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SURFACE TENSIONS OF THE SYSTEM ANILINE-HEXANE

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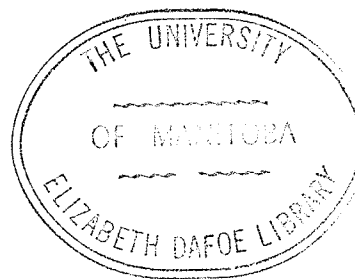
Master of Science

by

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TO MY FAMILY

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ABSTRACT

Surface tensions of the system aniline-hexane, in the range of temperatures 25° to 68°C were determined by three methods, viz. the Stalogmometer method, the Drop-Weight method and the Capillary Rise method. The method of capillary rise was used in the temperature range 55°C to 68°C.

Density measurements on this system were made, using an Ostwald-Sprengel type pycnometer (50) at 25°C and a dilatometer at higher temperatures (55° - 68°C).

An investigation of the surface tension isotherms just above the critical temperature was of primary concern. No horizontal portion in these isotherms was observed, although their slopes were slight.

A convexity in the three isotherms at 66°, 67° and 68°C was found to extend from a composition of 39.2% to 57.4% hexane by weight. The miscibility gap extended from 35.3% to 56.9% hexane by weight according to the coexistence curve.

The hydrogen bonded aniline associates into a complex. Plots of molecular surface energy versus composition and surface heat versus composition indicated that this complex undergoes dissociation.

The excess concentration of hexane in the surface layer of the system aniline-hexane was determined by means

of the Gibbs Adsorption Isotherm Equation and was found to be constant at 18.363×10^{-11} moles cm^{-2} on the high hexane side.

Guggenheim's relation $(T_c - T)^{1/3}$ was found to apply neither to surface tension nor molecular surface energy in a determination of whether the coexistence curve obeys a cubic relationship or not.

GLOSSARY OF SYMBOLS

T_m	the temperature at which the meniscus between liquid and gas phases appears to vanish.
T_c	the true critical temperature or the temperature at which the meniscus actually disappears.
x'_a	the mole fraction of component A in the phase-prime solution.
x''_a	the mole fraction of component A in the phase double-prime solution.
x'_b	the mole fraction of component B in the phase-prime solution.
$\bar{S}''_a$	the partial molal entropy of component A in the phase double-prime solution.
γ	surface tension in dynes/cm.
S	separation factor for the enrichment of the surface layer in A, the component of lower surface tension.
$\sum_1, \sum_2$	molal surface areas of components 1 and 2 respectively.
η	viscosity in centipoise.
a, b	empirical constants.
H	the vertical distance between the lowest points of the two menisci in two capillary tubes.
D	density in gm/ml.
R	universal gas constant.
X_i	mole fraction of component i in the liquid.
V_f	orthobaric volume of liquid phase.

GLOSSARY OF SYMBOLS CONTINUED

V_s	orthobaric volume of vapor phase.
V_{fm}	orthobaric volume of liquid at T_m .
V_{sm}	orthobaric volume of vapor at T_m .
F	number of degrees of freedom.
ΔS_A	the change in entropy of component A when material is transferred from the more concentrated to the less concentrated solution.
ΔS_B	the change in entropy of component B when material is transferred from the more concentrated to the less concentrated solution.
μ'_A	chemical potential of component A in the primed solution.
k	Boltzmann's constant.
T	absolute temperature.
ΔH	the heat of evaporation per mole of mixture.
m	mole % aniline in a solution.
H_s	surface heat in calories/cm ² .
Γ_2	excess concentration of hexane in the surface layer of an aniline-hexane mixture.
η_{Hexane}	viscosity of hexane in centipoise.
η_{Aniline}	viscosity of aniline in centipoise.
γ_{Aniline}	surface tension of aniline in dynes/cm.
γ_{Hexane}	surface tension of hexane in dynes/cm.

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CHAPTER I

INTRODUCTION

In this research surface tension has been investigated for the system aniline-hexane, which exhibits partial miscibility at lower temperatures and an upper critical solution temperature.

The purpose of this work was to determine whether there is a range of temperatures for which an isotherm shows constant surface tension, or some derived function of surface tension, for a binary mixture over a range of concentrations in a region just above the critical temperature.

Rice (1) developed a theory on the behaviour of certain thermodynamic properties at the critical solution temperature, which will be described later.

(A) Application of the Phase Rule

The system under investigation exhibits partial or limited miscibility. If a small quantity of a second liquid is added to a pure liquid in equilibrium with its vapor, a bivariant system is obtained from the original univariant system.

$$\text{i.e. } F = C - P + 2 = 2 - 2 + 2 = 2$$

where C is the number of components and P the number of phases.

The solution is homogeneous and two of the three variables

(T, P, composition) may alter. If more of the second component (liquid) is added, the system will at first remain homogeneous with its composition and pressure undergoing a continuous change. Then, when the concentration has reached a definite value (at constant temperature), solution no longer takes place and two liquid phases appear. Various points such as this occur for different temperatures, constituting what is known as the coexistence curve, when the compositions of the equilibrium phases are plotted against temperature.

The coexistence curve of the system aniline-hexane, which displays an upper critical solution temperature, was determined by Campbell and Kartzmark (1a) and is shown in Figure 1.

It is evident that the mutual solubility of the two liquids increases with increasing temperature, outlining a homogeneous and a heterogeneous area separated by the solubility curve as shown in Figure 1.

(B) The Theory of Mayer and Harrison

In order to understand clearly the theory of Rice, the one component system $L \rightleftharpoons V$ should first be considered.

Mayer and Harrison deduced certain equations (2) for the thermodynamic properties of a liquid system in the neighborhood of the critical point, which led to the P-V diagram of Figure 2. In this diagram, pressure is plotted as a function of volume at various temperatures so that the isotherms are represented by solid lines, with the temper-

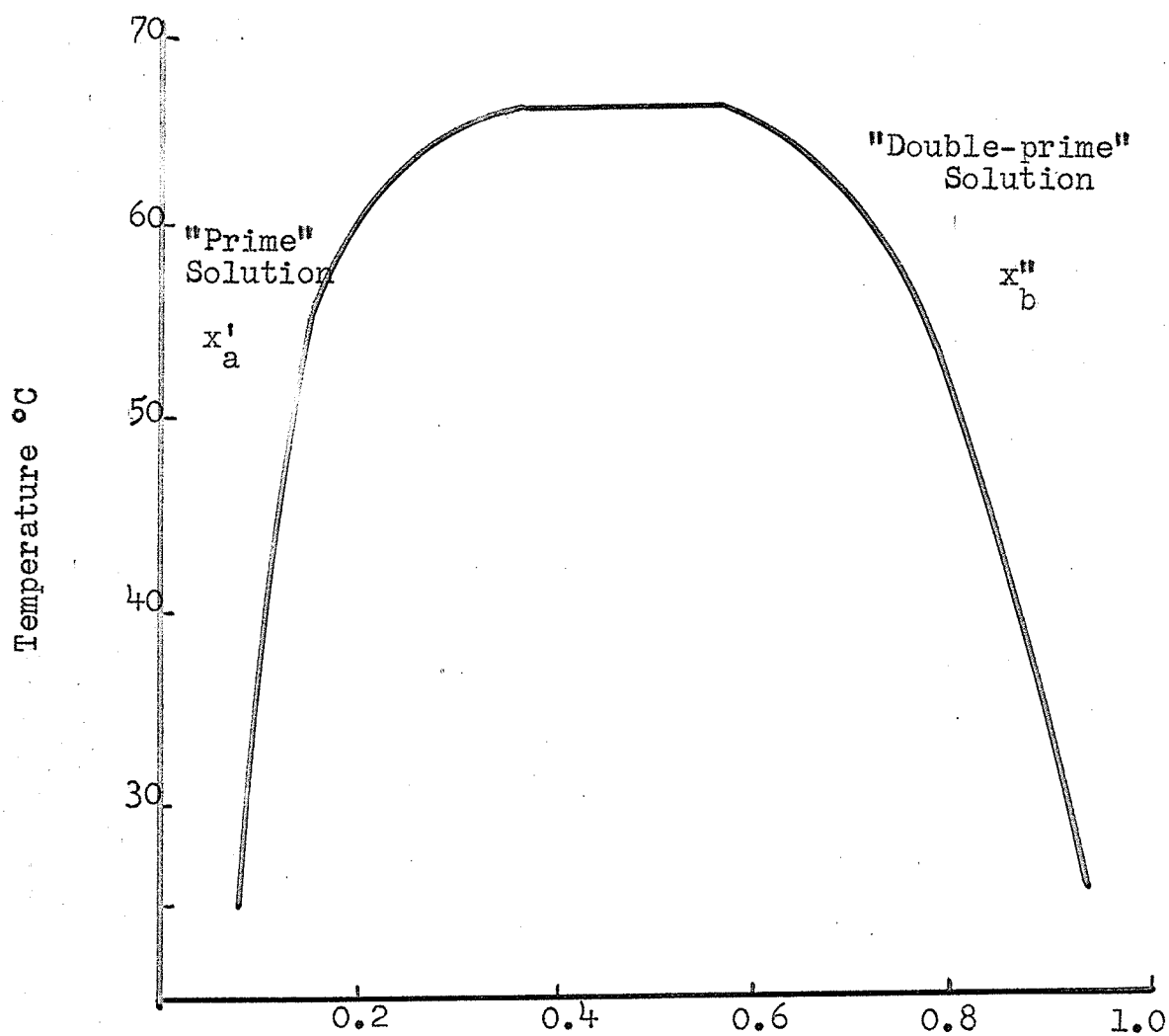


FIGURE 1. Coexistence Curve of the System Aniline-Hexane

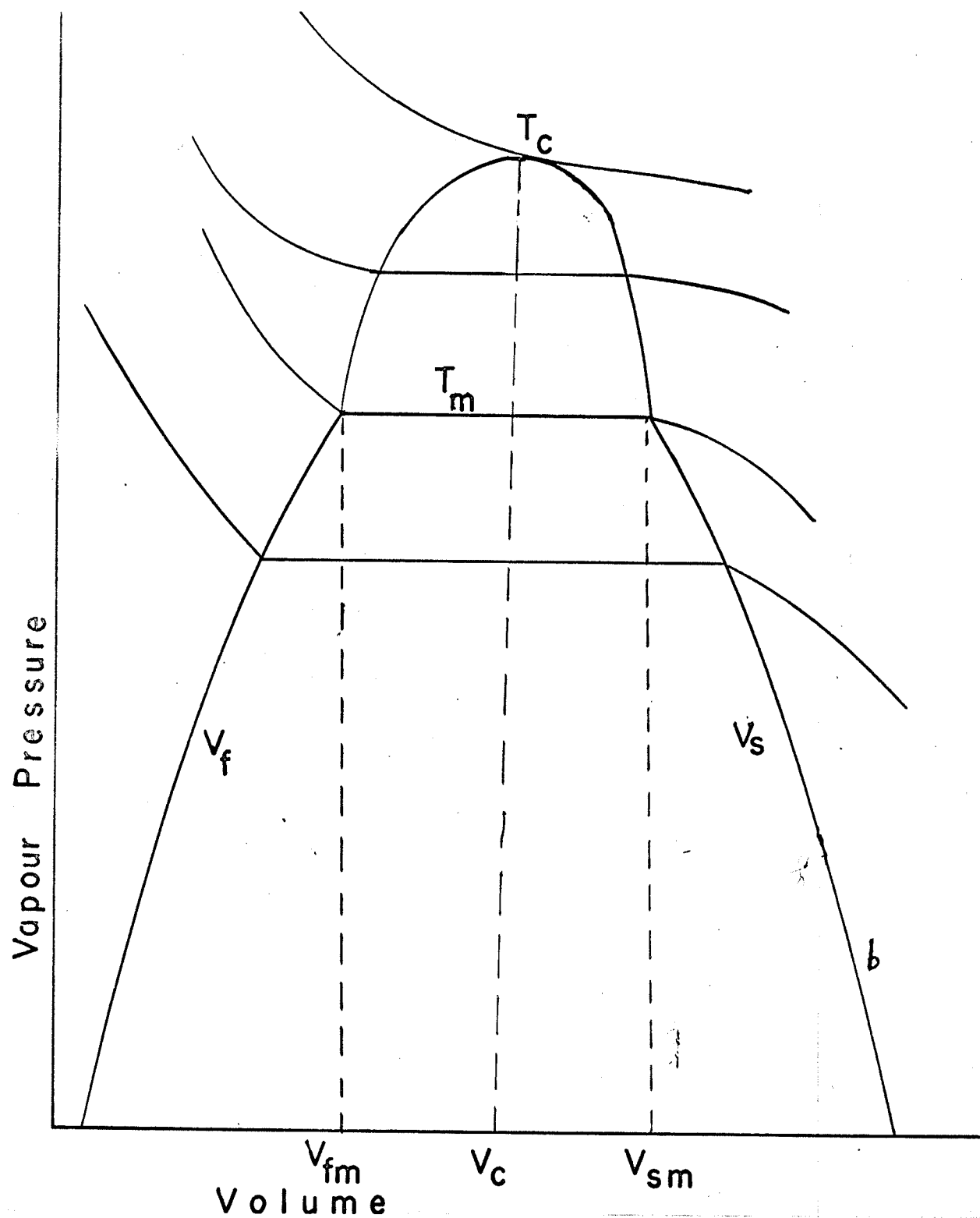


FIGURE 2. Mayer and Harrison's Proposed Coexistence Curve

atures T_m and T_c clearly indicated. T_m is the temperature at which the meniscus between liquid and gas appears to vanish, while T_c is the true critical temperature or the temperature at which the two phases become identical.

The region enveloped by the solid curve contains lines which are horizontal, that is $\left(\frac{\partial P}{\partial V}\right)_T = 0$. Below T_m the isothermal lines have zero slope, within the area of heterogeneity, and between T_m and T_c they have a continuous change of slope only outside curve b.

Mayer and Harrison state that at T_m the surface tension of the liquid is zero and above T_m no interface between liquid and vapor can be detected. At T_c the isothermal has a horizontal tangent at only one point, V_c, P_c . Above T_c the isothermal lines are never horizontal. Mayer and Harrison believed that the area between T_m and T_c would have certain unusual properties. Below T_m compression of the system through the volume region v_s and v_f was accompanied by the separation of two distinct phases of density $\frac{1}{v_f}$ and $\frac{1}{v_s}$, where v_s (Figure 2) is a point on the right-hand boundary of the P - V curve^b representing the volume of the saturated vapor, and v_f the corresponding point on the left-hand boundary, representing the volume of the condensed phase. Between T_m and T_c , however, there is no surface tension between the phases and corresponding to this, the isothermals pass smoothly through this region. Indeed all microscopic densities, within the area of the solid curve, in the region

between T_m and T_c correspond to the same pressure (at the same temperature) and to the same Gibb's free energy.

After a certain length of time, due to the higher pressure at the bottom and the gravitational gradient, the system will have a higher density at the bottom than at the top. The gravitational pressure gradient, however, amounts to only about one part in 10^5 per cm. of height and it would, therefore, seem that uniform density would be maintained for weeks.

Various experimenters have observed discontinuities in different properties of the condensed phase near the critical temperature T_m (the temperature of disappearance of the meniscus). These results are summarized by O. Maass (3). Solubility, dielectric constant and adsorption values have been found to change rapidly at this temperature. The most striking change is in the reactivity of HCl with propylene, which shows the usual increase in reaction rate with temperature as long as the HCl is liquid, but the rate drops suddenly to zero as the critical temperature (T_m) of HCl is exceeded (4).

(C) Rice's Theory

Rice disagrees, in some respects, with the theory of Mayer and Harrison and states that there is no constant-pressure portion of an isotherm above the temperature T_m . Rice contends that in the theory of Mayer and Harrison there

appear certain cluster integrals which are assumed to be volume independent. The integrals, however, which involve large numbers of molecules become volume dependent when the volume actually filled by these molecules is comparable to the total volume. Since these integrals are an important basis of Mayer and Harrison's equations, their theory breaks down. According to Rice, the breakdown occurs when the spongy mass, which will be described shortly, is formed.

The three-phase two-component system ($L_1 \rightleftharpoons L_2 \rightleftharpoons V$) of two partially miscible liquids is similar to the two-phase one-component system ($L \rightleftharpoons V$) already described.

For the two component system, $F = C - P + 2 = 2 - 3 + 2 = 1$.

For the one component system, $F = 1 - 2 + 2 = 1$.

By the application of the phase rule to the two cases, the same variance is obtained.

The critical phenomena of such a system, upon which the present work is based, are described by Rice as follows. According to van der Waals theory, the coexistence curve has a rounded, parabolic shape in the neighborhood of the critical point. Careful study and observation by Rice, however, indicate that for a plot of either pressure or temperature as ordinate against concentration as abscissa, the coexistence curve frequently has a flat top. This means that there is a range of concentration over which the meniscus disappears, within the limits of error, at the temperature designated as T_m .

Data on carbon dioxide (5), however, definitely indicate

that the horizontal portion is of finite length on the critical isotherm, which has a horizontal portion, while only 0.15° above the critical temperature, the isotherms have everywhere a finite slope.

Rice's theory considers two questions:

(1) Does the coexistence curve have a horizontal portion (constant temperature over a range of concentrations) at the critical temperature?

(2) Just above or below the critical temperature, in the region where there is complete miscibility, is there a range of temperatures for which an isotherm shows a constant fugacity or chemical potential for a liquid mixture over a range of concentrations?

To answer these questions from a theoretical point of view, Rice derives the following thermodynamic equations which determine the coexistence curve:

$$\frac{d \ln x_a'}{dT} = \frac{\Delta S_a - \left(\frac{x_b''}{x_a'} \right) \Delta S_b}{A' RT \left(\frac{x_a' x_b''}{x_b' x_a''} - 1 \right)} \quad (1)$$

and

$$\frac{d \ln x_b''}{dT} = \frac{\Delta S_b - \left(\frac{x_a'}{x_b''} \right) \Delta S_a}{A'' RT \left(\frac{x_a' x_b''}{x_b' x_a''} - 1 \right)} \quad (2)$$

where x_a' = mole fraction of component A in the phase-prime solution (as shown in Figure 1) x_a'' = mole fraction of component A in the phase double-prime solution.

x_b^I and x_b^{II} have a similar meaning except that they apply to component B.

ΔS_a is equal to $\bar{S}_a^{II} - \bar{S}_a^I$

where $\bar{S}_a^{II}$ is the partial molal entropy of component

A in the phase double-prime solution and,

$\bar{S}_a^I$ is that in the phase-prime solution.

ΔS_b is equal to $\bar{S}_b^I - \bar{S}_b^{II}$ and refers to component B,

but has a similar meaning as above.

$$A^I \text{ is } \frac{1}{RT} \left[\frac{\partial \mu_a^I}{\partial \ln x_a^I} \right]_{T,P} = \frac{1}{RT} \left[\frac{\partial \mu_b^I}{\partial \ln x_b^I} \right]_{T,P} \quad (3)$$

$$A^{II} \text{ is } \frac{1}{RT} \left[\frac{\partial \mu_a^{II}}{\partial \ln x_a^{II}} \right]_{T,P} = \frac{1}{RT} \left[\frac{\partial \mu_b^{II}}{\partial \ln x_b^{II}} \right]_{T,P} \quad (4)$$

Rice then derives the formula

$$\frac{d^2 n}{\left(\frac{x_b^{II}}{x_a^{II}} \right)^2} = - 2 \left[\frac{\partial \Delta S_b}{\partial \left(\frac{x_b^{II}}{x_a^{II}} \right)} \right]_T \quad (5)$$

to determine whether the coexistence curve has an upper or lower critical temperature. n is equal to $\Delta S_a - \frac{x_b^{II}}{x_a^{II}} \Delta S_b$.

$n = 0$ at the critical point and must be negative in the neighbourhood of an upper critical solution point. Since

$$\frac{dn}{d \left(\frac{x_b^{II}}{x_a^{II}} \right)} \text{ is also zero at the}$$

critical point, the second derivative must also be negative.

Since $\frac{x_b^{II}}{x_a^{II}}$ increases on leaving the critical point along the

coexistence curve, it is seen that this requires that ΔS_b increase also. Since ΔS_b starts at zero, it must be positive near an upper critical solution temperature.

This discussion is for a rounded coexistence curve. If the coexistence curve is flat at the critical temperature then, $\frac{d \ln x_a'}{d T}$ and $\frac{d \ln x_b''}{d T}$ are infinite for a range of concentrations so that we have $x_a' = x_a''$ and $x_b' = x_b''$ at the critical temperature.

A theoretical answer by O. K. Rice to the questions put forward earlier, is based on the point of view of associating molecules (6-8). He considers equilibrium between single molecules, double molecules, triplets, and higher clusters or droplets and states that these molecules are held together by van der Waals or dipole forces. As the system is compressed to smaller volumes, more and more of the larger clusters are formed. If sufficient compression is exerted, clusters of macroscopic size suddenly become stable, i.e. condensation begins.

Nevertheless, events will proceed in this way only if the surface tension of the droplets is positive. Since the surface tension of a liquid decreases with increasing temperature (9) and will eventually approach zero, the sudden shift of stability to the large clusters will not occur. Instead, the number and average size of the large clusters will gradually increase until finally, when the free volume of the large clusters is reduced to zero, they coalesce into

cone. Here the free volume is determined by the limits within which the cluster as a whole can move without becoming joined to other clusters. The coalescence of the droplets will then produce a spongy, complexly interconnected mass of variable density. Condensation will now compress the spongy mass, and there will be a decrease in the surface, but there will be no resistance to the compression, since the surface tension is zero. The pressure will remain constant until this process is finished; further compression requires the actual squeezing of the liquid. This process which takes place at constant pressure corresponds to the change of concentration across the flat top of the coexistence curve in question.

Above T_m , Rice states that the surface tension will become negative and the spongy mass, once formed, will require a small but steady increase in pressure to squeeze out the interstices, because this requires a decrease in the total amount of surface which is now resisted by the negative surface tension. Therefore, according to Rice's theoretical view, there will not be any horizontal isotherm above T_m .

It was the purpose of this research to determine whether the same applies to surface tension isotherms.

The manner in which interfacial tension vanishes is governed by the equation,

$$\gamma = n - T \sigma$$

where n and σ are, respectively, proportional to the

enthalpy and entropy.

If n and σ are positive, then at a sufficiently high temperature γ vanishes, giving an upper critical temperature. If they are negative, then at a sufficiently low temperature γ vanishes, giving a lower critical temperature.

The interfacial tension is of interest because it is related to surface tension viz: the interfacial tension of two mutually saturated liquids is equal to the difference between their surface tensions, measured when each liquid is thoroughly saturated with the other.

In the interfacial tension equation, if there are no special forces between the molecules of the two components of a binary system, then σ is expected to be positive, because the interface is then a place where the two species of molecules mix, with more disorder than in the bulk of the solution. ΔS_1 and ΔS_2 , the change in the entropies of both species, will be positive and an upper critical temperature will result. On the other hand, if special forces between the molecules of both components exist, then there is a tendency for these molecules to be bound to each other at the interface. This leads to a negative σ and a lower critical temperature will be evident.

Extensive experimental evidence on the shape of co-existence curves is given in the Landolt-Börnstein tables and it is found that many of them are extremely flat at the critical temperature as shown for example by Woodburn, Smith

and Tetewsky (10). There is, however, still some doubt about this because one may be dealing with an extremely flat maximum. Experimental evidence also shows that there are coexistence curves with rounded tops and that impurities have an appreciable effect in determining their shape (11). Zimm (12), for instance, found no evidence of a flat top in the system perfluoromethylcyclohexane-carbon tetrachloride because his samples were possibly not extremely pure. Gopal and Rice (13) later found evidence of a flat top although the amount of the truncation was within experimental error.

Thompson and Rice (14) here suggested an equation for coexistence curves of both binary liquid systems and liquid-vapor systems, of the form, $X_1 - X_2 = K(T_c - T)^{1/n}$ in the immediate vicinity of the critical region, where $X_1 - X_2$ is a measure of the difference in composition between coexisting phases. T_c is the critical temperature, T is the temperature at which the phases are in equilibrium, K is a proportionality constant and, n is very close to 3.

When $(T_c - T)^{1/3}$ is plotted versus some function such as density, the resultant graph will have the form shown in Figure 3. If the two lines meet at the base, as shown, then the coexistence curve will have a rounded, parabolic shape at the critical temperature and will obey a cubic relationship. If the two lines do not meet, as in Figure 4, and intersect the base of the graph at points a and b, then the coexistence curve will not obey a cubic relationship and will

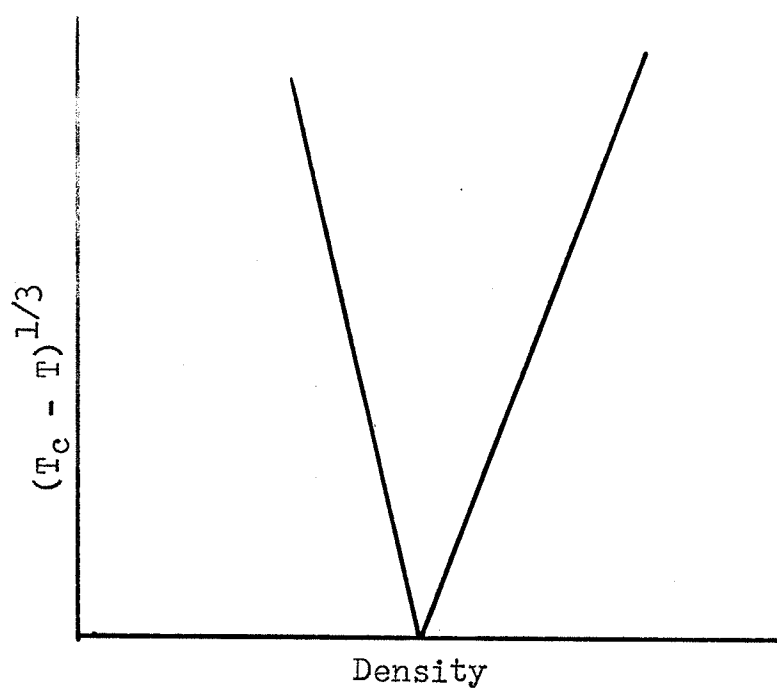


FIGURE 3. $(T_c - T)^{1/3}$ vs. Density

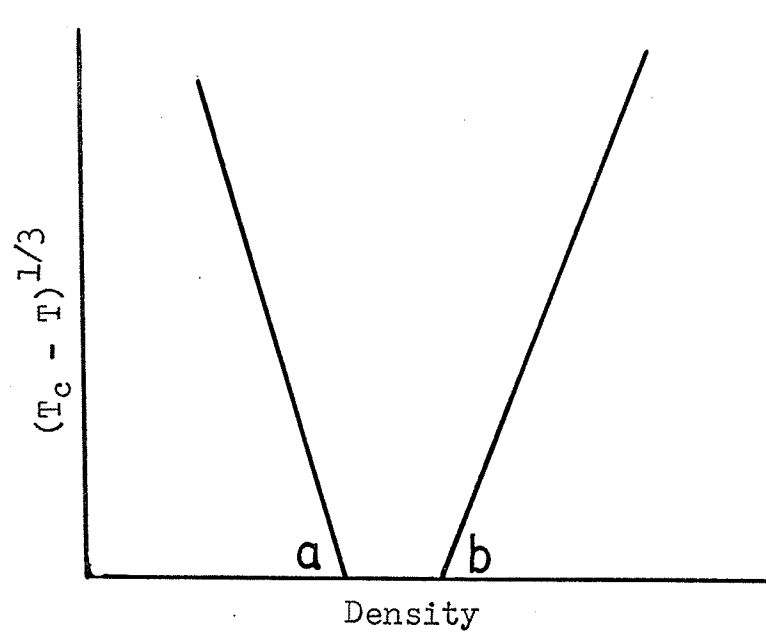


FIGURE 4. $(T_c - T)^{1/3}$ vs. Density

have a flat top extending over a distance of length a b .
 Similar plots were made to determine whether this applies to surface tension.

(D) Temperature Dependence of Surface Tension

Surface tension is very dependent on temperature. The following attempts have been made to correlate it with temperature.

One of the earlier empirical relations is that of Katayama (15), who modified Eötvös' equation

$$\gamma v_l^{2/3} \propto (1-T/T_c) \text{ to get}$$

$$\gamma y^{-2/3} \propto (1-T/T_c)$$

where y is defined as $\frac{1}{v_l} - \frac{1}{v_c}$

v_l is the molar volume of the liquid at temperature T and
 v_c is the molar volume at the critical temperature T_c .

Another well-known relationship between surface tension and temperature is that of Ramsey and Shields (16), which is based on the equation of Eötvös.

$$\gamma \left\{ \frac{M}{d_l} \right\}^{2/3} = k(t_c - t - b)$$

where γ is the surface tension at temperature t ,

M is the molecular weight

d_l is the density of the liquid and,

t_c is the critical temperature of the liquid.

The left-hand side of the equation represents what is known

as the molecular surface energy.

Guggenheim (17) suggested the empirical relation

$$\gamma = \gamma_0 (1 - T/T_c)^{1+r}$$

where T_c is the critical temperature

r is a constant and

γ is the surface tension of the liquid at the temperature T .

γ_0 is an arbitrarily assumed constant for each substance.

(E) Surface Tension of Binary Liquid Mixtures

Schmidt (18) proposed a theory known as "The Surface Model," which treats the liquid-vapor interface in the manner of Bakker (19), Verschaffelt (20), and Guggenheim (21). This theory shows that surface tension does not obey the simple mixture rule which is of the form

$$\sigma = y_A \sigma_A + y_B \sigma_B$$

where σ is the surface tension

y_A and y_B are the mole fractions of the two liquids in the surface layer and,

σ_A and σ_B are the surface tensions of the pure components.

Schmidt contends, however, that surface tension is not a linear function of the bulk mole fraction but is possibly a linear function of the surface mole fraction. By a thermodynamic treatment he derived a new equation for the surface tension of a mixture, which is expressed in terms of the bulk liquid composition of the mixture.

$$\sigma = \frac{S x_A \sigma_A + x_B \sigma_B}{S x_A + x_B}$$

where x_A and x_B are the mole fractions of the two liquid components.

S is a separation factor for the enrichment of the surface layer in A, the component of lower surface tension and is defined as,

$$S = \frac{K_A}{K_B} = \frac{b_A}{b_B} \bigg/ \frac{a_A}{a_B} = \frac{\delta_A}{\delta_B} \bigg/ \frac{\gamma_A}{\gamma_B} \cdot \frac{y_A}{y_B} \bigg/ \frac{x_A}{x_B}$$

where δ and γ are surface layer and bulk liquid activity coefficients, respectively.

K_A and K_B are distribution constants depending on temperature only, with "b" and "a" representing the activities in the surface layer and bulk liquid, respectively. For mixtures with components of similar properties between two bulk phases, or one bulk phase and one absorbed phase, it is assumed that

$$\left(\frac{\delta_A}{\delta_B} \right) \bigg/ \left(\frac{\gamma_A}{\gamma_B} \right) = 1$$

so that S becomes

$$\frac{y_A}{y_B} \bigg/ \frac{x_A}{x_B}$$

Closely related to Schmidt's formula (22) is an equation relating the surface tension of a mixture to pure component properties and properties of the bulk and surface phase of a mixture, proposed by Belton and Evans (23).

$$\sigma = \sigma_1 + \frac{RT}{\sum 1} \ln \frac{a_{1s}}{a_1} = \sigma_2 + \frac{RT}{\sum 2} \ln \frac{a_{2s}}{a_2}$$

where σ is the surface tension of the mixture
 σ_1 and σ_2 are the surface tensions of the pure

components.

Σ_1 and Σ_2 are the molal surface areas of the pure components and,

a_{is} and a_i are the activities of component i in the surface phase and bulk phase, respectively.

The combined ratio of the surface and bulk-phase activities can be expressed in terms of pure component parameters as

$$\left(\frac{a_{1s}}{a_1}\right) / \left(\frac{a_{2s}}{a_2}\right)^{\Sigma_1/\Sigma_2} = \exp \left[-\frac{\sigma_1 - \sigma_2}{RT} \Sigma_1 \right]$$

By assuming (a) equal surface areas, $\Sigma_1 = \Sigma_2 = \Sigma$ and (b) the ratio of the activity coefficients equal to unity,

$$\text{i.e. } \left(\frac{\gamma_{1s}}{\gamma_1}\right) / \left(\frac{\gamma_{2s}}{\gamma_2}\right) = 1$$

where $a \approx \gamma X$ and γ is the activity coefficient of the component in the respective phase, the equation is then solved for X_{1s} in terms of X_1 and X_2 .

$$\text{i.e. } \sigma = \sigma_1 - \frac{RT}{\Sigma} \ln (X_1 + X_2 C)$$

where $C = \exp \left[(\sigma_1 - \sigma_2) / RT \right] \Sigma$ (an empirical parameter)

It is not possible to calculate surface tension by this equation in the present research because the activities and surface areas have not been determined.

(F) Surface Tension-Viscosity Relation for Liquids

Several relations have been postulated (24) relating surface tension of a liquid in air to its viscosity. Silver-

man and Roseveare (25) suggested that,

$$\gamma - 1/4 = A/\eta + B$$

where γ is the surface tension

η is the viscosity and,

A and B are empirical constants for a given substance.

Murkerjee (26) proposed the formula

$$\gamma = K \eta^{1/3}$$

where K is an empirical constant.

Sanyal and Mitra (27) derived the following relations:

Associated liquids: $T \log \eta - a \gamma^{5/6} = b$

Non-associated liquids: $T \log \eta - a \gamma = b$

where a and b are empirical constants.

CHAPTER II

NATURE OF THE PROBLEM

The present research was carried out to test the theory of Rice, which states that slightly above the critical temperature there is no range of temperatures for which an isotherm can show constant fugacity or chemical potential for a liquid mixture over a range of concentrations. This was extended to the property of surface tension in order to determine whether there were horizontal isotherms above the critical temperature, in a plot of surface tension or some derived function versus composition.

The system aniline-hexane was chosen because the co-existence curve, which was used throughout this research, had an upper critical solution temperature and was already determined by Campbell and Kartzmark. It was found by Campbell and Kartzmark that the top of this coexistence curve was horizontal, or approximately so.

No surface tension data have been reported in the literature for the system aniline-hexane in the area of the critical temperature. The only investigation of this system is that of Keyes and Hildebrand (28), who made six surface tension determinations at 25°C, in the composition range 0 to 100 weight % hexane, by the method of capillary rise.

Some surface tension work has been done on the pure components. Jasper, Kerr and Gregorich (29) measured the

orthobaric surface tensions of n-hexane at 10° intervals between 0° and 60°C, by the capillary rise method.

Jasper and Kring (30) determined the surface tension of n-hexane orthobarically, in an atmosphere of nitrogen, over a temperature range 0° to 60°C by means of a capillarimeter (a capillary apparatus) connected to a pressure-regulating manometer.

The surface tension of hexane between 10° and 20°C was measured by Verschaffelt (31), by the lifting of circular disks from the liquid surface.

Teitelbaum, Gortalova and Ganelina (32) determined the surface tension of aniline by the method of maximum pressure in bubbles, between the temperatures 20° and 40°C.

Surface Tension by the Drop-Weight Method

The theory for surface tension measurements by the "drop-weight" method is based on the law of Tate (33).

$$W = mg = 2 \pi r \gamma \quad (6)$$

where W is the weight of the drop, m is its mass, g is the acceleration due to gravity, r is the radius of the capillary tip and γ is the surface tension.

If a drop which hangs at the end of a tip were cylindrical and of the same diameter as the tip, it is evident that the maximum weight of drop which could be supported would be exactly equal to the weight of the liquid upheld in a capillary tube of the same diameter. This is because, in

both cases, the force of surface tension acts on a line $2\pi r$ long, so that the force is $2\pi r\gamma$ as in equation (6) above (Tates Law).

Both observation and theory indicate that, on tips of ordinary size, only a fraction of the drop falls, so the weight of the drop which falls must be less than that given by equation (6). However, as the tip is made smaller, the fraction which falls becomes larger and larger, and extrapolation of the curve to zero diameter indicates that here all of the drop falls, or the hanging and falling drops have the same weight. Both the theory of the preceeding section and the extrapolation of experimental values show that equation (6) gives the correct weight of the drop when r/a or $r/v^{1/3}$ is zero, where "a" is a capillary constant and "v" is the volume of the drop.

The weight of a drop must, therefore, be a function of the shape of the drop. The shape depends on the ratio between some linear dimension of the tip, such as r , and a linear dimension of the drop l , or

$$W = mg = 2\pi r\gamma f(r/l) .$$

Now, the cube root of the volume of the drop $v^{1/3}$ varies as a linear dimension of the drop, so

$$W = mg = 2\pi r\gamma f_1(r/v^{1/3}) = 2\pi r\gamma \phi = 2\pi r\gamma f_2(r/a)$$

and since $W = mg$ the surface tension equation is of the form

$$= \frac{mg}{2\pi r} \cdot f_1(r/v^{1/3}) = \frac{mg}{2\pi r} \cdot f_2(r/a) = \frac{mg\phi}{2\pi r} = \frac{mg}{r} \cdot F$$

If the vapor is dilute, it is simplest to let "m" represent the weight in grams of one drop as weighed in air.

Surface Tension by Capillary Rise

The theory of the capillary tube has been discussed by the late Lord Rayleigh (34). For a narrow tube of radius r in which the meniscus stands at a height "h" above a plane surface of liquid, Rayleigh gives the equation:

$$a^2 = 2\alpha^2 = r(h + r/3 - 0.1288 r^2/h + 0.1312 r^3/h^2) \quad (7)$$

$$\text{Here } a^2 = 2\alpha^2 = \frac{2\gamma}{g(D - d)}$$

where γ is the surface tension, g the acceleration due to gravity, D the density of the liquid, and d the density of the vapor or air and vapor if the surface tension is measured against air. This formula holds accurately as long as r/h is small compared with r , for example, for water in tubes of 1 mm. radius or less.

It was shown by Richards and Coombs (35) that the wide tubes employed by many workers were not large enough to give a plane surface from which to measure the rise in the narrow tube and that a considerable correction for capillary rise in the wide tube was necessary. To calculate this correction, Rayleigh gives the formula:

$$r/\alpha - \log_e \alpha/h = 0.8381 + 0.2798 \alpha/r + 1/2 \log_e r/\alpha \quad (8)$$

The correction in h is calculated by substituting the value of α from equation (7).

The range of application of these formulae limits the size of tube (36) which may be used for accurate measurement of surface tension. It could be much facilitated if

tubes of intermediate size could be employed and the surface tension deduced from measurements of the difference in height between two menisci in comparatively small tubes.

The general equation for such a case, given by Samuel Sugden (37) is:

$$\gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) = g Z (D - d) + \text{a constant} \quad (9)$$

which applies to the free surface of a liquid in equilibrium, under the influence of surface tension and gravity at a particular point P on the meniscus of the liquid.

R_1 and R_2 are the principal radii of curvature of the surface at P. Z is the vertical distance of P above the lowest point of the meniscus O. By considering the case of $Z = 0$, the constant is seen to have the value $2 \gamma/b$, where b is the radius of curvature at O. Further, since the meniscus is a surface of revolution, one of the radii of curvature is $PC = x/\sin \phi$, where ϕ is the angle subtended by lines joining O and P from the center of curvature C. (Figure 4a) If P is the second radius of curvature, then equation (9) becomes:

$$\frac{1}{P/b} + \frac{\sin \phi}{x/b} = 2 + \frac{g(D - d)b^2}{\gamma} \cdot Z/b \quad (10)$$

This equation represents a family of curves which are determined by the value of the parameter B , where

$$B = \frac{g(D - d) b^2}{\gamma}$$

It then follows, from the general equation to the free surface of a liquid that:

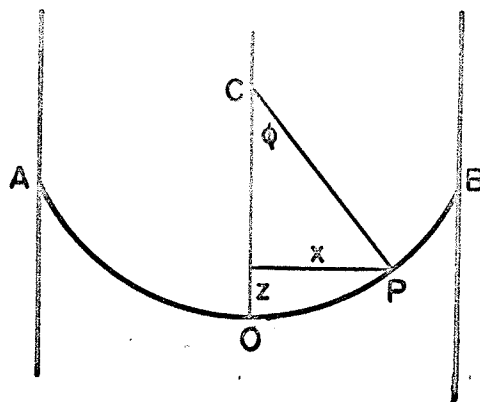


Figure 4 a: Cross Section of a Meniscus in a Vertical Cylindrical Tube

$$2\gamma\left(\frac{1}{b_1} - \frac{1}{b_2}\right) = H g(D - d)$$

where H is the vertical distance between the lowest points of the menisci in two vertical tubes of radii r_1 and r_2 , b_1 and b_2 are the radii of curvature at these points.

CHAPTER III

EXPERIMENTAL

A. Purification of Materials

Hexane

Spectroanalyzed Hexane (A.C.S.) from the Fisher Scientific Company was used without further purification. The refractive index observed for this hexane is compared with literature values in the following table at 25°.

TABLE 1
Refractive Indices of Pure Hexane

Relevant Investigations	Refractive Index	$n_{25^{\circ}}^D$
1) This Research	1.37536	
2) Lama and Lee (38)	1.37230	
3) Dow Chemical Co. (39)	1.37226	

Since all hexanes are distillation products, the results of this research are only good for the product used.

Aniline

Aniline obtained from the Fisher Scientific Company was purified by distillation over zinc dust. New samples were distilled each week, because aniline is decomposed by light. This decomposition was minimized by placing the sample in a

brown bottle, which was stored in a dark compartment. Care was taken to avoid unnecessary exposure of the aniline to air. A comparison of the refractive index of my product with the literature is shown in the table below.

TABLE 2
Refractive Indices of Pure Aniline

Relevant Investigations	Refractive Index	$n_D^{25^\circ}$
1) This Research	1.5837	
2) Dreisbach and Martin (40)	1.58318	
3) Smith, Foecking & Barber (41)	1.5840	
4) Hough, Mason & Sage (42)	1.5826	

Benzene

Thiophene-free benzene (A.C.S.) from the Fisher Scientific Company was frequently shaken with conc. H_2SO_4 until the yellow color in the acid layer disappeared. It was then washed with a solution of sodium bicarbonate and the product dried by anhydrous sodium sulfate and metallic sodium. Finally it was distilled twice from sodium metal.

Water

Water was purified by distillation from a Barnstead electric, water still. At $25^\circ C$ the specific conductivity of this water was 5×10^{-6} mho/cm.

B. Experimental Procedure

Determination of Surface Tensions

In this work, three methods have been employed for measuring surface tension, viz.

- 1) The Stalagmometer Method
- 2) The Drop-Weight Method
- 3) The Capillary Rise Method

This research was begun using the well-known stalagmometer method (43) of surface tension determination. It was found, however, that this method required 45 to 60 minutes for each determination and this indicated that, at temperatures higher than 25°C, a large amount of evaporation would take place in this period of time and the sample composition would not remain constant.

The Drop Weight Method was then tried and found satisfactory at 25°C but, again, excessive evaporation of the liquid sample at higher temperatures introduced considerable error, so that the Capillary Rise Method had to be employed for temperatures above 25°C.

Drop-Weight Method

The drop-weight apparatus used was that devised by Harkins and Brown (44) and was designed to give a precision of 0.3%.

The apparatus, shown in Figure 5, was supported by a heavy iron rod, held upright by a secure clamp. During a

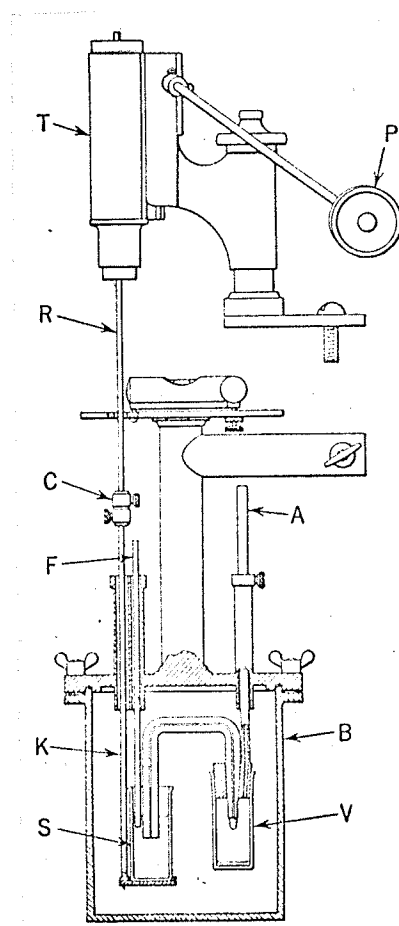


FIGURE 5. Drop-Weight Apparatus.

determination, it was suspended in the water of a thermostat, which was constant to $\pm 0.02^{\circ}\text{C}$.

The fundamental part of this apparatus consisted merely of an inverted U of heavy walled, pyrex, capillary tubing, one end of which was ground until it was perpendicular to the length of the tube. The diameter of the tip was then measured by means of a travelling microscope: it was found to be 0.674 cm.

The outside casing, B, was constructed of glass while the water-proof lid was made of brass. The supply bottle, S, which contained the liquid under investigation, was made adjustable in height by using a stand with a ratchet and pinion, P, from an old microscope. The supply bottle was held by a metal support, K, which was fastened to a metal rod, R, by means of connection piece C. Rod R was fastened to a moveable bar T. By turning P, a pinion wheel, T, was raised or lowered and the height of S thus regulated. By adjustment of the supply bottle, S, and by suction applied at A, the rate of formation of the drops from the capillary tip was controlled. These drops were collected in the collecting bottle, V, and weighed. Several determinations on each sample were made.

Control of the Drop

The drop was controlled by the method of Harkins and Brown (45). Gravity alone was allowed to control the formation of the last tenth of the drop. To accomplish this,

the level of the liquid in the supply bottle was made just a little higher than the level of the capillary tip and by applying suction, the drop was drawn over to as nearly full size as possible without causing the drop to fall under the influence of suction. Then the drop was allowed to complete its growth and fall under the influence of gravity. Thirty drops, which were allowed to form in this manner, were collected.

Collecting and Weighing the Drops

The above method of drop control was used rather than allowing three minutes for the natural formation of each drop (46), because the possible errors due to evaporation would have more than compensated for the accuracy gained by slow formation. The method of making a run was as follows: The capillary tube was cleaned (with chromic acid, distilled water and acetone in this order, followed by several washings with the liquid under investigation), the level in the supply bottle was adjusted slightly above the capillary tip, a clean weighing bottle was placed in position and the apparatus was suspended in the thermostat for 30 minutes in order that thermal equilibrium might be attained. The first drop was then drawn over and kept at full size for five minutes in order to saturate the space in the collecting bottle with vapor, so that each drop would fall in its own saturated vapor. Thirty such drops were drawn over. The apparatus was removed from the thermostat and the collec-

ting bottle was cooled with acetone to prevent loss of vapor. The collecting bottle, with the drops, was weighed.

A blank run was then made exactly as before, except that only five drops were allowed to be formed and collected. Therefore, the weight of the bottle and 30 drops, diminished by the weight of the bottle and five drops, gave the weight of 25 drops. The distillation from the convex drop to the concave surface in the bottle, the weight of the vapor in the bottle, and all other causes for loss or gain in weight were nearly the same in both cases and were, therefore, approximately eliminated by this procedure.

The drop-weight apparatus was checked against benzene. My value for the surface tension of benzene at 25°C was 28.19 dynes/cm. against a literature value of 28.25 dynes/cm. (47).

Capillary Rise Method

A diagram of this apparatus, as designed by Sugden (48), is shown in Figure 6. The essential feature is the use of two heavy-walled capillary tubes mounted close together with the junction of the tubes sealed on to a small glass rod, A, which slid easily into a socket, B, formed of narrow glass tubing joined on to the lower end of the wide tube C. This allowed the capillaries to be removed readily for cleaning and by this arrangement, both menisci could be seen simultaneously in the field of view of a travelling microscope. The tube, C, was fitted with a stopper, D, which was connected

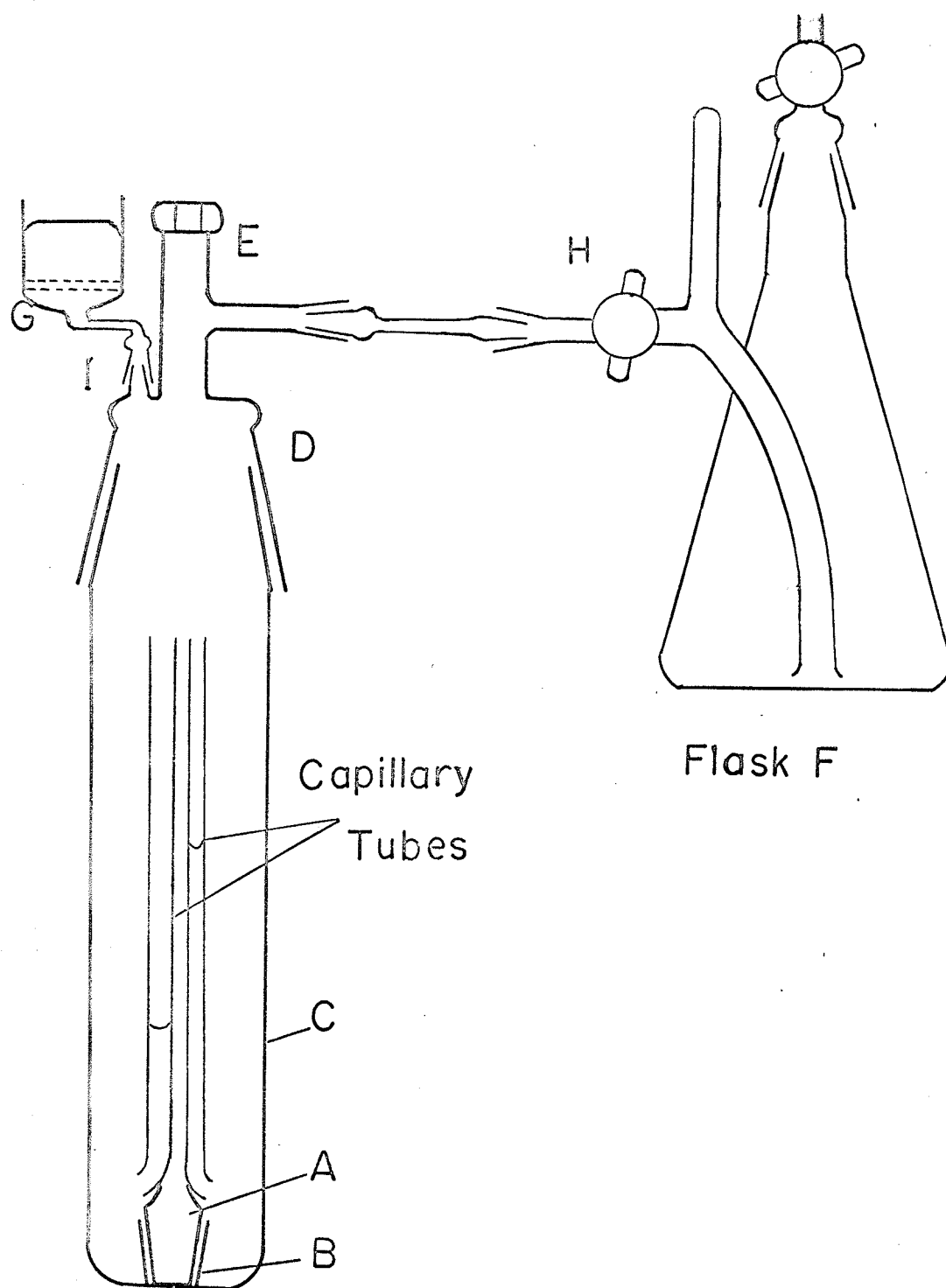


FIGURE 6. Capillarimeter and Filling Flask.

to a teflon stopcock, E, for regulating the filling of the apparatus.

The vertical distance between the lowest points of the two menisci was measured for each solution.

Selection of Capillary Tubes

A number of capillary tubes were tested for constancy of radius by the mercury thread length method. Two capillaries were found, each with a length of approximately six cms. of constant bore. The radius of the capillary of smaller bore was found to be 0.01009 cm. while that of the larger bore was found to be 0.04996 cm.

Such an arrangement, using two capillary tubes, made it possible to read both menisci more accurately, since the bulk solution did not have to be used as a reference point.

Filling of the Apparatus

The sample solution was made up in a flask similar to F, of Figure 6, and was connected to the capillarimeter by means of teflon tubing and a stopcock H. After placing the apparatus in the thermostant for 30 minutes, the solution was forced, by way of stopcock E and H, into the capillarimeter by the vapor pressure in flask F. The air in C was displaced through crucible, G, which was half-filled with mercury. When a sufficient amount of solution was transported, stopcocks E and I were closed to prevent evaporation and to maintain constant composition of the solution. The capillarimeter was then tilted so that the liquid in the capillaries would rise above the equilibrium level. After

adjustment to the vertical position, the distance between the lowest points of the two menisci was measured. Several trials were made for each solution and the mean height was taken.

The capillarimeter was checked against benzene and hexane in order to test its accuracy. The experimental values for benzene and hexane at 25°C were 28.17 and 17.98 respectively, which corresponded well with the literature values of 28.25 (47) and 17.93 (49) dynes/cm.

Cleaning of the Apparatus

Before each set of measurements, the capillaries and apparatus were thoroughly cleaned with a hot mixture of chromic and nitric acids, then washed with distilled water. This was followed by rinsing with acetone and drying with vacuum suction.

Preparation of Solutions

Solutions ranging from 0 to 100% Hexane by weight were prepared in the 250 ml. flask, F, shown in Figure 6. A two-pan balance was used for weighing both components at room temperature. The weighings were accurate to two units in the fourth decimal place.

Density Measurement

The Ostwald-Sprengel type of pycnometer described by Daniels et al (50) was used for density measurements at 25°C. A buoyancy correction was employed. At higher temperatures, a dilatometer method was employed (see Figure 7).

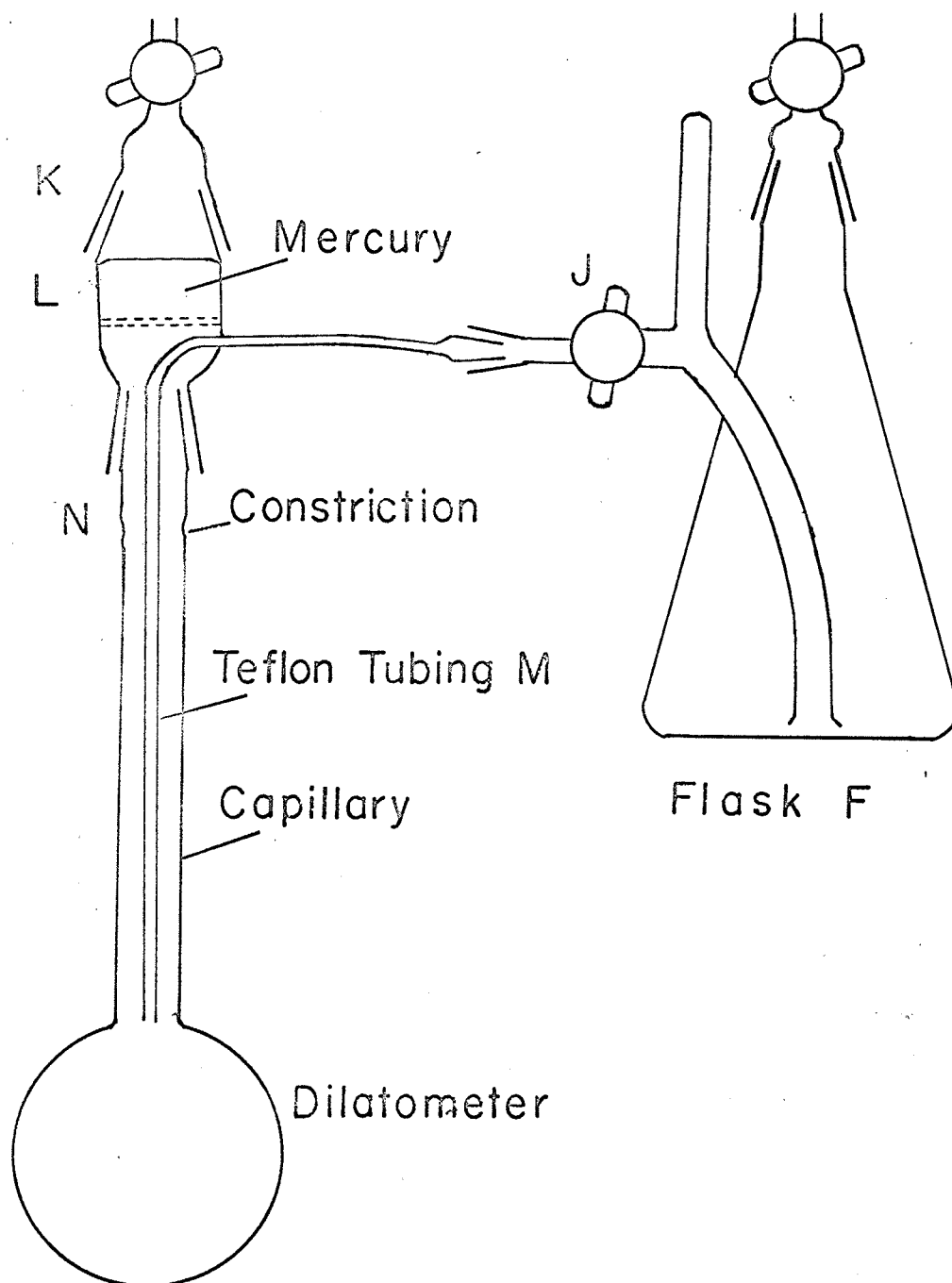


FIGURE 7. Dilatometer and Filling Flask.

Calibration of the Dilatometer

After thorough cleaning of the dilatometer with chromic acid and distilled water, it was dried and filled with clean mercury by means of a hypodermic syringe. One cm. above the neck of the dilatometer flask, a mark was etched on the capillary tubing, behind which was fastened a scale taken from a broken Beckmann thermometer. It was arranged so that this mark coincided with a specific mark on the Beckmann scale. The apparatus was then immersed in the thermostat, to within a cm. of the top of the capillary, for thirty minutes.

Using a syringe, the mercury meniscus was adjusted to coincide with a specific mark on the Beckmann scale. The dilatometer was then removed from the thermostat, dried, and weighed without the Beckmann scale. This was repeated for each of the main marks on the Beckmann scale and the volume per unit mark of the scale was calculated, using the density of mercury at the appropriate temperature.

The solution was made up in flask F shown in Figure 7. It was then connected to the dilatometer and placed in the thermostat constant to $\pm 0.02^{\circ}\text{C}$. After thermal equilibrium was attained, stopcocks K and J were opened and the dilatometer was filled with solution. The crucible, L, and the teflon tubing M, were removed and the excess solution at the top of the capillary was withdrawn by means of a syringe in order to prevent drops of heterogeneous solution, formed

in the lower temperature part of the capillary protruding out of the thermostat, from falling downward into the homogeneous portion. A constriction at N aided in removing the heterogeneous drops at the top of the capillary when the teflon tubing was removed.

As before, the solution was brought to a particular mark on the Beckmann scale by using a syringe and the portion of the capillary above the meniscus was dried with a piece of filter paper. The capillary opening was then stoppered with a crucible half-filled with mercury. For each temperature, a reading on the Beckmann scale was made, after thermal equilibrium was attained. The dilatometer was then removed quickly from the thermostat, sprayed with acetone to cool it, and wiped dry. After allowing it to remain in the atmosphere for a few minutes, it was weighed. Values for the same solution were reproducible to the extent of one unit in the fourth decimal.

CHAPTER IV

EXPERIMENTAL RESULTS

TABLE 3

Surface Tensions of Pure Liquids by the
Stalagmometer Method at 25°C

Liquid	Density (gm. ml ⁻¹)	Surface Tension (dynes cm ⁻¹)
Benzene	0.8735	27.19
Distilled Water	0.9971	71.49
Pure Hexane	0.6623	17.47
Pure Aniline	1.0175	42.52

TABLE 4

Surface Tensions of Pure Liquids by the
Method of Capillary Rise (25°C)

Liquid	H (cm.)	Density (gm. ml ⁻¹)	Surface Tension (dynes cm ⁻¹)
Benzene	5.181	0.8735	28.17
Distilled Water	11.565	0.9971	71.58
Pure Hexane	4.395	0.6610	17.91
Pure Aniline	6.615	1.0175	41.79

TABLE 5

Surface Tensions of the System Aniline-Hexane
by the Drop Weight Method at 25°C

Weight % Hexane	Mole % Hexane	Density (gm. ml ⁻¹)	Surface Tension (dynes cm. ⁻¹)
0	0	1.0173	42.89
1.00	1.08	1.0125	39.57
2.99	3.20	1.0062	35.90
3.77	4.06	0.9989	31.47
5.05	5.44	0.9927	28.66
5.12	5.51	0.9924	28.49
5.81	6.23	0.9890	27.12
5.97	6.42	0.9882	26.54
7.44	7.99	0.9810	24.58
93.03	93.52	0.6812	18.41
95.06	95.41	0.6725	18.32
95.09	95.44	0.6724	18.59
96.02	96.31	0.6702	18.19
97.94	98.09	0.6657	18.20
100	100	0.6612	18.13

TABLE 6

Surface Tensions of the System Aniline-Hexane at 55°C

Weight % Hexane	Mole % Hexane	H (cm.)	Density (gm. ml ⁻¹)	Surface Tension (dynes cm. ⁻¹)
100	100	3.803	0.6331	14.83
90.07	90.74	3.832	0.6554	15.47
79.91	81.13	3.778	0.6833	15.84
9.99	10.71	3.513	0.9425	20.44
0	0	6.379	0.9914	39.13

Results in Tables (6) to (15) were obtained by the Method of Capillary Rise.

TABLE 7

Surface Tensions of the System Aniline-Hexane at 60°C

Weight % Hexane	Mole % Hexane	H (cm.)	Density (gm. ml ⁻¹)	Surface Tension (dynes cm. ⁻¹)
100	100	3.710	0.6284	14.35
90.07	90.74	3.753	0.6526	15.07
79.91	81.13	3.703	0.6790	15.48
9.99	10.71	3.658	0.9392	21.20
0	0	3.753	0.9869	38.51

TABLE 8

Surface Tensions of the System Aniline-Hexane at 61°C

Weight % Hexane	Mole % Hexane	H (cm.)	Density (gm. ml ⁻¹)	Surface Tension (dynes cm. ⁻¹)
100	100	3.682	0.6278	14.22
90.07	90.74	3.729	0.6517	14.95
79.91	81.13	3.688	0.6783	15.40
70.27	71.87	3.581	0.7051	15.62
20.63	21.93	3.022	0.8890	16.56
9.99	10.71	3.688	0.9366	21.32
0	0	3.729	0.9862	38.42

TABLE 9

Surface Tensions of the System Aniline-Hexane at 62°C

Weight % Hexane	Mole % Hexane	H (cm.)	Density (gm. ml ⁻¹)	Surface Tension (dynes cm. ⁻¹)
100	100	3.664	0.6264	14.12
90.07	90.74	3.712	0.6501	14.86
79.91	81.13	3.673	0.6772	15.31
70.27	71.87	3.577	0.7043	15.54
20.63	21.93	3.031	0.8880	16.59
9.99	10.71	3.702	0.9357	21.38
0	0	3.712	0.9854	38.29

TABLE 10

Surface Tensions of the System Aniline-Hexane at 63°C

Weight % Hexane	Mole % Hexane	H (cm.)	Density (gm. ml ⁻¹)	Surface Tension (dynes cm. ⁻¹)
100	100	3.650	0.6254	14.04
90.07	90.74	3.692	0.6492	14.76
79.91	81.13	3.658	0.6759	14.23
70.27	71.87	3.563	0.7038	15.47
20.63	21.93	3.040	0.8872	16.62
9.99	10.71	3.719	0.9349	21.46
0	0	3.692	0.9843	38.19

TABLE 11

Surface Tensions of the System Aniline-Hexane at 64°C

Weight % Hexane	Mole % Hexane	H (cm.)	Density (gm. ml ⁻¹)	Surface Tension (dynes cm. ⁻¹)
100	100	3.638	0.6245	13.97
90.07	90.74	3.673	0.6487	14.67
79.91	81.13	3.642	0.6757	15.16
70.27	71.87	3.548	0.7036	15.39
25.06	26.54	2.993	0.8671	15.98
20.63	21.93	3.049	0.8863	16.66
9.99	10.71	3.743	0.9343	21.59
0	0	3.673	0.9835	37.91

TABLE 12

Surface Tensions of the System Aniline-Hexane at 65°C

Weight % Hexane	Mole % Hexane	H (cm.)	Density (gm. ml ⁻¹)	Surface Tension (dynes cm. ⁻¹)
100	100	3.638	0.6234	13.86
90.07	90.74	3.660	0.6473	14.58
79.91	81.13	3.625	0.6741	15.05
70.27	71.87	3.534	0.7023	15.30
29.36	30.99	2.962	0.8474	15.49
25.06	26.54	3.003	0.8662	16.00
20.63	21.93	3.071	0.8855	16.76
9.99	10.71	3.763	0.9337	21.69
0	0	3.660	0.9825	37.52

TABLE 13

Surface Tensions of the System Aniline-Hexane at 66°C

Weight % Hexane	Mole % Hexane	H (cm.)	Density (gm. ml ⁻¹)	Surface Tension (dynes cm. ⁻¹)
100	100	3.588	0.6223	13.73
90.07	90.74	3.637	0.6461	14.46
79.91	81.13	3.603	0.6729	14.93
70.26	71.87	3.520	0.7009	15.21
57.21	59.10	3.337	0.7434	15.27
54.09	56.46	3.258	0.7524	15.08
49.37	51.31	3.197	0.7703	15.10
44.37	46.63	3.122	0.7887	15.16
40.79	42.68	3.082	0.8021	15.22
39.24	41.10	3.078	0.8081	15.32
33.16	34.90	2.990	0.8317	15.34
29.36	30.99	2.978	0.8473	15.54
25.06	26.54	3.013	0.8654	16.07
20.63	21.93	3.084	0.8846	16.81
9.99	10.71	3.776	0.9330	21.75
0	0	3.637	0.9816	37.31

TABLE 14

Surface Tensions of the System Aniline-Hexane at 67°C

Weight % Hexane	Mole % Hexane	H (cm.)	Density (gm. ml ⁻¹)	Surface Tension (dynes cm. ⁻¹)
100	100	3.566	0.6211	13.62
90.07	90.74	3.618	0.6455	14.37
79.91	81.13	3.590	0.6727	14.87
70.26	71.87	3.508	0.7008	15.16
57.21	59.10	3.327	0.7425	15.21
54.09	56.46	3.246	0.7516	15.02
49.37	51.31	3.178	0.7697	15.06
44.37	46.63	3.121	0.7879	15.14
40.79	42.68	3.082	0.8013	15.21
39.24	41.10	3.080	0.8073	15.31
33.16	34.90	3.018	0.8312	15.45
29.36	30.99	2.986	0.8467	15.57
25.06	26.54	3.040	0.8647	16.20
20.63	21.93	3.094	0.8838	16.85
9.99	10.71	3.814	0.9324	21.95
0	0	3.618	0.9807	37.19

TABLE 15

Surface Tensions of the System Aniline-Hexane at 68°C

Weight % Hexane	Mole % Hexane	H (cm.)	Density (gm. ml ⁻¹)	Surface Tension (dynes cm. ⁻¹)
100	100	3.546	0.9202	13.52
90.07	90.74	3.602	0.6446	14.29
79.91	81.13	3.581	0.6718	14.81
70.26	71.87	3.492	0.6999	15.07
57.21	59.10	3.321	0.7416	15.16
54.09	56.46	3.236	0.7507	14.95
49.37	51.31	3.155	0.7692	14.94
44.37	46.63	3.118	0.7869	15.11
40.79	42.68	3.081	0.8004	15.18
39.24	41.10	3.089	0.8063	15.34
33.16	34.90	3.030	0.8302	15.49
29.36	30.99	2.993	0.8457	15.59
25.06	26.54	3.072	0.8637	16.35
20.63	21.93	3.129	0.8829	17.03
9.99	10.71	3.828	0.9313	22.01
0	0	3.602	0.9798	37.10

TABLE 16

Density (gm. ml⁻¹) of the System Aniline-Hexane at Different Temperatures

Temperature (°C)	0	3.01	5.61	8.19	18.19	27.55	38.25	47.68
Mole % Aniline								
62.0	0.6264	0.6336	0.6404	0.6472	0.6753			
63.0	0.6255	0.6328	0.6395	0.6463	0.6745			
64.0	0.6245	0.6320	0.6388	0.6457	0.6737			
65.0	0.6235	0.6309	0.6378	0.6445	0.6728			
65.5	0.6229	0.6303	0.6372	0.6439	0.6723			
65.8	0.6226	0.6300	0.6369	0.6436	0.6721	0.7008	0.7352	0.7667
66.0	0.6224	0.6298	0.6365	0.6433	0.6719	0.7005	0.7350	0.7669
67.0	0.6212	0.6288	0.6354	0.6424	0.6710	0.6994	0.7341	0.7659
68.0	0.6202	0.6277	0.6344	0.6414	0.6703	0.6987	0.7333	0.7650
Mole % Aniline								
Temperature (°C)	52.47	58.49	67.72	78.75	90.90	94.38	100	
62.0				0.8907	0.9433	0.9591	0.9854	
63.0				0.8899	0.9423	0.9584	0.9844	
64.0			0.8439	0.8894	0.9414	0.9577	0.9836	
65.0			0.8430	0.8887	0.9407	0.9568	0.9826	
65.5			0.8427	0.8884	0.9404	0.9564	0.9821	
65.8		0.8065	0.8424	0.8881	0.9403	0.9562	0.9823	
66.0	0.7841	0.8064	0.8423	0.8879	0.9401	0.9560	0.9816	
67.0	0.7839	0.8058	0.8415	0.8872	0.9394	0.9553	0.9808	
68.0	0.7832	0.8050	0.8407	0.8863	0.9388	0.9545	0.9798	
	0.7824							

Density Data

The graphical method of representing density versus composition was not suitable because of the large difference in the density between pure aniline and hexane.

Density was, therefore, expressed as a function of the molar concentration of aniline at constant temperature by the equation,

$$D = a + b m + c m^2$$

where a, b and c are constants; m is the mole % of aniline and a is the density of hexane at a particular temperature, b and c were determined by the method of averages.

These equations at different temperatures are as follows:

TABLE 17

Density Equations at Different Temperatures

Temperature (°C)	Density Equation (gm./ml)
62	$D = 0.6264 + (2.450 \times 10^{-3})m + (1.140 \times 10^{-5})m^2$
63	$D = 0.6255 + (2.480 \times 10^{-3})m + (1.108 \times 10^{-5})m^2$
64	$D = 0.6245 + (2.509 \times 10^{-3})m + (1.081 \times 10^{-5})m^2$
65.5	$D = 0.6229 + (2.510 \times 10^{-3})m + (1.082 \times 10^{-5})m^2$
65.8	$D = 0.6226 + (2.513 \times 10^{-3})m + (1.084 \times 10^{-5})m^2$
66	$D = 0.6224 + (2.520 \times 10^{-3})m + (1.074 \times 10^{-5})m^2$
67	$D = 0.6212 + (2.528 \times 10^{-3})m + (1.070 \times 10^{-5})m^2$
68	$D = 0.6202 + (2.533 \times 10^{-3})m + (1.065 \times 10^{-5})m^2$

The preceding formulae have an accuracy of $\pm 1 \times 10^{-4}$ to $\pm 3 \times 10^{-4}$ for various concentrations.

FIGURE 8. Surface Tension Versus Weight % Hexane for the System Aniline-Hexane at 25°C

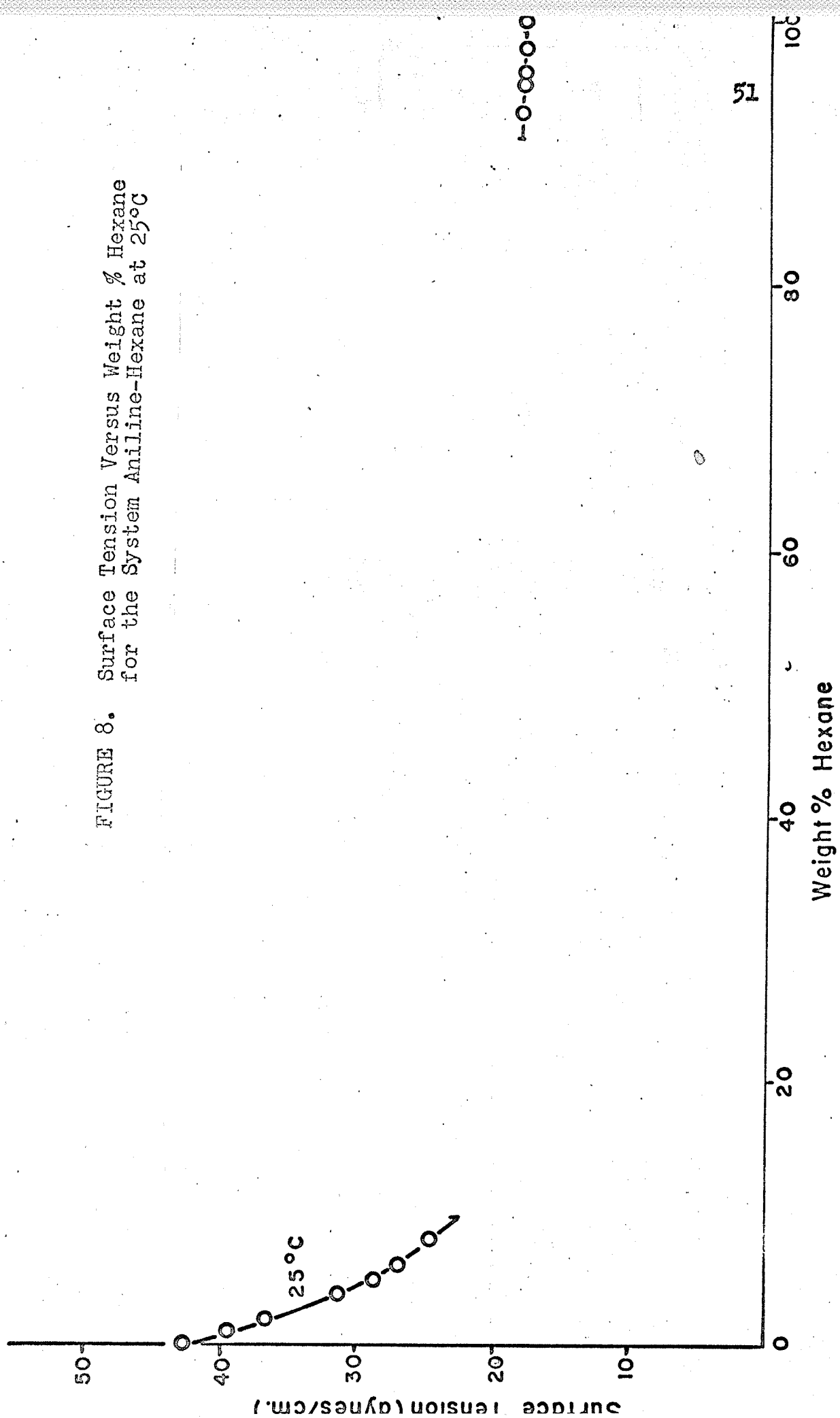
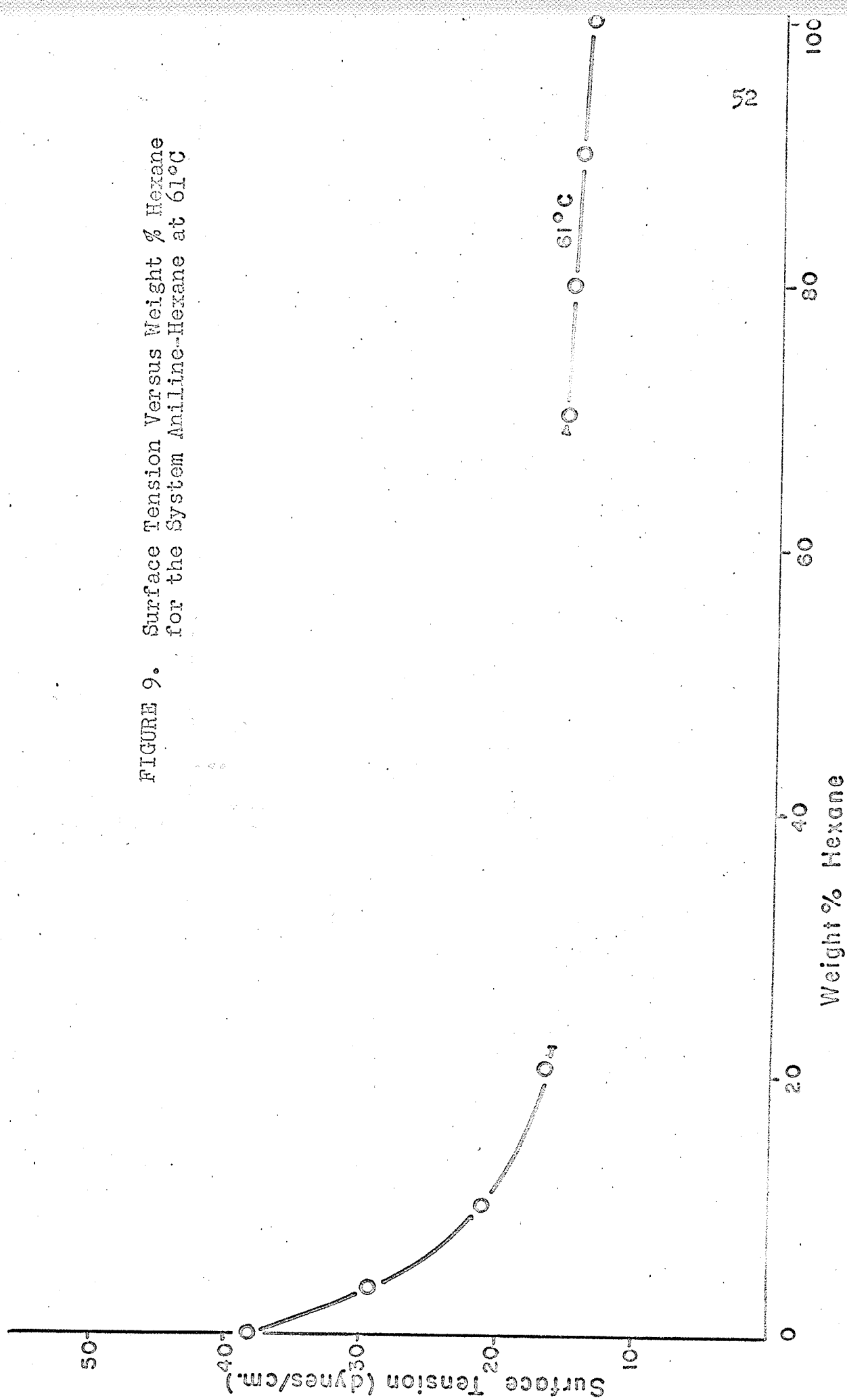


FIGURE 9. Surface Tension Versus Weight % Hexane
for the System Aniline-Hexane at 61°C



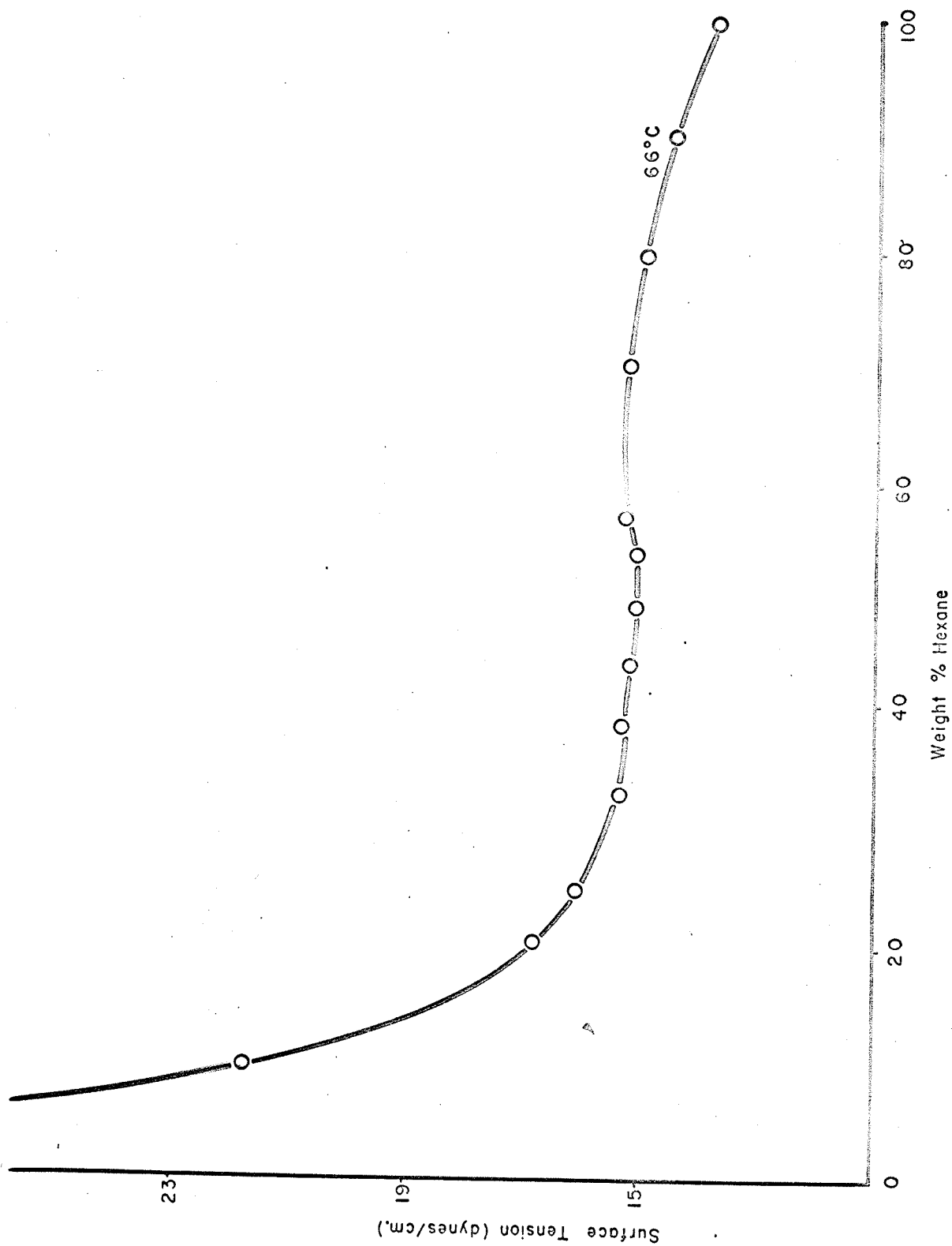


FIGURE 10. Surface Tension Versus Weight % Hexane for the System Aniline-Hexane at 66°C

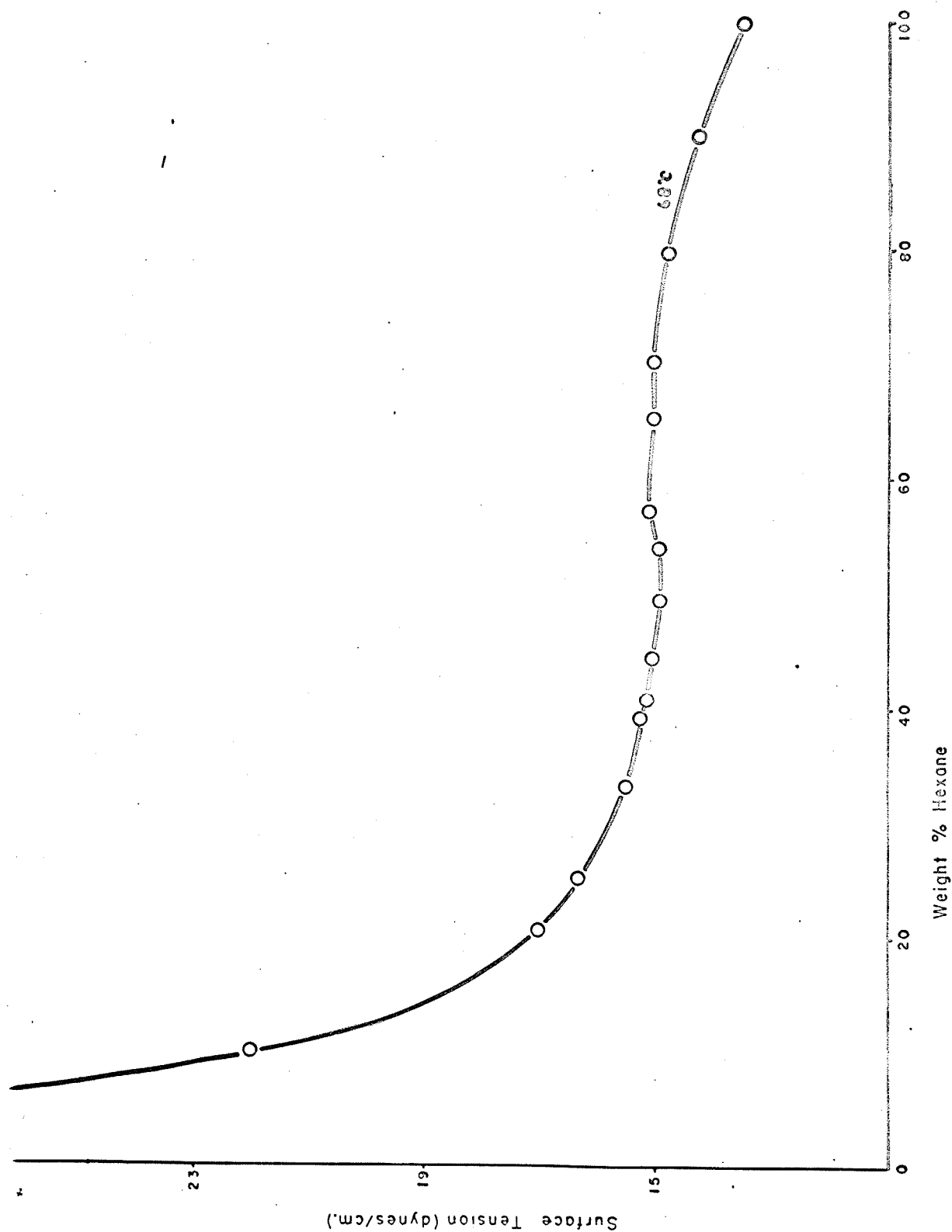


FIGURE 11. Surface Tension Versus Weight % Hexane for the System Aniline-Hexane at 68°C

Surface tension (dynes/cm.)

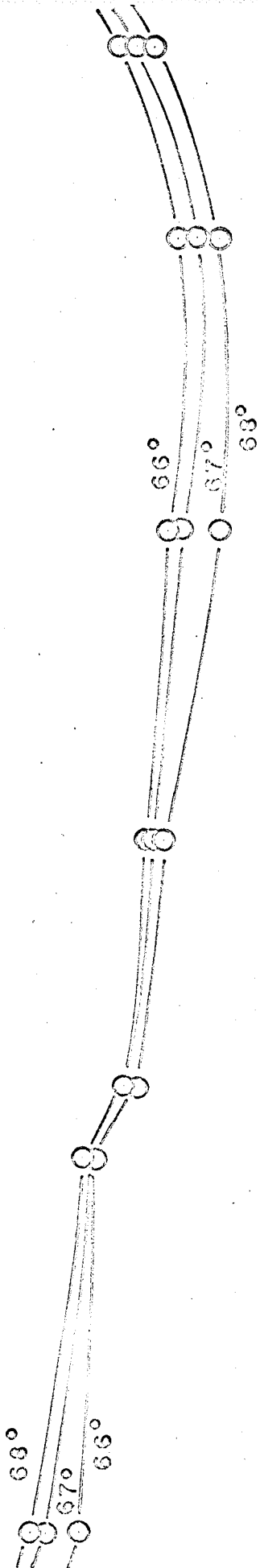
17

16

15

FIGURE 12. Surface Tension Versus
Composition Isotherms
at 66°, 67° and 68°C

68°
67°
66°



35

40

45

50

55

Weight % Hexane

55

CHAPTER V

DISCUSSION

Experimental surface tension data, when plotted against composition, show that there is no range of temperatures for which an isotherm has a region of constant surface tension (or some derived function of surface tension) for an aniline-hexane mixture. Figures (10) and (11), which show isotherms at 66° and 68°C , show clearly that there is no such horizontal above the critical temperature, although the slope is very slight. The deviation or convexity in the curve is found to lie between the compositions 39.2% and 57.4% hexane by weight (determined by inspection of Figure 12) for each of the three isotherms at 66° , 67° and 68°C . The miscibility gap extends over the composition range between 35.3% and 56.9% hexane by weight.

The isotherms throughout the temperature range 55° to 68°C were found to lie very close together, making their representation on one graph impossible. Since the 66° and 68°C isotherms are characteristic of the shape of the others, they are shown in Figures (10) and (11). The 25° and 61°C isotherms are also shown in Figures (8) and (9).

Surface tension determinations could not be carried out at temperatures higher than 68°C because hexane boils, under atmospheric pressure, at 68° - 69°C , nor could they be carried out at the critical solution temperature (65.6°C) because the solution becomes heterogeneous.

A fundamental characteristic of these isotherms is that the addition of hexane to aniline causes a large decrease in surface tension, ie., in the range from 0% to 30% hexane by weight, while the addition of aniline to hexane increases the surface tension very slightly, ie., in the range 60% to 100% hexane by weight. The same effect is found with the viscosity measurements which were made by Mr. S. Anand (51), working in this laboratory. Keyes and Hildebrand (28) also found this to be characteristic of their 25°C isotherm.

This phenomenon can best be explained on the assumption that on the aniline rich side, the aniline molecules have a large attraction for each other, pushing the hexane molecules towards the surface to form a pseudo two-phase region. In other words, the aniline molecules resist dispersion into the hexane molecules and the hexane molecules are pushed to the surface forming an almost pure hexane surface.

On the aniline rich side of the graph, the highest surface tension is that of pure aniline at 25°C, while on the hexane rich side, the lowest surface tension is that of pure hexane at 68°C. There is a difference of 29.37 dynes/cm. between the two extreme values.

In the region between 39.8% and 100% hexane by weight, surface tension increases with decreasing temperature, while in the range from 4.0% to 39.0%, the surface tension decreases slightly with decreasing temperature. The three isotherms

at 66°, 67° and 68°C, therefore, cross at a composition of 29.2% hexane by weight, as shown in Figure (12), (which is an enlargement of the region above the gap) and at a composition of approximately 4.0% hexane by weight. The point of intersection near 4.0% could not be accurately determined because the isotherms were superimposed upon each other over a range of compositions.

No indication in the literature of hydrogen bond formation between aniline and hexane has been reported; hexane is considered to be an inert solvent. A possible explanation for the phenomenon just described is that of Pannetier et al (52) and Lutsker et al (53), who suggested that the aniline itself is strongly associated, by means of hydrogen bonds, to form a complex which is not very stable.

The decrease in surface tension with decreasing temperature, on the high aniline side, can be shown by comparing the surface tension of a certain solution at 25°C and at 55°C. The value for a solution of composition 7.44% hexane at 25°C is 24.58 dynes/cm. as plotted on Figure (13). The value for the same solution at 55°C is 24.83 as obtained from the 55°C isotherm, indicated a distinct decrease in surface tension with a decrease in temperature.

A plot of molecular surface energy against composition, which is shown in Figures (14) and (15) and tabulated in Tables (18) and (19), is similar to that of surface tension

FIGURE 13. Surface Tension Versus Weight
% Aniline for the System
Aniline-Hexane at 25°C

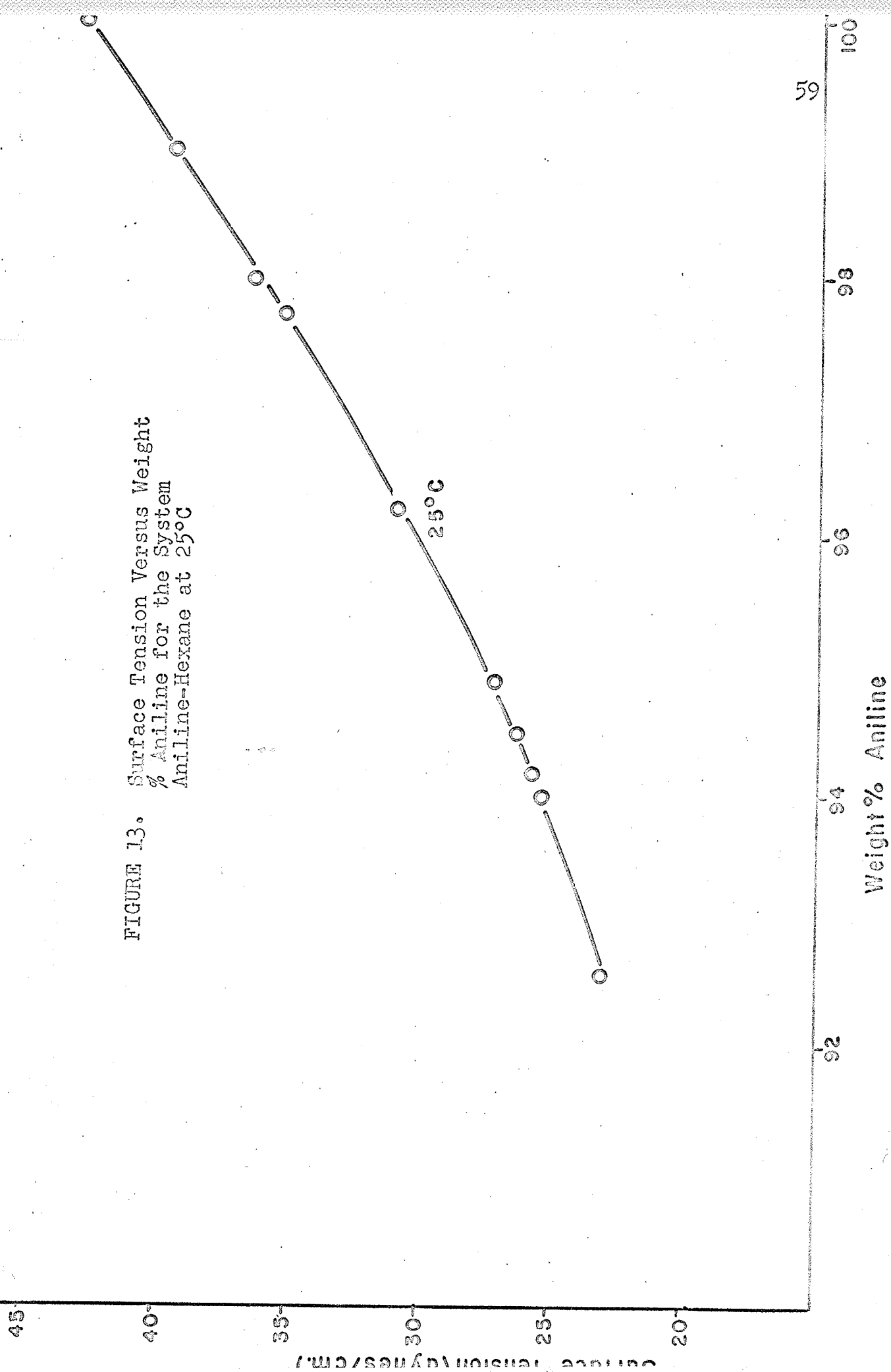


FIGURE 14. Molecular Surface Energy Versus Composition for the System Aniline-Hexane at Various Temperatures

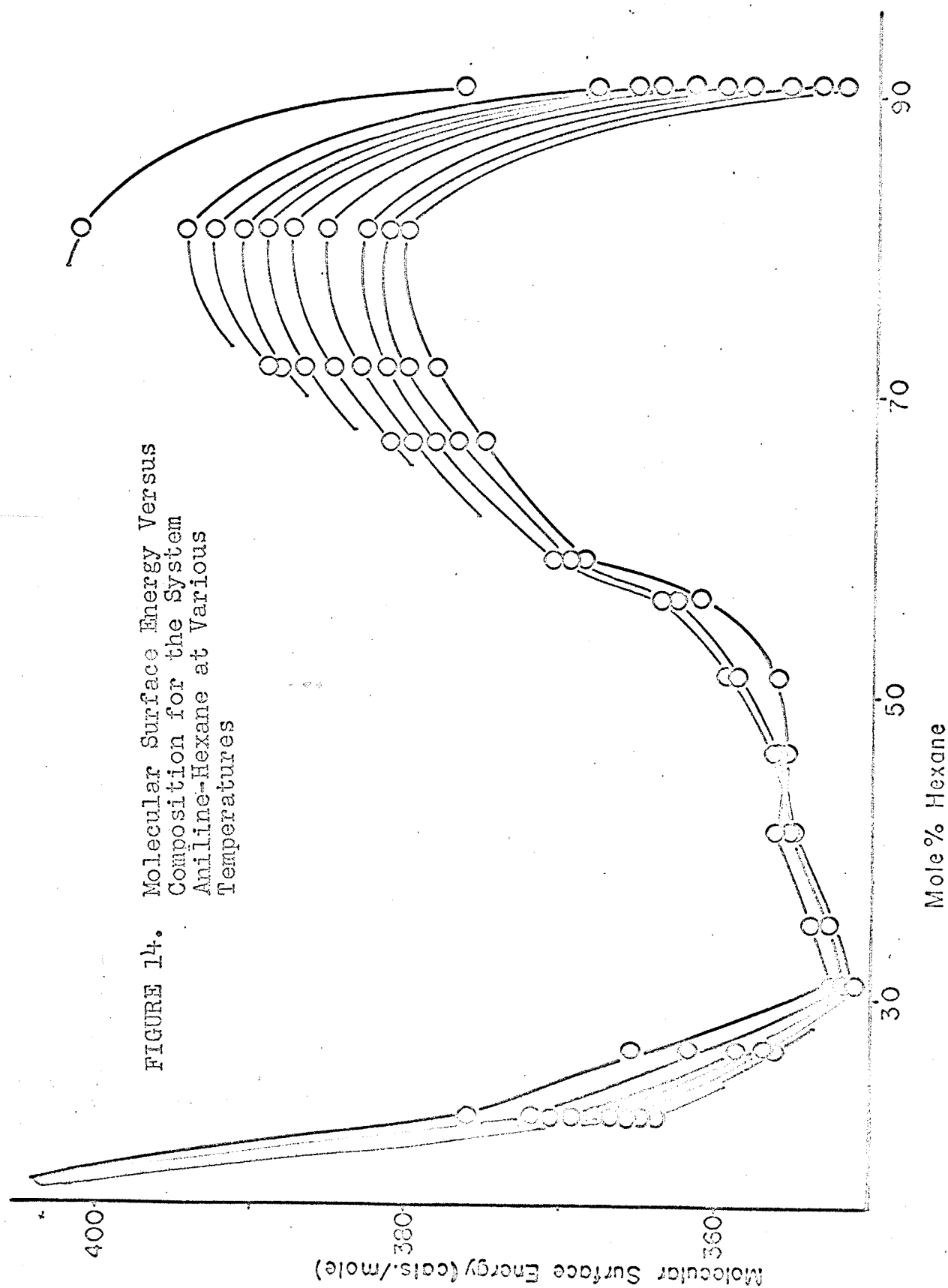


TABLE 18

Molecular Surface Energy (cals. mole⁻¹) at Different Temperatures

Temperature (°C)	90.74	81.13	71.87	59.10	30.99	34.90	41.10	51.31
55	376.93	401.85						
60	368.23	394.91						
61	365.63	393.14	390.49					
62	364.03	391.27	388.79					
63	361.91	389.72	387.22					
64	359.89	388.01	385.29					
65	358.19	385.79	383.51	349.90				
66	355.69	383.18	381.76	370.99	350.16	355.35		359.72
67	353.69	381.72	380.54	369.83	352.81	355.35		358.95
68	352.05	380.52	378.61	368.91	354.01	356.34		356.24

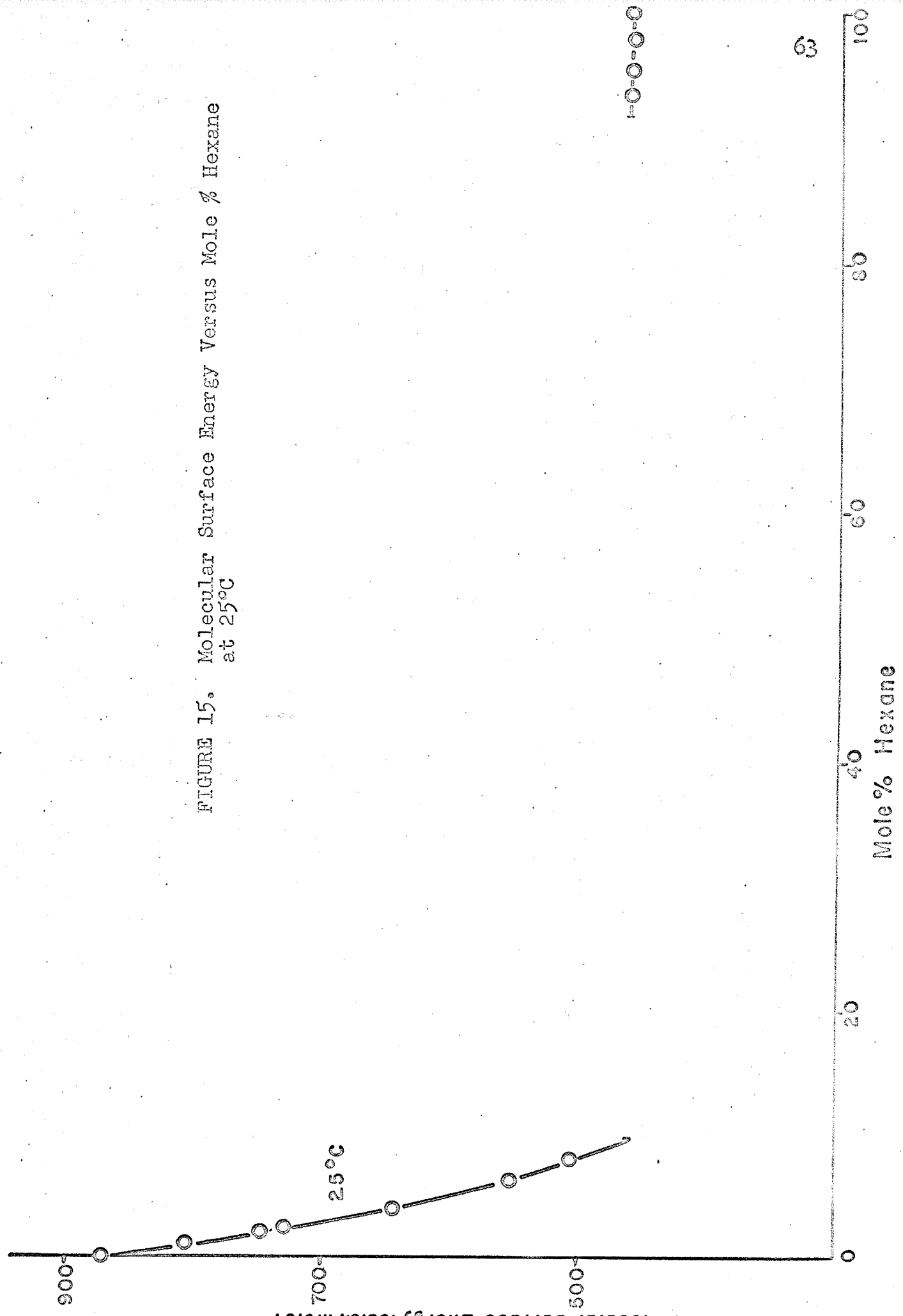
Temperature (°C)	21.93	10.71	26.54	56.46	46.29	42.68
55		434.54				
60		451.75				
61	363.98	455.15				
62	364.91	456.72				
63	365.79	458.69				
64	366.92	461.67	356.29			
65	369.34	464.01	356.98			
66	370.69	465.52	358.76	363.94	356.43	354.49
67	371.80	470.01	361.86	362.75	356.19	354.50
68	376.03	471.66	365.49	361.35	355.79	354.07

TABLE 19

Molecular Surface Energy at 25°C

Mole % Hexane	Molecular Surface Energy (cals. mole ⁻¹)
0	871.10
1.08	805.65
2.13	747.41
4.07	645.45
2.47	733.44
6.42	552.90
6.24	559.49
5.44	590.40
7.99	509.30
95.41	466.79
93.52	465.41
96.30	457.11
98.09	466.10
100.0	465.76

FIGURE 15. Molecular Surface Energy Versus Mole % Hexane
at 25°C



versus composition. On the aniline rich side, the molecular surface energy decreases sharply with the addition of hexane. At a composition of 30.9 mole % hexane, a minimum is reached. In this region, extending to 30.9 mole % hexane, the molecular surface energy decreases with decreasing temperature, while on the high hexane side the molecular surface energy decreases with increasing temperature in the region 44.9 to 100 mole % hexane, exhibiting a maximum for each isotherm in the range 78 to 80 mole % hexane. The change in molecular surface energy on the high hexane side is less pronounced than on the high aniline side.

Pure Aniline has the highest molecular surface energy at 25°C, as shown in Table (19) while pure hexane has the lowest molecular surface energy at a temperature of 68°C. This shows that the intermolecular forces between the aniline molecules are much higher than those of the hexane molecules.

As before, no horizontal isotherms occur just above the critical temperature, indicating that no isotherm has constant molecular surface energy over any range of compositions in this region. Just above the gap of the co-existence curve, the isotherms curve in a convex fashion and then cross at a composition of 44.2 mole % hexane.

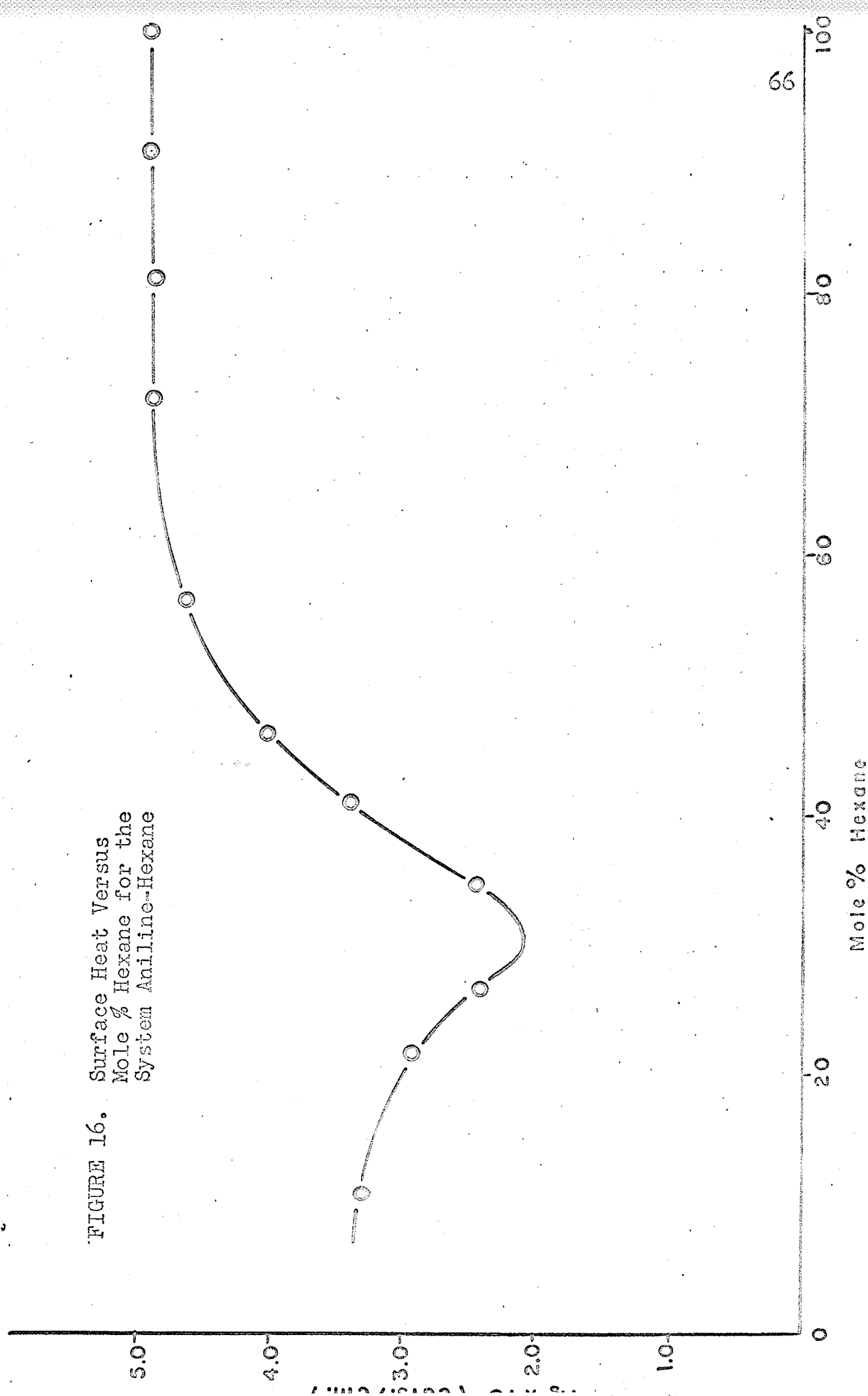
Surface heat, defined by the formula $H_s = \gamma - T \frac{d\gamma}{dT}$, and tabulated in Table (20), has a curve of the form shown in Figure (16). Since it is not affected by temperature,

TABLE 20

Surface Heat of the System Aniline-Hexane
at Different Compositions

Mole % Hexane	Surface Heat $\times 10^{-7}$ (cals. cm^{-2})
100	4.899
90.74	4.894
81.13	4.836
71.87	4.879
57.21	4.517
56.46	4.630
51.31	4.877
46.29	4.019
42.68	3.954
41.10	3.421
34.90	2.486
26.54	2.394
21.93	2.967
10.71	3.311

FIGURE 16. Surface Heat Versus
Mole % Hexane for the
System Aniline-Hexane



only one value was obtained for each composition over the entire temperature range 25° to 68°C.

A minimum is exhibited at 30.5 mole % hexane. Such a minimum was obtained by Mr. S. Skrynyk (54), working in this laboratory, in a plot of ΔH (the heat of evaporation per mole) versus composition, in the high aniline region of the system aniline-hexane. According to Yarym-Agaev (55), a minimum in ΔH shows that compound formation has taken place. Since a survey of the literature has shown no evidence of compound formation or hydrogen bonding between aniline-hexane molecules or hexane-hexane molecules, the only compound that can be formed is a hydrogen bonded aniline complex.

The surface heat reaches a constant value at 71.8 mole % hexane and remains constant at a value of 4.89×10^{-7} cal./cm², to 100 mole % hexane.

The Gibbs Adsorption Isotherm Equation

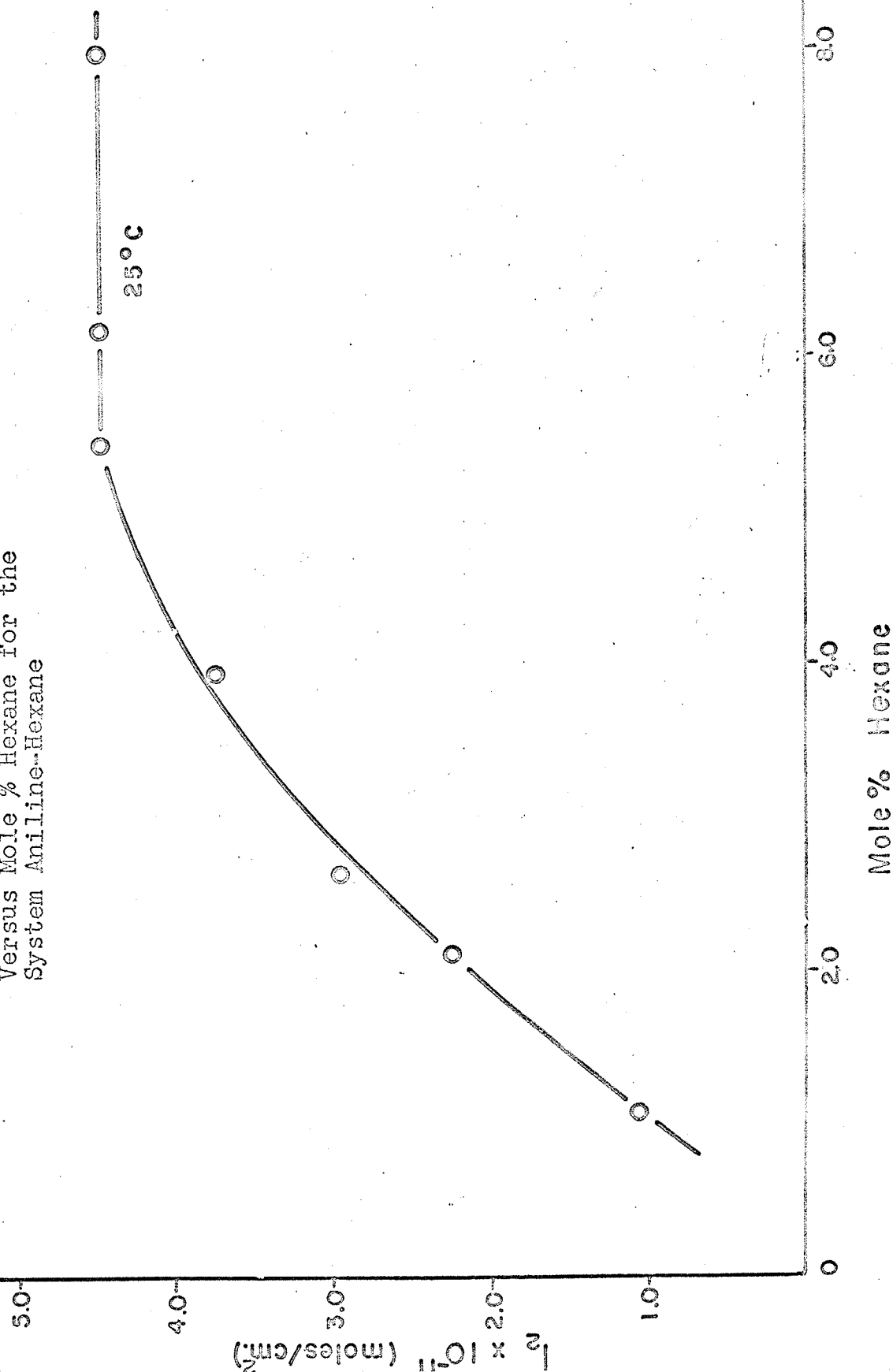
$\Gamma_2 = \frac{1}{RT} \frac{d\gamma}{d \ln X_2}$ was used to calculate the excess concentration of hexane in the surface layer of an aniline-hexane solution at 25°C. The data of Table 21 are represented in Figure (17), in which Γ_2 is plotted against mole % hexane on the high aniline side. The excess concentration of hexane in the surface layer increases with the addition of hexane to an aniline rich solution until a value of 5.43 mole % hexane is reached. At this point, a constant value of

TABLE 21

Excess Concentration of Hexane in the Surface Layer
at Different Compositions (On the High Aniline Side)

Surface Tension (dynes cm ⁻¹)	x_2 ($\times 10^{-2}$)	$\log x_2$	$\Gamma_2 \times 10^{-11}$ (moles cm ⁻²)
39.57	1.08	-1.967	1.08
36.62	2.12	-1.674	2.25
35.90	2.47	-1.607	2.99
31.47	4.07	-1.390	3.71
28.66	5.43	-1.265	4.46
27.12	6.25	-1.204	4.46
24.58	7.99	-1.098	4.46

FIGURE 17. Excess Concentration of Hexane in the Surface Layer Versus Mole % Hexane for the System Aniline-Hexane



4.459×10^{-11} moles/cm² is maintained up to the heterogeneous region of the coexistence curve. This constant value of Γ_2 indicates that the surface layer has been saturated with hexane between the values of 4.3 and 8.16 mole % hexane.

On the high hexane side, the excess concentration of hexane in the surface layer remains constant at 18.363×10^{-11} moles/cm², throughout the composition range, as shown in Table (22).

Guggenheim's relation $(T_c - T)^{1/3}$ was found to apply neither to surface tension nor molecular surface energy since straight line plots were not obtained for $(T_c - T)^{1/3}$ versus γ or for $(T_c - T)^{1/3}$ versus $\gamma \left(\frac{M}{d} \right)^{2/3}$ as shown in Figures (18) and (19), which are tabulated in Tables 23 and 24. It was, therefore, not possible to determine whether the coexistence curve obeyed a cubic relationship or not. As mentioned in the introduction, if Guggenheim's relation had applied, then it would have been possible to determine whether the coexistence curve had a flat or rounded top. According to Campbell and Kartzmark (1a), the coexistence curve for the system aniline-hexane is horizontal at the top or very nearly so.

The viscosity data of Mr. S. Anand (51) were used in a plot of $\log \gamma$ versus $1/n$ (where n = viscosity). Straight lines were obtained for the pure components aniline and hexane, as in Figure (20), on the scale used by Pelofsky (24), but for an enlarged scale no straight line could be

TABLE 22

Excess Concentration of Hexane in the Surface Layer
at Different Compositions (On the High Hexane Side)

Surface Tension (dynes cm ⁻¹)	X_2 ($\times 10^{-1}$)	$\log X_2$ ($\times 10^{-2}$)	$\Gamma_2 \times 10^{-11}$ (moles cm ⁻²)
18.20	9.81	-0.840	18.36
18.19	9.63	-1.640	18.36
18.32	9.54	-2.050	18.36
18.41	9.35	-2.910	18.36

FIGURE 18. $(T_c - T)^{1/3}$ Versus Surface Tension

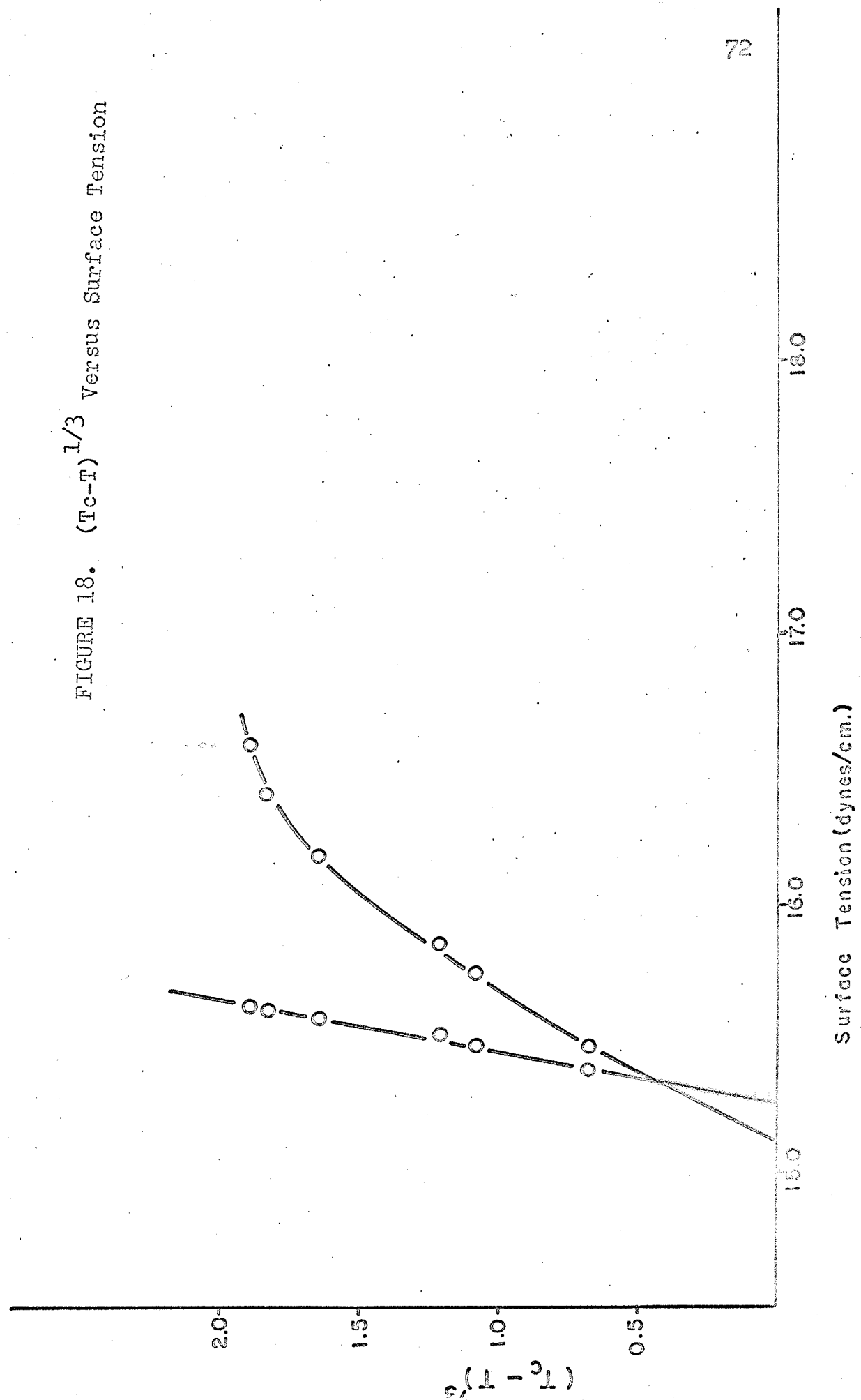


FIGURE 19. $(T_c - T)^{1/3}$ Versus Molecular Surface Energy

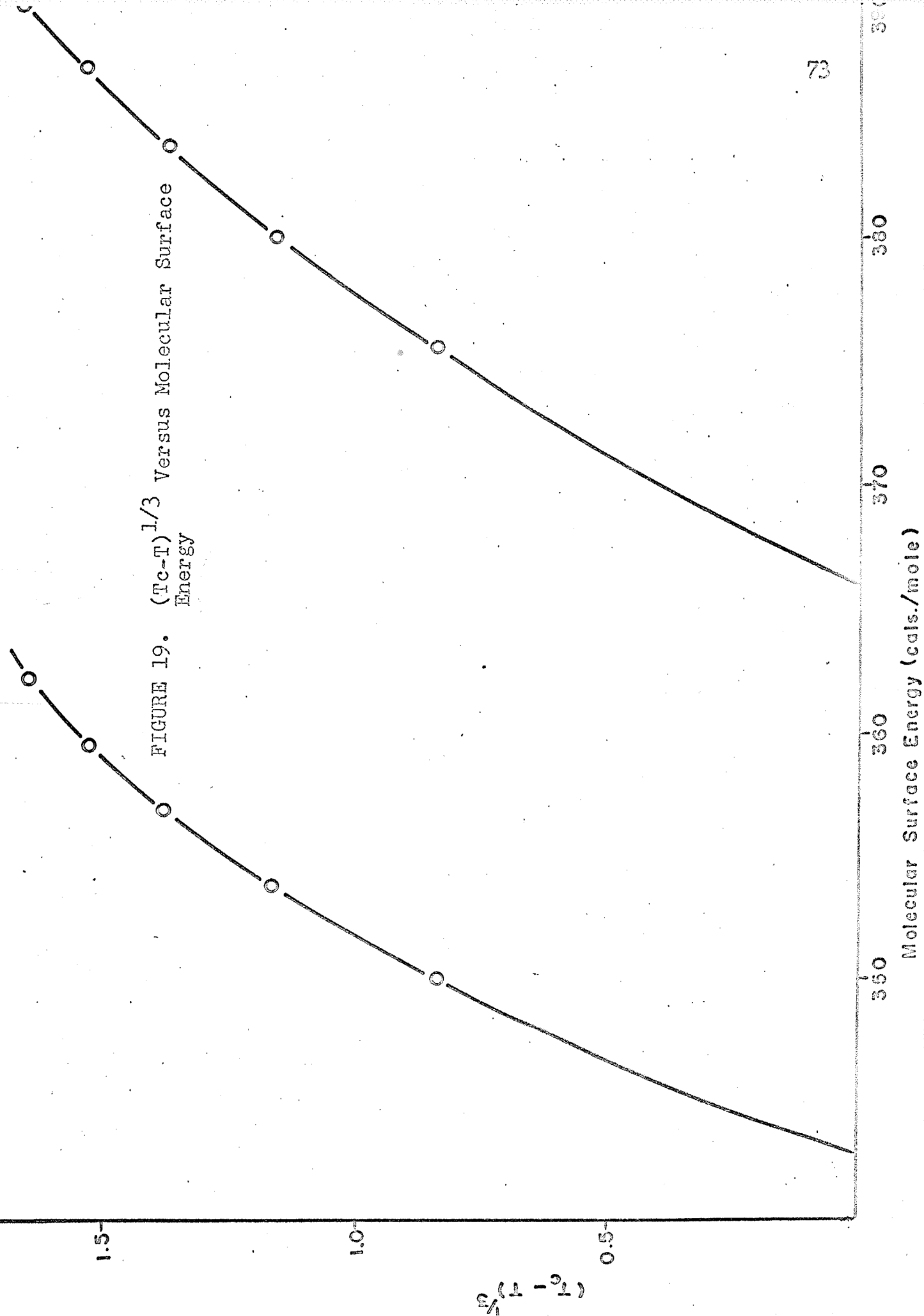


TABLE 23

Surface Tension and $(T_c - T)^{1/3}$
in the Heterogeneous Region

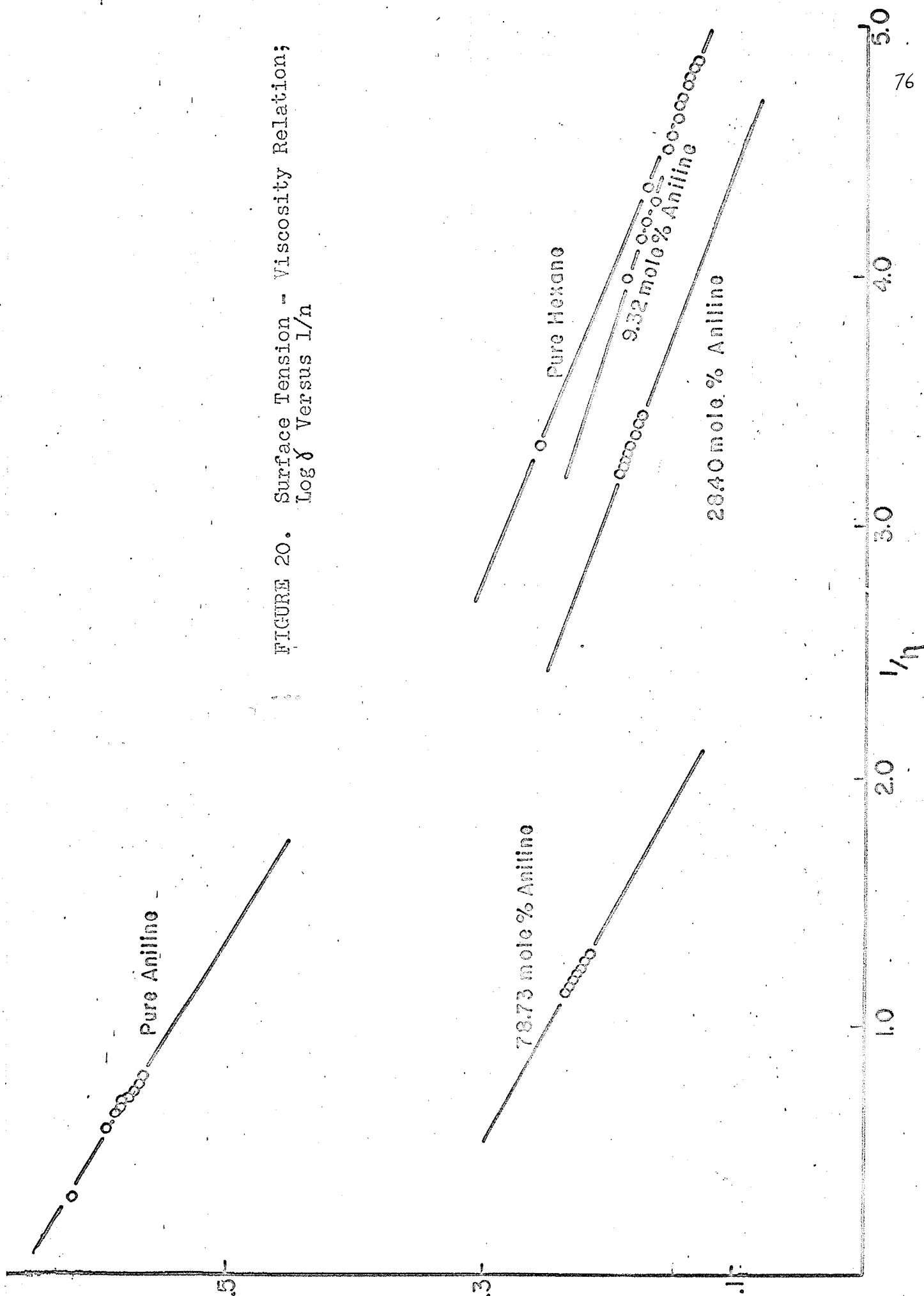
Temperature (°C)	Surface Tension (dynes cm ⁻¹)	(T _c -T)	(T _c -T) ^{1/3}
65	15.39	0.60	0.8434
64	15.49	1.60	1.1696
63	15.54	2.60	1.3751
62	15.57	3.60	1.5326
61	15.61	4.60	1.6631
60	15.65	5.60	1.7758
55	15.90	10.60	2.1967
25	18.41	40.60	3.4369
High Hexane Side			
65	15.46	0.60	0.8434
64	15.74	1.60	1.1696
63	15.98	2.60	1.3751
62	16.17	3.60	1.5326
61	16.40	4.60	1.6631
60	16.58	5.60	1.7758
25	24.52	40.60	3.4369

TABLE 24

Molecular Surface Energy and $(T_c - T)^{1/3}$
in the Heterogeneous Region

Temperature (°C)	Molecular Surface Energy (cals. mole ⁻¹)	(T _c -T)	(T _c -T) ^{1/3}
65	375.6	0.60	0.8434
64	380.0	1.60	1.1696
63	383.8	2.60	1.3751
62	386.9	3.60	1.5326
61	389.3	4.60	1.6631
60	391.8	5.60	1.7758
High Hexane Side			
65	350.0	0.60	0.8434
64	353.8	1.60	1.1696
63	356.9	2.60	1.3751
62	359.5	3.60	1.5326
61	362.1	4.60	1.6631

FIGURE 20. Surface Tension - Viscosity Relation;
Log γ Versus $1/\eta$



drawn. This relationship was also plotted for various compositions as shown in Figure (20) and tabulated in Tables (25 - 28).

TABLE 25

Surface Tension-Viscosity Relation
for the Pure Components Aniline and Hexane

Temperature (°C)	η_{Hexane} (centipoise)	γ_{Hexane} (dynes/cm)	η_{Aniline} (centipoise)	γ_{Aniline} (dynes/cm)
25	0.302	17.94	3.778	41.79
55	0.230	14.80	1.722	39.13
60	0.222	14.35	1.557	38.51
61	0.219	14.22	1.552	38.42
62	0.216	14.12	1.503	38.29
63	0.214	14.04	1.475	38.08
64	0.213	13.97	1.449	37.91
65	0.211	13.86	1.423	37.52
66	0.209	13.73	1.403	37.31
67	0.208	13.62	1.384	37.19
68	0.207	13.52	1.365	37.10

TABLE 26

Surface Tension-Viscosity Relation for the
System Aniline-Hexane at 9.32 Mole % Aniline

Temperature (°C)	Viscosity (centipoise)	Surface Tension (dynes/cm)
55	0.251	15.47
60	0.241	15.07
61	0.237	14.95
62	0.233	14.86
63	0.230	14.76
64	0.227	14.67
65	0.225	14.58
66	0.223	14.46
67	0.220	14.37
68	0.218	14.29

TABLE 27

Surface Tension-Viscosity Relation for the
System Aniline-Hexane at 28.40 Mole % Aniline

Temperature (°C)	Viscosity (centipoise)	Surface Tension (dynes/cm)
61	0.313	15.62
62	0.310	15.53
63	0.307	15.48
64	0.305	15.40
65	0.301	15.32
66	0.298	15.22
67	0.294	15.16
68	0.291	15.06

TABLE 28

Surface Tension-Viscosity Relation for the
System Aniline-Hexane at 78.73 Mole % Aniline

Temperature (°C)	Viscosity (centipoise)	Surface Tension (dynes/cm)
60	0.876	17.20
61	0.862	17.10
62	0.844	17.06
63	0.834	16.94
64	0.824	16.80
65	0.812	16.74
66	0.798	16.68
67	0.791	16.64
68	0.784	16.60

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