

THE UNIVERSITY OF MANITOBA

KINETIC STUDIES ON THE FORMATION
OF BERYLLIUM-5-SULPHOSALICYLIC ACID AND
BERYLLIUM-5-CHLOROSALICYLIC ACID COMPLEXES

by

Mark Kon Shing Mak

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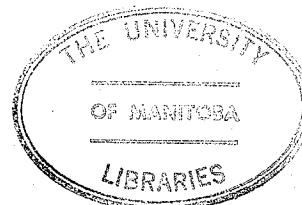
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of the degree of

MASTER OF SCIENCE

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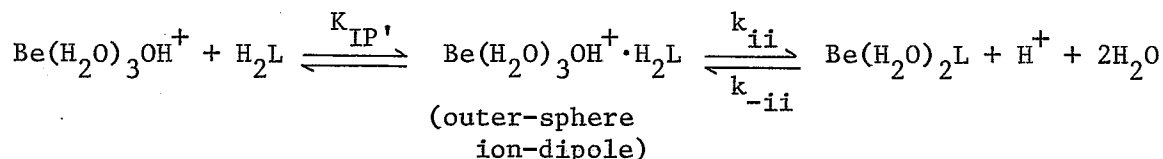
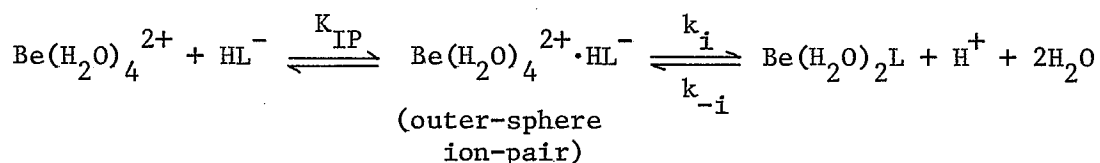


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ABSTRACT

The kinetics of the reactions of $\text{Be}(\text{H}_2\text{O})_4^{2+}$ with 5-sulphosalicylic acid and 5-chlorosalicylic acid were studied by a spectrophotometric stopped-flow technique over the acidity range from 1.58×10^{-4} M to 5.01×10^{-4} M. Two competitive reaction pathways were identified:



At 25.1°C and an ionic strength of 3.0 M, k_i and k_{ii} for the chelation of Be(II) with the ligand 5-sulphosalicylic acid were determined to be 63 sec^{-1} and $6.6 \times 10^6 \text{ sec}^{-1}$ respectively. In the case of the ligand 5-chlorosalicylic acid, k_i and k_{ii} were found to be 66 sec^{-1} and $2.7 \times 10^6 \text{ sec}^{-1}$ respectively. From a Fuoss-Eigen type outer-sphere ion-pair treatment of the experimental data, the rate-determining step in the complex formation appears to be the loss of the first water molecule from the inner coordination sphere of Be(II). The dissociative ($\text{S}_{\text{N}}1 - \text{I}_{\text{d}}$) reaction mechanism is in agreement with the conclusions of other substitution studies of the hydrated beryllium

cation and solvent exchange studies. Activation enthalpies for the formation of Be(II)-5-sulphosalicylate and Be(II)-5-chlorosalicylate are 12.23 Kcal/mole and 11.93 Kcal/mole respectively. These values are slightly higher than the activation energies reported for the formation of the monofluoroberyllium complex. The difference is discussed in terms of the solvent effect proposed by Bennetto and Caldin. The associated activation entropies for the formation of both complexes are also reported.

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(A) INTRODUCTION

(1) FAST REACTIONS.

In recent years, the investigation of many fast reactions has been made possible with the advent of new techniques. Reactions that were previously regarded as "instantaneous" or "upon-mixing" can now be studied by methods like stopped-flow, quenching techniques, low-temperature experiments, polarography, ion-molecule reactions, shock-tubes, flash photolysis, ESR & NMR spectroscopy, and, most often, perturbation-relaxation methods.¹⁻⁴ Consequently, these techniques have provided us with a new time range for chemical rate studies.⁵ Present microwave spectroscopy techniques which have been used extensively to study solvent or ligand molecule exchange in complexes^{6,7} require only a suitable equilibrium in solution before exchange rate constants can be determined. Reported first order rate constants range from $10^4 - 10^8 \text{ sec}^{-1}$.

Complex formations are generally investigated by either of the following two methods. Faster substitutions with rate constants anywhere from $10^2 - 10^9 \text{ sec}^{-1}$ are commonly followed by equilibrium perturbation methods.^{5,8,9} These methods are essentially relaxation techniques. An external parameter of an equilibrium system (e.g. temperature, pressure, electrical field density or sound absorption) is perturbed rapidly, and its subsequent relaxation to a new equilibrium is followed spectrophotometrically, or via conductimetric, polarographic or fluorimetric measurements.^{5,10,11} This particular technique has two important advantages, (i) it can be applied to study reactions that

approach diffusion-controlled rates, (ii) actual chemical transformation is not necessary.

The other common technique used to study complex formation is the "stopped-flow" method, one of the many "flow" methods.^{1,2,3} The mechanism of "stopped-flow" spectrophotometry will be discussed in the experimental section. An outstanding advantage of this method is that a whole reaction cycle may be followed very rapidly. In addition, reactant consumption proves to be very economical. However, there are two severe limitations in the application of the method, namely, (i) the reaction being observed must possess a half-life, $t_{1/2}$, which is much longer than the mixing time, and (ii) actual chemical transformation is absolutely necessary. Eigen⁵ has suggested, in view of the time factor in mixing, that the effective time range of flow methods is restricted to reactions with half-lives between $10^0 - 10^3 \text{ sec}^{-1}$. Nevertheless, the developement of "stopped-flow" has enabled chemists to elucidate the reaction kinetics and mechanisms of many complex formations.

(2) KINETICS AND MECHANISMS.^{12,13,14}

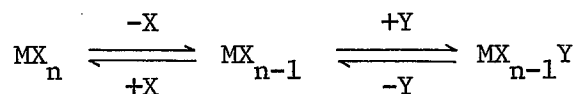
Generally, all reactions involving coordination compounds, except those of redox processes, can be classified as substitutions. There are two types of substitutions, abbreviated " S_N " & " S_E ". " S_N " represents "substitution nucleophilic", a term which implies the replacement of a ligand in a substrate by another ligand that is an electron donor seeking for a positive center for reaction, e.g.



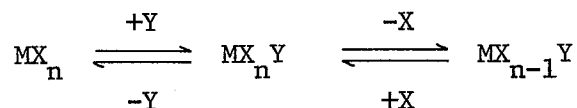
"S_E" denotes "substitution electrophilic". It is the opposite of "S_N" reactions in the sense that it involves an electron-deficient reagent attacking an electron-rich center. Reactions of this sort often involve the replacement of one metal by another, e.g.



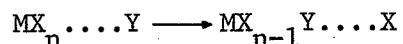
There are various sub-classifications of "S_N" reactions, and it is these reactions that constitute most of the complex formations. Three possible mechanisms are envisaged for nucleophilic substitution according to the following "stoichiometrically" distinct pathways.¹⁴



(D = dissociative mode of activation, definite intermediate of reduced coordination number.) (2)(a)



(A = associative mode of activation, definite intermediate of increased coordination number.) (2)(b)

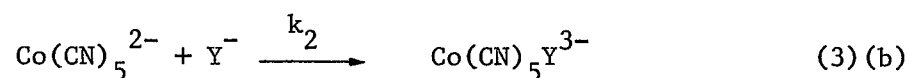
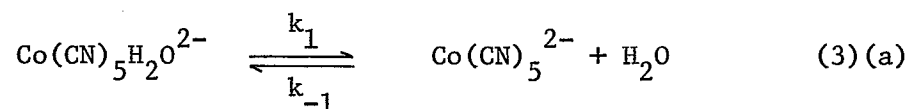


(I = an interchange, concerted process with no kinetically detectable intermediate.) (2)(c)

The crucial factor in distinguishing nucleophilic substitution

mechanisms then, is obviously the nature of the intermediate.

According to the Hughes-Ingold¹⁴ scheme, reaction type (2)(a) corresponds to the limiting S_N1 process. Reactions of this kind often display a characteristic unimolecular rate-determining step. Significant bond stretching prior to the formation of an intermediate with a reduced coordination number is also important. An example of a recently studied reaction that conforms to a limiting S_N1 mechanism is,^{15,16}



Assuming the steady-state approximation for the intermediate, i.e.

$d[\text{Co(CN)}_5^{2-}]/dt = 0$, the following rate expression is obtained.

$$\frac{-d[\text{Co(CN)}_5\text{H}_2\text{O}^{2-}]}{dt} = \frac{k_1 k_2 [\text{Co(CN)}_5\text{H}_2\text{O}^{2-}] [\text{Y}^-]}{k_{-1} + k_2 [\text{Y}^-]} \quad (3)(c)$$

Various forms of the above rate expression can exist, depending upon the relative magnitudes of the rate constants k_{-1} and k_2 .

The first instance would be:

$$(i) \quad k_{-1} \approx k_2.$$

The kinetics observed under this condition is dependent on the concentration of $[\text{Y}^-]$. If $[\text{Y}^-]$ is kept in large excess so that its concentration is considered to be relatively constant throughout the reaction and such that $k_2[\text{Y}] > k_{-1}$, the rate is pseudo-first order in

the complex, i.e.

$$\frac{-d[\text{Co}(\text{CN})_5\text{H}_2\text{O}^{2-}]}{dt} = k_1[\text{Co}(\text{CN})_5\text{H}_2\text{O}^{2-}] \quad (3)(d)$$

However, if $[\text{Y}^-]$ is low enough so that $k_{-1} > k_2[\text{Y}^-]$, a second order kinetic expression would result.

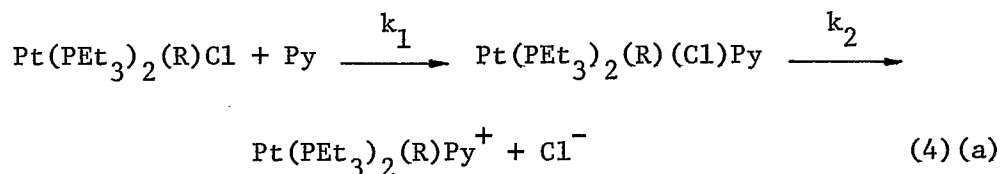
$$\frac{-d[\text{Co}(\text{CN})_5\text{H}_2\text{O}^{2-}]}{dt} = \frac{k_1 k_2}{k_{-1}} [\text{Co}(\text{CN})_5\text{H}_2\text{O}^{2-}] [\text{Y}^-] \quad (3)(e)$$

Consequently, if $k_{-1} \approx k_2$, the rate obtained should have a second-order dependence on $[\text{Y}^-]$ at relatively low $[\text{Y}^-]$ and be independent of the concentration and nature of Y^- at higher $[\text{Y}^-]$. Expression (3)(e) has illustrated that second-order kinetics do not necessarily represent an $\text{S}_{\text{N}}2$ direct substitution. It is also interesting to note that the ratio k_2/k_{-1} measures the nucleophilicity of the incoming ligand Y^- .

Another situation would arise if reaction (3)(b) is fast, i.e. (ii) $k_2 \gg k_{-1}$. Under this limiting condition, the rate constant for the formation of the complex would be dependent solely upon the value for water exchange and independent of the nature of the entering ligand.

Reactions of type (2)(b) are commonly known as limiting " $\text{S}_{\text{N}}2$ " processes. It has been concluded from some platinum complex studies that such an associative (A) mechanism is both sterically and

electronically favoured in square-planar (d^8) substitutions.¹⁴ The following example would depict the second-order rate law for a " S_N2 " substitution.



By assuming $d[\text{Pt}(\text{PEt}_3)_2(\text{R})(\text{Cl})\text{Py}]/dt = 0$, i.e. a steady state calculation, the following rate expression is obtained:

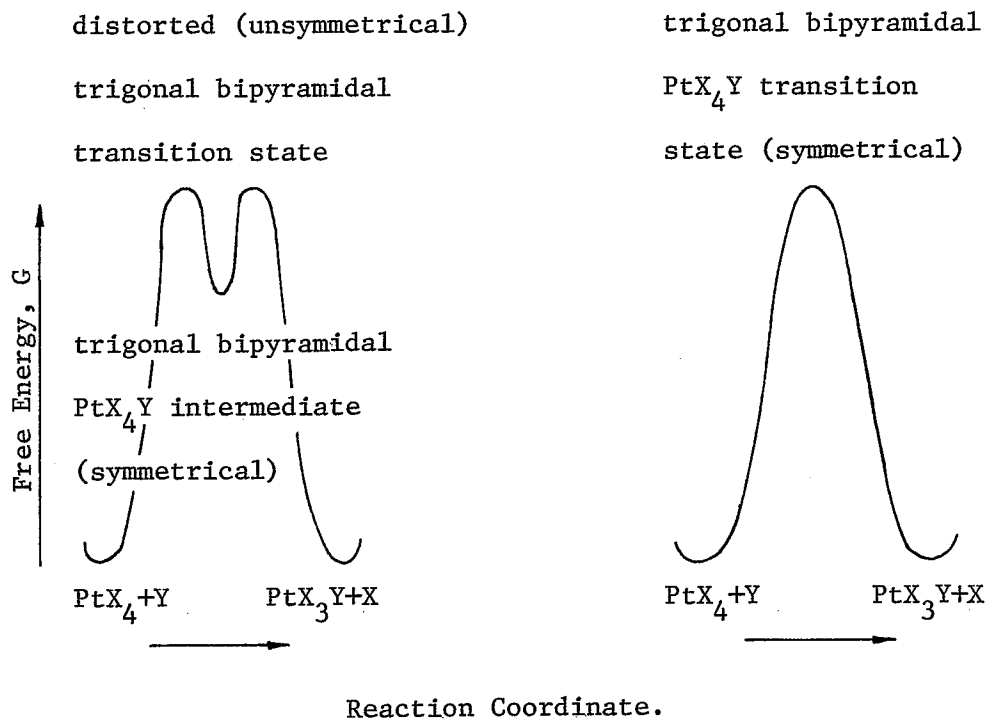
$$\frac{-d[\text{Pt}(\text{PEt}_3)_2(\text{R})\text{Cl}]}{dt} = (k_1 + k_2[\text{Py}]) [\text{Pt}(\text{PEt}_3)_2(\text{R})\text{Cl}] \quad (4) (b)$$

$$k_{\text{obs}} = k_1 + k_2[\text{Py}] \quad (4) (c)$$

The term $k_2[\text{Py}][\text{Pt}(\text{PEt}_3)_2(\text{R})\text{Cl}]$ in expression (4)(b) is evidently second-order dependent, but the remaining $k_1[\text{Pt}(\text{PEt}_3)_2(\text{R})\text{Cl}]$ term appears to be first-order. It was suggested that a dual mechanism was possible with the $k_1[\text{Pt}(\text{PEt}_3)_2(\text{R})\text{Cl}]$ term representing a dissociative S_N1 mode of activation. However, later evidences¹⁷ seemed to support the thesis of a strictly associative mechanism with the solvent involved as reagent in the k_1 rate term, i.e. $k_1 = k_3[\text{S}]$. Consequently, the idea of a partial S_N1 mechanism was discarded. It is expected that all S_N2 reaction rates are dependent upon the nucleophilicity of the entering ligand. The gradient k_2 from a plot of k_{obs} vs. the concentration of entering ligand, $[\text{Y}]$, is a measure of the reactivity of Y. Contrary to

the S_N1 mechanism, considerable bond making, instead of bond breaking, prior to the actual formation of the intermediate is significant.

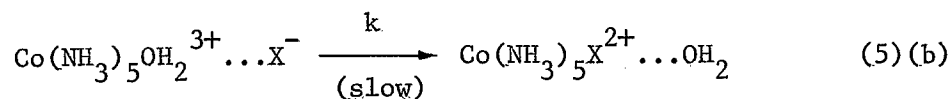
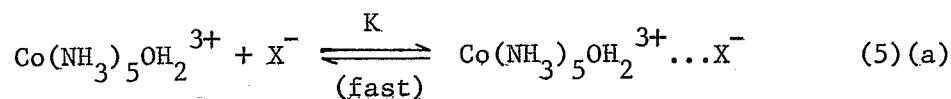
The final mechanism depicted in expression (2)(c) is interchange (I). There are two major categories, I_a & I_d ; both of them exhibit no kinetically detectable intermediates. The I_a type denotes a mechanism similar to the S_N2 (Not limiting) process. According to Basolo & Pearson,¹⁸ this would be a process in which the rate step involves about equal bond breaking and bond making. The following free-energy diagrams demonstrate the intimate differences between the S_N2 -(A) limiting and S_N2 -(I_a) not limiting mechanisms.



The only apparent way to distinguish the two intimate mechanisms is from the symmetry of the transition state. Experimental evidence like

trans and cis effects, entering and leaving group effects, etc. can sometimes aid the elucidation. Kinetically, the rate laws are identical for the two mechanisms.

The I_d mechanism has been a subject of controversy because of its ambiguity when classified under the Hughes-Ingold scheme. Reactions in this category would share all the mechanistic features of an S_N1 limiting process if not for the following discrepancies, (i) the characteristic unimolecular intermediate of reduced coordination number is absent, (ii) kinetically, they display a second-order bimolecular rate constant. To resolve this apparently conflicting evidence, most authors have adopted the collision theory in reaction mechanisms. Concepts such as "ion-pair" and "solvent cage" are widely accepted occurrences in this theory. When a complex collides with a ligand, the two form a highly activated, short-lived "ion-pair" trapped in a "solvent cage". Energy transfer is very rapid in the condensed phase, and consequently the complex would receive enough energy to dissociate readily. The ligand which enters the complex via such a mechanism does not contribute significantly to the activation. Essentially it is an "accidental" bimolecular process. The characteristic leaving group effect of an S_N1 limiting mechanism is, as expected, an important aspect of the activation. The following example (Reference 14, P.87) demonstrates the kinetics of the mechanism.



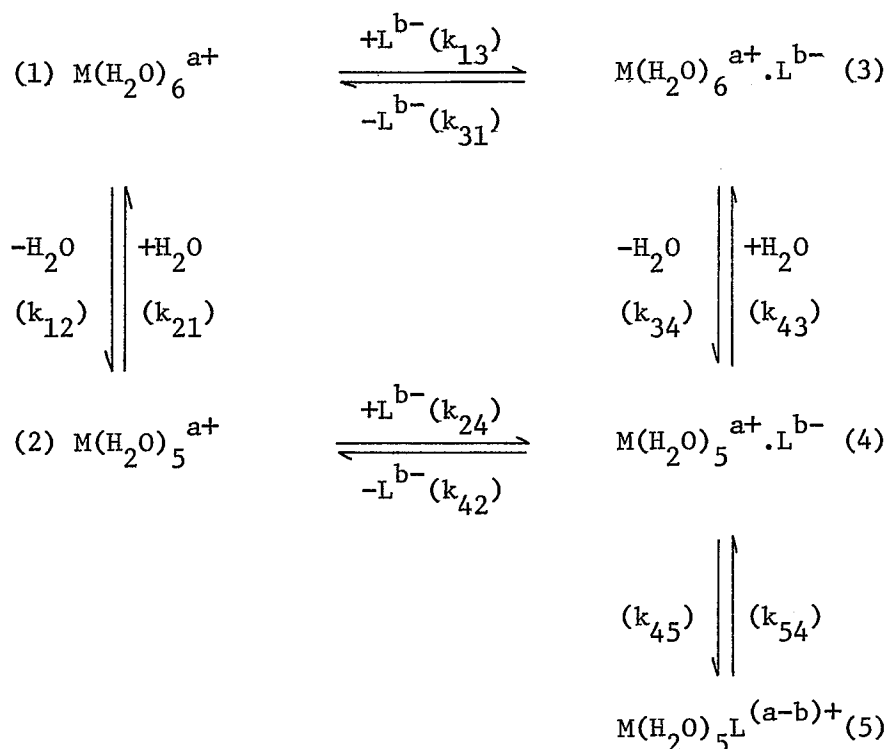
The bimolecular rate expression in terms of K, the formation constant of the first outer-sphere complex, and k, the rate constant of the conversion of the outer-sphere complex into an inner-sphere complex is:

$$\frac{-d[\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}]}{dt} = kK[\text{Co}(\text{NH}_3)_5\text{OH}_2^{3+}][\text{X}^-] \quad (5) \text{ (c)}$$

Generally, the formation of the outer-sphere complex is very fast and the formation of the inner-sphere complex is comparatively slow. Therefore, the latter is the rate-determining step for the overall reaction.

(3) METAL COMPLEX FORMATION.

Most of the substitutions involving octahedral metal aquo complexes studied so far have indicated the prevalence of S_N1 mechanisms. Eigen & Wilkins⁹ have put forth a general pathway including the S_N1 -(D) limiting mechanism as well as the S_N1 -(I_d) mechanism.



Substitutions can proceed via, (i) route (1), (2), (4) & (5), (ii) route (1), (3), (4) & (5), or possibly, (iii) a combination of both routes. It is not unreasonable to assume that k_{45} is very large, i.e. step (4) to (5) is fast, and hence, would not in any case be rate determining. Under this condition, the rate of route (1), (2), (4) & (5) would be identical with expression (3)(c) if $k_{24} \gg k_{42}$, and the alternative route (1), (3), (4) & (5) would have a rate identical with expression (5)(c) if $k_{34} \gg k_{43}$. It is very difficult to distinguish the fine mechanism of the reaction without extensive data. Various conventional tests of the rate dependence on steric effects, charge-type effects, isotope effects, effects of the change

of the leaving group, and the electronic effect of nonlabile substituent ligands introduced into the complexes, appear to have various degrees of success depending on the specificities of the reactants. An exception arises when both reactants involved are of similar charge signs. It is commonly acknowledged that the formation of outer-sphere complexes under such a condition is minimised, and therefore, reaction pathway (1), (3), (4) & (5) is very unlikely.

Entering group effects are sometimes subtly different between the two mechanistic pathways. For an $S_N1-(D)$ mechanism, the influence exerted by the entering anion on the rate-determining step is proportional to the relative affinity of the anion with water molecules to react with the five-coordinate intermediate. In the case of an $S_N1-(I_d)$ mechanism, the rate-determining influence of the entering anion depends upon the solvating power of the anion, i.e. the number of water molecules which the ligand can replace in the outer-sphere. As a consequence, an apparently entering-group dependent path emerges because the probability of reaction increases accordingly with the solvating power. Langford & Gray¹⁴ have had considerable success in resolving these rates by adjusting them with statistical factors. A logical choice for these statistical factors would be the ratio between the total number of water molecules replaced in the outer-sphere by the entering anion and the total number of possible water molecules occupying the outer-sphere. If these statistical corrections are applied, it is seen that the actual rate is insensitive to the nature

of the entering group. Additional evidence has led to some speculations about the factors leading to an $S_N1-(D)$ mechanism as opposed to the $S_N1-(I_d)$ substitutions. Some of the criteria are, (i) stabilization of the five-coordinate intermediate by either a good π -donor or a good π -acceptor group, (ii) less reactive solvent, and (iii) complex with an overall negative charge because it may be solvated in such a way that the solvent molecules are not properly oriented for entry.

Substitutions involving metal aquo complexes studied so far can be classified into three main categories:

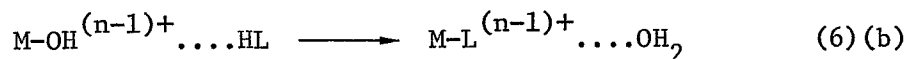
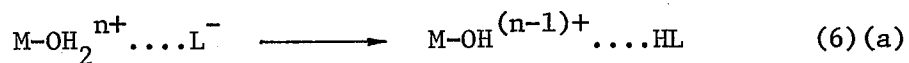
(i) Very fast reactions are observed with rate constants all exceeding 10^7 sec^{-1} . These include alkali metals - Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ and alkaline earth metals - Ca^{2+} , Ba^{2+} and Sr^{2+} . Specific effects were observed only with strongly chelating multidentate ligands. The general mechanism proposed by Eigen⁵ is a transformation of the diffusion-controlled ion-pair into an inner-sphere complex. Reaction rates of the metal ions in this group display a certain dependence on the nature of the chelating agent. Rate increase has been correlated with decrease in the heat of hydration of the metal ion. It is apparent that water loss is fast and the ligand attack is the rate-determining step. Eigen suggests that the rate-limiting step is the substitution of several water molecules by the ligand.

(ii) Reactions which belong to this category exhibit rate constants less than 10^7 sec^{-1} and are very nearly independent of the nature of the chelating compound if substitution is faster than hydrolysis. It includes cations like Mg^{2+} , most of the divalent metals

of the first transition series and some of the trivalent rare earth ions. The rate limiting step is the splitting of the metal water bond and the rates are characteristic of the metal ion only. The relatively low rate of substitution for Mg^{2+} is attributed to the size of the ion for its given valency. Divalent metal ions with $s^0 p^0$ inert-gas configurations like Zn^{2+} , Cd^{2+} , Hg^{2+} and most of the trivalent rare earth metal ions have substitution kinetics which reflect the electrostatic behaviour of these ions. The reaction rates of the transition metal series can be explained satisfactorily in terms of the difference ΔE in the crystal-field stabilization energy (C.F.S.E.) between the reactant octahedral state and the transition state. The geometry of the transition state depends on whether an S_N1 or S_N2 mechanism is involved. A large positive ΔE entails a slow reaction while a zero or negative value indicates a relatively fast reaction. It is important to consider the spin state of the initial reactant because the energy of a particular spin state would determine the magnitude of ΔE for a given transition state. Metal ions with d^1 , d^2 , d^3 (i.e. t_{2g}^1 , t_{2g}^2 , t_{2g}^3) and d^8 or d^9 ($t_{2g}^6 e_g^2$ and $t_{2g}^6 e_g^3$) configurations can have only one possible ground state, but with d^4 , d^5 , d^6 and d^7 ions, there can be high-spin and low-spin states. It has been concluded that among high-spin systems, only the d^3 and d^8 states would show an appreciable stabilization regardless of whether an S_N1 or S_N2 mechanism is involved. Both Cu^{2+} and Cr^{2+} in the first row are

expected to behave differently in the rate of water substitution because of their change in the coordination structure from octahedral to square planar.

(iii) The few cations including Fe^{3+} , Al^{3+} , and Be^{2+} which exhibit very slow rates of ligand entry and water exchange. The rate of hydrolysis for these ions is often greater than the rate of water substitution by orders of magnitude, and pH effects show that the hydrolysed species undergo faster substitution. Complex formations in this category display a very strong dependence upon the basicity of the entering ligand. Apparently, the rate-limiting step in these cases is an internal hydrolysis, i.e. the splitting of a H_2O molecule in the inner coordination sphere of the cation, and the rate constant is therefore dependent on the basicity of the ligand. Schematically, it can be represented by the following steps:



It is quite natural to assume that the $\text{S}_{\text{N}}1-(\text{I}_{\text{d}})$ mechanism is predominantly active here.

(4) COORDINATION CHEMISTRY OF BERYLLIUM.

The coordination number of Be^{2+} aquo ion was first elucidated by Connick & Fiat¹⁹ from O^{17} NMR measurements. It was reported to be 4.0 ± 0.2 and the average lifetime of the water molecule in the inner coordination sphere was $\sim 3 \times 10^{-4}$ sec at 298°K . Connick²⁰ has since reported a value for the rate constants of water exchange k_{ex} at 298°K to be $3 \times 10^4 \text{ sec}^{-1}$. Since then, Be^{2+} has been studied with other solvent systems including dimethylformamide²¹, water-hexamethylphosphoramide²² mixtures and trimethyl phosphate²³, all reporting a coordination number of four solvent molecules. The corresponding k_{ex} values can be found within these references.

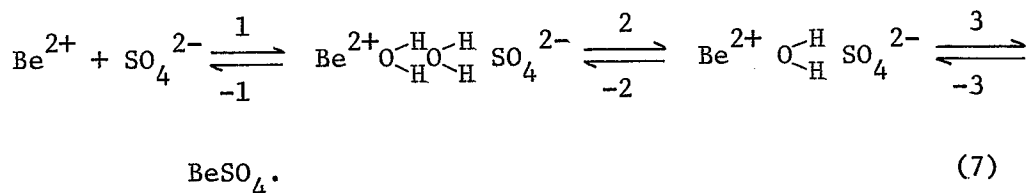
(5) BERYLLIUM COMPLEX FORMATION STUDIES.

(i) Beryllium-thenoyltrifluoroacetone (T.T.A.) complex formation.

A qualitative observation of the Be^{2+} - T.T.A. complex formation was reported by Taft and Cook²⁴ without any proposed reaction mechanism. The general conclusions were that the rate constant was less than $10^6 \text{ l mole}^{-1} \text{ min}^{-1}$ and the rate-determining step involved the metal ion. These authors have correlated the rate constant of the first complex formation with the Born charging energy of the central ion.

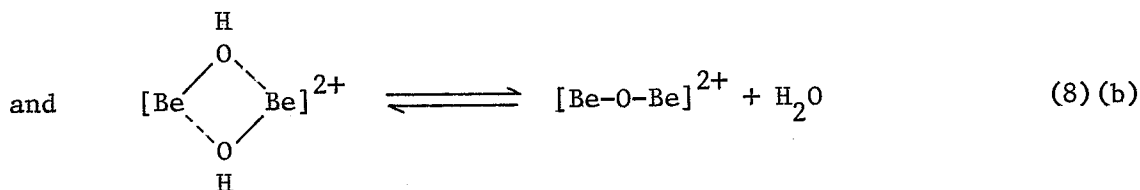
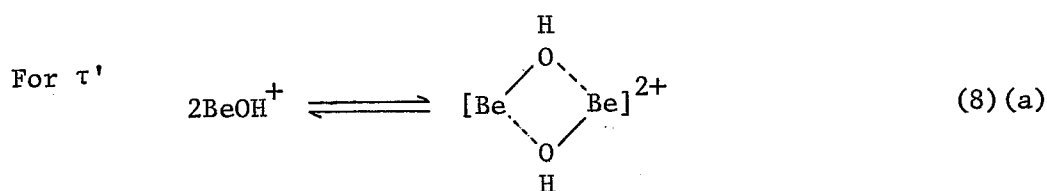
(ii) Beryllium-Sulphate complex formation.

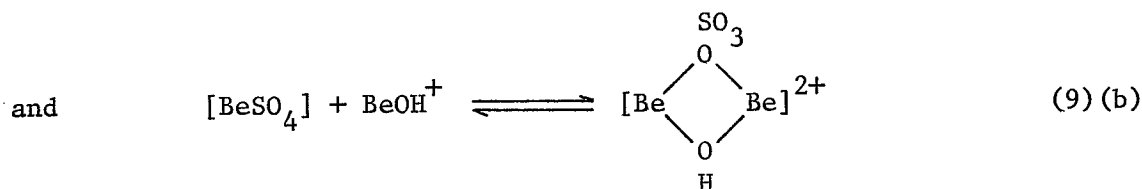
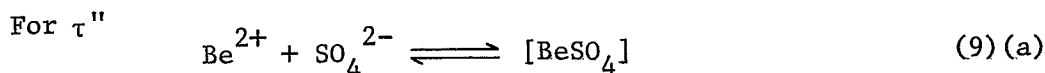
Diebler & Eigen²⁵ reported an initial study of the Be^{2+} - SO_4^{2-} complex formation by the ultrasonic absorption technique. The following reaction pathways were postulated:



Step (1) and (2) were suggested to be very rapid with relaxation times $\tau_1, \tau_2 \geq 10^{-6}$ msec. The value of τ_3 which was found to be both hydrogen and beryllium ion concentration independent, was 0.8 ± 0.2 msec. at 35°C . It is obvious from the experimental data that step (3) is the rate-determining step. Tamm & Eigen²⁶ later reported values of k_3 and k_{-3} to be 10^2 and 10^{-3} sec^{-1} respectively.

Two extra relaxation times τ' and τ'' were observed between pH 3 and 4.5; both have relaxation time values which are dependent upon the hydrogen and beryllium ion concentrations. Each of these relaxation effects was individually interpreted by Diebler & Eigen, with the following proposed mechanisms:





A study on the temperature dependence of the reaction was not followed, consequently, the energies of activation cannot be determined.

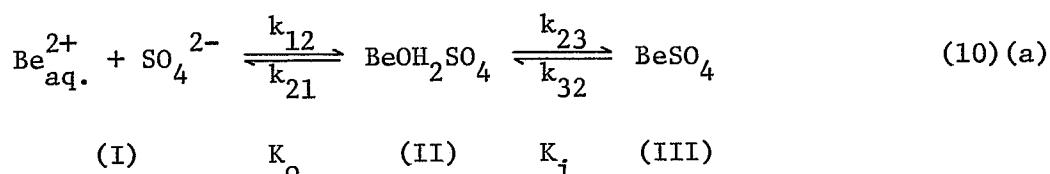
Strehlow and Becker²⁷ in the same year published a paper on a similar study of the formation of beryllium sulphate using the pressure-jump method as opposed to the temperature-jump method of Diebler and Eigen. These authors reported to have observed only one relaxation time, $\tau = 0.4(\pm 50\%)$ msec at 12°C, which was relatively pH and concentration independent. There is apparently a discrepancy between the two reports since the value obtained by Strehlow and Becker would be considerably shorter at 35°C, which was reported to be the temperature at which Diebler and Eigen performed their experiment.

A series of studies dealing with the formation of beryllium sulphate have surfaced since then. Wendt^{28a} in 1960 reported the values, $\tau = 2.9$ msec at 25°C and $\tau \approx 6.7$ msec at 8°C for the only relaxation time observed by pressure-jump measurements. The activation energy was estimated to be approximately 13 Kcal/mole. Hoffmann, Stuehr and Yeager^{28b}, assuming the reaction pathway of Diebler and Eigen, reported yet another value of τ to be 2.5 ± 0.2 msec at 25°C. This single relaxation time was found to be independent of concentration

from $2 \times 10^{-3} \text{M}$ to 0.2M and independent of pH from 2.5 to 4.5. There was not any obvious isotope effect on the relaxation time because τ was reported to be 2.2 msec for 0.04M BeSO_4 at pH 3.2 in D_2O . The temperature dependence of the relaxation was followed, and an apparent activation energy was determined to be $14 \pm 1 \text{ Kcal/mole}$. Using this value, the authors were able to calculate a relaxation time expected from their pressure-jump measurements at 35°C . They concluded that the relaxation time τ of BeSO_4 as determined by pressure-jump measurements ($1.1 \pm 0.1 \text{ msec}$ at 35°C), compared favourably with the temperature-jump measurements τ_3 made by Diebler and Eigen ($0.8 \pm 0.2 \text{ msec}$ at 35°C). Their attempt to resolve the discrepancy between the observations of Eigen et. al.²⁵ and Strehlow et. al.²⁷ remained unsuccessful. These authors in the same paper have also pointed out that the extra relaxation times observed with the temperature-jump technique should be attributed to the nature of the detection system. The temperature-jump technique which uses pH-sensitive organic indicators would be very sensitive to the hydrolysis processes as well as the dissociation processes which are coupled to them. On the other hand, the relaxing portion of the conductivity is relatively insensitive to hydrolysis even if dissociation is considered to have coupled with hydrolysis. Consequently, the effect of hydrolysis on the relaxation of the conductivity may be sufficiently small to have evaded detection in pressure-jump measurements. Calculations similar to those of Tamm & Eigen²⁵ were performed and yielded values of k_3 and k_{-3} of 40 sec^{-1}

and $400 \pm 40 \text{ sec}^{-1}$ at 25°C .

Strehlow and Kalarickal^{28c} using an improved temperature-jump technique and Köhler and Wendt^{28d} using the pressure-jump method both reported further studies on the formation of BeSO_4 in 1966. The general mechanism adopted was:



The overall stability constant is K , and

$$K = \frac{[\text{BeOH}_2\text{SO}_4] + [\text{BeSO}_4]}{[\text{Be}^{2+}][\text{SO}_4^{2-}]} = K_o(1 + K_i) \quad (10) (b)$$

The stability constant of the outer-sphere complex is denoted by K_o

$$K_o = \frac{[\text{BeOH}_2\text{SO}_4]}{[\text{Be}^{2+}][\text{SO}_4^{2-}]} = \frac{k_{12}}{k_{21}} \quad (10) (c)$$

Similarly, K_i denotes the stability of the inner-sphere complex, and

$$K_i = \frac{[\text{BeSO}_4]}{[\text{BeOH}_2\text{SO}_4]} = \frac{k_{23}}{k_{32}} \quad (10) (d)$$

The work performed by Strehlow and Kalarickal was principally a temperature dependence study on the relaxation time. An apparent activation energy of $8.5 \pm 0.4 \text{ Kcal/mole}$ was determined. This value is obviously in disagreement with the previously reported values of

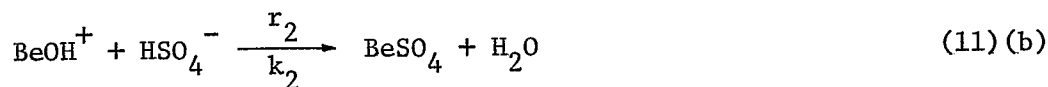
Wendt^{28a} and Hoffmann, Stuehr and Yeager^{28b}. Unfortunately, the discrepancy was not discussed by these authors. In the meantime, Köhler and Wendt reported another study on the subject. Contrary to most of the other observations, there was apparently a beryllium ion concentration dependence for the relaxation time. The concentrations at which the investigation was conducted ranged from $5 \times 10^{-2} \text{ M}$ to $2 \times 10^{-1} \text{ M}$. No specific pH value was reported at which measurements were made, though it is assumed to be relatively low. Values of K_i and K_o can be determined from the measurements of τ as a function of concentration if a value of K is assumed. K_o and K_i were reported to be 50 M^{-1} and 0.8 ± 0.2 respectively, at 25°C and infinite dilution, if K is equal to 90 M^{-1} .

Strehlow and Knoche^{28e} in their attempt to elucidate the mechanism of ligand substitution in weak complexes, repeated some measurements on the relaxation time, τ , of BeSO_4 using a pressure-jump method. Temperature and pH dependent investigations were carried out at a concentration of 0.1 M between temperatures ($5^\circ \text{C} < T < 50^\circ \text{C}$) and pH values of ($1.71 < \text{pH} < 2.86$). Identical measurements of Köhler and Wendt^{28d} on the concentration dependence of τ were also reported. The results were found to have agreed with the reported values of Köhler and Wendt. The apparent activation energies for the formation, E_A^{23} , and dissociation, E_A^{32} , of the inner sphere complex were determined to be $13.2 \pm 0.6 \text{ Kcal/mole}$ and $11.0 \pm 1.2 \text{ Kcal/mole}$ respectively. These authors explained that the relatively low value^{28c} of activation

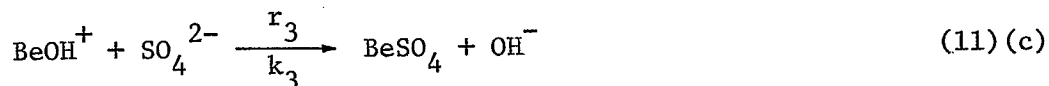
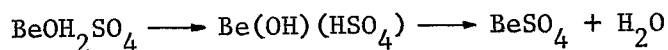
energy (~ 8 Kcal/mole) as was determined by temperature-jump measurements was due to a systematic error which they have eliminated for these pressure-jump measurements. A theoretical activation energy based on corrected electrostatic considerations was calculated and compared to the experimental value. It was concluded that a pure S_N1 -(D) mechanism would lead to an activation energy which was much too high. Consequently, it was suggested that a concerted mechanism would be most likely. These authors have also noted that with such a mechanism, all ligands in the inner sphere would be involved if one ligand was to be substituted. The cation and anion were postulated to be separated by three equivalent water molecules and the fourth water molecule was the one to leave the coordination shell in the formation of the inner complex. The rate determining step was assigned to be:



The other possible rate-determining steps were rejected on the basis of the experimental evidence.



or



Reaction (11)(c) would be pH dependent, and since no such evidence was

forthcoming, the following rate relationship was established.

$$r_1 + r_2 \gg r_3 \quad (12)(a)$$

In the pH range studied, $[\text{SO}_4^{2-}] > [\text{HSO}_4^-]$ so that

$$r_3 > r_2 \quad (12)(b)$$

if the rate constants k_2 and k_3 were of comparative magnitudes.

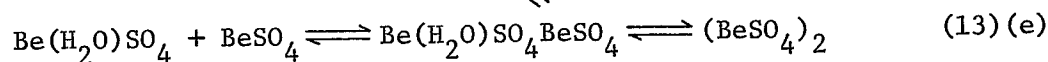
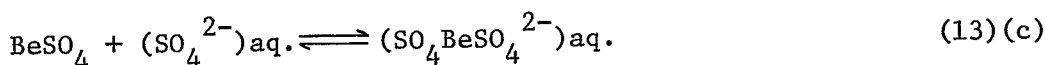
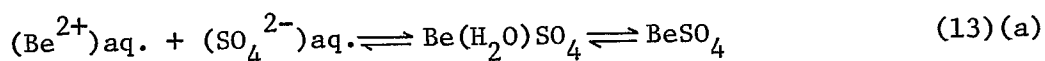
Expression (12)(a) combined with (12)(b) to yield another inequality,

$$r_1 \gg r_2 \quad (12)(c)$$

which has eliminated any possible contribution of reaction (11)(b) in the rate-determining process. By assuming the same $K = 90\text{M}^{-1}$ (29), these authors reported a value of $K_0 = 60 \pm 10\text{M}^{-1}$ which is comparable to the value obtained by Köhler and Wendt^{28d}.

Using the enhanced accuracy of a repetitive temperature-jump technique, Brumm and Ruppel^{28f} reported some more data from their detailed studies on the subject. Values of τ measured at pHs 2.5 - 4.2 were reported to be within $\pm 2\%$ of each other, consequently, hydrolysis was negligible. The temperature dependence of τ was studied at temperatures between 8 - 35°C and a concentration of 0.1M BeSO_4 , subsequent activation energies A_{23} and A_{32} were reported to be 8 ± 1 Kcal/mole and 5.8 ± 0.5 Kcal/mole, respectively. Positive concentration dependence of τ was also observed and found to have deviated from the calculated values in the ms-range. In light of this

discrepancy between the values of activation energy obtained by temperature and pressure-jump techniques, these authors concluded that the formation of BeSO_4 might involve a superposition of two processes with relaxation times of equal order of magnitude in which high complex aggregation, particularly $(\text{Be}(\text{H}_2\text{O})\text{SO}_4)_2$ were participating. A mechanism of the following was suggested:



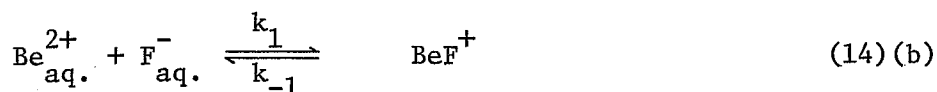
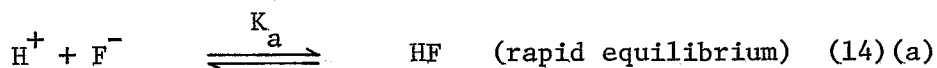
A value of $K = 100 \text{ l/mole} \pm 30\%$ was used by these authors and the subsequent value of K_0 was reported to be $60 \pm 20 \text{ l/mole}$.

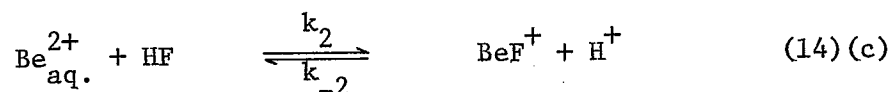
Despite of the amount of work which has been performed by various authors on the subject, there remain discrepancies which are not resolved. A fundamental difference which stems apparently from the nature of the experimental technique involved, prevails over the measurements obtained by two popular methods. The relaxation time, τ , measured by the temperature-jump technique at a specific temperature²⁵ disagrees obviously with the result of an identical measurement made

by the pressure-jump method²⁷. Activation energies elucidated by the two methods differ by as much as 4 Kcal/mole. Instead of dismissing it as a systematic error of the temperature-jump technique^{28e}, Brumm and Ruppel^{28f} suggested that because of the different modes of excitation, the phenomena under observation might not have been identical with the two methods. Since Brumm and Ruppel^{28f}, using the temperature-jump method, have reported that the τ values were relatively constant at pH 2.5 - 4.2, the discrepancy between the hydrogen ion concentration dependence of τ values^{25,27} is apparently resolved^{28b}. Finally, as Strehlow and Knoche^{28e} has pointed out, the concentration dependence of τ has not always been observed by pressure-jump measurements^{27,28b}. No attempt, however, has been made by any author to explain this inconsistency. Nothing very decisive can be concluded about the formation of BeSO_4 from this conflicting evidence except that maybe the reaction proceeds via a concerted ion-pairing mechanism.

(iii) Beryllium-fluoride complex formation.

The formation of the monofluoroberyllium species $\text{Be}(\text{OH}_2)_3\text{F}^+$ through reactions of the hydrated beryllium cation with both hydrogen fluoride and fluoride ion was reported by Baldwin and Stranks³⁰ using a conductimetric stopped-flow technique. The following parallel reaction pathways were confirmed at acid concentrations exceeding 0.01M:





The rate expression that corresponds to this reaction scheme at constant hydrogen ion concentration would be:

$$\frac{d[\text{BeF}^+]}{dt} = k_a [\text{Be}_T] [\text{F}_T] - k_d [\text{BeF}^+] [\text{H}^+] \quad (15) (a)$$

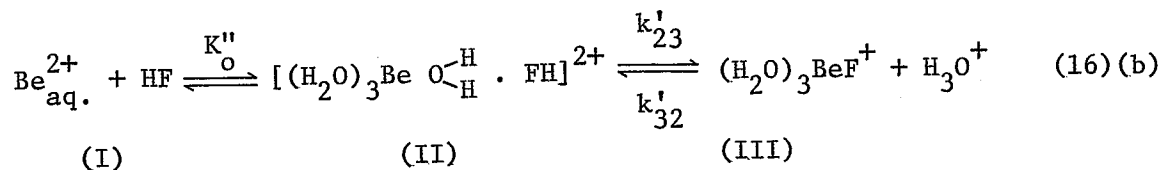
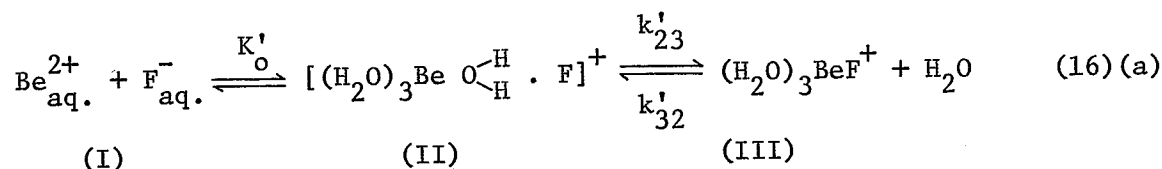
Where

$$k_a = \left\{ \frac{k_1 K_a}{[\text{H}^+]} + k_2 \right\} \left\{ \frac{1}{1 + K_a / [\text{H}^+]} \right\} \quad (15) (b)$$

$$k_d = k_{-2} + k_{-1} / [\text{H}^+] \quad (15) (c)$$

$$K_a = [\text{H}^+] [\text{F}^-] / [\text{HF}] \quad (15) (d)$$

A substitution mechanism that is analogous to the formation of $\text{Be}(\text{OH}_2)_3\text{SO}_4$ was proposed:



The observed second-order rate constants can be expressed in terms of K_o , the outer-sphere complex stability constant, and k_{23} , the first-order rate constant for the formation of the BeF^+ species.

$$k_1 = K'_O \times k'_{23} \quad (17)(a)$$

$$k_2 = K''_O \times k''_{23} \quad (17)(b)$$

The observed rate law was reported to be second-order forward and second-order reversible, in accordance with expression (15)(a).

The hydrogen ion concentration dependence of k_a was observed between pH 0.3 and pH 2.1 at an ionic strength of 0.2M. The $[Be_T]$ and $[F_T]$ were set at 0.01M and 0.005M respectively. This set of measurements was repeated at four different temperatures, 15.9°C, 23.0°C, 25.0°C and 39.8°C. The magnitudes of k_1 and k_2 at each temperature were determined by a plot of $k_a\{1 + K_a/[H^+]\}$ versus $1/[H^+]$, and were reported to be:

TABLE 1

Temperature	k_1 (litre/mole-sec)	k_2 (litre/mole-sec)
15.9	503 ± 194	46.1 ± 5.5
23.0	801 ± 204	82.3 ± 5.3
25.0	724 ± 95	72.8 ± 3.4
39.8	1566 ± 123	165 ± 2

The mean value of the activation energy, which presumably was calculated from the temperature dependence of k_a , was reported to be $8.9_1 \pm 0.8$ Kcal/mole. This value was reported to be more preferable than the activation energies of 10.0 ± 2.0 and 9.4 ± 1.1 Kcal/mole corresponding to the listed values of k_1 and k_2 respectively. The common activation energy of (8.9 ± 0.8) Kcal/mole was compared by these authors to the activation energy of (8.5 ± 0.4) Kcal/mole observed by Strehlow and Kalarickal^{28c} for the formation of BeSO_4 . The enthalpy of association for the outer-sphere complex, ΔH^{IP} , was calculated by these authors using both the Bjerrum and Fuoss treatment. The reported value was $\Delta H^{\text{IP}} = +1.1$ Kcal/mole. It was expected that the enthalpies of activation for the two reaction paths (k'_{23} , k''_{23}) would be similar, therefore,

$$\Delta H^{\ddagger}_{23}' = \Delta H^{\ddagger}_{23}'' = 8.9 - 1.1 - 0.6 = 7.2 \text{ Kcal/mole}$$

The authors have also speculated that the magnitude and sign of ΔH^{IP} for the BeSO_4 system would be very similar to the BeF^+ system. Consequently, it is not unreasonable to assume that the two substitution reactions proceed with the same enthalpy of activation (7.2 Kcal/mole).

The K'_o and K''_o values can be estimated by an adaptation of the Fuoss-type equation.³¹ And since the values of k_1 and k_2 are known, the first-order substitution rate constants k'_{23} and k''_{23} can be determined. Also available are the known^{32,33} values of the overall stability constants K for BeF^+ . According to expression (10)(b),

these authors reported the subsequent K_i values for the two parallel reaction pathways. The values are tabulated as the following:

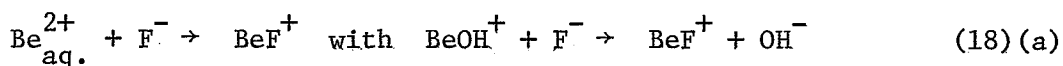
TABLE 2

Reaction (25°C)	K	K_o	K_i	$k_1(k_2)$	k_{23}
$\text{Be}_{\text{aq.}}^{2+} + \text{F}^- \rightarrow \text{BeF}^+$	1.05×10^5	1.53	6.9×10^4	724	473
$\text{Be}_{\text{aq.}}^{2+} + \text{HF} \rightarrow \text{BeF}^+ + \text{H}_{\text{aq.}}^+$	1.32×10^2	0.36	3.7×10^2	73	203

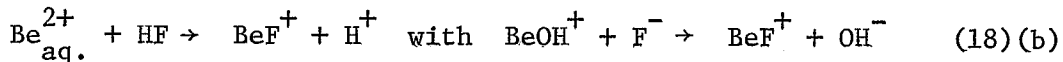
K and K_o in litre/mole; k_1, k_2 in litre/mole-sec; k_{23} in sec^{-1} .

Reactions which could have proceeded through mononuclear and polynuclear hydrolysed species of beryllium were rejected by these authors on two criteria. First of all, the species Be_2OH^+ , $\text{Be}_3(\text{OH})_3^{3+}$ and $\text{Be}(\text{OH})_2$ were all excluded because they would not comply with the experimental rate law which was first order in $[\text{Be}_T]$ and essentially first order in $[\text{H}^+]^{-1}$. The formation of these species according to Schwarzenbach³⁴, would require times of at least 100 msec which was actually slower than several of the half-times observed for fluoride substitution. Consequently, these hydrolysis equilibria could not be treated as rapid pre-equilibria and this constituted the second point of inconsistency with the observed rate law.

The first two pairs of reaction paths for substitution via BeOH^+ , the "internally" hydrolysed product, were,

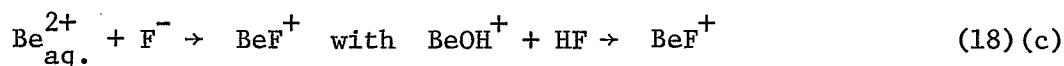


and

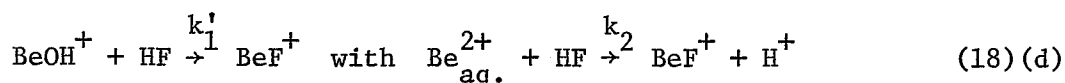


Both of these reactions would exhibit a term in $[\text{H}^+]^{-2}$ which was incompatible with the observed $[\text{H}^+]^{-1}$ dependence of the rate law.

The third possible pair of reaction path was



This, however, was also rejected because it would not exhibit any dependence upon the $[\text{H}^+]$. The final combination,



apparently, was compatible with the observed rate law. Nevertheless, it was ultimately rejected on the basis that such a reaction if valid would give an anomalously high value for $k_1' = 1.1 \times 10^6$ litre/mole-sec at 25°C, while k_2 would retain its previous value.

(iv) Other studies on the chelation of the beryllium ion.

Hoffmann, Stuehr and Yeager^{28b} in their initial study on the formation of BeSO_4 using the pressure-jump technique, have reported brief measurements on the relaxation times of some organo-beryllium complexes. The results are listed in Table 3.

TABLE 3

Cation	Ligand	τ	τ_1	τ_2	τ_3
Be^{2+}	H-citrate	2			
	d-tartrate		6	100	
	Acetate		15	200	5000
	Aminoacetate		6	20	
	Oxalate	20			
	Glycollate		3	700	
	Formate	6			
	Chloroacetate	3			

These relaxation times were reported in msec at 25°C and concentrations of 0.04M. No further investigation on the subject was pursued by these authors; therefore, the relaxation times given are the only available information.

Fleet and Rechnitz³⁵ while developing a rapid-mixing continuous-flow system utilizing liquid membrane ion-selective electrodes as sensors, reported the complex formation rates of Be^{2+} with some biologically important ligands. The internally hydrolysed cation, $\text{Be}(\text{OH})^+$, was assumed to be involved in the reaction mechanism (Eq.(6)(a) and Eq.(6)(b)). Therefore, the parallel of reactivity with the basicity of the ligand was anticipated by these authors. Their observed rate constants are tabulated in Table 4.

TABLE 4

Cation	Ligand	pH	k
$\text{Be}^{2+}_{\text{aq.}}$	gluconate	7.15	4.45×10^4
	lactate	7.05	6.15×10^4
	tartrate	7.15	5.50×10^4
	malate	7.15	8.75×10^4

Ionic strength $\mu = 0.04\text{M}$ TMACHloride, $[\text{Be}^{2+}] = 1 \times 10^{-4}\text{M}$,
 $[\text{Ligand}] = 1 \times 10^{-4}\text{M}$, and k in sec^{-1} . The magnitudes of these rate constants were considerably higher than anticipated, unfortunately, no attempt to resolve the discrepancy was reported. The correlation between the rate constant, k , and the basicity of the ligand, $1/K_{\text{Diss.}}$, appeared to be fairly satisfactory over the range of ligands used.

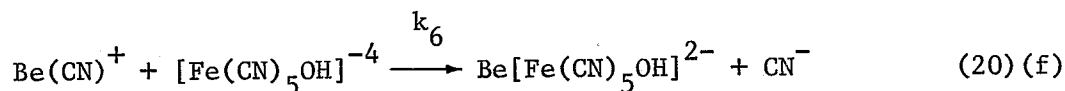
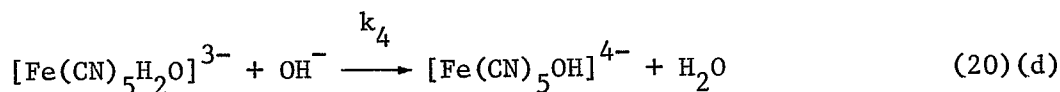
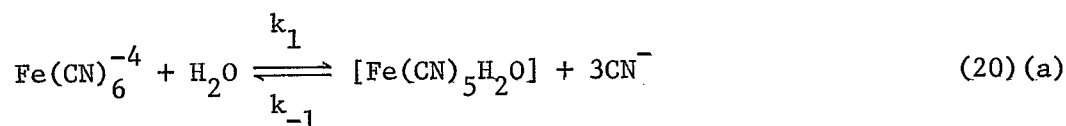
Malik, Srivastava and Thallam³⁶ reported a study on the complex formation between Be(II) and potassium ferrocyanide. The reaction was followed by measuring the absorbance at $440\text{ m}\mu$ at different intervals of time, using a Spectronic-20 spectrophotometer. All measurements were conducted at $\text{pH} = 1.0$ except those of the $[\text{H}^+]$ dependence of k studies. The concentration dependence of the rate constant k was followed by varying (2.5×10^{-2} to $0.6 \times 10^{-2}\text{M}$) each of the reactants in turn, keeping the other constant ($3.3 \times 10^{-3}\text{M}$). The reaction was found to be first order w.r.t. Be(II) and zero order w.r.t. Fe(CN)_6^{-4} . The temperature dependence of k was also investigated from 298°K to

318°K, the activation energy thus obtained was ~ 17.1 Kcal/mole and the entropy of activation $\Delta S^\ddagger \approx 22 \text{ e.u.}$. It was found that at pH 4.92 precipitation occurred, therefore, $[\text{H}^+]$ dependence studies of k was performed from pH 1.0 to 4.35, maintained by sodium acetate-hydrochloric acid buffer. The reaction rate constant was found to be inversely proportional to pH. These authors have reported an apparent relationship $\Delta S^\ddagger = -10Z_A Z_B \text{ e.u.}$ which would lead to the value $Z_A Z_B = -2$, suggesting that the reaction was between a bivalent ion and a univalent ion of opposite charge. The salt effect was investigated using KCl as the neutral salt. This result has also suggested that the rate determining step was a reaction between a bivalent ion and a univalent ion of opposite charge. The reaction was considered to be relatively insusceptible to specific ionic effect. Rates were investigated with various ions, namely Na^+ , K^+ , Mg^{2+} , NO_3^- , Cl^- , CH_3COO^- and SO_4^{2-} , and found to be literally constant. To determine the solvent effect, the reaction was observed in different compositions of methanol-water, ethanol-water, and dioxane-water mixtures, used as the solvent. The reaction was found to obey the general expression

$$\ln k = \ln k_o - \frac{Z_A Z_B e}{DdABKT} \quad (19)$$

in other words, the plot of $\log k$ vs $1/D$ is linear. (D is the dielectric constant of the medium.)

A reaction mechanism of the following was proposed,



The steps (20)(a), (b) and (c) were considered by these authors as rapid equilibria, and reaction (20)(d) was to be rapid because it involved the substitution of a H_2O molecule by a OH^- ion in the coordination sphere. Reaction (20)(e) which is a reaction between a divalent and a univalent ion of opposite charge, was naturally adopted as the rate-determining step. The rate equation was derived as:

$$\frac{dx}{dt} = k' C_{\text{Be}^{2+}} \quad (21)$$

if C_{CN^-} was at any moment very small and constant, and reaction (20)(f)

was fast.

(B) OBJECT OF RESEARCH

A limited number of studies on the formation of Be(II) complexes have been reported in the literature. In particular, there has not been any extensive investigation on the kinetics and mechanisms of the reactions which involve the cation and some bidentate ligands. Complexation studies with unidentate ligands SO_4^{2-} and F^- both produced very low rate constants. This is in accordance with the postulate from electrostatic considerations that the reaction rate would slow down as the charge of the cation increases and its size decreases. Be(II) has been found to have a tendency to form bonds largely covalent in nature. The rate-determining step in the mechanism is agreed to be the conversion of the outer-sphere complex into the inner-sphere. This research was an attempt to provide a better understanding of the role of Be(II) in the chelation with bidentate ligands.

The substituted salicylic acids with a rigid benzene ring were selected for a variety of reasons. Structurally, the salicylic acids are in many respects similar to some aromatic acids which are ligands of great biological interest. Furthermore, according to a molecular model, the chelate ring enclosure between the carboxyl and the hydroxyl groups should be relatively free of strain despite the smaller size of the cation. And finally, the complex formation of salicylic acids with various cations has been the subject of a number of recent studies, including (i) the chelation of Ni(II) and Co(II) with salicylic acids³⁷, (ii) the complex formation between Mg(II) and 5-Nitrosalicylic acid³⁸,

and (iii) the complexation between Fe(III) and salicylic acids.^{39,40,41}

The present work, hopefully, would supplement the overall understanding of the complex formation between salicylic acids and various cations.

(C) EXPERIMENTAL

(1) THEORY OF THE STOPPED-FLOW TECHNIQUE.^{1,2,3}

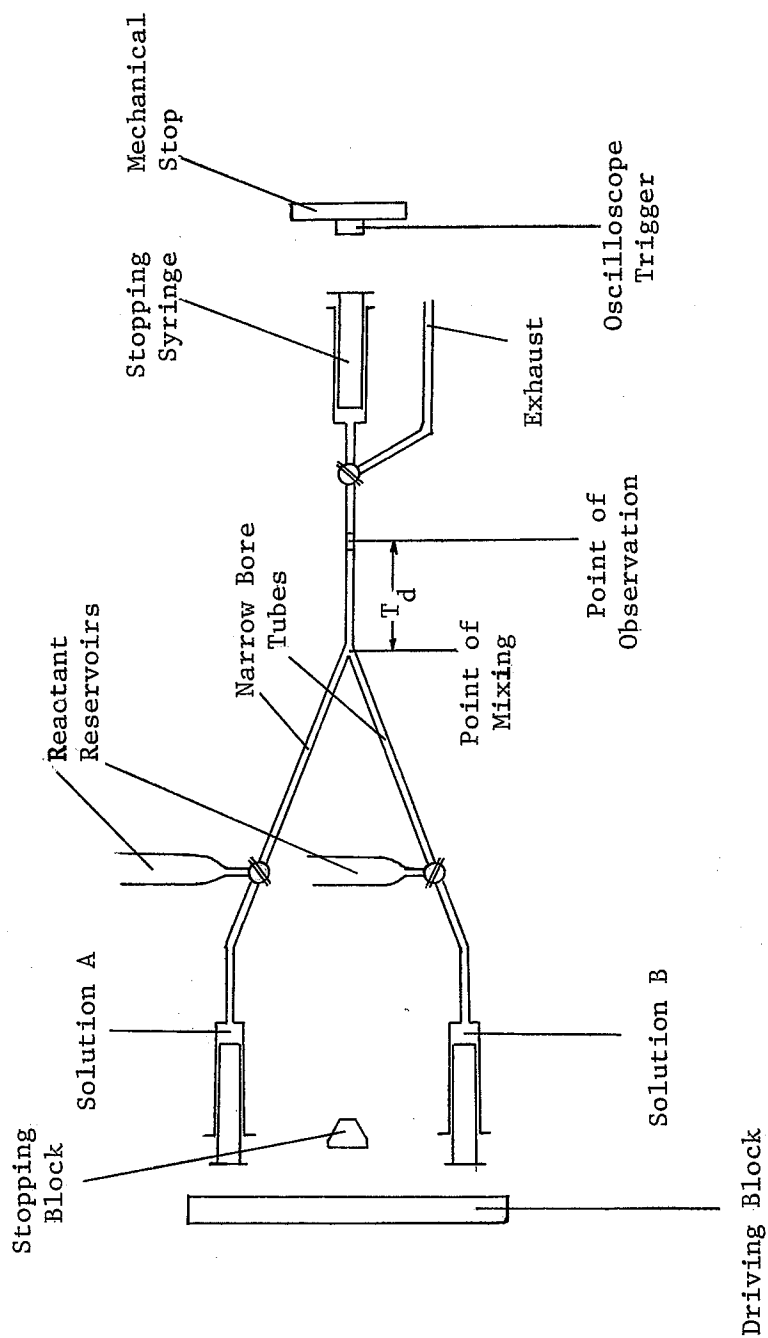
Much of the developement of the stopped-flow method, particularly the stopping device, should be credited to Gibson.⁴² The basic components of a stopped-flow apparatus is schematically represented in Figure 1.

There are four stages to every complete run, (i) driving, (ii) mixing, (iii) stopping, and (iv) observing.

Reactants A and B, which are contained in two robust and leak-free syringes, are driven through the narrow bore tubes either manually or mechanically at a very high flow velocity. Both pneumatic and hydraulic devices are feasible as driving units although the former appears to be more common. Narrow bore tubes in conjunction with a high flow velocity are necessary in order to achieve a turbulent flow, which is the closest possible to the ideal "mass" flow. In general, the effects of such an imperfect flow introduce a discrepancy of ~2% in the measured k values.

The mixing is performed by a rapid mixer which has to mix the reactants efficiently in a time much shorter than $t_{1/2}$. A multitude of rapid mixers have been designed, each according to the researcher's specifications and discretion. The simplest type is a three-way glass T-tap (T-mixer) of capillary bore which can be used for reactions with half-lives of 10 msec and up. For faster reactions, the more sophisticated jet-mixers are often used. A simple four-jet mixer has four 0.5 to 1 mm. bore capillaries arranged semi-tangentially such

FIGURE 1. Basic components of a stopped-flow apparatus.



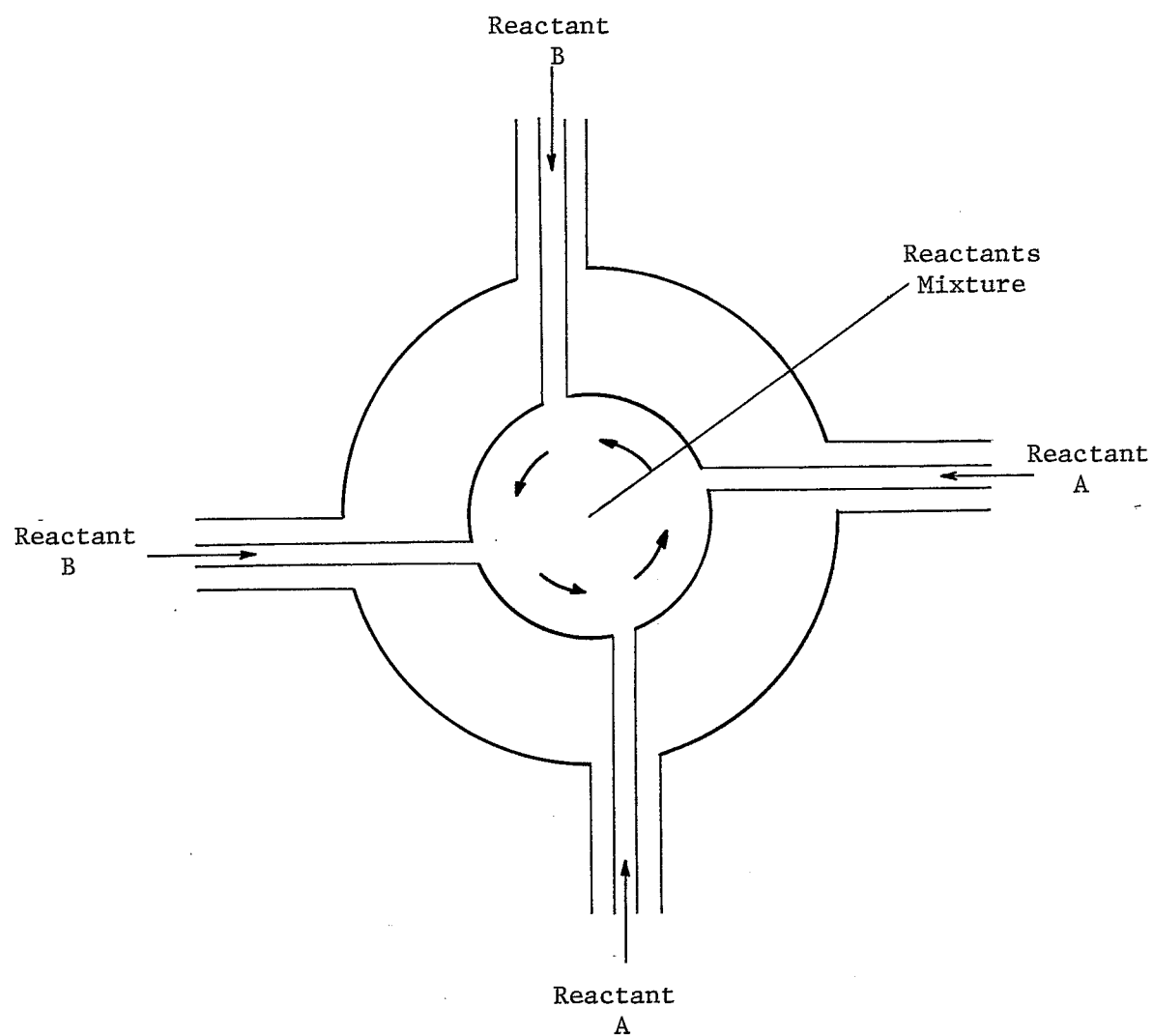
T_d = "Dead" time.

that the reactants acquire a rotary motion which accelerates mixing. A four-jet mixer is illustrated diagrammatically in Figure 2. Materials such as glass, plastic or metal are often used for the construction of such mixing-chambers. Generally speaking, the efficiency of mixing is directly proportional to the number of jets in the mixer. The more exotic multi-jet (8, 10, 12 jets) mixers have been used by many workers despite the fact that these mixers are sometimes difficult to engineer. Another common practice to achieve better mixing is to arrange in a series a number of mixers adjacent to each other. The series can be comprised solely of jet-mixers, T-mixers, or of both types of mixers.

The dead time is the time required for the reacting solution to travel from the point of mixing to the point of observation, provided that, when the flow is stopped, it is an instantaneous or "dead" stop. For a constant flow velocity, the dead time is a function of the instrument only and is constant. That is why laminar flow, which has a parabolic velocity profile at lower flow velocities, should be avoided. The existence of the dead time means that the reaction has been in progress for a specified time (the dead time) before the first observation can be made. For any satisfactory kinetic study, the observation of at least 50% of a reaction is essential. It is recommended that only reactions with half-lives which are equal to or slower than the dead time should be studied.

The most common method of observation is spectrophotometry. The light source is a lamp (U.V. or visible) preferably with a monochromator and the optical density change is monitored by a photomultiplier on the

FIGURE 2. A four-jet mixer.



receiving end. When the flow is stopped "dead", a trigger will initiate a trace of the photomultiplier's output on an oscilloscope screen with a time-base. The trace is subsequently photographed and analysed. Alternative means of detection include e.m.f. measurements with a glass electrode and conductivity measurements.

The stopping mechanism consists of a simple syringe whose plunger is displaced by the reaction mixture, coming to rest abruptly against the oscilloscope trigger on a mechanical stop. This simple arrangement will stop the flow "dead" in 1 - 2 msec. A very sudden stoppage has the advantages of an increased efficiency of mixing and of earlier reaction observation.

Most of the existing stopped-flow apparatus are capable of following the temperature dependence of reactions. The desired operation temperature can be achieved by thermostating the reactant reservoirs, mixing-chamber, observation tube and the stopping syringe with a constant-temperature bath.

(2) APPARATUS.

The earlier kinetic runs (pH 3.5 - 5.5) in this work were done with an "Aminco-Morrow" commercial stopped-flow apparatus⁴³ (Cat. No. 4-8409). The detailed specifications of the instrument can be found in the company's literature. Roughly, the driving mechanism incorporates two teflon syringes whose plungers are driven by a pneumatic device operating under air pressure of 70 psig.. Two 5-ml glass syringes serve as reactant reservoirs for loading reactants into the driving syringes. The on-off valves function to separate two operations, the

loading of the driving syringes from the driving of the reactants. Two teflon tubes (0.091" o.d. x 0.059" i.d.) transport the reactants to the entrance of the "Triple-T" mixer. The components of the rather compact mixing chamber which incorporates the observation path are shown diagrammatically in Figure 3.

Mixing initially occurs at the first "T" near the bottom of the mixer. The mixed reactants are then reunited to enter the second "T" (refer to Figure 3) which subsequently splits it up again. The course after will take two 90° turns and recombine at the third "T" where observation is to begin. The efficiency of mixing is reported to be greater than 98% in less than 1 msec or at the point of observation. The total path length in the observation cell is 10 mm.. An ordinary deuterium lamp with a Beckman prism monochromator is used as the light source. The optical density change is monitored by a photo-multiplier which is connected to the input of a high performance kinetic photometer. The plunger of the stopping syringe when displaced by the mixed reactants would be stopped "dead" by the oscilloscope trigger switch which is mounted on a micrometer tip. A 14-volt signal triggers a trace of the output from the kinetic photometer when the switch is closed. Figure 4 is a block diagram of the final assembly. The two driving syringes and the stopping syringe are mounted in an aluminium block which has appropriate inlet and outlet nipples drilled and fitted to facilitate circulation of liquid through the block for thermostating with an external constant-temperature water bath. A small thermistor is attached to the observation cell so that the exact

FIGURE 3. "Triple-T" mixing chamber and observation cell
of an Aminco-Morrow stopped-flow apparatus.

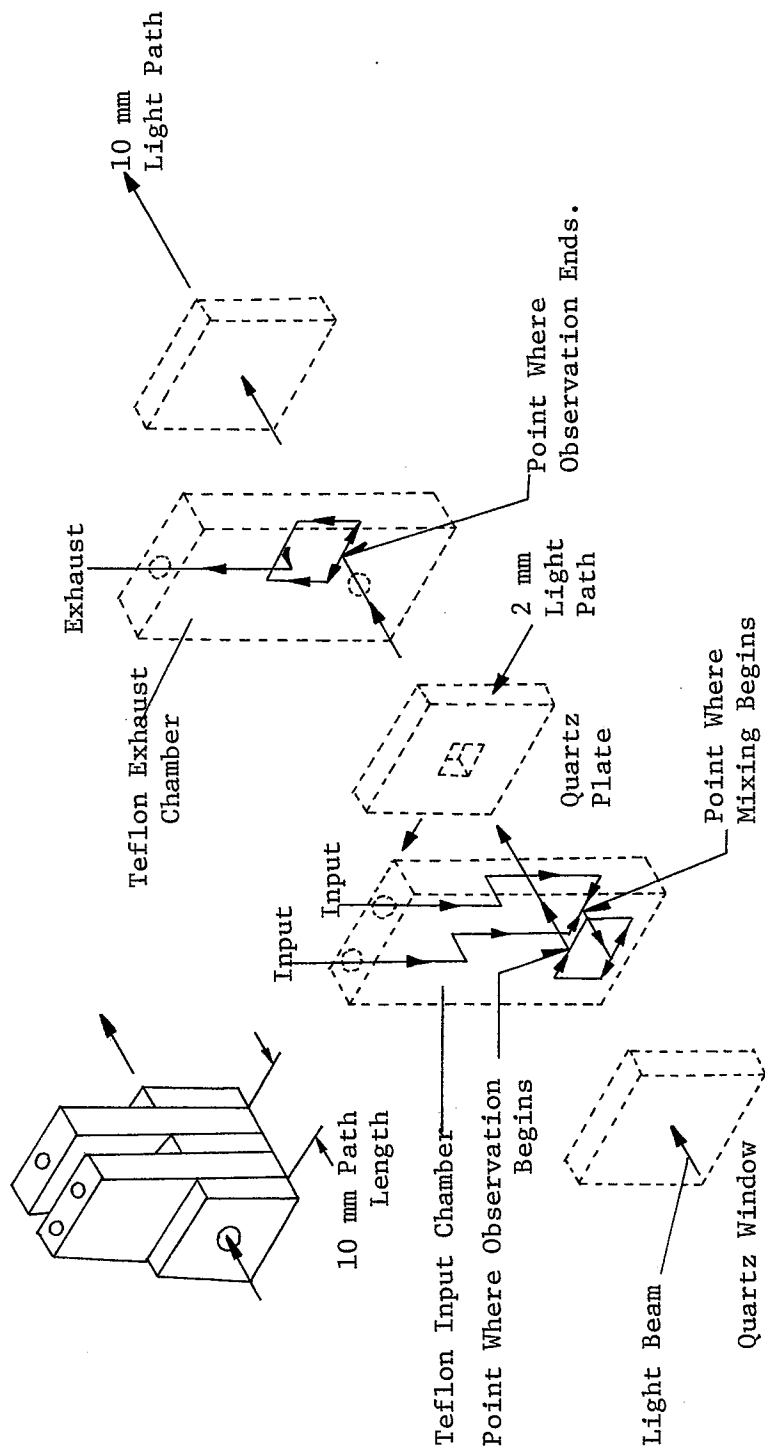
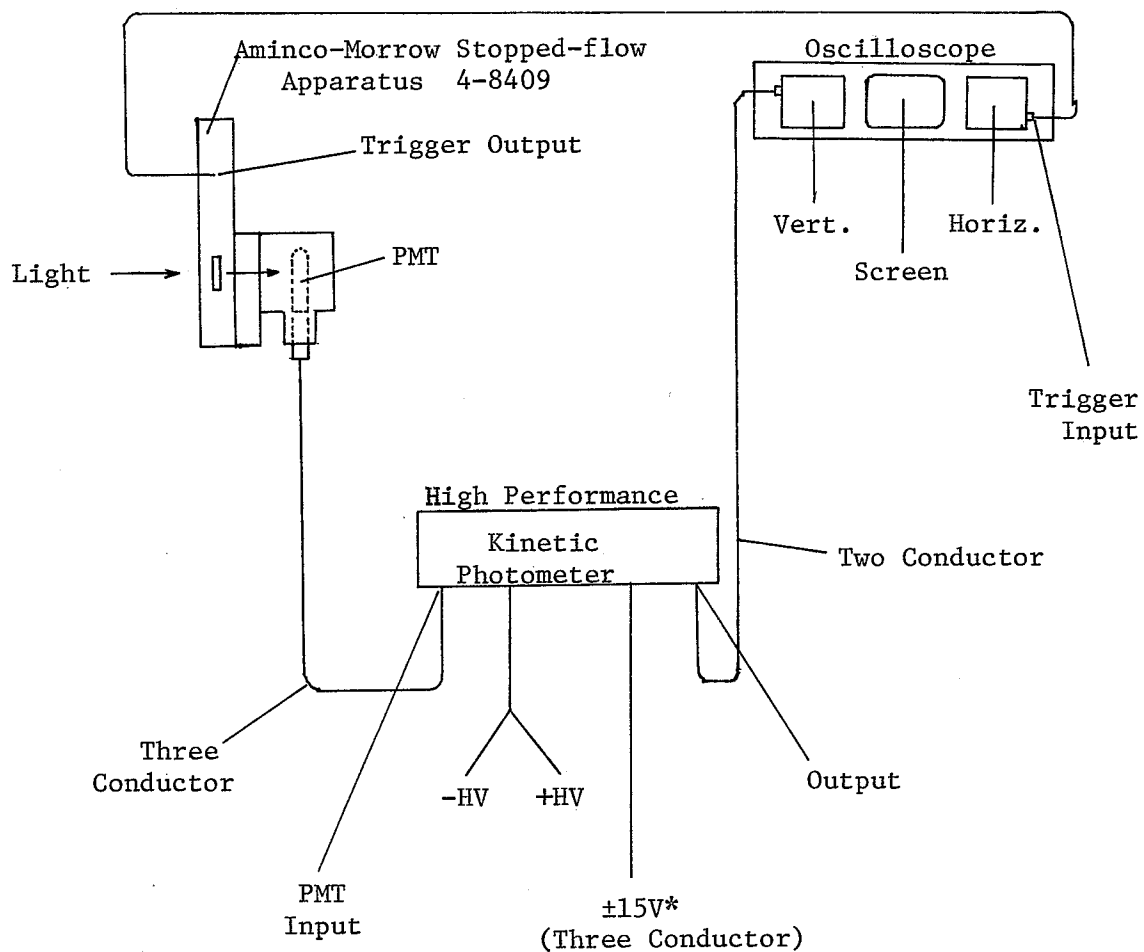


FIGURE 4. Block diagram of the final assembly of
an Aminco-Morrow stopped-flow apparatus.



PMT - Photomultiplier Tube.

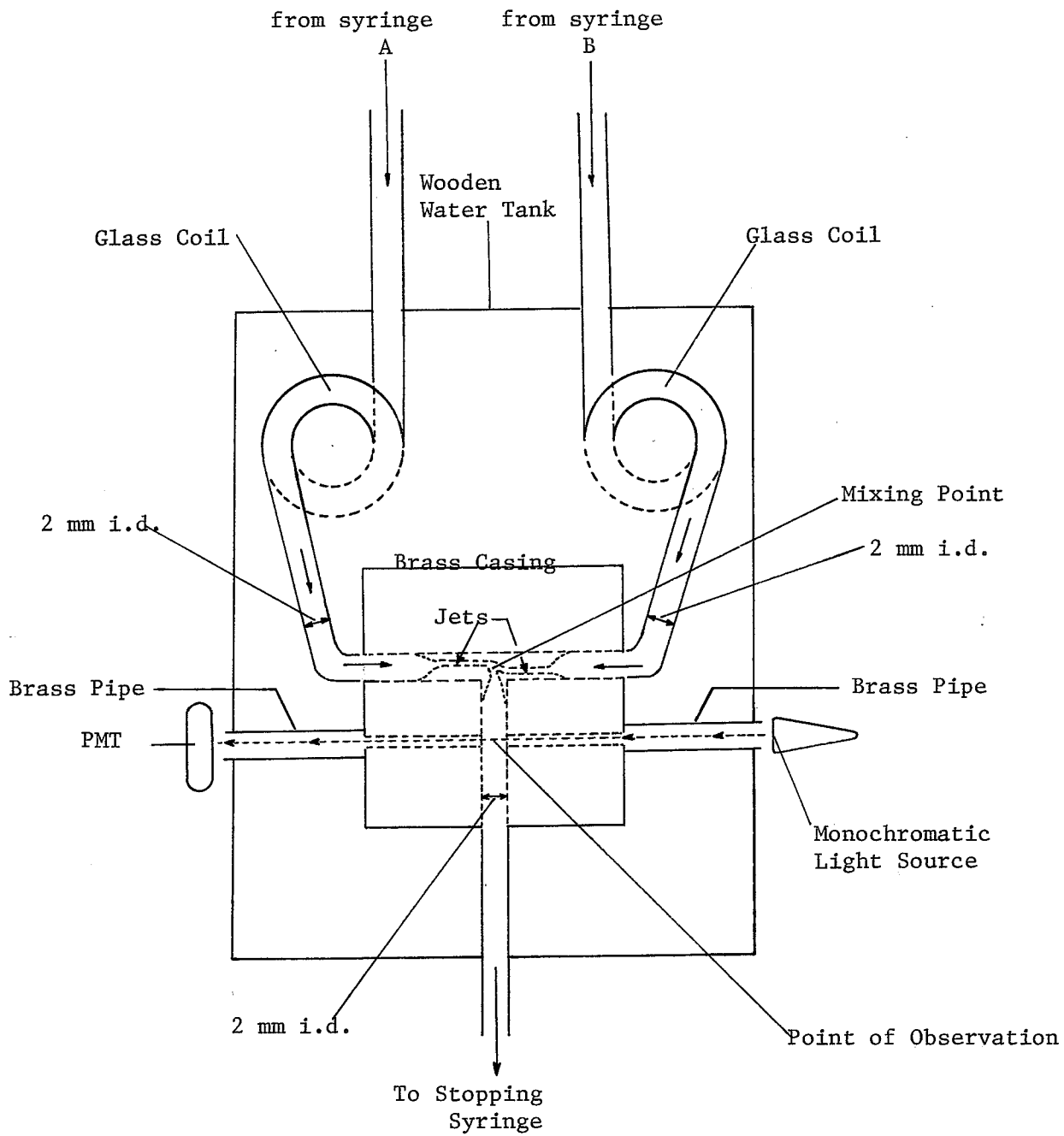
HV - High voltage power supply (Kepco Model ABC-1000).

* The $\pm 15V$ output signal from the high performance kinetic photometer can be coupled to any low voltage analog device for fast data process.

effective temperature can be monitored. Under normal operating conditions, the average flow velocity is 12 ml/sec, and, depending on the volume of reactants delivered, the transport time, which is the interval during which the reactants flow, ranges from 6.6 msec. to 20 msec.. The corresponding "dead" time of the 10 mm. observation cell at a flow rate of 12 ml/sec is 4 msec..

The kinetic runs at lower pHs (3.3 - 3.85) and the temperature dependent studies were carried out in a "Canterbury" designed stopped-flow apparatus. A detail description of the apparatus can be found in a paper by Caldin, Crooks and Queen⁴⁴. The present apparatus is the same as the one described by these authors except for a few minor adjustments. The driving system is generally the same. Two B-D 2 ml glass driving syringes are fed by reactants in the 10 ml glass reservoirs through three-way teflon taps. These are mounted horizontally on a metal deck which is adjacent to an adjoining thermostat bath (10.5" length x 8.5" width x 9.5" height). Enclosed in the bath are two coils of glass tubing, a mixing chamber, the observation tube and part of the exit tube. Each of the coils is made from about 1 m. of Pyrex tubing of internal diameter 4 mm., and both are mounted vertically to the panel through which the driving syringes entered. The two coils serve two functions, (i) as the effective thermostated internal reservoirs and, (ii) as the connections between the driving syringes and the mixing chamber. Figure 5 is a description of the quartz T-mixer used in the present work. The reactants to be mixed are forced through two side-arms, each leading to a 1/2 mm. jet, slightly offset;

FIGURE 5. The "T-mixer" and observation unit of a
"Canterbury" designed stopped-flow apparatus.



Internal Diameter of the jets = $1/2$ mm

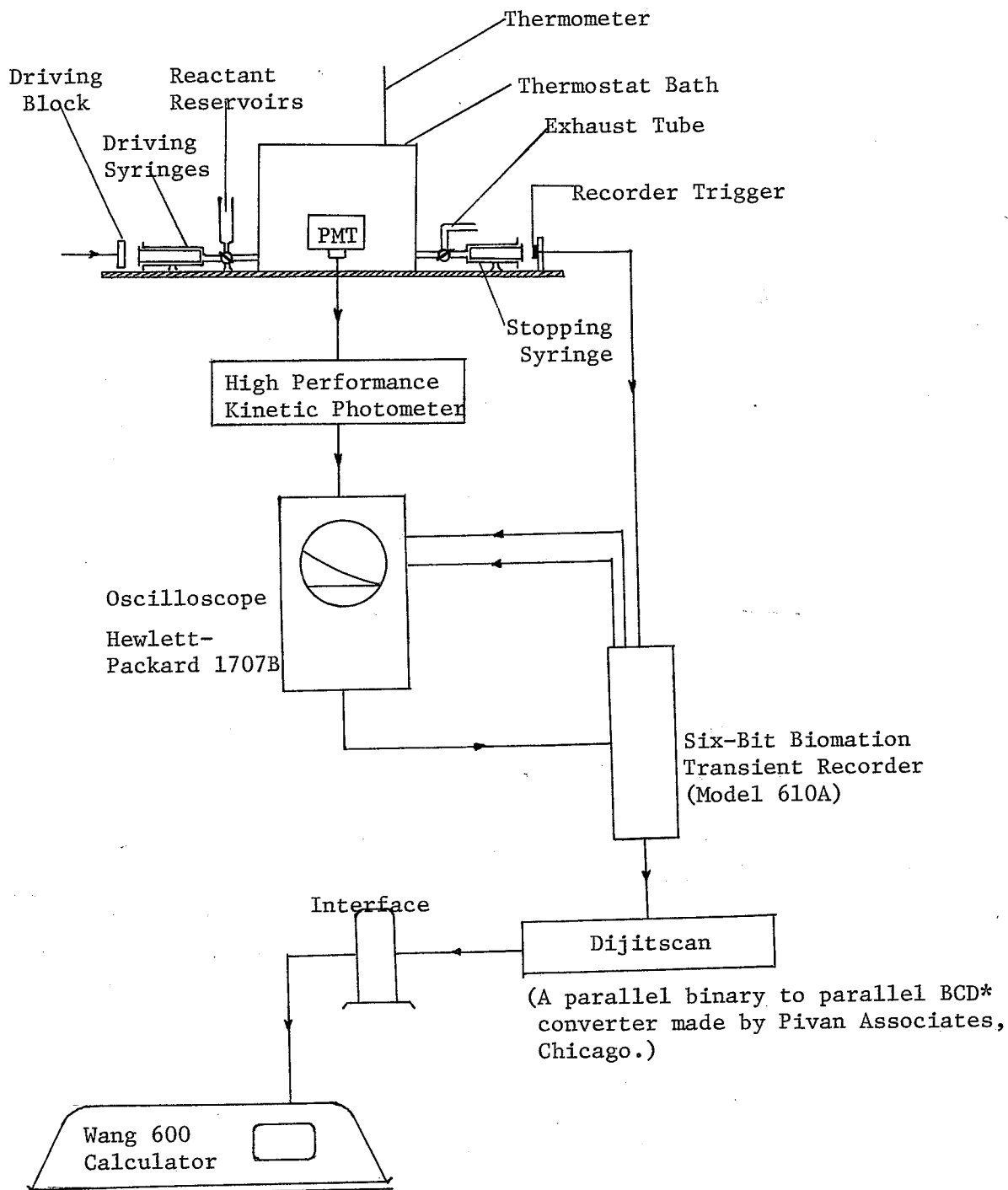
Distance between point of mixing and point of observation = 8 mm

the mixed solution emerges through the observation tube which measures 18 mm. long and has an internal diameter of 2 mm.. The mixing chamber and part of the observation tube are housed rigidly, and protected from stray light, by a brass casing cemented to the bottom of the bath. Spectrophotometric observation is achieved in the manner described by Bennetto and Caldin⁴⁵. Two small circular holes, aligned to receive and transmit an incident beam at 90° to the observation tube, have been drilled, one on each side of the casing. Brass tubes were subsequently fitted to connect these holes with holes cut in the opposite walls of the tank, thus providing a linear passage for the incidence and transmittance of a monochromatic beam of light. The point of observation is approximately 8 mm. from the point of mixing. A deuterium lamp coupled with a Bausch and Lomb high-intensity grating monochromator is the light source used in the present apparatus. The intensity of the transmitted beam is monitored by a photomultiplier mounted at the exit opening of the brass tube. An "on-line" method has been developed to determine the rate constant directly from the signals of the photomultiplier. Details of the computation method will be described in the Result section. The arrangement of the electronic implements involved is schematically depicted in Figure 6.

The flow is stopped by the normal means of a stopping syringe through a three-way tap. The microswitch trigger when closed initiates the input into the memory of a Biomation transient recorder the output signals from the photomultiplier.

The effective temperature range of the present apparatus is at

FIGURE 6. Block diagram of the on-line computation instruments for the "Canterbury" designed stopped-flow apparatus.



BCD* - Binary coded decimal.

least -10° to $+55^{\circ}\text{C}$. Since the mixing chamber and the two glass coil reservoirs are immersed in the thermostat bath, it is expected that the reactants would take up the bath temperature within about 10 mins..

The total observation light path is 2 mm. and the volume of solution from mixing to observation is 0.03 cm^3 . With a driving pressure of 10 lbs. in^{-2} or its manual equivalent, the linear flow velocity is 2.7 m/sec and observation starts 3 msec after mixing. The corresponding dead time under these conditions is 3 msec..

(3) CHEMICALS AND STANDARD SOLUTIONS.

Two substituted salicylic acids were used, 5-Sulphosalicylic acid, reagent grade, supplied by Fisher Scientific Co. and 5-Chlorosalicylic acid, technical grade, supplied by Aldrich Chemical Co.. Both acids were recrystallized twice, the 5-Chlorosalicylic acid from benzene and the 5-Sulphosalicylic acid from triply distilled water. The final products were dried in a vacuum desiccator, and their purities were checked by melting point determinations using a Fisher Johns melting point apparatus. Some information on the acids is listed in Table 5.

TABLE 5

	Crystal description	Melting point	Reference
5-Sulphosalicylic acid	hygroscopic needles (+2H ₂ O)	198-199°C(d)	46
	hygroscopic crystals (+2H ₂ O)	197-198°C(d)	This work
5-Chlorosalicylic acid	Needles from water or ethanol	173-4°C	46
	off-white needles	173-4°C	This work

Both the hydrated and anhydrous salts of sodium acetate were used to prepare the necessary buffer solutions. Anhydrous sodium acetate of reagent grade was supplied by Matheson, Coleman and Bell. At lower hydrogen ion concentrations, hydrated sodium acetate (NaC₂H₃O₂·3H₂O) reagent grade supplied by Shawinigan was used because of the greater solubility of the salt.

Stock sodium perchlorate was prepared from sodium carbonate (reagent grade supplied by MacArthur Chemical Co. Ltd.) and perchloric acid (Baker Analyzed Reagent) and analysed as described by Biedermann⁴⁷.

Be(II) perchlorate was prepared by the following method. A hot solution of BeSO₄·4H₂O (Reagent Grade supplied by Fisher Scientific Company) was treated with sodium hydroxide solution. The precipitate Be(OH)₂ was filtered off, washed several times with triply distilled water and dried on the vacuum line. It was then dissolved in perchloric

acid and re-precipitated with sodium hydroxide. After another series of washing and drying, the purified $\text{Be}(\text{OH})_2$ was used to saturate a hot solution of perchloric acid with heating. The final $\text{Be}(\text{ClO}_4)_2$ solution was stored in a cold room for a few days to equilibrate, and the excess $\text{Be}(\text{OH})_2$ eventually filtered off.

The concentration of the stock $\text{Be}(\text{II})$ perchlorate was determined gravimetrically⁴⁸. $\text{Be}(\text{II})$ was precipitated as the hydroxide and subsequently ignited to the oxide at 1000°C .

Stock perchloric acid (Analysed Reagent) supplied by Baker was standardized⁴⁹ against mercuric oxide using methyl purple as an indicator.

A standard solution of 5-sulphosalicylic acid (10^{-2}M) was prepared by weighing out a calculated amount of the recrystallized acid and dissolving it in triply distilled water.

The standard solutions of $\text{Be}(\text{II})$ perchlorate (10^{-1}M) and perchloric acid (2M) were each prepared from the respective standardized (in moles/gm of stock solution) stock solutions. The necessary quantity of stock solution was weighed out and subsequently diluted to the required volume with triply distilled water.

In the present work, it was necessary to conduct a series of studies on the $[\text{H}^+]$ dependence of the complex formations. Therefore, an effective means of attaining a constant hydrogen ion concentration was necessary. This was accomplished using a suitable acetic acid (acid) - sodium acetate (salt) buffer in the reactant solution. Depending upon the pH desired, the ratio of acid to salt comprising the buffer was

calculated from the Henderson-Hasselbach equation, i.e.

$$\text{pH} = \text{pK}_a + \log \frac{C_b}{C_a} \quad (22)$$

Experimentally, the buffer used was generated internally. Instead of mixing directly C_a moles of acetic acid with C_b moles of sodium acetate, the equivalent solution was achieved by simply mixing C_a moles of perchloric acid with $(C_a + C_b)$ moles of sodium acetate. With this method, C_a moles of sodium perchlorate was produced internally along with the desired buffer. With C_a for HClO_4 set at 2M, a value of C_b was calculated via expression (22) for each pH level desired. The corresponding standard solution of sodium acetate was prepared according to the sum of $(C_a + C_b)$. In a 3M NaClO_4 medium, the pK_a value of acetic acid was reported to be 5.014⁵⁰.

(4) KINETIC RUNS.

Reactants for the kinetic runs were prepared from the standard solutions. Small quantities of the standard solutions (HClO_4 , $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$, Be(II) or 5-sulphosalicylic acid) involved were mixed and diluted according to the concentrations and pH's desired. Typical examples of the preparations are as follows.

For a 100 ml of $3 \times 10^{-3}\text{M}$ Be(II) at $\text{pH} = 3.5$, 3 ml of standard 10^{-1}M $\text{Be(ClO}_4)_2$, 10 ml of standard 2M HClO_4 and 10 ml of standard $\text{NaC}_2\text{H}_3\text{O}_2$ for $\text{pH} = 3.5$ were pipetted into a clean 100 ml volumetric

flask. The total ionic strength of the medium, μ , was adjusted to 3M by the addition of an appropriate quantity of the analysed NaClO_4 . The rest of the volume was made up with triply distilled water.

A 100 ml of $1 \times 10^{-4}\text{M}$ 5-sulphosalicylic acid (SSA) was prepared in the same manner described for Be(II) , except for the substitution of the 3 ml of standard 10^{-1}M $\text{Be(ClO}_4)_2$ with 1 ml of standard 10^{-2}M 5-sulphosalicylic acid.

In the case of 5-chlorosalicylic acid (5Cl-SA), the reactant solution was prepared by a slightly different procedure. Owing to its extremely low solubility in water, a standard solution of the acid at reasonable concentrations was impossible to prepare. Therefore, the alternative practice was to dissolve the prescribed amount of solid acid directly in 10 ml of standard sodium acetate, which was slightly basic. The perchloric acid and sodium perchlorate were added to the solution only after the acid had completely dissolved.

It is generally acknowledged that the use of vacuum-degassed solutions eliminate all the problems which are caused by air bubbles. Nevertheless, the reactants used in this work were not degassed. Experiments have shown that, with the apparatus purged carefully with fresh reactants to remove all traces of air, there were no symptoms of an interference of the spectrophotometric detection system by an air bubble.

After the reactants were loaded into the driving syringes (Aminco-Morrow) or the internal glass coil reservoirs in the case of the "Canterbury" apparatus, a period of incubation was allowed for the

system to reach thermal equilibrium before the kinetic runs were started. Approximately fifteen minutes was enough for the runs at 25°C and a minimum of 90 minutes was required for the runs at elevated or depressed temperatures. Six kinetic runs could be done with each filling of the driving syringes. The resolving power of the spectrophotometric detection system was adjusted by off-setting the output signals from the photomultiplier. Details of the procedure are described in the Result section (D)(1). The result of the first run was generally considered to be slightly erroneous because diffusion could have occurred during incubation. An average of ten to fifteen runs were done for each concentration of beryllium and hydrogen ion to be measured.

Generally, both the preparation of the reactants and the subsequent kinetic experiments were carried out in the same day, particularly with studies which were above pH 4.

(D) RESULTS

(1) TREATMENT OF THE DATA.

Many complex formations with an overall equation of



obey the following kinetics,

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt} = k_1[A][B] - k_{-1}[C] \quad (24)$$

If one of the reactants (e.g. B) is present in at least a tenfold excess, the concentration of that reactant can be considered as constant through a run, and the reaction is said to be pseudo-first order. The rate expression (Appendix A) is as follows,

$$\frac{d[C]}{dt} = k_{\text{obs}} ([C]_{\text{eq.}} - [C]_t) \quad (25)$$

where

$$k_{\text{obs}} = (k_1/K_1 + k_1[B]) \quad (26)$$

and

$$K_1 = \frac{k_1}{k_{-1}} = \frac{[C]_{\text{eq.}}}{[A]_{\text{eq.}}[B]_{\text{eq.}}} \quad (27)$$

$[C]_{\text{eq.}}$ and $[C]_t$ are the concentrations of the product C at equilibrium and at time t. Expression (25) can be integrated and rearranged to give expression (28) which describes the change of concentration of product

C in a time t.

$$([C]_{eq.} - [C]_t) = ([C]_{eq.} - [C]_o)e^{-k_{obs}t} \quad (28)$$

$[C]_o$ is the initial concentration of product C. The value of k_{obs} is readily evaluated using the following equation (29),

$$k_{obs} = \frac{1}{t} \ln \frac{([C]_{eq.} - [C]_o)}{([C]_{eq.} - [C]_t)} \quad (29)$$

The theory of light absorption by an absorbing species makes spectrophotometry a very convenient method of following concentration changes. The concentration of the absorbing species $[C]$ is related to the absorbance (A), which is a ratio of the intensities of the radiation transmitted through the absorbing medium (I) and the radiation incident upon that medium (I_o).

$$A = \log \frac{I_o}{I} = \text{constant} \times [C] \quad (30) (a)$$

Therefore,

$$[C]_t = \frac{1}{\text{constant}} \log \frac{I_o}{I_t} \quad (30) (b)$$

$$[C]_{eq.} = \frac{1}{\text{constant}} \log \frac{I_o}{I_{eq.}} \quad (30) (c)$$

and $[C]_o = 0. \quad (30) (d)$

In terms of expressions (30)(b), (c) and (d), equation (29) can be rewritten in the form of,

$$\log(\log I_o/I_{eq.} - \log I_o/I_t) = \text{KONSTANT} - k_{obs} t/2.303 \quad (31)(a)$$

or

$$\log \log (I_t/I_{eq.}) = \text{KONSTANT} - k_{obs} t/2.303 \quad , \quad (31)(b)$$

where

$$\text{KONSTANT} = \log \log (I_o/I_{eq.}) \quad . \quad (31)(c)$$

If the values of I_o , $I_{eq.}$ and I_t at various times t are known, k_{obs} may be readily evaluated by a standard linear regression programme via equation (31)(a).

The intensity of the transmitted beam is generally monitored by a photomultiplier. The output signal is amplified and converted to a potential which is applied to the y-axis of the oscilloscope. Consequently, d_t , the displacement of the oscilloscope trace along the y-axis from the 0% transmittance line at any time t , is directly proportional to I_t , the intensity of light transmitted by the absorbing solution at the same time. The following relationships are established,

$$\frac{I_o}{I_t} = \frac{d_o}{d_t} \quad (32)(a)$$

$$\frac{I_o}{I_{eq.}} = \frac{d_o}{d_{eq.}} \quad (32)(b)$$

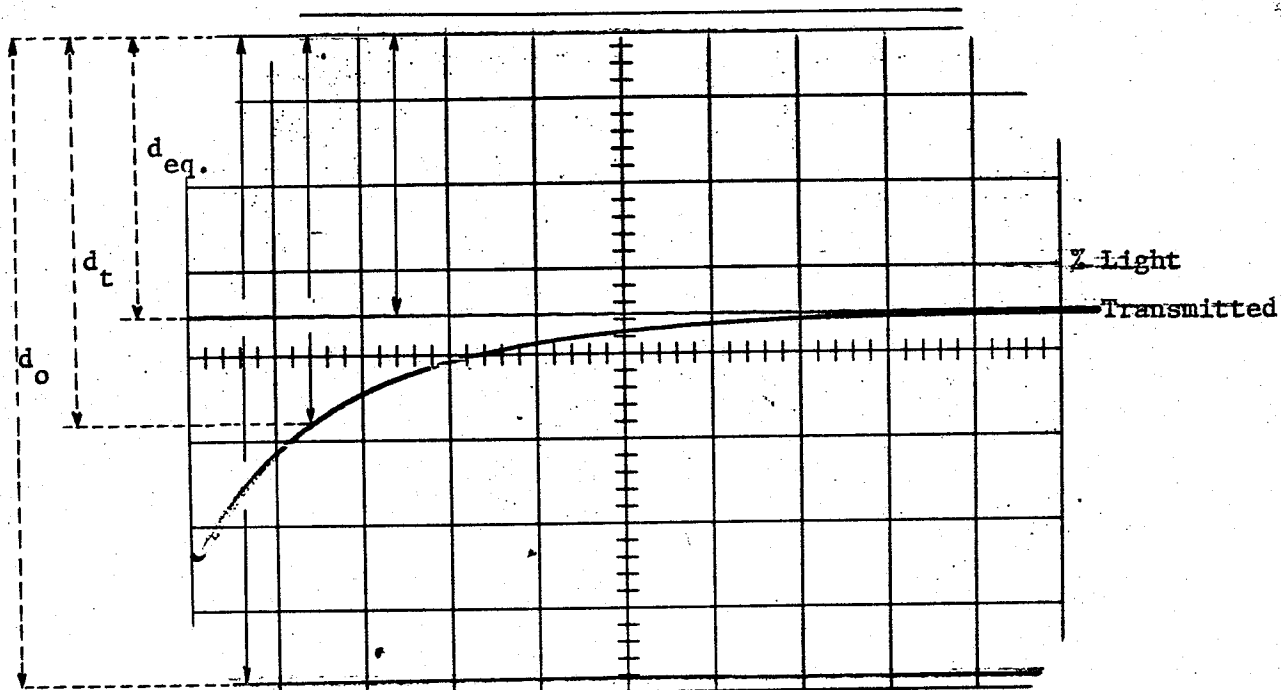
For computations which are based upon expression (31)(a), the quantities I_o , I_{eq} and I_t can be conveniently substituted by the corresponding d_o , d_{eq} and d_t values.

At pH's 3.5, 4.0, 4.5, 5.0 & 5.5, the formation of beryllium-5-Sulphosalicylate and beryllium-5-Chlorosalicylate were followed by the "Aminco-Morrow" stopped-flow apparatus. Typical traces of a complete kinetic run are shown in Figures (7)(a) & (b). The pictures were photographed by a Tektronix oscilloscope (CRO) camera using Polaroid Projection film type 46-L (continuous tone). Each negative was then projected onto a graph paper by a Kodak overhead enlarger, and the magnified image was drawn on the paper. Experimentally, the displacement d_o (in mm.) was obtained with the electronics adjusted such a way that, (i) with the shutter closed, a 0% transmittance line was traced across the top of the oscilloscope, (ii) with triply distilled water in the observation cell, and the shutter opened, a 100% transmittance line was traced across the bottom of the oscilloscope. The result of such stipulations was that only a relatively low voltage could be applied to amplify the signal from the photomultiplier. In order to establish the value of d_{eq} , a kinetic run of the reaction was performed and allowed to reach an equilibrium under identical operating conditions. The displacement between the transmittance line at time $t = \infty$ and the dark current line, d_{eq} , was measured and recorded in millimeters along with d_o . The resolution of the trace (an exponential decay) was severely limited by the insufficient amplification, and therefore, was not used

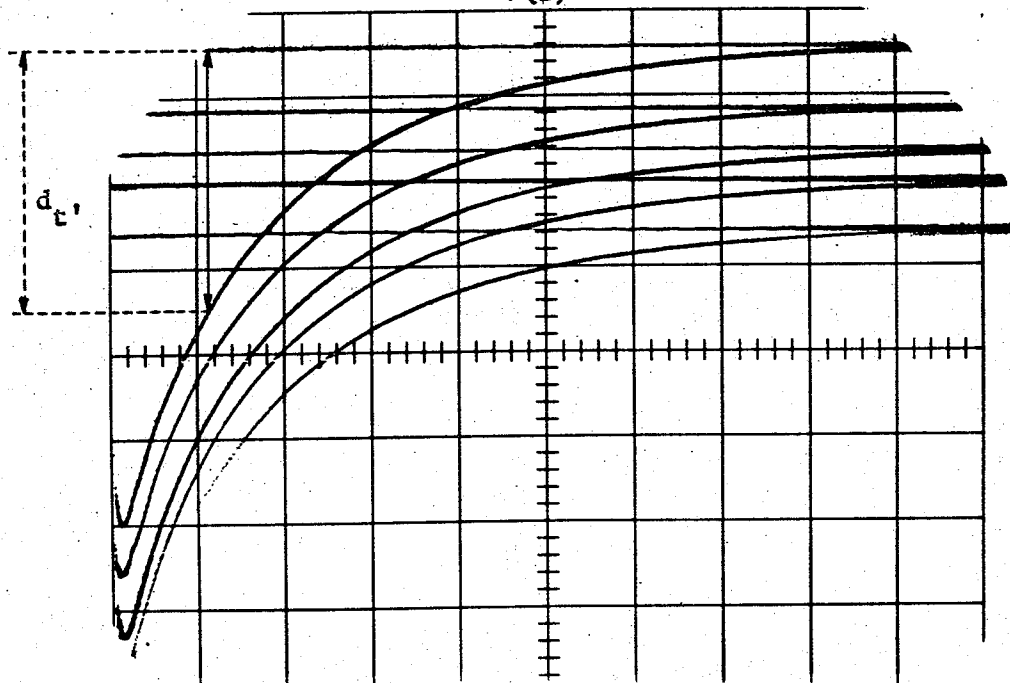
FIGURE 7(a). A typical example of a kinetic trace before magnification.

FIGURE 7(b). Traces of several "magnified" kinetic runs.

7(a)



7(b)



for the measurements of the d_t values.

The magnified traces in Figure (7)(b) were obtained through an appropriate increase in the amplification of the signal from the photomultiplier. This was achieved by a combination of adjusting the "off-set" of the kinetic photometer and increasing the voltage supplied to the oscilloscope. A magnification factor (M) was calculated from the total increase in amplification. From a suitable point chosen near the beginning of the trace, values of d_t' (in mm.) were measured at regular 10 mm intervals along the time base. Generally, at least three half-lives were measured, i.e. the last value of d_t' measured was one-tenth in magnitude of the first value. In order that the set of d_t' values could be used directly in the computation of the pseudo first-order rate constant k_{obs} , values of d_o and d_{eq} were converted into the respective d_o' and d_{eq}' :

$$d_o' = d_o \times M \quad (33)(a)$$

$$d_{eq}' = d_{eq} \times M \quad (33)(b)$$

A computer programme written in FORTRAN (Appendix B) was used in the final analysis of the data. The programme was basically an attempt to fit a best straight line for the plot of $\log \log (d_t'/d_{eq}')$ against t via a linear regression. (A sample of the data inputs is given in Appendix B.)

The print-out from the computer consists of principally, (i) a tabulation of the time measured in msec., (ii) a tabulation of the

values of $\log \log (d_t'/d_{eq}')$, (iii) the half-life of the reaction in msec., and (iv) the pseudo first-order rate constant k_{obs} in sec^{-1} .

Rate constants of the kinetic runs performed with the "Canterbury" stopped-flow apparatus were speedily evaluated by an on-line computation method developed by Queen et. al.⁵¹. The theoretical basis of the method is still based upon expressions (30) and (31). Consider expression (30). Since the output of the photomultiplier is directly proportional to the intensity of the incident beam, the absorbance can also be expressed in terms of the voltages generated by the photomultiplier.

$$A = \log \frac{V_o}{V} \quad (34)$$

By comparing equation (34) to equation (31)(a), a relationship between the intensities (I) of the radiation transmitted and the output voltages (V) of the photomultiplier is developed,

$$\frac{I_o}{I_t} = \frac{V_o}{V_t} \quad (35) (a)$$

$$\frac{I_o}{I_{eq}} = \frac{V_o}{V_{eq}} \quad (35) (b)$$

The set-up of the present apparatus has been described in detail by Queen et. al.⁵¹. The signal from the photomultiplier was fed to both an oscilloscope for display and a six bit Biomation transient recorder (model 610A) for storage. Simultaneously with the stoppage of

the flow, a switch was closed, thereby supplying the necessary voltage for triggering the recorder. A "Dijitscan" unit (made by Pivan Associates, Chicago), which is essentially a parallel binary to parallel binary coded decimal converter, was coupled to the transient recorder. Finally, a Wang 600 calculator was suitably interfaced with the output of the "Dijitscan". Signals from the output of the interface were processed by the calculator using two programmes (Appendix C) stored on magnetic tape cassettes.

According to equations (35)(a) and (b), the intensities (I) in expression (31)(a) or (b) can be rewritten in terms of the corresponding voltage outputs (V) and subsequently used to evaluate the value of k_{obs} . However, even in the case of the simpler equation (31)(b), the calculations require a knowledge of the values of V_{eq} and V_t at various times t . Therefore, it is necessary to arrange for both the base line voltage corresponding to 0% transmittance, and the transient signals of a kinetic run to be within the voltage range of the recorder. To operate under such conditions, it was demonstrated in Figure (7)(a) that the spread of the transient signals would cover only a small part of the scale, and consequently, suffered a considerable loss in resolution. This is not a serious problem if the voltage resolution of the recorder is at least 0.1%, e.g. a ten-bit instrument. Unfortunately, the voltage resolution of the six-bit Biomation unit is short of the 0.1%. It is therefore necessary to amplify the transient signal and thus moving the 0% transmittance baseline off-scale. The amount of off-set which was given to the baseline must be known and stored in the memory of the

calculator so that it can be added during the calculations to the values obtained from the transient recorder. Generally, if the offset controls of an apparatus are properly calibrated, an accurate value of the total offset of any signal may be determined directly from the settings of these controls. Queen et. al.⁵¹ have reported a calibrated offset using a regulated D.C. voltage suitably divided by an accurate 10 turn potentiometer and applied to a differential amplifier in opposition to the signal from the photomultiplier.

For kinetic runs which have small transmittance change, ΔT up to 5% or so, the absorbance and transmittance changes are linearly related to within 3%,

$$A \propto \Delta T \quad (36)$$

Therefore, for most purpose, the voltage output from the photomultiplier can be fed directly to the transient recorder and the calculations carried out directly. Under this circumstance, it is not necessary to establish the baseline voltage at 0% transmittance.

Experimentally, a kinetic trace was recorded under the optimum resolving power of the recorder. The signal offset and the voltage amplification were adjusted so that the maximum transmittance change just fell within the voltage range of the recorder. The time base was adjusted to be at least ten half-lives in total so that V_{eq} could be recorded.

An averaged V_{eq} value was calculated and stored in the memory by a preliminary programme in the calculator. Generally, the last 20 to 40 of the total 256 available storing points in the transient

recorder were used in the calculation of this average V_{eq} value.

The k_{obs} value was evaluated by a second programme which was loaded into the memory of the calculator from the magnetic tape. The programme was essentially a linear regression based upon expression (31)(b). (A typical example of the inputs for both programmes is given in Appendix C.)

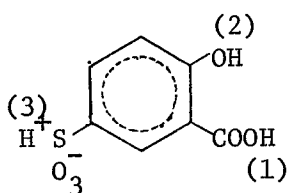
By varying the location of the starting point, different segments of the decay curve were sampled and used in the calculation of k_{obs} . Provided that the trace was satisfactory, the k_{obs} values computed from different starting points should be the same within experimental error. The final k_{obs} in the output was the average of 15 to 20 calculated values.

The output from the second programme included a tabulation of all the k_{obs} values calculated and a final average of these values.

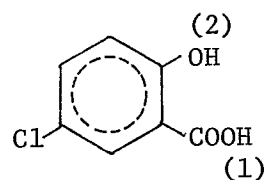
To ensure that there was no discrepancy between the "Aminco-Morrow" and the "Canterbury" apparatus, kinetic runs of the formation of both complexes at pH = 3.5 were performed and interpreted by both methods. The results were found to be the same within experimental error. In the present work, kinetic runs which were conducted at pH's below 4.0 could be followed by either of the two methods. However, at pH's above 4.0, the use of the present on-line computation programme described was not recommended since the total transmittance change of the reaction was in excess of 5%.

(2) THE DEPENDENCE OF THE FORMATION RATE ON BERYLLIUM AND HYDROGEN ION CONCENTRATIONS.

The structures of the ligands, 5-sulphosalicylic acid (I) and 5-chlorosalicylic acid (II) are depicted as follows,



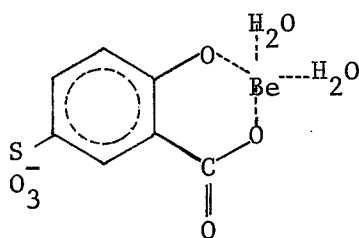
(I)



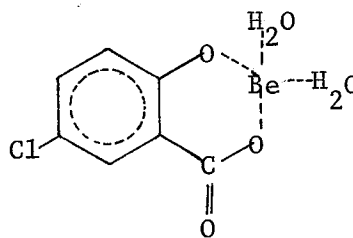
(II)

Owing to the high dissociation constant of the sulphonic group, proton H(3) of the ligand 5-sulphosalicylic acid is expected to be dissociated from the SO_3^- group at all times in solution.

The ligands (I) and (II) will react with Be(II) to form the corresponding complexes (III) and (IV),



(III)



(IV)

Closure of the chelate ring in each complex involves only the salicylic acid structure of the ligands, i.e. the carboxyl (COOH) and hydroxyl (OH) group of the benzene ring. The protons H(1) and H(2) are lost either prior to or immediately after the formation of the complex. It is not unreasonable to assume that the kinetics and mechanisms are the same for the formations of these complexes. Any difference in the formation rates may be attributed to the effects of the different substituent groups (SO_3^- vs Cl) on the salicylic acid structure. Generally speaking, for purpose of elucidating the kinetics of the complex formation, ligands (I) and (II) can be treated the same.

5-sulphosalicylic acid in solution can exist in various proportions of H_2SSA^- , HSSA^{2-} , SSA^{3-} , depending upon the pH of the solution. The dissociations of protons H(1) and H(2) are governed by the following relationships,



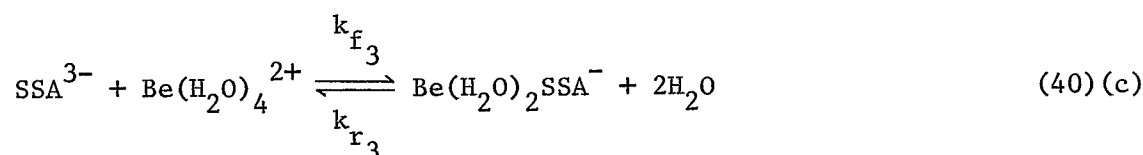
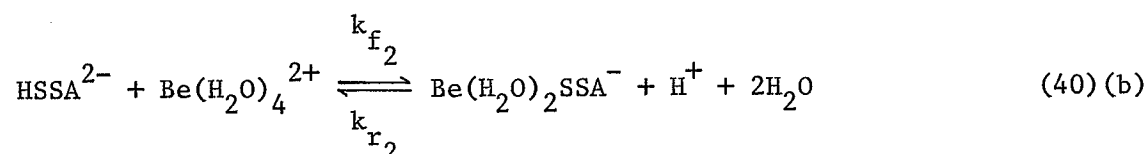
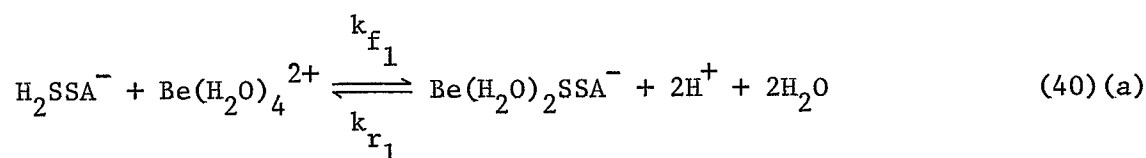
$$K_{2A} = \frac{[\text{H}^+][\text{HSSA}^{2-}]}{[\text{H}_2\text{SSA}^-]} \quad (38) (b)$$



$$K_2 = \frac{[\text{HSSA}^{2-}]}{[\text{SSA}^{3-}][\text{H}^+]} \quad (39) (b)$$

K_{2A} , K_2 are the dissociation and association constants respectively.

Conceivably, it is possible for all three species of the ionized acid to react with Be(II) and form the complex BeSSA. Complexation can proceed via the following pathways :



Assuming that the reverse reactions are slow compared to the forward reactions, the rate of complex formation can be written as,

$$\frac{d[\text{BeSSA}^-]}{dt} = [\text{Be}^{2+}]_{\text{total}} \{ k_{f1} [\text{H}_2\text{SSA}^-] + k_{f2} [\text{HSSA}^{2-}] + k_{f3} [\text{SSA}^{3-}] \} \quad (41)$$

It is obvious from equation (41) that the formation rate of the complex will have a definite dependence upon the concentration of Be(II). This conclusion is further supported by equations (25) and (26) if the reaction was conducted under a pseudo-first order condition, i.e. the concentration of Be(II) was presented in excess at least ten-fold of the ligand concentration. According to equation (26), the observed rate constant of the complex formation is a function of the

concentration of Be(II).

$[\text{Be}^{2+}]_{\text{total}}$ is not the only variable in the rate expression (41).

Rate of formation of the complex is also governed by the proportions of H_2SSA^- , HSSA^{2-} and SSA^{3-} present in the solution. Since the proportions of H_2SSA^- , HSSA^{2-} , and SSA^{3-} vary, depending upon the pH, it is then logical to assert that the formation rate of the complex will be dependent upon the pH as well.

In light of the $[\text{Be}^{2+}]_{\text{total}}$ and pH dependence of the formation rates, a series of experiments, which included studies on both variables, was performed. Kinetic runs were conducted at eight different pH levels from 3.3 - 5.5. At each pH level, studies were conducted with at least five or six different concentrations of Be(II) reacting with a fixed concentration of the ligand, generally one-tenth of the lowest $[\text{Be}^{2+}]_{\text{total}}$ used. The reactions at lower pH values, i.e. 3.3, 3.5, 3.65, & 3.8, were followed by the "Canterbury" apparatus connected with an "on-line" computation set-up. At the higher pH levels, i.e. 4.0, 4.5, 5.0, & 5.5, due to larger transmittance changes, the reactions were investigated with the more suitable "Aminco-Morrow" stopped-flow apparatus.

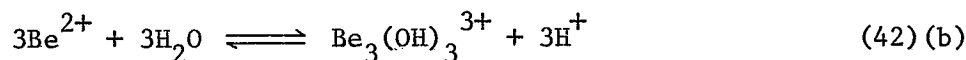
At pH = 3.3, formation of the beryllium salicylate complexes could not be detected by ultraviolet spectrophotometry unless the complex was presented at a relatively high concentration. This was achieved by increasing the otherwise low concentrations of Be(II) ($1.0 \times 10^{-3}\text{M}$ to $3.5 \times 10^{-3}\text{M}$) by a factor of 10, thus bringing the

concentrations to a range of $1.0 \times 10^{-2} \text{M}$ to $3.5 \times 10^{-2} \text{M}$. For the rest of the seven pHs, low concentrations of Be(II) were essential in an attempt to curb the hydrolysis of the cation, which can be quite extensive at high concentrations. The effort was rather successful at pH levels below 4. However, at pH 4 and above, the effort was futile unless $[\text{Be}^{2+}]_{\text{total}}$ was reduced to such a level that proper measurements on the subsequent formation of the beryllium complex was not feasible. In the present work, it was hoped that the kinetic runs conducted at pH's 4.0, 4.5, 5.0, & 5.5, despite extensive hydrolysis of the cation, would provide some insights into the effect of hydrolysis on the formation rate.

According to Kakihana & Sillen⁵², the main product from the hydrolysis of Be^{2+} is $\text{Be}_3(\text{OH})_3^{3+}$, a polynuclear species. The equilibrium constant,

$$\beta_{33} = \frac{[\text{Be}_3(\text{OH})_3^{3+}][\text{H}^+]^3}{[\text{Be}^{2+}]^3}, \quad (42) (a)$$

of the reaction



is equal to 2.187×10^{-9} .

The experimental value of $[\text{Be}^{2+}]_{\text{total}}$ can be written as,

$$[\text{Be}^{2+}]_{\text{total}} = [\text{Be}^{2+}]_{\text{eff.}} + 3[\text{Be}_3(\text{OH})_3^{3+}] \quad (43) (a)$$

where $[\text{Be}^{2+}]_{\text{eff.}}$ is the concentration of the unhydrolysed cation. By substituting equation (42)(a) into (43)(a), (43)(a) can be rewritten in terms of β_{33} and $[\text{Be}^{2+}]_{\text{eff.}}$.

$$[\text{Be}^{2+}]_{\text{total}} = [\text{Be}^{2+}]_{\text{eff.}} \left\{ 1 + 3\beta_{33} \frac{[\text{Be}^{2+}]_{\text{eff.}}^2}{[\text{H}^+]^3} \right\} \quad (43)(b)$$

or

$$[\text{Be}^{2+}]_{\text{eff.}} = [\text{Be}^{2+}]_{\text{total}} / \left\{ 1 + 3\beta_{33} \frac{[\text{Be}^{2+}]_{\text{eff.}}^2}{[\text{H}^+]^3} \right\} \quad (43)(c)$$

With equation (43)(c), concentrations of the unhydrolysed cation, $[\text{Be}^{2+}]_{\text{eff.}}$, at each pH were calculated by successive approximations.

$[\text{Be}^{2+}]_{\text{total}}$ was used as the first $[\text{Be}^{2+}]_{\text{eff.}}$ input for the initial approximation calculation.

The wavelengths, 250 mμ and 253 mμ, were chosen for the observations of the respective BeSSA^- and Be5Cl-SA complex formations. A partitioned cuvette (2 compartments) was used to establish the transmittances of the reactants before and after the complexation. In Figure 8, UV spectrum (A) was recorded before the reaction, with equal volumes of the reactants (Be(II) , SSA) occupying the separate compartments. After shaking the cuvette gently for a minute, reaction was completed, and spectrum (B) was recorded. At the chosen wavelength 250 mμ, the total transmittance change is approximately 5%. Similar spectra of the reactants Be(II) and 5Cl-SA are shown in Figure 9. The

FIGURE 8. UV spectra of the reactants before (A) and after (B) the BeSSA^- complex formation.

Conditions under which the spectra were recorded:

$\text{pH} = 3.5$

$[\text{Be}^{2+}] = 6 \times 10^{-3} \text{ M}$ & $[\text{SSA}] = 2 \times 10^{-4} \text{ M}$.

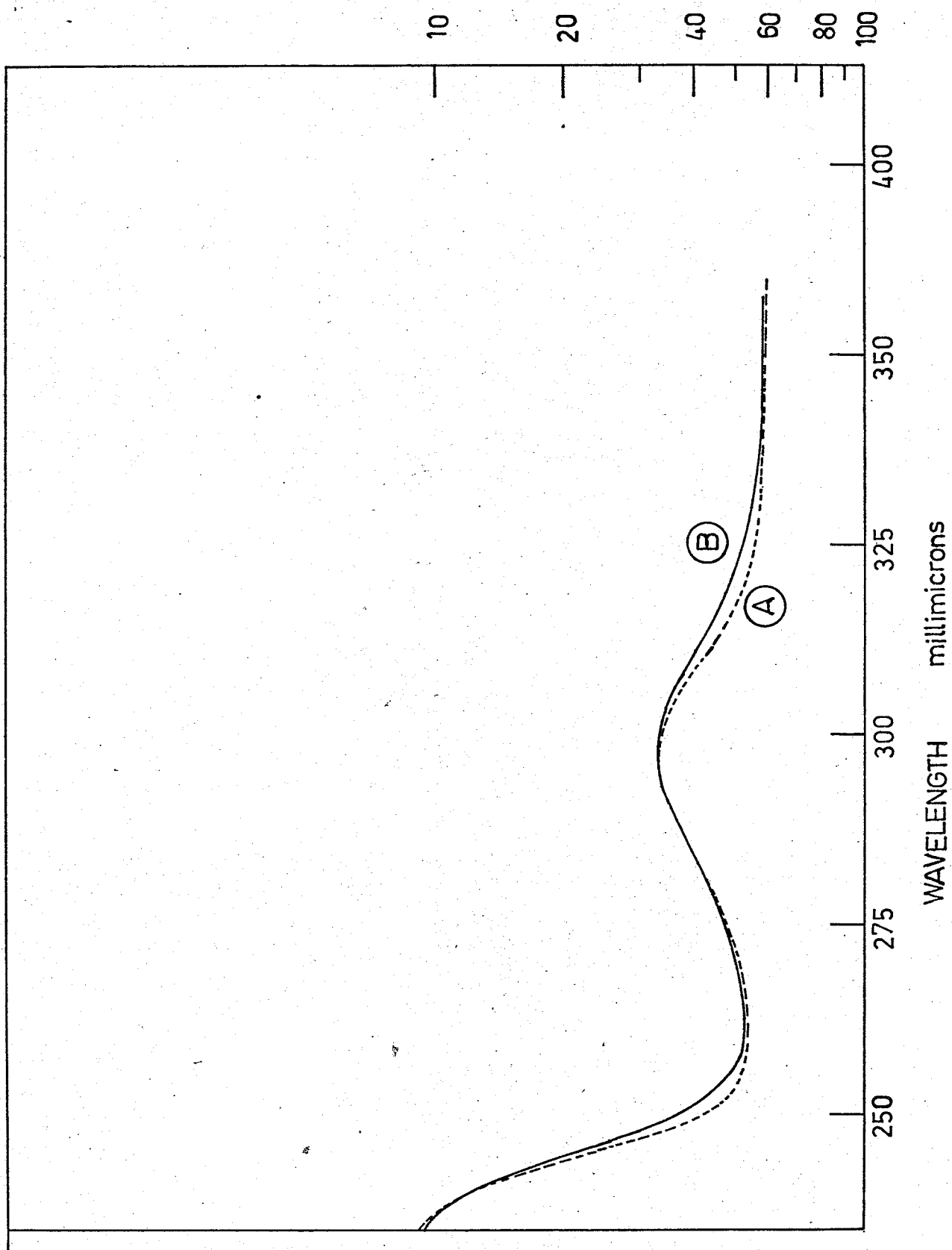
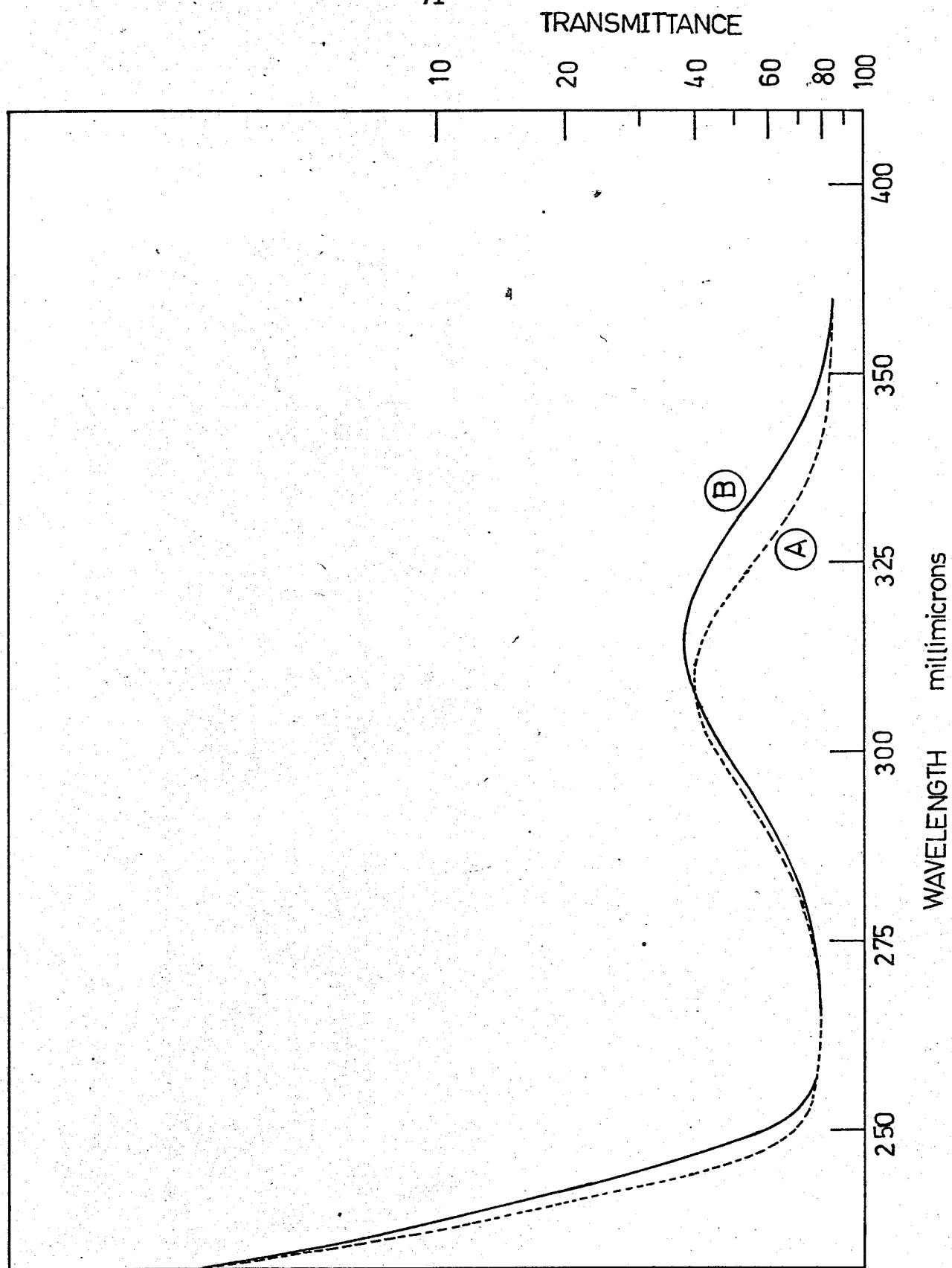


FIGURE 9. UV spectra of the reactants before (A) and after (B) the Be5Cl-SA complex formation.

Conditions under which the spectra were recorded:

pH = 3.5

$[\text{Be}^{2+}] = 6 \times 10^{-3} \text{ M}$ & $[\text{5Cl-SA}] = 2 \times 10^{-4} \text{ M}$.



total transmittance change at 253 mμ is also approximately 5%.

Generally, the UV method was more sensitive for detecting the Be5Cl-SA complex compared to the BeSSA⁻ complex.

The observed rate constants of the formations of both complexes, BeSSA⁻ and Be5Cl-SA, are listed in Table 6 & Table 7 together with values of the calculated $[\text{Be}^{2+}]_{\text{eff.}}$.

(3) DEPENDENCE OF THE FORMATION RATE ON LIGAND CONCENTRATION.

Complex formation rates of the reactions investigated so far were assumed to be pseudo first-order in $[\text{Be}^{2+}]_{\text{total}}$. Experimentally, the concentration of Be^{2+} in each kinetic run was kept in large excess compared to that of the ligand. This is, of course, a kinetic "trick" used to eliminate the complexity of second-order kinetics. Therefore, it is necessary to verify if the concentration ratios of (Be^{2+} to ligand) chosen indeed led to valid pseudo first-order kinetic values.

The set of Be-SSA⁻ experiments at pH 3.5 (as listed in Table 6), was reported with the SSA concentration doubled from 2×10^{-4} M to 4×10^{-4} M. The results are tabulated in Table 8. If the k_{obs} values obtained at the lower ligand concentration agree with the ones obtained at the higher concentration within experimental uncertainties, then, the pseudo first-order relationship is true in both cases. Theoretically, the value of k_{obs} will be doubled with the doubling of the ligand concentration under kinetic conditions which are not pseudo first-order in $[\text{Be}^{2+}]_{\text{total}}$.

TABLE 6

KINETIC DATA FOR BeSSA^- FORMATION - A $[\text{H}^+]$ RATE DEPENDENCE STUDY.

pH	$k_{\text{obs}} \text{ sec}^{-1}$	$[\text{Be}^{2+}]_{\text{total}} \times 10^3 \text{ M}$	$[\text{Be}^{2+}]_{\text{eff.}} \times 10^3 \text{ M}$	$[\text{SSA}] \times 10^4 \text{ M}$
3.30	3.03(0.02)	10	9.95	14
	3.63(0.02)	15	14.83	"
	4.13(0.02)	20	19.61	"
	4.65(0.03)	25	24.25	"
	5.18(0.03)	30	28.75	"
	5.68(0.03)	35	33.10	"
3.50	1.33(0.01)	1	1	1.50
	1.45(0.01)	2	2	"
	1.56(0.01)	3	2.99	"
	1.69(0.01)	4	3.99	2
	1.83(0.01)	5	4.97	"
	1.91(0.02)	6	5.96	"
	2.06(0.02)	7	6.93	"
	2.12(0.02)	8	7.90	"
3.65	1.02(0.002)	1	1	1.50
	1.07(0.001)	1.50	1.50	"
	1.12(0.003)	2	2	"
	1.18(0.001)	2.50	2.49	"
	1.26(0.002)	3	2.98	"

TABLE 6 - Continued.

pH	$k_{\text{obs}} \text{ sec}^{-1}$	$[\text{Be}^{2+}]_{\text{total}} \times 10^3 \text{ M}$	$[\text{Be}^{2+}]_{\text{eff.}} \times 10^3 \text{ M}$	$[\text{SSA}] \times 10^4 \text{ M}$
3.65	1.32(0.001)	3.50	3.48	1.50
3.80	0.76(0.002)	1	1	1.40
	0.81(0.001)	1.50	1.49	"
	0.87(0.003)	2	1.99	"
	0.94(0.003)	2.50	2.47	"
	1.02(0.003)	3	2.96	"
	1.07(0.002)	3.50	3.43	"
4.00	0.43(0.003)	0.80	0.80	2
	0.57(0.003)	2	1.95	"
	0.69(0.004)	3	2.85	"
	0.82(0.004)	4	3.67	"
	0.91(0.001)	5	4.43	"
	1.03(0.001)	6	5.11	"
	1.13(0.003)	7	5.75	"
	1.23(0.001)	8	6.33	"
4.50	0.24(0.004)	2	1.41	2
	0.39(0.004)	4	2.09	"
	0.43(0.003)	5	2.33	"
	0.50(0.004)	6	2.55	"
	0.57(0.004)	7	2.74	"
	0.63(0.004)	8	2.90	"

TABLE 6 - Continued.

pH	$k_{\text{obs}} \text{ sec}^{-1}$	$[\text{Be}^{2+}]_{\text{total}} \times 10^3 \text{ M}$	$[\text{Be}^{2+}]_{\text{eff.}} \times 10^3 \text{ M}$	$[\text{SSA}] \times 10^4 \text{ M}$
5.00	0.12(0.001)	2	0.59	2
	0.20(0.004)	4	0.78	"
	0.22(0.001)	5	0.85	"
	0.26(0.001)	6	0.91	"
	0.30(0.003)	7	0.97	"
	0.33(0.002)	8	1.02	"
5.50	0.08(0.001)	2	0.20	2
	0.12(0.001)	4	0.25	"
	0.14(0.001)	5	0.28	"
	0.17(0.001)	6	0.29	"
	0.19(0.001)	7	0.31	"
	0.21(0.002)	8	0.33	"

TABLE 7

KINETIC DATA FOR Be - 5ClSA FORMATION - A $[H^+]$ RATE DEPENDENCE STUDY.

pH	$k_{obs} \text{ sec}^{-1}$	$[Be^{2+}]_{total} \times 10^3 \text{ M}$	$[Be^{2+}]_{eff.} \times 10^3 \text{ M}$	$[5Cl-SA] \times 10^4 \text{ M}$
3.30	4.75(0.02)	10	9.95	8
	5.15(0.02)	15	14.83	"
	5.47(0.02)	20	19.61	"
	5.89(0.01)	25	24.25	"
	6.27(0.01)	30	28.75	"
	6.63(0.02)	35	33.10	"
3.50	2.71(0.01)	1	1	1.50
	2.82(0.01)	2	2	"
	2.93(0.004)	3	2.99	"
	3.04(0.004)	4	3.99	"
	3.13(0.003)	5	4.97	"
	3.22(0.004)	6	5.96	"
3.65	1.90(0.01)	1	1	1.50
	1.96(0.01)	1.50	1.50	"
	2.02(0.01)	2	2	"
	2.07(0.04)	2.50	2.49	"
	2.13(0.04)	3	2.98	"
	2.19(0.01)	3.50	3.48	"
3.80	1.51(0.003)	1	1	1.50
	1.58(0.003)	1.50	1.49	"

TABLE 7 - Continued.

pH	$k_{\text{obs}} \text{ sec}^{-1}$	$[\text{Be}^{2+}]_{\text{total}} \times 10^3 \text{ M}$	$[\text{Be}^{2+}]_{\text{eff.}} \times 10^3 \text{ M}$	$[\text{5Cl-SA}] \times 10^4 \text{ M}$
3.80	1.65(0.003)	2	1.99	1.50
	1.71(0.002)	2.50	2.47	"
	1.77(0.002)	3	2.96	"
	1.85(0.003)	3.50	3.43	"
4.00	1.37(0.01)	4	3.67	2
	1.50(0.01)	5	4.43	"
	1.58(0.01)	6	5.11	"
	1.69(0.02)	7	5.75	"
	1.78(0.003)	8	6.33	"
4.50	0.56(0.004)	4	2.09	2
	0.64(0.01)	5	2.33	"
	0.67(0.01)	6	2.55	"
	0.75(0.003)	7	2.74	"
	0.79(0.01)	8	2.90	"
5.00	0.26(0.002)	4	0.78	2
	0.30(0.01)	5	0.85	"
	0.33(0.001)	6	0.91	"
	0.37(0.004)	7	0.97	"
	0.42(0.003)	8	1.02	"
5.50	0.15(0.001)	4	0.25	2
	0.18(0.002)	5	0.28	"

TABLE 7 - Continued.

pH	$k_{\text{obs}} \text{ sec}^{-1}$	$[\text{Be}^{2+}]_{\text{total}} \times 10^3 \text{ M}$	$[\text{Be}^{2+}]_{\text{eff.}} \times 10^3 \text{ M}$	$[\text{5Cl-SA}] \times 10^4 \text{ M}$
5.50	0.20(0.001)	6	0.29	2
	0.23(0.001)	7	0.31	"
	0.24(0.002)	8	0.33	"

TABLE 8
LIGAND CONCENTRATION DEPENDENCE OF THE
BeSSA⁻ COMPLEX FORMATION AT pH 3.5

pH	k _{obs} sec ⁻¹	[Be ²⁺] _{total} × 10 ³ M	[Be ²⁺] _{eff.} × 10 ³ M	[SSA] × 10 ⁴ M
3.50	1.71(0.01)	4	3.99	4
	1.79(0.01)	5	4.97	"
	1.91(0.02)	6	5.96	"
	2.01(0.03)	7	6.93	"
	2.25(0.04)	8	7.90	"
3.50	1.33(0.01)	1	1	1.50
	1.45(0.01)	2	2	"
	1.56(0.01)	3	2.99	"
	1.69(0.01)	4	3.99	2
	1.83(0.01)	5	4.97	"
	1.91(0.02)	6	5.96	"
	2.06(0.02)	7	6.93	"
	2.12(0.02)	8	7.90	"

The k_{obs} values at pH = 5.5 were very small comparing to the ones at pH = 3.5. Therefore, the k_{obs} values determined were very susceptible to errors caused by experimental uncertainties. Under such circumstances, if the ligand concentration was simply doubled as before (at pH = 3.5), there was a very good chance that the true value of the new k_{obs} would be masked by the experimental uncertainties. In light of this, a new set of experiments which included four different concentrations of ligand (2×10^{-4} M, 4×10^{-4} M, 6×10^{-4} M & 8×10^{-4} M) reacting with a fixed concentration of Be(II) (8×10^{-3} M) was adopted. Results from this set of experiments are listed in Table 9.

(4) DEPENDENCE OF THE FORMATION RATE ON THE HYDROLYSIS RATE OF Be(II).

It is suspected that the hydrolysis rate of the cation Be(II) is much faster than the rate of complex formation. However, it is still necessary to prove experimentally that the overall rate-controlling step is independent of the rate of hydrolysis.

In the previous kinetic runs, each of the reactants was prepared individually buffered, i.e. the pH level was attained before the complex formation. An alternative method of pH control is to have one of the reactants prepared in the acid component (HClO_4) of the buffer with the other reactant in the salt component ($\text{NaC}_2\text{H}_3\text{O}_2$). In this way, the desired pH is attained "instantaneously" upon mixing of the reactants. For the present study, at pH = 5.5, Be(II) was prepared in a solution of HClO_4 (which consisted of twice the amount of HClO_4 normally required to buffer the reactants individually), and therefore,

TABLE 9
LIGAND CONCENTRATION DEPENDENCE OF THE
BeSSA⁻ COMPLEX FORMATION AT pH 5.5

pH	k _{obs} sec ⁻¹	[Be ²⁺] _{total} × 10 ³ M	[Be ²⁺] _{eff.} × 10 ³ M	[SSA] × 10 ⁴ M
5.5	0.21(0.002)	8	0.33	2
	0.27(0.001)	"	"	4
	0.37(0.002)	"	"	6
	0.52(0.01)	"	"	8

should remain completely unhydrolysed. Various concentrations of Be(II) prepared in this fashion were to react with 2×10^{-4} M of SSA in sodium acetate (the quantity of $\text{NaC}_2\text{H}_3\text{O}_2$ used was also doubled accordingly).

The kinetic runs were first followed with the same time base previously used (at pH = 5.5) to observe the complex formation between reactants that were individually buffered. A reaction between each of the different concentrations of Be(II) and SSA was observed. The k_{obs} values are listed in Table 10.

To detect if there were any faster reaction(s), a number of faster time bases ranging from seconds to milliseconds were used to follow the kinetic runs. No reaction with rates in this range was observed. Investigations carried out with slower time bases also produced no result.

Hoffmann, Stuehr and Yeager^{28b} using a pressure-jump method, have reported three relaxation times for 0.04M of beryllium acetate (pH not specified); the values were, $\tau_1 = 15$ msec, $\tau_2 = 200$ msec, and $\tau_3 = 5000$ msec. The results of our work, however, do not show any evidence of such beryllium acetate formations. It rather supports the suggestion of Malik, Srivastava and Thallam³⁶ that acetate anions do not interfere with the progress of a Be(II) reaction. Theoretically, if indeed there was a $\text{Be}^{2+} - \text{CH}_3\text{COO}^-$ reaction, the observed rate constants obtained (at pH = 5.5) by using reactants which were individually buffered (Table 6) and reactants as described in this section (Table 10) should be different. This was not the case, since the two groups of results were the same within experimental uncertainties.

TABLE 10
DEPENDENCE OF BeSSA^- COMPLEX FORMATION RATE ON
THE HYDROLYSIS RATE OF Be(II) .

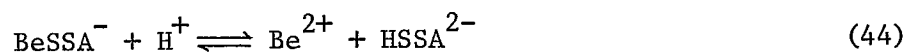
pH	$k_{\text{obs}} \text{ sec}^{-1}$	$[\text{Be}^{2+}]_{\text{total}} \times 10^3 \text{ M}$	$[\text{Be}^{2+}]_{\text{eff.}} \times 10^3 \text{ M}$	$[\text{SSA}] \times 10^4 \text{ M}$
5.5	0.08(0.001)	2	0.20	2
	0.13(0.001)	4	0.25	"
	0.18(0.004)	6	0.29	"
	0.22(0.003)	8	0.33	"

Thus, it was concluded that hydrolysis was very fast and could not have contributed to the rate-determining step.

(5) DEPENDENCE OF THE DISSOCIATION RATE (OF THE COMPLEX) ON THE HYDROGEN ION CONCENTRATION.

Generally, an investigation of the dissociation rates of the complex is favoured since the additional information will most certainly improve the understanding of the reaction pathways.

The BeSSA⁻ complex at each of the three pH levels (5.5, 5.0, & 4.5) was prepared by reacting 4 ml of the 0.1M Be(ClO₄)₂ standard solution with 2 ml of the 0.01M SSA standard solution in a 50 ml volumetric flask. The solution was suitably buffered and the ionic strength adjusted with stock NaClO₄ to 3M. Conceivably, if the dissociation rate of the complex is indeed pH dependent, i.e.



it is then feasible to follow the dissociation simply by bringing down the pH from its original level. Experimentally, this was achieved by injecting a proper quantity of HClO₄ (calculated according to equation (22)) into the prepared complex solution which was buffered at a specific pH. Five different sets of experiment were conducted which included pH changes from pH 5.5 - 3.5, 5.5 - 4.0, 5.0 - 3.5, 5.0 - 4.0, and 4.5 - 3.5. With each set of experiments, only a very slow reaction was observed. The pseudo first-order rate constants obtained are listed in Table 11. The results, it is apparent that the rate of dissociation of the complex is independent of pH.

TABLE 11

DISSOCIATION STUDIES OF THE BeSSA^- COMPLEX BY $[\text{H}^+]$ PERTURBATION.

$\text{pH}_{\text{initial}}$	pH_{final}	$k_{\text{obs}} \text{ sec}^{-1}$
5.5	3.5	0.06(0.003)
5.5	4.0	0.10(0.01)
5.0	3.5	0.04(0.002)
5.0	4.0	0.06(0.002)
4.5	3.5	0.04(0.001)

(6) DEPENDENCE OF THE FORMATION RATE ON TEMPERATURE.

According to the Arrhenius equation,^{1,53}

$$k = A \exp (-E_A/RT) \quad (45)$$

E_A , the temperature independent Arrhenius activation energy of any unimolecular reaction or reactions in solutions, can be determined from the slope of a plot of $\log k$ against $1/T$.

$$d (\log k)/d(1/T) = -E_A/2.303R \quad (46)$$

The quantity A in expression (45) is a constant which is also temperature independent. In transition-state theory, equation (45) is rewritten in the form of the Eyring function⁵³, i.e.

$$k_{(obs)} = \frac{k'T}{h} \exp (-\Delta H^\ddagger/RT) \exp (\Delta S^\ddagger/R) \quad (47)$$

where k' is the Boltzmann constant, h is Planck's constant, and $\Delta H^\ddagger$, $\Delta S^\ddagger$ are the enthalpy and entropy of activation respectively. These activation parameters can be determined from a plot of $\log (k/T)$ against $1/T$.

$$\frac{d \log(k/T)}{d(1/T)} = - \frac{\Delta H^\ddagger}{2.303R} \quad (48) (a)$$

$$\text{Intercept} = \log \frac{k}{h} + \frac{\Delta S^\ddagger}{2.303R} \quad (48) (b)$$

The convenient and direct temperature control of the "Canterbury" stopped-flow apparatus has been described in the EXPERIMENTAL section.

Complex formation of BeSSA^- and Be5Cl-SA at pH levels, 3.5 & 3.8, were followed at four additional temperatures beside 25.1°C , these included 20°C , 30°C , 35°C , & 40°C . Rate constants determined at the various temperatures are listed in Table 12.

TABLE 12
TEMPERATURE DEPENDENCE OF THE RATE OF

pH	Ligand	[Ligand] $\times 10^3$ M	[Be ²⁺] _{total} $\times 10^3$ M	k _{obs} sec ⁻¹
3.30	SSA ⁻	1.40	15	2.75(0.01)
				3.70(0.01)
				6.12(0.01)
				8.33(0.02)
				10.61(0.03)
3.30	5Cl-SA	1.00	10	3.84(0.01)
				4.75(0.02)
				7.25(0.04)
				10.24(0.03)
				13.10(0.03)
3.80	SSA ⁻	0.14	2.00	0.70(0.003)
				0.86(0.003)
				1.45(0.01)
				1.98(0.01)
				2.66(0.01)
3.80	5Cl-SA	0.15	1.00	1.15(0.01)
				1.51(0.002)
				2.46(0.01)
				3.47(0.01)
				4.68(0.01)

TABLE 12

BeSSA⁻ AND Be-5ClSA COMPLEX FORMATIONS.

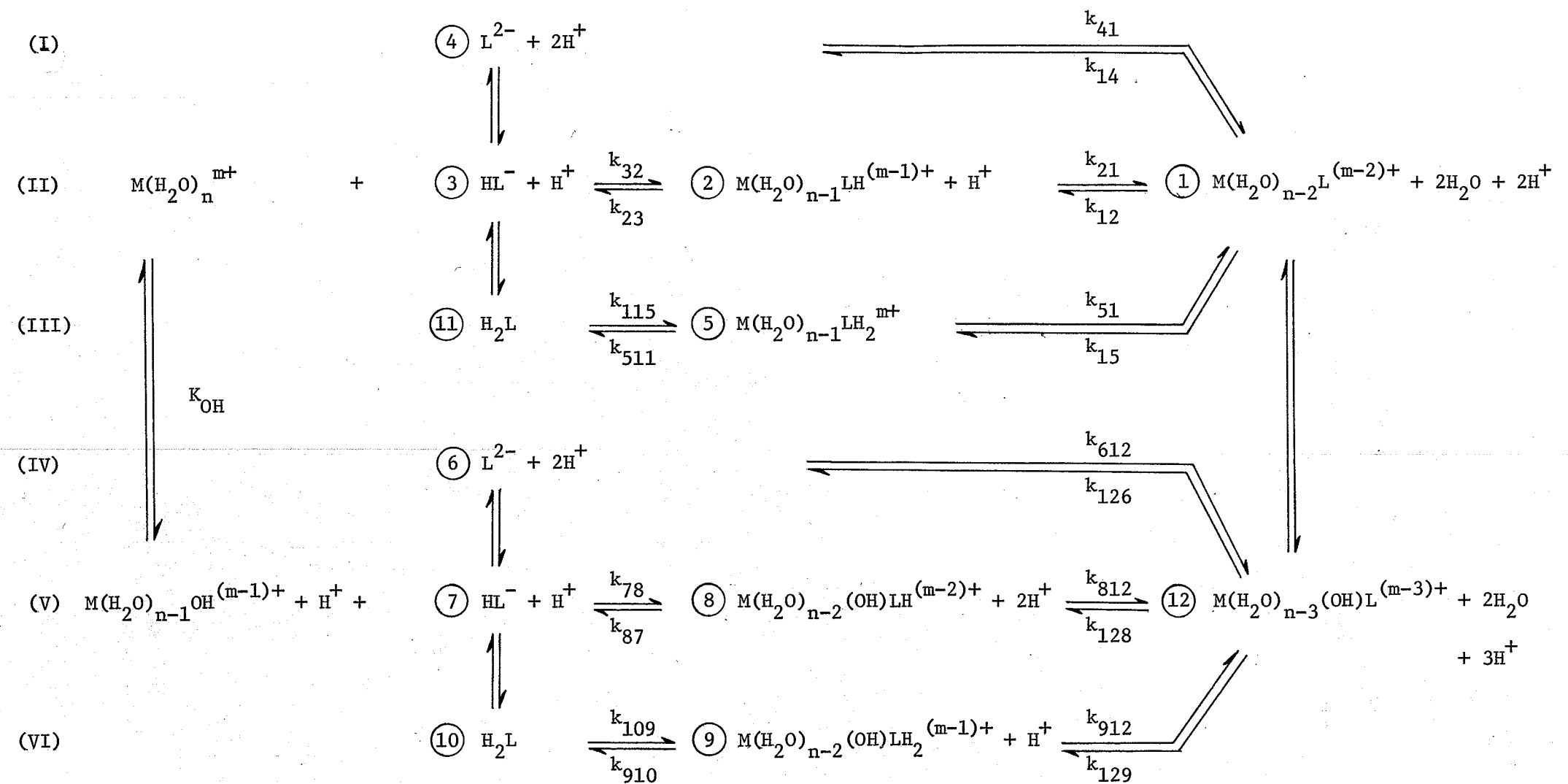
Temperature T°C	1/T °K ⁻¹ x 10 ³	Log (k _{obs} /T) sec ⁻¹ °K ⁻¹
20(0.05)	3.41	-2.0277
25.1(0.05)	3.35	-1.9059
30(0.05)	3.30	-1.6945
35(0.05)	3.25	-1.5678
40(0.05)	3.20	-1.4697
20(0.05)	3.41	-1.8823
25.1(0.05)	3.35	-1.7973
30(0.05)	3.30	-1.6212
35(0.05)	3.25	-1.4785
40(0.05)	3.20	-1.3782
20(0.05)	3.41	-2.6237
25.1(0.05)	3.35	-2.5397
30(0.05)	3.30	-2.3215
35(0.05)	3.25	-2.1920
40(0.05)	3.20	-2.0707
20(0.05)	3.41	-2.4075
25.1(0.05)	3.35	-2.2959
30(0.05)	3.30	-2.0914
35(0.05)	3.25	-1.9481
40(0.05)	3.20	-1.8257

(E) DISCUSSION

(1) KINETICS OF CHELATION STUDIES WITH BIDENTATE LIGANDS.

Many metal chelate formations involving bidentate ligands have been reported in the literature. Unfortunately, these do not include any study on the chelation of the $\text{Be}(\text{H}_2\text{O})_4^{2+}$ ion. Therefore, a general understanding of the kinetics and mechanism of other metal complex formations with bidentate ligands will facilitate the interpretation of the data from our present work. Typical examples of various metal complex formations are found in a series of studies including the kinetics of formation of (i) cobalt (II) monomalonate complex⁵⁴, (ii) nickel (II) monomalonate⁵⁵, (iii) monoazide complex of iron (III)⁵⁶, (iv) iron (III) monochelates with substituted malonic acids⁵⁷, (v) nickel (II) methyl- and n-butyl- malonato-complexes⁵⁸, and (vi) monophthalatonickel (II) complex⁵⁹ reported by Cavasino and his co-workers. Studies which involve the formation of $\text{Fe}(\text{III})$ complexes are particularly relevant, since the cation $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ is often compared with $\text{Be}(\text{H}_2\text{O})_4^{2+}$ because of their analogous rates of ligand substitution and water exchange (P.14, Section A). The complex formations were conducted over a variety of pH ranges and a general reaction Scheme (A) was proposed. Future references in connection with Scheme (A) will be made in the interpretation of our present results.

In the presence of an excess of $\text{M}(\text{H}_2\text{O})_n^{m+}$, assuming that the protolytic reactions (all vertical steps) are sufficiently fast and that $[\text{M}(\text{H}_2\text{O})_{n-1}\text{OH}^{(m-1)+}] \ll [\text{M}(\text{H}_2\text{O})_n^{m+}]$, the observed rate constant of



SCHEME A

the complex formation between a metal ion and a diprotic bidentate ligand can be expressed as follows, (derivation of the kinetic expression appears in Appendix D),

$$\begin{aligned}
 k_{\text{obs}} = & \frac{[M(H_2O)_n^{m+}]_{\text{eq}}}{\Omega} \left\{ k_{41} + \frac{k_{21}k_{32}K_2[H^+]}{(k_{23}+k_{21})} + \frac{k_{51}k_{115}[H^+]^2K_2}{(k_{511}+k_{51})K_{2A}} \right. \\
 & + \frac{K_{OH}}{[H^+]} k_{612} + \frac{K_{OH}k_{812}k_{78}K_2}{(k_{87}+k_{812})} + \frac{K_{OH}k_{912}k_{109}K_2[H^+]}{(k_{910}+k_{912})K_{2A}} \left. \right\} + \\
 & \left\{ \frac{k_{23}k_{12}[H^+]}{k_{23}+k_{21}} + \frac{k_{511}k_{15}[H^+]^2}{k_{511}+k_{51}} + \frac{k_{87}k_{128}}{k_{87}+k_{812}} + \frac{k_{910}k_{129}[H^+]}{k_{910}+k_{912}} \right. \\
 & \left. + k_{14} + k_{126} \right\} , \quad (49)
 \end{aligned}$$

where $K_{OH} = \frac{[M(H_2O)_{n-1}OH^{(m-1)+}][H^+]}{[M(H_2O)_n^{m+}]}$, $K_{2A} = \frac{[H^+][HL^-]}{[H_2L]}$,

$K_2 = \frac{[HL^-]}{[H^+][L^{2-}]}$, and $\Omega = \frac{(1 + K_2[H^+])}{\alpha_A}$; α_A is the degree of

dissociation of the ligand and is equal to $K_{2A}/(K_{2A} + [H^+])$. Equation (49) is a general expression effective over a wide range of pH levels. Since the degree of dissociation of the ligand H_2L and the hydrolysis of the cation $M(H_2O)_n^{m+}$ are both dependent on pH, special cases of expression (49) (generally simpler expressions) can arise by manipulating

the pH condition of the experiment.

In equation (49), the slope (S) of a plot of k_{obs} against $[M(H_2O)_n^{m+}]_{eq.}$ is equal to,

$$\begin{aligned} \text{Slope} = S = \frac{1}{\Omega} \{ & k_{41} + \frac{k_{21}k_{32}K_2[H^+]}{(k_{23}+k_{21})} + \frac{k_{51}k_{115}[H^+]^2K_2}{(k_{511}+k_{51})K_{2A}} \\ & + \frac{K_{OH}}{[H^+]} k_{612} + \frac{K_{OH}k_{812}k_{78}K_2}{(k_{87}+k_{812})} + \frac{K_{OH}k_{912}k_{109}K_2[H^+]}{(k_{910}+k_{912})K_{2A}} \}. \end{aligned} \quad (50)$$

Intercept (I) of the same plot is equal to,

$$\begin{aligned} \text{Intercept} = I = \{ & \frac{k_{23}k_{12}[H^+]}{k_{23}+k_{21}} + \frac{k_{511}k_{15}[H^+]^2}{k_{511}+k_{51}} + \frac{k_{87}k_{128}}{k_{87}+k_{812}} \\ & + \frac{k_{910}k_{129}[H^+]}{k_{910}+k_{912}} + k_{14} + k_{126} \}. \end{aligned} \quad (51)$$

It can be readily shown (Appendix D) that the slope (S) and intercept (I) are related by the following,

$$(S)(\Omega) = \frac{k_{41}}{k_{14}} (I) \quad (52)$$

According to expression (50), the quantity (S)(Ω) can depend on the hydrogen ion concentration in three ways, (i) $[H^+]$, (ii) $[H^+]^{-1}$, and (iii) $[H^+]^2$. Of course, it is also possible for the quantity (S)(Ω) to

exhibit a complex hydrogen ion concentration dependence or no hydrogen ion concentration dependence at all. Very often, a particular kind of hydrogen ion concentration dependence is exhibited because of the dominant activity of a certain group of reactions in the general reaction Scheme (A). For example, the $K_{OH} k_{612}/[H^+]$ term in equation (50) is generally associated with the reactions via the hydrolysed species, $M(H_2O)_{n-1}OH^{(m-1)+}$. A $[H^+]^{-1}$ dependence of the quantity $(S)(\Omega)$ in some cases is an indication that, in the range of acidity investigated, complex formation is predominantly between species of the ligand and $M(H_2O)_{n-1}OH^{(m-1)+}$.

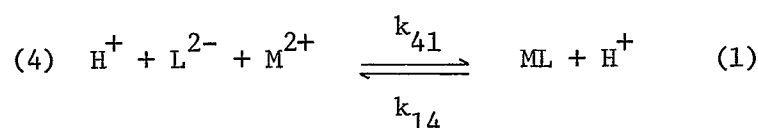
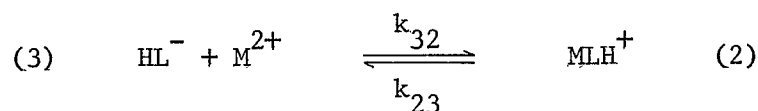
Cavasino et. al. have reported a series of complex formation studies of Co(II) and Ni(II) using malonic acid^{54,55} or substituted malonic acids⁵⁸ and phthalic acid⁵⁹ as the bidentate ligands. In the range of acidity investigated, $2 \times 10^{-6} M \leq [H^+] \leq 5 \times 10^{-4} M$, ($5.7 \geq pH \geq 3.3$), chelate formation was reported to have proceeded via two competitive reaction paths, i.e. the cation reacting with the dianionic and monoanionic forms of the ligand. The reaction pathways can be found in any of the references 54, 55, 58, & 59. The quantity $(k_{obs})(A)^{58,59}$, where A was a constant, was found to be a linear function of the hydrogen ion concentration over the acidity range investigated. Various rate constants were determined from the plot and with these values it was concluded that complex formation occurred by

an "I_d" mechanism. Reactions of the cation with the two reacting forms of the ligands were controlled by loss of the first water molecule from the inner co-ordination sphere of the metal ion. The observed different rates were attributed to the differences in the outer-sphere association constants, K_o . The ring enclosure step was found to be generally faster than the dissociation of the monodentate $(H_2O)_5Ni(O_2C \cdot CH_2 \cdot CO_2)$ by at least 32 times. In the case of the ligands methyl- and n-butyl malonic acids, the length of the alkyl group has practically no effect upon the ring-closure rate. The series of works have also confirmed that, if the proton-transfer process is relatively slow, the rate of a metal ion reacting with an unprotonated ligand is much faster than the rate with its corresponding monoprotonated species.

William and Petrucci³⁷ at about the same time reported a study of the chelation of Ni(II) and Co(II) with some aromatic ligands including anthranilic acid, salicylic acid, and 5-sulphosalicylic acid. Studies were conducted in the basic region from pH 7.63 to 8.35. The results reported by these authors using the aromatic ligands with a rigid benzene ring were surprisingly quite different from what were observed by Cavasino et. al.^{58,59} in the analogous studies with aliphatic ligands at lower pHs. The "normal" Eigen chelation mechanism in which ring enclosure is much faster than the back dissociation of the monodentate intermediate was conspicuously absent; instead, the reverse situation was found to prevail. The discrepancy was first interpreted in terms of a sterically controlled substitution mechanism. However, a comparison

of the activation parameters for Ni(II) salicylate and the bulkier Ni(II) sulphosalicylate revealed that the $\Delta H_f^\ddagger$ and $\Delta S_f^\ddagger$ values for these two ligands were the same within experimental error. The indistinguishability of the two energetic profiles was obviously inconsistent with the proposed sterically controlled substitution mechanism. Finally, using Ni(II) salicylate as an example, the activation parameters for solvent exchange around Ni^{2+} , ΔH_{ex} and ΔS_{ex} , were compared with the quantities $(\Delta H_f^\ddagger - \Delta H_o)$ and $(\Delta S_f^\ddagger - \Delta S_o)$ (with ΔH_o and ΔS_o the outer-sphere activation parameters), and these authors were able to conclude that the source of the deviation from the normal chelation mechanism was entropic rather than enthalpic in nature. No systematic study of the pH dependence of the k_{obs} value was reported and complex formation was assumed to be between the cation and the dianionic form of the ligand.

Hague et. al. in their investigation of the role of metals in enzymatic reactions have reported a series of studies on the complex formation of Mg(II) and Mn(II) with ligands such as 8-hydroxyquinoline^{60,61,62} and 5-nitrosalicylic acid³⁸. The kinetics of these complex formations were investigated through a wide range of acidities, generally from the slightly acidic pH 5 to the very basic pH 11. The reaction pathways postulated for the complex formation were similar to those put forth by Cavasino and his co-workers.^{58,59}



SCHEME (B)

The kinetic expression derived from mechanism B was,

$$k_{\text{obs}} = [\text{M}^{2+}] \left\{ \frac{k_{41}}{1 + K_2 [\text{H}^+]} + \frac{k_{32}k_{21}}{k_{23} + k_{21}} \right\} + [\text{H}^+] \left\{ \frac{k_{12}k_{23}}{k_{23} + k_{21}} \right\} + k_{14} \quad (53)$$

where $K_2 = k_{43}/k_{34}$. At a constant metal ion concentration, k_{obs} has a

U-shaped pH profile which was explained in terms of three types of

dependence of the k_{obs} value on the hydrogen ion concentration. At low

pH, the term $[\text{M}^{2+}]k_{41}(1 + K_2[\text{H}^+])^{-1}$ was negligible compared with

$[\text{H}^+](k_{12}k_{23}/k_{23} + k_{21})$, and a plot of k_{obs} against $[\text{H}^+]$ yielded a straight

line of slope $(k_{12}k_{23}/k_{23} + k_{21})$ and intercept $\{([\text{M}^{2+}]k_{32}k_{21}/(k_{23} + k_{21})) + k_{14}\}$

which was hydrogen ion concentration independent. At high pH, the reverse happened, i.e. $[M^{2+}]k_{41}(1 + K_2[H^+])^{-1} \gg [H^+](k_{12}k_{23}/k_{23}+k_{21})$, and a plot of k_{obs} against $(1 + K_2[H^+])^{-1}$ was linear with a slope of $[M^{2+}]k_{41}$ and the same intercept as before. In the intermediate regions, terms $[M^{2+}]k_{41}(1 + K_2[H^+])^{-1}$ and $[H^+](k_{12}k_{23}/k_{23}+k_{21})$ were comparable in magnitude, and k_{obs} displayed a complex hydrogen ion concentration dependence. By varying $[M^{2+}]$ at a fixed pH, and by varying the pH at a fixed $[M^{2+}]$, it was possible to evaluate k_{41} and k_{32} if ring enclosure was assumed to be fast, i.e. $k_{21} \gg k_{23}$. The k_{41} values for the formation of the complex between Mg(II) and 8-hydroxyquinoline⁶² and 5-nitrosalicylic acid³⁸ were, $6.0 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$ and $7.0 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$ at 25°C respectively. It was concluded that substitution rate was relatively independent of the nature of the incoming ligand, and that chelation proceeded via the normal dissociative (I_d) mechanism. For the reaction between Mn(II) and 8-hydroxyquinoline^{61,62}, the k_{41} value was $3.3 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$ at 25°C. The faster substitution rate of Mn(II) compared to the substitution rate of the analogous reaction with Mg(II) was in keeping with the previous findings.⁵

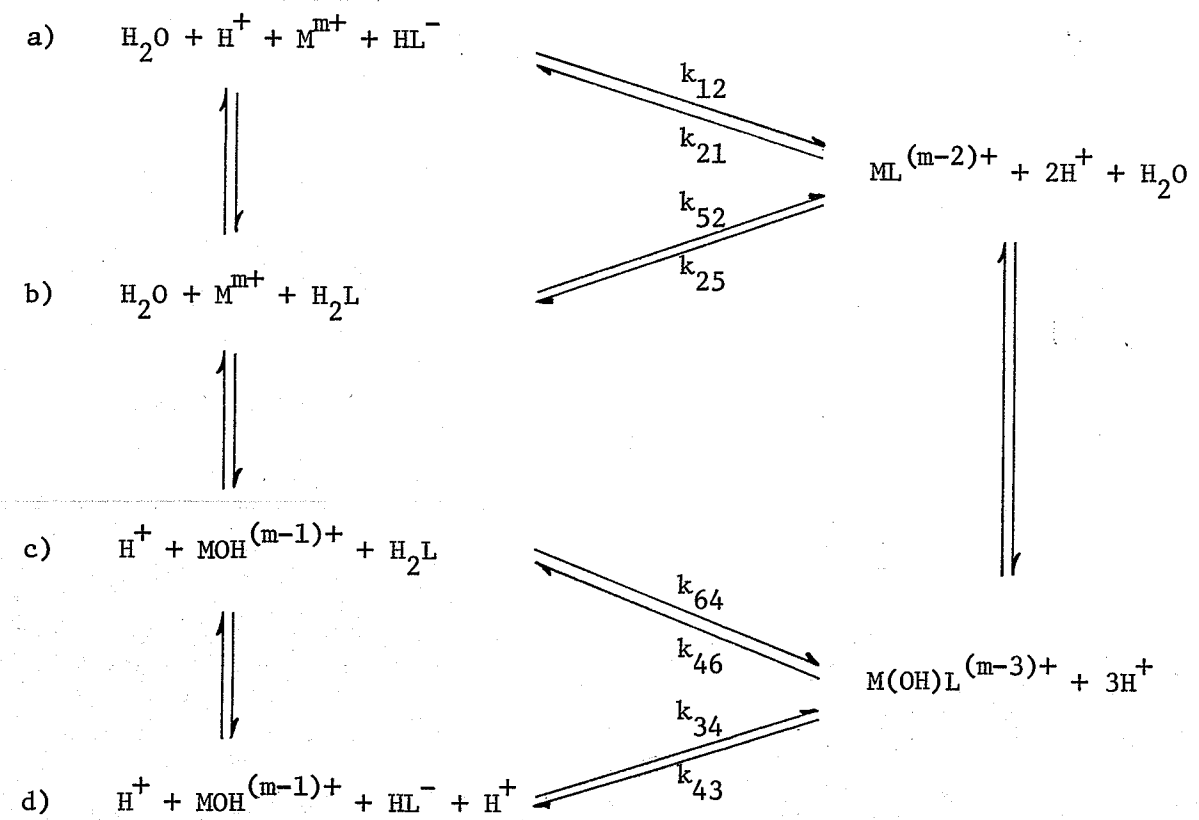
Discussions so far have focused on reported kinetic studies which were carried out at intermediate acidity ranges^{54,55,58,59}

$(10^{-7} \leq [H^+] \leq 10^{-4})$ by Cavasino and his co-workers) and fairly basic

regions^{38,60,61,62} ($10^{-11} \leq [H^+] \leq 10^{-5}$ by Hague et. al.). It was concluded that complex formation was exclusively between the cation and the monoanionic and dianionic forms of the ligand.

A number of kinetic studies which were conducted at considerably higher acidity levels have also been reported in the literature. These included, (i) the formation of the monoazide complex of iron (III)⁵⁶, FeN_3^{2+} , (ii) the formation of iron (III) monochelates with substituted malonic acid⁵⁷, and (iii) the formations of the monosulphosalicylato complex^{39,40} and monosalicylato complex^{39,41} of iron (III). Reactions of the cation $Fe(III)$ have been specifically selected for detailed description because of the resemblance in behaviour between this ion and $Be(II)$. Saini and Mentasti^{40,41} and Cavasino et. al.⁵⁶ both agreed on the reaction pathways depicted in Scheme C.

The authors Saini and Mentasti^{40,41} in adopting the reaction pathways in Scheme C had assumed that ring enclosure was fast compared to the dissociation of the monodentate intermediate, $MLH^{(m-1)+}$ or $MOHLH^{(m-2)+}$. If protonation and deprotonation reactions are considered faster than complex formation reactions and if $[MOH^{(m+1)+}] \ll [M^{m+}]$, the observed reaction rate constant in the presence of an excess of M^{m+} is given by: (derivation of the following kinetic expression appears in Appendix E)



SCHEME C

$$k_{\text{obs}} = \left(k_{12} + k_{52} \frac{[\text{H}^+]}{K_{2A}} + k_{64} \frac{K_{\text{OH}}}{K_{2A}} + k_{34} \frac{K_{\text{OH}}}{[\text{H}^+]} \right) (B) \quad (54)$$

where $B = ([\text{M}^{m+}] \alpha_A + \frac{[\text{H}^+]}{K_c})$, $K_{\text{OH}} = \frac{[\text{MOH}^{(m-1)+}][\text{H}^+]}{[\text{M}^{m+}]}$,

$$K_c = \frac{[\text{ML}^{(m-2)+}][\text{H}^+]}{[\text{M}^{m+}][\text{HL}^-]}, \text{ and } \alpha_A \text{ is the degree of dissociation}$$

of the ligand. The equilibrium constant K_{2A} is the same as previously defined in equation (49). At a fixed pH, the quantity

$$k_{\text{obs}} / ([\text{M}^{m+}] \alpha_A + \frac{[\text{H}^+]}{K_c}) \text{ or } k_{\text{obs}} / B \text{ is a constant.}$$

According to expression (54), a plot of k_{obs} against $[\text{M}^{m+}]$, at constant pH, will have a slope

$$S' = \alpha_A \left(k_{12} + k_{52} \frac{[\text{H}^+]}{K_{2A}} + k_{64} \frac{K_{\text{OH}}}{K_{2A}} + k_{34} \frac{K_{\text{OH}}}{[\text{H}^+]} \right) \quad (55)$$

and an intercept

$$I' = (k_{21}[\text{H}^+] + k_{25}[\text{H}^+]^2 + k_{46}[\text{H}^+] + k_{43}) \quad (56)$$

Initially, reaction Scheme C was proposed by Cavasino et. al.⁵⁶ in their interpretation of the formation of FeN_3^{2+} . The quantity k_{obs}/C ,

in which C was a term similar to $([M^{m+}]_{\alpha_A} + \frac{[H^+]}{K_c})$, was found to be relatively independent of the hydrogen ion concentration in the range 0.01M to 0.09M. The observed quantity was subsequently attributed to k, the sum of $(k_{12} + k_{64}K_{OH}/K_{2A})$. It was remarked by these authors that neither k_{12} nor $k_{64}K_{OH}/K_{2A}$ could be identified a priori with k. The k_{12} and k_{64} values were finally evaluated by making comparisons with the rate constants previously obtained in Fe(III) complex formation studies with other unidentate ligands⁶³. The average k value established by these authors was equal to $(5.28 \pm 0.40) \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$. If this value was ascribed to the rate constant k_{12} , it would be inconsistent with the k_{12} values previously determined in the Fe(III) complex formation studies⁶³ with ligands Br^- ($20 \text{ M}^{-1} \text{ sec}^{-1}$ at 22°C), Cl^- ($9.4 \text{ M}^{-1} \text{ sec}^{-1}$ at 25°C) and CNS^- ($127 \text{ M}^{-1} \text{ sec}^{-1}$ at 25°C). Since the ligand N_3^- was not radically different from the ligands described, it was assumed unlikely that k could be equated with k_{12} . However, when k was assigned to $k_{64}K_{OH}/K_{2A}$, and if the equilibrium constants K_{OH} and K_{2A} assumed the values $2.75 \times 10^{-3} \text{ M}$ and $3.88 \times 10^{-5} \text{ M}$ respectively, the rate constant k_{64} computed would be equal to $7.45 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$. This was in excellent agreement with the k_{64} values previously reported for the complex formations⁶³ between Fe(III) and HF ($3.2 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$ at 25°C), and N_3^- ($6.8 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$ at 25°C). Complex formation of FeN_3^{2+} was interpreted in terms of the reactions of the FeOH^{2+} ion with the

undissociated acid ligands and the corresponding monoanions. The rate-determining step was the release of the "first" water molecule from the inner coordination sphere of Fe(III). The authors concluded that their findings were consistent with an earlier report of the same study at lower pH's ($0.95M \gg [H^+] \gg 0.2M$) by Seewald and Sutin⁶⁴.

In their interpretations of the formations of the monosulfo-salicylato⁴⁰ and monosalicylato⁴¹ complex of Fe(III), Saini and Mentasti have successfully adopted Scheme C as the reaction pathways despite the fact that it was originally proposed for the monodentate ligands, HN_3 and N_3^- . The experiments reported were performed in solutions of acidities from 0.01M to 0.5M. It was demonstrated by these authors that k_{obs}/B , where B in this case was equal to $([Fe^{3+}]_{\alpha_A} + [H^+]/K_C)$, was constant for a constant hydrogen ion concentration. Two types of behaviour in the variation of k_{obs}/B with hydrogen ion concentration were observed. For $[H^+] < 0.1M$, k_{obs}/B was clearly a function of $1/[H^+]$ for both of the ligands. It was concluded that the term $k_{52}[H^+]/K_{2A}$ was negligible with respect to the other terms in expression (54). From the slope of the plot of k_{obs}/B vs $1/[H^+]$, the rate constant k_{34} at 25°C was evaluated and found to be $1.2 \pm 0.1 \times 10^4 M^{-1} sec^{-1}$ for the ligand 5-sulphosalicylic acid and $1.4 \pm 0.1 \times 10^4 M^{-1} sec^{-1}$ for salicylic acid. The intercept, k, was a sum of $[H^+]$ independent terms, k_{12} and $k_{64}K_{OH}/K_{2A}$. It was pointed out earlier that to identify a priori the intercept k either with k_{12} or with $k_{64}K_{OH}/K_{2A}$ was incorrect. Consequently a number

of criteria were considered in an attempt to identify the major contributing term.

The possible contribution of k_{12} or reaction (a) to the value of k (if the incoming ligand was very weakly basic) was discussed by these authors. The coefficient K_{OH}/K_{2A} for the formation of the monosulphosalicylato complex of Fe(III) was calculated to be 0.33. From previous studies,⁶³ it was observed that k_{64} and k_{12} were largely independent of the properties of the entering ligand, and the kinetic constants of $FeOH^{2+}$ were about three order higher than those of Fe^{3+} . It was concluded that $k_{64}K_{OH}/K_{2A}$ was large compared to k_{12} , and that reaction (c) was predominant in the formation of the Fe(III) complex.

Since reaction (c) was between the ion $FeOH^{2+}$ and a singly charged species, while reaction (d) was between $FeOH^{2+}$ and a doubly charged species, it was expected that k_{34} would be greater than k_{64} . If the reverse was true, i.e. $k_{64} > k_{34}$, the intercept k was to be identified with k_{12} instead of k_{64} . The experimental quantity, k_{34}/k_{64} reported by these authors was equal to ~ 2 . Therefore, complex formation was assumed to have proceeded via reaction (c) in addition to the already established reaction (d).

Finally, by assuming $k_{64}K_{OH}/K_{2A} \gg k_{12}$, the value of k_{64} was computed to be $5.5 \pm 0.5 \times 10^3 M^{-1} sec^{-1}$ at 25°C for both ligands. The finding was in good agreement with the k_{64} values reported for ligands such as HF and HN_3 ⁶³, which have about the same basicity as the ligands

under study.

For both of the ligands, when $[H^+] \geq 0.1M$, k_{obs}/B as a function of $1/[H^+]$ was nonlinear. In the case of 5-sulphosalicylic acid, the plot k_{obs}/B vs $1/[H^+]$ was clearly horizontal in the region $[H^+] \geq 0.1M$. With salicylic acid, k_{obs}/B was almost an inverse function of $1/[H^+]$ if $[H^+] \geq 1$, particularly at low temperatures. In both cases, the nonlinear behaviour was viewed as an increase in contribution of the $k_{52}[H^+]/K_{2A}$ term or reaction (b), which became important in strongly acidic solutions. An approximate value of k_{52} at 25°C was reported as $1.5 \pm 1 M^{-1} sec^{-1}$ for the ligand 5-sulphosalicylic acid and $3.0 \pm 1 M^{-1} sec^{-1}$ for salicylic acid.

Thermodynamic data for the formation of Fe(III) monosulphosalicylate was not reported. For the ligand salicylic acid, activation parameters were estimated from the results obtained at temperatures 20°C, 25°C and 30°C. At 25°C, values of $\Delta H_f^\ddagger$, $\Delta S_f^\ddagger$ for the reaction (c) and (d) were 12 Kcal/mole, -2 cal/deg-mole, and 11 Kcal/mole, -3 cal/deg-mole, respectively. The data were compared with activation parameters for the formation of other monocomplexes⁶⁵ of Fe(III), and found to be in good agreement.

The reaction mechanism was assumed to be " I_d " and the rate-determining step was the transition from the outer-sphere complex into the inner-sphere complex. The assumption was supported by a very satisfactory comparison between values of the rate constants k_{52} , k_{64}

and k_{34} and the rate constants of water exchange from the co-ordination sphere of $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ and $\text{Fe}(\text{H}_2\text{O})_5\text{OH}^{2+}$ ions reported in the literature⁶⁶.

No attempt was made to evaluate the outer-sphere ion-pair association constant, K_o , with the Fuoss-Eigen relation^{31,37}. The authors explained that the bases (the approximation of a ligand having a spherical form, and with the charge uniformly distributed on it) on which the Fuoss-Eigen relation was derived, were simply not realistic for the kinds of ligand under study. Furthermore, within experimental error, the rate constants for the formation of both complexes were demonstrated to be the same. This was inconsistent with the thesis that the K_o value (and hence, the formation rate constant) was to increase if the charge of either of the ions for the outer-sphere complex formation was increased. The inconsistency was suggested to be due to, (i) the unrealistic approximation of the spherical form for the ligand, and (ii) the electrostatic attraction of the sulphonic group being not favourable for the complex formation.

A similar study of the formation of monocomplexes of Fe(III) with salicylic acid and 5-sulphosalicylic acid was later reported by Fogg and Hall³⁹. The reactions were observed in the acidity range of 0.0145 M - 0.08 M, which was within the range of acidities reported by Saini and Mentasti^{40,41}. Reaction Scheme (C) was adopted and the experimental data were interpreted in terms of expression (55). The kinetic behaviour shared by both ligands was found to be quite different from the previous findings of Saini and Mentasti. The quantity,

($k_{12} + k_{52}[H^+]/K_{2A} + k_{64}K_{OH}/K_{2A} + k_{34}K_{OH}/[H^+]$) or k_{obs}/B , obtained by these authors using expression (55) as opposed to expression (54) which was employed by Saini and Mentasti, was found to be constant over the range of acidities investigated. The $1/[H^+]$ dependence of k_{obs}/B , reported by Saini and Mentasti in this $[H^+]$ region, was not observed. Therefore, k_{obs}/B was identified as k , the sum of k_{12} and $k_{64}K_{OH}/K_{2A}$. No attempt was made to assign the value of k_{obs}/B to either one of the term in k . Instead, both limiting conditions of k , i.e.

$k_{12} \gg k_{64}K_{OH}/K_{2A}$ and $k_{64}K_{OH}/K_{2A} \gg k_{12}$, were considered by the authors.

In the case of complex formation proceeding predominantly via reaction (c), the value of k_{64} at 25°C was reported to be $5.7 \times 10^3 M^{-1} sec^{-1}$ for ligand 5-sulphosalicylic acid and $2.9 \times 10^3 M^{-1} sec^{-1}$ for salicylic acid. These values were in fairly good agreement with the ones reported by Saini and Mentasti. The rate constant, k_o , for the transformation of the outer-sphere complex into the inner-sphere complex, was calculated with the relationship,

$$k_o = k_{64}/K_o \quad (57)(a)$$

in which K_o was the ion-pair association constant. The values of k_o at 25°C were $14.5 \times 10^3 sec^{-1}$ and $2.9 \times 10^3 sec^{-1}$ for the ligands salicylic acid and 5-sulphosalicylic acid respectively. The rate-determining step was suggested to be the release of a coordinated

water molecule, since k_o did not display any significant dependence on the nature of the entering ligand. For reaction (c), complex formation proceeded via a dissociative (I_d) mechanism.

In the reverse situation when reaction (a) became the major complex formation contributor, the value of k_{obs}/B would then have to be identified with k_{12} . The rate constant k_o was calculated by the expression,

$$k_o = k_{12}/K_o \quad (57)(b)$$

For the ligands $HSSA^{2-}$ and $HSaI^-$, the k_o values at 25°C were reported to be $2.6 \times 10^2 \text{ sec}^{-1}$ and $1.3 \times 10^3 \text{ sec}^{-1}$ respectively. Other k_o values of reaction (a) from Fe(III) studies with unidentate ligands were compared, and it was concluded that k_o was a function of the basicity of the incoming ligand. Therefore, complex formation via an associative mechanism (I_a) was considered very likely, if reaction (a) was the predominant pathway.

Additional evidence on the kinetics of the chelation of Fe(III) (with bidentate ligands) at low acidities, was reported by Cavasino et. al.⁵⁷ in their study of the formation of Fe(III) monochelates with substituted malonic acids. Kinetic measurements were recorded over the acidity range 0.04 - 0.45 M, the data obtained were interpreted in terms of reaction Scheme (A) and expression (49). Ring closure was assumed to be faster than the dissociation of the monodentate intermediate. Equation (49) was re-expressed by the authors as follow,

$$\frac{k_{\text{obs}}}{A} = (k_{41} + k_{32}K_2[H^+] + \frac{k_{115}K_2[H^+]^2}{K_{2A}} + \frac{K_{\text{OH}}}{[H^+]} k_{612} + K_{\text{OH}}k_{78}K_2 + \frac{K_{\text{OH}}k_{109}K_2[H^+]}{K_{2A}}) \quad (58)$$

where A was a term similar to $(\frac{[\text{Fe}^{3+}]}{\Omega} + \frac{k_{14}}{k_{41}})$.

Over the acidity range investigated, the quantity k_{obs}/A was a linear function of the hydrogen ion concentration, $[H^+]$. This was interpreted as an indication that the contributions from the terms involving $[H^+]^2$ and $1/[H^+]$ to k_{obs} were negligible. A plot of k_{obs}/A vs $[H^+]$ yielded a slope of,

$$S'' = k_{32}K_2 + K_{\text{OH}}k_{109}\frac{K_2}{K_{2A}} \quad (59)$$

and an intercept,

$$I'' = k_{41} + K_{\text{OH}}k_{78}K_2 \quad (60)$$

The reactions (I) and (V) (in Scheme A) associated with expression (60), were kinetically indistinguishable. Consequently, a direct evaluation of the corresponding rate constants, k_{41} and k_{78} respectively, was impossible. However, by making considerations similar to those discussed earlier (i.e. values of k_{41} and k_{78} , calculated from

the limiting conditions $k_{41} \gg K_{OH} k_{78} K_2$ and $K_{OH} k_{78} K_2 \gg k_{41}$, were compared with the available values of similar rate constants from other Fe(III) complex ion studies with univalent unidentate and bidentate anions), the authors were able to conclude that $K_{OH} k_{78} K_2 \gg k_{41}$. The value of k_{78} subsequently calculated, compared favourably with values of the equivalent rate constant obtained in other Fe(III) complex ion studies⁵⁷.

As for reactions (II) and (VI), associated with expression (59), it was assumed that $k_{109} > k_{32}$, and consequently, $K_{OH} k_{109} K_2 / K_{2A} > k_{32} K_2$. The estimated value of k_{109} was in good agreement with those found with other neutral ligands.

Since reactions (V) and (VI) were the dominant pathways, complex formation between Fe(III) and substituted malonic acids was interpreted in terms of the $FeOH^{2+}$ ion reacting with the undissociated acid ligand and the corresponding monoanions. The k_{78} values were practically the same for all the dicarboxylic acids investigated, (malonic acid, methylmalonic acid, n-butylmalonic acid, benzylmalonic acid, and cyclobutane-1,1-dicarboxylic acid); therefore, the rate-determining step in reaction (V) was the release of the "first" co-ordinate water molecule. The kinetics and mechanism of reaction (V) was independent of structural changes of the ligands. As for the values k_{109} , there was a rough correlation between the rate constant and the length or size of the substituent group on the malonic acid. This was rationalized by the authors as being due to the substituent group effect upon the

association constants, K_o , of the ion-dipole pair between the aquated cation and the neutral ligand.

A value of the stability constant of the Fe(III) complex, $K_c = k_{41}/k_{14}$, was calculated from a plot of k_{obs} vs A at constant hydrogen ion concentration. The K_c value established for the Fe(III) malonate complex was very satisfactory compared to the literature value.

(2) KINETICS OF THE FORMATION OF Be(II) MONOCHELATES WITH SUBSTITUTED SALICYLIC ACIDS.

In the present work, complex formation of Be(II) 5-sulphosalicylate and 5-chlorosalicylate was investigated in the acidity range of $5.01 \times 10^{-4} \text{ M} \geq [\text{H}^+] \geq 3.16 \times 10^{-6} \text{ M}$. However, only the experimental data obtained in the acidity range of $5.01 \times 10^{-4} \text{ M} \geq [\text{H}^+] \geq 1.59 \times 10^{-4} \text{ M}$ will be used in the interpretation of the kinetics involved. As it was illustrated in the Result section earlier, due to extensive hydrolysis of the cation at $[\text{H}^+] < 1.59 \times 10^{-4} \text{ M}$, values of $[\text{Be}^{2+}]_{\text{eff.}}$ decreased drastically compared to the corresponding $[\text{Be}^{2+}]_{\text{total}}$ values. Observation of the complex formation at $[\text{H}^+] > 5.01 \times 10^{-4} \text{ M}$ was not feasible because sensitivity for the detection of the Be(II) species at low pH's was generally poor. Even at $\text{pH} = 3.3$, the concentrations of Be(II) had to be increased tenfold before satisfactory results were obtained. The slow rates observed were in accordance with the postulate that Be(II) ion has a tendency to form bonds largely covalent in nature.

In the present study, the concentrations of the ligands in the dianionic form, L^{2-} (SSA^{3-} , 5Cl-SA^{2-}), are considered to be negligible compared to the concentrations of the corresponding monoanions and the undissociated acid ligands. In the case of 5-sulphosalicylic acid, since the sulphonic proton is always dissociated at low pH values, the species H_2SSA^- , HSSA^{2-} , & SSA^{3-} are generally recognized as the undissociated acid ligand, the corresponding monoanion, and the dianion of the ligand in the discussions below. The predominant species in the

acidity range 5.01×10^{-4} to 1.59×10^{-4} M is the corresponding monoanion of the ligands. The α_A values (α_A is the degree of dissociation of the ligand) for both ligands at each pH level are tabulated in Table 13.

It is unfortunate that the question of whether Be(II) complex formation can or cannot proceed via the BeOH^+ ion has remained unresolved, despite of the number of Be(II) complex formation studies with unidentate ligands which were reported in the literature.^{25,28e,30} Nevertheless, to exclude a priori the presence of such reaction pathways would be incorrect. After careful considerations, reaction Scheme (C) appears to be the most appropriate description for the complex formation of Be(II) 5-sulphosalicylate and 5-chlorosalicylate. Of course, the complex formation can also be interpreted in terms of the general reaction Scheme (A) which is valid for most metal chelations with bidentate ligands. In the present study, the experimental data will be treated with both schemes, and it is hoped that each scheme will serve as an internal check for the other, on the mechanism and rate constants of the complex formation.

As it was shown in the last section ((E)(1)), kinetics of the formation of Fe(III) salicylates have been discussed in terms of reaction Scheme (C). The same kinetic expressions (54), (55), and (56) derived from the scheme, will be applied to the present experimental data. The concentration of the cation, $[\text{M}^{m+}]$, corresponds to the concentration of the unhydrolysed $\text{Be}(\text{H}_2\text{O})_4^{2+}$ species, $[\text{Be}^{2+}]_{\text{eff.}}$. Plots of k_{obs} vs $[\text{Be}^{2+}]_{\text{eff.}}$ for both the ligands (SSA, 5Cl-SA) are

TABLE 13

DEGREE OF DISSOCIATION OF THE LIGANDS 5-SULPHOSALICYLIC ACID
AND 5-CHLOROSALICYLIC ACID AT VARIOUS pH, α_A , AT 25°C IN A
3M NaClO₄ MEDIUM.

Ligand	pH	$K_{2A} \times 10^3 \text{ M}$	$\alpha_A \left(\frac{K_{2A}}{K_{2A} + [H^+]} \right)$	Reference
SSA	3.3	2.14	0.81	50
	3.5		0.87	
	3.65		0.91	
	3.8		0.93	
5-ClSA	3.3	0.82	0.62	68
	3.5		0.72	
	3.65		0.79	
	3.8		0.84	

shown in Figures 10(a) & (b) and 11(a) & (b). Values of the slope, S' , the quantity, S'/α_A , and the intercept, I' , are given in Table 14.

The value of S'/α_A according to equation (55) is equal to $(k_{12} + k_{52}[H^+]/K_{2A} + k_{64}K_{OH}/K_{2A} + k_{34}K_{OH}/[H^+])$. From Table 14, it can be seen that the values of S'/α_A are relatively independent of $[H^+]$ over the pH range measured. The average value of S'/α_A for the ligands 5-sulphosalicylic acid, and 5-chlorosalicylic acid are $(1.39 \pm 0.04) \times 10^2 \text{ sec}^{-1} \text{ M}^{-1}$ and $(1.47 \pm 0.02) \times 10^2 \text{ sec}^{-1} \text{ M}^{-1}$ respectively. The independence of the S'/α_A value with $[H^+]$ indicates that the terms $k_{52}[H^+]/K_{2A}$ and $k_{34}K_{OH}/[H^+]$ are negligible in comparison with the sum of k_{12} and $k_{64}K_{OH}/K_{2A}$, k .

For 5-sulphosalicylic acid,

$$k = k_{12} + k_{64}K_{OH}/K_{2A} = (1.39 \pm 0.04) \times 10^2 \text{ sec}^{-1} \text{ M}^{-1} \quad (61)(a)$$

and for 5-chlorosalicylic acid,

$$k = k_{12} + k_{64}K_{OH}/K_{2A} = (1.47 \pm 0.02) \times 10^2 \text{ sec}^{-1} \text{ M}^{-1} \quad (61)(b)$$

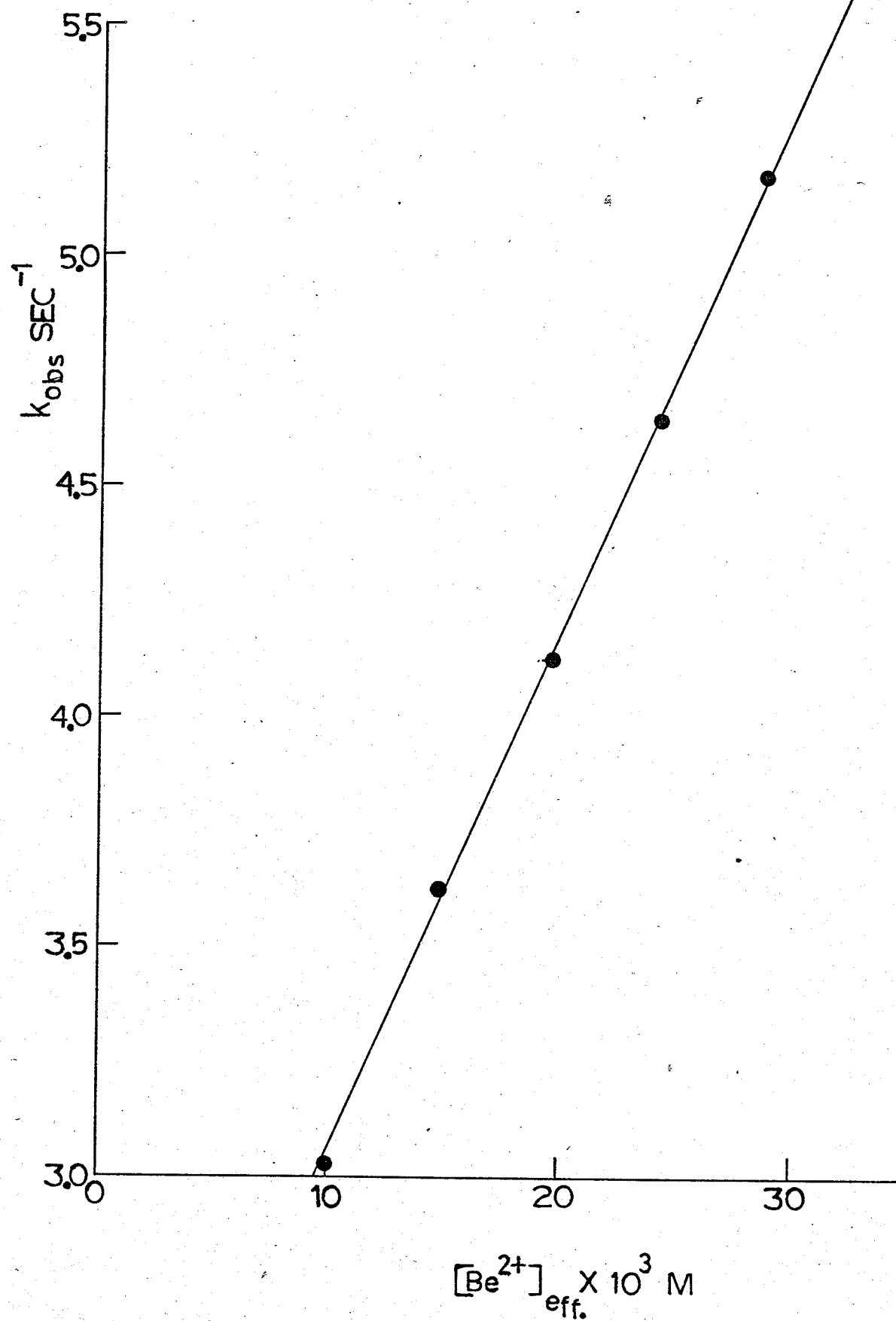
It has been shown previously that the value of k cannot be identified a priori either with k_{12} or $k_{64}K_{OH}/K_{2A}$. Therefore, reactions (a) and (c) of Scheme (C) are kinetically indistinguishable. Consequently, the corresponding rate constants cannot be evaluated directly from the experimental k value.

If the limiting condition $k_{12} \gg k_{64}K_{OH}/K_{2A}$ is assumed, the

FIGURE 10(a). Dependence of BeSSA^- complex formation rate upon the effective (unhydrolysed) beryllium concentration.

At $\text{pH} = 3.3$; 25.1°C ; and ionic strength = 3.0M.

- 116(a) -



$$k_{\text{obs}} = \left(k_{12} + k_{52} \frac{[\text{H}^+]}{K_{2A}} + k_{64} \frac{K_{\text{OH}}}{K_{2A}} + k_{34} \frac{K_{\text{OH}}}{[\text{H}^+]} \right) (B) \quad (54)$$

where $B = ([\text{M}^{m+}] \alpha_A + \frac{[\text{H}^+]}{K_c})$, $K_{\text{OH}} = \frac{[\text{MOH}^{(m-1)+}][\text{H}^+]}{[\text{M}^{m+}]}$,

$$K_c = \frac{[\text{ML}^{(m-2)+}][\text{H}^+]}{[\text{M}^{m+}][\text{HL}^-]}, \text{ and } \alpha_A \text{ is the degree of dissociation}$$

of the ligand. The equilibrium constant K_{2A} is the same as previously defined in equation (49). At a fixed pH, the quantity

$$k_{\text{obs}} / ([\text{M}^{m+}] \alpha_A + \frac{[\text{H}^+]}{K_c}) \text{ or } k_{\text{obs}} / B \text{ is a constant.}$$

According to expression (54), a plot of k_{obs} against $[\text{M}^{m+}]$, at constant pH, will have a slope

$$S' = \alpha_A \left(k_{12} + k_{52} \frac{[\text{H}^+]}{K_{2A}} + k_{64} \frac{K_{\text{OH}}}{K_{2A}} + k_{34} \frac{K_{\text{OH}}}{[\text{H}^+]} \right) \quad (55)$$

and an intercept

$$I' = (k_{21}[\text{H}^+] + k_{25}[\text{H}^+]^2 + k_{46}[\text{H}^+] + k_{43}) \quad (56)$$

Initially, reaction Scheme C was proposed by Cavasino et. al.⁵⁶ in their interpretation of the formation of FeN_3^{2+} . The quantity k_{obs}/C ,

in which C was a term similar to $([M^{m+}]_{\alpha_A} + \frac{[H^+]}{K_c})$, was found to be relatively independent of the hydrogen ion concentration in the range 0.01M to 0.09M. The observed quantity was subsequently attributed to k, the sum of $(k_{12} + k_{64}K_{OH}/K_{2A})$. It was remarked by these authors that neither k_{12} nor $k_{64}K_{OH}/K_{2A}$ could be identified a priori with k. The k_{12} and k_{64} values were finally evaluated by making comparisons with the rate constants previously obtained in Fe(III) complex formation studies with other unidentate ligands⁶³. The average k value established by these authors was equal to $(5.28 \pm 0.40) \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$. If this value was ascribed to the rate constant k_{12} , it would be inconsistent with the k_{12} values previously determined in the Fe(III) complex formation studies⁶³ with ligands Br^- ($20 \text{ M}^{-1} \text{ sec}^{-1}$ at 22°C), Cl^- ($9.4 \text{ M}^{-1} \text{ sec}^{-1}$ at 25°C) and CNS^- ($127 \text{ M}^{-1} \text{ sec}^{-1}$ at 25°C). Since the ligand N_3^- was not radically different from the ligands described, it was assumed unlikely that k could be equated with k_{12} . However, when k was assigned to $k_{64}K_{OH}/K_{2A}$, and if the equilibrium constants K_{OH} and K_{2A} assumed the values $2.75 \times 10^{-3} \text{ M}$ and $3.88 \times 10^{-5} \text{ M}$ respectively, the rate constant k_{64} computed would be equal to $7.45 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$. This was in excellent agreement with the k_{64} values previously reported for the complex formations⁶³ between Fe(III) and HF ($3.2 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$ at 25°C), and N_3^- ($6.8 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$ at 25°C). Complex formation of FeN_3^{2+} was interpreted in terms of the reactions of the FeOH^{2+} ion with the

undissociated acid ligands and the corresponding monoanions. The rate-determining step was the release of the "first" water molecule from the inner coordination sphere of Fe(III). The authors concluded that their findings were consistent with an earlier report of the same study at lower pH's ($0.95M \gg [H^+] \gg 0.2M$) by Seewald and Sutin⁶⁴.

In their interpretations of the formations of the monosulfo-salicylato⁴⁰ and monosalicylato⁴¹ complex of Fe(III), Saini and Mentasti have successfully adopted Scheme C as the reaction pathways despite the fact that it was originally proposed for the monodentate ligands, HN_3 and N_3^- . The experiments reported were performed in solutions of acidities from 0.01M to 0.5M. It was demonstrated by these authors that k_{obs}/B , where B in this case was equal to $([Fe^{3+}]_{\alpha_A} + [H^+]/K_C)$, was constant for a constant hydrogen ion concentration. Two types of behaviour in the variation of k_{obs}/B with hydrogen ion concentration were observed. For $[H^+] < 0.1M$, k_{obs}/B was clearly a function of $1/[H^+]$ for both of the ligands. It was concluded that the term $k_{52}[H^+]/K_{2A}$ was negligible with respect to the other terms in expression (54). From the slope of the plot of k_{obs}/B vs $1/[H^+]$, the rate constant k_{34} at 25°C was evaluated and found to be $1.2 \pm 0.1 \times 10^4 M^{-1} sec^{-1}$ for the ligand 5-sulphosalicylic acid and $1.4 \pm 0.1 \times 10^4 M^{-1} sec^{-1}$ for salicylic acid. The intercept, k, was a sum of $[H^+]$ independent terms, k_{12} and $k_{64}K_{OH}/K_{2A}$. It was pointed out earlier that to identify a priori the intercept k either with k_{12} or with $k_{64}K_{OH}/K_{2A}$ was incorrect. Consequently a number

of criteria were considered in an attempt to identify the major contributing term.

The possible contribution of k_{12} or reaction (a) to the value of k (if the incoming ligand was very weakly basic) was discussed by these authors. The coefficient K_{OH}/K_{2A} for the formation of the monosulphosalicylato complex of Fe(III) was calculated to be 0.33. From previous studies,⁶³ it was observed that k_{64} and k_{12} were largely independent of the properties of the entering ligand, and the kinetic constants of $FeOH^{2+}$ were about three order higher than those of Fe^{3+} . It was concluded that $k_{64}K_{OH}/K_{2A}$ was large compared to k_{12} , and that reaction (c) was predominant in the formation of the Fe(III) complex.

Since reaction (c) was between the ion $FeOH^{2+}$ and a singly charged species, while reaction (d) was between $FeOH^{2+}$ and a doubly charged species, it was expected that k_{34} would be greater than k_{64} . If the reverse was true, i.e. $k_{64} > k_{34}$, the intercept k was to be identified with k_{12} instead of k_{64} . The experimental quantity, k_{34}/k_{64} reported by these authors was equal to ~ 2 . Therefore, complex formation was assumed to have proceeded via reaction (c) in addition to the already established reaction (d).

Finally, by assuming $k_{64}K_{OH}/K_{2A} \gg k_{12}$, the value of k_{64} was computed to be $5.5 \pm 0.5 \times 10^3 M^{-1} sec^{-1}$ at 25°C for both ligands. The finding was in good agreement with the k_{64} values reported for ligands such as HF and HN_3 ⁶³, which have about the same basicity as the ligands

under study.

For both of the ligands, when $[H^+] \geq 0.1M$, k_{obs}/B as a function of $1/[H^+]$ was nonlinear. In the case of 5-sulphosalicylic acid, the plot k_{obs}/B vs $1/[H^+]$ was clearly horizontal in the region $[H^+] \geq 0.1M$. With salicylic acid, k_{obs}/B was almost an inverse function of $1/[H^+]$ if $[H^+] \geq 1$, particularly at low temperatures. In both cases, the nonlinear behaviour was viewed as an increase in contribution of the $k_{52}[H^+]/K_{2A}$ term or reaction (b), which became important in strongly acidic solutions. An approximate value of k_{52} at 25°C was reported as $1.5 \pm 1 M^{-1} sec^{-1}$ for the ligand 5-sulphosalicylic acid and $3.0 \pm 1 M^{-1} sec^{-1}$ for salicylic acid.

Thermodynamic data for the formation of Fe(III) monosulphosalicylate was not reported. For the ligand salicylic acid, activation parameters were estimated from the results obtained at temperatures 20°C, 25°C and 30°C. At 25°C, values of $\Delta H_f^\ddagger$, $\Delta S_f^\ddagger$ for the reaction (c) and (d) were 12 Kcal/mole, -2 cal/deg-mole, and 11 Kcal/mole, -3 cal/deg-mole, respectively. The data were compared with activation parameters for the formation of other monocomplexes⁶⁵ of Fe(III), and found to be in good agreement.

The reaction mechanism was assumed to be " I_d " and the rate-determining step was the transition from the outer-sphere complex into the inner-sphere complex. The assumption was supported by a very satisfactory comparison between values of the rate constants k_{52} , k_{64}

and k_{34} and the rate constants of water exchange from the co-ordination sphere of $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ and $\text{Fe}(\text{H}_2\text{O})_5\text{OH}^{2+}$ ions reported in the literature⁶⁶.

No attempt was made to evaluate the outer-sphere ion-pair association constant, K_o , with the Fuoss-Eigen relation^{31,37}. The authors explained that the bases (the approximation of a ligand having a spherical form, and with the charge uniformly distributed on it) on which the Fuoss-Eigen relation was derived, were simply not realistic for the kinds of ligand under study. Furthermore, within experimental error, the rate constants for the formation of both complexes were demonstrated to be the same. This was inconsistent with the thesis that the K_o value (and hence, the formation rate constant) was to increase if the charge of either of the ions for the outer-sphere complex formation was increased. The inconsistency was suggested to be due to, (i) the unrealistic approximation of the spherical form for the ligand, and (ii) the electrostatic attraction of the sulphonic group being not favourable for the complex formation.

A similar study of the formation of monocomplexes of Fe(III) with salicylic acid and 5-sulphosalicylic acid was later reported by Fogg and Hall³⁹. The reactions were observed in the acidity range of 0.0145 M - 0.08 M, which was within the range of acidities reported by Saini and Mentasti^{40,41}. Reaction Scheme (C) was adopted and the experimental data were interpreted in terms of expression (55). The kinetic behaviour shared by both ligands was found to be quite different from the previous findings of Saini and Mentasti. The quantity,

($k_{12} + k_{52}[H^+]/K_{2A} + k_{64}K_{OH}/K_{2A} + k_{34}K_{OH}/[H^+]$) or k_{obs}/B , obtained by these authors using expression (55) as opposed to expression (54) which was employed by Saini and Mentasti, was found to be constant over the range of acidities investigated. The $1/[H^+]$ dependence of k_{obs}/B , reported by Saini and Mentasti in this $[H^+]$ region, was not observed. Therefore, k_{obs}/B was identified as k , the sum of k_{12} and $k_{64}K_{OH}/K_{2A}$. No attempt was made to assign the value of k_{obs}/B to either one of the term in k . Instead, both limiting conditions of k , i.e.

$k_{12} \gg k_{64}K_{OH}/K_{2A}$ and $k_{64}K_{OH}/K_{2A} \gg k_{12}$, were considered by the authors.

In the case of complex formation proceeding predominantly via reaction (c), the value of k_{64} at 25°C was reported to be $5.7 \times 10^3 M^{-1} sec^{-1}$ for ligand 5-sulphosalicylic acid and $2.9 \times 10^3 M^{-1} sec^{-1}$ for salicylic acid. These values were in fairly good agreement with the ones reported by Saini and Mentasti. The rate constant, k_o , for the transformation of the outer-sphere complex into the inner-sphere complex, was calculated with the relationship,

$$k_o = k_{64}/K_o \quad (57)(a)$$

in which K_o was the ion-pair association constant. The values of k_o at 25°C were $14.5 \times 10^3 sec^{-1}$ and $2.9 \times 10^3 sec^{-1}$ for the ligands salicylic acid and 5-sulphosalicylic acid respectively. The rate-determining step was suggested to be the release of a coordinated

FIGURE 10(b). Dependence of BeSSA^- complex formation rate upon the effective (unhydrolysed) beryllium concentration. (at 25.1°C , and ionic strength = 3.0M)

■ denotes the plot of k_{obs} vs $[\text{Be}^{2+}]_{\text{eff.}}$ at $\text{pH} = 3.50$.
The values of $[\text{Be}^{2+}]_{\text{eff.}}$ used in the plot are half of the actual values reported in Table 6. (p.73)

◆ denotes the plot of k_{obs} vs $[\text{Be}^{2+}]_{\text{eff.}}$ at $\text{pH} = 3.65$.

▲ denotes the plot of k_{obs} vs $[\text{Be}^{2+}]_{\text{eff.}}$ at $\text{pH} = 3.80$.
The k_{obs} values used in this plot are the sum of the actual k_{obs} values reported in Table 6 (p.74) and a constant, 0.5 .

- 116(b) -

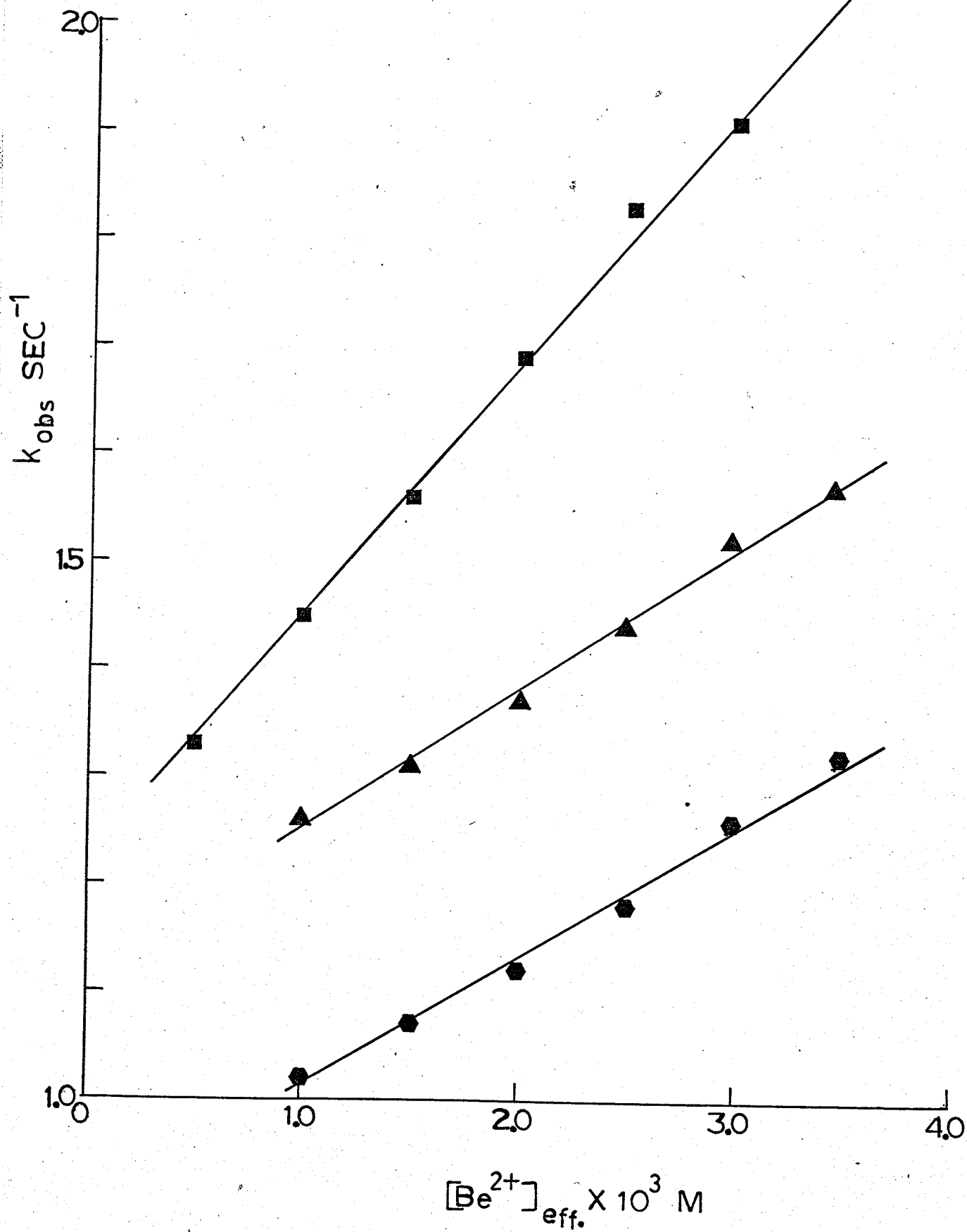


FIGURE 11(a). Dependence of Be5Cl-SA complex formation rate upon the effective (unhydrolysed) beryllium concentration.

At pH = 3.3; 25.1°C; and ionic strength = 3.0M.

- 117(a) -

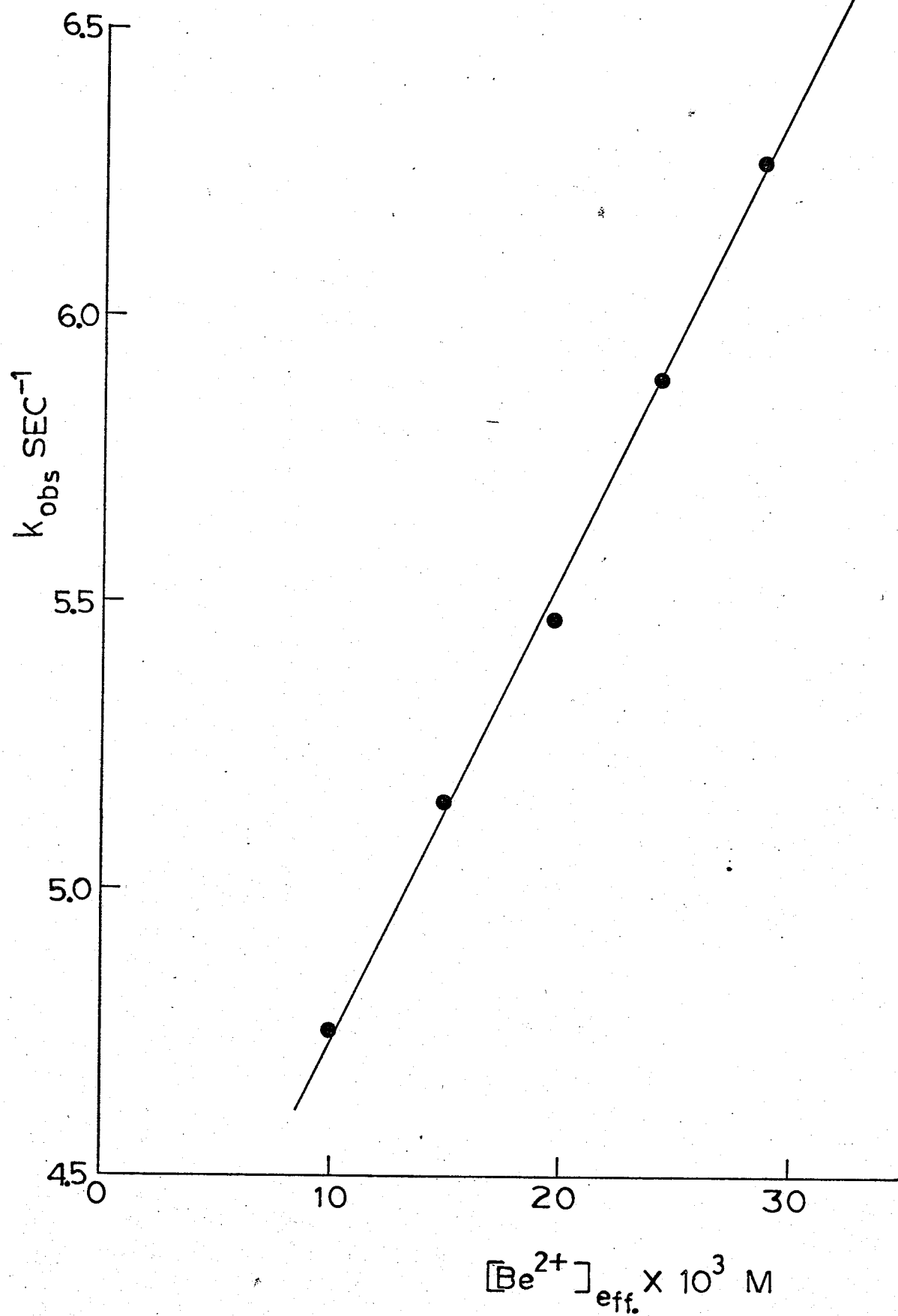


FIGURE 11(b). Dependence of Be5Cl-SA complex formation rate upon the effective (unhydrolysed) beryllium concentration. (at 25.1°C, and ionic strength = 3.0M)

■ denotes the plot of k_{obs} vs $[\text{Be}^{2+}]_{\text{eff.}}$ at pH = 3.50 .
The values of $[\text{Be}^{2+}]_{\text{eff.}}$ used in the plot are half of the actual values reported in Table 7. (p.76)

● denotes the plot of k_{obs} vs $[\text{Be}^{2+}]_{\text{eff.}}$ at pH = 3.65 .
The k_{obs} values used in this plot are the sum of the actual k_{obs} values reported in Table 7 (p.76) and a constant, 0.7 .

▲ denotes the plot of k_{obs} vs $[\text{Be}^{2+}]_{\text{eff.}}$ at pH = 3.80 .
The k_{obs} values used in this plot are the sum of the actual k_{obs} values reported in Table 7 (p.76) and a constant, 1.0 .

- 117(b) -

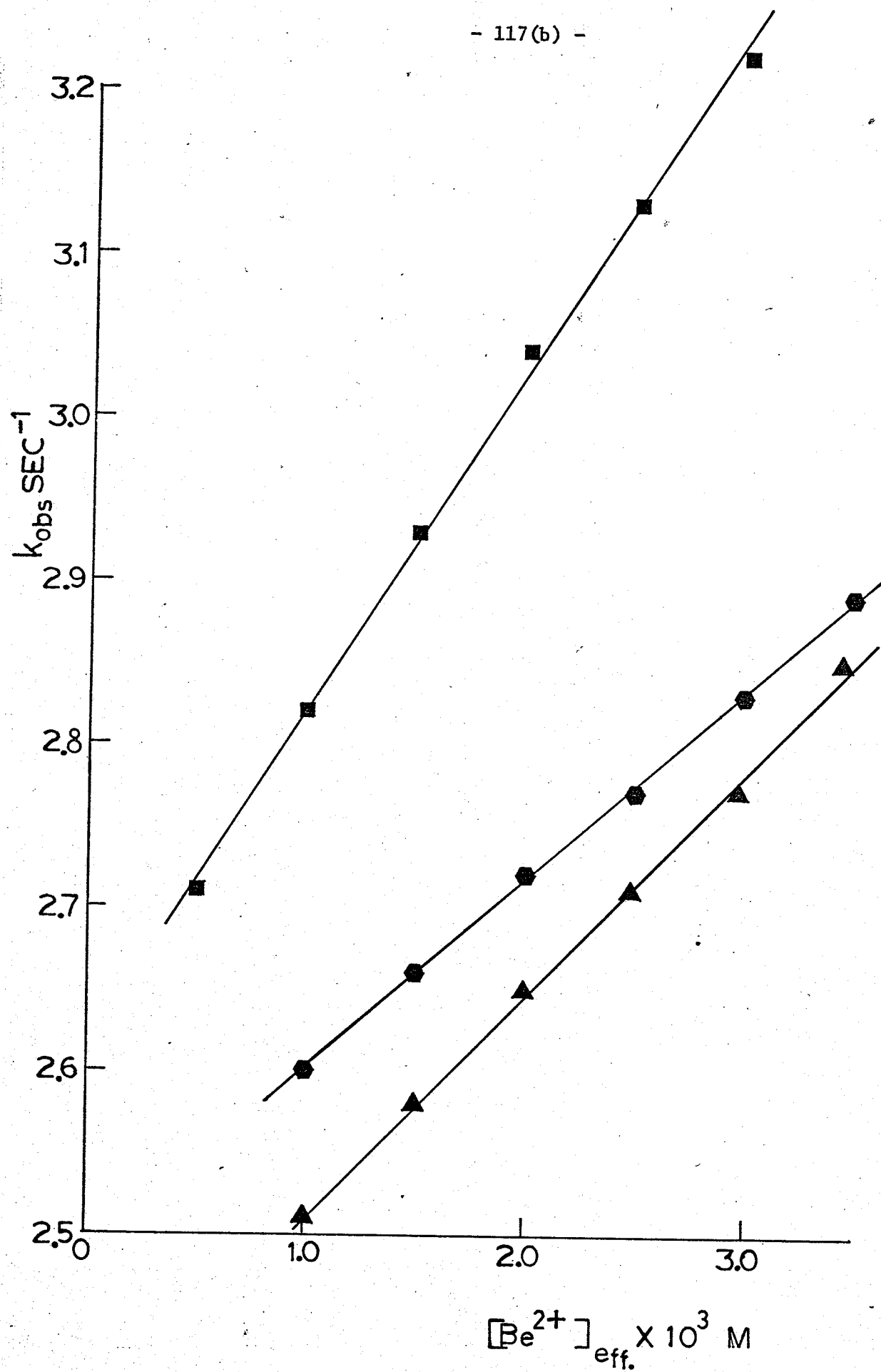


TABLE 14

RESULTS OBTAINED FROM PLOTS OF k_{obs} vs $[\text{Be}^{2+}]_{\text{eff}}$ at 25°C.

Ligand	pH	Slope (S') $\times 10^{-2}$ $\text{sec}^{-1} \text{M}^{-1}$	$S'/\alpha_A \times 10^{-2}$ $\text{sec}^{-1} \text{M}^{-1}$	Intercept (I') sec^{-1}
SSA	3.3	1.14(0.01)	1.40(0.01)	1.91(0.02)
	3.5	1.18(0.03)	1.36(0.03)	1.22(0.01)
	3.65	1.24(0.05)	1.37(0.05)	0.88(0.01)
	3.8	1.32(0.04)	1.42(0.04)	0.62(0.01)
		Average : 1.39(0.03)		
5Cl-SA	3.3	0.81(0.02)	1.31(0.02)	3.93(0.04)
	3.5	1.04(0.02)	1.44(0.02)	2.61(0.01)
	3.65	1.17(0.02)	1.49(0.02)	1.79(0.01)
	3.8	1.38(0.02)	1.65(0.02)	1.37(0.01)
		Average : 1.47(0.02)		

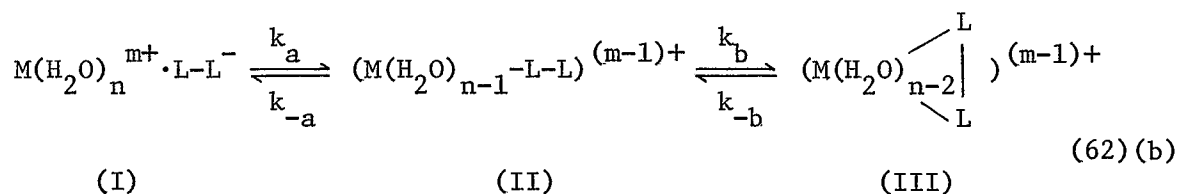
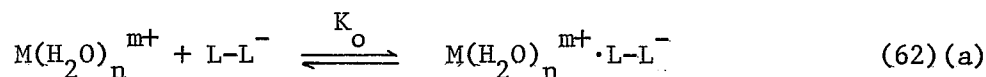
value of k_{12} will simply be the value of k . The corresponding reaction (a) is a reaction between $\text{Be}(\text{H}_2\text{O})_4^{2+}$ and the monoanion of the ligand. It is unfortunate that not many values of the formation rate constant of $\text{Be}(\text{II})$ complexes are available. The only two extensive studies which have been reported are the $\text{Be}(\text{II})$ complex formation with unidentate ligands, SO_4^{2-} (26,28a,b) and HF, F^- (30). Actually, the k_{12} value for the formation of BeSO_4 is expected to be higher because SO_4^{2-} is a dianion instead of a monoanion. The k_{12} value of the reaction between $\text{Be}(\text{H}_2\text{O})_4^{2+}$ and F^- is however, most useful. It has been suggested by Saini and Mentasti⁴⁰ that the ligand HSSA^{2-} is very likely to have roughly the same basicity as unidentate ligands such as F^- and N_3^- . The ligand H5Cl-SA^- is slightly more basic than HSSA^{2-} , because the K_{2A} value for 5-chlorosalicylic acid is 8.18×10^{-4} M, slightly smaller than the value of 2.14×10^{-3} M for 5-sulphosalicylic acid. Therefore, if the rate-determining step in reaction (a) is assumed to be the formation of the inner-sphere ion-pair, the k_{12} values obtained in the present work may be compared with the k_{12} values reported³⁰ for the formation of BeF^+ . The k_{12} values for the formation of BeSO_4 and BeF^+ , together with k_{12} values from the present work, are given in Table 15. It is shown that the k_{12} values of the present work are slightly lower than that obtained with the unidentate ligand F^- .

According to the Eigen multistep mechanism, complex formation

TABLE 15
VALUES OF THE RATE CONSTANT k_{12} (Scheme (C)) FOR
REACTIONS OF $\text{Be}(\text{H}_2\text{O})_4^{2+}$ WITH VARIOUS LIGANDS. (25°C)

Ligand	Ionic Strength(μ)M	$k_{12} \times 10^{-2} \text{ sec}^{-1} \text{ M}^{-1}$	Reference
SO_4^{2-}	-	12.5(35°C)	26
SO_4^{2-}	-	3.40	28a
SO_4^{2-}	-	4.00	28b
SO_4^{2-}	0.2	1.64	28d
HF	0.2	0.73	30
F^-	0.2	7.24	30
HSSA^{2-}	3.0	1.39	Present Work
5Cl-SA^-	3.0	1.47	Present Work

(with bidentate ligands) via reaction (a) can be represented by the following sequence,



where K_o is the outer-sphere ion-pair association constant. At $\mu = 0$, i.e. zero ionic strength, K_o can be calculated by the Fuoss equation³¹,

$$K_o = 4\pi N \bar{a}^3 e^b / 3000 = 2.524 \times 10^{-3} \bar{a}^3 e^b \quad (63)$$

where $b = |Z_1 Z_2| e^2 / \bar{a} D k T$, N is the Avagadro's number and $\bar{a}$ is the centre-to-centre distance of the ions in the outer-sphere ion-pair (I). At a finite ionic strength, the value of K_o has to be adjusted with the activity coefficients of the ion, (f_i),

$$K_{IP} = \frac{f(M) f(L-L)}{f(M \cdot L-L)} K_o \quad (64)$$

$$\text{where } \log f_i = - \{ 0.0509 Z_i^2 \sqrt{I} / (1 + \sqrt{I}) \} + 0.3I \quad (65)$$

According to the Eigen multistep mechanism (expressions (62)(a) & (62)(b), the overall rate constant of the forward (formation) reaction, k_f , and the reverse (dissociative) reaction, k_r can be written as,

$$k_f = K_{IP} k_a k_b / (k_b + k_{-a}) \quad (66)(a)$$

$$k_r = k_{-a} k_{-b} / (k_b + k_{-a}) \quad (66)(b)$$

if a steady state condition on the intermediate (II), i.e.

$$d(M(H_2O)_{n-1}-L-L)^{(m-1)+}/dt = 0, \text{ is assumed.}$$

In a majority of the complex formations, chelate ring enclosure is faster than the breaking of the first metal-ligand bond ("normal" chelation), i.e. $k_b \gg k_{-a}$. For reaction (a), the overall forward rate constant, k_{12} , in terms of a "normal" chelation process is equal to,

$$k_{12} = K_{IP} k_a \quad (67)$$

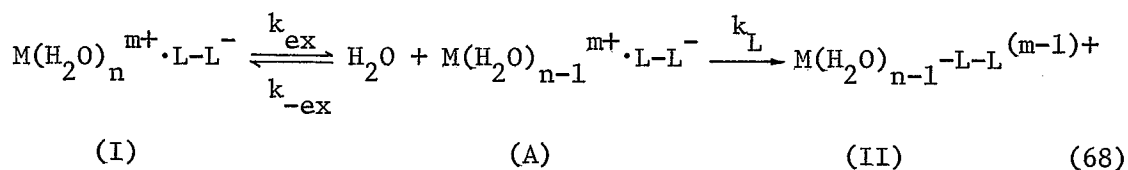
where k_a is characteristic of the formation rate of the inner-sphere monodentate intermediate (II) from the outer-sphere ion-pair (I) in expression (62)(b). The mechanism associated with such a reaction is generally assumed to be dissociative ($SN_1 - (D)$ or I_d) rather than associative ($SN_2 - (A)$ or I_a). An active associative mechanism is generally characterized by the dependence of the complex formation rate on the nature of the entering ligand. At the present, there are not enough studies reported in the literature to provide a definitive statement on the role of the entering ligand in the rate-determining process of the complex formation. However, according to the rate constants tabulated in Tables 15 and 16, rates of the forward reactions are rather insensitive to the nature of the entering ligand (from the small F^- ion to the relatively bulky 5-sulphosalicylic acid). Thus, the

TABLE 16

VALUES OF K_{IP} AND k_a AT 25°C FOR REACTIONS OF $Be(H_2O)_4^{2+}$ WITH VARIOUS LIGANDS.

Ligand	Ionic Strength (μ) M	$K_{IP} M^{-1}$	$k_a \text{ sec}^{-1}$	$s \times 10^3$	$\frac{k_{-ex}}{k_L}$	Reference
F^-	0.2	1.53	473	15.77	63	30
HF	0.2	0.36	203	6.77	148	30
SO_4^{2-} (18°C)	0.2	4.10	40	1.33	752	30
HSSA ²⁻ (formal charge)	3.0	19.37	7.18	0.24	4167	Present Work
HSSA ²⁻ (charge delocalized)	3.0	2.22	62.61	2.09	479	Present Work
H5Cl-SA ⁻	3.0	2.22	66.22	2.21	453	Present Work

possibility of complex formation via an associative pathway is not likely, but rather a dissociative mechanism of the following is favoured.



For the cation Be(II), both group of authors, Strehlow and Knoche^{28e}, and Crea and Lincoln²³ agreed that the formation of the intermediate (A) is a concerted I_d process rather than a pure SN₁ - (D) process. Calculations based on an electrostatic model by Strehlow & Knoche^{28e} have shown that formation of a trigonal-planar transition state for the [Be(H₂O)₄]²⁺ system, although requiring a smaller ΔH[‡] value than a trigonal-pyramidal transition state, still required a ΔH[‡] value which is a number of orders of magnitude too high. On this basis, the authors Crea and Lincoln²³ concluded that the solvent-exchange mechanism between the intermediates (I) and (A) must be viewed as a concerted solvent-assisted dissociative process.

According to expression (68), the rate constant k_a in equation (67) for a given ligand L-L⁻ is thus dependent partially upon the rate constant of water exchange, k_{ex}, and partially upon the relative reactivities for nucleophilic attack of water and ligand, (k_{-ex}/k_L), on the three-coordinate intermediate (A). The formation rate of the monodentate intermediate (II) can be expressed as,

$$d(M(H_2O)_{n-1}^{-L-L})^{(m-1)+}/dt = \frac{k_{ex}[M(H_2O)_n^{m+} \cdot L-L^-]}{1 + k_{-ex}/k_L} = k_a[M(H_2O)_n^{m+} \cdot L-L^-] , \quad (69)(a)$$

and therefore,

$$k_a = k_{ex}/(1 + k_{-ex}/k_L) = sk_{ex} \quad (69)(b)$$

where s is a statistical factor dependent upon the number of water molecules the monoanionic ligand can replace in the outer coordination sphere of the cation. If the statistical factors, s , are known, the ratio k_{-ex}/k_L of the ligands can be calculated by equation (69)(b).

In the present work, the centre-to-centre distance, $\bar{a}$, between $Be(H_2O)_4^{2+}$ and the ligand is approximated to be $4.66\text{\AA}$ in each case. The rate of water exchange, k_{ex} , for $Be(H_2O)_4^{2+}$ is $3 \times 10^4 \text{ sec}^{-1}$, as reported by Connick and Fiat¹⁹. Using these values in equations (64), (67) and (69)(b), the values of K_{IP} , k_a , s , and k_{-ex}/k_L were calculated and listed in Table 16. The two sets of values for the ligand $HSSA^{2-}$ were calculated on the assumption of two different charge distribution models. With the first model, the negative charge of the SO_3^- group is treated as a formal charge. The reactants $Be(H_2O)_4^{2+}$ and $HSSA^{2-}$, in this case, will constitute a 2:2 electrolyte. The corresponding K_{IP} value (Table 16) calculated by equation (64)(a) is shown to be very large comparing to that of a 2:1 electrolyte. On the basis of simple electrostatic theory, one would expect the k_{12} value for

the reaction between $\text{Be}(\text{H}_2\text{O})_4^{2+}$ and ligand HSSA^{2-} to be much larger than with ligand 5Cl-SA^- . This was not the case, however, since according to the results in Table 15 the k_{12} values for both reactions are the same within experimental error. Therefore, the proposed model appears to be invalid if complex formation is to proceed via the outer-sphere association of an ion-pair. Another discrepancy of the model can be seen when the energy profiles of the reaction of $\text{Be}(\text{II})$ with both ligands are considered (values of the activation parameters will be reported in the next section). Both $\Delta H_f^\ddagger$ and $\Delta S_f^\ddagger$ for the two ligands, HSSA^{2-} and 5Cl-SA^- , are the same within experimental error. These thermodynamic data indicate that the HSSA^{2-} dianion acts as a monovalent anion in terms of the outer-sphere ion-pair formation.

The second charge distribution model is found by assuming the delocalization of the SO_3^- group charge with respect to the reaction site, namely the carboxylic-hydroxylic position. The principle of this theory has been discussed previously^{37,38,41} in the literature. According to this model, the observed monoanionic behaviour of the ligand HSSA^{2-} can be rationalized if only the local charge densities on the metal ion and the coordinating atom of the incoming ligand are considered, rather than the overall charges. The local charge densities can be approximated by the Huckle LCAO method. For example, Cayley and Hague³⁸, using the dianion of 5-nitrosalicylic acid, $5\text{NO}_2\text{-SA}^{2-}$, and the monoanion of 8-hydroxyquinoline, OX^- , as a pair have demonstrated that the sums of the charges on the two atoms in $5\text{NO}_2\text{-SA}^{2-}$ and OX^- which are

involved in coordination to the cation Mg^{2+} (assuming outer-sphere association) differ by less than half an electronic charge (-1.64 and -1.21 respectively). In the present work, the local charge densities of the active reaction site (the oxygen atoms of the carboxylic-hydroxylic position) of the ligands, HSSA^{2-} and 5Cl-SA^- , cannot be radically different from each other. This thesis is supported by the similar values of k_{12} obtained, and the indistinguishability of the energy profiles for the reaction of Be(II) with both ligands. In light of this, the K_{IP} , k_a , s and $k_{-\text{ex}}/k_L$ values calculated by assuming HSSA^{2-} to be a monoanion, will be more reliable than the analogous values for the dianion.

Since the k_a values ($\sim 10^2 \text{ sec}^{-1}$) given in Table 16 are much smaller than the k_{ex} value ($3 \times 10^4 \text{ sec}^{-1}$, Connick & Fiat¹⁹) of the $\text{Be(H}_2\text{O)}_4^{2+}$ ion, the rate-determining step of reaction (a) (of Scheme (C)) cannot possibly be the rate of release of a water molecule from the inner coordination shell of the cation. A strictly dissociative " I_d " mechanism in this case is very unlikely, particularly when water exchange can be strongly accelerated in a medium of high ionic strength. The observed condition of $k_{\text{ex}} \gg k_a$ is best understood when the s value of the various ligands reported in Table 16 are considered. The average order of magnitude of the s factor is 10^{-3} which indicates that the probability of a ligand molecule replacing a water molecule in the outer coordination sphere of $\text{Be(H}_2\text{O)}_4^{2+}$ is very small. For the ligands F^- , HF and SO_4^{2-} , the corresponding $k_{-\text{ex}}/k_L$ values of the s

factors reported by Baldwin & Stranks³⁰ were 62, 148 and 750 respectively; these values largely favour nucleophilic attack of the $\text{Be}(\text{H}_2\text{O})_3^{2+} \cdot \text{L-L}^-$ intermediate by a water molecule. In other words, the relatively slow complex formation rate (k_a) observed in comparison with the water exchange rate (k_{ex}) is a consequence of the condition, $k_{\text{-ex}} \gg k_L$. The high reactivity with water was attributed (by Baldwin & Stranks³⁰) to the large negative free energy associated with addition of the fourth, highly polarizable, aquo ligand to the high surface charge of the beryllium cation. Later solvent exchange studies involving systems like $[\text{Be}(\text{dmf})_4]^{2+}$, $[\text{Be}(\text{acac})(\text{dmf})_2]^+(21)$ and $[\text{Be}(\text{MeO})_3\text{PO}_4]^{2+}(23)$ have all reported activation enthalpies of approximately 14-15 Kcal/mole. The relatively high values were also attributed to the high surface charge density of Be^{2+} by Crea and Lincoln²³.

The $k_{\text{-ex}}/k_L$ value of the ligands HSSA^{2-} and 5Cl-SA^- are, 480, 450 respectively. These values were obtained in a 3.0 M NaClO_4 medium and corrections should be made to allow for the primary salt effect. Such corrections are, however, not possible at the present since the classical treatment of Brønsted-Bjerrum on ionic effects is valid only in media of relatively low ionic strengths. Nevertheless, it has been established for reactions between ions of different charge, rate constant k decreases with increasing ionic strength. If the present work was conducted in a medium of 0.2 M NaClO_4 instead of 3.0 M NaClO_4 , the subsequent values of the rate constant k_a would be comparatively

larger than those reported in Table 16. In the case of the reactivity ratio k_{-ex}/k_L , the reverse is true, a decrease in the ionic strength of the medium will reduce the value of k_{-ex}/k_L substantially. Nevertheless, the values of k_{-ex}/k_L for the ligands HSSA^{2-} and 5Cl-SA^- in a medium of 0.2 M NaClO_4 are still expected to be much larger than unity. The actual values are relatively unimportant for it is only necessary to demonstrate that the condition $k_{-ex} \gg k_L$ is predominant in all of the Be(II) complex formations with various ligands. In the present work, the different substituent groups in the 5-position of the 2-hydroxyl benzoic acid do not seem to have any significant effect on the values of the rate constant k_L . This can be explained if the distance between the reaction centre (carboxylic-hydroxylic position) and the substituent group in the 5-position is assumed to be large. In that case, any steric effect of the substituent group will be minimal on the rate-determining process. ~~The electronic effects of the sulphonate and chloride group are~~ not expected to differ drastically from each other.

For systems with the same solvent (e.g. H_2O), it is apparent that the rate-determining step of complex formation is characteristic of the rate constant k_L . The magnitude of k_L varies with each ligand, depending upon the basicity and steric structure of the specific ligand involved. The magnitude of k_L is a function of the free energy associated with the addition of the incoming ligand. Therefore, with the present assumption of $k_{ex} = 3.0 \times 10^4 \text{ sec}^{-1}$ (19), the reaction mechanism of the complex formation must be considered to be at least partially associative

(I_a), in addition to the (I_d) mechanism already established for the solvent exchange. Such a conclusion is contrary to the earlier suggestion that an active associative mechanism is highly unlikely, since the observed complex formation rates are rather insensitive to the nature of the entering ligand. With the present situation, the nature of the reaction mechanism for the Be(II) complex formations will remain unresolved.

Crea and Lincoln²³ in their study of the exchange of Trimethyl Phosphate on the Tetrakis (Trimethyl Phosphato) Be(II) complex have quoted from the same study reported by Connick & Fiat¹⁹, a k_{ex} value of H₂O exchange of the Be(H₂O)₄²⁺ ion. However, the k_{ex} value used by these authors was $3.0 \times 10^2 \text{ sec}^{-1}$ instead of the $3.0 \times 10^4 \text{ sec}^{-1}$ adopted by the authors Baldwin & Stranks³⁰ earlier. Unfortunately, it is not known at the present which of these values is more reliable. If the former k_{ex} value of $3.0 \times 10^2 \text{ sec}^{-1}$ is accepted, the water exchange rate will be roughly of the same order of magnitude as the complex formation rate represented in k_a (Table 16), i.e. $k_{ex} \approx k_a$.

The rate of ligand attack of the three coordinated intermediate Be(H₂O)₃²⁺·L-L⁻, k_L , is expected to be relatively fast in comparison with the rate of solvent exchange, k_{ex} . Under such circumstances, the rate-determining step of the complex formation is the rate of release of a water molecule from the inner coordination sphere of the Be(H₂O)₄²⁺ ion, and the reaction mechanism is positively dissociative (I_d). This thesis is in agreement with the conclusion of Baldwin and Stranks³⁰ in

their studies of Be(II) complex formation with nucleophiles F^- and HF.

So far, the k values ($k_{12} + k_{64}K_{OH}/K_{2A}$) established from the plot of k_{obs} vs $[Be^{2+}]_{eff}$. (equation (54) & (55)), have been interpreted only in terms of the limiting condition $k_{12} \gg k_{64}K_{OH}/K_{2A}$ associated with the reaction (a) in Scheme (C). In the reverse situation, i.e. $k_{64}K_{OH}/K_{2A} \gg k_{12}$, complex formation is assumed to have proceeded via reaction (c) of Scheme (C). Value of the equilibrium constant, K_{OH} , as given by Diebler and Eigen²⁵ is equal to 3.0×10^{-7} M. If the value of k is assumed to be equal to $k_{64}K_{OH}/K_{2A}$, the rate constant k_{64} can be expressed as kK_{2A}/K_{OH} . Values of the rate constant k_{64} for the reaction of $Be(H_2O)_4^{2+}$ with various ligands are given in Table 17.

A discussion of the results in Table 17 is very difficult since there has not been any extensive report on Be(II) complex formation via the $BeOH^+$ species. The k_{64} value for the ligand SO_4^{2-} is obviously much larger than the rest of the values reported. It is possible that such an interpretation of $BeSO_4$ formation via the pathway of reaction (c) is not valid. The dissociation constant, $[SO_4^{2-}][H^+]/[HSO_4^-]$, of the ion HSO_4^- is larger than the analogous equilibrium constants of the other ligands by almost a factor of 10. In this case the alternative reaction (a) is more preferable. If reaction (c) is the valid pathway, in order for the k_{64} value of $BeSO_4$ formation to be compatible with the values given in Table 17 for the other ligands, k_{obs} value for the

TABLE 17
VALUES OF THE RATE CONSTANT k_{64} FOR THE REACTION
OF $\text{Be}(\text{H}_2\text{O})_4^{2+}$ WITH VARIOUS LIGANDS. (25°C)

Ligand	Ionic Strength(μ) M	$k_{64} \times 10^{-5} \text{ sec}^{-1} \text{ M}^{-1}$	Reference
SO_4^{2-}	0.2	54.67	30
HF	0.2	2.43	30
H_2SSA^-	3.0	9.92	Present Work
$\text{H}_2\text{5Cl-SA}$	3.0	4.02	Present Work

complex formation would have to be in the region of $\sim 10 \text{ sec}^{-1} \text{ M}^{-1}$. Considered that the k_{obs} value used in the present calculation is $164 \text{ sec}^{-1} \text{ M}^{-1}$, as used by Baldwin and Stranks,³⁰ and that there are other k_{obs} values ranging from 400 - 1000 $\text{sec}^{-1} \text{ M}^{-1}$ reported in the literature, the chance of reaction (c) being the predominant BeSO_4 formation pathway is very remote.

Baldwin & Stranks,³⁰ in their study of the formation of BeF^+ , have rejected the reaction ($\text{BeOH}^+ + \text{HF}$) as an active pathway. The reason was, for such a reaction to operate, the rate of complex formation would have to be 30 times faster than the rate of water exchange, k_{ex} . In the case of the cation, Fe^{3+} , it has been shown that the rate of water exchange in the coordination shell of $\text{Fe}(\text{H}_2\text{O})_6\text{OH}^{2+}$ is generally faster by a factor of $\sim 10^3$, compared to the rate of water exchange in the $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ coordination shell^{41,66}. It was generalized later by Saini & Mentasti⁴⁰ that the kinetic constants of FeOH^{2+} are often three orders higher than those of Fe^{3+} . In light of this, it is not unreasonable to expect the rate of water exchange, k_{ex} , in the coordination sphere of $\text{Be}(\text{H}_2\text{O})_3\text{OH}^+$ to be $10^2 - 10^3$ times faster than that of $\text{Be}(\text{H}_2\text{O})_4^{2+}$. Consequently, the result of Baldwin & Stranks³⁰ has been reinterpreted in terms of the possible reaction ($\text{BeOH}^+ + \text{HF}$), and the k_{64} value obtained compared with the k_{64} values of the present work (Table 17).

Analyses of the k_{64} values with outer-sphere ion-pair association calculations (Fuoss equation (63), (64)(a)) are unreliable for two reasons, (i) reaction (c) is an interaction between a charged ion and a dipole, unlike the ion-pair interactions encountered previously, association constant of an ion-dipole equilibrium cannot be calculated by the Fuoss equation, (ii) since the k_{ex}' value of water exchange in the $\text{Be}(\text{H}_2\text{O})_3\text{OH}^+$ coordination shell is not available at the present, only estimated value of k_{ex}' can be used in the calculations. A rough value of the ion-dipole association constant, K_{id} , can be obtained with the following expression suggested by Prue⁶⁸,

$$K_{id} = 4\pi r^2 \Delta r N \quad (70)$$

The symbol r is an arbitrary distance between two reaction centres, and Δr , is the fraction of r reduced between the two reactant centres when a charge-transfer absorption occurs from one reactant to the other. According to the authors, reasonable values assumed for the quantities, r and Δr , are $\sim 5\text{\AA}$ and $\sim 0.94\text{\AA}$ respectively. Generally, the value of K_{id} is approximately 0.2 M^{-1} .

In terms of the Eigen multistep complex formation mechanism (expression (62)(a) & (62)(b)), values of the rate constant k_a' are calculated by substituting the quantities k_{12} and K_{IP} in equation (67) with k_{64} and K_{id} . If the value $3.0 \times 10^5 \text{ sec}^{-1}$ is adopted as the rate constant of water exchange, k_{ex}' , in the coordination sphere of $\text{Be}(\text{H}_2\text{O})_3\text{OH}^+$, (i.e. about 10^3 higher than k_{ex} for $\text{Be}(\text{H}_2\text{O})_4^{2+}$), values of

the statistical factor s' can also be established via equation (69)(b).

Results of these calculations are given in Table 18.

Unlike the reaction between $\text{Fe}(\text{H}_2\text{O})_5\text{OH}^{2+}$ and various ligands, which was well studied and documented with plenty of data available on the values of the rate constant k_{64} , there has not been any reported value of the rate constant k_{64} for the reaction of the $\text{Be}(\text{H}_2\text{O})_3\text{OH}^+$ ion. Consequently, the mechanism of reaction (c) can only be conjectured, using the findings on $\text{Fe}(\text{H}_2\text{O})_5\text{OH}^{2+}$ as references. A comparison of the k_a' values of reaction (c) in Table 18 with the k_a values of reaction (a) in Table 16 shows that the kinetic constants of $\text{Be}(\text{H}_2\text{O})_3\text{OH}^+$ are about four to five orders higher than those of $\text{Be}(\text{H}_2\text{O})_4^{2+}$. The rate increase is attributed to the increase in lability of the hydroxo complex, $\text{Be}(\text{H}_2\text{O})_3\text{OH}^+$. This is supported by the much smaller values of $k_{\text{-ex}}'/k_L'$ in Table 18 indicating a faster substitution rate by the incoming ligand molecules. In comparison with the rate of water exchange, k_{ex}' , the values of k_a' are slightly larger. However, for all practical purposes, it is valid to conclude that $k_a' \approx k_{\text{ex}}'$ since there are considerable uncertainties associated with the estimation of both rate constants. Therefore, the rate-determining step of the complex formation appears to be essentially the release of water molecules from the inner coordination sphere of $\text{Be}(\text{H}_2\text{O})_3\text{OH}^+$. With the present study, the reaction mechanism of reaction (c) in Scheme (C) is concluded to be also dissociative (I_d).

TABLE 18

VALUES OF K_{id} AND k_a , AT 25°C FOR REACTION OF $Be(H_2O)_3 OH^+$ WITH VARIOUS LIGANDS.

Ligand	Ionic Strength (μ) M	$K_{id} M^{-1}$	$k_a, \times 10^{-6}$ sec ⁻¹	s'	$\frac{k_{-ex'}}{k_L'}$	Reference
HF	0.2	0.14	1.74	5.80	0.172	30
H_2SSA^-	3.0	0.15	6.61	22.03	0.045	Present Work
$H_2SCl-SA$	3.0	0.15	2.68	8.93	0.112	Present Work

It is necessary to point out that a second contribution to the complex formation by reaction (a) is possible via the pathway of reaction (c). The sequence of elementary steps suggested by Eigen⁵ involves, (i) formation of the outer-sphere ion-pair, $\text{Be}(\text{H}_2\text{O})_4^{2+} \cdot \text{HSSA}^{2-}$, (ii) the "internal" hydrolysis of the cation which increases the basicity of the attacking ligand, thus forming $\text{Be}(\text{H}_2\text{O})_3\text{OH}^+ \cdot \text{H}_2\text{SSA}^-$, and (iii) transition from the outer-sphere ion-pair to the inner-sphere complex. It is apparent that the two reactions (a) and (c) are indistinguishable, and that both of these reactions could contribute extensively to the complex formation.

The k_{obs} data in the present work can be interpreted alternatively using the general reaction Scheme (A). Expression (49) is the general kinetic expression of the scheme which can be simplified to expression (58) if ring enclosure is assumed to be faster than the dissociation of the first metal-ligand bond. The term A in equation (58) is equal to $([\text{Be}^{2+}]_{\text{eff.}} / \Omega + k_{14}/k_{41})$, where Ω has been previously defined as $(1 + K_2[\text{H}^+]/\alpha_A)$. According to equation (58), the values of S' and I' (the slope and intercept obtained from a plot of k_{obs} vs $[\text{Be}^{2+}]_{\text{eff.}}$) reported in Table 14, are equal to:

$$S' = \frac{1}{\Omega} \{ k_{41} + k_{32}K_2[\text{H}^+] + k_{115}K_2[\text{H}^+]^2/K_{2A} + K_{\text{OH}}k_{612}/[\text{H}^+] + K_{\text{OH}}k_{78}K_2 + K_{\text{OH}}k_{109}K_2[\text{H}^+]/K_{2A} \} \quad (71) (a)$$

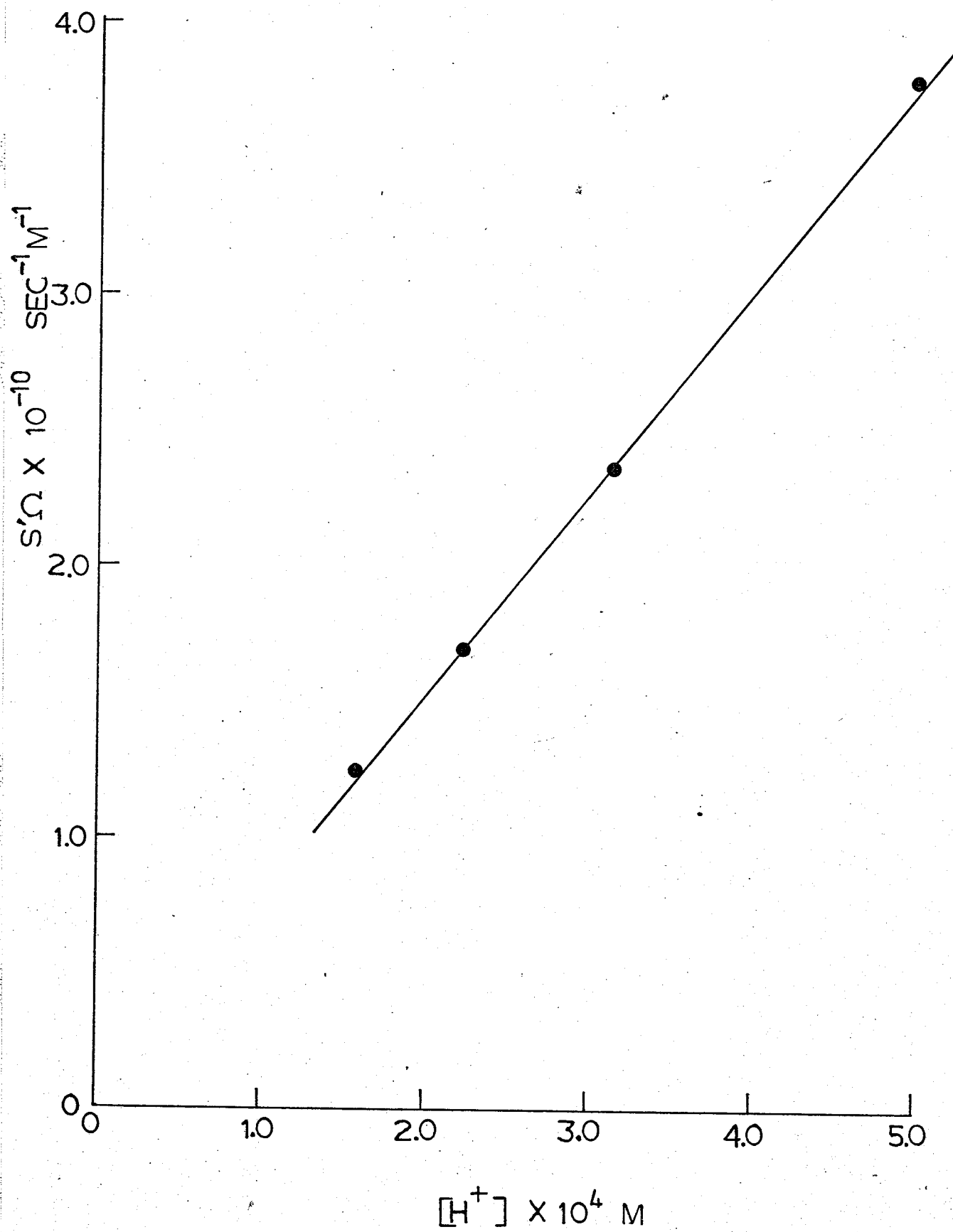
and,

$$I' = \{ k_{14} + k_{126} + k_{23}k_{12}[H^+]/k_{21} + k_{511}k_{15}[H^+]^2/k_{51} \\ + k_{87}k_{128}/k_{812} + k_{910}k_{129}[H^+]/k_{912} \} \quad (71)(b)$$

For the ligands SSA and 5Cl-SA, a plot of the quantity $S'\Omega$ in equation (71)(a) against $[H^+]$ (Figure 12 & 13) was found to be linear with a slope S'' and an intercept I'' which are described by equation (59) and (60) respectively. The values of S'' and I'' for the two ligands are given in Table 19.

The quantity I'' , $(k_{41} + K_{OH}k_{78}K_2)$, is associated with the reactions (I) and (V) of Scheme (A). Kinetically, the two reactions are indistinguishable and, consequently a direct evaluation of the corresponding rate constant is not possible. However, the assumption of limiting condition, $K_{OH}k_{78}K_2 \gg k_{41}$, is well justified with two criteria. Firstly, the rate constant k_{41} with a magnitude of $\sim 10^8 \text{ sec}^{-1} \text{ M}^{-1}$ is simply too fast, even if the reaction was between $\text{Be}(\text{H}_2\text{O})_4^{2+}$ and a dianion. This conclusion is quite reasonable considered that the rate constant of a reaction between $\text{Be}(\text{H}_2\text{O})_4^{2+}$ and a monoanion is only in the range of $\sim 10^2 - 10^3 \text{ sec}^{-1} \text{ M}^{-1}$. (30) Secondly, a value of $7.0 \pm 0.2 \times 10^5 \text{ sec}^{-1} \text{ M}^{-1}$ was reported by Cayley and Hague³⁸ for the rate constant k_{41} of the reaction between $\text{Mg}(\text{H}_2\text{O})_6^{2+}$ and the dianion of 5-nitrosalicylic acid. Previous studies⁵ have shown that the rate constants for H_2O substitution in the inner sphere of Mg^{2+} are normally

FIGURE 12. A plot of the quantity $S'\Omega$ in equation (71)(a) vs $[H^+]$ for the complex formation between $Be(H_2O)_4^{2+}$ and the ligand SSA.



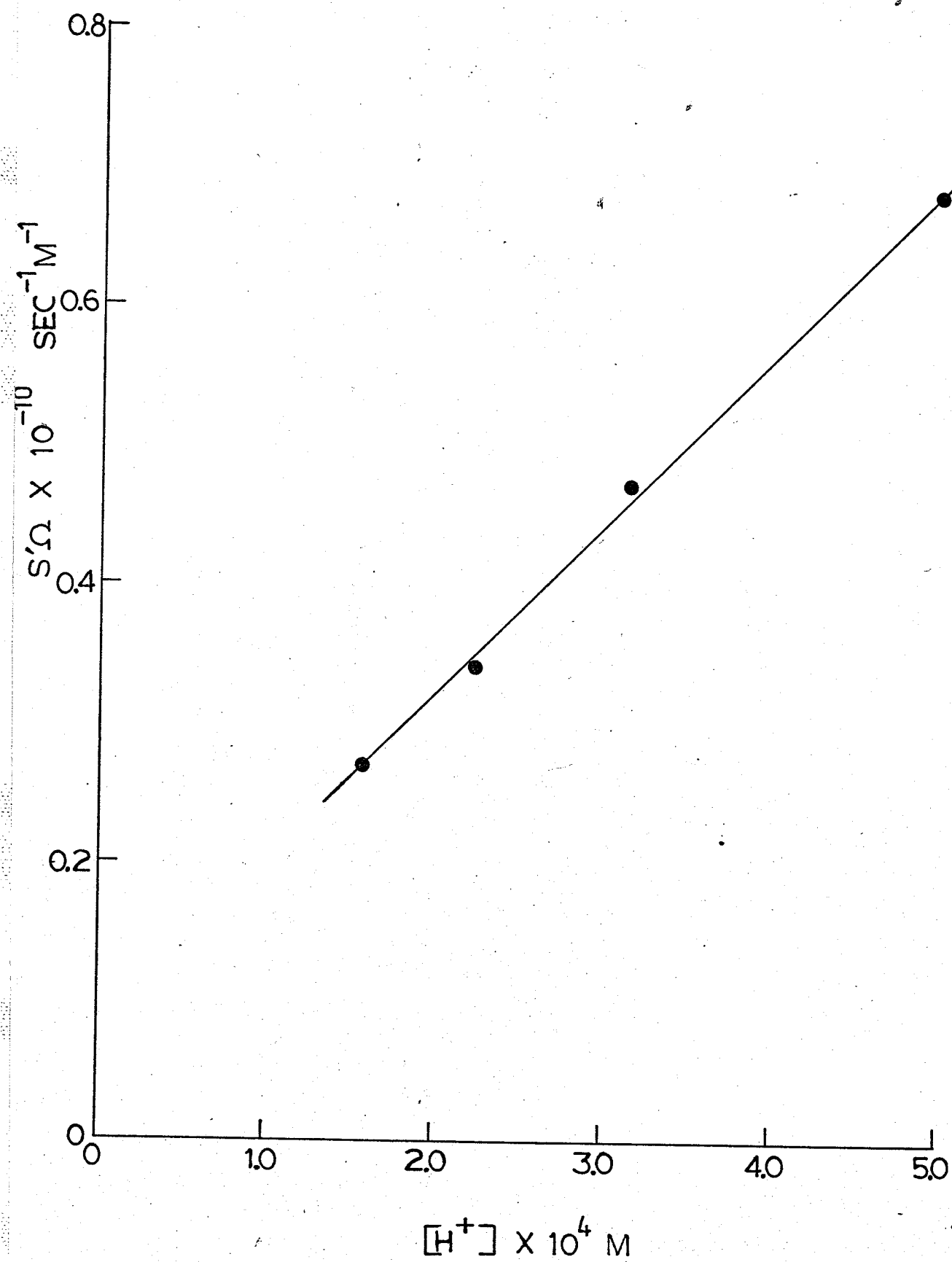


TABLE 19

RESULTS OBTAINED FROM PLOTS OF $S'\Omega$ vs $[H^+]$ AT 25°C.

Ligand	$S' \times 10^{-2}$ $\text{sec}^{-1} \text{ M}^{-1}$	$\Omega \times 10^{-8}$	$S'\Omega \times 10^{-10}$ $\text{sec}^{-1} \text{ M}^{-1}$	$[H^+] \times 10^4$ M	$S'' \times 10^{-13}$ sec^{-1}	$I'' \times 10^{-8}$ $\text{sec}^{-1} \text{ M}^{-1}$
SSA ⁻	1.32	0.94	1.24	1.58	7.49(0.12)	2.36(0.40)
	1.24	1.36	1.69	2.24		
	1.18	1.99	2.36	3.16		
	1.14	3.34	3.79	5.01		
5Cl-SA	1.38	0.20	0.27	1.58	1.19(0.36)	8.20(0.12)
	1.17	0.29	0.34	2.24		
	1.04	0.45	0.47	3.16		
	0.81	0.83	0.68	5.01		

three orders faster than those of Be^{2+} . Therefore, the present value of $\sim 10^8 \text{ sec}^{-1} \text{ M}^{-1}$ would have to be identified with $K_{\text{OH}} k_{78} K_2$. The equilibrium constants are $K_{\text{OH}} = 3 \times 10^{-7} \text{ M}^{(25)}$, $K_2 = 5.50 \times 10^{11} \text{ M}^{-1(50)}$ for 5-sulphosalicylic acid and $K_2 = 1.03 \times 10^{11} \text{ M}^{-1(67)}$ for 5-chlorosalicylic acid. The value of k_{78} computed from the relationship, $I'' = K_{\text{OH}} k_{78} K_2$, is equal to $1.43 \times 10^3 \text{ sec}^{-1} \text{ M}^{-1}$ and $2.65 \times 10^4 \text{ sec}^{-1} \text{ M}^{-1}$ for the ligand SSA and 5Cl-SA respectively.

If the rate constant k_{78} (reaction (V) in Scheme (A)) associated with the reaction between $\text{Be}(\text{H}_2\text{O})_3\text{OH}^+$ and the monoanion of the ligand is compared with the rate constant k_{64} (reaction (c) in Scheme (C)) associated with the reaction between $\text{Be}(\text{H}_2\text{O})_3\text{OH}^+$ and the undissociated form of the ligand, it can be seen that the value of k_{78} is smaller than the value of k_{64} . This is inconsistent with the theory that a ligand with charge -1 should react faster than a neutral ligand. Under such circumstances, reaction (V) must be considered as insignificant in contributing to the formation of $\text{Be}(\text{II})$ complexes according to Scheme (A). A similar finding of $k_{78} > k_{64}$ was reported by Cavasino et.al.⁵⁷ in their studies of the $\text{Fe}(\text{III})$ monochelates formation with substituted molonic acids.

The reactions (II) and (VI) associated with the slope S'' , $(k_{32} K_2 + K_{\text{OH}} k_{109} K_2 / K_{2A})$, are also kinetically indistinguishable from

the experimental data. In the discussion of the results interpreted with Scheme (C), it was shown that reactions (a) and (c) are probably equivalent pathways for the complex formation. Since reactions (a) and (c) of Scheme (C) are identical with reaction (II) and (VI) of Scheme (A), the two limiting conditions, (i) $k_{32}K_2 \gg K_{OH}k_{109}K_2/K_{2A}$, and (ii) $K_{OH}k_{109}K_2/K_{2A} \gg k_{32}K_2$, should be considered as equivalent and treated individually.

If $k_{32}K_2 \gg K_{OH}k_{109}K_2/K_{2A}$ is true, then the value of k_{32} obtained from the relationship $S'' = k_{32}K_2$ is, $1.36 \times 10^2 \text{ sec}^{-1} \text{ M}^{-1}$ and $1.16 \times 10^2 \text{ sec}^{-1} \text{ M}^{-1}$ for the ligands SSA and 5Cl-SA respectively. These values of k_{32} , within experimental uncertainty, are the same as the k_{12} values reported in Table 15 (interpreted with Scheme (C)). The minor discrepancy between the k_{32} and k_{12} values of the ligand 5Cl-SA is probably due to the uncertainty in the K_2 value reported in reference (67).

When $K_{OH}k_{109}K_2/K_{2A} \gg k_{32}K_2$, the value of S'' is identified with $K_{OH}k_{109}K_2/K_{2A}$. The value of rate constant k_{109} established for the ligands SSA and 5Cl-SA is $9.71 \times 10^5 \text{ sec}^{-1} \text{ M}^{-1}$ and $3.15 \times 10^5 \text{ sec}^{-1} \text{ M}^{-1}$ respectively. These values are found to be in very good agreement with the k_{64} values reported in Table 17.

From the kinetic data of the present study, it is concluded that over the acidity range $1.58 \times 10^{-3} \text{ M} - 5.01 \times 10^{-3} \text{ M}$, the formation of

Be(II) monochelates with substituted salicylic acids proceeds via two pathways, (i) $\text{Be}(\text{H}_2\text{O})_4^{2+} + \text{HL}^-$ (monoanion), and (ii)

$\text{Be}(\text{H}_2\text{O})_3\text{OH}^+ + \text{H}_2\text{L}$ (undissociated acid ligand). The mechanism of both pathways is a dissociative " I_d " process in which the rate-determining step is the release of a coordinated water molecule from the inner coordination sphere of the Be(II) cation.

The corresponding stability constant, $K_c = k_{41}/k_{14}$, of the complexes Be(II) 5-sulphosalicylate and Be(II) 5-chlorosalicylate were calculated by equation (52), and the results are given in Table 20. The results obtained here are in good agreement with those which were determined potentiometrically^{69,67}. This agreement does not only reaffirm the reliability of all the K_c values determined kinetically, but also supports indirectly the validity of the present data interpretation using the kinetics of Scheme (A).

The overall rate of the reverse (aquation) reactions, i.e. the intercept of a plot of k_{obs} against $[\text{Be}^{2+}]_{\text{eff.}}$, is described by either equation (71)(b) of reaction Scheme (A) or equation (56) of reaction Scheme (C). A linear relationship is observed when the I' values of the two ligands (reported in Table 14) are plotted against $[\text{H}^+]$, as shown in Figure 14 & 15. The corresponding slope and intercept of the plot I' vs $[\text{H}^+]$ are denoted by S''' and I''' respectively. In terms of equation (71)(b) of the general reaction Scheme (A), S''' and I''' are expressed as follows,

TABLE 20

STABILITY CONSTANT, k_{41}/k_{14} , OF THE COMPLEXES

Be(II) 5-SULPHOSALICYLATE AND Be(II) 5-CHLOROSALICYLATE. (25°C)

Complex	pH	$K_c (k_{41}/k_{14}) \times 10^{-10}$ M^{-1}	Average $K_c \times 10^{-10}$ M^{-1}	Literature $\times 10^{-10}$ M^{-1}	Reference
BeSSA ⁻	3.3	1.99	1.96	9.95	69
	3.5	1.93	(in 3M NaClO ₄)	(in 0.5M NaClO ₄)	
	3.65	1.92			
	3.8	1.99			
Be5Cl-SA	3.3	0.17	0.19	0.69	67
	3.5	0.18	(in 3M NaClO ₄)	(in 3M NaClO ₄)	
	3.65	0.19			
	3.8	0.20			

FIGURE 14. Hydrogen ion concentration dependence of the overall dissociation (reverse reactions) rate of the complex, BeSSA^- .

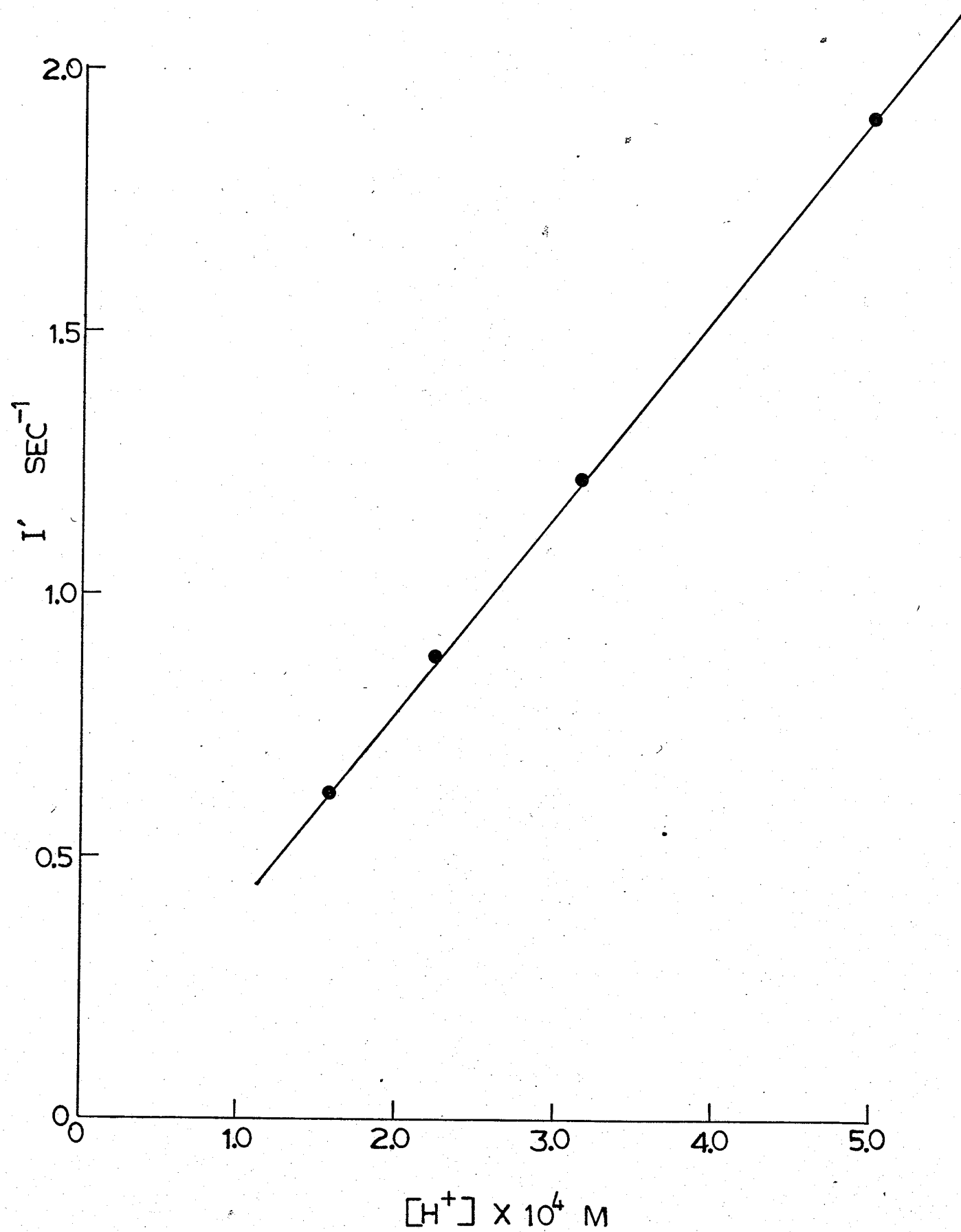
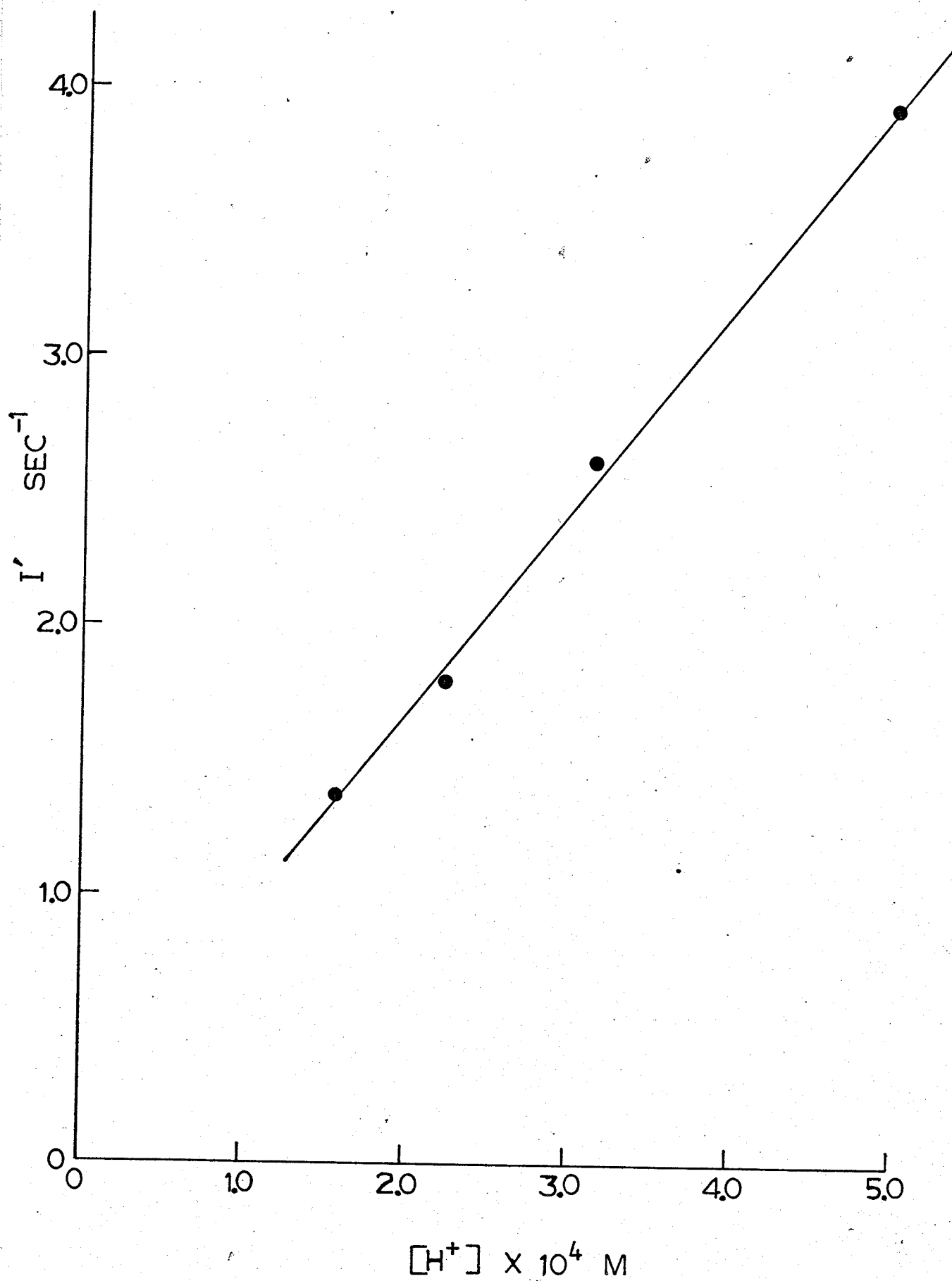


FIGURE 15. Hydrogen ion concentration dependence of the overall dissociation (reverse reactions) rate of the complex, Be-5ClSA.



$$S''' = (k_{23}k_{12}/k_{21} + k_{910}k_{129}/k_{912}) \quad (72)(a)$$

and

$$I''' = (k_{14} + k_{126} + k_{87}k_{128}/k_{812}) \quad (72)(b)$$

Expressions similar to (72)(a) & (b) can be derived from an interpretation of the I' vs $[H^+]$ plot with equation (56) of reaction Scheme (C).

The analogous equations are:

$$S''' = (k_{21} + k_{46}) \quad (73)(a)$$

and

$$I''' = k_{43} \quad (73)(b)$$

For the ligand 5-sulphosalicylic acid, the S''' and I''' values are $(3.76 \pm 0.04) \times 10^3 \text{ sec}^{-1} \text{ M}^{-1}$ and $(2.95 \pm 1.18) \times 10^{-2} \text{ sec}^{-1}$ respectively; and for the ligand 5-chlorosalicylic acid, the values are $(7.57 \pm 0.26) \times 10^3 \text{ sec}^{-1} \text{ M}^{-1}$ and $(1.55 \pm 0.84) \times 10^{-1} \text{ sec}^{-1}$ respectively. It can be seen that in both cases the value of S''' is much larger than that of I''' . This indicates that the contribution of the $[H^+]$ dependent pathways (reaction (I), (IV) and (V) of Scheme (A) or reaction (d) of Scheme (C)) to the overall rate of the reverse (aquation) reaction is negligible in comparison with the contribution from the $[H^+]$ dependent pathways (reactions (II) and (VI) of Scheme (A) or reactions (a) and (c) of Scheme (C)).

From the discussion of the rate of forward (complexation) reactions, it is obvious that reaction Scheme (C) is just a special

case of the general Scheme (A). Therefore, in the present discussion of the reverse rate, only equation (72)(a) and (b) of Scheme (A) will be considered. According to equation (72)(a), the reverse reactions (II) and (VI) are kinetically indistinguishable and consequently, it is impossible to evaluate the corresponding rate constants directly from the experimental value of S''' . This is the same situation as in the case of the forward reactions (II) and (VI) discussed earlier in this section. It was then concluded that both forward reactions were equally possible, and should be weighted the same in contributing to the formation of the Be(II) complex. In light of this conclusion, and the lack of evidence supporting the predominance of a particular reverse reaction, the overall rate of reverse reaction is then presumed to be the result of both reverse reactions (II) and (VI). The experimental value of S''' provides an upper limit for the value of the rate constants $k_{23}k_{12}/k_{21}$ and $k_{910}k_{129}/k_{912}$. If the magnitudes of these rate constants are comparable, and assuming $k_{21} \gg k_{23}$ and $k_{912} \gg k_{910}$, the value of the rate constants k_{12} and k_{129} for both ligands is much greater than the corresponding S''' values determined. In other words, according to the present results, if ring enclosure in the formation of the complex is assumed to be fast, then ring opening in the dissociation of the complex is equally fast as well. Values of k_{12} and k_{129} are estimated to be orders larger than $10^3 \text{ sec}^{-1} \text{ M}^{-1}$.

The $[\text{H}^+]$ independent values of I''' for both ligands are associated with the rate constants k_{14} , k_{126} and $k_{87}k_{128}/k_{812}$ of expression (72)(b).

If the values of I''' ($10^{-2} - 10^{-1} \text{ sec}^{-1}$) are identified with the reverse rate constants k_{14} and k_{126} , then according to the stability constants ($10^9 - 10^{10} \text{ M}^{-1}$) established, values of the forward rate constants k_{41} and k_{612} would have to be in the range of $10^8 \text{ sec}^{-1} \text{ M}^{-1}$ for the formation of both complexes. This is obviously in disagreement with the value of k_{41} which was suggested earlier in this section to be smaller than $10^5 \text{ sec}^{-1} \text{ M}^{-1}$. Therefore, it is apparent that the value of I''' should be identified with the rate constant $k_{87}k_{128}/k_{812}$. A direct evaluation of k_{128} is not possible because the values of k_{87} and k_{812} are not known. However, if it is assumed $k_{812} \gg k_{87}$, the value of k_{128} will be much greater than 10^{-1} sec^{-1} .

According to the results reported in Table 11, the dissociation rate constant of the complex BeSSA in an equilibrium system is apparently independent of $[\text{H}^+]$. The average k_{obs} value was $6.02 \times 10^{-2} \text{ sec}^{-1}$, which is in the same order as the $[\text{H}^+]$ independent I''' value ($2.95 \times 10^{-2} \text{ sec}^{-1}$) of the complex BeSSA. It is possible that an equilibrium system of the complex BeSSA, if perturbed by a change in $[\text{H}^+]$, relaxes exclusively via the reverse reaction mechanism of pathway (V) in Scheme (A).

At pH = 4.0 and above, the kinetic pathways of Scheme (A) or (C) are not valid due to the extensive hydrolysis of the cation $\text{Be}(\text{H}_2\text{O})_4^{2+}$ to its trinuclear species $\text{Be}_3(\text{OH})_3^{3+}$ (52). Figure 16 is an example of

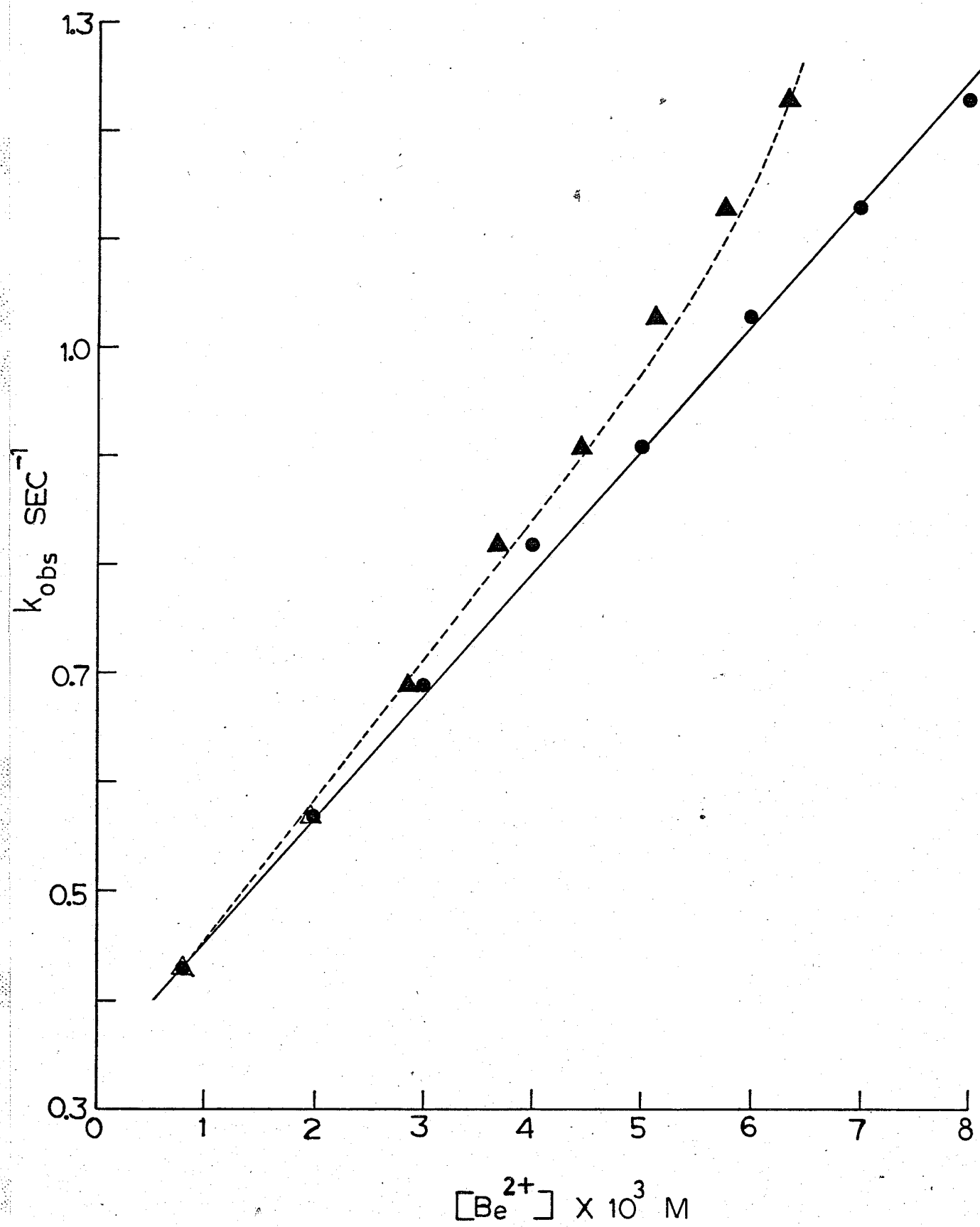
FIGURE 16. Plots of k_{obs} vs $[\text{Be}^{2+}]_{\text{total}}$ and $[\text{Be}^{2+}]_{\text{eff.}}$

for the complex formation of BeSSA^- at

25.1°C, pH = 4.0, and in a 3.0M ionic medium.

● $[\text{Be}^{2+}]_{\text{total}}$

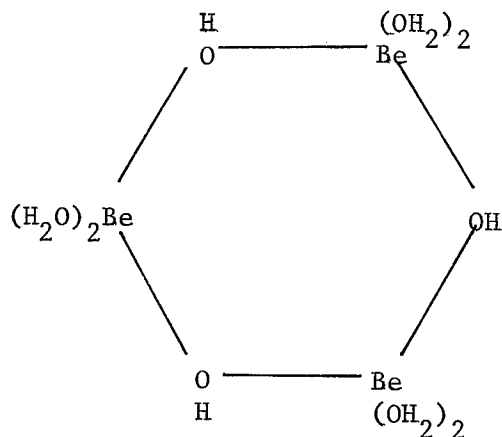
▲ $[\text{Be}^{2+}]_{\text{eff.}}$



the relationship between k_{obs} and $[\text{Be}^{2+}]_{\text{eff}}$ at pH = 4.0. The nonlinearity could have been the consequence of a reaction between the hydroxo complex, $\text{Be}_3(\text{OH})_3^{3+}$, and the salicylic acid type ligand.

At pH's 4.5, 5.0 & 5.5, it can be easily shown (exemplified in Figure 16) that the plots of k_{obs} vs $[\text{Be}^{2+}]_{\text{total}}$ are linear while the plots of k_{obs} vs $[\text{Be}^{2+}]_{\text{eff}}$ are not. A model which is consistent with the observed kinetic behaviour would have to include $\text{Be}_3(\text{OH})_3^{3+}$ as a reactive species along with the ligand. Thus, at higher pH's, the total transmittance change is caused by the presence of two absorbing species, (i) BeSSA (or Be-5ClSA) formed by the reaction between $\text{Be}(\text{H}_2\text{O})_4^{2+}$, $\text{Be}(\text{H}_2\text{O})_3\text{OH}^+$ and the ligand, and (ii) an absorbing species that is spectrophotometrically indistinguishable from BeSSA (or Be-5ClSA), formed by the reaction between $\text{Be}_3(\text{OH})_3^{3+}$ and the ligand. The value of k_{obs} , in such a case, will be dependent upon the value of $[\text{Be}^{2+}]_{\text{total}}$ instead of the value of $[\text{Be}^{2+}]_{\text{eff}}$.

In addition to the kinetic evidence, the structure of $\text{Be}_3(\text{OH})_3^{3+}$ also supports the thesis that the hydroxo species will react with the ligand. A probable structure proposed by Kakihana & Sillen⁵² is a six-membered ring with tetrahedra being linked by sharing OH corners. Structurally, there is a certain amount of distortion of the original geometry (tetrahedral) of the $\text{Be}(\text{H}_2\text{O})_4^{2+}$ ion in the formation of the six-membered ring. Nevertheless, orientations of the two H_2O molecules



around each beryllium centre are not expected to change radically since a majority of the rearrangements is restricted to the Be-OH bonds only. Furthermore, the OH group is not particularly bulky spatially, and therefore, should not have any steric effect upon the original orientations of the two water molecules. On the basis of this conclusion, it is speculated that the water molecules of the hydroxo complex, $\text{Be}_3(\text{OH})_3^{3+}$, would be susceptible to ligand substitutions similar to the water molecules of the $\text{Be}(\text{H}_2\text{O})_4^{2+}$ ion. The electronic effects of the hydroxide groups on the lability of the water molecules are not known. However, there is no evidence indicating the inhibition of the substitution reactions by the presence of these hydroxide groups. It must be emphasized that the present discussion is strictly conjectural, no attempt has been made to elucidate the actual structure(s)

of the complex(es) formed at the higher pH levels.

According to the data reported in Table 8 & 9, it would seem that the complex formation rate is independent of the ligand concentration at pH = 3.5, but dependent upon it at pH = 5.5. Considering that hydrolysis of the cation is greater than 90% at pH = 5.5 and is negligible at pH = 3.5, it would not be unreasonable to attribute the apparent ligand concentration dependence of the complex formation rate to the reaction between the hydroxo complex $\text{Be}_3(\text{OH})_3^{3+}$ and the ligand. Values of the rate constant, k_{obs} , in Table 9 were determined by using the kinetic expressions derived for the interpretation of a strictly pseudo-first order reaction (excess of cation). Due to the extensive hydrolysis occurred at pH = 5.5, the condition under which the kinetics were observed was not pseudo-first order as originally intended. Therefore, application of the pseudo-first order kinetic expressions in this case was erroneous. A proper treatment of the kinetic data would involve taking into consideration the variation of $[\text{Be}^{2+}]_{\text{total}}$, which is equal to $[\text{Be}^{2+}]_{\text{eff.}} + 3[\text{Be}_3(\text{OH})_3^{3+}]$, at any time t (sec). The apparent ligand concentration dependence of the complex formation rate could have been caused simply by the deviation of the reaction at higher pH's from the pseudo-first order condition. In the present work, this would appear to be more likely than the thesis which suggests that the reaction rate between $\text{Be}_3(\text{OH})_3^{3+}$ and the ligand was concentration dependent.

(3) ACTIVATION PARAMETERS.

Data of the studies on the temperature dependence of the complex formation rate of both ligands are listed in Table 12. The plots of $\log (k_{\text{obs}}/T)$ against $1/T$ in Figures 17 & 18 are shown to be linear. The temperature studies of both complexes were conducted at pH = 3.3 & 3.8, and the results agree with each other within experimental uncertainties. From the slope of the plots, the average activation energy for the formation of BeSSA and Be-5ClSA is computed to be 12.83 Kcal/mole and 12.53 Kcal/mole respectively. Therefore, it can be assumed that the same reaction mechanism is operating from pH 3.3 to 3.8 for the complex formation with both ligands. The similar activation energies support the thesis that electronically and structurally, the ligands SSA and 5Cl-SA are very similar in the chelation of the $\text{Be}(\text{H}_2\text{O})_4^{2+}$ ion. The difference in size of the functional groups (the bulky SO_3^- group vs Cl^-) and formal charge of the ligands (SSA^{2-} vs 5Cl-SA^-) do not seem to have any significant effect on the activation energies of the complex formations.

The enthalpy of activation, $\Delta H^\ddagger$, for the ligand 5-sulphosalicylic acid and 5-chlorosalicylic acid are, 12.23 Kcal/mole and 11.93 Kcal/mole respectively, according to calculations based on equation (48)(a). These values are slightly different from the 8.5 Kcal/mole observed by Strehlow and Kalarickal^{28c} for the beryllium-sulphate substitution and 8.9 Kcal/mole observed by Baldwin & Stranks³⁰ for the beryllium-fluoride substitution reaction. The difference is best understood in

FIGURE 17. Temperature dependence of complex formation
rate of BeSSA^- and Be-5ClSA at pH 3.3 .

● BeSSA^-
▲ Be-5ClSA

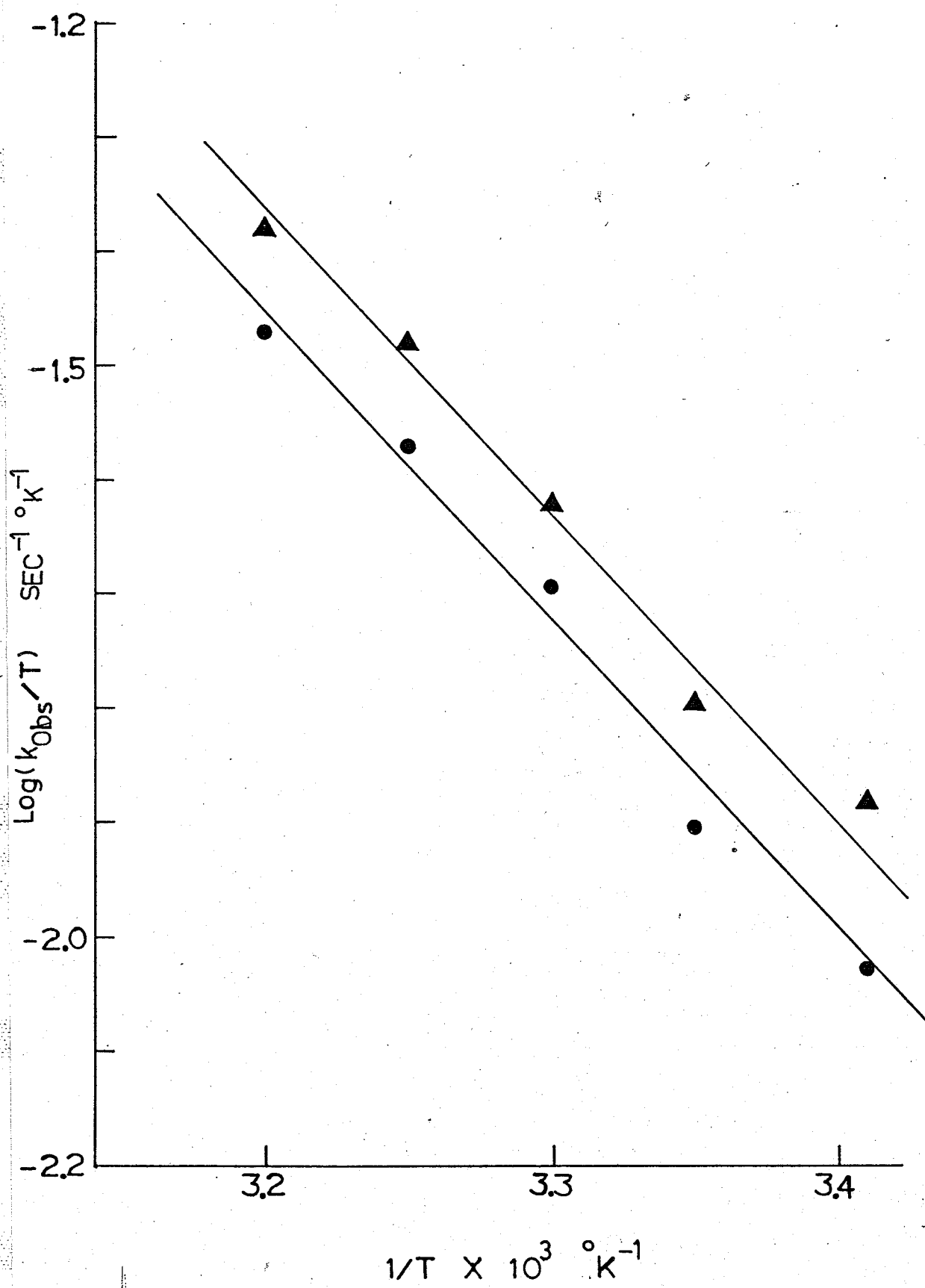
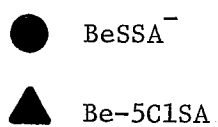
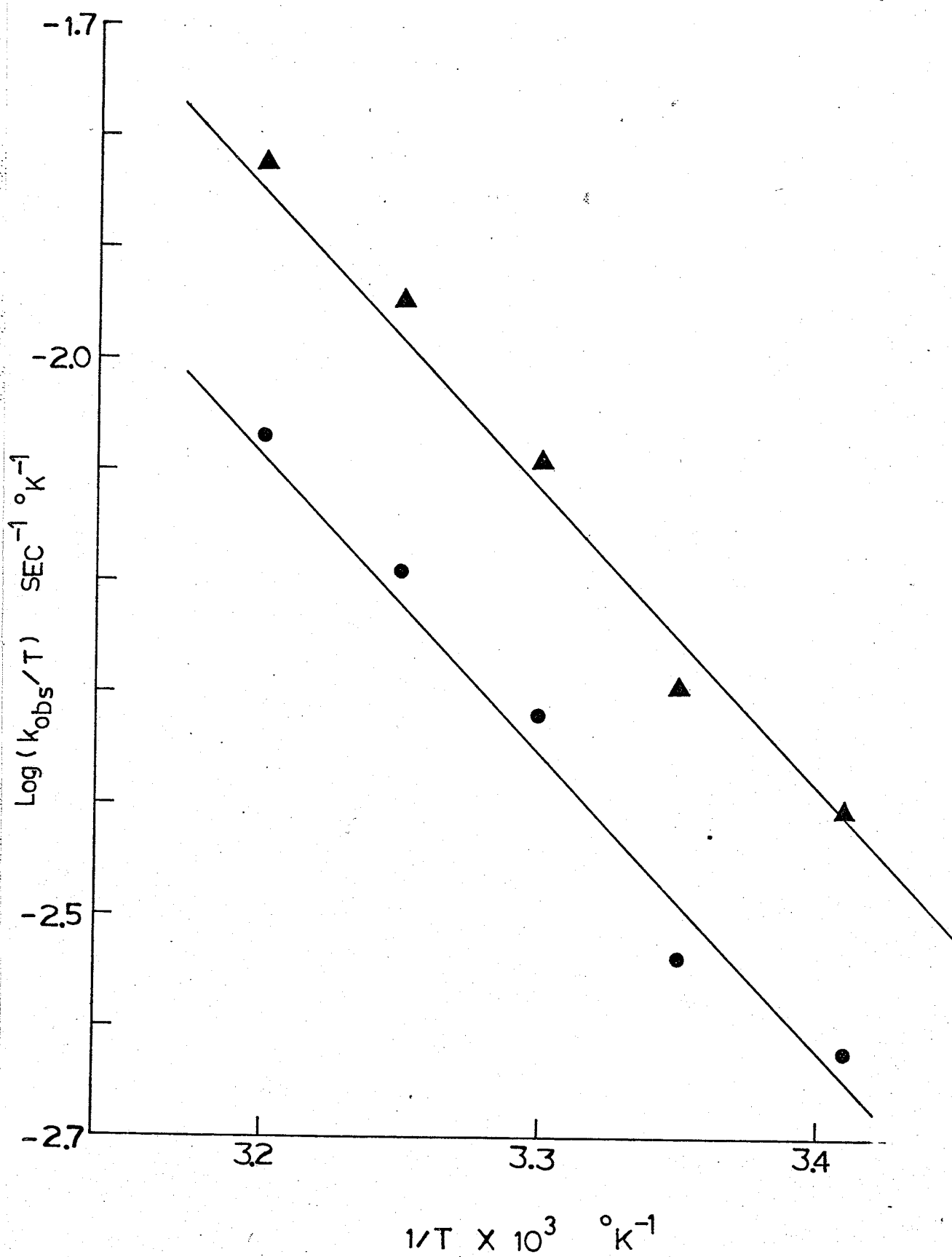
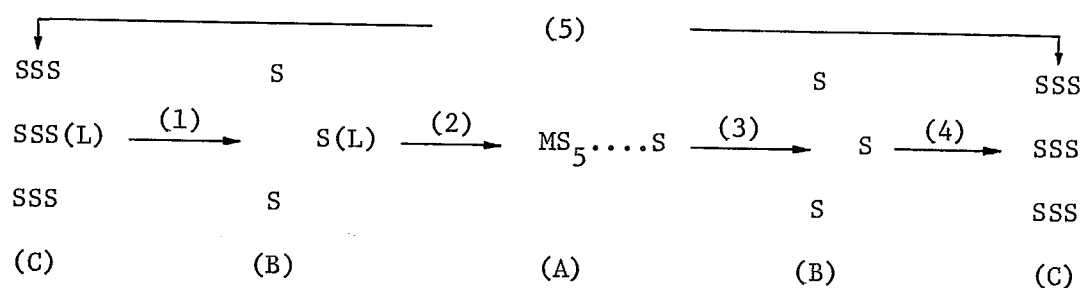


FIGURE 18. Temperature dependence of complex formation
rate of BeSSA^- and Be-5ClSA at pH 3.8 .





terms of the mechanism of solvent exchange and ligand substitution proposed by Bennetto and Caldin⁷⁰. According to these authors, the surroundings of a solvated ion can be divided into three regions, (i) the innermost solvation shell A, (ii) an intermediate region B which is extended not far beyond region A, where the molecules will have a short stay in a state of high energy and high entropy relative to the bulk solvent, and (iii) the bulk solvent C outside region B. Solvent exchange and ligand substitution are understood as the following scheme,



The corresponding enthalpies of activation for substitution and exchange are,

$$\Delta H_f^\ddagger = \Delta H_{MS} + \Delta H_{st}^\ddagger \quad (74)(a)$$

$$\Delta H_{ex}^\ddagger = \Delta H_{MS} + \Delta H_{st} \quad (74)(b)$$

The enthalpy change, ΔH_{MS} , is associated with process (3) which is independent of the entering ligand since the breaking of an ion-solvent bond is common to both the substitution and exchange processes. ΔH_{st} and $\Delta H_{st}^\ddagger$ are the enthalpy changes accompanying the respective

reorganization of the solvent structure, and therefore, are associated with the processes 1, 4 and 5. In the case of solvent exchange, ΔH_{st} is a property of the solvent molecules only. However, in the case of ligand substitution, ΔH_{st} , is characteristic of both the ligand and solvent molecules. The relative magnitudes of the quantities ΔH_{MS} and ΔH_{st} , characterise the kinetic behaviour of a ligand substitution process.

In the presence of a ligand, solvent structure can alter considerably depending upon the effects of the electrostatic properties of the ligand. For a ligand with high intermolecular attractive forces, the attraction between neighbouring solvent molecules is increased; thus "stiffening" the solvent structure. Under such an influence, ΔH_{st} , in expression (74)(a) will be more negative and thus, making $\Delta H_f^\ddagger$ smaller than $\Delta H_{ex}^\ddagger$. Conversely, a ligand with weak intermolecular attractive forces will "loosen" the solvent structure and thus lead to $\Delta H_f^\ddagger$ values higher than $\Delta H_{ex}^\ddagger$ values of solvent exchange.

It is unfortunate that $\Delta H_{ex}^\ddagger$ for H_2O exchange of the $Be(H_2O)_4^{2+}$ ion is not available at the present. However, with the aid of the proposed model, the minor difference between the substitution enthalpies of the ligands SO_4^{2-} , F^- and the 5-substituted salicylic acids can still be explained. From the results of Baldwin and Stranks³⁰, it is apparent that the intermolecular interactions between the ligands F^- and SO_4^{2-} and an aqueous solvent of low ionic strength ($< 1.0M$) are similar. This is supported by comparable substitution enthalpies, $\Delta H_f^\ddagger$,

of the two systems. The slightly higher values of $\Delta H_f^\ddagger$ from the present study is an indication of a possibly different intermolecular interaction between the 5-substituted salicylic acid and the present solvent system. For the F^- and SO_4^{2-} systems studied,^{30,28c} it is speculated that the highly-organized structure characteristic of an aqueous solvent system is basically retained. This is suggested in light of the smaller sizes of the anions and the relatively low ionic strengths used in these systems. In the present studies, the solvent used is a 3 M ionic medium which is made up of ~ 2.8 M $NaClO_4$ and ~ 0.2 M $NaC_2H_3O_2$. The presence of an excess of ClO_4^- and CH_3COO^- could have disrupted the basic structure of the well-organized aqueous solvent system. In addition to that, the 5-substituted salicylic acids are relatively bulkier than unidentate ligands and hence, will contribute further to the disruption of the basic aqueous solvent structure. Therefore, it is concluded that the lower substitution enthalpies of ligands F^- and SO_4^{2-} are due to a more rigid solvent structure in comparison to the solvent structure of the present system. In other words, ΔH_{st} of the former systems are more negative than those of the latter system.

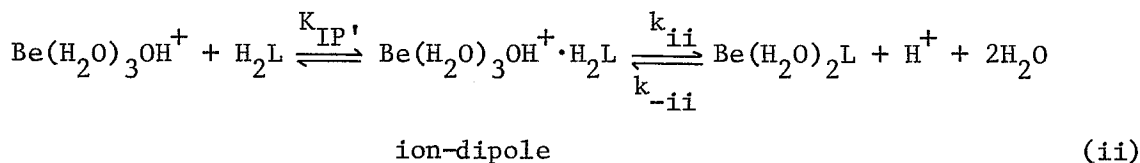
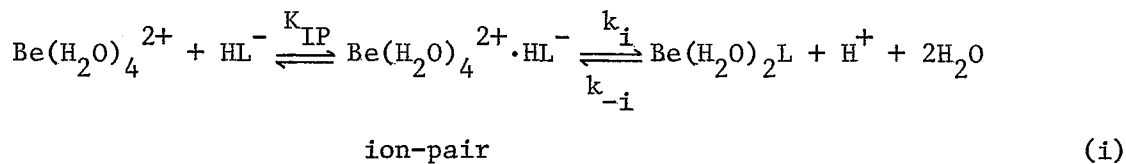
From the reported studies of $Be(II)$ solvent exchange with trimethyl phosphate,²³ dimethylformamide and acetylacetonato dimethylformamide²¹ systems, enthalpies of activation were found to have average values of ~ 14 Kcal/mole and the solvent-exchange mechanism was a solvent-assisted " I_d " process. If this average $\Delta H_{ex}^\ddagger$ value is assumed to be the upper limit of activation enthalpy of water exchange

of the $\text{Be}(\text{H}_2\text{O})_4^{2+}$ complex, then $\Delta H_f^\ddagger$ values of the present systems and the F^- and SO_4^{2-} systems^{30,28c} are attributable to $\Delta H_{\text{ex}}^\ddagger$ of the $\text{Be}(\text{H}_2\text{O})_4^{2+}$ ion in an aqueous medium. The discrepancies in the activation parameters observed in the various systems studied are probably a consequence of the different solvent (medium) backgrounds used in the kinetic runs.

Entropies of activation, $\Delta S_f^\ddagger$, for the ligands 5-sulphosalicylic acid and 5-chlorosalicylic acid are, -16.15 cal/deg-mole and -16.37 cal/deg-mole respectively. This is in agreement with the slightly negative entropy of activation, $\Delta S_{\text{ex}}^\ddagger$, for solvent exchange in most of the systems studied (~ -7.5 cal/deg-mole)²³.

(F) CONCLUSION

Formation of the chelates of beryllium, $\text{Be}(\text{H}_2\text{O})_2\text{-SSA}^-$ and $\text{Be}(\text{H}_2\text{O})_2\text{-5ClSA}$, were found to have proceeded via the following parallel reaction pathways:



Both pathways are expected to contribute actively, particularly when the tetra-aquo beryllium complex, $\text{Be}(\text{H}_2\text{O})_4^{2+}$, can be easily hydrolysed into the tri-aquo hydroxo beryllium complex, $\text{Be}(\text{H}_2\text{O})_3\text{OH}^+$, via an "internal hydrolysis" mechanism suggested by Eigen⁸. For the chelation of Be(II) with the ligand 5-sulphosalicylic acid, the corresponding values of the rate constants k_i and k_{ii} are $6.3 \times 10^1 \text{ sec}^{-1}$ and $6.6 \times 10^6 \text{ sec}^{-1}$ respectively. In the case of the ligand 5-chlorosalicylic acid, the rate constants k_i and k_{ii} are, $6.6 \times 10^1 \text{ sec}^{-1}$ and $2.7 \times 10^6 \text{ sec}^{-1}$ respectively.

The reaction mechanism is determined to be " I_d ", in agreement with the findings reported by Baldwin and Stranks³⁰. There is no apparent dependence of the complex formation rate on the nature of the

entering ligand, hence, no evidence of an associative mechanism being active.

Activation parameters associated with the formation of $\text{Be}(\text{H}_2\text{O})_2\text{-SSA}^-$ are,

$$\Delta H_f^\ddagger = 12.23 \text{ Kcal/mole}$$

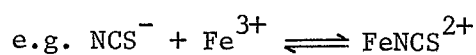
$$\Delta S_f^\ddagger = -16.15 \text{ cal/deg-mole} \quad .$$

The corresponding activation parameters for the formation of $\text{Be}(\text{H}_2\text{O})_2\text{-5ClSA}$ are,

$$\Delta H_f^\ddagger = 11.93 \text{ Kcal/mole}$$

$$\Delta S_f^\ddagger = -16.37 \text{ cal/deg-mole} \quad .$$

APPENDIX A



$$K_1 = k_1/k_{-1} = \frac{[C]_{\text{eq.}}}{[A]_{\text{eq.}}[B]_{\text{eq.}}} \quad (2)$$

$$d[C]/dt = k_1[A][B] - k_{-1}[C] \quad (3)$$

$$= k_1[A][B] - k_{-1}[C]/K_1$$

Total concentration of A at any time t is:

$$[A]_{\text{total}} = [A]_t + [C]_t \quad (4)$$

Similarly, at equilibrium,

$$[A]_{\text{total}} = [A]_{\text{eq.}} + [C]_{\text{eq.}} \quad (5)$$

If $[B] \gg [A]$, so that $[B]_{\text{eq.}} \approx [B]_{\text{total}}$, we can write

(from equation (2)),

$$[A]_{\text{eq.}} = \frac{[C]_{\text{eq.}}}{K_1[B]_{\text{total}}} \quad (6)$$

and equation (5) can be re-written

$$[A]_{\text{total}} = [C]_{\text{eq.}} \left(1 + \frac{1}{K_1[B]_{\text{total}}}\right) \quad (7)$$

APPENDIX A

On substituting $[A]_{\text{total}}$ into equation (4), we obtain

$$[A]_t = [C]_{\text{eq.}} \left(1 + \frac{1}{K_1[B]_{\text{total}}}\right) - [C]_t \quad (8)$$

The rate equation (3) becomes

$$d[C]/dt = (k_1/K_1 + k_1[B]_{\text{total}})([C]_{\text{eq.}} - [C]_t) \quad (9)$$

or

$$d[C]/dt = k_{\text{obs}}([C]_{\text{eq.}} - [C]_t) \quad (10)$$

APPENDIX B

```

$JOB WATER MARK K.S. MAK
C SE REACTION_RATES FROM STOPPED-FLOW DATA
1 INTEGER RN,S(30)
2 REAL IC,IE,A,DL*8
3 DIMENSION T(30),DT(30),V(30),Z(30)
4 9 READ(5,10,END=999)DL,RN
5 10 FORMAT(15)
6 READ(15,N,IC,IE,X
7 PRINT11
8 11 FORMATT(1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,19,20,21,22,23,24,25,26,27,28,29,30)
9 PRINT12,DL,RN
10 FORMAT(1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16)
11 PRINT13
12 13 FORVAT(1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,19,20,21,22,23,24,25,26,27,28,29,30)
13 REAL,S(1),DT(1),I=1,N
14 DO 1 I=1,N
15 DT(I)=IE+IS*DT(I)
16 DT(I)=ALCG10(IC/DT(I))
17 1 T(I)=X*S(I)
18 IF=ALCG10(I0/IF)
19 DO 2 I=1,N
20 Y(I)=ALOG(A+S*(DT(I)-IF))
21 Z(I)=Y(I)/2.3026+3.
22 PRINT14,S(1),T(1),DT(1),Z(1)
23 14 FORMATT(1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,19,20,21,22,23,24,25,26,27,28,29,30)
24 PRINT15,IF
25 15 FORMATT(1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,19,20,21,22,23,24,25,26,27,28,29,30)
26 PRINT16
27 16 FORVAT(1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,19,20,21,22,23,24,25,26,27,28,29,30)
28 A=0.
29 B=0.
30 D=0.
31 E=0.
32 G=0.
33 DO 3 I=1,N
34 A=AT(I)
35 B=RT(I)
36 D=DT(I)*2
37 3 E=AT(I)*Y(I)
38 F=N*C-A*A
39 M=(N+E-A*R)/F
40 C=(R+E-A*E)/F
41 DO 4 I=1,N
42 G=G+(M*(T(I)-C-Y(I)))**2
43 DY=SQRT(G/(N-2))
44 ZM=1000.*M
45 DDY=1000.*DY*SQRT(N/F)
46 PRINT17,M,CCY
47 17 FORMATT(1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,19,20,21,22,23,24,25,26,27,28,29,30)
48 A=1,5X,E50=1,E11,4, SECONDS(1))
49 PRINT19,MM
50 18 FORMATT(1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,19,20,21,22,23,24,25,26,27,28,29,30)
51 GO TO 9
52 999 STOP
53 SNO
3ENTRY

```

APPENDIX B

An example of the data inputs were:

CARD 1 - This card was reserved for a data label which was allowed to occupy up to 14 columns. The columns 1 to 8 inclusive were allocated to characters which denoted the nature of the run. In columns 9 to 14 inclusive, the serial number of the run was registered. e.g.

bbBe/SSAbbb801

Columns 1 8 14

CARD 2 - The first input value was an INTEGER* number, either a +1 or a -1 depending on the slope of the optical density change as the reaction proceeded. If the transmittance was increasing, a value of +1 was input and vice versa. Another INTEGER* number was next which represented the total number of d_t ' values being used in the computation. The third and fourth entries were REAL* numbers, the values of d_o ' and d_{eq} ' respectively. Finally, a time conversion factor in the form of (1mm $\equiv$ X msec) was entered as a REAL* number. The following is an example of the format free card 2.

1b13b636b244b0.495

Columns 1....

CARD 3 - The d_t ' values and the corresponding time measurements were entered as data pairs. The time measurement of each data pair was entered first as an INTEGER* number, followed by the d_t ' value in REAL*.

APPENDIX B

The numbers 0, 10, 20, 30 etc. (multiples of 10) were characteristic of the time measurements. This resulted from the 10 mm intervals taken along the time base between d_t ' measurements.

INTEGER*, REAL* - FORTRAN language.

APPENDIX C

0000	00 00	E 0
0001	06 14	ST14
0002	06 15	ST15
0003	09 00	* M
0004	08 06	* SN
0005	15 13	D13
0006	07 00	RE 0
0007	00 15	E 15
0008	00 01	E 1
0009	02 15	+15
0010	07 15	RE15
0011	09 02	* α
0012	08 04	* J ₆
0013	08 00	* S
0014	08 06	* SN
0015	00 00	E 0
0016	06 00	ST 0
0017	06 01	ST 1
0018	06 02	ST 2
0019	06 03	ST 3
0020	06 04	ST 4
0021	06 05	ST 5
0022	06 14	ST14
0023	06 15	ST15
0024	09 00	* M
0025	08 07	* CS
0026	00 15	E 15
0027	00 01	E 1
0028	02 00	+ 0
0029	06 15	ST15
0030	00 15	E 15
0031	15 13	D13
0032	07 00	RE 0
0033	02 01	+ 1
0034	06 02	ST 2
0035	07 06	RE 6
0036	03 15	-15
0037	08 04	* J ₆
0038	08 00	* S
0039	08 07	* CS
0040	07 06	RE 6
0041	05 02	÷ 2
0042	06 03	ST 3
0043	07 03	RE 3
0044	08 02	* W
0045	03 04	-14
0046	09 03	* SP

APPENDIX C

0000	00 00	E 0
0001	06 01	ST 1
0002	06 05	ST 5
0003	06 07	ST 7
0004	06 08	ST 8
0005	06 09	ST 9
0006	06 10	ST 10
0007	06 11	ST 11
0008	06 12	ST 12
0009	06 13	ST 13
0010	06 14	ST 14
0011	06 15	ST 15
0012	00 15	E 15
0013	09 00	* M
0014	08 08	* TN
0015	15 13	D 13
0016	07 00	RE 0
0017	00 15	E 15
0018	00 01	E 1
0019	02 15	+ 15
0020	07 15	RE 15
0021	09 02	* α
0022	08 04	* J ₆
0023	08 00	* S
0024	08 08	* TN
0025	00 15	E 15
0026	15 13	D 13
0027	07 00	RE 0
0028	06 01	ST 1
0029	07 01	RE 1
0030	08 02	* W
0031	04 06	x 6
0032	07 03	RE 3
0033	06 14	ST 14
0034	07 01	RE 1
0035	03 14	- 14
0036	06 13	ST 13
0037	07 13	RE 13
0038	08 02	* W
0039	05 06	÷ 6
0040	08 02	* W
0041	00 15	E 15
0042	00 00	E 0
0043	06 01	ST 1
0044	06 14	ST 14
0045	06 15	ST 15
0046	09 00	* M
0047	08 07	* CS
0048	00 01	E 1
0049	02 01	+ 1
0050	15 13	D 13
0051	07 00	RE 0
0052	00 15	E 15
0053	07 01	RE 1
0054	06 14	ST 14
0055	07 04	RE 4
0056	03 14	- 14
0057	08 04	* J ₆
0058	08 00	* S
0059	08 07	* CS

0060	00 00	E 0
0061	06 14	ST 14
0062	00 15	E 15
0063	15 13	D 13
0064	07 00	RE 0
0065	06 15	ST 15
0066	07 03	RE 3
0067	06 14	ST 14
0068	07 15	RE 15
0069	03 14	- 14
0070	06 05	ST 5
0071	07 05	RE 5
0072	08 02	* W
0073	06 06	ST 6
0074	00 00	E 0
0075	06 14	ST 14
0076	06 15	ST 15
0077	07 13	RE 13
0078	06 12	ST 12
0079	07 05	RE 5
0080	05 12	÷ 12
0081	08 10	* LN
0082	06 14	ST 14
0083	07 06	RE 6
0084	08 15	* ½
0085	04 14	x 14
0086	06 10	ST 10
0087	00 15	E 15
0088	00 01	E 1
0089	02 08	+ 8
0090	07 08	RE 8
0091	06 15	ST 15
0092	07 15	RE 15
0093	05 10	÷ 10
0094	07 10	RE 10
0095	08 02	* W
0096	07 06	RE 6
0097	08 02	* W
0098	00 15	E 15
0099	00 00	E 0
0100	06 01	ST 1
0101	07 10	RE 10
0102	02 07	+ 7
0103	07 02	RE 2
0104	06 15	ST 15
0105	07 08	RE 8
0106	03 15	- 15
0107	08 04	* J ₆
0108	08 00	* S
0109	08 07	* CS
0110	07 07	RE 7
0111	06 09	ST 9
0112	07 02	RE 2
0113	06 14	ST 14
0114	07 14	RE 14
0115	05 09	÷ 9
0116	06 11	ST 11
0117	07 11	RE 11
0118	08 02	* W
0119	02 06	+ 6
0120	09 03	* ¾

APPENDIX C

Inputs for the first programme were as follows,

- (i) a starting point where calculation was to begin, was entered in register 00, e.g. 230,
- (ii) the number of points to be counted after 230 for the averaging, e.g. 20. This number was entered in register 06. The average value of V_{eq} was stored in register 03 for further applications.

For the second programme, the inputs included:

- (iii) A starting point, generally from 5 to 7 depending upon how satisfactory the trace was, was entered in register 00. By varying the location of the starting point, the different segments of the decay curve were sampled and used in the calculation of the final k_{obs} values. Provided that the trace was satisfactory, these final k_{obs} values computed from different starting points should be very close to each other within experimental error.
- (iv) The final k_{obs} value in the output was an average of a number of k_{obs} values computed by the programme. The total number of k_{obs} values to be used in the averaging was chosen in the range of 15 to 20 and stored in register 02.
- (v) A suitable point interval (n), e.g. 2, was taken regularly after every point which was sampled. This procedure was designed to ensure that a good part of the decay curve would be sampled instead of just the first few half-lives. The desired point interval was stored in register 04.

APPENDIX C

(vi) Finally, the time interval (in sec.) between two sampling points was calculated and stored in register 06. Depending on the value of the point interval (n), the corresponding time interval was calculated with the following,

$$t = \frac{(n+1) \times (\text{sample interval in msec})}{1000} \text{ sec.}$$

APPENDIX D

To simplify the derivation, the number of coordinated H_2O and charge(s) on each chemical specie are neglected.

According to Scheme (A) and assuming that $M(OH)L$ is in a steady state,

$$\begin{aligned} d[ML]/dt = & k_{41}[L][M] + k_{21}[MLH] + k_{51}[MLH_2] + k_{612}[MOH][L] \\ & + k_{812}[M(OH)LH] + k_{912}[M(OH)LH_2] - k_{14}[ML] \\ & - k_{12}[ML][H^+] - k_{15}[ML][H^+]^2 - k_{126}[ML] \\ & - k_{128}[ML] - k_{129}[ML][H^+] \end{aligned}$$

Assuming steady state for $[MLH]$, i.e.

$$\begin{aligned} d[MLH]/dt = 0 = & k_{32}[M][HL] + k_{12}[ML][H^+] \\ & - k_{23}[MLH] - k_{21}[MLH] \\ [MLH] = & \frac{k_{32}[M][HL] + k_{12}[ML][H^+]}{(k_{23} + k_{21})} \end{aligned}$$

Steady state for $[MLH_2]$, i.e.

$$\begin{aligned} d[MLH_2]/dt = 0 = & k_{115}[M][H_2L] + k_{15}[ML][H^+]^2 \\ & - k_{511}[MLH_2] - k_{51}[MLH_2] \\ [MLH_2] = & \frac{k_{115}[M][H_2L] + k_{15}[ML][H^+]^2}{(k_{511} + k_{51})} \end{aligned}$$

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Steady state for $[M(OH)LH]$, i.e.

$$\begin{aligned} d[M(OH)LH]/dt = 0 &= k_{78}[MOH][HL] + k_{128}[ML] \\ &- k_{87}[M(OH)LH] - k_{812}[M(OH)LH] \end{aligned}$$

$$[M(OH)LH] = \frac{k_{78}[MOH][HL] + k_{128}[ML]}{(k_{87} + k_{812})}$$

Steady state for $[M(OH)LH_2]$, i.e.

$$\begin{aligned} d[M(OH)LH_2]/dt = 0 &= k_{109}[MOH][H_2L] + k_{129}[ML][H^+] \\ &- k_{910}[M(OH)LH_2] - k_{912}[M(OH)LH_2] \end{aligned}$$

$$[M(OH)LH_2] = \frac{k_{109}[MOH][H_2L] + k_{129}[ML][H^+]}{(k_{910} + k_{912})}$$

After some algebraical manipulations, the rate expression can be expressed as,

$$d[ML]/dt = K_A + K_B$$

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where,

$$\begin{aligned}
 K_A = & k_{41}[M][L] + [M]\left\{\frac{k_{21}k_{32}[HL]}{(k_{23} + k_{21})}\right\} + [M]\left\{\frac{k_{51}k_{115}[H_2L]}{(k_{511} + k_{51})}\right\} \\
 & + [M]\left\{\frac{K_{OH}}{[H^+]}k_{612}[L]\right\} + [M]\left\{\frac{K_{OH}}{[H^+]} \frac{k_{812}k_{78}[HL]}{(k_{87} + k_{812})}\right\} \\
 & + [M]\left\{\frac{K_{OH}}{[H^+]} \frac{k_{912}k_{109}[H_2L]}{(k_{910} + k_{912})}\right\} \\
 K_B = & \left\{\frac{k_{21}k_{12}[H^+]}{(k_{23} + k_{21})} + \frac{k_{51}k_{15}[H^+]^2}{(k_{511} + k_{51})} + \frac{k_{812}k_{128}}{(k_{87} + k_{812})}\right. \\
 & + \frac{k_{912}k_{129}[H^+]}{(k_{910} + k_{912})} - k_{14} - k_{12}[H^+] - k_{15}[H^+]^2 \\
 & \left. - k_{126} - k_{128} - k_{129}[H^+]\right\} [ML]
 \end{aligned}$$

K_{OH} is as defined in text.

Total concentration of the ligand can be written as

$$\begin{aligned}
 C_L = & [H_2L] + [HL] + [L] + [ML] \\
 = & [H_2L]_{eq.} + [HL]_{eq.} + [L]_{eq.} + [ML]_{eq.}
 \end{aligned}$$

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In terms of K_{2A} , K_2 and α_A (also defined in text), C_L can be rewritten:

$$\begin{aligned} C_L &= [L] \left(1 + \frac{K_2 [H^+]}{\alpha_A} \right) + [ML] \\ &= [L]_{eq.} \left(1 + \frac{K_2 [H^+]}{\alpha_A} \right) + [ML]_{eq.} \end{aligned}$$

or

$$[L] = [L]_{eq.} + [ML]_{eq.} / \Omega - [ML] / \Omega$$

Under experimental condition pseudo first-order in $[M]$

$$[M]_{total} \approx [M]_{eq.}$$

K_A and K_B can be expressed in terms of K_{2A} , K_2 , Ω_A and

$$\begin{aligned} K_A &= [M]_{eq.} \left\{ [L]_{eq.} + \frac{[ML]_{eq.}}{\Omega} - \frac{[ML]}{\Omega} \right\} \left\{ k_{41} + \frac{k_{21} k_{32} K_2 [H^+]}{(k_{23} + k_{21})} \right. \\ &\quad + \frac{k_{51} k_{115} [H^+]^2 K_2}{(k_{511} + k_{51}) K_{2A}} + \frac{K_{OH}}{[H^+]} k_{612} + \frac{K_{OH} k_{812} k_{78} K_2}{(k_{87} + k_{812})} \\ &\quad \left. + \frac{K_{OH} k_{912} k_{109} [H^+] K_2}{(k_{910} + k_{912}) K_{2A}} \right\} \end{aligned}$$

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$$K_B = - \left\{ \frac{k_{23}k_{12}[H^+]}{(k_{23} + k_{21})} + \frac{k_{511}k_{15}[H^+]^2}{(k_{511} + k_{51})} + \frac{k_{87}k_{128}}{(k_{87} + k_{812})} \right. \\ \left. + \frac{k_{910}k_{129}[H^+]}{(k_{910} + k_{912})} + k_{14} + k_{126} \right\} [ML]$$

$$\text{Since } [M]_{eq.} [L]_{eq.} = \frac{k_{14}}{k_{41}} [ML]_{eq.}$$

$$K_A = \theta + [M]_{eq.} \left\{ \frac{[ML]_{eq.}}{\Omega} - \frac{[ML]}{\Omega} \right\} \left\{ k_{41} + \frac{k_{21}k_{32}K_2[H^+]}{(k_{23} + k_{21})} \right. \\ \left. + \frac{k_{51}k_{115}[H^+]^2K_2}{(k_{511} + k_{51})K_{2A}} + \frac{K_{OH}}{[H^+]} k_{612} + \frac{K_{OH}k_{812}k_{78}K_2}{(k_{87} + k_{812})} \right. \\ \left. + \frac{K_{OH}k_{912}k_{109}[H^+]K_2}{(k_{910} + k_{912})K_{2A}} \right\}$$

where

$$\theta = \frac{k_{14}}{k_{41}} \left\{ k_{41} + \frac{k_{21}k_{32}K_2[H^+]}{(k_{23} + k_{21})} + \frac{k_{51}k_{115}[H^+]^2K_2}{(k_{511} + k_{51})K_{2A}} + \frac{K_{OH}}{[H^+]} k_{612} \right. \\ \left. + \frac{K_{OH}k_{812}k_{78}K_2}{(k_{87} + k_{812})} + \frac{K_{OH}k_{912}k_{109}[H^+]K_2}{(k_{910} + k_{912})K_{2A}} \right\} [ML]_{eq.}$$

It can be easily shown that:

$$\theta/[ML]_{eq.} = -K_B/[ML]$$

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Therefore,

$$\begin{aligned} d[ML]/dt = & -K_B [ML]_{eq.} / [ML] + K_B + [M]_{eq.} \left\{ \frac{[ML]_{eq.}}{\Omega} - \frac{[ML]}{\Omega} \right\} \\ & \left\{ k_{41} + \frac{k_{21}k_{32}K_2[H^+]}{(k_{23} + k_{21})} + \frac{k_{51}k_{115}[H^+]^2K_2}{(k_{511} + k_{51})K_{2A}} + \frac{K_{OH}}{[H^+]} k_{612} \right. \\ & \left. + \frac{K_{OH}k_{812}k_{78}K_2}{(k_{87} + k_{812})} + \frac{K_{OH}k_{912}k_{109}[H^+]K_2}{(k_{910} + k_{912})K_{2A}} \right\} \end{aligned}$$

From Appendix A, it has been shown

$$d[ML]/dt = k_{obs} ([ML]_{eq.} - [ML])$$

Since,

$$\begin{aligned} d[ML]/dt = & \left(\frac{[M]_{eq.}}{\Omega} \left\{ k_{41} + \frac{k_{21}k_{32}K_2[H^+]}{(k_{23} + k_{21})} + \frac{k_{51}k_{115}[H^+]^2K_2}{(k_{511} + k_{51})K_{2A}} \right. \right. \\ & \left. \left. + \frac{K_{OH}}{[H^+]} k_{612} + \frac{K_{OH}k_{812}k_{78}K_2}{(k_{87} + k_{812})} + \frac{K_{OH}k_{912}k_{109}[H^+]K_2}{(k_{910} + k_{912})K_{2A}} \right\} \right. \\ & \left. - \frac{K_B}{[ML]} \right) ([ML]_{eq.} - [ML]) \end{aligned}$$

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Therefore,

$$\begin{aligned}
 k_{\text{obs}} = & \frac{[M]_{\text{eq}}}{\Omega} \cdot \left\{ k_{41} + \frac{k_{21}k_{32}K_2[H^+]}{(k_{23} + k_{21})} + \frac{k_{51}k_{115}[H^+]^2K_2}{(k_{511} + k_{51})K_{2A}} \right. \\
 & + \frac{K_{\text{OH}}}{[H^+]} k_{612} + \frac{K_{\text{OH}}k_{812}k_{78}K_2}{(k_{87} + k_{812})} + \frac{K_{\text{OH}}k_{912}k_{109}[H^+]K_2}{(k_{910} + k_{912})K_{2A}} \Big\} \\
 & + \left\{ \frac{k_{23}k_{12}[H^+]}{(k_{23} + k_{21})} + \frac{k_{511}k_{15}[H^+]^2}{(k_{511} + k_{51})} + \frac{k_{87}k_{128}}{(k_{87} + k_{812})} \right. \\
 & \left. + \frac{k_{910}k_{129}[H^+]}{(k_{910} + k_{912})} + k_{14} + k_{126} \right\}
 \end{aligned}$$

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$$\begin{aligned} d[ML]/dt = & k_{12}[M][HL] - k_{21}[ML][H^+] + k_{52}[M][H_2L] - k_{25}[ML][H^+]^2 \\ & + k_{64}[MOH][H_2L] - k_{46}[ML][H^+] \\ & + k_{34}[MOH][HL] - k_{43}[ML] \end{aligned}$$

In terms of K_{OH} and K_{2A} , it can be rewritten as

$$\begin{aligned} d[ML]/dt = & (k_{12} + k_{52}[H^+]/K_{2A} + k_{64}K_{OH}/K_{2A} + k_{34}K_{OH}/[H^+]) \\ & [M][HL] - (k_{21}[H^+] + k_{25}[H^+]^2 + k_{46}[H^+] + k_{43})[ML] \end{aligned}$$

K_{OH} and K_{2A} are as defined in text.

Total concentration of the ligand,

$$C_L = \frac{[HL]}{\alpha_A} + [ML] = \frac{[HL]_{eq.}}{\alpha_A} + [ML]_{eq.}$$

or

$$[HL] = [HL]_{eq.} + [ML]_{eq.} \alpha_A - [ML] \alpha_A$$

Under experimental condition pseudo first-order in $[M]$, i.e.

$$[M]_{total} = [M]_{eq.}$$

The rate expression can be written as:

$$d[ML]/dt = \beta \{ [M]_{eq.} ([HL]_{eq.} + [ML]_{eq.} \alpha_A - [ML] \alpha_A) \} - \gamma [ML]$$

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where

$$\beta = (k_{12} + k_{52}[H^+]/K_{2A} + k_{64}K_{OH}/K_{2A} + k_{34}K_{OH}/[H^+])$$

and

$$\gamma = (k_{21}[H^+] + k_{25}[H^+]^2 + k_{46}[H^+] + k_{43})$$

In terms of the constant K_C defined in text,

$$[M]_{eq.}[HL]_{eq.} = [ML]_{eq.} \frac{[H^+]}{K_C}$$

It can be easily shown that,

$$\frac{[H^+]}{K_C} \beta = \gamma$$

The final rate expression is written as:

$$d[ML]/dt = ([M]_{eq.} \alpha_A \beta + \gamma)([ML]_{eq.} - [ML])$$

Therefore,

$$k_{obs} = [M]_{eq.} \alpha_A (k_{12} + k_{52}[H^+]/K_{2A} + k_{64}K_{OH}/K_{2A} + k_{34}K_{OH}/[H^+]) \\ + (k_{21}[H^+] + k_{25}[H^+]^2 + k_{46}[H^+] + k_{43})$$

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