	0.443
0.0099	0.607
0.0149	0.689
0.0248	0.722
0.0499	0.729
0.1011	0.732
0.197	0.735
0.348	0.738
0.496	0.742
0.644	0.749
0.793	0.772
0.858	0.783
0.924	0.830
0.975	0.905
1.000	1.000

Figure 15. Liquid-Vapor Equilibrium Compositions for
the System Triethylamine-Water at 17°C.

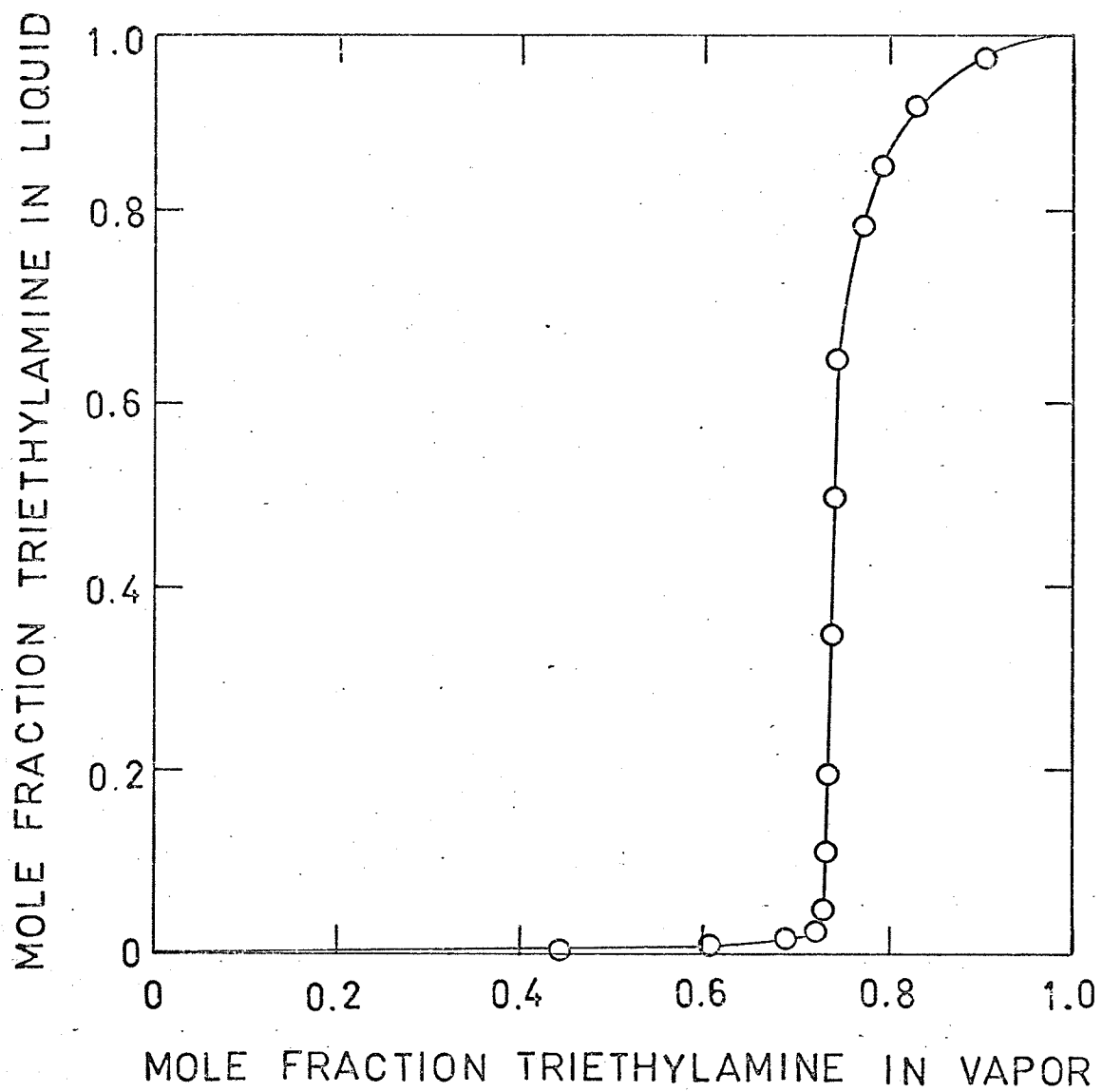


TABLE 10

Total and Partial Vapor Pressures for the System
Monoethylamine-Water at Rounded Concentrations at 25°C

x_B^* Mole Fraction Amine in Liquid	x_B^{*v} Mole Fraction Amine in Vapor	p Total Pressure in mm Hg	p_A Partial Pressure of Water in mm Hg	p_B Partial Pressure of Amine in mm Hg
0.00	0.000	23.75	23.75	0.0
0.01	0.158	27.9	23.5	4.4
0.02	0.274	32.3	23.5	8.8
0.03	0.363	36.5	23.3	13.2
0.04	0.436	41.0	23.1	17.9
0.05	0.498	45.9	23.0	22.9
0.06	0.556	51.0	22.6	28.4
0.07	0.610	56.4	22.0	34.4
0.08	0.652	62.1	21.6	40.5
0.09	0.691	68.4	21.3	47.1
0.10	0.718	74.5	21.0	53.5

TABLE 11

Total and Partial Vapor Pressures for the System
Diethylamine-Water at Rounded Concentrations at 25°C

x_B^* Mole Fraction Amine in Liquid	x_B^{*V} Mole Fraction Amine in Vapor	p Total Pressure in mm Hg	p_A Partial Pressure of Water in mm Hg	p_B Partial Pressure of Amine in mm Hg
0.00	0.000	23.75	23.75	0.0
0.01	0.277	32.5	23.5	9.0
0.02	0.432	41.0	23.3	17.7
0.04	0.595	56.3	22.8	33.5
0.06	0.668	67.7	22.5	45.2
0.08	0.702	74.5	22.2	52.3
0.10	0.724	79.6	22.0	57.6
0.15	0.759	89.3	21.5	67.8
0.20	0.785	97.7	21.0	76.7
0.30	0.832	115.3	19.4	95.9
0.40	0.871	134.5	17.4	117.1
0.50	0.902	154.1	15.1	139.0
0.60	0.927	173.7	12.6	161.1
0.70	0.947	191.4	10.1	181.3
0.80	0.964	207.6	7.4	200.2
0.90	0.981	222.8	4.3	218.5
0.95	0.990	230.7	2.4	228.3
1.00	1.000	238.8	0.0	238.8

TABLE 12

Total and Partial Vapor Pressures for the System
Triethylamine-Water at Rounded Concentrations at 17°C

Mole Fraction Amine in Liquid	x_B^*	Mole Fraction Amine in Vapor	x_B^v	Total Pressure in mm Hg	p	Partial Pressure of Water in mm Hg	p_A	Partial Pressure of Amine in mm Hg	p_B
0.000		0.000		14.51		14.51		0.0	
0.005		0.455		26.3		14.3		12.0	
0.010		0.606		36.2		14.3		21.9	
0.015		0.685		45.5		14.3		31.2	
0.020		0.716		50.2		14.3		35.9	
0.030		0.726		52.4		14.4		38.0	
0.050		0.729		52.6		14.3		38.3	
0.100		0.732		52.8		14.2		38.6	
0.200		0.735		53.1		14.1		39.0	
0.300		0.737		53.5		14.1		39.4	
0.400		0.740		53.8		14.0		39.8	
0.500		0.742		54.1		14.0		40.1	
0.600		0.748		54.3		13.7		40.6	
0.700		0.756		54.7		13.4		41.3	
0.800		0.771		54.9		12.6		42.3	
0.900		0.808		54.1		10.4		43.7	
0.950		0.863		52.2		7.2		45.0	
1.000		1.000		46.7		0.0		46.7	

IV.C Activities and Activity Coefficients

The water activities and amine activities in the usual way were obtained by dividing the partial vapor pressures of the components by the vapor pressures of pure water and the amine respectively. The vapor pressures of pure water at 25°C and 17°C were obtained from the work of Keyes⁽¹¹⁰⁾. These values are

$$p_A^\circ = 23.75 \text{ mm Hg at } 25^\circ\text{C}; 14.51 \text{ mm Hg at } 17^\circ\text{C}$$

From the vapor pressure of pure monoethylamine at 25°C, 1066 mm Hg according to Bittrich⁽¹¹¹⁾, that of pure diethylamine at 25°C, 238.8 mm Hg, and of pure triethylamine at 17°C, 46.7 mm Hg, both measured by me, the activities and activity coefficients, i.e., the quotients of the activities to the mole fractions at rounded concentrations were computed and given in Tables 13-15.

After converting the mole fractions into molalities, the logarithms of amine activities were plotted against the logarithms of molalities in Figures 16, 17 and 18, since these curves are useful in the theoretical treatment of diffusion. The water activities of the systems as functions of molarities were presented in Figure 19 through 21. The mean activity coefficient of the free ionic species, $\bar{\gamma}'_{\pm}$ involved in the evaluation of the basic dissociation constants appearing in Equation (73), requires a preliminary computation of the stoichiometric mean activity coefficient of the "aminium hydroxide", $\bar{\gamma}_{\pm}$, as given by Equation (70), which in turn necessitates an estimation of the constant k_{\pm} expressed in Equation (66). Unfortunately, a finite value of k_{\pm} for each amine could not be obtained because, on the one hand, from the measured partial pressures of amine it appeared that they are proportional directly to mole fraction rather than to the square of the mole fraction in the di-

lute region, and hence the limit of $\frac{p}{p_B^0} \cdot \frac{1}{\tilde{\chi}_B^2}$ appears infinite; on the other hand, even Henry's law implies that the vapor pressures of amine are proportional to $\tilde{\chi}_B^2$ for these dissociating "solutes" in extreme dilution, but to perform the highly accurate vapor pressure measurements in very dilute solutions and derive from these the proportionality constant is experimentally, a matter of great difficulty. Therefore the mean ionic activity coefficients of the aminium and hydroxyl ions were not obtained. Hence for the estimation of the mean activity coefficients required in the calculation of the dissociation constants, I have to resort to some other means. Evaluation of the activity coefficient of the undissociated species by Equation (74) had to be postponed until the degree of dissociation was available, as mentioned in the section dealing with conductivity.

TABLE 13

Activities and Activity Coefficients for the System
Monoethylamine-Water at Rounded Concentrations at 25°C

x_B^*	a_A	f_A^*	a_B	f_B^*
Mole Fraction Amine	Water Activity	Water Activity Coefficient	Amine Activity	Amine Activity Coefficient
0.00	1.000	1.000	0.0000	-
0.01	0.989	0.999	0.0041	0.41
0.02	0.987	1.007	0.0083	0.42
0.03	0.979	1.003	0.0124	0.414
0.04	0.973	1.013	0.0168	0.419
0.05	0.968	1.019	0.0215	0.430
0.06	0.952	1.013	0.0266	0.443
0.07	0.926	0.996	0.0323	0.461
0.08	0.909	0.988	0.0380	0.475
0.09	0.897	0.986	0.0442	0.491
0.10	0.884	0.982	0.0502	0.502

TABLE 14

Activities and Activity Coefficients for the System
Diethylamine-Water at Rounded Concentrations at 25°C

x_B^*	a_A	f_A^*	a_B	f_B^*
Mole Fraction Amine	Water Activity	Water Activity Coefficient	Amine Activity	Amine Activity Coefficient
0.00	1.000	1.000	0.0000	-
0.01	0.990	1.000	0.0377	3.77
0.02	0.980	1.000	0.0741	3.71
0.04	0.959	0.999	0.140	3.51
0.06	0.946	1.006	0.189	3.16
0.08	0.935	1.016	0.219	2.74
0.10	0.926	1.029	0.241	2.41
0.15	0.906	1.066	0.284	1.89
0.20	0.882	1.103	0.321	1.606
0.30	0.816	1.165	0.402	1.339
0.40	0.733	1.222	0.490	1.226
0.50	0.635	1.270	0.582	1.164
0.60	0.529	1.322	0.675	1.124
0.70	0.424	1.413	0.759	1.085
0.80	0.311	1.554	0.838	1.048
0.90	0.181	1.810	0.915	1.017
0.95	0.101	2.022	0.956	1.006
1.00	0.000	-	1.000	1.000

TABLE 15

Activities and Activity Coefficients for the System
Triethylamine-Water at Rounded Concentrations at 17°C

x_B^*	a_A	f_A^*	a_B	f_B^*
Mole Fraction Amine	Water Activity	Water Activity Coefficient	Amine Activity	Amine Activity Coefficient
0.000	1.000	1.000	0.000	-
0.005	0.988	0.992	0.256	51.3
0.010	0.983	0.993	0.470	47.0
0.015	0.988	1.003	0.667	44.5
0.020	0.983	1.004	0.770	38.5
0.030	0.990	1.021	0.815	27.2
0.050	0.982	1.034	0.821	16.42
0.100	0.975	1.083	0.828	8.28
0.200	0.970	1.213	0.836	4.18
0.300	0.970	1.386	0.844	2.81
0.400	0.964	1.61	0.852	2.13
0.500	0.962	1.92	0.860	1.720
0.600	0.943	2.36	0.870	1.450
0.700	0.920	3.08	0.885	1.264
0.800	0.866	4.33	0.906	1.133
0.900	0.716	7.16	0.936	1.040
0.950	0.49	9.9	0.965	1.017
1.000	0.00	-	1.000	1.000

Figure 16. $\ln a_B$ vs. $\ln m$ for Aqueous Mono-ethylamine Solutions at 25°C.

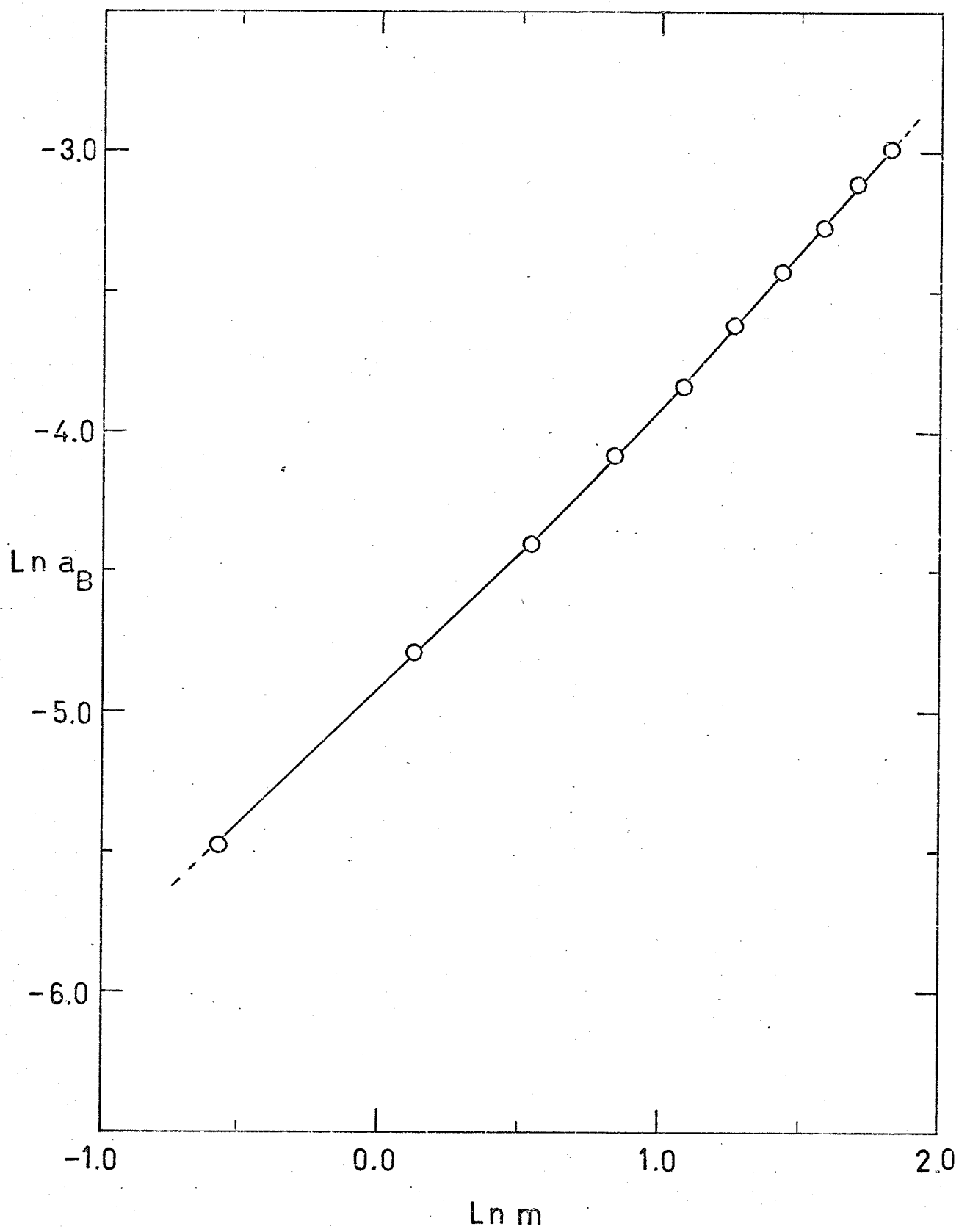


Figure 17. $\ln a_B$ vs. $\ln m$ for Aqueous Diethylamine Solutions at 25°C.

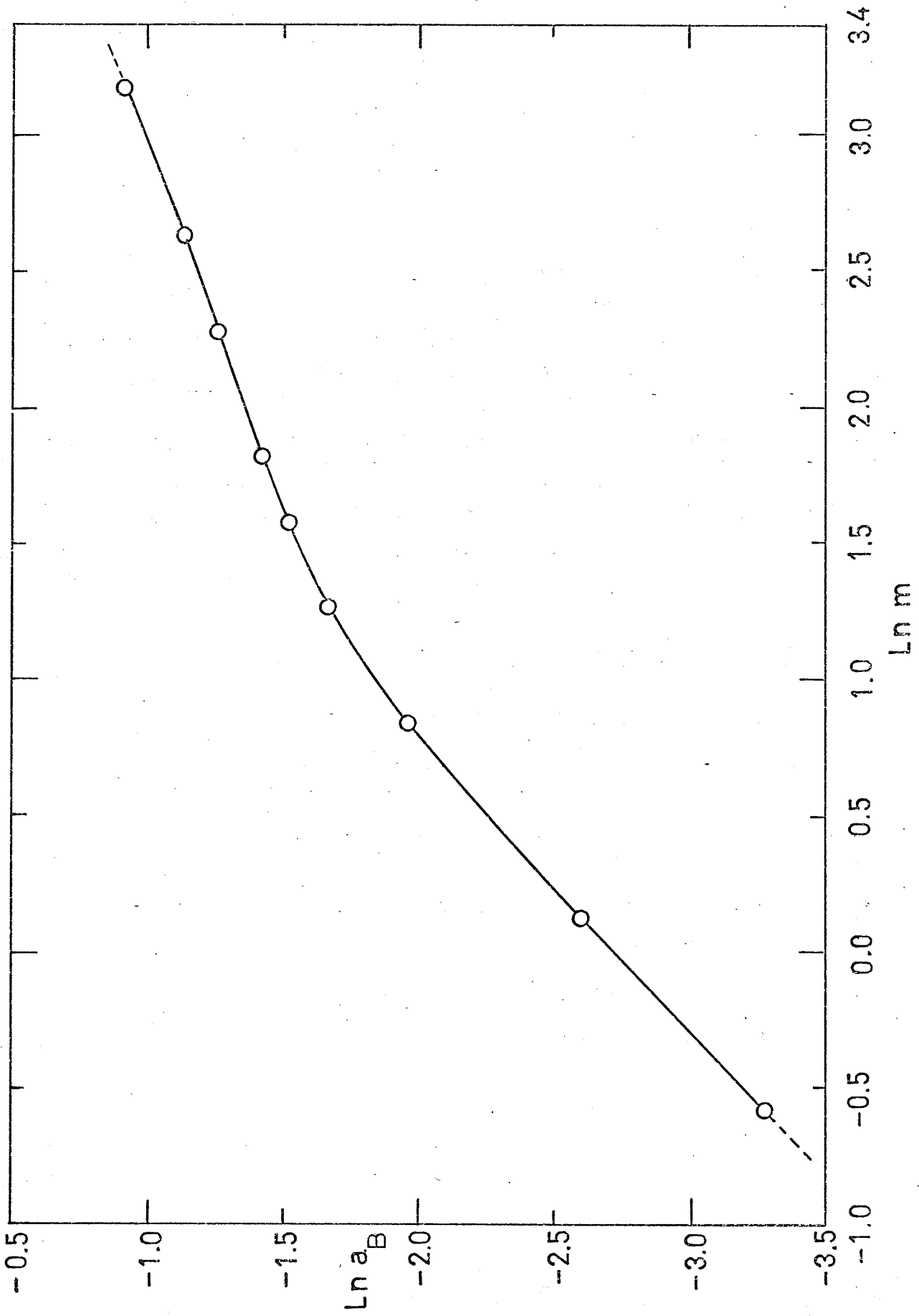


Figure 18. $\ln a_B$ vs. $\ln m$ for Aqueous Triethylamine Solutions at 17°C.

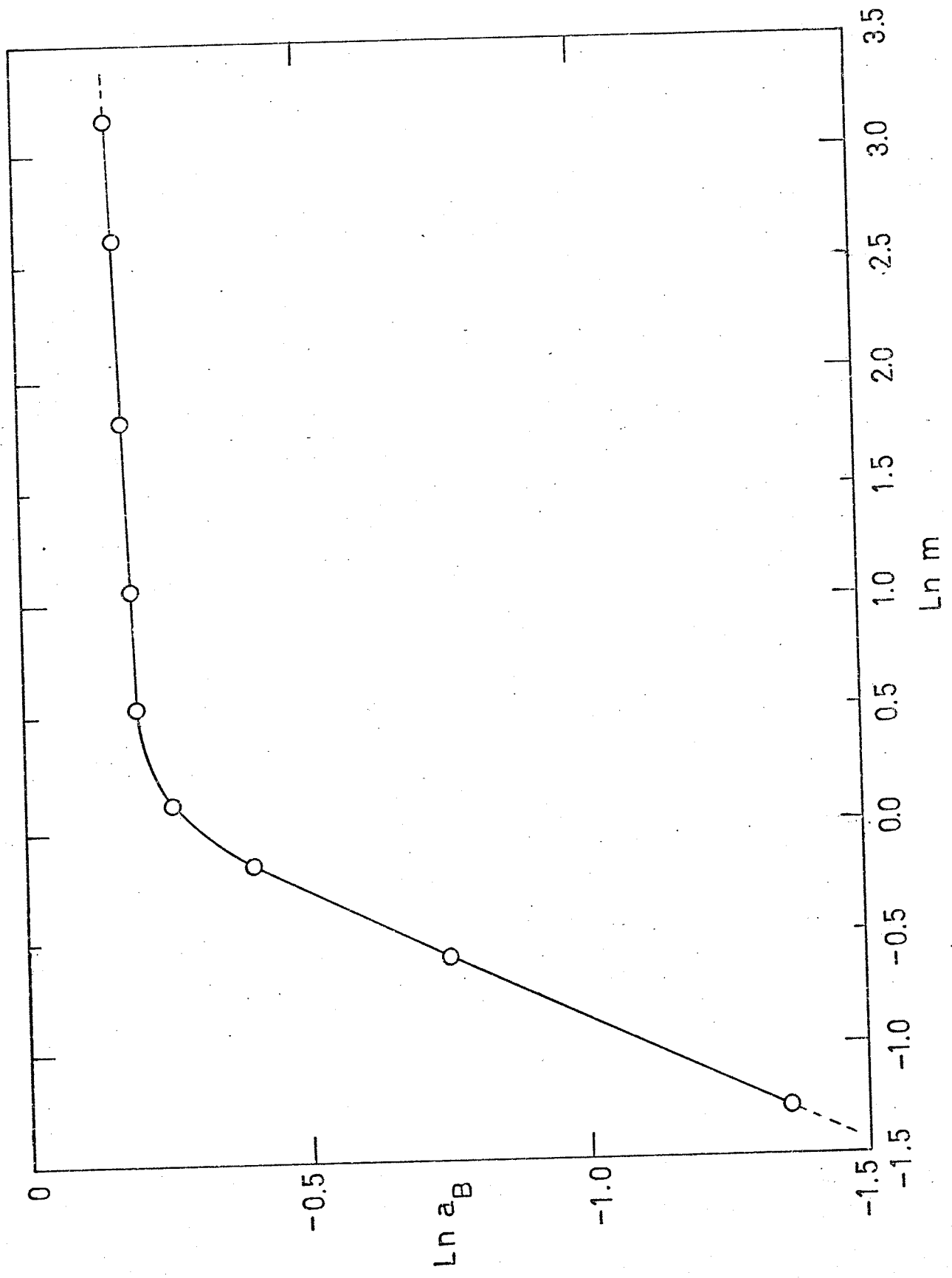


Figure 19. Water Activities of Monoethylamine Solutions
vs. Molarities of Monoethylamine at 25°C.

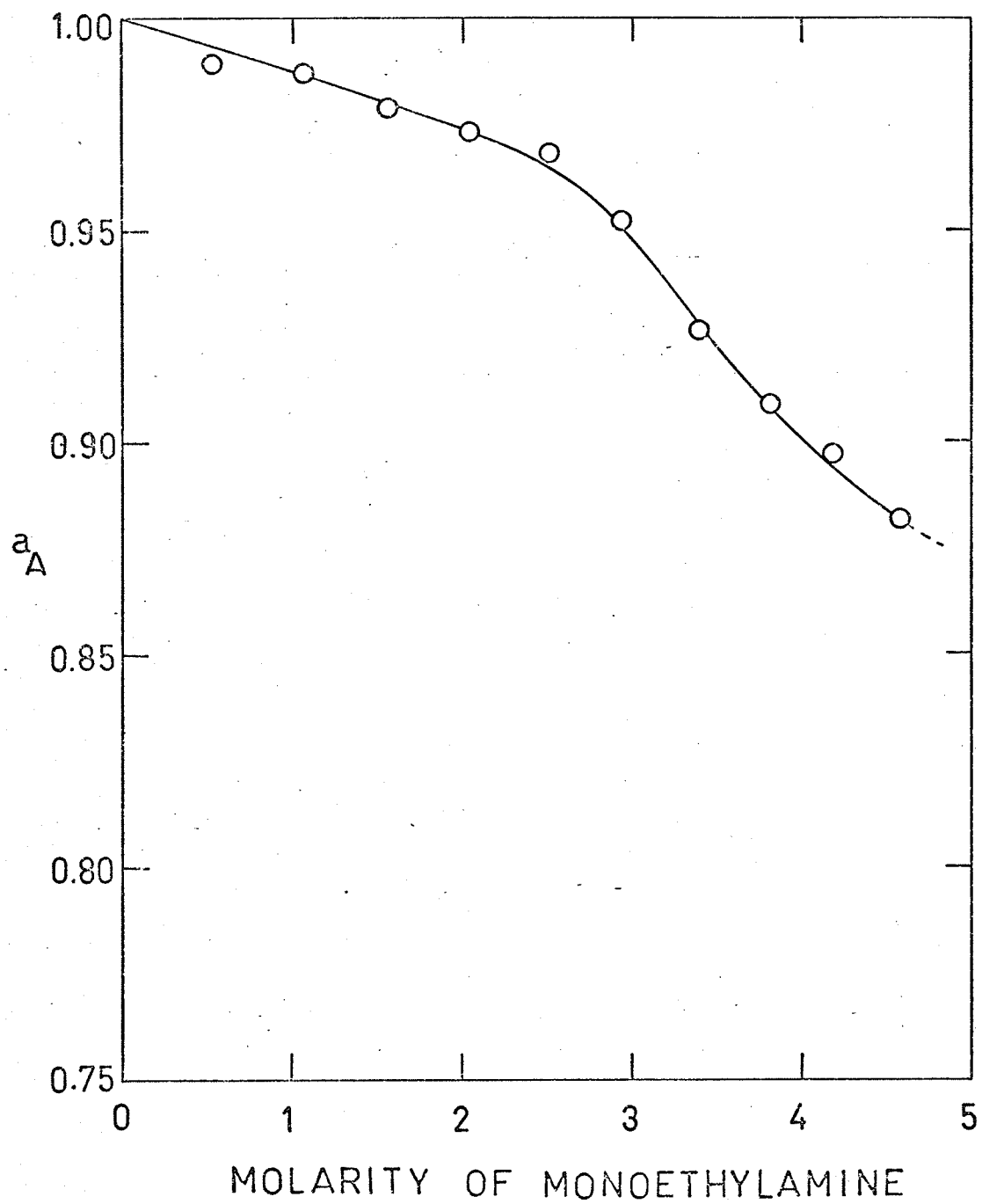


Figure 20. Water Activities of Diethylamine Solutions
vs. Molarities of Diethylamine at 25°C.

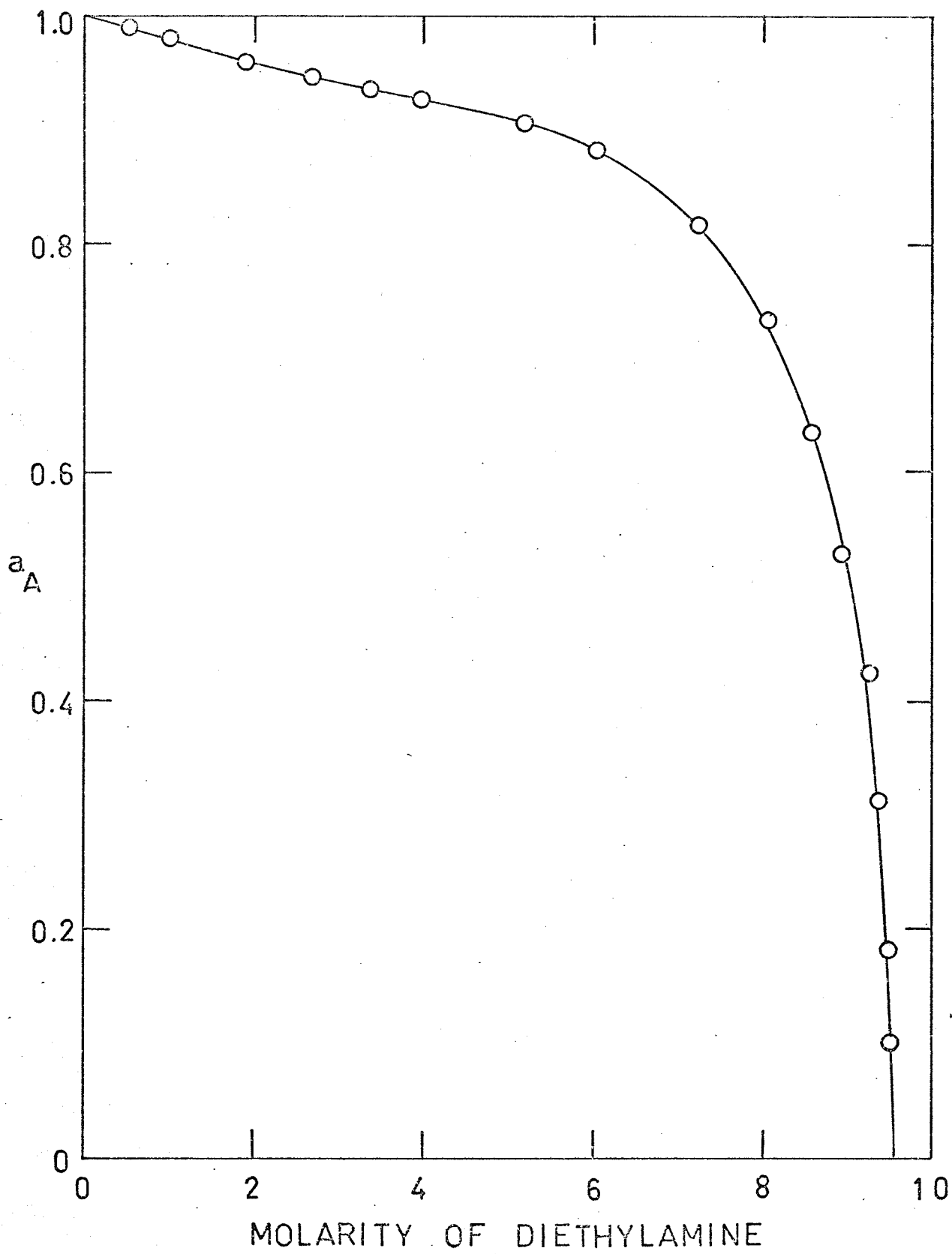
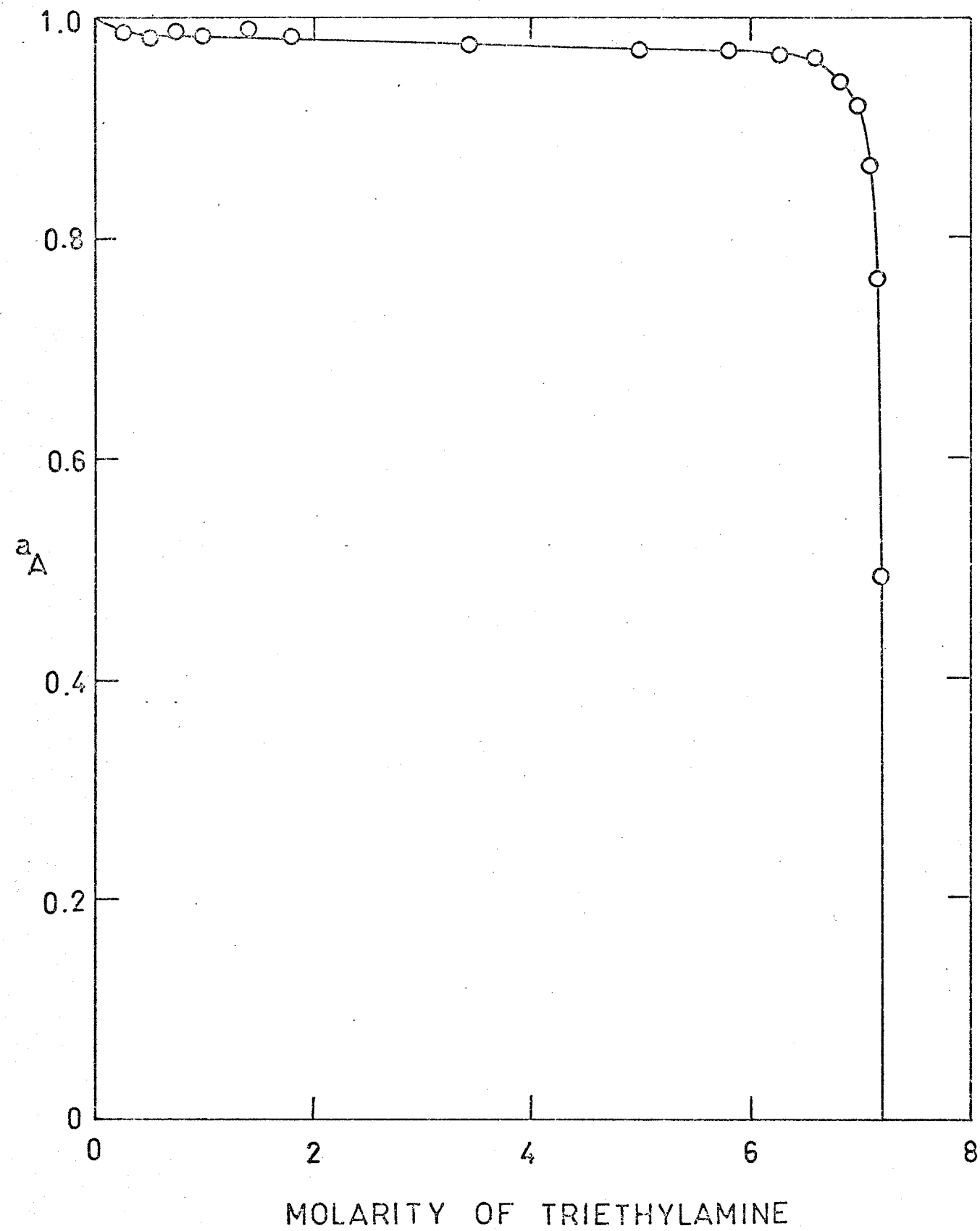


Figure 21. Water Activities of Triethylamine Solutions
vs. Molarities of Triethylamine at 17°C.



IV.D Conductivities and Dissociation Constants

1. Preliminary Values of Equivalent Conductances of Amine Hydrochlorides

The experimental equivalent conductances of the hydrochlorides of mono-, di-, and triethylamine, in which the hydrolysis effect has not been allowed for, are presented as functions of their stoichiometric concentrations in Tables 16, 17 and 18 respectively. The preliminary values of the limiting conductances of the salts were found by plotting the equivalent conductances against the square roots of the concentrations and extrapolating the resulting curves to infinite dilution. These are shown in Figures 22, 23 and 24 respectively. Values of the limiting conductances thus obtained are as follows:

$$\text{(monoethylamine hydrochloride at } 25^{\circ}\text{C)} = 122.85 \text{ cm}^2\text{ohm}^{-1} \text{ equil.}^{-1}$$

$$\text{(diethylamine hydrochloride at } 25^{\circ}\text{C)} = 112.90 \quad "$$

$$\text{(triethylamine hydrochloride at } 17^{\circ}\text{C)} = 91.20 \quad "$$

In order to calculate the limiting conductances of the "aminium hydroxides" by means of the Kohlrausch law, (Equation (179)), it is necessary to have the limiting equivalent conductivities of hydroxyl and chloride ions. Values of the ionic conductivities at 25°C and the graphically interpolated values at 17°C were obtained from tables given by Robinson and Stokes (112), namely

$$\Lambda_{\text{OH}^-}^{\circ} = 198.3 \text{ at } 25^{\circ}\text{C}; \quad 167.1 \text{ at } 17^{\circ}\text{C}$$

$$\Lambda_{\text{Cl}^-}^{\circ} = 76.35 \text{ at } 25^{\circ}\text{C}; \quad 64.47 \text{ at } 17^{\circ}\text{C}$$

From these values and those of the hydrochlorides, the preliminary limiting equivalent conductances of "aminium hydroxides" were derived.

These are

TABLE 16

Equivalent Conductances of Monoethylamine Hydrochloride
in Aqueous Solutions at 25°C

$c \times 10^4$		Λ	
in Moles per Litre		in $\text{cm}^2\text{ohm}^{-1}$ equivalent $^{-1}$	
Uncorrected for Hydrolysis	Corrected For Hydrolysis	Uncorrected for Hydrolysis	Corrected for Hydrolysis
(0.0000)	(0.0000)	(122.85)	(122.76)
0.8591	0.8587	122.04	121.98
3.6080	3.6071	121.12	121.09
4.9227	4.9217	120.87	120.87
8.313	8.311	120.28	120.26
8.757	8.756	120.23	120.21
17.192	17.190	119.19	119.17
21.042	21.040	118.77	118.76
31.895	31.892	117.93	117.92
37.205	37.202	117.55	117.54
54.76	54.76	116.50	116.49
97.92	97.92	114.57	114.56
158.41	158.40	112.57	112.56
246.65	246.64	110.37	110.36

Figure 22. Equivalent Conductance vs. \sqrt{c} for Mono-ethylamine Hydrochloride in Water at 25°C.

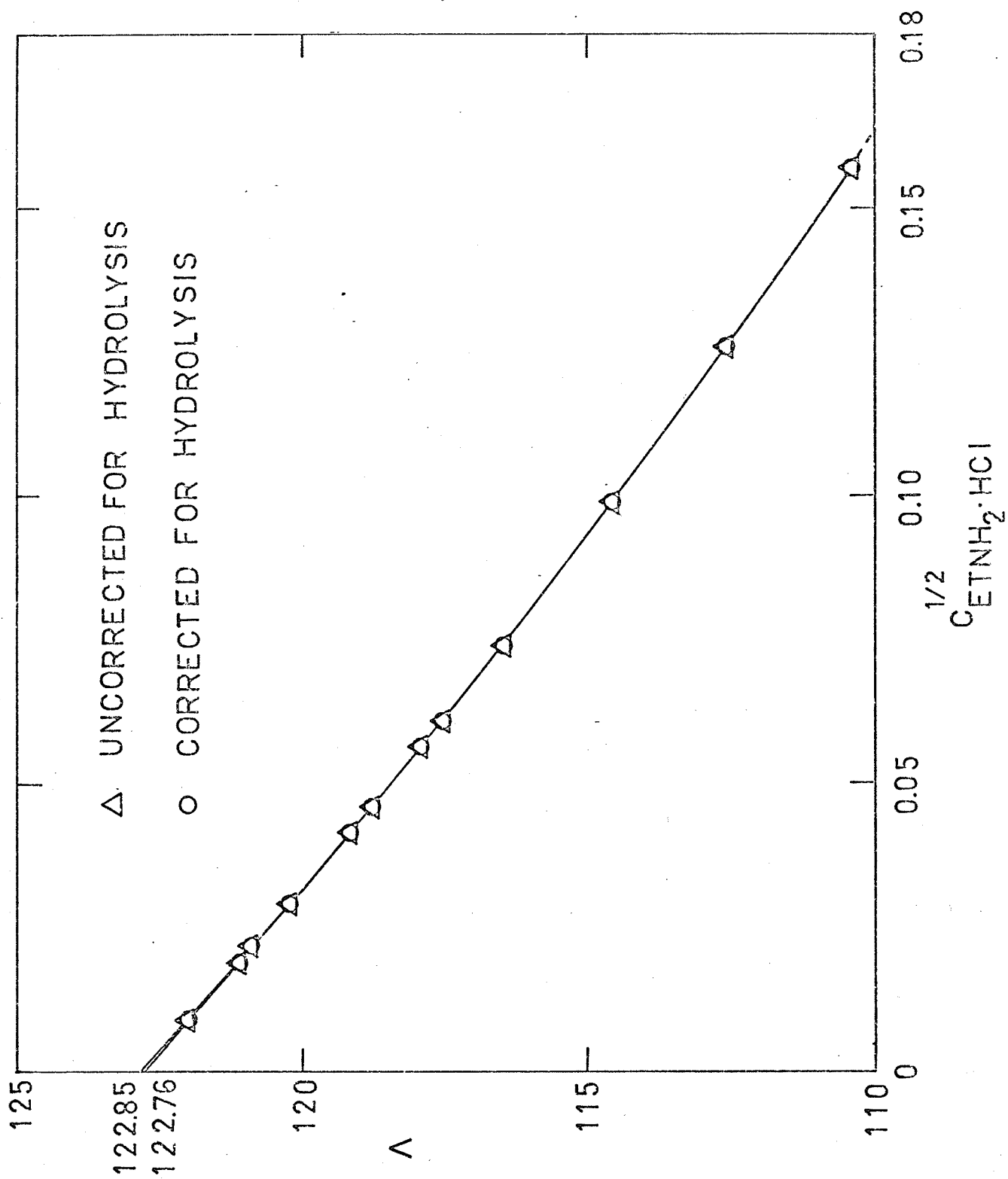


TABLE 17

Equivalent Conductances of Diethylamine Hydrochloride
in Aqueous Solutions at 25°C

$c \times 10^4$		Λ	
in Moles per Litre		in $\text{cm}^2 \text{ohm}^{-1}$ equivalent $^{-1}$	
Uncorrected for Hydrolysis	Corrected for Hydrolysis	Uncorrected for Hydrolysis	Corrected for Hydrolysis
(0.0000)	(0.0000)	(112.90)	(112.82)
1.1304	1.1301	112.02	111.98
4.0470	4.0464	111.17	111.15
8.967	8.966	110.33	111.31
16.278	16.277	109.45	109.44
25.140	25.138	108.66	108.66
35.832	35.830	107.88	107.88
63.37	63.37	106.27	106.27
120.03	120.03	103.95	103.95
215.75	215.75	101.24	101.24
413.71	413.71	97.34	97.34
631.2	631.2	94.23	94.23
913.7	913.7	91.17	91.17

Figure 23. Equivalent Conductance vs. \sqrt{c} for Diethylamine Hydrochloride in Water at 25°C.

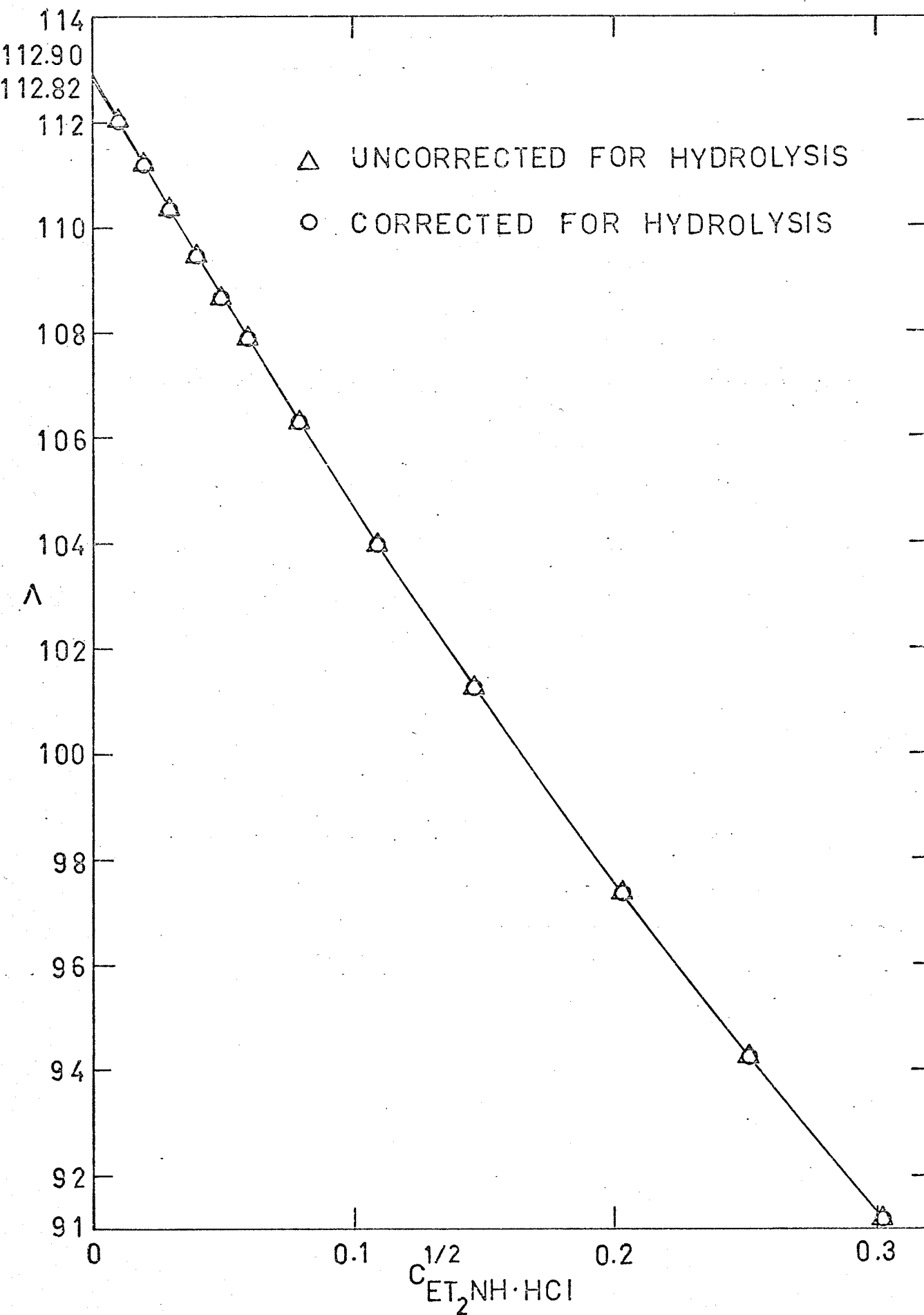
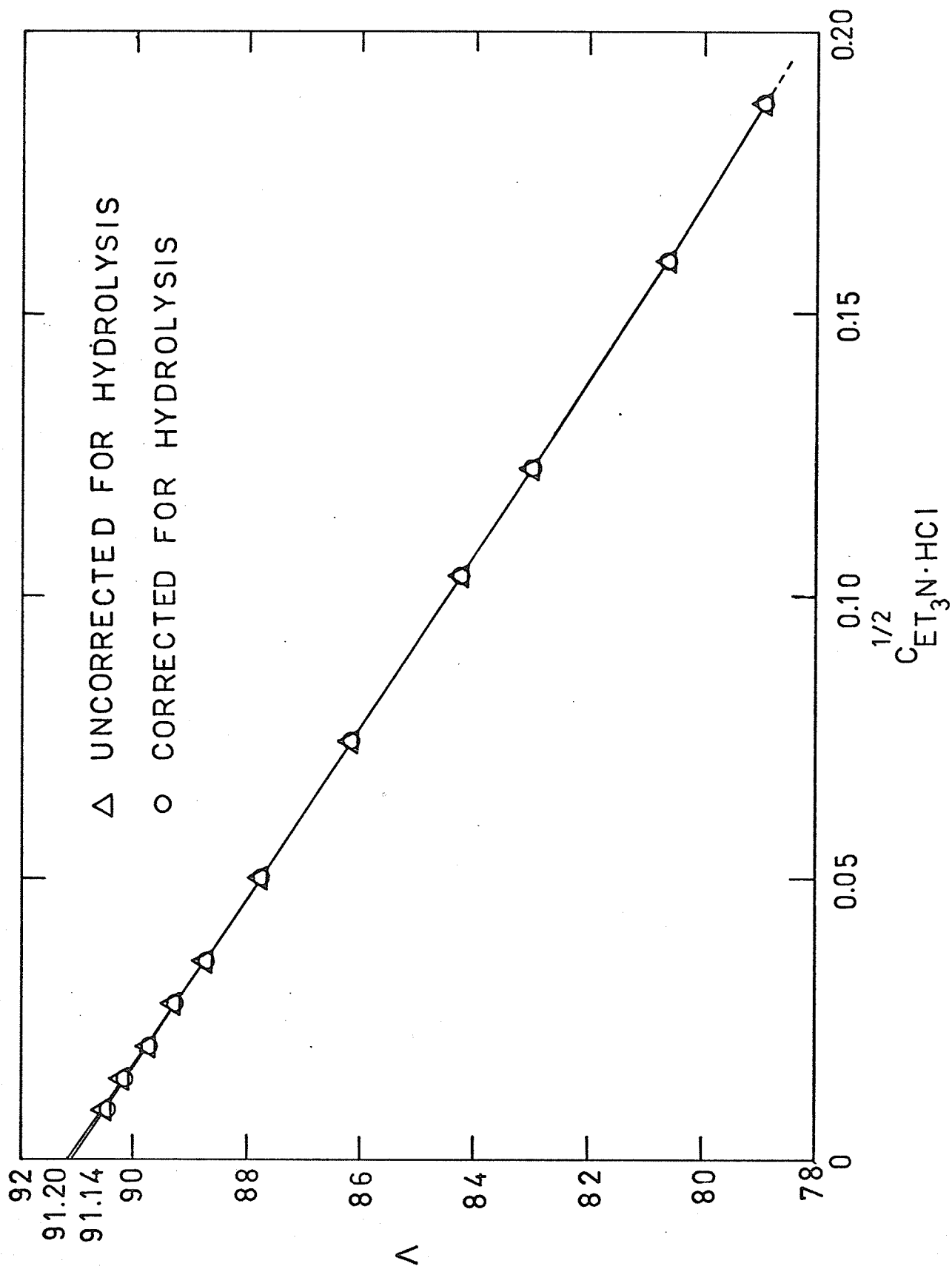


TABLE 18

Equivalent Conductances of Triethylamine Hydrochloride
in Aqueous Solutions at 17°C

$c \times 10^4$ in Moles per Litre		\wedge in $\text{cm}^2 \text{ohm}^{-1}$ equivalent ⁻¹	
Uncorrected for Hydrolysis	Corrected for Hydrolysis	Uncorrected for Hydrolysis	Corrected for Hydrolysis
(0.0000)	(0.0000)	(91.20)	(91.14)
0.8468	0.8465	90.53	90.49
2.1855	2.1850	90.20	90.18
4.1264	4.1257	89.74	89.72
7.836	7.835	89.29	89.28
12.603	12.602	88.73	88.72
24.999	24.997	87.76	87.75
55.10	55.10	86.18	86.17
107.26	107.26	84.24	84.23
150.62	150.62	82.96	82.96
253.77	253.76	80.63	80.63
350.42	350.41	78.93	78.93

Figure 24. Equivalent Conductance vs. \sqrt{c} for Tri-ethylamine Hydrochloride in Water at 17°C.



$$\Lambda_{\text{uncorr}}^{\circ}(\text{"monoethylaminium hydroxide" at } 25^{\circ}\text{C}) = 244.8$$

$$\Lambda_{\text{uncorr}}^{\circ}(\text{"diethylaminium hydroxide" at } 25^{\circ}\text{C}) = 234.9$$

$$\Lambda_{\text{uncorr}}^{\circ}(\text{"triethylaminium hydroxide" at } 17^{\circ}\text{C}) = 193.8$$

2. Preliminary Values of Conductances of "Aminium Hydroxide" and Approximated Dissociation Constants

In Tables 19, 20 and 21, the specific conductances of the weak bases are given. The solvent corrections have not been applied to these conductivities, and therefore are approximations to the true values. The equivalent conductances were computed. From the approximated conductances of the "aminium hydroxides" previously obtained, the degrees of dissociation were roughly calculated. By using the Ostwald dilution law and a free hand extrapolation, preliminary values of basic dissociation constant for the amines were found; they are:

$$\text{Monoethylamine at } 25^{\circ}\text{C} = 4.8 \times 10^{-4} \text{ moles litre}^{-1}$$

$$\text{Diethylamine at } 25^{\circ}\text{C} = 1.1 \times 10^{-3} \text{ moles litre}^{-1}$$

$$\text{Triethylamine at } 17^{\circ}\text{C} = 4.8 \times 10^{-4} \text{ moles litre}^{-1}$$

TABLE 19

Specific Conductances of "Monoethylammonium Hydroxide" in Aqueous Solutions without Solvent Correction at 25°C

c in Moles per Litre	$L_{unc} \times 10^4$ in $\text{cm}^{-1}\text{ohm}^{-1}$	η_{rel} Relative Viscosity
0.0020372	1.8689	-
0.0049720	3.2269	-
0.008495	4.4028	1.002
0.017009	6.472	1.005
0.040912	10.377	1.011
0.09488	15.974	1.020
0.20250	23.010	1.043
0.5064	33.482	1.111
0.9992	38.789	1.221
2.0241	36.288	1.498
3.1594	27.160	1.845
4.5532	16.290	2.265
5.714	9.856	2.510
7.079	5.089	2.595
8.397	2.4485	2.477
9.801	1.0188	2.186
11.316	0.3862	1.708
12.639	0.2014	1.197

TABLE 20

Specific Conductances of "Diethylaminium Hydroxide" in Aqueous
Solutions without Solvent Corrections at 25°C

c in Moles per Litre	$L_{unc} \times 10^4$ in $\text{cm}^{-1}\text{ohm}^{-1}$	$\frac{\eta}{\eta_0}$ Relative Viscosity
0.007935	5.683	1.001
0.009955	6.461	1.001
0.023662	10.708	1.005
0.048966	15.886	1.016
0.06537	18.441	1.030
0.09044	21.695	1.033
0.11566	24.430	1.050
0.20285	31.359	1.080
0.33129	37.640	1.134
0.5117	42.256	1.225
0.6791	44.085	1.309
0.9099	44.162	1.439
1.4439	38.782	1.782
2.1508	27.903	2.293
2.7334	19.706	2.696
3.9849	7.804	3.364
5.009	3.0037	3.589
6.065	0.8746	3.424
7.047	0.2204	2.819
8.075	0.0931	1.822
8.576	0.0486	1.274
8.900	0.0175	0.935
9.188	0.0029	0.648
9.361	0.0003	0.493
9.555 (100% amine)	-	0.323

TABLE 21

Specific Conductances of "Triethylaminium Hydroxide" in Aqueous Solutions without Solvent Corrections at 17°C

c	$L_{\mu\text{nc}} \times 10^4$	η_{rel}
in Moles per Litre	in $\text{cm}^{-1}\text{ohm}^{-1}$	Relative Viscosity
0.004156	2.3777	1.001
0.009953	3.9285	1.001
0.022953	6.213	1.008
0.06816	10.740	1.023
0.11917	13.856	1.062
0.22066	17.585	1.128
0.38469	20.415	1.245
0.7878	20.204	1.583
1.1501	16.652	1.921
1.4795	13.540	2.257
2.2038	8.210	4.049
2.9887	4.1993	3.764
3.7569	1.7634	4.031
4.5179	0.5497	3.876
5.279	0.1167	3.235
5.999	0.0261	2.142
6.694	0.0080	0.990
6.992	0.0004	0.601
7.213 (100% amine)	-	0.346

3. Final Values of Equivalent Conductances

From the above obtained values of dissociation constants of amines and the ionization constants⁽¹¹³⁾ of water at 25°C, 1.01×10^{-14} , and at 17°C, 5.33×10^{-15} , the effect of hydrolysis upon the conductivity was computed for each salt by using Equations (184) and (186). In general, these corrected values are practically unchanged for higher concentrations, and in very dilute solutions, the conductances are close to those uncorrected ones. From fresh plots of these values in Figures 22-24, limiting conductances were obtained. These are

$$\text{(monoethylamine hydrochloride at 25°C)} = 122.76 \text{ cm}^2\text{ohm}^{-1} \text{ equiv.}^{-1}$$

$$\text{(diethylamine hydrochloride at 25°C)} = 112.82 \text{ cm}^2\text{ohm}^{-1} \text{ equiv.}^{-1}$$

$$\text{(triethylamine hydrochloride at 17°C)} = 91.14 \text{ cm}^2\text{ohm}^{-1} \text{ equiv.}^{-1}$$

and differ from those uncorrected by less than 0.1%. Since subsequent improved values of basic dissociation constants do not alter the correction factors appreciably, it is therefore sufficient to tabulate these conductances in Tables 16, 17 and 18 as the true conductivities of these salts against the corrected stoichiometric concentrations of the hydrochlorides, i.e., the concentrations of the unhydrolyzed portions of the salts. Accordingly, the final limiting equivalent conductances computed for the aminium cations and "aminium hydroxides" are as follows:

$$\text{(monoethylaminium ion at 25°C)} = 46.41 \text{ cm}^2\text{ohm}^{-1} \text{ equivalent}^{-1}$$

$$\text{(diethylaminium ion at 25°C)} = 36.47 \quad "$$

$$\text{(triethylaminium ion at 17°C)} = 26.67 \quad "$$

$$\text{(monoethylaminium hydroxide at 25°C)} = 244.7 \quad "$$

$$\text{(diethylaminium hydroxide at 25°C)} = 234.8 \quad "$$

$$\text{(triethylaminium hydroxide at 17°C)} = 193.8 \quad "$$

For ammonium ion and ammonium hydroxide at 25°C, the limiting conductances are 73.55 (112) and 271.9 (112) respectively. The decrease in the limiting conductance in going from ammonia to triethylamine is mainly due to the size difference of the conducting species.

4. Basic Dissociation Constants of Amines

The method of finding the dissociation constants of amines is essentially that of Shedlovsky and Kay, with modifications including the water activity and molar activity coefficient of amine. According to Equation (73), the basic dissociation constant is

$$K = \frac{\alpha^2 c y_{\pm}^{\prime 2}}{(1-\alpha) y_B' a_A}$$

The Shedlovsky-Kay equation becomes

$$1000 L = 1000 L_0 + \frac{\Lambda^{\circ} y_B^{\prime \frac{1}{2}} a_A^{\frac{1}{2}} K^{\frac{1}{2}} c^{\frac{1}{2}}}{S(z) y_{\pm}'} \left[1 - \frac{\Lambda^*}{\Lambda^{\circ}} S(z) \left(1 - \frac{L_0}{L} \right) \right]^{\frac{1}{2}}$$

$$\text{or } 1000 L = 1000 L_0 + \frac{\Lambda^{\circ} y_B^{\prime \frac{1}{2}} a_A^{\frac{1}{2}} K^{\frac{1}{2}} c^{\frac{1}{2}}}{S(z) y_{\pm}'} \left[1 - \frac{\Lambda^*}{\Lambda^{\circ}} S(z) \right]^{\frac{1}{2}}$$

here the symbols have their significances given previously. Since the method is founded on the Shedlovsky conductance equation, (122), which is valid for solutions of ionic strength less than 0.01, the method will not be applied to amine solutions of concentrations considerably higher than $\alpha c = 0.01$. I have found that the relative viscosity of solution plays an important role in obtaining the straight line relationship when the Shedlovsky-Kay plot is carried out, as will be shown later.

Therefore in the following calculations and presentations, emphasis is

laid on the set of data for which the specific conductance used is the product of the measured conductance and the relative viscosity. This is equivalent to obtaining a set of conductance data measured in a solvent of unit relative viscosity. Comparison between the conductances viscosity corrected and uncorrected will be given in graphs later.

To proceed with this method of finding the solvent corrections for the three systems, first, the constants B_1 and B_2 appearing in the Fuoss-Onsager equation, i.e., Equation (116) were calculated from the dielectric constants of water given by Malmberg and Maryott⁽¹¹⁴⁾,

$$B_1 = 0.2300 \text{ at } 25^\circ\text{C}; \quad 0.2268 \text{ at } 17^\circ\text{C}$$

$$B_2 = 60.65 \text{ at } 25^\circ\text{C}; \quad 49.74 \text{ at } 17^\circ\text{C}$$

From the limiting conductances of the "aminium hydroxides" above, the values of $(B_1 \Lambda^\circ + B_2)$ were calculated,

$$B_1 \Lambda^\circ + B_2 = 116.9 \text{ for "monoethylaminium hydroxide" at } 25^\circ\text{C}$$

$$= 114.7 \text{ for "diethylaminium hydroxide" at } 25^\circ\text{C}$$

$$= 94.0 \text{ for "triethylaminium hydroxide" at } 17^\circ\text{C}$$

Then the necessary quantities involved, namely, $\frac{\Lambda^*}{\Lambda^\circ}$ and β of Equation (171) were computed with the inclusion of the relative viscosity factor.

From the interpolation table for $S(\beta)$ given by Daggett⁽⁷⁷⁾, values of $S(\beta)$ for each concentration were obtained. The degree of dissociation,

$\frac{\Lambda^*}{\Lambda^\circ} S(\beta)$ was then evaluated.

The mean activity coefficients of the free ionic species were calculated by using the Davies equation,

$$\log \gamma_{\pm} = -A \left(\frac{|z_1 z_2| \sqrt{I}}{1 + \sqrt{I}} - 0.3 I \right)$$

with $A = 0.5115$ at 25°C ; 0.5045 at 17°C .

The ionic strength here was set equal to αC .

The molar activity coefficients of the free amine molecules were evaluated according to Equations (74) and (75). An example of obtaining the limiting value of $\frac{c(1-\alpha)}{a_B}$ for monoethylamine is given in Figure 25 where $\frac{c(1-\alpha)}{a_B}$ is plotted against c . Since the vapor pressures of amines in very dilute solutions were not determined due to experimental difficulty, I was obliged to use the data for higher concentrations, where α can only be calculated approximately, $\sim \frac{\Delta}{\Lambda^c}$. Although such an extrapolation, from the plot, may lead to only an approximate limiting value of k , nevertheless the activity coefficient in any dilute solution is the ratio of k to the value read off from the curve in this particular concentration, and is fairly insensitive to the variation of k , provided the slope in the dilute region is not exceptionally large. In all cases, the activity coefficients of amine molecules in dilute solutions are close to unity and the fact that they are practically unity in very dilute solutions justifies the neglect of this term by many well known authors.

The water activities of the aqueous amine solutions were obtained from Figures 19, 20 and 21, and were equal to unity in dilute solutions.

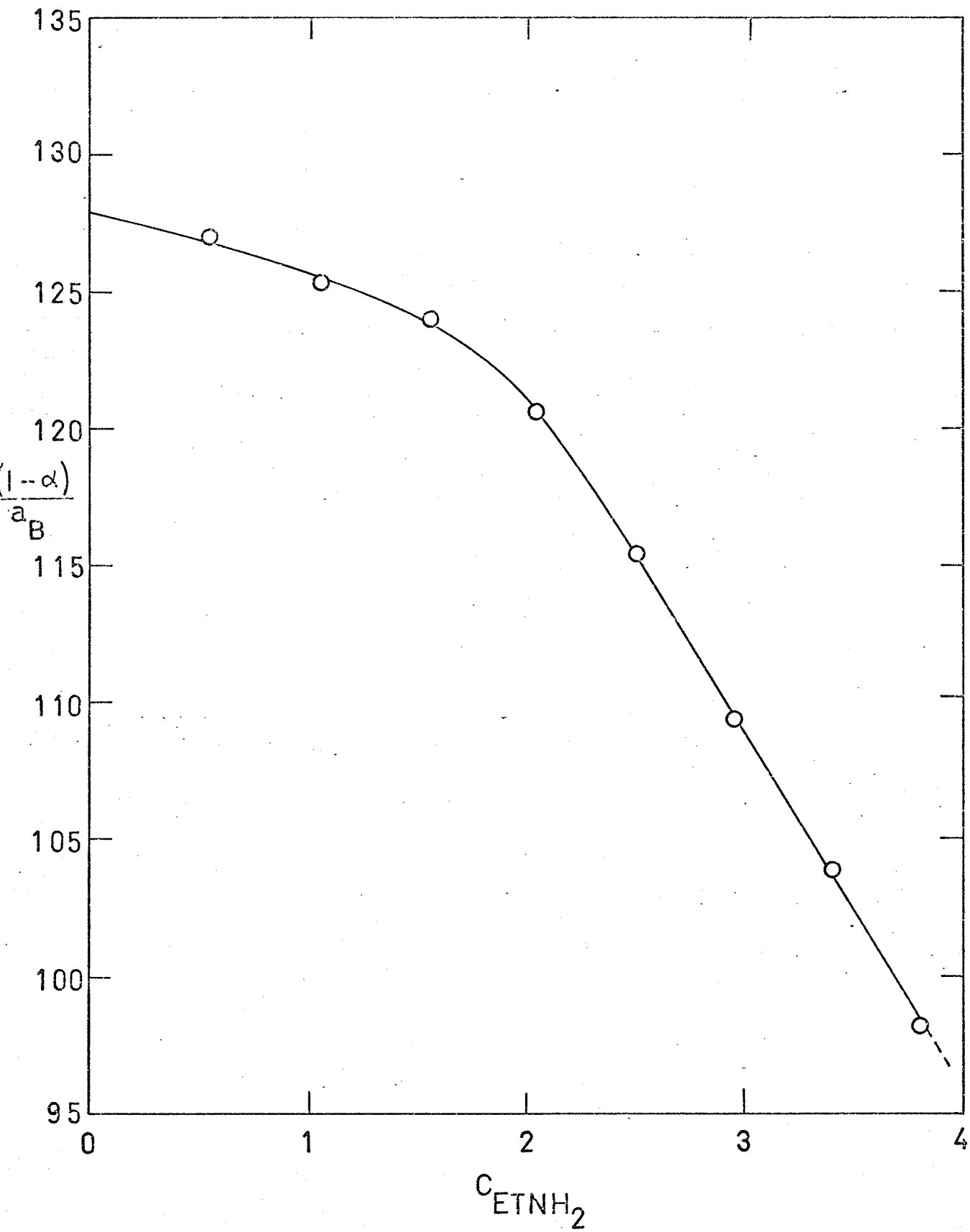
With these activity coefficients, water activities and the other quantities, values of $\frac{y_B'^{\frac{1}{2}} a_A'^{\frac{1}{2}} c^{\frac{1}{2}}}{y_2' S_2'} \left[1 - \frac{\Delta^*}{\Lambda^c} S_2' \right]^{\frac{1}{2}}$ were calculated, and plotted against the viscosity corrected specific conductances. The plots are entirely similar to the final plots subsequently shown which give rise to the dissociation constants, except that the former give the solvent corrections L_0 's for the aqueous amine solutions. These are

4.5 x 10⁻⁶ for monoethylamine solutions

3.5 x 10⁻⁶ for diethylamine solutions

and 4.0 x 10⁻⁶ for triethylamine solutions

Figure 25. $\frac{c(1 - \alpha)}{a_B}$ vs. c for Monoethylamine at 25°C.



The empirical corrections are several times larger than the original specific conductance of water used which contained some carbonic acid, because the amines converted the weak acid into the completely ionized salts.

The true specific conductances of solutions were then computed. The stoichiometric concentrations of the amines were also corrected for the portions of amines converted into salts by the method below, using monoethylamine solution as an example. By using the limiting conductivity of monoethylaminium ion in a previous section, and those of HCO_3^- and CO_3^{--} ions (115) at 25°C , the concentrations of bicarbonate and carbonate were estimated by the relation $\frac{L_o \times 10^3}{\Lambda_{\text{salt}}^\circ}$, assuming that neutralization is complete entirely to bicarbonate or carbonate. These concentrations are

$$C_{\text{bicarbonate}} = 4.9 \times 10^{-5}$$

$$C_{\text{carbonate}} = 2.0 \times 10^{-5}$$

The concentration of monoethylaminium ion is αC . From the estimated dissociation constant of monoethylamine, $K = 4.8 \times 10^{-4}$, the ion product of water and the dissociation constants of carbonic acid, viz., $K_1 = 4.4 \times 10^{-7}$ and $K_2 = 4.7 \times 10^{-11}$, the following equilibria can be formulated,

$$\frac{[\text{aminium}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3][\text{"aminium hydroxide"}]} = \frac{\alpha}{1-\alpha} \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 2.1 \times 10^4$$

$$\frac{[\text{aminium}^+][\text{CO}_3^{--}]}{[\text{HCO}_3^-][\text{"aminium hydroxide"}]} = \frac{\alpha}{1-\alpha} \frac{[\text{CO}_3^{--}]}{[\text{HCO}_3^-]} = 2.3$$

Since the degree of dissociation is less than 0.4 for the most dilute

monoethylamine solution, the ratio $\frac{[CO_3^{--}]}{[HCO_3^-]}$ is larger than 3. Therefore for simplicity I assumed that portion of base was completely converted to dibasic salt. The correction for monoethylamine solutions is therefore 4.0×10^{-5} rather than 4.9×10^{-5} , and was constantly subtracted from the concentrations of monoethylamine to obtain the corrected values. In a similar manner, corrections found for diethylamine and triethylamine solutions are 3.3×10^{-5} and 4.7×10^{-5} respectively.

With the corrected concentrations and specific conductances, new values of λ , β , $S(\beta)$, α and y_{\pm}' , for which the ionic strength included the contribution from the salt, were calculated. In Tables 22, 23 and 24, the relevant quantities are given and the final plots of corrected specific conductance vs. $\left[1 - \frac{\Lambda^*}{\Lambda^0} S(\beta) \left(1 - \frac{L_0}{L}\right)\right]^{\frac{1}{2}} \frac{y_{\pm}'^{\frac{1}{2}} a_A^{\frac{1}{2}} c^{\frac{1}{2}}}{S(\beta) y_{\pm}'}$ are shown in Figures 26-28. Points in low concentration regions lie on straight lines which intercept the origins. The slopes were measured. Knowing the limiting conductances, the basic dissociation constants were calculated. These are

$$4.57 \times 10^{-4} \quad \text{for monoethylamine at } 25^{\circ}\text{C}$$

$$1.02 \times 10^{-3} \quad \text{for diethylamine at } 25^{\circ}\text{C}$$

and $4.93 \times 10^{-4} \quad \text{for triethylamine at } 17^{\circ}\text{C}$

Separate calculations, neglecting the viscosity factor, were also made for the three systems. The results are given in the same figures. It is obvious that without viscosity corrections, deviations from the straight lines are much larger than those with the same corrections in higher concentrations. In less dilute solutions, for which values of αc are still less than 0.01, and therefore still within the working range of the Shedlovsky conductance equation, the deviations of the viscosity corrected values from the straight lines are presumably due mainly

to the decreases of dielectric constants as the neutral amine molecules become more and more parts of the solvent media for the moving ions, when the concentration increases.

TABLE 22

Data Relevant to the Shedlovsky-Kay Plot for Aqueous Monoethylamine
Solutions at 25°C

$L_0 = 4.5 \times 10^{-6}$ $\lambda^\circ = 244.7$

C_{corr}	$L_{corr} \times 10^4$	λ	δ	$S(\delta)$	α	y'_\pm	y'_B	$a_A^{1/2}$	$\frac{c \frac{1}{2} a_A^{1/2}}{5g y'_\pm} \left[1 - \frac{\lambda^\circ (1 - \frac{\lambda^\circ}{L})}{\lambda^\circ} \right]^{1/2}$
0.001997	1.825	91.34	0.01305	1.0130	0.3782	0.968	1.000	1.000	0.0362
0.004932	3.186	64.59	0.01724	1.0173	0.2686	0.959	1.000	1.000	0.0616
0.008455	4.372	51.70	0.02021	1.0203	0.2156	0.953	1.000	1.000	0.0844
0.016969	6.457	38.05	0.02456	1.0249	0.1594	0.944	1.000	1.000	0.1235
0.040872	10.443	25.55	0.03124	1.0310	0.1074	0.930	1.000	1.000	0.1992
0.09482	16.252	17.14	0.03895	1.0397	0.0728	0.915	1.001	1.000	0.3118
0.20245	23.941	11.83	0.04728	1.0484	0.0507	0.900	1.001	.999	0.4642
0.5064	37.140	7.335	0.05890	1.0605	0.03179	0.881	1.004	.997	0.750

TABLE 23

Data Relevant to the Shedlovsky-Kay Plot for Aqueous Diethylamine
Solutions at 25°C

$$L_0 = 3.5 \times 10^{-6} \quad \Lambda^\circ = 234.8$$

C_{corr}	$L_{\text{corr}} \times 10^4$	Λ	δ	$S(\delta)$	α	y'_B	y'_B	α_A	$\frac{c^{\frac{1}{2}} y'_B \alpha_A^{\frac{1}{2}}}{S(\delta) y'_B} \left[1 - \frac{\Lambda^\circ (1 - \frac{L_0}{L})}{\Lambda^\circ} \right]^{\frac{1}{2}}$
0.007902	5.656	71.58	0.02397	1.0242	0.3122	0.946	1.000	1.000	0.0762
0.009922	6.437	64.88	0.02557	1.0259	0.2835	0.943	1.001	1.000	0.0873
0.023629	10.729	45.41	0.03301	1.0336	0.1990	0.928	1.002	1.000	0.1440
0.048933	16.104	32.91	0.04045	1.0413	0.1460	0.915	1.002	1.000	0.2150
0.06534	18.963	29.02	0.04389	1.0448	0.1292	0.908	1.003	.999	0.2522
0.09040	22.367	24.74	0.04766	1.0488	0.1105	0.902	1.004	.999	0.3006
0.11563	25.626	22.16	0.05102	1.0524	0.0993	0.896	1.005	.998	0.3436
0.20282	33.841	16.69	0.05863	1.0603	0.0753	0.883	1.008	.998	0.4654
0.33126	42.662	12.88	0.06583	1.0681	0.0586	0.872	1.013	.997	0.605

TABLE 24

Data Relevant to the Shedlovsky-Kay Plot for Aqueous Triethylamine Solutions at 17°C

$$L_0 = 4.0 \times 10^{-6} \quad \Lambda^\circ = 193.8$$

C_{corr}	$L_{\text{corr}} \times 10^4$	Λ	\bar{z}	$S(\bar{z})$	α	γ_{\pm}	$\gamma_{\pm}^{1/2}$	$\alpha^{1/2}$	$\frac{c^{1/2} \gamma_{\pm}^{1/2} a_{\pm}^{1/2}}{S(\bar{z}) \gamma_{\pm}^{1/2}} \left[1 - \frac{\Lambda^\circ (1 - \frac{L_0}{L})}{\Lambda^\circ} \right]^{1/2}$
0.00411	2.339	56.90	0.01680	1.0169	0.2986	0.971	1.000	1.000	0.0554
0.00990	3.894	39.33	0.02167	1.0218	0.2074	0.951	1.000	1.000	0.0915
0.02290	6.221	27.17	0.02739	1.0278	0.1441	0.935	0.998	1.000	0.1457
0.06811	10.945	16.07	0.03634	1.0369	0.0860	0.922	0.994	0.999	0.2594
0.11912	14.678	12.32	0.04208	1.0429	0.0663	0.912	0.990	0.999	0.3470
0.22061	19.803	8.977	0.04887	1.0502	0.04869	0.900	0.980	0.997	0.4742
0.38464	25.388	6.600	0.05534	1.0568	0.03599	0.889	0.963	0.996	0.622
0.7877	31.943	4.055	0.06207	1.0640	0.02226	0.879	0.910	0.994	0.848

Figure 26. Shedlovsky-Kay Plot for Aqueous Mono-ethylamine Solutions at 25°C.

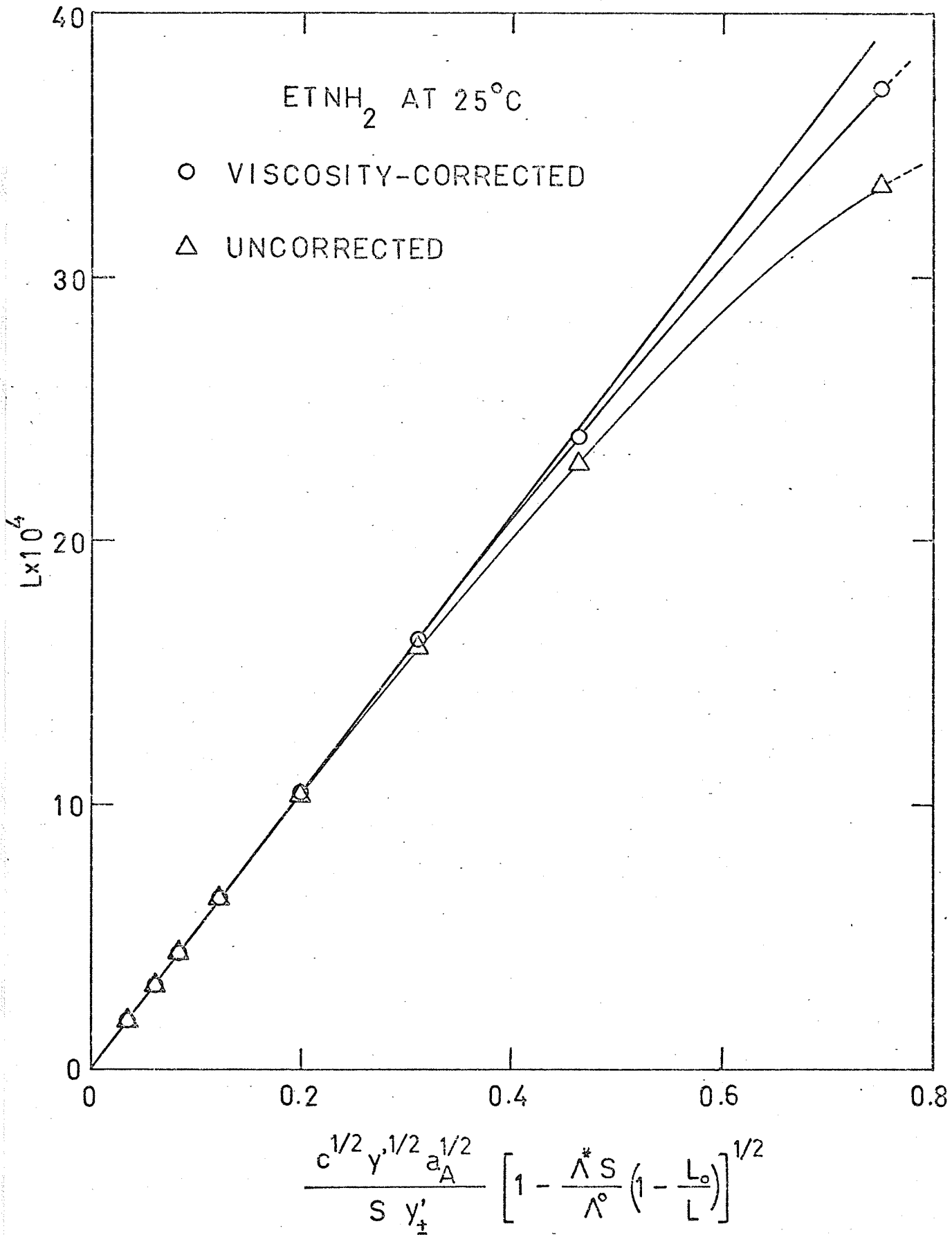


Figure 27. Shedlovsky-Kay Plot for Aqueous
Diethylamine Solutions at 25°C.

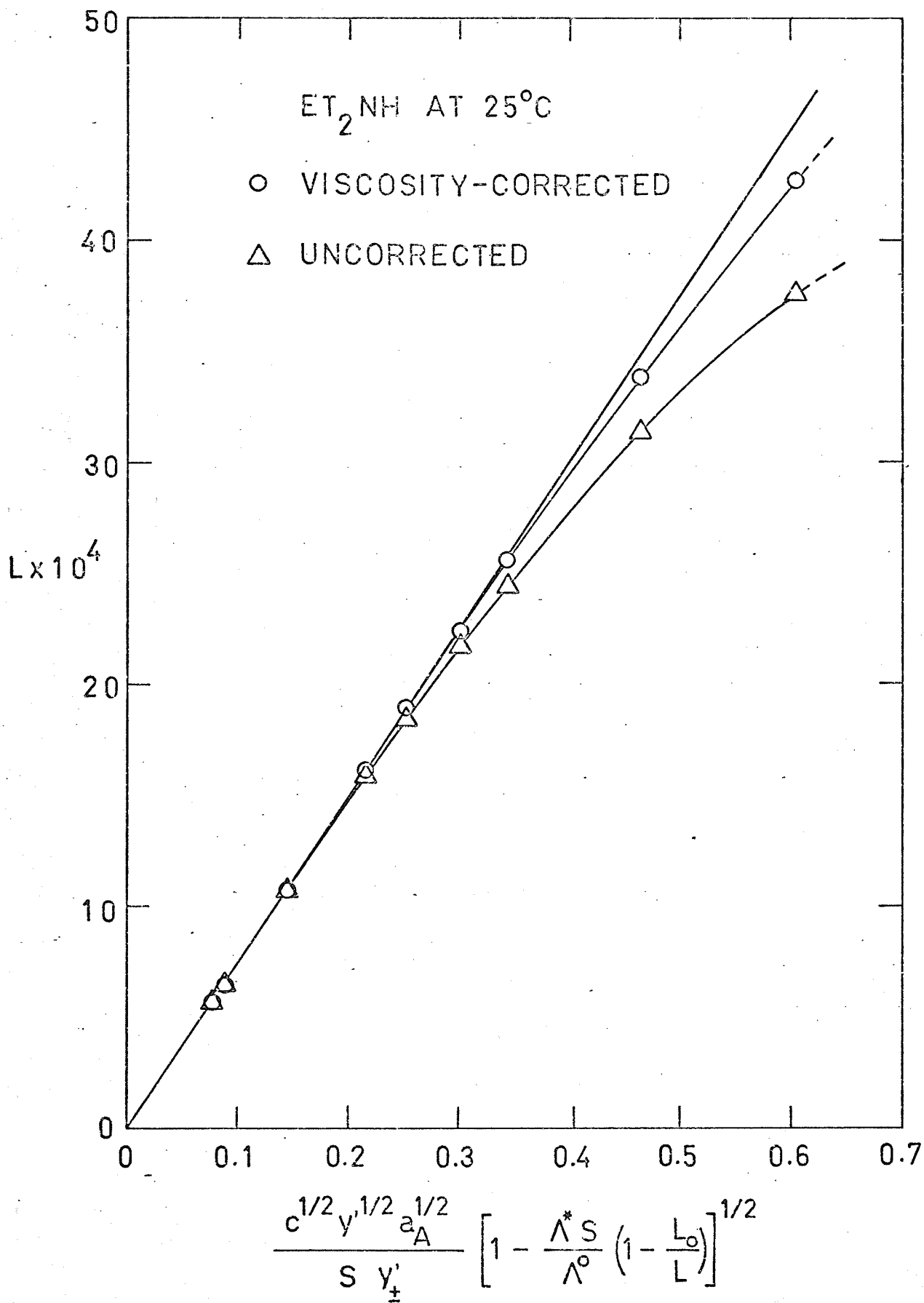
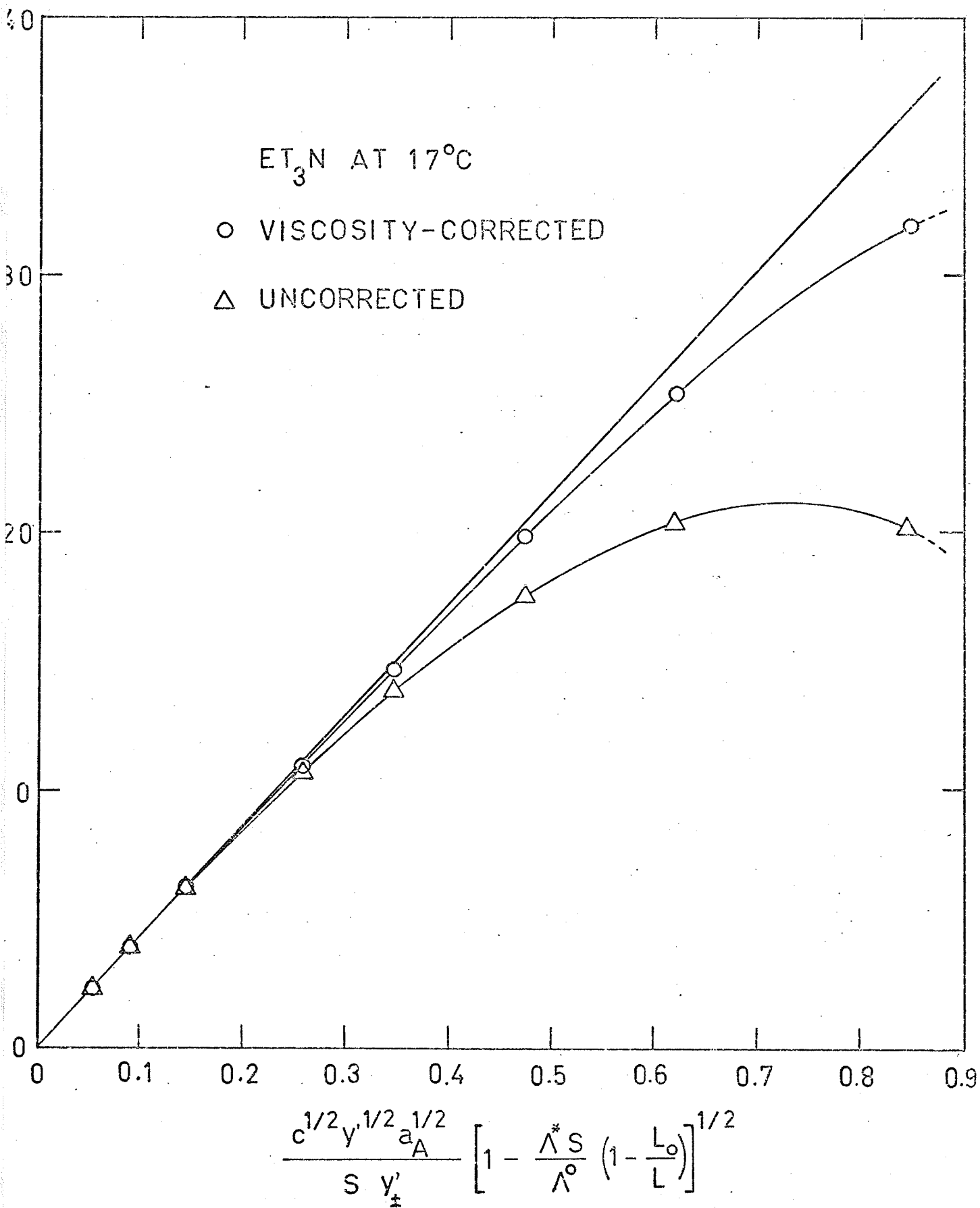


Figure 28. Shedlovsky-Kay Plot for Aqueous Tri-ethylamine Solutions at 17°C.



IV.E Diffusion Coefficients

The theory for calculating the diffusion coefficients for concentration dependent systems from diaphragm cell experiments was given by Gordon⁽¹⁰⁶⁾ and extended by Stokes^(104,107,116). The principle assumptions of the theory are as follows: (1) The diaphragm is considered to be equivalent to a collection of parallel pores, i.e., the diffusion process is assumed to be unidirectional. (2) The concentrations of the solutions are assumed to be uniformly constant up to the diaphragm, and (3) stagnant layers on the surface of the diaphragm do not exist. (4) Transport from one compartment to the other is only by diffusion. (5) There is no streaming through the diaphragm or surface transport effect along the pore walls. (6) The diaphragm assumes a steady state throughout the experiment, i.e., there is no gain or loss of solute from the diaphragm. (7) The volumes of the two solutions are assumed constant during the experiment.

In a diaphragm cell diffusion measurement, there is a set of four concentrations, $c_1 > c_3 > c_4 > c_2 = 0$, where c_1 and c_2 represent the initial concentrations, and c_3 and c_4 denote the final concentrations. Let the volume of one compartment of the cell associated with the more concentrated solution, c_1 or c_3 be V_1 , and the volume of the other compartment with the less concentrated solution, c_2 or c_4 by V_2 . Let the pores have a total effective cross-sectional area A , and an average length l . Let c' and c'' be the concentrations of the more concentrated and less concentrated solutions at any time during an experiment. At time $t = 0$, $c' = c_1$, and $c'' = c_2$; at the end of the experiment $c' = c_3$ and $c'' = c_4$. The rates of change of c' and c'' are related to the flux $J(t)$ by

$$\frac{dc'}{dt} = -J(t) \frac{A}{V_1} \quad (253)$$

and

$$\frac{dc''}{dt} = J(t) \frac{A}{V_2} \quad (254)$$

A combination of the two relations gives

$$\frac{d(c' - c'')}{dt} = -J(t) A \left(\frac{1}{V_1} + \frac{1}{V_2} \right) \quad (255)$$

By introducing the time dependent quantity $\bar{D}(t)$, i.e., the average value of the diffusion coefficient D with respect to concentration over the concentration range c' to c'' prevailing in the experiment, then

$$\begin{aligned} \bar{D}(t) &= \frac{1}{c' - c''} \int_{c''}^{c'} D dc = - \frac{1}{c' - c''} \int_{x=0}^l D \left(\frac{\partial c}{\partial x} \right) dx \\ &= \frac{l J(t)}{c' - c''} \end{aligned} \quad (256)$$

for $J(t) = -D \frac{\partial c}{\partial x}$ is constant at all points within the diaphragm at time t , x being the distance of the plane from the surface of the diaphragm that is in contact with the more concentrated solution. From Equations (255) and (256), one obtains

$$- \frac{d \ln(c' - c'')}{dt} = \frac{A}{l} \left(\frac{1}{V_1} + \frac{1}{V_2} \right) \bar{D}(t) \quad (257)$$

By integrating this equation subject to the boundary conditions, one arrives at

$$\ln \frac{c_1 - c_2}{c_3 - c_4} = \frac{A}{l} \left(\frac{1}{V_1} + \frac{1}{V_2} \right) \int_0^t \bar{D}(t) dt \quad (258)$$

Defining the diaphragm cell integral diffusion coefficient \bar{D} as the time-average of $\bar{D}(t)$, i.e.,

$$\bar{D} = \frac{1}{t} \int_0^t \bar{D}(t) dt \quad (259)$$

and writing the cell constant β for $\frac{A}{l} \left(\frac{1}{V_1} + \frac{1}{V_2} \right)$, the following diffusion cell equation is obtained,

$$\bar{D} = \frac{l}{\beta t} \ln \frac{c_1 - c_2}{c_3 - c_4} \quad (260)$$

The value \bar{D} calculated from the initial and final concentrations and time by the above expression is a complicated double average which is not easy to convert immediately into the more fundamental differential diffusion coefficient D . Fortunately it has been shown by Gordon⁽¹⁰⁶⁾ and confirmed by Stokes^(104,107,116), that a negligible error is introduced in all ordinary cases if instead of using the exact relation,

$$\bar{D} = \frac{1}{t} \int_0^t \bar{D}(t) dt \quad (261)$$

the integrand is treated as having a constant value equal to its value when the concentrations c' and c'' are half-way between their initial and final values. This constant value is equal to \bar{D} by virtue of the integrated form of the above equation and calculable from Equation (260), and is related to the differential diffusion coefficient by

$$\bar{D} = \frac{l}{c_{m'} - c_{m''}} \int_{c_{m''}}^{c_{m'}} D dc \quad (262)$$

where $c_{m'} = \frac{c_1 + c_3}{2}$, $c_{m''} = \frac{c_2 + c_4}{2} = \frac{c_4}{2}$

Further to resolve \bar{D} into D , it is expedient to define a new integral diffusion coefficient as that which would be obtained in a run of vanishingly short duration with initial concentrations c and zero on

opposite sides of the diaphragm,

$$\bar{D}^{\circ} = \frac{1}{c} \int_0^c D dc \quad (263)$$

The values of \bar{D}° in such hypothetical experiments with initial concentrations $c_{m'}$ and $c_{m''}$, are denoted by $\bar{D}^{\circ}(c_{m'})$ and $\bar{D}^{\circ}(c_{m''})$ respectively

$$\bar{D}^{\circ}(c_{m'}) = \frac{1}{c_{m'}} \int_0^{c_{m'}} D dc \quad (264)$$

$$\bar{D}^{\circ}(c_{m''}) = \frac{1}{c_{m''}} \int_0^{c_{m''}} D dc \quad (265)$$

By means of the relation

$$\int_{c_{m''}}^{c_{m'}} D dc = \int_0^{c_{m'}} D dc - \int_0^{c_{m''}} D dc \quad (266)$$

it follows from Equations (262), (264), and (265) that

$$\bar{D}^{\circ}(c_{m'}) = \bar{D} - \frac{c_{m''}}{c_{m'}} [\bar{D} - \bar{D}^{\circ}(c_{m''})] \quad (267)$$

In this formula \bar{D} , $c_{m'}$, and $c_{m''}$ are experimental quantities. If in some way values of $\bar{D}^{\circ}(c_{m''})$ can be estimated and hence of $\bar{D}^{\circ}(c_{m'})$, then the differential diffusion coefficient can be calculated by using an equivalent form of Equation (263). This can be done by successive approximations to find true values of $\bar{D}^{\circ}(c_{m'})$. The first step is to plot \bar{D} vs. c_1 and extrapolate the curve to the Nernst limiting value at infinite dilution. From this curve approximated values of $\bar{D}^{\circ}(c_{m''})$ are first determined for each run and substituted in the square brackets of Equation (267). The resulting values of $\bar{D}^{\circ}(c_{m'})$ are then plotted against $c_{m'}$; this curve gives a better approximation to the true value of $\bar{D}^{\circ}(c_{m''})$. The processes of substitution and fresh plotting are repeated until con-

stant values of $\bar{D}^0(c_{m'})$ are obtained. From these $\bar{D}^0(c_{m'})$ data the differential diffusion coefficient D can be calculated, since Equation (263) or (264) is readily differentiable to give

$$D = \bar{D}^0 + c \frac{d\bar{D}^0}{dc} \quad (268)$$

or

$$D = \bar{D}^0 + \frac{1}{2} \sqrt{c} \frac{d\bar{D}^0}{d\sqrt{c}} \quad (269)$$

The diaphragm cell integral diffusion coefficients for the three aqueous amine systems are given in Tables 25-27. Values of $c_{m'}$ and $c_{m''}$ were calculated. To obtain approximated values of $\bar{D}^0(c_{m''})$, values of \bar{D} vs c_1 were plotted. Curves were extrapolated to the Nernst Limiting values calculated from Equation (201). These are

$$\begin{aligned} \bar{D}^0 &= 2.002 \times 10^{-5} \quad \text{for monoethylamine at } 25^\circ\text{C} \\ &= 1.640 \times 10^{-5} \quad \text{for diethylamine at } 25^\circ\text{C} \\ &= 1.192 \times 10^{-5} \quad \text{for triethylamine at } 17^\circ\text{C} \end{aligned}$$

The graphs of \bar{D} against c_1 are similar to the plots of $\bar{D}^0(c_{m'})$ vs. $c_{m'}$ shown in Figures 29-31. From these last plots values of $\bar{D}^0(c_{m''})$ and accordingly $\bar{D}^0(c_{m'})$ were determined. In all cases, three series of approximations are sufficient to give constant values of \bar{D}^0 of Equation (267). Values of $\frac{d\bar{D}^0}{dc}$ were computed from these figures. By using Equation (268), the differential diffusion coefficients were calculated. Tables 28-30 summarize the necessary quantities from which the values of D were derived. In Figures 32-34 graphical presentation of differential diffusion coefficients as functions of concentration are given.

TABLE 25

Integral Diffusion Coefficients for Aqueous Monoethylamine Solutions
at 25°C

$$c_2 = 0$$

c_1	c_3	c_4	$c_{m'}$	$c_{m''}$	β in cm^{-2}	t in sec	$\bar{D} \times 10^5$ in $\text{cm}^2\text{sec}^{-1}$
0.1130	0.0836	0.0338	0.0983	0.0169	0.3840	171780	1.245
0.2589	0.1934	0.0745	0.2262	0.0373	0.3802	168300	1.216
0.4411	0.3277	0.1280	0.3840	0.0640	0.3790	175440	1.192
0.7840	0.5916	0.2173	0.6378	0.1087	0.3775	169560	1.156
1.334	1.020	0.355	1.177	0.178	0.3750	166200	1.116
2.270	1.740	0.598	2.005	0.299	0.3742	172860	1.062
3.490	2.725	0.889	3.108	0.445	0.3734	166260	1.009
4.680	3.683	1.116	4.182	0.558	0.3718	165840	0.974
5.404	4.206	1.351	4.805	0.676	0.3848	174120	0.952
5.929	4.632	1.470	5.281	0.735	0.3713	180480	0.938
7.200	5.776	1.633	6.488	0.817	0.3706	165720	0.900
8.598	6.845	2.029	7.722	1.015	0.3695	176160	0.890
9.749	7.827	2.261	8.788	1.132	0.3690	170280	0.894
11.366	9.123	2.688	10.245	1.344	0.3685	169140	0.913
12.639	10.306	3.087	11.473	1.544	0.3675	161280	0.904
13.966	11.234	3.657	12.600	1.829	0.3670	159720	1.044

TABLE 26

Integral Diffusion Coefficients for Aqueous Diethylamine Solutions
at 25°C

$$c_2 = 0$$

c_1	c_3	c_4	$c_{m'}$	$c_{m''}$	β in cm^{-2}	t in sec	$\bar{D} \times 10^5$ in $\text{cm}^2 \text{sec}^{-1}$
0.1072	0.0761	0.0345	0.0916	0.0173	0.3530	283740	9.45
0.2042	0.1522	0.0575	0.1782	0.0288	0.3419	247800	9.09
0.2045	0.1511	0.0596	0.1778	0.0298	0.3526	252720	9.03
0.3488	0.2552	0.1036	0.3020	0.0518	0.3494	275220	8.70
0.3530	0.2592	0.1033	0.3062	0.0517	0.3512	268560	8.67
0.5478	0.4130	0.1491	0.4805	0.0746	0.3477	255180	8.22
0.6329	0.4899	0.1572	0.5614	0.0786	0.3399	228840	8.27
0.8054	0.6086	0.2172	0.7068	0.1086	0.3472	261840	7.93
1.1669	0.9607	0.2250	1.0638	0.1225	0.3457	176760	7.51
1.2249	0.8912	0.3670	1.0581	0.1835	0.3382	336840	7.46
1.6415	1.3812	0.2848	1.5514	0.1424	0.3357	168600	7.13
1.7005	1.3386	0.3980	1.5196	0.1990	0.3535	239640	6.99
2.1438	1.8210	0.3533	1.9824	0.1767	0.3345	170160	6.66
2.6656	2.0181	0.7120	2.3419	0.3560	0.3305	355740	6.07
3.3078	2.6109	0.7786	2.9594	0.3893	0.3284	327900	5.49
3.882	3.107	0.848	3.495	0.424	0.3266	329340	5.03
4.628	3.820	0.915	4.224	0.458	0.3230	315680	4.57
5.387	4.452	1.070	4.920	0.535	0.3215	355500	4.07
6.207	5.079	1.283	5.652	0.642	0.3197	398040	3.83
6.965	5.917	1.270	6.441	0.635	0.3167	344400	3.77
7.724	6.635	1.365	7.180	0.683	0.3152	325200	3.73
8.480	7.522	1.305	8.003	0.653	0.3139	255960	3.87
9.225	8.137	1.645	8.681	0.823	0.3452	244080	4.17
9.555	8.465	1.884	9.010	0.924	0.3444	241380	4.49

TABLE 27

Integral Diffusion Coefficients for Aqueous Triethylamine Solutions
at 17°C

$$c_2 = 0$$

c_1	c_3	c_4	$c_{m'}$	$c_{m''}$	β in cm^{-2}	t in sec	$\bar{D} \times 10^5$ in $\text{cm}^2 \text{sec}^{-1}$
0.0754	0.0532	0.0241	0.0643	0.0121	0.3645	405000	6.45
0.1001	0.0847	0.0163	0.0924	0.0082	0.3665	161400	6.26
0.1948	0.1491	0.0510	0.1720	0.0255	0.3647	322200	5.84
0.4572	0.3510	0.1132	0.4041	0.0566	0.3622	326700	5.53
0.6500	0.5060	0.1538	0.5780	0.0769	0.3616	323700	5.24
0.9192	0.7396	0.1950	0.8294	0.0975	0.3611	312060	4.64
1.1047	0.8989	0.2226	0.9518	0.1113	0.3605	325860	4.17
1.3837	1.1146	0.2925	1.2491	0.1462	0.3650	409680	3.48
1.5644	1.2815	0.3090	1.4230	0.1545	0.3646	423180	3.08
1.5989	1.3295	0.2927	1.4642	0.1464	0.3598	403680	2.98
2.1860	1.9468	0.2560	2.0664	0.1280	0.3587	314640	2.28
2.906	2.718	0.226	2.812	0.113	0.3583	254280	1.69
3.658	3.415	0.282	3.537	0.141	0.3580	318600	1.36
4.416	4.204	0.246	4.310	0.123	0.3575	350620	1.22
5.071	4.776	0.351	4.924	0.176	0.3571	329280	1.16
5.804	5.534	0.333	5.669	0.167	0.3562	256740	1.20
6.330	6.042	0.360	6.186	0.180	0.3555	242520	1.25
6.984	6.641	0.487	6.812	0.244	0.3549	268860	1.33
7.213	6.972	0.471	7.093	0.236	0.3543	158700	1.85

Figure 29. \bar{D}° vs. c for Monoethylamine in
Aqueous Solutions at 25°C.

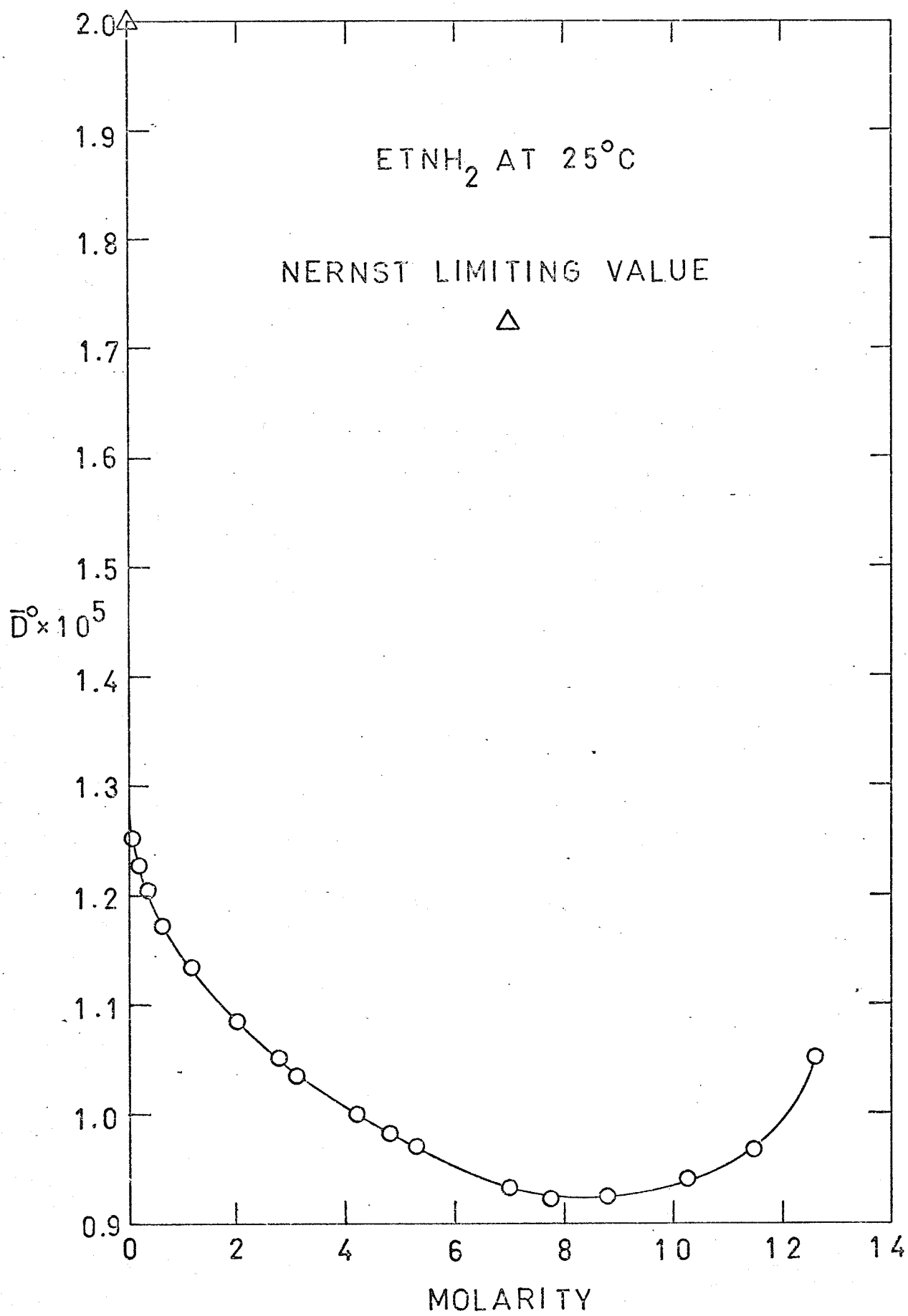


Figure 30. \bar{D}° vs. c for Diethylamine in
Aqueous Solutions at 25°C.

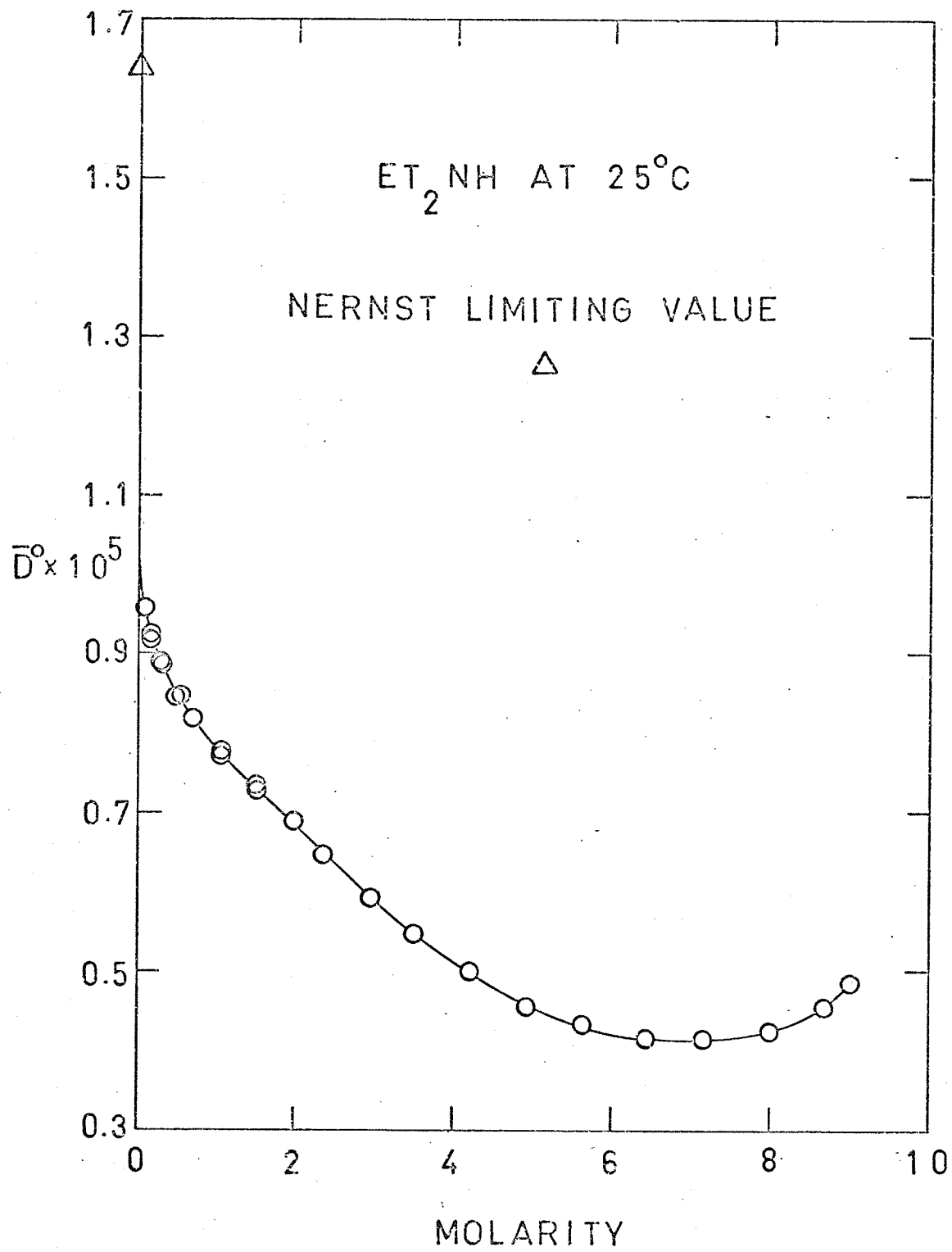


Figure 31. \bar{D}° vs. c for Triethylamine in
Aqueous Solutions at 17°C.

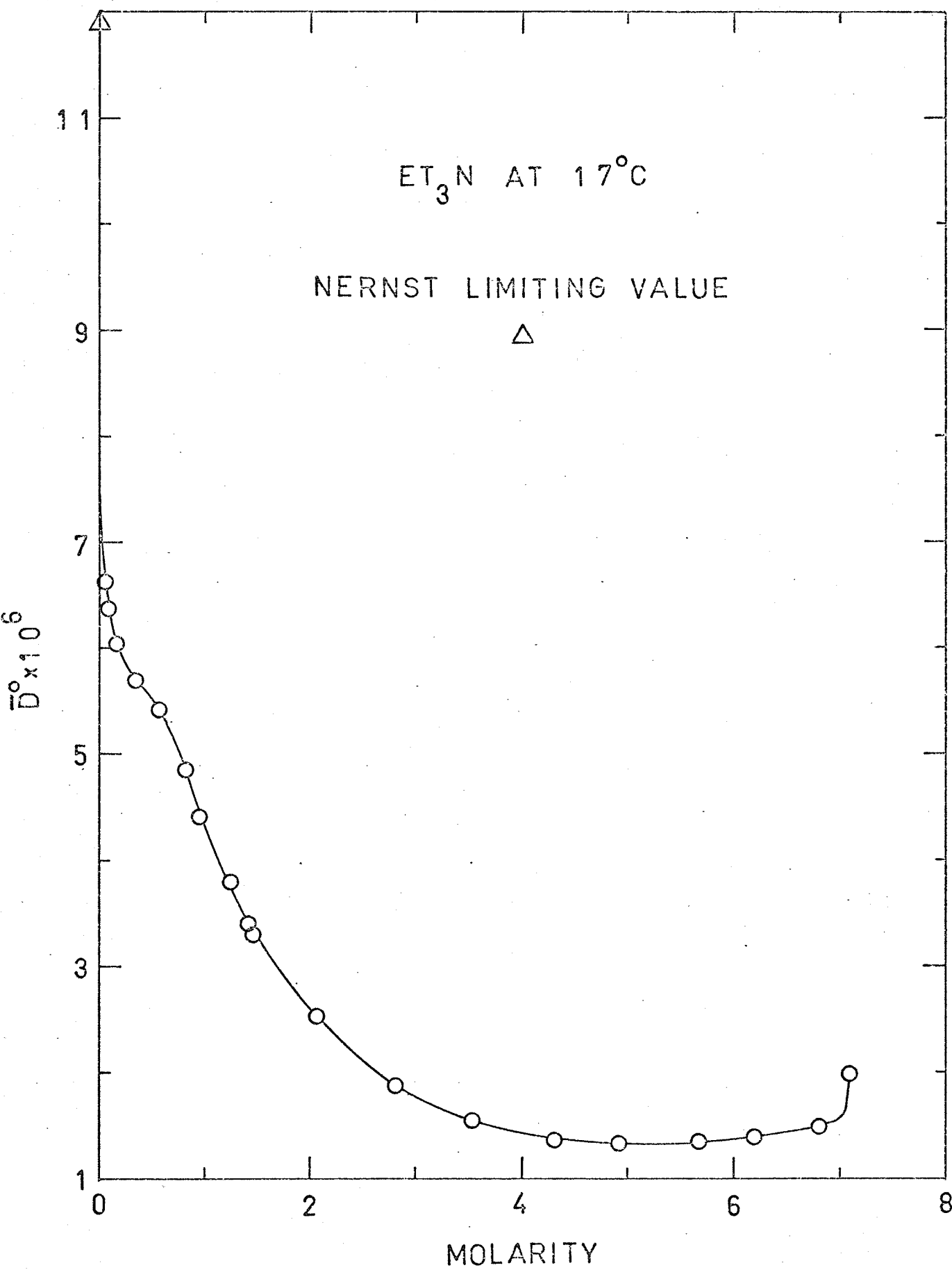


TABLE 28

Integral Diffusion Coefficients for Runs of Vanishingly Short Duration and
Differential Diffusion Coefficients for Monoethylamine in Aqueous Solutions
at 25°C

$C = C_m'$	C_m''	$\bar{D}(C_m') \times 10^5$ in $\text{cm}^2 \text{sec}^{-1}$	$\bar{D}(C_m'') \times 10^5$ in $\text{cm}^2 \text{sec}^{-1}$	$C \frac{d\bar{D}}{dC} \times 10^5$ in $\text{cm}^2 \text{sec}^{-1}$	$D \times 10^5$ in $\text{cm}^2 \text{sec}^{-1}$
0.0983	0.0169	1.252	1.285	-0.025	1.227
0.2262	0.0373	1.226	1.275	-0.036	1.190
0.3844	0.0640	1.204	1.265	-0.049	1.155
0.6378	0.1087	1.172	1.251	-0.059	1.113
1.177	0.178	1.134	1.234	-0.080	1.054
2.005	0.299	1.085	1.216	-0.099	0.986
3.108	0.445	1.035	1.194	-0.114	0.921
4.182	0.558	1.001	1.179	-0.128	0.873
4.805	0.676	0.983	1.169	-0.136	0.847
5.281	0.735	0.970	1.165	-0.145	0.825
6.488	0.817	0.932	1.158	-0.106	0.826
7.722	1.015	0.923	1.144	-0.046	0.877
8.788	1.132	0.925	1.137	0.035	0.960
10.245	1.344	0.940	1.122	0.169	1.109
11.473	1.544	0.967	1.109	0.377	1.344
12.600	1.829	1.051	1.093	-	-

TABLE 29

Integral Diffusion Coefficients for Runs of Vanishingly Short Duration and
Differential Diffusion Coefficients for Diethylamine in Aqueous Solutions
at 25°C

$C = C_{m'}$	$C_{m''}$	$\bar{D}^o(c_{m'}) \times 10^5$ in $\text{cm}^2 \text{sec}^{-1}$	$\bar{D}^o(c_{m''}) \times 10^5$ in $\text{cm}^2 \text{sec}^{-1}$	$c \frac{d\bar{D}^o}{dc} \times 10^5$ in $\text{cm}^2 \text{sec}^{-1}$	$D \times 10^5$ in $\text{cm}^2 \text{sec}^{-1}$
0.0916	0.0173	0.957	1.011	-0.052	0.905
0.1782	0.0288	0.923	0.995	-0.060	0.863
0.1778	0.0298	0.918	0.995	-0.060	0.858
0.3020	0.0518	0.889	0.979	-0.068	0.821
0.3062	0.0517	0.886	0.979	-0.070	0.816
0.4805	0.0746	0.845	0.967	-0.083	0.762
0.5614	0.0786	0.846	0.963	-0.087	0.759
0.7068	0.1086	0.816	0.945	-0.095	0.721
1.0581	0.1835	0.776	0.917	-0.115	0.661
1.0638	0.1125	0.771	0.942	-0.115	0.656
1.5114	0.1424	0.733	0.928	-0.142	0.591
1.5196	0.1991	0.726	0.913	-0.142	0.584
1.9824	0.1767	0.689	0.919	-0.203	0.486
2.3419	0.3560	0.647	0.872	-0.230	0.417
2.9594	0.3893	0.591	0.867	-0.254	0.337
3.495	0.424	0.547	0.862	-0.262	0.285
4.224	0.458	0.500	0.854	-0.262	0.238
4.920	0.535	0.454	0.840	-0.236	0.218
5.652	0.642	0.433	0.826	-0.180	0.235
6.441	0.635	0.416	0.827	-0.086	0.330
7.180	0.683	0.415	0.820	0.021	0.436
8.003	0.653	0.423	0.825	0.191	0.614
8.681	0.823	0.453	0.800	0.639	1.092
9.010	0.942	0.484	0.787	-	-

TABLE 30

Integral Diffusion Coefficients for Runs of Vanishingly Short Duration and
Differential Diffusion Coefficients for Triethylamine in Aqueous Solutions
at 17°C

$c = c_{m'}$	$c_{m''}$	$\bar{D}^0(c_{m'}) \times 10^6$ in $\text{cm}^2 \text{sec}^{-1}$	$\bar{D}^0(c_{m''}) \times 10^6$ in $\text{cm}^2 \text{sec}^{-1}$	$c \frac{d\bar{D}^0}{dc} \times 10^6$ in $\text{cm}^2 \text{sec}^{-1}$	$D \times 10^6$ in $\text{cm}^2 \text{sec}^{-1}$
0.0643	0.0121	6.61	7.27	-0.48	6.13
0.0924	0.0082	6.36	7.38	-0.51	5.85
0.1721	0.0255	6.04	7.15	-0.59	5.45
0.4041	0.0566	5.69	6.64	-0.65	5.04
0.5780	0.0769	5.41	6.50	-1.14	4.27
0.8294	0.0975	4.84	6.35	-2.08	2.76
0.9518	0.1113	4.40	6.25	-2.52	1.88
1.2491	0.1462	3.79	6.10	-2.80	0.99
1.4230	0.1545	3.40	6.05	-2.66	0.74
1.4642	0.1464	3.29	6.10	-2.63	0.66
2.0664	0.1280	2.52	6.17	-2.19	0.33
2.812	0.1130	1.87	6.25	-1.67	0.20
3.537	0.1411	1.55	6.10	-1.15	0.40
4.310	0.1232	1.36	6.23	-0.58	0.78
4.924	0.1757	1.33	5.95	-0.16	1.17
5.669	0.1667	1.34	6.00	0.39	1.73
6.186	0.1798	1.39	5.95	0.77	2.16
6.812	0.2435	1.49	5.82	1.19	2.68
7.093	0.2355	1.98	5.83	-	-

Figure 32. D vs. c for Monoethylamine in
Aqueous Solutions at 25°C .

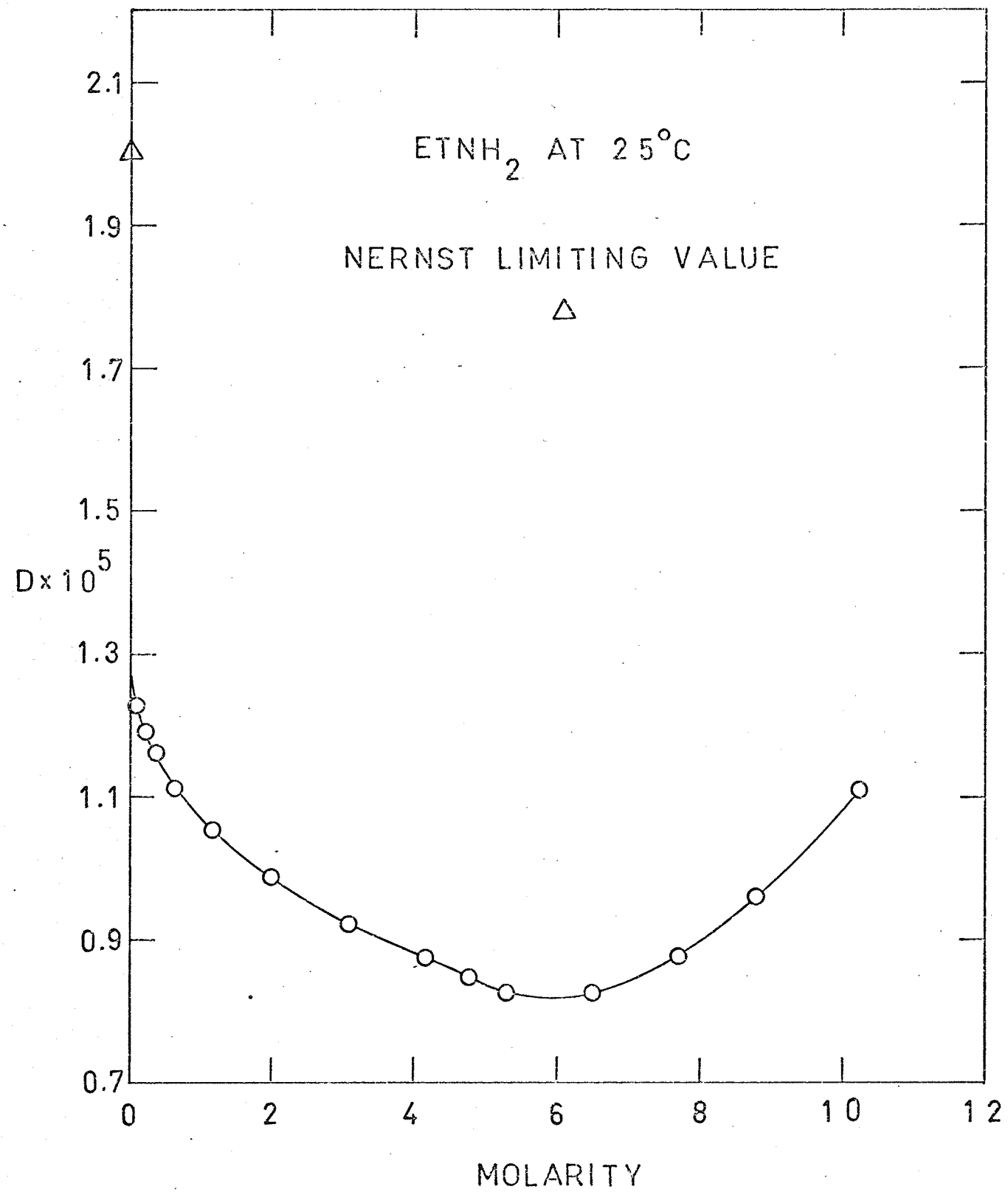


Figure 33. D vs. c for Diethylamine in
Aqueous Solutions at 25°C .

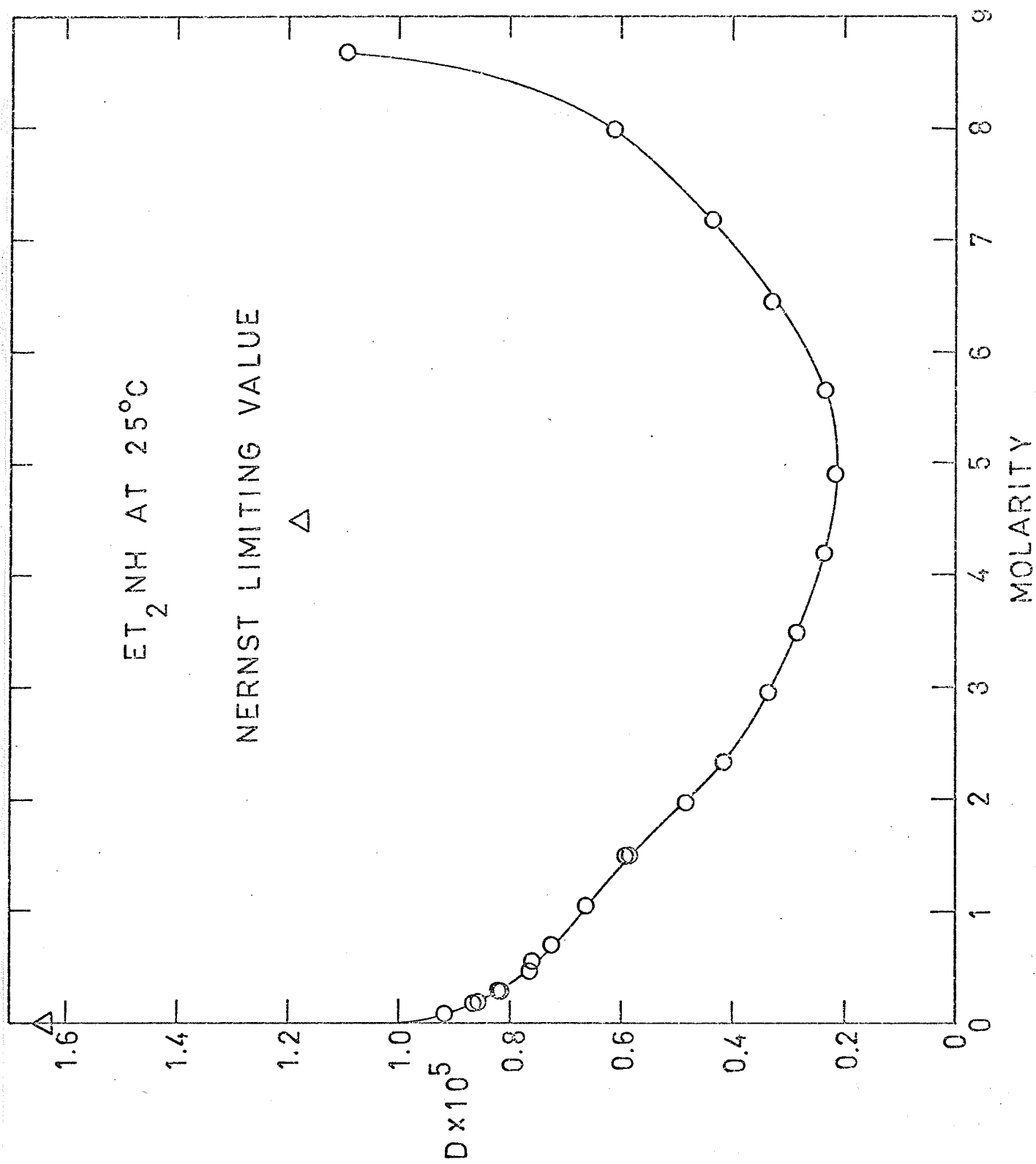
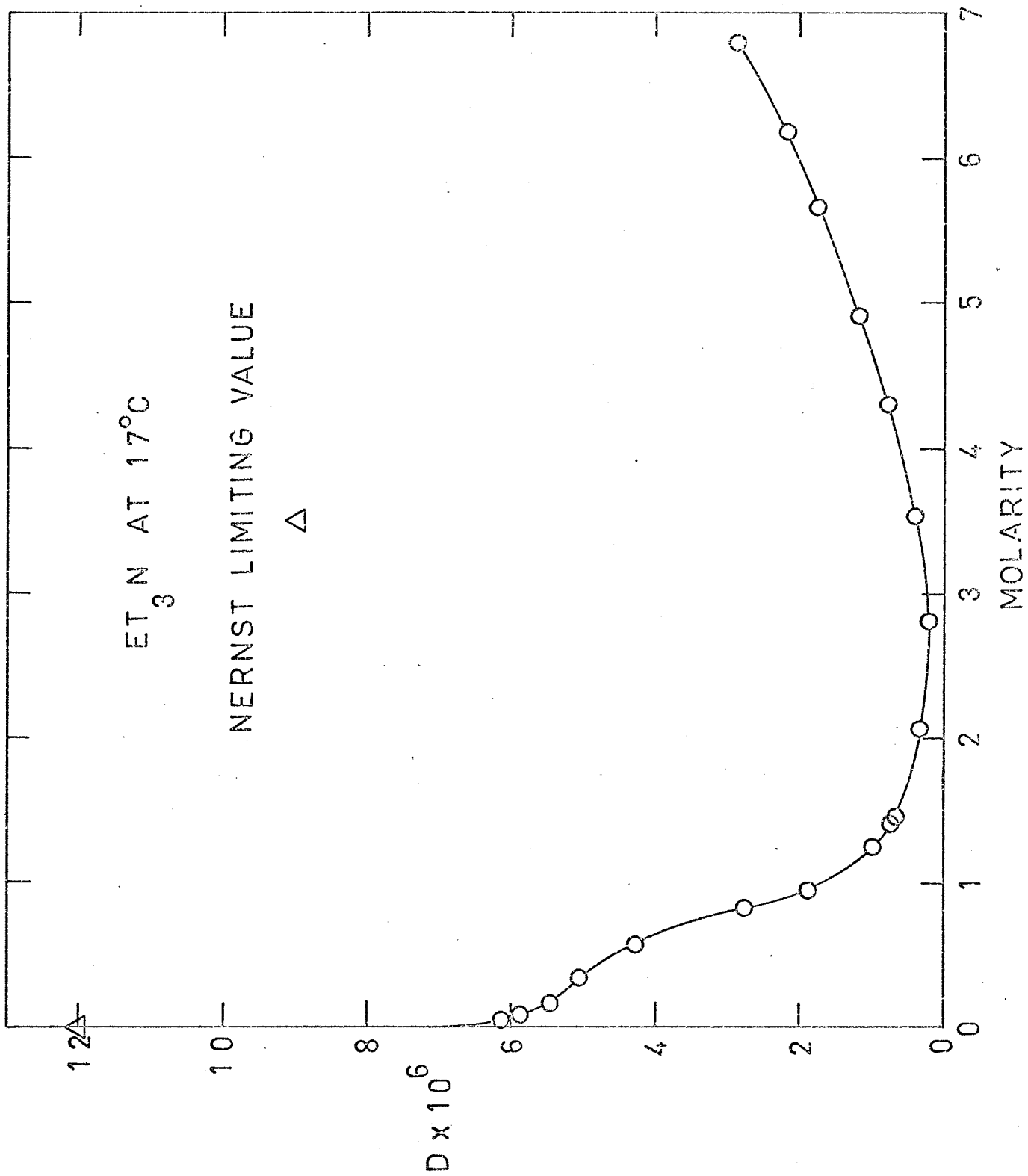


Figure 34. D vs. c for Triethylamine in
Aqueous Solutions at 17°C.



V DISCUSSION

V.A Thermodynamic Consistency in Vapor Pressure Measurements

The partial vapor pressures of amines and water, and hence the activity coefficients in Tables 13, 14 and 15 were derived from the total vapor pressures and liquid-vapor equilibrium compositions, assuming the validity of Dalton's law. Since the activity coefficients of the two components in a binary system are related to each other through the Gibbs-Duhem equation, the internal consistency of the activity coefficients can be checked. From the activity coefficients of amines in these tables, values of water activity coefficient for these systems were calculated by means of the Gibbs-Duhem equation, and compared with the values previously obtained. In all cases the average deviations are in the order of $\pm 1\%$, and this is about the uncertainty of the experimental measurements. For the systems: diethylamine-water and triethylamine-water, large deviations arise where the mole fractions of amine are higher than 0.8 or 0.9, where the partial vapor pressures of water are low. For example, a difference in 6% is found in concentrated solutions of diethylamine and triethylamine having mole fraction 0.95. In view of the decreasing relative accuracy with which partial pressures of water can be determined in this range, the results in vapor pressure measurements in general are consistent and satisfactory.

V.B Comparison of Results in Vapor Pressure Measurements and Derived Thermodynamic Quantities

1. Monoethylamine-Water at 25°C

a. Vapor Pressures

Vapor pressure measurements for the system monoethylamine-water reported in literature are scanty. Butler⁽¹¹⁷⁾ determined the partial pres-

TABLE 31

A Comparison of the Partial Pressures of Monoethylamine According to Dailey and Felsing⁽¹¹⁸⁾ with the Data of This Investigation at 25°C

x_B^* Mole Fraction Amine	p_B Partial Pressure in mm Hg	
	Dailey and Felsing ⁽¹¹⁸⁾	This Work
0.01	4.5	4.4
0.02	9.1	8.8
0.03	13.7	13.2
0.04	18.3	17.9

TABLE 32

Excess Chemical Potential and Excess Free Energy of Mixing x_B^* Moles of
Monoethylamine and $(1 - x_B^*)$ Moles of Water at 25°C

x_B^* Mole Fraction Amine	μ^E Excess Chemical Potential in Cal.		G^E Excess Free Energy of Mixing in Cal.
	Amine	Water	
0.00	-	0	0
0.01	-828	0	-5
0.02	-514	4.1	-6
0.03	-522	1.4	-14
0.04	-516	7.5	-13
0.05	-499	10.9	-14
0.06	-482	7.5	-22
0.07	-458	-2.0	-34
0.08	-441	-6.8	-42
0.09	-422	-8.2	-46
0.10	-385	-10.9	-48

sure of monoethylamine at 25°C for a very dilute solution with mole fraction of amine lower than 5×10^{-4} , by bubbling dry air through the solution, condensing the vapor carried over and determining the concentration of solute in the condensate. By a similar method, Dailey and Felsing⁽¹¹⁸⁾ measured the partial pressures of monoethylamine in aqueous solutions in the mole fraction range of amine from 0.004 to 0.04 at 25°C. From the latter results, values of partial pressure of amine at rounded concentrations were obtained and compared with values from my work in Table 31. There is agreement within 3% on the average between these two sets of data.

b. Excess Chemical Potentials and Free Energy of Mixing

The excess chemical potential of component i , μ_i^E , and the excess free energy of mixing G^E are given by the expressions,

$$\mu_i^E = RT \ln f_i^* \quad (270)$$

and

$$G^E = X_A^* RT \ln f_A^* + X_B^* RT \ln f_B^* \quad (271)$$

From the activity coefficients in Table 13, values of the excess quantities were calculated and are given in Table 32. Since no data on the heat of mixing exist for this system, nor sufficient data on vapor pressure for an evaluation of the temperature coefficient, the excess entropy of mixing cannot be computed.

2. Diethylamine-Water at 25°C

a. Vapor pressure of pure diethylamine

The vapor pressure of diethylamine was found to be 238.8 mm Hg at 25°C in good agreement with the value 237.2 mm of Bolas⁽¹¹⁹⁾. Pohland and Mehl⁽¹²⁰⁾ made six measurements from -41°C to 21°C and established an analytical expression for the amine. This equation gives a

TABLE 33

A Comparison of the Partial Pressures of Diethylamine According to Dailey and Felsing⁽¹¹⁸⁾ with the Data of This Investigation at 25°C

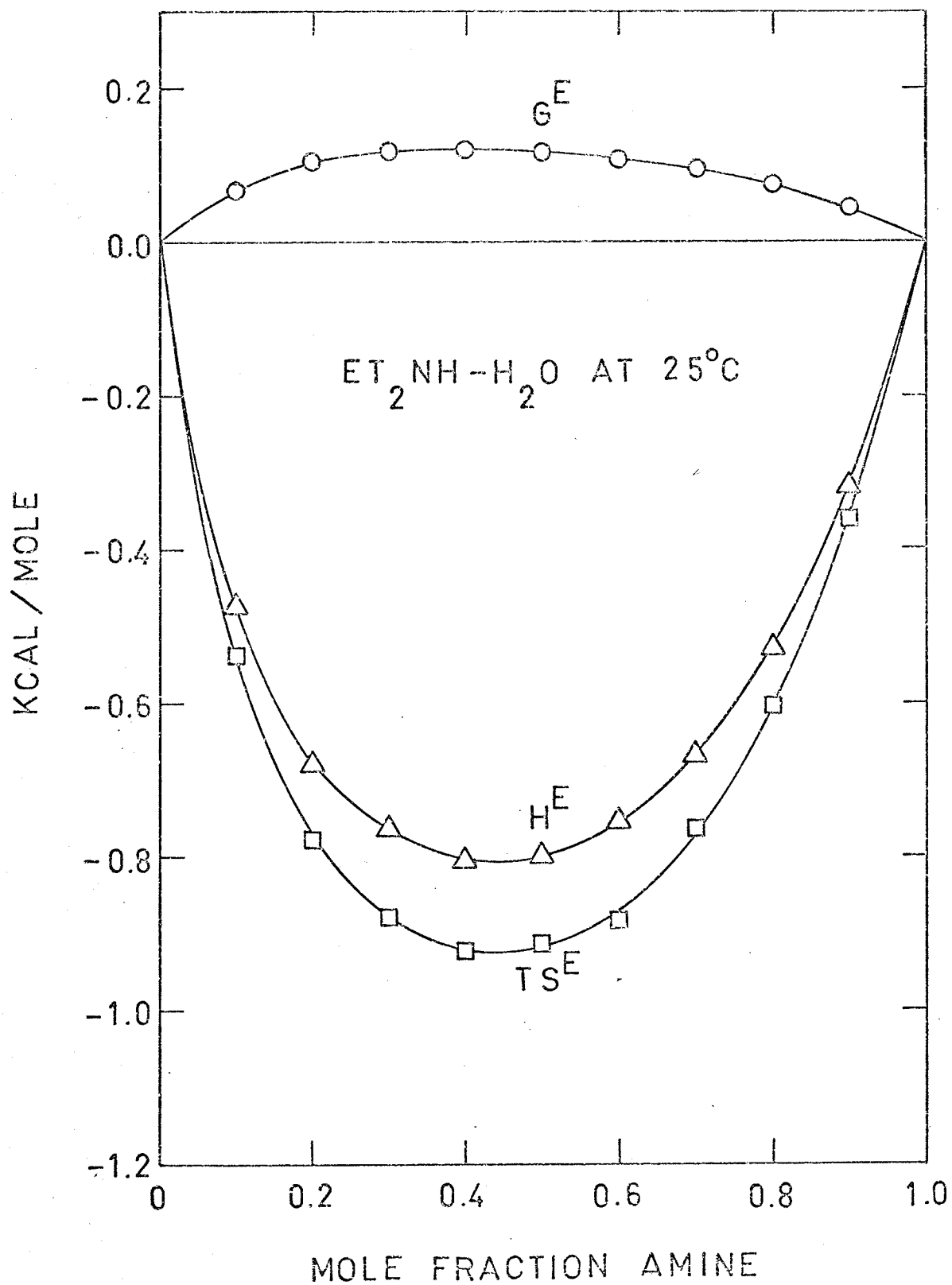
x_B^* Mole Fraction Amine	p_B Partial Pressure in mm Hg	
	Dailey and Felsing	This Work
0.01	9.3	9.0
0.02	18.5	17.7
0.04	36.8	33.5

TABLE 34

Excess Thermodynamic Functions of Mixing χ_B^* Moles of Diethylamine
and $(1 - \chi_B^*)$ Moles of Water at 25°C

Mole Fraction χ_B^* Amine	Excess Chemical Potential μ^E in Cal.		G^E Excess Free Energy of Mixing in Cal.	H^E Heat of Mixing in Cal.	S^E Entropy of Mixing in e.u.
	Amine	Water			
0.00	-	0.0	0.0	0.0	0.0
0.01	787.1	0.0	7.9	-	-
0.02	777.6	0.0	15.6	-	-
0.04	743.5	0.0	29.7	-	-
0.06	682.1	4.1	44.8	-	-
0.08	597.5	9.5	56.5	-	-
0.10	521.1	16.4	66.9	-475	-1.82
0.15	376.5	38.2	89.0	-	-
0.20	281.0	58.7	103.2	-680	-2.63
0.30	173.3	90.0	115.0	-765	-2.95
0.40	121.4	118.7	119.8	-805	-3.10
0.50	90.0	141.9	116.0	-800	-3.07
0.60	69.6	165.1	107.8	-755	-2.89
0.70	47.7	204.6	94.8	-670	-2.57
0.80	28.6	260.5	75.0	-530	-2.03
0.90	9.5	350.6	43.7	-320	-1.22
0.95	4.1	417.4	24.8	-	-
1.00	0.0	-	0.0	0.0	0.0

Figure 35. Excess Thermodynamic Functions for the
System Diethylamine-Water at 25°C.



value 235.5 mm at 25°C. Static and dynamic measurements by Copp and Everett⁽¹²¹⁾ in the temperature range 15°C to 55°C gave by interpolation a value at 25°C of 235.7 mm Hg. Bittrich⁽¹²²⁾ carried out a series of measurements from 21°C to 96°C which lead to a value of 234.0 mm at 25°C. My value is thus about 3 mm or 1.3% higher than the average of other workers.

b. Total Vapor Pressures of the System Diethylamine-Water

The only work in the literature on total vapor pressure measurements of diethylamine-water is due to Copp and Everett⁽¹²¹⁾. Their experiments were conducted at 56.80°, 49.10° and 38.35°C. I attempted to extrapolate to 25°C, but the result was not satisfactory, because the plot of $\log p$ against reciprocal temperature did not give a smooth curve.

c. Partial Vapor Pressures of Diethylamine-Water

Using the same method as for monoethylamine, Daley and Felsing⁽¹¹⁸⁾ obtained partial pressures of diethylamine in the dilute concentration region. Their higher values at rounded concentrations are compared with mine in Table 33. The average discrepancy is 6%.

d. Excess Thermodynamic Functions

The excess chemical potentials and free energy of mixing were calculated by means of Equations (270) and (271). The only available heats of mixing for this system at 25°C are those of Copp and Everett⁽¹²¹⁾. Using their figures, the excess entropy of mixing was calculated. Since the accuracy claimed for the heats of mixing is about 4%, I estimated the derived entropies to have about 5% uncertainty. These excess functions are shown in Table 34 and are presented graphically in Figure 35.

3. Triethylamine-Water at 17°C

a. Vapor Pressure of Pure Triethylamine

Lathey⁽¹²³⁾ gave a value 50.4 mm compared with a lower value 46.7 mm

in this research. The work of Pohland and Mehl⁽¹²⁰⁾ resulted in a higher value, 53.2 mm. Thompson and Linnett's analytical expression gives 47.9 mm in closer agreement with my value. Interpolation from Kohler's results⁽¹²⁵⁾ at 0°, 10° and 18°C yielded the same value as mine. Copp and Everett⁽¹²¹⁾ summarized their findings in an expression, viz., Equation (2) in their publication. This equation gave 303 mm at 17°C and must therefore be misprinted. Fortunately the vapor pressure of pure triethylamine in association with the total vapor pressure measurements for the system triethylamine-ethanol at 34.85°, 49.60° and 64.85°C by Copp and Everett produced a straight line relationship when the logarithm of pressure was plotted against the reciprocal of absolute temperature. Extrapolation of this straight line led to 46.2 mm at 17°C. A series of measurements in the temperature range 13.58° to 79.12°C by Krichevskii *et al.*⁽¹²⁶⁾ gave 46.3 mm at 25°C. Bittrich⁽¹²²⁾ deduced a vapor pressure-temperature relation from experiments in the high temperature range, 50° to 59°C. This predicts 46.4 mm at 17°C, sufficiently close to my value. Recently, Christie and Crisp⁽¹²⁷⁾ measured the vapor pressure of the amine in a higher but more narrow temperature range. The only presentation is in condensed graphical form which does not warrant a satisfactory extrapolation to 17°C. However, it suffices to say that within agreement with the majority of the above mentioned sources, the general correctness of the vapor pressure of triethylamine in this work has been established.

b. Total Vapor Pressures of the System Triethylamine-Water

The total vapor pressures for this system over the entire concentration range were investigated by Lattey⁽¹²³⁾ at 16°, 18°, 20° and 22°C, by Roberts and Mayer⁽¹²⁸⁾ at 0°, 13°, 16° and 18°C, and by Kohler⁽¹²⁵⁾

TABLE 35

Comparison of Total Vapor Pressures for the System
Triethylamine-Water at 17°C

Mole Fraction Amine	Total Vapor Pressure in mm Hg					This Work
	Latley (123)	Roberts and Mayer (128)	Kohler (125)	Krichevskii (126)		
0.01	-	-	-	39.8	36.2	
0.02	-	-	-	50.2	50.2	
0.03	-	-	-	52.1	52.4	
0.05	50.1	-	-	52.1	52.6	
0.10	52.7	53.0	51.8	-	52.8	
0.20	54.6	53.2	52.0	-	53.1	
0.30	55.4	53.3	52.3	-	53.5	
0.40	56.0	53.4	52.6	-	53.8	
0.50	56.1	53.7	52.9	-	54.1	
0.60	56.3	54.0	53.3	-	54.3	
0.70	56.4	54.3	53.8	-	54.7	
0.80	56.4	54.7	53.7	-	54.9	
0.90	54.8	54.7	52.4	-	54.1	
1.00	50.4	-	46.7	-	46.7	

TABLE 36

Comparison of Liquid-Vapor Equilibrium Compositions for the System
Triethylamine-Water at 17°C

Mole Fraction Amine in Liquid	Mole Fraction Amine in Vapor	
	Roberts and Mayer ⁽¹²⁸⁾	This Work
0.05	0.742	0.729
0.10	0.742	0.732
0.20	0.742	0.735
0.30	0.743	0.737
0.40	0.748	0.740
0.50	0.752	0.742
0.60	0.758	0.748

TABLE 37

Comparison of Partial Vapor Pressures in mm Hg for the System
Triethylamine-Water at 17°C

Mole Fraction Amine	Roberts and Mayer (128)		Kohler (125)		Lattey (123)		This Work	
	Amine	Water	Amine	Water	Amine	Water	Amine	Water
.00	-	-	0.0	15.1	0.0	14.4	0.0	14.5
.05	-	-	-	-	36.0	14.1	38.3	14.3
.10	39.3	13.7	37.1	14.7	38.7	14.0	38.6	14.2
.20	39.5	13.7	37.3	14.7	40.9	13.7	39.0	14.1
.30	39.6	13.7	37.6	14.7	41.8	13.6	39.4	14.1
.40	39.9	13.5	38.0	14.6	42.4	13.6	39.8	14.0
.50	40.4	13.3	38.6	14.3	42.5	13.6	40.1	14.0
.60	40.9	13.1	39.2	14.1	42.7	13.6	40.6	13.7
.70	-	-	40.1	13.7	42.9	13.5	41.3	13.4
.80	-	-	41.3	12.4	43.7	12.7	42.3	12.6
.90	-	-	42.2	9.3	45.7	9.1	43.7	10.4
1.00	-	-	46.7	0.0	50.4	0.0	46.7	0.0

at 0°C, 10°C and 18°C. Krichevskii et al.⁽¹²⁶⁾ also made measurements below 0.08 mole fraction of amine in the range 10° to 25°C. Values for the total vapor pressure at 17°C and at rounded concentrations were obtained by interpolation and are compared with this research in Table 35. Lattey's results are consistently higher than mine by an average of 1.8 mm, but Kohler's are consistently lower by 1.1 mm. Krichevskii's vapor pressures at low concentrations differ from mine by 1 mm on the average. However, there is very good agreement within 0.3 mm, on the average, between the set of vapor pressures by Roberts and Mayer⁽¹²⁸⁾, and that obtained in my work. Roberts and Mayer felt that Lattey's higher readings were probably due to a less complete removal of air.

c. Liquid-Vapor Equilibrium Compositions and Partial Vapor Pressures

The only experimental liquid-vapor equilibrium compositions in the literature for this system are those of Roberts and Mayer⁽¹²⁸⁾ at 0°, 13°, 16° and 18°C. Values at 17°C were interpolated and are listed in Table 36. The vapor compositions in terms of amine determined by me are lower than theirs by an average of 1.3%.

Partial pressures, calculated from total pressure data and liquid-vapor equilibrium compositions of Roberts and Mayer at 17°C, are given in Table 37. Lattey⁽¹²³⁾ and Kohler⁽¹²⁵⁾ resolved their total vapor pressures into partial pressures of components by an approximation process on the basis of the Gibbs-Duhem equation, Dalton's law and the assumption of ideal gas behaviour. Interpolation of their partial pressures gave the values at 17°C in Table 37. The discrepancy between Roberts and Mayer's and my work is mainly due to the differences in the measured liquid-vapor equilibrium compositions, since both sets of total pressures are almost identical. The partial pressures of amine according to Lattey

are higher, and those of water are lower, compared with my work. This is because a higher value for pure amine and a lower value for pure water were employed by them in carrying out the approximation procedure to obtain the partial pressures for the mixtures. Although Kohler's total pressures in general are lower than mine the measured vapor pressure of pure water is much higher than that I have adopted from a better established standard by Keyes⁽¹¹⁰⁾. As a result, Kohler's partial pressures for water are higher and those for amine are lower in comparison with all other work. There is no doubt, however, as to the internal consistency of the partial vapor pressures, as given by Kohler as well as by Lattey, for this system.

d. Excess Thermodynamic Functions

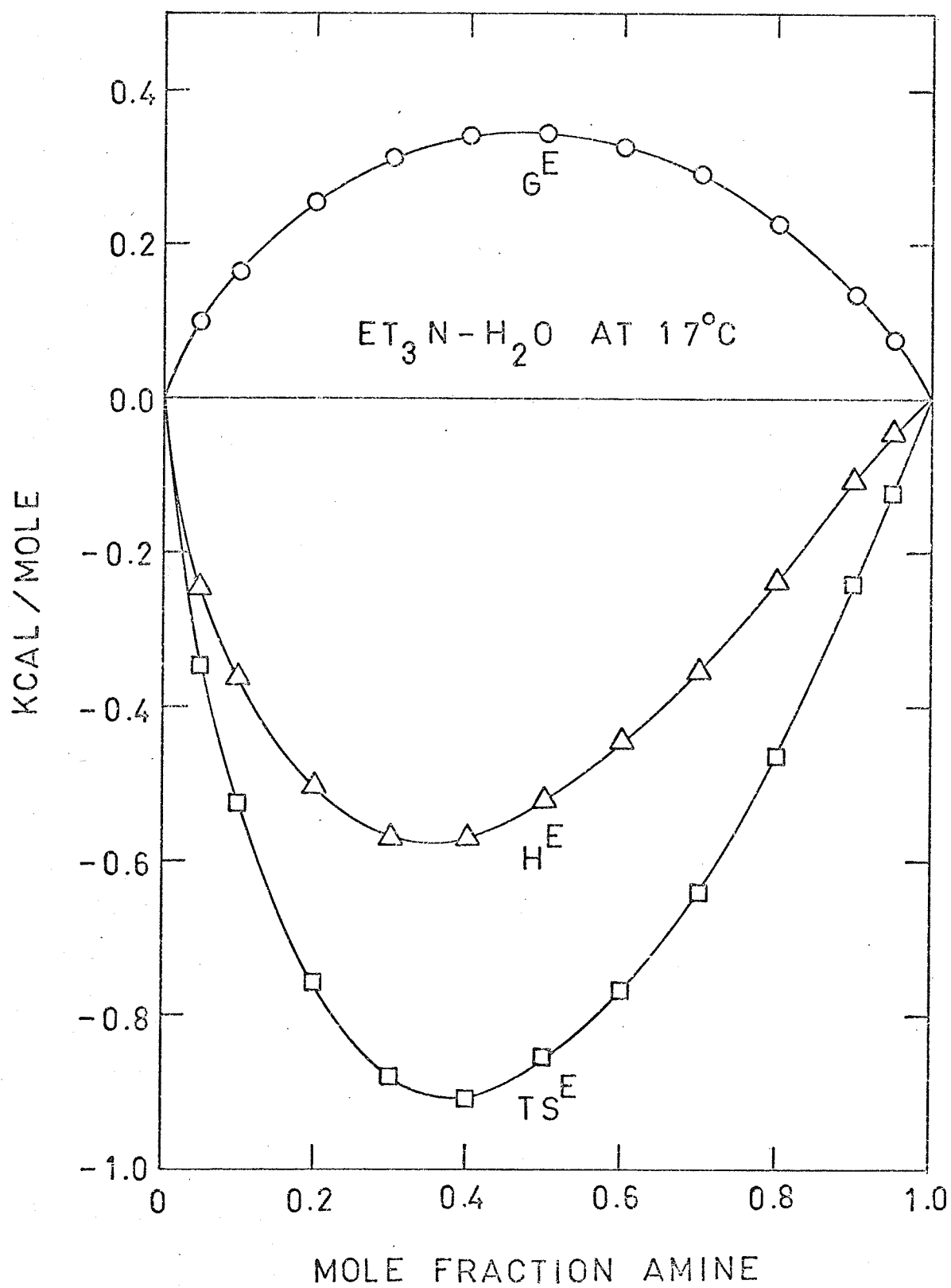
Using the activity coefficients of Table 15, the excess chemical potentials and free energies of mixing were computed. The heats of mixing for this system at 10°C were derived by Kohler⁽¹²⁵⁾ by differentiation of his vapor pressure data at 0°, 10° and 18°C. Copp and Everett⁽¹²¹⁾ measured directly the heats of mixing at 15°C. Matizen and Kustova⁽¹²⁹⁾ repeated these measurements, at the same temperature, but principally in the low triethylamine concentration region. The most recent work at 15°C is due to Betrand et al.⁽¹³⁰⁾. I believe this work gives the best thermal data presently available for this system over the full concentration range, judging from its internal consistency, the scattering of points and the better accuracy claimed. By incorporating the heats by Betrand et al. at 15°C for 17°C, values of excess entropy of mixing were calculated. Table 38 gives the excess functions. Figure 36 shows the relation between these quantities. Since according to Betrand the estimated maximum uncertainty for the heats is 10 cal. per mole and 1% uncertainty in

TABLE 38

Excess Thermodynamic Functions for Mixing X_B^* Moles of
Triethylamine and $(1 - X_B^*)$ Moles of Water at 17°C

Mole Fraction X_B^* Amine	ΔC^E Excess Chemical Potential in. Cal.		G^E Excess Free Energy of Mixing in Cal.	H^E Heat of Mixing in Cal.	S^E Entropy of Mixing in e.u.
	Amine	Water			
0.000	-	0.0	0.0	0	0.00
0.005	2270	-4.0	7.4	-52	-.21
0.010	2220	-4.0	18.2	-93	-.38
0.015	2189	1.3	34.1	-124	-.54
0.020	2106	2.7	44.7	-144	-.65
0.030	1905	11.9	68.7	-185	-.87
0.050	1614	19.9	99.6	-246	-1.19
0.100	1219	46.5	163.8	-362	-1.81
0.200	826	111.5	254.3	-503	-2.61
0.300	596	188.5	310.8	-569	-3.03
0.400	436.8	274.8	339.6	-570	-3.14
0.500	312.0	375.7	343.9	-522	-2.98
0.600	213.7	495.2	326.3	-442	-2.65
0.700	134.7	649	289.1	-353	-2.21
0.800	71.7	846	226.5	-238	-1.60
0.900	22.6	1135	133.8	-109	-0.84
0.950	9.7	1322	75.3	-47	-0.42
1.000	0.0	-	0.0	0	0.00

Figure 36. Excess Thermodynamic Functions for the
System Triethylamine-Water at 17°C.



activity coefficients causes another maximum difference about 6 cal. per mole in the resulting excess chemical potentials, the calculated excess entropies and TS^E are believed to be accurate within 0.05 entropy units and 16 cal. respectively.

4. General Discussion

All these systems exhibit nonideality on mixing. The activity coefficients of monoethylamine, calculated from the partial pressures, below mole fraction of amine $x_B^* = 0.1$, are less than unity. A comparison of the total vapor pressure curve with that of ideal behaviour, shown in Figure 10, shows that negative deviation exists below mole fraction of amine of about 0.65; above this, there is some evidence of positive deviation. The other two systems show positive deviations from the ideal vapor pressure curve in Figures 11 and 12. The behaviour of triethylamine-water is much more pronounced. The total pressure rises sharply to $x_B^* = 0.03$ and reaches a plateau with small slope in the region $x_B^* = 0.03$ and 0.85. This is consistent with the characteristics of systems having lower critical solution temperatures. For partial miscible liquid at temperatures slightly higher than the critical temperature, it is thermodynamically necessary that each of the two phases, at equilibrium must have the same chemical potentials. The partial pressures for each component are identical, and hence the total pressures are equal. The miscibility gap may extend to cover a wide concentration range. As the temperature decreases to the critical temperature, the partial pressures are constant over a wide range of composition. It is experimentally found that this feature persists more or less even if the temperature is further lowered by 1 or 2 degrees, as demonstrated in Figure 12 for triethylamine-water, which has a lower critical temperature at 18.3°C ⁽¹²⁶⁾. For di-

ethylamine-water which has a lower critical temperature around 140°C ⁽¹²¹⁾, the equality of vapor pressure does not persist at room temperature.

The large relative viscosity of amine solutions and the negative values of the heats of mixing, for the systems diethylamine-water and triethylamine-water, are some indications that strong molecular interaction takes place⁽¹³⁴⁾. Perhaps this interaction is best expressed by the excess entropy of mixing, which is a measure of order and disorder. In both cases, the positive excess free energies of mixing augment the heats of mixing to give large negative values of excess entropy. These entropies suggest that the amines are hydrated to a considerable extent. Judging from the magnitude of the excess quantity for both mixtures, the degrees of hydration are similar.

C. Diffusion

The graphs of differential diffusion coefficients against molarities for the amines are shown in Figure 32, 33 and 34. Although the temperatures are not the same, the shapes of the curves bear some similarity. In general, the diffusion coefficient decreases from monoethylamine to triethylamine. This is in qualitative agreement with what is expected from a consideration of the size of the molecule and the viscosity of the solution, triethylamine being largest and its solution most viscous. The position of the minimum shifts gradually from about $c = 6$ to $c = 3$ or roughly from $m = 10$ to $m = 4$, in going from monoethylamine to triethylamine. It is interesting to note that at their minima the magnitude of the diffusion coefficients diminishes from about $1 \times 10^{-5} \text{ cm}^2$ per sec. of monoethylamine to $1 \times 10^{-6} \text{ cm}^2$ per sec. for diethylamine and to $1 \times 10^{-7} \text{ cm}^2$ per sec. for triethylamine, and this is very low in comparison with that usually found, viz., $1 \times 10^{-5} \text{ cm}^2$ per sec. This is in accordance at

least qualitatively with the concept that the driving force for diffusion is the gradient of chemical potential or logarithm of activity, as can be seen by referring to Figures 16, 17 and 18, where the gradient is shown. Most remarkably, for triethylamine the minimum occurs where the plot of $\ln a$ against $\ln m$ is almost horizontal. Also, Krichevskii and Tsekhan-skaya⁽¹³¹⁾ found the diffusion rate to be very small for triethylamine.

I attempted to fit the experimental diffusion coefficients into the Hartley-Crank equation, i.e., Equation (251), in order to calculate the hydration numbers for the amines. As this equation implies that the diffusing entity is amine rather than "aminium" cation and hydroxyl anion, I did not attempt the treatment for very dilute solutions, for which the degree of dissociation is more than 2 to 3%. By transforming molarity into molality as the independent variable, the values of $\frac{d \ln a}{d \ln m}$ and relative viscosity were evaluated from Figures 16, 17, 18 and 8. Table 39 summarizes these quantities. The Hartley-Crank plots are shown in Figures 37, 38 and 39. The influence of the viscosity factor on the appearance of the curve is marked; even the sign of the slope changes. From the straight line portions of these curves, at low concentrations, values of the intercept, D_{BA}^0 , and the slope, $0.036 \left(\frac{D_{H_2O}^*}{2} - h D_{BA}^0 \right)$ of Equation (251) were obtained. Hypothetical values of D_{BA}^0 , i.e., the diffusion coefficient of the amine molecule at infinite dilution are

$$1.21 \times 10^{-5} \text{ cm}^2/\text{sec} \text{ for monoethylamine at } 25^\circ\text{C}$$

$$8.9 \times 10^{-6} \text{ cm}^2/\text{sec} \text{ for diethylamine at } 25^\circ\text{C}$$

and $6.4 \times 10^{-6} \text{ cm}^2/\text{sec}$ for triethylamine at 17°C

By using the self-diffusion coefficient of water, $D_{H_2O}^*$, ($2.43 \times 10^{-5} \text{ cm}^2/\text{sec}$ at 25°C and $2.01 \times 10^{-5} \text{ cm}^2/\text{sec}$ at 17°C given by Partington, Hudson and Bagnall⁽⁹²⁾), hydration numbers for the amines were calculated. In

TABLE 39

Data Relevant to the Hartley-Crank Plots

Monoethylamine at 25°C

m	$D \times 10^5$	η_{rel}	$\frac{dlna}{dlnm}$	$D \frac{dlnm}{dlna} \times 10^5$	$\eta_{rel} D \frac{dlnm}{dlna} \times 10^5$
0.3952	1.555	1.080	0.97	1.16	1.25
0.6665	1.113	1.135	0.97	1.12	1.27
1.195	1.054	1.250	0.97	1.06	1.32
2.270	0.986	1.474	1.06	0.93	1.39
3.773	0.921	1.820	1.10	0.84	1.52
5.481	0.873	2.160	1.14	0.78	1.65
6.592	0.847	2.330	1.14	0.74	1.73

Dichthylamine at 25°C

0.5033	0.762	1.210	0.94	0.81	0.98
0.5923	0.759	1.250	0.94	0.80	1.01
0.7556	0.721	1.330	0.94	0.76	1.02
1.172	0.661	1.530	0.93	0.71	1.09
1.178	0.656	1.535	0.93	0.71	1.09
1.752	0.591	1.830	0.90	0.66	1.21
1.767	0.584	1.835	0.87	0.65	1.20
2.410	0.486	2.170	0.78	0.62	1.35
2.949	0.417	2.430	0.68	0.62	1.50
4.003	0.337	2.840	0.52	0.65	1.86
5.092	0.285	3.145	0.41	0.70	2.19
6.885	0.238	3.440	0.37	0.64	2.20
7.764	0.218	3.520	0.37	0.59	2.06

Triethylamine at 17°C

0.4251	0.504	1.260	0.88	0.57	0.72
0.6191	0.427	1.410	0.88	0.49	0.69
0.9181	0.276	1.635	0.58	0.48	0.78
1.071	0.188	1.740	0.44	0.43	0.75
1.468	0.099	2.035	0.07	1.4	2.8
1.716	0.074	2.205	0.01	7.0	15.0

Figure 37. Hartley-Crank Plot for Monoethylamine at 25°C.

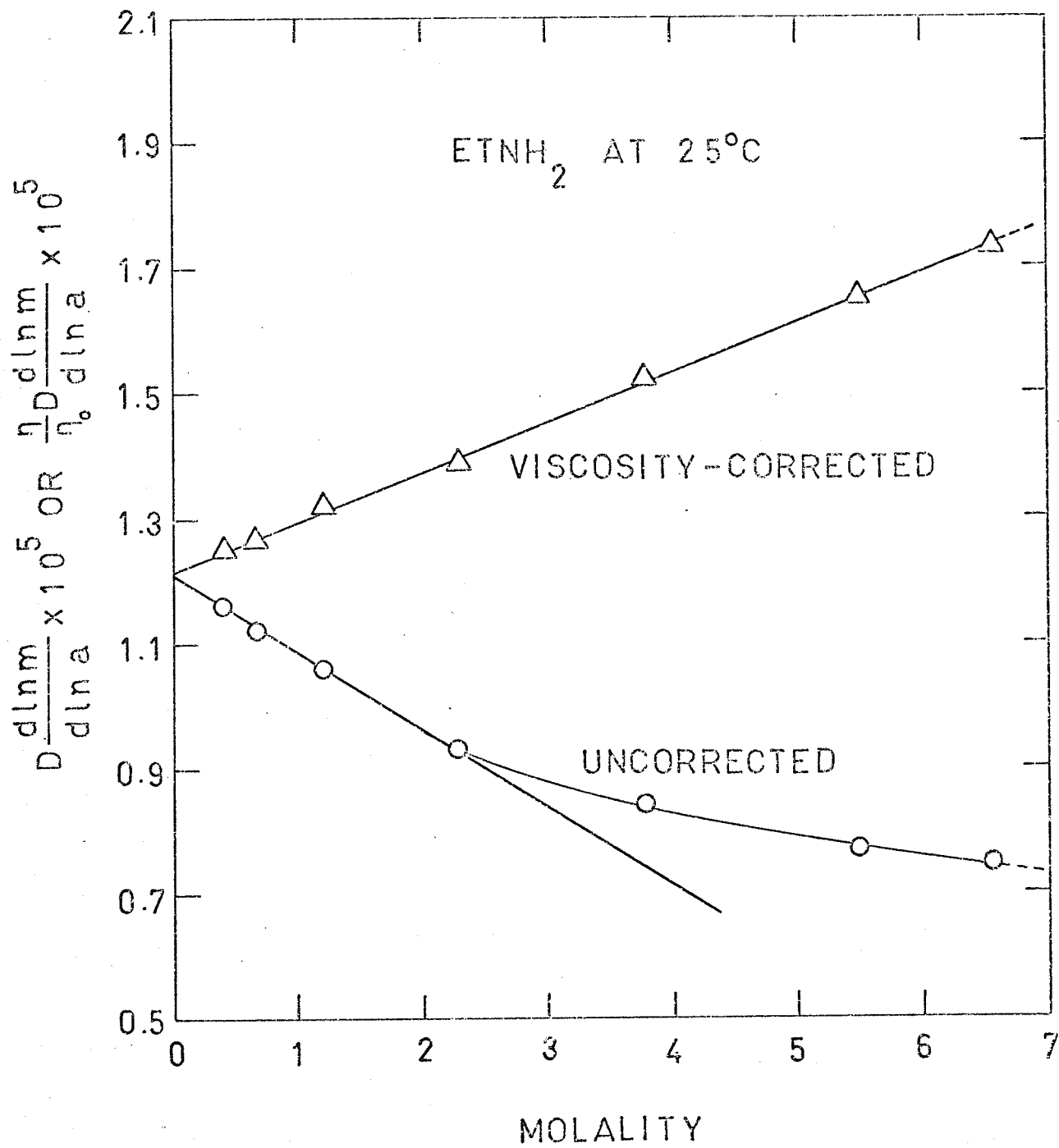
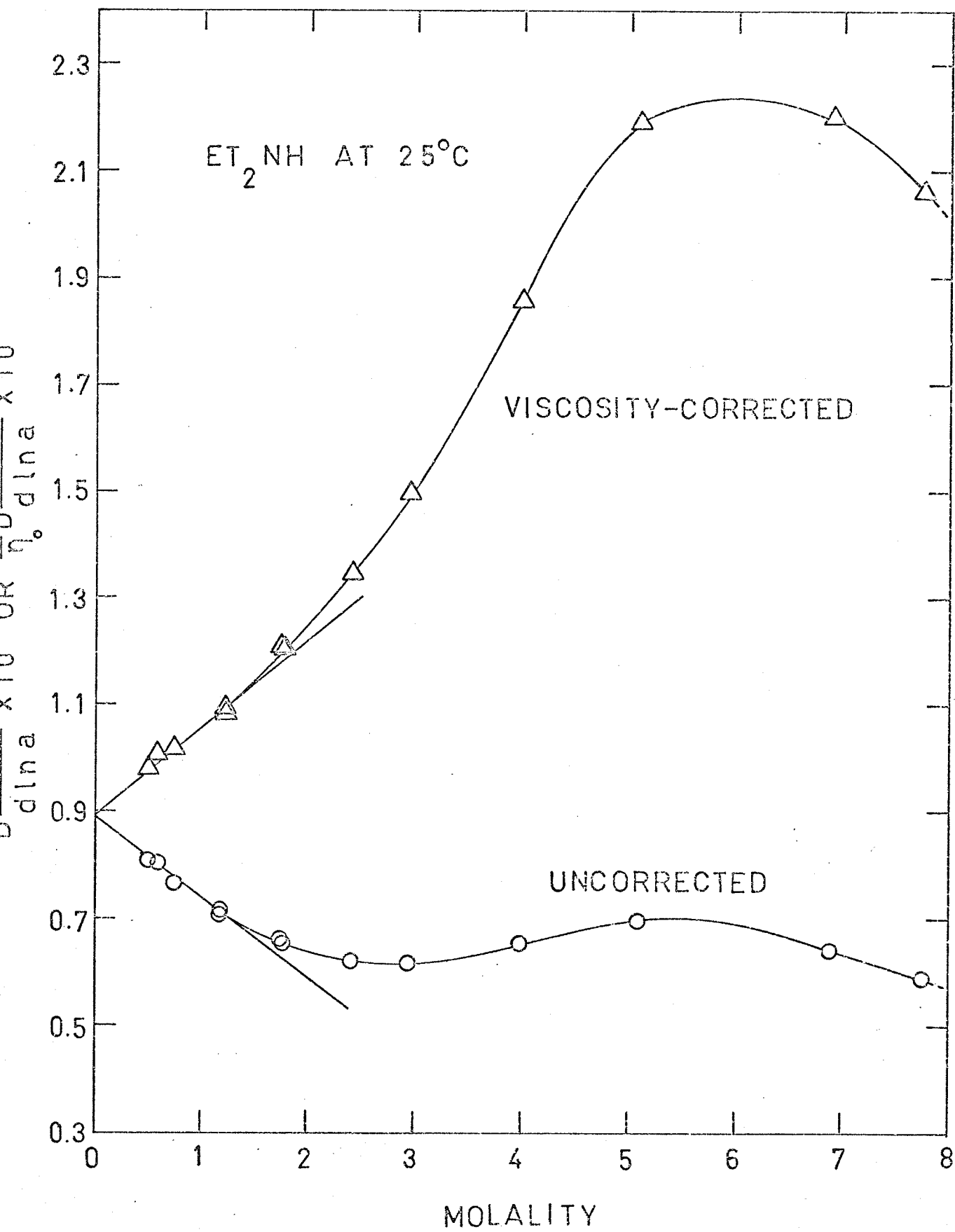
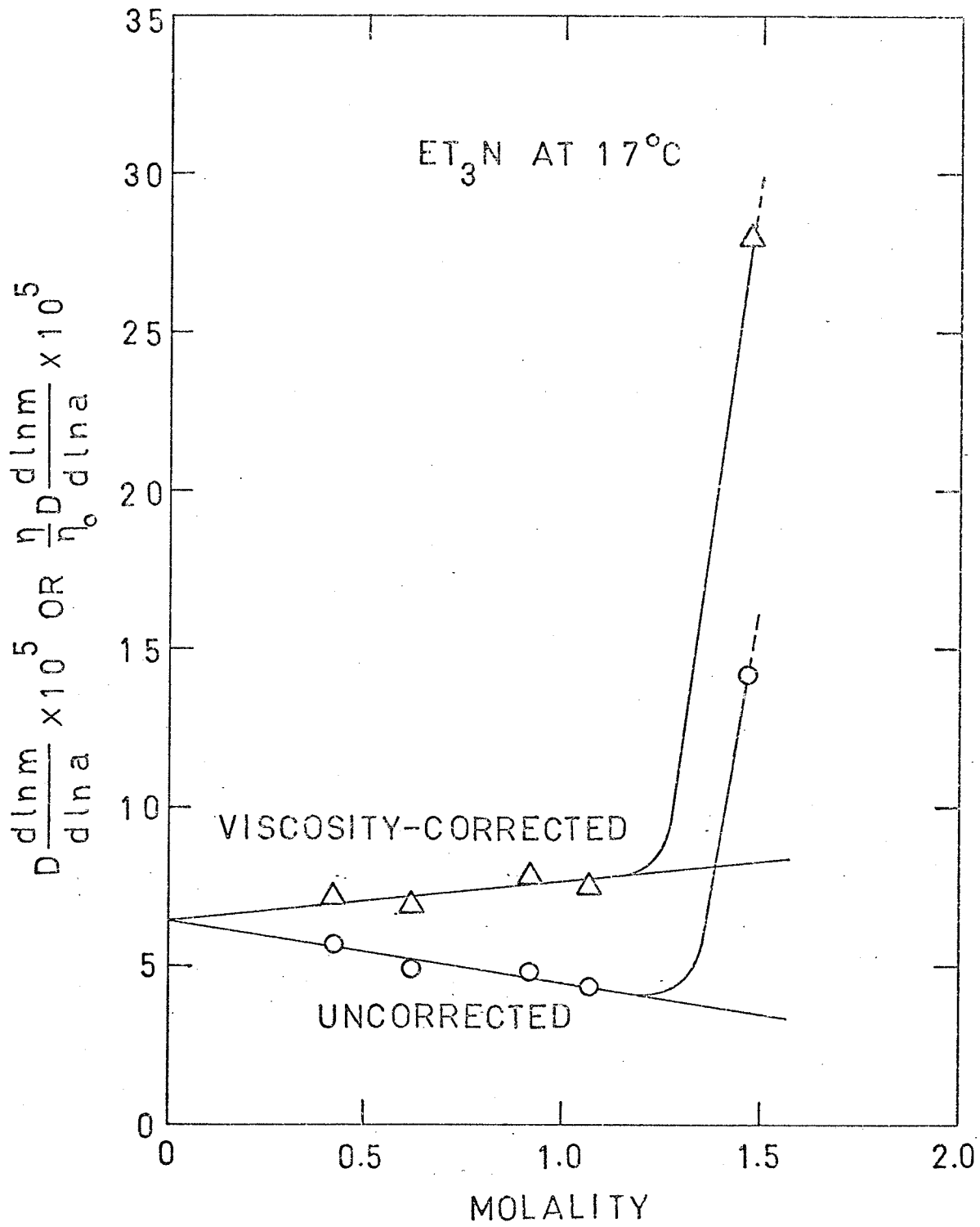


Figure 38. Hartley-Crank Plot for Diethylamine at 25°C.





the absence of viscosity factor, these numbers are

3.8 for monoethylamine at 25°C

6.0 for diethylamine at 25°C

and 10 for triethylamine at 17°C

However, if the viscosity factory is introduced into the calculation, the hydration numbers for mono-, di-, and triethylamine will be negative, -1.0, -3.8 and -4.0 respectively. These do not have any physical meaning. There is an unknown error introduced by taking the bulk viscosity as the viscosity experienced by discrete diffusing molecules. The same difficulty arises with the effect of viscosity in conductance. The relative viscosity will probably minimize this error if the solution has a viscosity very close to that of the solvent, or the solution is very dilute, for the deviation from the truth may be cancelled to a considerable extent by taking the ratio of two bulk viscosities. This is why in many cases the inclusion of the relative viscosity in theoretical equations can fit the experimental diffusion coefficients and conductances better. In high concentrations, however, where the relative viscosity is much greater than unity, e.g., the amine solutions, the inclusion of it as a multiplying factor does not account accurately for the true effect. Judging from the hydration numbers derived in both cases, it seems that this factor over corrects the theory, despite the fact that it gives the best straight line fit for the diffusion coefficients up to 7 molal, for monoethylamine.

If the viscosity factor is omitted, the equation fits the experimental data within $\pm 1\%$, below 2 m for monoethylamine, within $\pm 2\%$ below 1.5 m for diethylamine, and $\pm 6\%$ below 1 m for triethylamine. The order of hydration in this series of amines is tri > di > mono, in agree-

ment with the conclusion of Somerville⁽¹³²⁾.

When repeating the work of Pickering⁽¹³³⁾ on the freezing point curves of the aqueous amine solutions, Somerville⁽¹³²⁾ found that the amines could exist as solid hydrates at low temperatures. The formula of the hydrates which contained the greatest proportion of water and gave definite maxima on the freezing point diagrams were $\text{MeNH}_2 \cdot 3\text{H}_2\text{O}$, $\text{Me}_2\text{NH} \cdot 7\text{H}_2\text{O}$, $\text{Me}_3\text{N} \cdot 10\text{H}_2\text{O}$, $\text{EtNH}_2 \cdot 5\frac{1}{2}\text{H}_2\text{O}$ and $\text{Et}_2\text{NH} \cdot 8\text{H}_2\text{O}$. The position of triethylamine was not certain. From the thermal analysis of triethylamine-water over the full concentration range, Kartzmark⁽¹³⁴⁾ found that the only hydrate which could exist as a solid at low temperature is the dihydrate. The freezing point curves for which ice is the crystallizing substance lie below the ideal curve. On the assumption that the deviations from the ideal curve were entirely due to hydration, Somerville estimated the relative degree of hydration for the amines. Although the hydration numbers so obtained do not agree with the isolated hydrates, they do give the same trend of hydration for monoethylamine and diethylamine. For triethylamine, because the freezing point curve deviates from the normal course, the calculation was not made by Somerville, but, since the curve below 1 molal does show a greater deviation from ideal behaviour in comparison with mono-, and diethylamine, this is some indication that the tertiary amine is more hydrated in less concentrated solutions. The hydration of the amine in solution is usually ascribed to hydrogen bonding. As the bonding is necessarily weak, the loss of stability of the hydrate in solution, at higher temperature is to be expected. The hydration numbers at room temperature will presumably be smaller.

Among the amines, monoethylamine has the highest hypothetical diffusion coefficient at infinite dilution. Examination of diffusion data in

the literature reveals an increase of about 25% in value when temperature increases by 10°C . Even with this allowance, the hypothetical diffusion coefficient of triethylamine is still the smallest. This is entirely due to the size difference of the molecules. By regarding the diffusing entity as "aminium" and hydroxyl ions, the Nernst limiting values calculated by using Equation (201) are

$2.002 \times 10^{-5} \text{ cm}^2$ per sec. for monoethylamine at 25°C

$1.640 \times 10^{-5} \text{ cm}^2$ per sec. for diethylamine at 25°C

and $1.192 \times 10^{-5} \text{ cm}^2$ per sec. for triethylamine at 17°C

These are higher than the corresponding hypothetical values. This is due to the exceptional high mobility of hydroxyl ion which enters into the calculation of Nernst limiting values.

D. Dissociation Constants

The dissociation constants obtained in my work are 4.57×10^{-4} moles per litre for monoethylamine, 1.02×10^{-3} moles per litre for diethylamine at 25° and 4.93×10^{-4} moles per litre for triethylamine at 17°C . These agree well with the values obtained by Somerville⁽¹³²⁾, Ablard *et al.*⁽¹³⁵⁾, Everett and Wynne-Jones⁽¹³⁶⁾, Evans and Hamann⁽¹³⁷⁾, de Ligny⁽¹³⁸⁾, van der Linde *et al.*⁽¹³⁹⁾, Moore⁽¹⁴⁰⁾ and Hansson⁽¹⁴¹⁾. There is no doubt that for this series of substituted ammonias, diethylamine is the strongest base and ammonia is the weakest, $K = 1.77 \times 10^{-5}$ moles per litre at 25°C ⁽¹⁴²⁾. This "abnormal" trend of base strength in aqueous solutions, di > tri ~ mono > ammonia was interpreted satisfactorily by Palit⁽¹⁴³⁾. According to Palit, since nitrogen is strongly electronegative compared with hydrogen, the bonding electron pairs in N-H bonds in ammonia will be drawn closer to nitrogen, and hence the hydrogen atoms will acquire weak positive charges. Approaching hydrogen ion is attracted by the unshared

pair of electrons but repelled by the three positively charged hydrogen atoms. As a result of this, ammonia behaves as a weak base. If one or more hydrogens are substituted by groups, the strength of the resulting base will depend on three factors, (1) the polar factor or the electron attracting power of the replacing group, (2) the repulsion factor, i.e., the repulsion between the remaining hydrogen atoms around the nitrogen atom and the approaching hydrogen ion, and (3) the availability of the unshared pair of electrons as influenced by the steric interference between the unshared pair and the alkyl group present around the central nitrogen atom. The first factor which depends on the inductive effect is known to be very weak with alkyl groups, and hence can be neglected for alkylamines. The second and third effects act in opposite directions with ethylamines. For monoethylamine, the approaching hydrogen ion is repelled only by two hydrogen atoms. This diminution of repulsion causes an increase in the base strength of ethylamine. The increment of strength, on passing to diethylamine is less, since the compensating steric factor is increasing. For triethylamine, the steric factor is enough to compensate for the repulsion effect, and a decrease in strength is observed. It appears that a balance of two opposing factors is reached at the secondary amine which is therefore the strongest base in this series. This behaviour seems to be common to other series of alkylamine⁽¹⁴³⁾. By using the correlation between substituent effects and reaction rates and equilibria developed by Hammett⁽¹⁴⁴⁾ and Taft⁽¹⁴⁵⁾, Hall⁽¹⁴⁶⁾ found that the secondary amine should be the strongest base in a given series of alkylamines.

VI SUMMARY

Certain physical properties of the systems, ethylamine-water and diethylamine-water both at 25°C, and triethylamine-water at 17°C have been studied experimentally.

The total vapor pressures were measured by a differential manometer using mercury as the manometer fluid and water as the reference liquid. The liquid-vapor equilibrium compositions were determined by isothermal air saturation methods. The partial vapor pressures, activities and activity coefficients, calculated on the basis of Dalton's law are thermodynamically consistent. The relevant excess thermodynamic functions were also obtained.

The densities and relative viscosities were found experimentally. The conductances of the amines and hydrochlorides in aqueous solutions were determined. Corrections for the formation of aminium carbonates and the hydrolysis of the halides were made. By using the Kohlrausch law and the method of Shedlovsky and Kay, basic dissociation constants for the amines were computed. The base strength of this series was found to conform to the usual trend for other series of aliphatic amines.

The diffusion coefficients of the amines were obtained by using Stokes' diaphragm cell method. The larger the size of the molecule is, the smaller is the diffusion rate. Hydration numbers and hypothetical diffusion coefficients at infinite dilution for the amines were evaluated by using the extended treatment of Hartley and Crank. These values are lower than the corresponding Nernst limiting values for the reason of exceptionally high mobility of hydroxyl ion.

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