Fall 1974

SOLVENT EFFECTS UPON SUBSTITUTION REACTIONS OF METAL COMPLEXES

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ALVAREZ, Dagoberto Pacheco, 1941-
    SOLVENT EFFECTS UPON SUBSTITUTION REACTIONS
    OF METAL COMPLEXES.

    University of New Hampshire, Ph.D., 1974
    Chemistry, physical

University Microfilms, A XEROX Company, Ann Arbor, Michigan

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DAGOBERTO PACHECO ALVAREZ

SOLVENT EFFECTS UPON SUBSTITUTION

REACTIONS OF METAL COMPLEXES

by

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B.S., University of New Hampshire, 1969

A THESIS

Submitted to the University of New Hampshire

In Partial Fulfillment of

The Requirements for the Degree of

Doctor of Philosophy

Graduate School

Department of Chemistry

August, 1973

This thesis has been examined and approved.

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THIS THESIS IS DEDICATED TO

My parents, Maria and Aureliano;

and my wife, Carmen.

ACKNOWLEDGEMENTS

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ABSTRACT

SOLVENT EFFECTS UPON SUBSTITUTION
REACTIONS OF METAL COMPLEXES[*]

by

DAGOBERTO PACHECO ALVAREZ

The kinetics of the reactions leading to the formation of the 1:1 metal ion complexes of Ni(II), Zn(II), and Cu(II) with the ligands 1-(2-pyridylazo)-2-naphthol, 4-(2-pyridylazo)-resorcinol and 2-2'-bipyridine were studied in water and in the solvent mixtures 1-4 dioxane-water, methanol-water and acetone-water. An heuristic proof of an overall second order rate constant (k_{12}) is presented. This second order rate constant was found to be a composite of first order dependency upon each of the concentrations of the ligands and the metal ions. In the pure aqueous solvent k_{12} has the following dependency on the ligand:

$$k_{12\,(Bipy)} \cong 10\ k_{12\,(PAR)}$$

$$k_{12\,(Bipy)} \cong 80\ k_{12\,(\beta-PAN)}$$

These results are not readily explained by the accepted Id mechanism for the metal ions studied. Modification of the Id mechanism is proposed in which, for steric reasons, five-membered ring closure in forming the metal ion complex may become the rate-determining step.

The magnitude of k_{12} in the solvent mixtures was found to decrease to a minimum value followed by a small increase as the content of the non-aqueous component of the mixture was increased. The magnitude of the difference between the value of k_{12} in pure water and k_{12} minimum was found to be larger in dioxane-water than in acetone-water, and larger in acetone-water than in methanol-water. This order of effects could be expected from the variation of the dielectric constant of the medium; nevertheless, no unique correlation was found. The solvent effect was interpreted in terms of selective solvation of the metal ions by the non-aqueous component of the mixtures and structural properties of the solvent mixtures.

Preliminary studies of the kinetics of the reactions leading to the formation of the 1:2 metal ion complexes of Ni(II) and Zn(II) with the ligand 1-(2-pyridylazo)-2-naphthol were studied in the solvent mixtures dioxane-water and methanol-water. An overall second order rate constant (k_{13}) composed of a first order dependence on both metal ion and ligand concentrations was found. These second order rate constants were estimated by means of mathematical techniques which assumed the applicability to kinetic models of the "boundary conditions" of differential equations characteristic of the systems studied.

INTRODUCTION

The study of the time dependence of a chemical reaction is
experimentally limited to the observation of the appearance or dis-
appearance of any moiety in a reaction, namely: products or reactants.
This observation leads to data from which the following information
can be obtained:

    a)   Determination of mathematical models connecting chemical rate

         processes with concentrations (empirical rate laws);

    b)   Correlation of the empirical rate law of equivalent or

         related reactions with structural or environmental changes.

These two types of information are the basis of the study of
chemical rate processes that in classical terms are considered as a
unique type of phenomena which are enclosed under the name of "chemical
kinetics."

Empirical rate laws should, in principle, yield enlightenment
about stoichiometric and topological properties of the reaction transi-
tion states and/or elementary steps, while their correlations suggested
in b) are energetic comparisons of the activation process. The knowledge
of the above implicit ideas is said to be necessary conditions to
establish a "kinetic mechanism," but their sufficiency is a completely
different matter. From a classical kinetic point of view they are not
sufficient, as pointed out in several standard textbooks (1, 2), but
seen as a rate process they would be sufficient if all the rate processes
related to the chemical reaction were observed before the equilibrium is
reached. In other words, in classical kinetic studies, the energy of

activation elucidates only ground and transition states.

Ambiguity may arise in defining a rate process, particularly when the time domain of a chemical reaction is of the same order of magnitude as the time domain of rate changes of microproperties of the system. Furthermore, the general form of the Arrhenius equation (Equation 1-1) (3) represents the functional dependence of a specific rate of a chemical reaction with temperature, as well as the temperature dependence of certain physical processes (for example, viscosity and diffusion (4)).

$$\ln k = \ln A - (E_e^*/RT) \qquad\qquad \underline{1\text{-}1}$$

where k is a rate constant; A, a statistical factor; E_e^*, the experimental energy of activation; R, the gas constant, and T, the absolute temperature.

Theoretically, this ambiguity does not exist, since chemical reactions are studied in Statistical Quantum or Mechanics as particular cases of general rate processes (5, 6).

The subject of this thesis is a study of the time dependence of the substitution of the solvent molecules complexed with the metal ions Cu(II), Ni(II), and Zn(II) by the tridentate ligands 1-(2-pyridylazo)-2-naphthol (β-PAN), and 4-(2-pyridylazo)-resorcinol (PAR) and by the bidentate ligand 2,2'-bipyridine (Bipy). These types of reactions are common and general ideas have been established as we will show in the following review.

<u>Classification and Characterization of the Mechanism of Substitution</u> <u>Reactions in Water.</u> The idea of coordination number and spatial arrangement first suggested by Werner in 1912 (7) encouraged research toward the determination of the structure of metal ion coordination complexes. As a consequence, questions about the dynamics of the formation of the complexes arose, due to qualitative observations that in solutions the formation of complexes are in effect substitution of one ligand (solvent molecules, in general) for

another, and that the rate of formation of the complexes presented an ample

domain in the time scale. In fact, the following examples show two extreme

values of the time scale expressed in terms of the rate constant of the re-

actions:

a) $Cd^{+2} + NTA^{-3} \xrightarrow{k_f} Cd(NTA)^{-1}$ $k_f = 2 \times 10^{10}$ (8)

$$\underline{1-2}$$

b) $Fe^{+3} + NH_3 \xrightarrow{k_f} Fe(NH_3)^{+3}$ $k_f = 0.5$ (9)
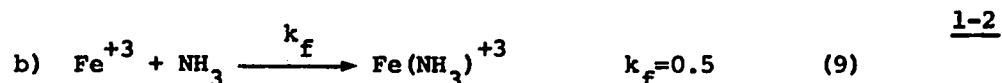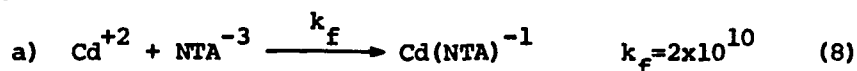
where k_f is expressed in $sec^{-1} M^{-1}$.

Furthermore, Taube in 1952 (10) reviewed those qualitative observa-

tions and proposed the empirical classification of the metal ion complexes

in two categories: "labile" and "inert." The first category refers to those

metal ions where the substitution of one ligand by another has a fast rate.

Although fast is a relative term, it is usually limited to the half lives

of these substitution reactions within the time domain 10^{-10} to 10^{+2} sec.

(i.e., Equation 1-2 a). The second category is used to label those metal

ions with a relatively slow rate compared with the labile group (i.e.,

Equation 1-2 b).

However, the nomenclature introduced by Basolo and Pearson (11)

specifically considers all the possible reaction pathways shown in Figure 1-1.

Their terminology is based on the analogous classification of organic subs-

titution reactions. For the inorganic substitution reactions it should be

theoretically possible to distinguish a particular pathway on the basis of

the presence or absence of a significant variation in the rate with a varia-

tion of the entering ligand in a series of related reactions. Basolo and

Pearson classified all possible reaction pathways in three simple stoichio-

metric mechanisms of substitution that may be envisioned as follows:
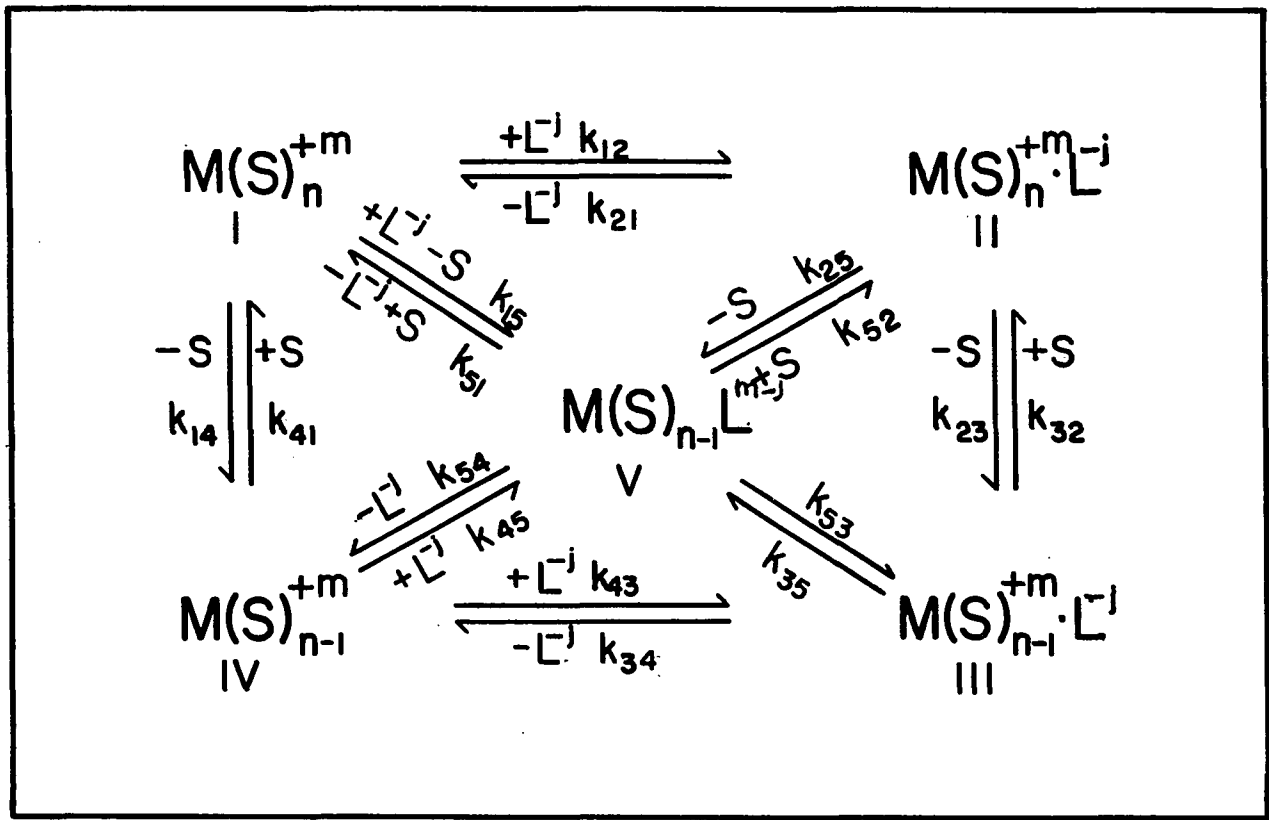
Figure 1-1. Generalization of Stoichiometric Mechanisms for Substitution Reactions in Metal Ions in Solution

a) $MX \underset{+X}{\overset{-X}{\rightleftharpoons}} X + M \underset{-Y}{\overset{+Y}{\rightleftharpoons}} MY$ (D)

b) $MX + Y \rightleftharpoons MY + X$ (I) **1-3**

c) $MX \underset{-Y}{\overset{+Y}{\rightleftharpoons}} MXY \underset{+X}{\overset{-X}{\rightleftharpoons}} MY + X$ (A)
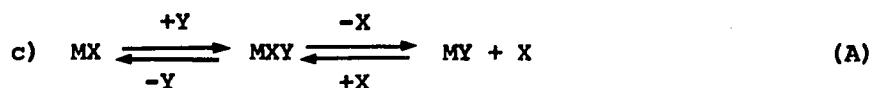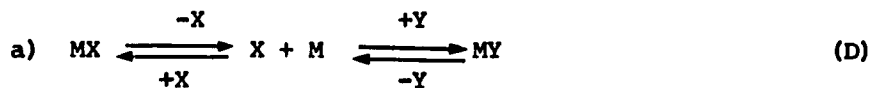
where X represents the leaving ligand, Y the entering ligand and M the remainder of the metal complex. The meaning of D, I, and A will be discussed later in this section.

They identified Equations a) and c) as the S_N1 (lim) and S_N2 (lim) mechanisms respectively, while the stoichiometric equation described in b) may or may not involve a lower coordination number in the intermediate species (S_N1 or S_N2, respectively).

Since no clear differentiation is made between the stoichiometric mechanism and the mode of activation in the above terminology, in this work we will use the nomenclature introduced by Langford and Stengle (12).

Based on the stoichiometric mechanism and referring to Figure 1-1 and Equation 1-3, the possible cases can be classified as:

1) Intermediates with higher coordination number than the starting metal complexes (mechanism A), as in the case of pathway I►V. The following example was reported by Haake (13):

a) $Cis[Pt(NH_3)_2NO_2Cl] + NO_2^- \xrightarrow{\text{Fast}} [Pt(NH_3)_2(NO_2)_2Cl]^-$

  1-4

b) $[Pt(NH_3)_2(NO_2)_2Cl]^- \xrightarrow{\text{Slow}} Cis[Pt(NH_3)_2(NO_2)] + Cl^-$
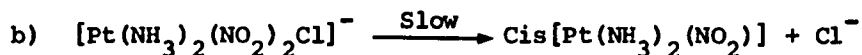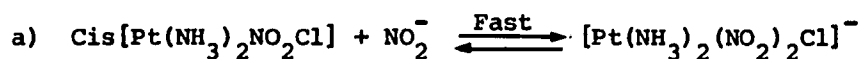
Haake reported spectroscopic evidence of the "five coordinate" intermediate.

2) Intermediates where the substituting ligands interact with the metal ion complex by an outer sphere coordination (interchange mechanism I), as would be the case if pathway I→II→III is followed. This stoichiometry

has been reported commonly in metal ion substitution reactions. The following examples show the possibility of ion pairs and dipole-ion pairs as outer sphere complexes:

a) $Ni(aq)^{+2} + SCN^- \xrightleftharpoons{Fast} Ni(aq)^{+2} \cdot SCN^-$

b) $Ni(aq)^{+2}SCN^- \xrightarrow{Slow} Ni(aq)SCN^{+1} + H_2O$
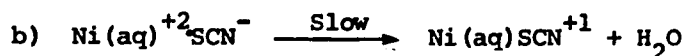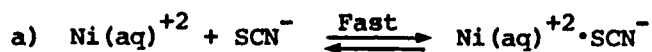
This example was reported by Davies and MacF. Smith (14).

Another example was reported by Melson and Wilkins (15):

a) $Ni(aq)^{+2} + NH_3 \xrightleftharpoons{Fast} Ni(aq)^{+2} \cdot NH_3$

1-6

b) $Ni(aq)^{+2} \cdot NH_3 \xrightarrow{Slow} Ni(aq)NH_3^{+2} + H_2O$
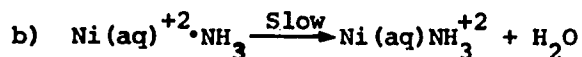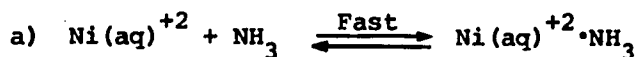
3) Intermediates with lower coordination number than the starting metal complexes (mechanism D), such as the cases if species III and/or IV are involved. This mechanism has not been commonly reported.

From the point of view of mode of activation, two categories are differentiated:

1) Associative activation (mode of activation a) if the transition state implies an increase in the coordination number of the metal ion.

2) Dissociative activation (mode of activation d) if the transition state implies a decrease in the coordination number of the metal ion.

Obviously, not all the combinations between the stoichiometric mechanism and the mode of activation are possible. The mechanism D can only be associated with a mode of activation d, and in order to avoid repetition, when referring to mechanism D, the mode of activation remains implicit. The same should be said about the mechanism A, which can only be associated with mode of activation a.

For the mechanism I (interchange substitution), both modes of activation are possible and Table 1-1 summarizes the terminology described above.

Eigen and Wilkins (16) in 1965 provided an extensive compilation of the rate constant of formation, k_f, for the following general reaction:

$$M(H_2O)_n^{+m} + L_{(i)}^{-j} \; \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \; M(H_2O)_{n-i}L^{m-j} + iH_2O \qquad \qquad \underline{1-7}$$
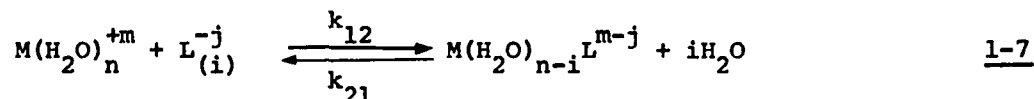
where the solvent molecules (H_2O) are displaced by the ligand L, with i sides of coordination and charge j, from the metal ion $M(H_2O)_n^{+m}$, and $k_{12}=k_f$. They concluded that the dissociative mode of activation predominates.

However, other authors (17-19) have presented evidence that both modes of activation are possible; nevertheless, the mode of activation seems to be specific for a particular coordination topological group. No general pattern has been found between stoichiometric mechanism and a particular geometry of metal ion complexes.

In addition, Basolo and Pearson (11, 20) have suggested that the mechanism Id plays an important role in the interpretation of experimental studies of octahedral substitution reactions. This idea has been widely supported, particularly following its initial formulation by Eigen (21).

a) $\quad M(H_2O)_6^{+2} + L^{-j} \rightleftharpoons (H_2O)_5M(H_2O)^{+2} \cdot L^{-j} \qquad K_o$

$$\underline{1-8}$$

b) $\quad (H_2O)_5M(H_2O)^{+2} \cdot L^{-j} \rightleftharpoons (H_2O)_5ML^{(2-j)} + H_2O \qquad k_o \, , \, k_{-o}$
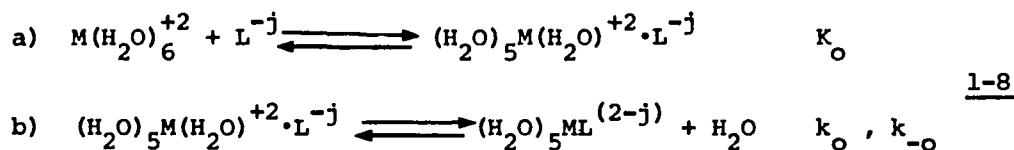
The following conclusions can be summarized:

a) Interchange stoichiometric mechanisms seem to be predominant ones, but not unique.

b) In octahedral complexes, the substitution reactions take place in a dissociative mode of activation.

TABLE 1-1

Classification of Ligand Substitution Mechanisms

Mode of Activation	Stoichiometric Mechanism			
	Pathway a Possibilities	Intermediate of Increased Coordination Number	One-Step Process b	Intermediate of Reduced Coordination Number
Associative	2	A	Ia	
Dissociative	2		Id	D

a) The pathway refers to Figure 1-1 expressing the full stoichiometric representation.

b) One-step process refers to Equation 1-2 as a theoretical simplification of the stoichiometry without any implication of the existence or not of the outer sphere complex.

c)   The I mechanism seems to be justified by the idea of an outer

sphere complex as in the so-called inert complex reactions.

d)   Half lives of the reactions can be correlated to the electro-

nic configurations of the metal ion (11, 12, 16).

Characterization of the Substitution Reactions in Other Solvents.
The above concluding observations were based on experimental results of

studies carried out in an aqueous medium, but the extrapolation of these

conclusions to other solvents is still not generally accepted, as is

pointed out in Wilkins' account (22). This is due to the limited

experimental results available, particularly in multicomponent mixtures,

whose structural and dynamic properties are far from fully understood.

The reaction of ligand substitution in non-aqueous pure solvents

does not present at the moment any specific mechanistic pattern. For

example, Glaeser et al. (23) studied the ammonia interchange with $Ni(S)_6^{+2}$

both in water and liquid ammonia, and suggested that their experimental

results were in agreement with an Id mechanism. In turn, Frankel (24)

studied the interchange of dimethylsulfoxide (DMSO) with $Ni(DMSO)_6^{+2}$ and

$Co(DMSO)_6^{+2}$ in DMSO and pointed out the ambiguity of assignment of either

an Id or an Ia mechanism. Frankel extended his study to the particular

solvent mixtures $DMSO-CH_3NO_2$ and $DMSO-CH_2Cl_2$. He suggested that as the

concentrations of CH_3NO_2 or CH_2Cl_2 (which are inert as ligands) increase,

more uncertainty in the mode of activation arises.

Characterization of Solvent Mixtures. At this point, it is important

to introduce certain ideas related to the structural and dynamic properties

of solvent mixtures before discussing further substitution reactions in

these media.

In studying liquid mixtures, there are several main constraints that

hinder the theoretical understanding necessary to develop a general formulation that could account for certain "anomalous" behaviors of the solvent mixtures (i.e., no linearity in physical properties such as density) as well as "normal" behavior of liquid mixtures. Experimental observations have yielded empirical and semiempirical correlations between different physical properties of liquids that has made possible qualitative descriptions of such systems. Since all molecules are aggregates of electric charges with specific configurations, it seems logical to correlate experimental observations of micro and macro properties of solvent mixtures with models based on the additive properties of molecular pairs. The interactions considered are electric and magnetic in nature. Virial-like corrections are used for the non-additive interactions of a van der Waals type, which are not necessarily defined in physical terms. This approach seems to work fairly well in elementary mixtures (for example, liquified noble gas mixtures, which are not particularly useful in chemical applications). Examples of such correlations are discussed in the literature (Eyring, Henderson, and Jost (25)).

This work deals with the particular mixtures water-methanol, water-acetone, and water-dioxane. Some qualitative characteristics of these mixtures are listed below (for more specific information, see Appendix A):

a) Water-methanol, a mixture with the following characteristics regardless of the proportions of either component: 1) protic-protic interactions typified by hydrogen bonding and dipole-dipole interactions; 2) high dielectric constant that changes almost linearly with respect to the composition of the mixture solvent from 80 in pure water to 32 in methanol; 3) molecular units with permanent dipole moment in the species H_2O, CH_3OH and in the possible short-term order of aggregates $(H_2O)_n$, $(CH_3OH)_m$, and $[(H_2O)_n \cdot (CH_3OH)_m]$; 4) the existence of the species $[(H_2O)_m \cdot (CH_3OH)_m]$ is

believed to contribute to the nonlinearity of both the intensive and extensive properties with respect to any pure component of the mixture.

b) Water-acetone, a mixture with the following characteristics regardless of the proportions of either component: 1) protic-aprotic properties typified by hydrogen bonding and dipole-dipole interactions; 2) high to medium dielectric constant that changes almost linearly with respect to the composition of the mixed solvent from 80 in pure water to 20 in acetone; 3) molecular units with permanent dipole moment in the species H_2O, $(CH_3)_2CO$, and the possible short-term order of the aggregates $(H_2O)_n$, $[(CH_3)_2CO]_m$, and $(H_2O)_n \cdot [(CH_3)_2CO]_m$; 4) the existence of the species $(H_2O)_n \cdot [(CH_3)_2CO]_m$ is believed to contribute to the nonlinearity of both the intensive and extensive properties with respect to any pure component of the mixture.

c) Water-dioxane, a mixture with the following characteristics depending on the composition: 1) protic-aprotic properties typified by hydrogen bonding; 2) high to low dielectric constant that changes almost linearly from 80 in pure water to 2 in dioxane; 3) molecular units with or without permanent dipole moments. The species H_2O, and the aggregates $(H_2O)_n$ have permanent dipole moments, while $O-C_2H_4-O-C_2H_4$ does not. The aggregates $(O-C_2H_4-O-C_2H_4)_n$ and $(H_2O)_m \cdot (O-C_2H_4-O-C_2H_4)_m$ have not been fully characterized with respect to dipole moments; 4) the nonlinearity of the extensive and/or intensive properties of the mixture is believed to be a result of the contribution of the species $(H_2O)_n \cdot (O-C_2H_4-O-C_2H_4)_m$.

The characteristics pointed out for these mixtures have been studied by several authors using different techniques (i.e., NMR, UV, IR, ESR, etc.). Horne's book (26) provides an excellent presentation of these experimental facts and their empirical and semi-empirical correlations. These correlations have the following very important qualitative implications:

a) The assumption of additive properties of molecule pairs breaks down and the non-additive interactions can no longer be invoked as virial-type corrections.

b) The concept of pH has a limited meaning, particularly because a scale definition can be meaningless in going from one composition to another.

c) Ionic strength cannot be uniquely defined, and the actual concentration of ions can be used as a qualitative representation of such operational properties.

d) Because of the dimeric and polymeric species present in these mixtures, models based on multi-thermodynamic equilibria can be used to justify the absolute maxima and minima, or both, of transport phenomena as functions of the solvent composition.

Another consideration, believed to be important in this particular type of study, is the idea that ions in mixed solvents are selectively solvated.

Strehlow and Koepp (27) determined the conductivity of silver nitrate solutions in acetonitrile-water mixtures, and their experimental results suggested that the silver ion was preferentially solvated by the larger acetonitrile molecules. Schneider (28) reviewed the subject and presented specific results which suggest that ions are selectively solvated by one of the components of the mixture independently of its composition, and he interpreted this selectivity in terms of the stability constants of the solvent ion in the outer and inner sphere complexes.

Solvent Effects Upon Substitution Reactions. With the review of the properties and behavior of solvent mixtures in mind, let us turn to

some kinetic studies in these media.

Recently, Hibbert and Long (29) studied the detritiation of several substituted malononitriles in the solvent mixtures dimethyl sulphoxide-water, ethanol-water, and dioxane-water, where the following mechanism was proposed:

a) $RCT + B \xrightarrow{k} RC^- + BT^+$ slow

b) $RC^- + \text{proton species} \longrightarrow RCH$ fast
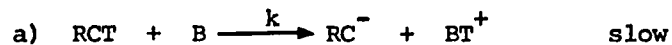
1-8

This mechanism may be identified in the nomenclature used in this work as a base catalyzed Id or D mechanism. Hibbert and Long reported a dependency of the rate of reaction upon the solvent composition functionally represented in plots of k versus the mole fraction of water. An increase of the rate of the reaction is shown relative to the rate in pure water, which leads to a maximum at approximately 0.9 mole fraction of H_2O in dioxane, 0.8 mole fraction of H_2O in dimethyl sulfoxide, and 0.7 mole fraction of H_2O in methanol. After the maximum, the rate of the reaction decreased to values 10^2, 10^2, and 10^4 times smaller than in pure water for the three mixed solvents: water in dimethyl sulfoxide, methanol, and dioxane respectively, when the molar fraction of water is below 0.1.

Hibbert and Long suggested that a direct relationship exists between the solvent effect upon the rate of the reaction and the ionic strength effect upon the rate of the reaction in pure water (in their own words, a salt effect). Their interpretation was:

a) Since the increase in the rate of the reaction by the addition of the non-aqueous solvent is parallel to the salt effect, the solvation of the reacting species does not play an important role and, therefore, the structural properties of the solvent mixtures are not the origin of the observed effect.

b) The acid-base characteristics of the solvent mixtures are a

critical factor to be considered. In fact, they consider their results as a "kinetic proof for solvent basicity."

Sanduja and MacF. Smith (30) studied the formation of the mono 1,10-phenanthroline (Phen) complex of Ni(II) in methanol-water mixtures in the specific range of 0.0 to 97% by weight of methanol. They reported the dependency of $[H^+]$ (0.5 to 4.0 x 10^{-2} M) in several different solvent compositions. The results show that such dependency is linear and the slope decreases with increments in the content of methanol in the solvent, the dependency being almost zero for 97% of methanol. This result suggests that acid-base characteristics of the solvent may play an important role in the interpretation of solvent effects in metal ion substitution reactions.

Bennetto and Caldin (31-33) presented a series of papers on solvent effects in substitution reactions of the metal ions Ni(II) and Co(II) with the ligands 2,2'-bipyridine (Bipy) and 2,2',2"-terpyridine (Terpy) in the following pure solvents: water, deuterium oxide, methanol, dimethyl formamide, dimethyl sulfoxide, ethylene glycol, and dimethyl phosphonate, as well as the specific reaction of Bipy with Ni(II) in the solvent mixture methanol-water.

They suggested relationships linking the variation of the rate of the reaction in different pure solvents with properties such as enthalpy of vaporization and fluidity which reflect the microstructure of the solvent.

The structural model of pure liquid was extended to the water-methanol mixtures and it was suggested that the decrease of the rate of the reaction with an increase in the concentration of methanol closely reflects the structure of the solvent mixtures. The justification for

such an idea came from the possibility of selective solvation in the outer sphere coordination; no emphasis was made on the stoichiometric composition of the first coordination sphere. Their analysis suggested an Id mechanism as common to all solvents.

MacKellar and Rorabacher (34) studied the solvent-ammonia exchange on Ni(II) in water and water-methanol mixtures. The dependency of the rate constant of the reaction shows a distinct maximum between 80 and 90% b/w of methanol followed by a decrease of the rate up to three times below the value for pure water at 99% b/w methanol. A postulation of an Id mechanism was used as a basis for the following conclusions:

a) Reaction of the species $Ni(H_2O)_{6-j}(CH_3OH)_j^{+2}$ is considered

to contribute on a statistical basis on the release of H_2O

or CH_3OH as ligands in the interpretation of their

experimental results.

b) The outer sphere solvation has little effect upon the

rate of the reaction, therefore, structural properties

of the solvent do not influence the rate of the reaction.

Shu and Rorabacher (35) minimized the possible inner sphere effect of the species $Ni(H_2O)_{6-j}(CH_3OH)_j^{+2}$ in their study of the solvent-ammonia exchange in H_2O-methanol mixtures of the N-hydroxyethylenediamine-N,N',N'-triacetate-solvent Ni(II) complex (Ni(HEEDTA)(S)$^-$). They found that the rate of the reaction increases steadily as the content of methanol increases in the solvent. They reported that the mechanism can be interpreted as either Id or D. This information, added to the previous example considered (34), leads to the following conclusions:

a) The competition between the selective outer sphere solvation

of the metal ions by H_2O and the stronger assistance of CH_3OH in the dissociation of the solvent-Ni(II) bond does not support a structural effect

of the solvent.

b) The changes of profile of the functional plot of the rate constant of formation of the $NH_3Ni(II)$ complexes with the change of the first coordination sphere (HEEDTA, a pentadentate ligand and $(H_2O)_{6-j}(CH_3OH)_j$) strongly suggest the stoichiometry of the inner sphere is a critical factor in the interpretation of the solvent effect.

c) The qualitative differences between the results presented by Bennetto and Caldin (32) and the results of the ammonia-solvent interchange study were interpreted in terms of the steric effects reported by Rorabacher and Melendez-Cepeda (36) in the study of the substitution reaction of water in Ni(II) by RR'NH (where R = H, CH_3, CD_3, CH_3CH_2, or $(CH_3)_2CH$, and R' = H or CH_3).

Although all groups of researchers seem to agree in the conservation of the mechanism in different solvents, an apparent contradiction is present in the interpretation of the role played by the solvent in the observed changes of the rate process from one system to another.

It is the view of the author of this work that this contradiction becomes less critical if it is considered that a concerted rearrangement of the outer sphere may account for structural effects of the solvent, as well as multiple equilibrium displacement of solvated metal ions. So it seems probable that the interpretations are not contradictory, but complementary in the sense of relative sizes of the reactants, the solvent composition, and the ligand characteristics.

The results presented in this work seem to indicate that the substitution reaction by a relatively large molecule with respect to the metal ion, should be influenced by the outer sphere coordination at least at intermediate solvent compositions; while at the extreme compositions,

the coordination of the innermost sphere should play the most important role, particularly if selective solvation acts as a thermodynamic control of the reaction.

EXPERIMENTAL SECTION

Reagents. - Analytical reagent grade hydrated nitrate salts

$(Ni(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, and $Cu(NO_3)_2 \cdot 3H_2O$; Fisher Scientific

Company, New Jersey) were used for stock metal ion solutions. These

solutions were titrated with EDTA using the standard procedure reported

by Schwarzenbach and Flaschka (37). The concentrations of the metal

ion solutions were set between 5.0×10^{-6} M and 1.0×10^{-5} M for Cu(II),

5.0×10^{-5} M and 5.0×10^{-4} M for Zn(II), and 5.0×10^{-4} M and 5.0×10^{-3}

M for Ni(II).

Reagent grade 1-(2-pyridylazo)-2-naphthol (β-PAN) and 4-(2 pyri-

dylazo)-resorcinol (PAR) (Eastman Organic Chemicals, New York) were re-

crystallized from methyl alcohol to m.p. 140-141, and 112-113°C respectively.

2,2'-bipyridine (Bipy) (Hopkin and Williams Ltd.) was used without further

purification (m.p. 70-71°C). The concentrations of the solutions of these

ligands were set between 1.0×10^{-7} M and 1.0×10^{-4} M.

Analytical stabilized 1,4-dioxane (Mallinckrodt Chemicals Works,

St. Louis) was purified and dried according to standard techniques,

described by Vogel (38). Absolute dried acetone and methyl alcohol

(Eastman Organic Chemicals, New York) were used without further purifi-

cation: samples of acetone and methyl alcohol were purified and dried

according to the technique described by Vogel (38) and no changes in

kinetic results were found, with respect to the solvents not specially

purified.

2,6-Dimethyl pyridine (Aldrich Chemical Co., Inc., Wisconsin),

distilled over potassium hydroxide was used as a base in the buffer

solution.

Appropriate quantities of analytical reagent grade sodium nitrate
(Mallinckrodt Chemical Works, St. Louis) were added to the solvents used
in this study to keep the ionic strength constant.

Distilled water, CO_2 free, with a conductance less than $1.0 \times 10^6 \Omega^{-1}$
was used in all experiments.

Experimental Control. - All solvent mixtures were prepared on a
weight percentage basis. In order to insure reproducibility of the sol-
vent composition in the related experiments, the following technique was
used:

Specific volumes of water were weighed in a volumetric flask and
then combined with the non-aqueous component of the mixture up to the cali-
bration mark. This technique yielded both the percent by weight and by
volume, and these procedures were cross checked by calculations using the
density of the pure solvents that are reported in the CRC handbook (39).
These tests showed agreement with the experimental values within 1 percent.

The solution of the reactants in the solvent mixtures were either
warmed up to about 50°C or allowed to stand overnight in order to degasify
the solvent up to a level that prevented air bubbles from forming in the
reaction chamber.

The pH for all solvent mixtures as well as water were determined
potentiometrically with a Beckmann Expandomatic SS-2 pH-meter, equipped
with a Beckman Combination electrode (Glass reference and saturated with
silver chloride in 4M potassium chloride solution). No scale of acidity
was used.

Most of the structural, transport, and physical properties of the
solvent mixtures were taken from the Critical Tables. However, in order
to obtain all the necessary data, some viscosity values were estimated

with an Ostwald viscosimeter, according to the general techniques reported
elsewhere (40). Dielectric constants were estimated in a Sargent Chemical
Oscillometer using methyl alcohol as a standard (the value of the dielectric
constant of the commercial methyl alcohol, used as a standard, was found
to be within 1% of the value accepted by IUPAC). Conductivity of the
metal ions were measured in a YSI Model 31 Conductivity Bridge.

These properties were temperature controlled in a water bath
thermostated between 20.0 and 40.0°C with a precision of ±0.1°C.

Spectroscopic Characterization of Products and Reactants. The
characterizations of the ligands and the complexes were made spectros-
copically using a Cary 14 spectrophotometer. The spectra were taken at
room temperature using specific compositions of solvent mixtures, and the
pH was chosen in such a way that direct comparison with previously reported
data by several authors (41-50) could be made (typical data are summarized
in Table 2-1). Figures 2-1 to 2-4 show the visible and U.V. spectra of
the species considered.

The validity of the Beer's law (Equation 2-4) for all the necessary
ligands and complexes at several pH values was confirmed.

The determination of the concentrations of the species considered
in the Beer's law confirmation were carried out by finding the numerical
solution of the mathematical system of equations which are implicit in
the stoichiometric equilibria represented in Equations 2-2. In addition,
the experimental values of the stability constants and acid dissociation
constants (41-48) that are summarized in Tables 2-2 and 2-3 respectively,
were used. It was assumed that the elementary definition

$$pH = - \log [H_3O^+] \qquad \text{2-1}$$

TABLE 2-1

Spectroscopy Characterization of Some of the Species Considered in This Study

Chemical Species	Solvent[a] % b/v	pH[b]	λ_{max} Reported (n m)	λ_{max} Found (n m)	Reference
β-PAN	20 D in W	5.6	470	468	41
β-PAN	50 M in W	5.0	470	470	42
β-PAN	50 D in W	5.8	470	470	43
PAR	W	5.5	383	384	41
PAR	50 D in W	5.3	392	391	41
PAR	50 D in W	6.3	415	416	44
PAR	50 D in W	3.6	383	384	43
Bipy	50 M in W	4.7	282	283	50
$Cu(\beta\text{-PAN})_2^{+2}$	70 E in W	5.0	576	577	43
$Cu(\beta\text{-PAN})_2^{+2}$	70 E in W	5.0	402	403	43
$Zn(\beta\text{-PAN})_2^{+2}$	70 E in W	5.0	572	572	43
$Zn(\beta\text{-PAN})_2^{+2}$	70 E in W	5.0	550	549	43
$Cu(\beta\text{-PAN})_2^{+2}$	50 M in W	5.0	552	552	42
$Zn(\beta\text{-PAN})^{+2}$	50 D in W	5.5	-	560	-
$Ni(\beta\text{-PAN})^{+2}$	70 E in W	5.0	592	592	43

a) The solvents are : D dioxane, W water, E ethanol, and M methanol.

b) The pH was chosen for identification with the literature but does not imply exclusion of other species in solution (Equation 2-2).

Legend of Figures 2-1, 2-2, 2-3 and 2-4

Figure 2-1 - Visible Spectra of $Ni(\beta-PAN)_2^{+2}$ and $Zn(\beta-PAN)_2^{+2}$

——————— for $Ni(\beta-PAN)_2^{+2}$

—·——·—— for $Zn(\beta-PAN)_2^{+2}$

Figure 2-2 - Visible Spectra of β-PAN, $Zn(S)_3(\beta-PAN)^{+2}$, $Ni(S)_3(\beta-PAN)^{+2}$ and $Cu(S)_3(\beta-PAN)^{+2}$

——————— for β-PAN

—·——·—— for $Zn(S)_3(\beta-PAN)^{+2}$

··——··—— for $Ni(S)_3(\beta-PAN)^{+2}$

···——···—— for $Cu(S)_3(\beta-PAN)^{+2}$

Figure 2-3 - U. V. Spectra of Bipy and $Zn(S)_4(Bipy)^{+2}$

——————— for Bipy

—·——·—— for $Zn(S)_4(Bipy)^{+2}$

Figure 2-4 - Visible Spectra of PAR, $Zn(S)_3(PAR)^{+2}$ and $Ni(S)_3(PAR)^{+2}$

——————— for PAR

—·——·—— for $Zn(S)_3(PAR)^{+2}$

··——··—— for $Ni(S)_3(PAR)^{+2}$

All spectra were taken in a 10 mm silica cuvette in 50% b/w methanol in water.

The pH were:

a) 5.4 for β-PAN and its complexes.

b) 5.0 for PAR and its complexes.

c) 4.7 for Bipy and its complex.
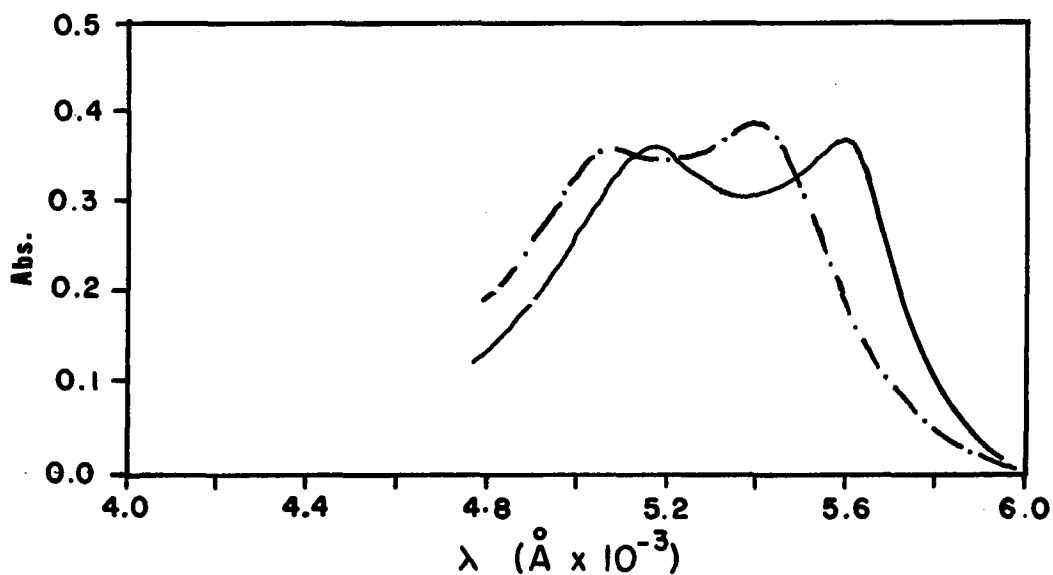
Figure 2-1. Visible Spectra of $Ni(\beta\text{-PAN})_2^{+2}$ and $Zn(\beta\text{-PAN})_2^{+2}$
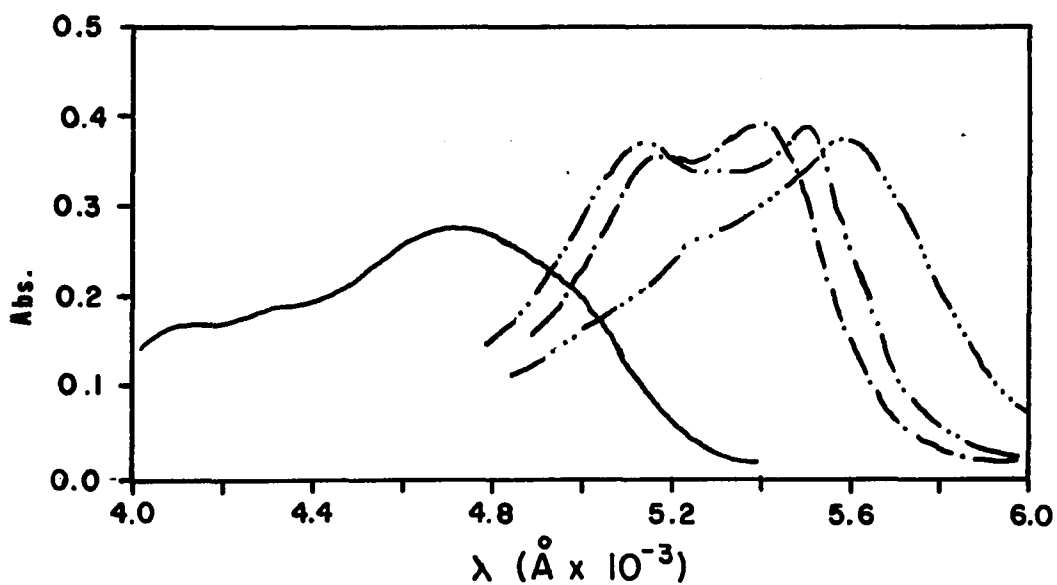
Figure 2-2. Visible Spectra of $\beta\text{-PAN}$, $Zn(S)_3(\beta\text{-PAN})^{+2}$ and $Ni(S)_3(\beta\text{-PAN})^{+2}$
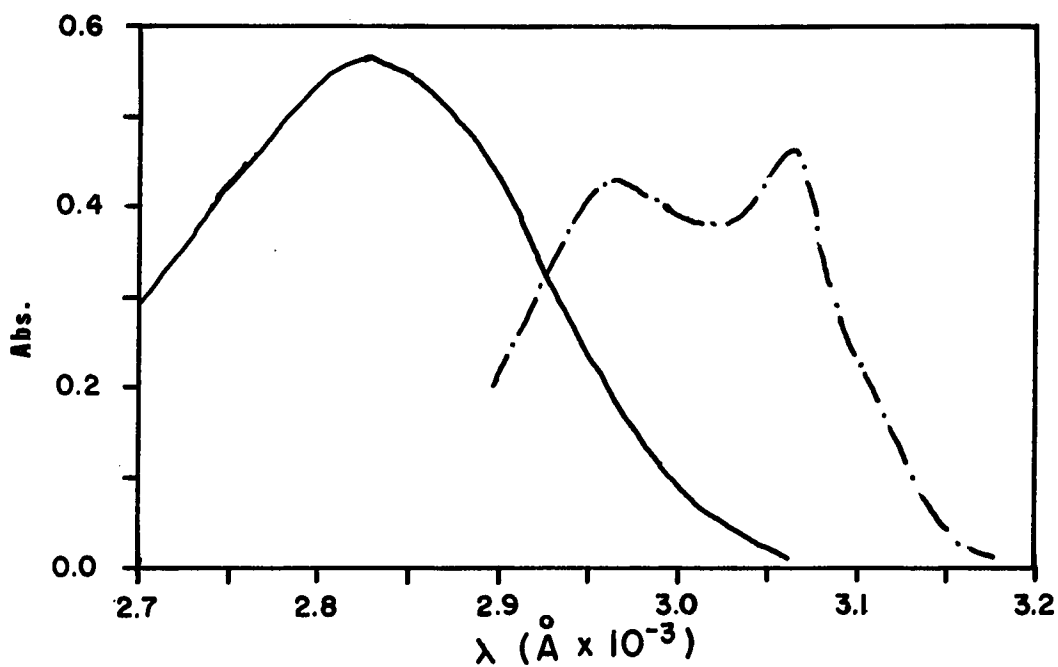
Figure 2-3. U.V. Spectra of Bipy and $Zn(S)_4(Bipy)^{+2}$
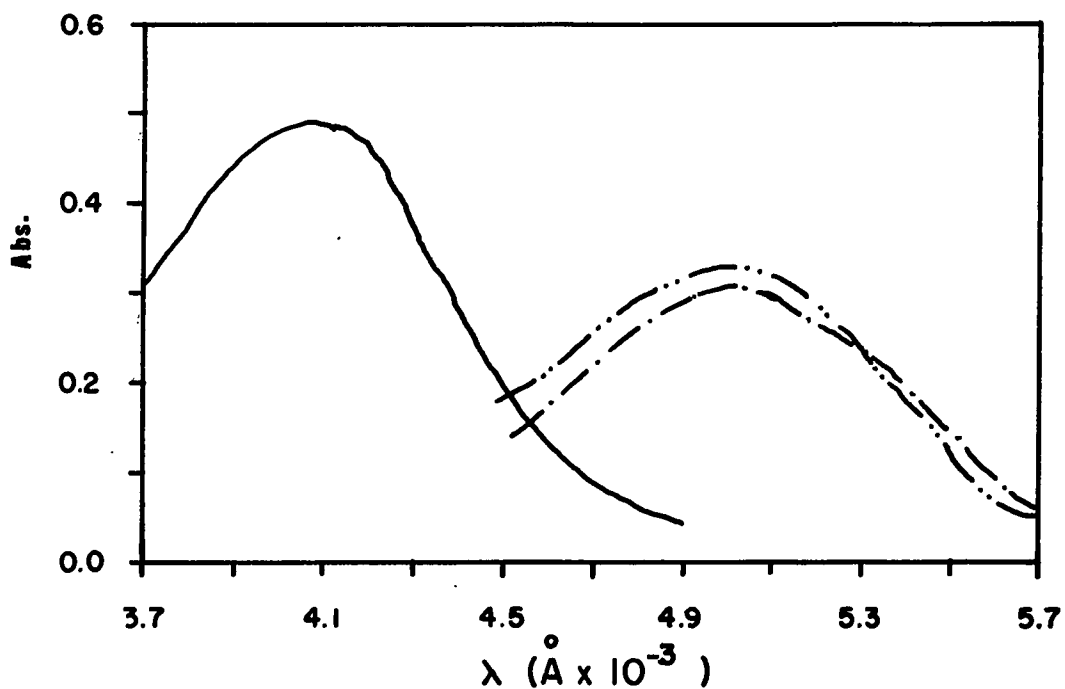
Figure 2-4. Visible Spectra of PAR and $Zn(S)_3(PAR)^{+2}$

is sufficiently accurate to calculate $[H^+]$ in solvent mixtures. In fact,
the balance of products were within an error of 1.% with respect to the
theoretical sum of the products (Equation 2-3)

a) $M(S)_6^{+2} + L_{(n)} \rightleftharpoons M(S)_{(6-n)}L_{(n)}^{+2}$ $\qquad K_1$

b) $M(S)_{(6-n)}L_{(n)}^{+2} + L_{(n)} \rightleftharpoons M(S)_{(6-2n)}L_{2(n)}^{+2}$ $\qquad K_2$

c) $M(S)_{(6-2n)}L_{2(n)} + L_{(n)} \rightleftharpoons ML_{3(n)}^{+2}$ $\qquad K_3$ $\qquad \underline{2-2}$

d) $LH^+ \rightleftharpoons H^+ + L$ $\qquad K_{a1}$

e) $L \rightleftharpoons H^+ + L^-$ $\qquad K_{a2}$

f) $L^- \rightleftharpoons H^+ + L^{-2}$ $\qquad K_{a3}$
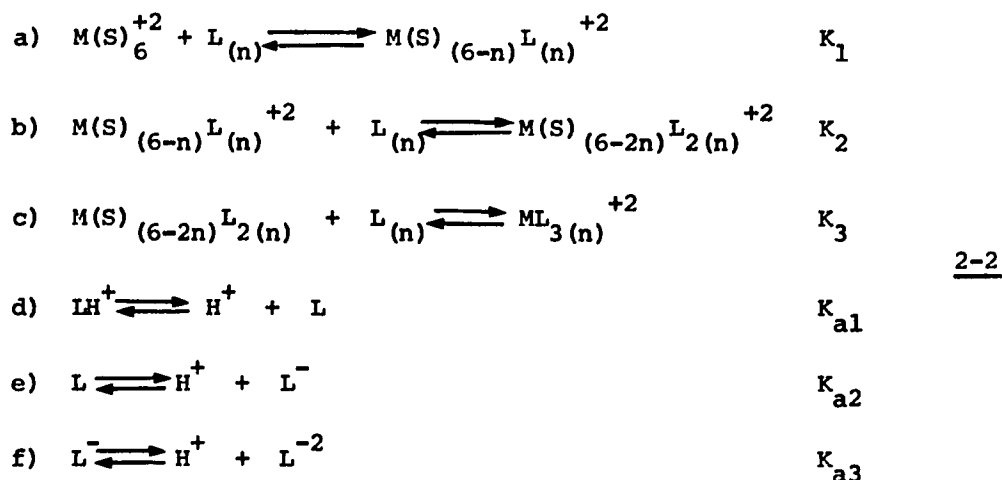
where n stands for the sites of coordination of the ligands, being n = 3
for β-PAN and PAR, and n = 2 for Bipy. The balance of products are
shown in the following equation:

a) $[L]_T = [L] + [M(S)_{(6-n)}L_{(n)}^{+2}] + 2 [M(S)_{(6-2n)}L_{2(n)}^{+2}] +$

$\qquad + 3 [ML_{3(n)}^{+2}] + [LH^+] + [L^-] + [L^{-2}]$ $\qquad \underline{2-3}$

b) $[M(S)_6^{+2}]_T = [M(S)_6^{+2}] + [M(S)_{(6-n)}L_{(n)}^{+2}] +$

$\qquad + [M(S)_{(6-2n)}L_{2(n)}^{+2}] + [ML_{3(n)}^{+2}]$
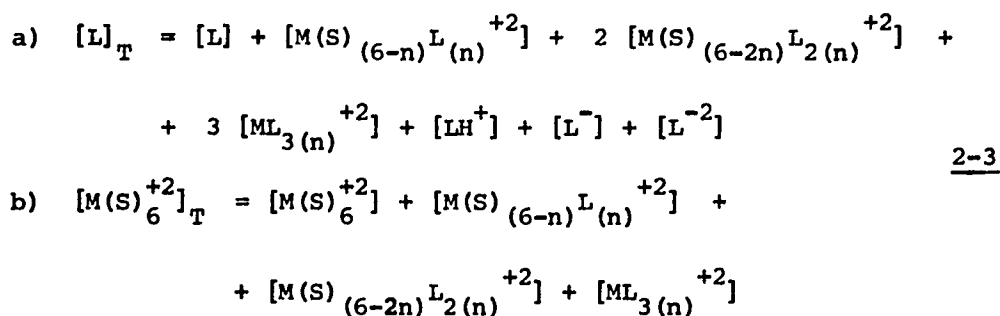
<u>Kinetic Measurements.</u> - The time dependence of the substitution
reactions was followed in a Durrum-Gibson stopped-flow single beam spectro-
photometer, with a Kel-F flow path and a 2 cm. path length cuvette. All
reactions were temperature controlled between 11.0 and 40.0°C, with a
precision of ±0.1°C by means of submersion of the drive syringes, the
Kel-F flow path and reaction cuvette in a water reservoir. The water

TABLE 2-2

Logarithm of the Equilibrium Constant of the Metal Complexes Considered in Equation 2-2

Ligand	Metal Ion	lg K_1	lg K_2	lg K_3	Reference
β-PAN	Ni^{+2}	12.5	12.6	-	45[a]
β-PAN	Zn^{+2}	11.2	10.5	-	45[a]
β-PAN	Cu^{+2}	17.0	-	-	42[a]
β-PAN	Cu^{+2}	15.5	8.4	-	47[b]
PAR	Ni^{+2}	13.2	12.8	-	45[a]
PAR	Zn^{+2}	12.4	11.2	-	45[a]
PAR	Cu^{+2}	14.8	9.1	-	45[c]
PAR	Cu^{+2}	16.4	8.9	-	45[a]
Bipy	Zn^{+2}	4.88	4.08	3.05	31[d]

a) Solvent 1-4 dioxane/water mixture   50% b/v

b) Solvent methanol/water mixture   50% b/v

c) Solvent water

d) Solvent ethanol/water mixture   40% b/v

TABLE 2-3

Negative Logarithm of Acid Dissociation Constants of Ligands

Ligands	pK_{a1} (pK_{NA})	pK_{a2} (pK_{OH})	pK_{a3} (pK'_{OH})	Reference
β-PAN	2.0	12.3	-	45[a]
β-PAN	2.32	12.0	-	42[b]
PAR	2.3	12.4	6.9	45[a]
PAR	2.66	12.31	5.48	48[a]
Bipy	4.33	-	-	77[c]

a) 1-4 dioxane-water mixture 50% b/v

b) methanol-water mixture 50% b/v

c) water

reservoir was connected in continuous flow with a thermostated P.M. Tamson (N.V.) bath.

The output information of the stopped-flow instrument was recorded in a Tektronix oscilloscope as a trace of voltage versus time. Deionized water, metal ion solutions, or specific solvent mixtures were used as reference in such a way that the voltage scale of the oscilloscope became linearly related to the transmittance in a relative 0% to 100% range, and so that the Bouguer-Lambert-Beer Equation 2-4 (51) could be applied;

$$a = \log(I/I_o) = - \xi Cd \qquad \underline{2-4}$$

where a is the absorption, ξ is the molar extinction coefficient, C the molar concentration, d the path length, $I_o = (OD_0 - OD_{100})$ (standard), and $I = (OD_{100} - OD_\infty)$ (general) (where OD is the optical density).

The analog recording of the oscilloscope was photographed on polaroid film. Digitalization of the data was performed manually by ruler measurement with an arbitrary decimal scale for the voltage, the horizontal scaling grid of the oscilloscope output was directly used as the time scale. Figure 2-5 shows a typical output reproduction of a plate with all parameters specifically indicated, and Figure 2-6 is the corresponding analysis.

Setting of Experimental Conditions. - The relative concentration of the metal ions with respect to the ligands, as well as the pH of the solutions, were chosen on the basis of the values of the stability constants of the complexes, and the acidic constants reported in Table 2-3 for their stoichiometric equilibria as shown in Equation 2-2. These equilibria were simulated in a 360-50 IBM Computer, Figures 2-7, and 2-8 show typical functional representations of the concentrations of the species $M(S)_{(6-n)}L_{(n)}^{+2}$ and $M(S)_{(6-2n)}L_{2(n)}^{+2}$ versus $M(S)_6^{+2}$ concentration and pH respectively for the specific case of β-PAN as a ligand, and with

Legend of Figures 2-5 and 2-6

Figure 2-5 - Typical Reproduction of the Oscilloscope Analog

Recording (Scale 1:1.26). Tabulation is Actual

Data From the Original Plate and its Primary Analysis.

Figure 2-6 - Actual Computer Plot of the Primary Analysis Showing

the Linearity of the Plot of Log (Absorbance -

Absorbance at Infinite Time) Versus Time.

This example corresponds to the reaction:

$$Ni(aq)^{+2} + PAR \longrightarrow Ni(aq)(PAR)^{+2}$$
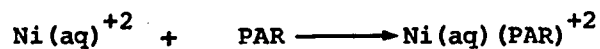
at the conditions:

$25.0^\circ C$

$\mu = 0.12$ M

pH = 5.2

$[Ni(aq)^{+2}] = 2.36 \times 10^{-3}$ M

$[PAR] = 7.75 \times 10^{-6}$

Stopped-flow cuvette: 20 mm.

Deflection shown was expanded 10 folds.

Reference for 100% transmittance: the nickel solution.

Solvent:water.

Figure 2-5. Typical Reproduction of the Oscilloscope Analog
Recording (Scale 1:1.26)

TIME = 5.0 sec

INF =   0.32566E-01

TIME	DEFLECTION	ABSORBANCE	LOG10(D(T)-D(INF)	D(T)-D(INF)
0.0	76.50	0.4640E-01	-0.18590E+01	0.1383E-01
2.00	64.50	0.4420E-01	-0.19342E+01	0.1163E-01
4.00	57.00	0.4283E-01	-0.19886E+01	0.1027E-01
6.00	50.50	0.4165E-01	-0.20418E+01	0.9083E-02
8.00	44.00	0.4047E-01	-0.21022E+01	0.7903E-02
10.00	37.00	0.3920E-01	-0.21781E+01	0.6636E-02
12.00	32.50	0.3839E-01	-0.22348E+01	0.5823E-02
14.00	28.00	0.3758E-01	-0.23000E+01	0.5012E-02
16.00	24.00	0.3686E-01	-0.23673E+01	0.4293E-02
18.00	21.00	0.3632E-01	-0.24255E+01	0.3754E-02
20.00	18.50	0.3587E-01	-0.24808E+01	0.3305E-02
22.00	16.00	0.3542E-01	-0.25441E+01	0.2857E-02
24.00	13.50	0.3498E-01	-0.26181E+01	0.2410E-02

◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆

-0.719695E+00   -0.186149E+01

◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆

Figure 2-6. Actual Computer Plot of the Primary Analysis showing the Linearity
of the Plot of log (Absorbance - Absorbance at Infinite Time)
Versus Time

Zn^{+2} as the metal ion.

From the above simulation, two extreme conditions were chosen:

a)   at least 20 times excess concentration of the metal ions

with respect to the ligands;

b)   at least 40 times excess concentration of the ligands

with respect to the metal ions.

A third condition was chosen on the basis of the general stoi-
chiometry of the reaction, namely:

c)   the concentration of the metal ions in two fold excess

with respect to the ligand concentrations.

The primary analysis of the data was carried out by standard

numerical techniques, using graphical mapping of logarithmic functions

versus time (Guggenheim type of plot) and inverse functions versus

time were usually extended over three half lives of the reaction. Least

square criteria was used as a basis for regression analysis and curve

fitting.

The results of the preliminary analysis using condition c) were

functionally corrected to the concentration of the ligand using Equation

2-4 in order to estimate the order of the reaction in the empirical rate

law.

The use of the condition c) was limited to mixed solvents for

concentrations of the non-aqueous component higher than 50% b/w as a

cross check of the estimated k_{13} of the empirical rate law of the

reaction when condition b) is assessed in relation to the limits of

the mathematical assumptions for the estimation of k_{13}.

The activation parameters were computed through observation of

at least three different temperatures in a range of 10.0 to 40.0°C and it

was found after regression analysis that the accuracy is probably ±0.5

kcal for E^* and $\Delta H^{\neq}$, and close to ± 1.0 e.u. for $\Delta S^{\neq}$ (where E^* is the experimental energy of activation, $\Delta H^{\neq}$ the heat of activation, and $\Delta S^{\neq}$ the entropy of activation). The formulation for the activation parameters will be presented in the next section.

A continuous modeling system program (analog-digital) (52-56) was used for computer simulation of the empirical rate law as a cross check of both the analytical closed solution and the general theoretical assumptions (general discussion and consideration are presented in Appendix B).
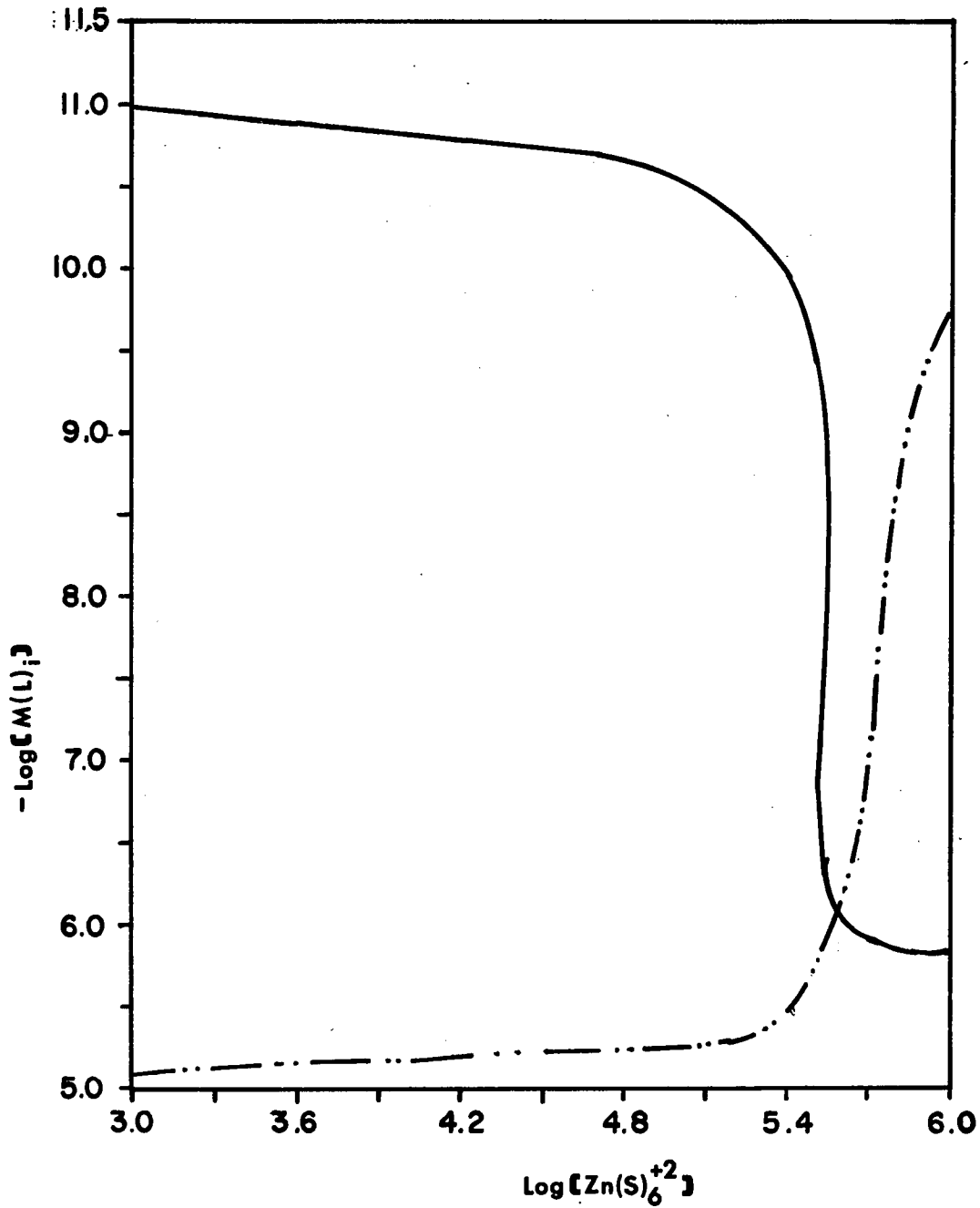
Figure 2-7. Logarithmic Representation of the Equilibrium Con-
centrations of $Zn(S)_3(\beta\text{-PAN})^{+2}$ and $Zn(\beta\text{-PAN})_2^{+2}$ as
a Function of the Concentration of Zn(II)
$([\beta\text{-PAN}] = 1.0 \times 10^{-5}$ M)

——————— $Zn(\beta\text{-PAN})^{+2}$
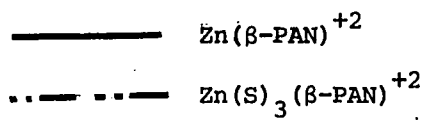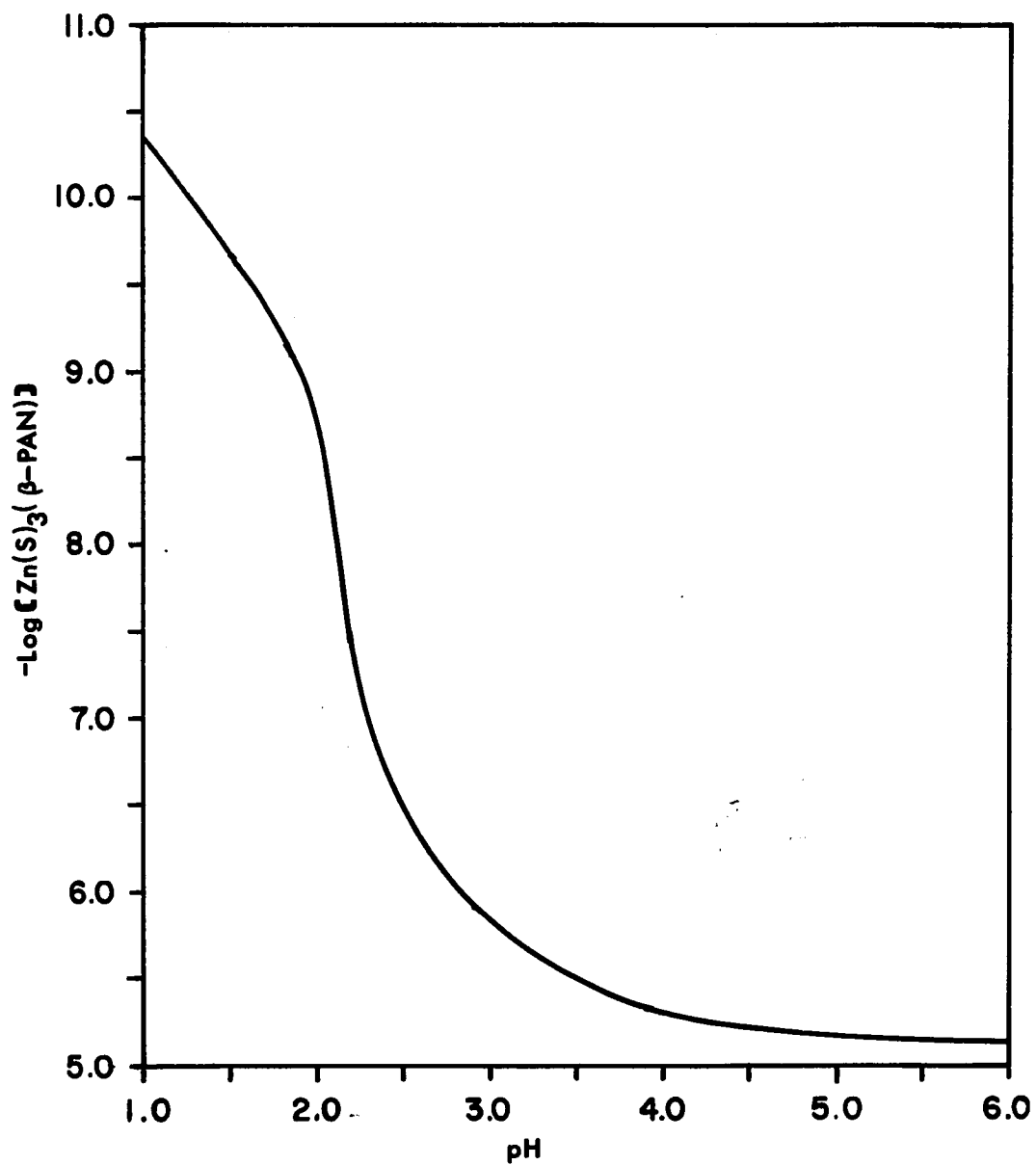
•• —— ••• —— $Zn(S)_3(\beta\text{-PAN})^{+2}$

Figure 2-8. Logarithmic Representation of the Equilibrium
Concentrations of $Zn(S)_3(\beta\text{-PAN})^{+2}$ as a Func-
tion of pH's

$$([\beta\text{-PAN}] = [Zn] = 1.0 \times 10^{-5} \text{ M})$$

RESULTS

The results of the kinetics of the reactions shown in Equation 2-2
(a, b, and c) of the previous section are presented in this section. The
study includes the reactions of the metal ions Cu(II), Zn(II), and Ni(II),
with the ligands β-PAN, PAR, and Bipy, in the solvents water, mixtures of
water-methanol, water-dioxane, and water-acetone.

It was found that the stoichiometries of the reactions studied
(for all ligands and metal ions combinations) correlate with an empirical
rate law of first order with respect to the concentration of each reacting
species. This section will be divided into the following parts:

   a)   Correlation of stoichiometry and empirical rate law.

   b)   pH dependency of k_{12} and other determinants of the
        rate constant.

   c)   Activation parameters.

Correlation of Stoichiometry and Empirical Rate Law.

Three different types of experiments, concerning the relative
initial concentration of the ligand with respect to the initial concen-
tration of the metal ions, were undertaken:

   I)   Excess initial concentration of the metal ions with respect
to the initial concentration of the ligands (pseudo first-order condition).
This type of experiment was applied to all metal ions.

   II)   The initial concentration of the metal ions in two fold excess
with respect to the initial concentration of the ligands.

   III)   Excess of the initial concentration of the ligands with respect
to the initial concentration of the metal ions.

In Appendix B a mathematical formulation for these types of experiments is presented.

The experiments type II and III were applied only to the ligand β-PAN because:

a) The scheme presented in Appendix B does not apply to Bipy which has possibilities of forming complexes with ratios of 1:1, 1:2, and 1:3 of metal ions to ligands;

b) Preliminary experiments using PAR as ligand yielded ambiguous results.

Experiments II and III of β-PAN with the mtal ion Cu(II) were excluded for thermodynamic reasons ($K_1 >> K_2$, see Table 2-2).

In Appendix C several examples of the primary analysis (plot) characteristic of each type of experiment previously enumerated are presented.

Experiment type I will assume the following rate equation:

$$- \frac{d[L]}{dt} = \frac{d[ML]}{dt} = k_{obs} [L] \qquad \text{3-1}$$

where

$$k_{obs} = k_{12} [M]_o.$$

Experiment type II uses an approximate solution for [L], as a boundary problem for the rate Equation B-12 which, after simplification becomes:

$$\frac{d^2[L]}{dt^2} + 2k_{13}[L]\frac{d[L]}{dt} + (2k_{12}k_{13} - k_{12}^2) \; [L]^3 = 0 \qquad \text{3-2}$$

whose solution presented in Equation B-19 implies [L] = [L](t) has a particular linear relationship. The slope of such a function is:

$$k_{obs} = k_{13} \pm \sqrt{k_{13}^2 + 8k_{12}k_{13} - k_{12}^2} \qquad \text{3-3}$$

Experiment type III assumes the following rate equation:

a) $\dfrac{d[M]}{dt} = -k_1[M]$

b) $\dfrac{d[ML]}{dt} = k_1[M] - k_2[ML]$ $\underline{3\text{-}4}$

c) $\dfrac{d[ML_2]}{dt} = k_2[ML]$

where

$k_1 = k_{12}[L]_o$, and $k_2 = k_{13}[L]_o$.

Before the presentation of any results, it seems to be in order to discuss the precision and the accuracy of the experiments.

It was pointed out in the experimental section that standarization of the voltage scale of the analog output of the stopped-flow against a particular solvent was necessary in order to correlate this scale with optical density; therefore, the determination of the absorption of any species can only be determined on a relative basis. In fact, comparison between the estimated absorptions from the stopped-flow and the equivalent taken from the Cary 14 spectrophotometer were found to agree within $\pm 8\%$.

If it is assumed that for any particular experiment this accuracy error is constant in sign and magnitude, then the error will be linearly related to the concentration (as the absorption is) and, therefore, any determination using the first derivative of a functional plot of the logarithms of the absorptions versus time should be independent of such error. In other words, the standard deviation of k_{obs}, k_2 or k_1 estimated in experiments type I or III should be bigger than the accuracy of the value of k_{obs}, k_2 or k_1.

For the experiments type II, the first derivative of the functional plot of the inverse of the absorption versus time is used. Therefore, the

observed constant is no longer independent of the accuracy error. This implies that the calculation of k_{13} is not estimated from an homogeneous set of data (k_{obs} and k_{12}), so all errors (accuracy and precision) become additive. A conservative estimate of the error is ±15%.

Reactions of the Ligand β-PAN With the Metal Ion $Zn(aq)^{+2}$, $Cu(aq)^{+2}$, and $Ni(aq)^{+2}$ in Water.

Experiments type I were carried out under the following conditions:

a) pH = 5.8 in buffer 2,6 lutidine - 2,6 lutidine nitrate;

b) Ionic strength (μ) = 0.12 ± 0.005 M adjusted with sodium nitrate;

c) Temperature = 25.0 ± 0.1°C.

The reaction of a 1.2×10^{-7} M solution of β-PAN with several solutions of each metal ion (whose concentrations were in excess with respect to the concentration of the ligand) was observed at 4600 Å in the stopped-flow instrument. Plots of the logarithm of the change of absorption ($D-D_\infty$) versus time (Guggenheim plot) were found to be linear. These results suggest a first-order empirical rate law with respect to the concentration of the ligand. Figure 3-1 shows a functional plot of the observed rate constant of formation of the mono-ligand complex versus the initial concentration of the metal ions. Linearity of such plots and their extrapolation to zero concentration of the metal ion with an intersection of O in the k_{obs} coordinate, suggests a first-order dependency on the concentration of the metal ions.

Table 3-1 condenses the results previously described.

Reactions of the Ligand β-PAN With the Metal Ions Zn(II), Cu(II), and Ni(II) in Dioxane-Water Mixtures.

Under the same conditions of pH, ionic strength, and temperature previously described, mixtures of 5.0, 10.5, 21.0, 31.4, 41.5, 51.5, 61.3, 71.0, 80.5, and 92.0% by weight of dioxane in water were used as solvents in the study of the reactions of the ligand β-PAN with the metal ions Zn(II) and Cu(II). For the metal Ni(II) only 10.5, 31.4, 51.5, 71.0 and 92.0% by weight of dioxane in water were used.

For experiments type I:

Reactions with the following initial concentrations were analyzed:

a)   8.5 x 10^{-6} M of β-PAN and 2.08 x 10^{-3} M of $Zn(S)_6^{+2}$

b)   8.5 x 10^{-6} M of β-PAN and 7.08 x 10^{-3} M of $Ni(S)_6^{+2}$

c)   8.6 x 10^{-7} M of β-PAN and 1.67 x 10^{-5} M of $Cu(S)_6^{+2}$

At all solvent compositions, it was found that the results were qualitatively equivalent to those previously reported for the same reactions in water.

Using selected solvent mixtures of dioxane-water experiments with different concentrations of ligands, as well as metal ions, were under-taken. Tables 3-2 to 3-7 summarize the results. These results show that k_{obs} is, within the experimental error, independent of the initial concen-tration of β-PAN. Functional plots of k_{obs} versus the initial concentration of the metal ions presented in Figure 3-2 show examples of the linear profile as well as a zero intersection with the k_{obs} coordinate at zero concentration of the metal ions. It is concluded that for all solvent compositions of the mixture dioxane-water, the correlation of the stoi-chiometry with the empirical rate law proposed for water as solvent is conserved.

For experiments type II (see Appendix D):

In the solvent mixtures 51.5, 61.3, 71.0, 80.5, and 92.0% by weight of dioxane, the following solutions were allowed to react:

a) 8.53×10^{-5} M of β-PAN and 4.25×10^{-5} M of $Zn(S)_6^{+2}$

b) 4.26×10^{-4} M of β-PAN and 2.14×10^{-4} M of $Ni(S)_6^{+2}$

Both reactions were observed at 4600 $\overset{o}{A}$. A plot of the inverse of the absorption versus time was found to be linear (examples are in Figure 3-3). The standard deviation of k_{obs} (slope of the linear plot) was found to be between 5-6% for at least four determinations for each particular solvent composition. It was suggested earlier that the value of k_{obs} and k_{12} were not homogeneous sets, so in order to calculate k_{13} from this data, the following scheme was used:

$$\overline{k}_{13}(k_{12}, k_{obs}) = \frac{\displaystyle\sum_{i=1}^{n} \sum_{j=1}^{m} \frac{k_{12(i)}^{2} + k_{obs(j)}^{2}}{8 k_{12(i)} + k_{obs(j)}^{2}}}{\binom{n+m}{2} - \binom{n}{2} - \binom{m}{2}} \qquad \text{3-5}$$

where in general:

$$\binom{p}{q} = \frac{p!}{q!(p-q)!} \qquad \text{3-6}$$

It is obvious that $\overline{k}_{13}$ (k_{12}, k_{13}) should be equal to k_{13} $(\overline{k}_{12}, \overline{k}_{obs})$ if the set $k_{12(i)}$ and $k_{obs(j)}$ were homogeneous. Experimentally this was not the case within the precision of the experiment (standard deviation of either k_{12} or k_{obs}), but there is still agreement within the error of $\overline{k}_{13}(k_{12}, k_{obs})$ (standard deviation of Equation 3-5).

Results of these experiments are summarized in Tables 3-8 and 3-9.

For experiments type III (see Appendix D):

In the solvent mixtures 21.0, 31.4, 41.5, 51.5, 61.3, 71.0, 80.5,

and 92.0% by weight of dioxane the following solutions were allowed to react:

a) 8.53 x 10^{-4} M of β-PAN and 2.54 x 10^{-5} M of $Zn(S)_6^{+2}$

b) 8.53 x 10^{-4} M of β-PAN and 3.54 x 10^{-5} M of $Ni(S)_6^{+2}$

The reactions were observed at 5550 $\overset{o}{A}$ and 5500 $\overset{o}{A}$ respectively.

Plots of the logarithm of the absorption change, $(D-D_\infty)$, versus time were

found to be linear (see Appendix C). The linearity of these plots suggests

that the reactions leading to $Zn(\beta-PAN)_2^{+2}$, and $Ni(\beta-PAN)_2^{+2}$ complexes are

first order with respect to the ligand concentration.

The slope of the Guggenheim plot was identified with k_2, but the

values of k_{13} becomes closer to the values of k_{12} for the solvent mixture

of 61.3% of dioxane, and no assignment was given to the slope of either

k_1 or k_2 in this particular solvent.

Limited experimentation was done regarding the dependence of k_2 on

the initial concentration of the metal ion. Figure 3-4 shows examples of

the linear dependence of k_2 on the initial concentration of the ligand.

These results, summarized in Tables 3-10 to 3-12, seem to confirm

the validity of the scheme proposed in Equation 3-4.

Reactions of the Ligand β-PAN With the Metal Ions Zn(II), Ni(II), and Cu(II) in the Solvent Mixtures Methanol-Water and Acetone-Water.

These reactions, in both solvent mixtures, were studied under the

same conditions of pH, ionic strength, and temperature previously described.

All the results for the experiments type I, II, and III, where applicable,

are qualitatively equivalent to those previously reported for dioxane-

water mixtures, in regard to the order of the reaction, validity of the

assumptions, and conservation of the correlation of the stoichiometry with the

empirical rate law.

Examples of the dependence of k_{obs} on the initial concentration of the metal ions (experiment type I) and on the initial concentration of β-PAN (experiment type III) are shown in Figures 3-5 to 3-7, respectively.

The results are summarized in Tables 3-13 to 3-26.

Reactions of the Ligand PAR With the Metal Ions Zn(II), and Ni(II) in Water.

For experiments type I:

At the following conditions:

a)   pH = 5.2 adjusted with buffer 2,6 lutidine-2,6 lutidine

     nitrate (the pH was chosen according to the description

     given in the experimental section);

b)   ionic strength (μ) = 0.10 ± 0.02 M adjusted with sodium nitrate;

c)   at the temperatures 25.0 and 14.7 ± 0.1°C the following

     reactions were observed:

     i) 7.75×10^{-6} M of PAR with 6.81×10^{-4} M of $Zn(S)_6^{+2}$

     ii) 7.75×10^{-6} M of PAR with 7.08×10^{-3} M of $Ni(S)_6^{+2}$
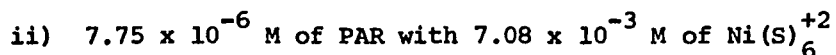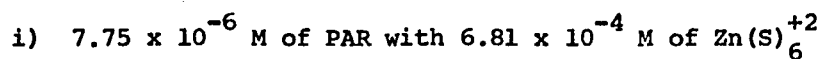
Guggenheim plots were found to be linear, and examples are shown in Appendix C. Variations of the initial concentration of the metal ions were found to correlate linearly with k_{obs}, this correlation is shown in Figure 3-8.

Table 3-27 summarizes the results of the above experiments.

Reactions of the Ligand PAR With the Metal Ions Zn(II), and Ni(II) in the Solvent Mixtures Dioxane-Water and Methanol-Water.

For experiments type I:

Under the same conditions described previously for the study of

this reaction in water, solutions of the following concentrations were

allowed to react;

a) 7.75×10^{-6} M of PAR and 2.27×10^{-4} M of $Zn(S)_6^{+2}$

b) 7.75×10^{-6} M of PAR and 3.54×10^{-3} M of $Ni(S)_6^{+2}$

Solvent mixtures used were dioxane-water with 10.5, 21.0, 31.4, 41.5, 51.5,

61.3, 71.0, 80.5, and 92.0% by weight of dioxane, and water-methanol with

9.4, 17.7, 26.8, 36.4, 45.9, 55.5, 65.8, 76.5, 87.8, and 96.1% by weight

of methanol.

It was found that at all solvent compositions the Guggenheim plots

were linear, and examples are shown in Appendix C. Experiments with dif-

ferent solvent compositions show k_{obs} to be independent of the initial

concentration of the ligand, similarly it was found that k_{obs} was linearly

correlated to the initial concentration of the metal ions (Figure 3-9).

These results, added to the results previously described, suggest that,

independently of the solvent, the reactions of the ligand PAR with the

metal ions $Zn(S)_6^{+2}$ and $Ni(S)_6^{+2}$ leading to $Zn(S)_3(PAR)^{+2}$ and $Ni(S)_3(PAR)^{+2}$

are first order with respect to the ligand as well as first order with

respect to the metal ions.

Tables 3-28 and 3-36 summarize the results of these experiments.

Reactions of the Ligand Bipy With the Metal Ion $Zn(S)_6^{+2}$

For experiments type I;

Under the following conditions:

a)   pH = 5.8 adjusted with buffer 2,6 lutidine - 2,6 lutidine

   nitrate;

b)   ionic strength $(\mu) = 5.7 \times 10^{-3}$ M adjusted with sodium

   nitrate;

c) temperature = 25.0 ± 0.1°C.

Solutions of 3.86×10^{-6} M of Bipy were reacted with solutions 5.35×10^{-5} M of $Zn(S)_6^{+2}$ in the solvents: water, and methanol-water mixtures of the same composition previously described.

The results of these experiments are qualitatively equivalent to those described for PAR.

Tables 3-37 to 3-39 summarize the results.

pH Dependency of k_{12} and Other Determinants of the Rate Constants.

Experiments at different pH's were undertaken in the study of the reaction of Zn(II) with β-PAN, in 50.5% b/w of dioxane in water, leading to the 1:1 and 1:2 metal ion to ligand complexes.

The results are tabulated in Tables 3-40 and 3-41. They show that in the limited range of pH (5.2 to 6.0) used in these experiments, both k_{12} and k_{13} have a noticeable dependency upon the pH. Furthermore, such dependency was found to be linear, as shown in Figures 3-10, and 3-11, for the functional plot $k = k(pH)$.

Similar experiments were carried out for the metal ion Ni(II) and the ligand PAR in the pH range 5.2 to 6.8 in pure water as solvent. The results summarized in Table 3-42 are qualitatively similar to those described above.

Other experiments relevant to this problem are summarized in Tables 3-43 to 3-46 concerning kinetic runs and conductivity of the metal ions in water and several mixed solvents.

Activation Parameters.

The activation parameters of the reaction rates for the formation of the $MS_{6-n}L_{(n)}$ complexes studied under the experiment type I were

estimates according to the formulation of Wymer-Jones and H. Eyring (4):

a) $\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq}$

b) $k_{soln.} = (\overline{k}T/\overline{h})\exp(-\Delta H^{\neq}/RT + \Delta S^{\neq}/R)$ 3-7

c) $E_e^* = RT + \Delta E^{\neq} = RT + \Delta H^{\neq} - p\Delta V^{\neq}$

where $k_{soln.}$ is a rate constant, $\overline{k}$ the Boltzmann constant (1.3804×10^{-16}

erg/$^\circ$K/molecule), $\overline{h}$ the Planck's constant (6.625×10^{-27} erg. sec/molecule),

T the temperature in $^\circ$K, $\Delta H^{\neq}$ the heat of activation in cal/mole, R the gas

constant (1.9872 cal/$^\circ$K/mole), and $\Delta S^{\neq}$ the entropy of activation in cal/$^\circ$K/mole),

E_e^* the experimental activation energy in cal/mole, $\Delta E^{\neq}$ is the internal

energy of activation in cal/mole, p is the pressure in atmosphere and

$\Delta V^{\neq}$ the volume of activation.

It was assumed that in all the solvents used in this experiment

$\Delta V^{\neq} = 0$. It is obvious that substitution of Equation 3-7b into 3-7a leads

to the Arrhenius equation:

$k_{soln.} = A \exp(-E_e^*/RT)$ 3-8

where A may be explicitly written as:

$A = 2.7182 \, \overline{k}T/\overline{h} \, \exp(\Delta S^{\neq}/R)$.   3-9

Provided $\Delta S^{\neq}$ is to be constant within a finite range of temperature

T_1 to T_2, Equations 3-7 and 3-8 imply that a plot of $\ln k_{soln.}$ versus T^{-1} in

the interval (T_1, T_2) (Arrhenius Plot) should be linear.

Arrhenius plots for the reactions of M(II) with the ligand β-PAN

between 11.0 and 40.0°C in the solvent mixtures previously described were

found to be linear. Examples are shown in Figures 3-12 to 3-15.

Linear least square curve fitting was applied for the estimation

of the slope and the intersect of such plots, direct application of the

Equations 3-7, 3-8, and 3-9 yielded the activation parameters E_e^*, $\Delta E^{\neq}$, $\Delta H^{\neq}$, $\Delta S^{\neq}$, and $\Delta G^{\neq}$. Results are summarized in Tables 3-47 to 3-54.

TABLES OF RESULTS

TABLE 3-1

Rate Constants for the Reactions of M(II) With the Ligand 1-(2-pyridylazo)-2-naphthol in Water [a, b, c].

Metal ion	Concentration of the metal ion (M)	k_{obs} [d] (sec^{-1})	k_{12} (sec^{-1} M^{-1})	# Runs
Zn^{+2}	8.46×10^{-5}	4.50 ± 0.21	$5.32 \pm 0.24 \times 10^{+4}$	4
Zn^{+2}	1.693×10^{-4}	9.10 ± 0.11	$5.37 \pm 0.12 \times 10^{+4}$	5
Zn^{+2}	2.54×10^{-4}	13.31 ± 0.23	$5.24 \pm 0.25 \times 10^{+4}$	4
Zn^{+2}	1.12×10^{-4}	6.15 ± 0.23	$5.49 \pm 0.23 \times 10^{+4}$	5
Ni^{+2}	1.18×10^{-3}	0.114 ± 0.012	97.3 ± 3.1	4
Ni^{+2}	2.38×10^{-3}	0.227 ± 0.010	96.3 ± 2.1	5
Ni^{+2}	3.54×10^{-3}	0.323 ± 0.008	91.3 ± 1.3	5
Cu^{+2}	3.82×10^{-5}	50.75 ± 0.81	$1.32 \pm 0.04 \times 10^{6}$	4
Cu^{+2}	7.64×10^{-5}	100.48 ± 1.0	$1.31 \pm 0.08 \times 10^{6}$	5
Cu^{+2}	1.146×10^{-4}	152.4 ± 4.5	$1.33 \pm 0.12 \times 10^{6}$	4
Cu^{+2}	2.164×10^{-6}	3.02 ± 0.03	$1.39 \pm 0.04 \times 10^{6}$	4

a) The concentration of β-PAN was 1.20×10^{-7} M for all experiments.

b) T = 25.0°C, pH = 5.8, μ = 0.12 M, and λ = 4600 Å.

c) Buffer 2,6 lutidine nitrate - 2,6 lutidine.

d) Errors are standard deviations.

TABLE 3-2

Rate Constants for the Reactions of Zn(II) With the Ligand 1-(2-pyridylazo)-
2-naphthol in Dioxane-Water Mixtures [a, b, c].

% Dioxane b/w	k_{obs} [d] (sec^{-1})	k_{12} x 10^{-3} (sec^{-1} M^{-1})	# Runs
5.52	120.9 [e]	48.7 ± 2.1	4
10.5	97.5 ± 5.1	46.8 ± 3.2	6
21.0	51.7 ± 3.8	24.8 ± 2.1	6
31.4	29.9 ± 2.1	14.3 ± 1.1	6
41.5	20.8 ± 0.9	10.0 ± 0.4	5
51.5	15.0 ± 0.3	7.4 ± 0.2	5
61.3	11.2 ± 0.2	5.4 ± 0.2	5
71.0	10.6 ± 0.1	5.1 ± 0.1	4
80.5	11.4 ± 0.6	5.4 ± 0.3	5
92.0	18.7 ± 0.2	8.9 ± 0.1	4

a) Concentration of β-PAN = 8.5 x 10^{-6} M.

b) Concentration of Zn(II) = 2.08 x 10^{-3} M.

c) T = 25.0°C, pH 5.8, μ = 0.12 M, λ = 4600 Å.

d) Errors are standard deviation.

e) Concentration of Zn(II) = 2.48 x 10^{-3} M.

TABLE 3-3

Rate Constants for the Reactions of Cu(II) With the Ligand 1-(2-pyridylazo)-
2-naphthol in Dioxane-Water Mixtures [a, b, c].

% Dioxane (b/w)	k_{obs} [d] (sec^{-1})	$k_{12} \times 10^{-5}$ (sec^{-1} M^{-1})	# Runs
10.5	15.87 ± 0.1	9.50 ± 0.1	4
21.0	6.87 ± 0.1	4.11 ± 0.1	4
31.8	3.01 ± 0.1	1.80 ± 0.08	5
41.5	1.78 ± 0.1	1.06 ± 0.07	4
51.5	1.39 ± 0.07	0.84 ± 0.06	5
61.7	1.21 ± 0.05	0.72 ± 0.04	4
71.0	1.68 ± 0.08	1.01 ± 0.07	5
80.5	2.20 ± 0.07	1.32 ± 0.06	4
92.0	3.86 ± 0.1	2.31 ± 0.09	5

a) Concentration of β-PAN = 7.58 x 10^{-7} M.

b) Concentration of Cu(II) = 1.67 x 10^{-5} M.

c) T = 25.0°C, pH=5.8, μ = 0.12 M, λ = 4600 Å.

d) Errors are standard deviations.

TABLE 3-4

Rate Constants for the Reactions of Ni(II) With the Ligand 1-(2-pyridylazo)-2-naphthol in Dioxane-Water Mixtures [a, b, c].

% Dioxane	k_{obs} [d] (sec^{-1})	k_{12} $(sec^{-1} M^{-1})$	# Runs
10.5	0.47 ± 0.01	$67.4 \pm 1.$	4
31.4	0.23 ± 0.01	$32.0 \pm 1.$	3
51.5	0.12 ± 0.01	17.9 ± 0.8	3
71.0	0.14 ± 0.01	20.8 ± 0.8	3
92.0	0.22 ± 0.01	$31.6 \pm 1.$	3

a) Concentration of β-PAN = 7.36×10^{-5} M.

b) Concentration of Ni(II) = 7.08×10^{-3} M.

c) T = 25.0°C, pH=5.8, μ = 0.12 M, λ = 4600 $\overset{o}{A}$.

d) Errors are standard deviations.

TABLE 3-5

Rate Constants for the Reactions of Zn(II) With the Ligand 1-(2-pyridylazo)-2-naphthol in Dioxane-Water Mixtures [a].

% Dioxane b/w	$[\beta\text{-PAN}] \times 10^{+6}\ M^{-1}$	$[Zn] \times 10^{3}\ M^{-1}$	$\lambda \times A^{-1}$	$k_{obs} \times sec$ [b]	$k_{12} \times 10^{-3}\ sec\ M$	# Runs
21.0	8.52	0.693	4600	17.27 ± 0.04	24.23 ± 0.03	3
41.5	8.52	0.693	4600	6.91 ± 0.06	9.98 ± 0.07	4
50.5	4.35	0.569	4600	4.54 ± 0.16	8.01 ± 0.10	4
50.5	8.69	1.138	4600	9.40 ± 0.08	8.26 ± 0.07	4
50.5	13.03	1.138	4600	8.74 ± 0.12	7.68 ± 0.12	4
50.5	26.06	1.706	4600	13.54 ± 0.08	7.93 ± 0.04	4
50.5	26.06	1.706	5300	13.39 ± 0.04	7.85 ± 0.03	4
50.5	26.07	2.276	5400	17.61 ± 0.02	7.73 ± 0.02	3
71.5	17.38	2.276	4600	7.58 ± 0.2	3.33 ± 0.12	4
71.5	17.38	2.276	5450	6.87 ± 0.13	3.01 ± 0.10	4
61.3	8.52	0.693	4600	3.73 ± 0.02	5.38 ± 0.02	3
80.5	8.52	0.693	4600	3.78 ± 0.08	5.46 ± 0.05	4

a) $T = 25.0^{\circ}C$, pH=5.8 and $\mu = 0.12$ M.

b) Errors are standard deviations.

TABLE 3-6

Rate Constants for the Reactions of Cu(II) With the Ligand 1-(2-pyridylazo)-2-naphthol in Dioxane-Water Mixtures [a].

% Dioxane b/w	$[\beta\text{-PAN}] \times 10^{+7}$ (M)	$[Cu(II)] \times 10^{+5}$ (M)	k_{obs} [b] (sec^{-1})	$k_{12} \times 10^{-5}$ $(sec^{-1} M^{-1})$	# Runs
10.5	7.58	3.34	31.5 ± 0.2	9.43 ± 0.1	4
10.5	7.58	5.02	47.8 ± 0.3	9.52 ± 0.2	4
31.8	7.58	3.34	6.03 ± 0.3	1.81 ± 0.2	3
31.8	7.58	5.02	9.15 ± 0.3	1.82 ± 0.2	4
31.8	11.37	3.34	6.10 ± 0.3	1.82 ± 0.21	4
51.5	7.58	5.02	4.23 ± 0.1	0.84 ± 0.1	3
51.5	7.58	3.34	2.70 ± 0.1	0.80 ± 0.1	3
80.5	7.58	3.34	4.48 ± 0.2	1.34 ± 0.1	4
80.5	11.37	3.34	4.37 ± 0.2	1.30 ± 0.1	3

a) T = 25.0°C, pH = 5.8, and μ = 0.12 M.

b) Errors are standard deviations.

TABLE 3-7

Rate Constants for the Reactions of Ni(II) With the Ligand 1-(2-pyridylazo)-2-naphthol in Dioxane-Water Mixtures [a].

% Dioxane b/w	$[\beta\text{-PAN}] \times 10^5$ (M)	$[Ni(II)] \times 10^2$ (M)	k_{obs} [b] (sec^{-1})	k_{12} $(sec^{-1} M^{-1})$	# Runs
10.5	7.36	1.02	0.65 ± 0.01	63.4 ± 1.	3
31.4	7.36	1.02	0.33 ± 0.01	32.2 ± 1.	3
51.5	10.84	1.02	0.18 ± 0.01	17.5 ± 1.	3
71.0	10.84	1.02	0.19 ± 0.01	18.5 ± 1.	2
92.0	10.84	1.02	0.32 ± 0.01	31.2 ± 1.	4

a) $T = 25.0°C$, pH = 5.8, and $\mu = 0.12$ M.

b) Errors are standard deviations.

TABLE 3-8

Rate Constants for the Reactions of Zn(II) With the Ligand 1-(2-pyridylazo)-2-naphthol in Dioxane-Water Mixtures (Preliminary Analysis) [a, b, c].

% Dioxane (b/w)	$k_2 \times 10^{-3}$ [d] $(\text{sec}^{-1} \text{ M}^{-1})$	$k_{13} \times 10^{-3}$ [e] $(\text{sec}^{-1} \text{ M}^{-1})$	# Runs
51.5 [f]	1.31 ± 0.04	-	3
61.5	1.21 ± 0.03	0.51 ± 0.1	4
71.0	1.4 ± 0.07	0.62 ± 0.08	5
80.5	8.3 ± 0.1	3.2 ± 0.5	4
92.0	16.3 ± 0.1	8.2 ± 1.	4

a) Concentration of β-PAN = 8.53 x 10^{-5} M.

b) Concentration of Zn(II) = 4.25 x 10^{-5} M.

c) T = 25.0°C, pH = 5.8, μ = 0.12 M, and λ = 4600 Å.

d) Errors are standard deviations.

e) Estimated values of k_{13}. This is based upon a model in which the mathematical formalism requires further refinement (see Appendix D).

f) No assignment was done to k_{13} (see Appendix B).

TABLE 3-9

Rate Constants for the Reactions of Ni(II) With the Ligand 1-(2-pyridylazo)-
2-naphthol in Dioxane-Water Mixtures (Preliminary Analysis) [a, b, c].

% Dioxane (b/w)	k_{obs}[d] ($sec^{-1} M^{-1}$)	k_{13}[e] ($sec^{-1} M^{-1}$)	# Runs
51.5	19.3 ± 0.4	7.0 ± 1.	5
71.0	24.3 ± 0.4	8.5 ± 1.	5
92.5	27.0 ± 0.5	30.2 ± 3.	5

a) Concentration of β-PAN = 4.26 x 10^{-4} M.

b) Concentration of Ni(II) = 2.14 x 10^{-4} M.

c) T = 25.0°C, pH = 5.8, μ = 0.12 M, λ = 4600 Å.

d) Errors are standard deviations.

e) Estimated values of k_{13}. This is based upon a model in which
the mathematical formalism requires further refinement (see
Appendix D).

TABLE 3-10

Rate Constants for the Reactions of Zn(II) With the Ligand 1-(2-pyridylazo)-
2-naphthol in Dioxane-Water Mixtures (Preliminary Analysis) [a, b, c].

% Dioxane (b/w)	k_2 [d] (sec^{-1})	$k_{13} \times 10^{-3}$ [e] $(sec^{-1} M^{-1})$	# Runs
10.5 [f]	-	-	3
21.0	23.6 ± 0.6	20.2 ± 0.3	3
31.8	7.62 ± 0.1	6.50 ± 0.1	4
41.5	2.05 ± 0.1	1.75 ± 0.06	3
51.5	0.67 ± 0.03	0.57 ± 0.06	4
61.7	0.64 ± 0.04	0.55 ± 0.06	3
71.0	0.72 ± 0.03	0.62 ± 0.06	3
80.5 [f]	-	-	4
92.5 [f]	-	-	3

a) Concentration of β-PAN = 8.53 x 10^{-4} M.

b) Concentration of Zn(II) = 2.54 x 10^{-5} M.

c) T = 25.0°C, pH = 5.8, and μ = 0.12 M.

d) Errors are standard deviations.

e) Estimated values of k_{13}. This is based upon a model in which
the mathematical formalism requires further refinement (see
Appendix D).

f) No assignment was done to k_2 or k_1 (see Appendix B).

TABLE 3-11

Rate Constants for the Reactions of M(II) With the Ligand 1-(2-pyridylazo)-2-naphthol in Solvent Mixtures

(Preliminary Analysis) [a].

Solvent	% non-aqueous (b/w)	Metal ion	[M(II)] (M)	[β-PAN] (M)	k_{13} [b] (sec^{-1} M^{-1})	# Runs
Dioxane/Water	10.5	Ni(II)	7.54×10^{-5}	8.53×10^{-4}	43.1	3
"	31.4	Ni(II)	7.54×10^{-5}	8.53×10^{-4}	13.5	3
"	21.0	Zn(II)	3.08×10^{-5}	8.53×10^{-4}	2.0×10^{4}	4
"	31.8	Zn(II)	3.08×10^{-5}	8.53×10^{-4}	6.4×10^{3}	4
"	41.5	Zn(II)	3.08×10^{-5}	8.53×10^{-4}	1.8×10^{3}	4
Methanol/Water	9.4	Ni(II)	6.25×10^{-5}	7.50×10^{-4}	67.8	3
"	55.4	Ni(II)	6.25×10^{-5}	7.50×10^{-4}	35.6	3
"	36.4	Zn(II)	3.91×10^{-5}	3.78×10^{-4}	5.7×10^{-3}	4
"	45.9	Zn(II)	3.91×10^{-5}	3.78×10^{-4}	4.1×10^{-3}	4
"	55.5	Zn(II)	3.91×10^{-5}	3.78×10^{-4}	5.4×10^{-3}	4

a) $T = 25.0^{\circ}C$, pH = 5.8, $\mu = 0.12$ M, and $\lambda = 5500$ Å.

b) Estimated values of k_{13}. This is based upon a model in which the mathematical formalism requires further refinement (see Appendix D).

TABLE 3-12

Rate Constants for the Reactions of Ni(II) With the Ligand 1-(2-pyridylazo)-2-naphthol in Dioxane-Water Mixtures (Preliminary Analysis) [a, b, c].

% Dioxane (b/w)	k_2 [d] (sec^{-1})	k_{13} [e] (sec^{-1} M^{-1})	# Runs
10.5	0.36 ± 0.03	42.5 ± 0.5	3
31.4	0.11 ± 0.01	13.8 ± 0.2	4
51.5 [f]	-	-	3
71.0 [f]	-	-	5
92.0 [f]	-	-	3

a) Concentration of β-PAN = 8.53 x 10^{-3} M.

b) Concentration of Ni(II) = 3.54 x 10^{-5} M.

c) T = 25.0°C, pH = 5.8, μ = 0.12 M, and λ = 5500 Å.

d) Errors are standard deviations.

e) Estimated values of k_{13}. This is based upon a model in which the mathematical formalism requires further refinement (see Appendix D).

f) No assignment was done to k_2 or k_1 (see Appendix B).

TABLE 3-13

Rate Constants for the Reactions of Zn(II) With the Ligand 1-(2-pyridylazo)-2-naphthol in Methanol-Water Mixtures [a, b, c].

% Methanol (b/w)	k_{obs} [d] (sec^{-1})	k_{12} x 10^{-4} (sec^{-1} M^{-1})	# Runs
9.4	137.8 ± 4.2	4.65 ± 0.22	3
17.7	104.0 ± 3.3	3.51 ± 0.13	5
26.8	52.8 ± 2.3	1.77 ± 0.16	4
36.4	46.6 ± 1.7	1.60 ± 0.08	6
45.9	40.1 ± 1.5	1.35 ± 0.05	6
55.5	41.4 ± 3.1	1.39 ± 0.16	5
65.8	43.3 ± 2.8	1.46 ± 0.14	5
76.5	46.5 ± 1.5	1.57 ± 0.06	5
87.8	45.9 ± 2.3	1.55 ± 0.12	3

a) Concentration of β-PAN = 8.31 x 10^{-5} M.

b) Concentration of Zn(II) = 2.96 x 10^{-3} M.

c) T = 25°C, pH = 5.8, μ = 0.12 M, λ = 4600 Å.

d) Errors are standard deviations.

TABLE 3-14

Rate Constants for the Reactions of Zn(II) With the Ligand 1-(2-pyridylazo)-
2-naphthol in Methanol-Water Mixtures [a, b, c].

% Methanol (b/w)	k_{obs}[d] (sec^{-1})	$k_{12} \times 10^{-4}$ $(sec^{-1} M^{-1})$
9.4	45.7 ± 0.6	4.63 ± 0.05
17.7	34.4 ± 0.3	3.49 ± 0.02
26.8	17.7 ± 0.4	1.79 ± 0.03
36.4	15.6 ± 0.3	1.58 ± 0.03
45.9	13.3 ± 0.1	1.35 ± 0.02
55.5	13.9 ± 0.2	1.41 ± 0.02
65.8	14.6 ± 0.1	1.44 ± 0.02
76.5	15.5 ± 0.1	1.57 ± 0.01
87.8	15.2 ± 0.1	1.54 ± 0.01

a) Concentration of β-PAN = 4.16×10^{-5} M.

b) Concentration of Zn(II) = 9.86×10^{-4} M.

c) T = 25.0°C, pH = 5.8, μ = 0.12 M, λ = 4600 $\overset{o}{A}$

d) Errors are standard deviations.

TABLE 3-15

Rate Constants for the Reactions of Cu(II) With the Ligand 1-(2-Pyridylazo)-
2-naphthol in Methanol-Water Mixtures [a, b, c].

% Methanol (b/w)	k_{obs}[d] (sec^{-1})	k_{12} x 10^{-5} (sec^{-1} M^{-1})	# Runs
9.4	19.49 ± 0.2	11.67 ± 0.1	5
17.7	14.74 ± 0.2	8.83 ± 0.1	4
26.8	10.22 ± 0.1	6.12 ± 0.1	4
36.4	8.21 ± 0.1	4.91 ± 0.1	4
45.9	7.21 ± 0.1	4.32 ± 0.1	4
55.5	7.22 ± 0.1	4.32 ± 0.1	5
65.8	8.36 ± 0.1	5.00 ± 0.1	4
76.5	8.87 ± 0.1	5.31 ± 0.1	4
87.4	8.86 ± 0.2	5.31 ± 0.1	4

a) Concentration of β-PAN = 7.58 x 10^{-7} M.

b) Concentration of Cu(II) = 1.67 x 10^{-5} M.

c) T = 25.0°C, pH = 5.8, μ = 0.12 M, λ = 4600 Å.

d) Errors are standard deviations.

TABLE 3-16

Rate Constants for the Reactions of Cu(II) With the Ligand 1-(2-pyridylazo)-2-naphthol in Methanol-Water Mixtures [a, b, c].

% Methanol b/w	k_{obs} [d] (sec^{-1})	k_{12} x 10^{-5} (sec^{-1} M^{-1})	# Runs
9.4	39.0 ± 0.3	11.7 ± 0.1	3
26.8	20.5 ± 0.2	6.13 ± 0.1	3
45.9	14.3 ± 0.2	4.28 ± 0.1	4
76.5	17.8 ± 0.2	5.32 ± 0.1	3
87.4	17.8 ± 0.2	5.32 ± 0.1	3

a) Concentration of β-PAN = 7.58 x 10^{-7} M.

b) Concentration of Cu(II) = 3.34 x 10^{-5} M.

c) T = 25.0°C, pH = 5.8, μ = 0.12 M.

d) Errors are standard deviations.

TABLE 3-17

Rate Constants for the Reactions of Ni(II) With the Ligand 1-(2-pyridylazo)-2-naphthol in Methanol-Water Mixtures [a, b, c].

% Methanol (b/w)	k_{obs}[d] (sec^{-1})	k_{12} $(sec^{-1} M^{-1})$	# Runs
9.4	0.57 ± 0.01	81.7 ± 1.	4
26.8	0.36 ± 0.01	51.9 ± 1.	3
55.4	0.29 ± 0.01	41.3 ± 1.	3
76.5	0.32 ± 0.01	45.0 ± 1.	4

a) Concentration of β-PAN = 7.36 x 10^{-5} M.

b) Concentration of Ni(II) = 7.08 x 10^{-3} M.

c) T = 25.0°C, pH = 5.8, μ = 0.12 M, λ = 4600 Å.

d) Errors are standard deviations.

TABLE 3-18

Rate Constants for the Reactions of Ni(II) With the Ligand 1-(2-pyridylazo)-2-naphthol in Methanol-Water Mixtures [a, b, c].

% Methanol b/w	k_{obs} [d] (sec^{-1})	k_{12} $(sec^{-1} M^{-1})$	# Runs
9.4	1.15 ± 0.02	81.2 ± 1.	3
26.8	0.75 ± 0.01	53.0 ± 1.0	3
55.4	0.58 ± 0.02	41.0 ± 1.0	3
76.5	0.63 ± 0.02	44.5 ± 1.0	3

a) Concentration of β-PAN = 7.36 x 10^{-4} M.

b) Concentration of Ni(II) = 1.42 x 10^{-2} M.

c) T = 25.0°C, pH = 5.8, and μ = 0.12 M.

d) Errors are standard deviations.

TABLE 3-19

Rate Constants for the Reactions of Zn(II) With the Ligand 1-(2-pyridylazo)-
2-naphthol in Acetone-Water Mixtures [a, b, c].

% Acetone (b/w)	k_{obs}[d] (sec^{-1})	$k_{12} \times 10^{-1}$ $(\text{sec}^{-1} M^{-1})$	# Runs
8.8	5.26 ± 0.07	4.69 ± 0.07	4
17.6	3.86 ± 0.07	3.45 ± 0.07	5
27.5	2.26 ± 0.03	2.02 ± 0.02	4
36.3	1.54 ± 0.04	1.38 ± 0.04	4
44.9	1.43 ± 0.03	1.27 ± 0.03	4
55.5	1.12 ± 0.06	1.00 ± 0.06	4
65.8	1.13 ± 0.04	1.01 ± 0.03	4
76.2	1.19 ± 0.04	1.07 ± 0.04	4
87.7	1.38 ± 0.03	1.23 ± 0.02	4

a) Concentration of β-PAN = 8.5 x 10^{-6} M.

b) Concentration of Zn(II) = 1.12 x 10^{-4} M.

c) T = 25.0°C, pH = 5.2, μ = 0.11 M, λ = 4600 Å.

d) Errors are standard deviations.

TABLE 3-20

Rate Constants for the Reactions of Zn(II) With the Ligand 1-(2-pyridylazo)-2-naphthol in Acetone-Water Mixtures [a, b, c].

% Acetone b/w	k_{obs} [d] (sec^{-1})	k_{12} x 10^{-4} (sec^{-1} M^{-1})	# Runs
8.8	10.66 ± 0.2	4.75 ± 0.1	4
17.6	7.66 ± 0.1	3.41 ± 0.1	3
36.3	3.04 ± 0.1	1.35 ± 0.1	4
36.3[e]	4.58 ± 0.1	1.36 ± 0.1	3
55.5	2.26 ± 0.1	1.08 ± 0.1	4
76.2	2.46 ± 0.1	1.10 ± 0.1	4

a) Concentration of β-PAN = 1.701 x 10^{-5} M.

b) Concentration of Zn(II) = 2.24 x 10^{-4} M unless otherwise stated.

c) T = 25.0°C, pH = 5.2, and μ = 0.12 M.

d) Errors are standard deviations.

e) Concentration of Zn(II) = 3.36 x 10^{-4} M.

TABLE 3-21

Rate Constants for the Reactions of Cu(II) With the Ligand 1-(2-pyridylazo)-2-naphthol in Acetone-Water Mixtures [a, b, c].

% Acetone (b/w)	k_{obs}[d] (sec^{-1})	k_{12} x 10^{-5} (sec^{-1} M^{-1})	# Runs
8.8	19.27 ± 0.3	11.5 ± 0.2	4
17.6	12.20 ± 0.1	7.3 ± 0.1	4
27.5	5 99 ± 0.1	3.6 ± 0.1	5
36.3	4.58 ± 0.2	2.7 ± 0.2	4
44.9	3.56 ± 0.2	2.1 ± 0.2	5
55.5	3.11 ± 0.1	1.8 ± 0.1	5
65.8	4.31 ± 0.1	2.5 ± 0.1	5
76.2	6.10 ± 0.1	3.7 ± 0.1	4
87.7	7.20 ± 0.1	4.3 ± 0.1	4

a) Concentration of β-PAN = 7.58 x 10^{-7} M.

b) Concentration of Cu(II) = 1.67 x 10^{-5} M.

c) T = 25.0°C, pH = 5.8, μ = 0.12 M, λ = 4600 Å.

d) Errors are standard deviations.

TABLE 3-22

Rate Constants for the Reactions of Cu(II) With the Ligand 1-(2-pyridylazo)-2-naphthol in Acetone-Water Mixtures [a].

% Methanol b/w	$[\beta\text{-PAN}] \times 10^7$ (M)	$[Cu(II)] \times 10^{+5}$ (M)	k_{obs} [b] (sec^{-1})	$k_{12} \times 10^{-5}$ $(sec^{-1} M^{-1})$	# Runs
8.8	7.58	5.01	57.54 ± 0.2	11.4 ± 0.1	5
8.8	7.58	3.34	38.40 ± 0.2	11.5 ± 0.1	4
8.8	10.31	1.67	19.32 ± 0.2	11.6 ± 0.1	4
36.3	7.58	5.01	13.60 ± 0.3	2.71 ± 0.1	4
36.3	10.31	5.01	13.32 ± 0.2	2.65 ± 0.1	4
36.3	10.31	1.67	4.63 ± 0.2	2.77 ± 0.1	4
65.8	10.31	1.67	4.36 ± 0.2	2.61 ± 0.1	3
65.8	7.58	5.01	13.10 ± 0.3	2.60 ± 0.1	4
65.8	7.58	3.34	8.63 ± 0.3	2.58 ± 0.1	4

a) $T = 25.0°C$, pH = 5.8, and $\mu = 0.12$ M.

b) Errors are standard deviations.

TABLE 3-23

Rate Constants for the Reactions of Zn(II) With the Ligand 1-(2-pyridylazo)-2-naphthol in Methanol-Water Mixtures (Preliminary Analysis) [a, b, c].

% Methanol (b/w)	k_{obs} x 10^{-3} [d] (sec^{-1} M^{-1})	k_{13} x 10^{-3} [e] (sec^{-1} M^{-1})	# Runs
65.8	17.2 ± 0.3	9.5 ± 1.	4
76.5	21.3 ± 0.2	13.9 ± 2.	3
87.4	23.3 ± 0.5	16.3 ± 2.	4
92.8	24.7 ± 0.6	17.5 ± 3.	4

a) Concentration of β-PAN = 8.17 x 10^{-5} M.

b) Concentration of Zn(II) = 4.08 x 10^{-5} M.

c) T = 25.0°C, pH = 5.8, μ = 0.12 M, and λ = 4600 Å.

d) Errors are standard deviations.

e) Estimated values of k_{13}. This is based upon a model in which the mathematical formalism requires further refinement (see Appendix D).

TABLE 3-24

Rate Constants for the Reactions of Ni(II) With the Ligand 1-(2-pyridylazo)-
2-naphthol in Methanol-Water Mixtures (Preliminary Analysis) [a,b,c].

% Methanol (b/w)	k_2 [d] (sec^{-1})	k_{13} [e] (sec^{-1} M^{-1})	# Runs
55.4	48.2 ± 0.5	37.1 ± 4.	4
76.5	57.3 ± 0.2	40.3 ± 5.	3

a) Concentration of β-PAN = 8.17 x 10^{-5} M.

b) Concentration of Ni(II) = 4.10 x 10^{-5} M.

c) T = 25.0°C, pH = 5.8, μ = 0.12 M, and λ = 4600 Å.

d) Errors are standard deviations.

e) Estimated values of k_{13}. This is based upon a model in which
the mathematical formalism requires further refinement (see
Appendix D).

TABLE 3-25

Rate Constants for the Reactions of Zn(II) With the Ligand 1-(2-pyridylazo)-2-naphthol in Methanol-Water Mixtures (Preliminary Analysis) [a, b, c].

% Methanol (b/w)	k_2 [d] (sec^{-1})	k_{13} x 10^{-3} [e] (sec^{-1} M^{-1})	# Runs
9.4 [f]	-	-	3
17.7	6.31 ± 0.06	16.7 ± 0.2	5
26.8 [f]	-	-	3
36.4	2.19 ± 0.08	5.80 ± 0.3	4
45.9	1.52 ± 0.05	4.03 ± 0.2	3
55.5	2.01 ± 0.03	5.32 ± 0.1	3
65.8	3.59 ± 0.06	9.50 ± 0.2	3

a) Concentration of β-PAN = 3.78 x 10^{-4} M.

b) Concentration of Zn(II) = 7.82 x 10^{-5} M.

c) T = 25.0°C, pH = 5.8, and μ = 0.12 M.

d) Errors are standard deviations.

e) Estimated values of k_{13}. This is based upon a model in which the mathematical formalism requires further refinement (see Appendix D).

f) No assignment was done to k_2 or k_1 (see Appendix B).

TABLE 3-26

Rate Constants for the Reactions of Ni(II) With the Ligand 1-(2-pyridylazo)-
2-naphthol in Methanol-Water Mixtures (Preliminary Analysis) [a, b, c].

% Methanol (b/w)	k_2[d] (sec^{-1})	k_{13}[e] $(sec^{-1} M^{-1})$	# Runs
9.4	0.51 ± 0.02	68.3 ± 0.4	4
26.8	0.33 ± 0.02	44.2 ± 0.4	4
55.4	0.27 ± 0.03	36.8 ± 0.6	4
76.5	30.3 ± 0.04	40.5 ± 0.8	3

a) Concentration of β-PAN = 7.50 x 10^{-4} M.

b) Concentration of Ni(II) = 3.12 x 10^{-5} M.

c) T = 25.0°C, pH = 5.8, μ = 0.12 M, and λ = 5500 Å.

d) Errors are standard deviations.

e) Estimated values of k_{13}. This is based upon a model in which
the mathematical formalism requires further refinement (see
Appendix D).

TABLE 3-27

Rate Constants for the Reactions of M(II) With the Ligand 4-(2-pyridylazo)-resorcinol in Water [a, b, c].

Metal ion	Concentration of the metal ion (M)	k_{obs}^d (sec^{-1})	k_{12} (sec^{-1} M^{-1})	# Runs
Zn^{+2}	6.81 x 10^{-4}	172.0 ± 5.2	2.52 ± 0.08 x 10^5	5
Zn^{+2}	3.41 x 10^{-4}	86.24 ± 0.82	2.52 ± 0.03 x 10^5	5
Zn^{+2}	2.27 x 10^{-4}	56.94 ± 0.03	2.50 ± 0.01 x 10^5	4
Zn^{+2}	4.42 x 10^{-5}	11 34 ± 0.21[e]	2.56 ± 0.06 x 10^5	4
Ni^{+2}	2.36 x 10^{-3}	0.818 ± 0.04	3.46 ± 0.04 x 10^2	3
Ni^{+2}	7.08 x 10^{-3}	2.51 ± 0.04	3.55 ± 0.04 x 10^2	4
Ni^{+2}	3.54 x 10^{-3}	1.23 ± 0.06	3.50 ± 0.05 x 10^2	3

a) Concentration of PAR = 7.75 x 10^{-6} M unless otherwise stated.

b) T = 25.0°C, pH = 5.2, μ = 0.12 M and λ = 3920 Å.

c) Buffer 2, 6 lutidine nitrate - 2, 6 lutidine

d) Errors are standard deviations.

e) Concentration of PAR = 2.13 x 10^{-6} M.

TABLE 3-28

Rate Constants for Reactions of Zn(II) with the Ligand 4-(2-pyridylazo)-
resorcinol in Dioxane-Water Mixtures [a, b, c].

% Dioxane (b/w)	k_{obs}^d (sec^{-1})	k_{12} x 10^{-5} (sec^{-1} M^{-1})	# Runs
10.5	47.53 ± 0.5	2.10 ± 0.03	4
21.0	36.64 ± 0.4	1.61 ± 0 02	5
31.4	29.97 ± 0,3	1.32 ± 0.01	4
41.5	27.25 ± 0.4	1.20 ± 0.02	5
51.5	25.08 ± 0.2	1.10 ± 0.01	5
61.7	24.61 ± 0.2	1.08 ± 0.01	5
71.0	25.22 ± 0.3	1.11 ± 0.02	5
80.5	27.12 ± 0.4	1.19 ± 0.02	5
92.0	28.75 ± 0.4	1.26 ± 0.03	4

a) Concentration of PAR = 7.75 x 10^{-6} M.

b) Concentration of Zn(II) = 2.27 x 10^{-4} M.

c) T = 25.0°C, pH = 5.2, μ = 0.11, λ = 3920 Å.

d) Errors are standard deviations.

TABLE 3-29

Rate Constants for Reaction of Zn(II) With the Ligand 4-(2-pyridylazo)-
resorcinol in Methanol-Water Mixtures [a, b, c].

% Metanol (b/w)	k_{obs}[d] (sec^{-1})	k_{12} x 10^{-5} $(sec^{-1} M^{-1})$	# Runs
9.4	55.49 ± 0.4	2.44 ± 0.02	4
17.7	48.19 ± 0.4	2.12 ± 0.02	4
26.8	45.60 ± 0.5	2.00 ± 0.02	4
36.4	45.60 ± 0.7	1.864 ± 0.03	5
45.9	47.72 ± 0.6	2.10 ± 0.03	5
55.5	48.07 ± 0.3	2.11 ± 0.01	4
65.8	49.56 ± 0.4	2.18 ± 0.02	4
76.5	49.19 ± 0.04	2.16 ± 0.02	5
87.8	49.02 ± 0.03	2.16 ± 0.021	5

a) Concentration of PAR = 7.75 x 10^{-6} M

b) Concentration of Zn(II) = 2.27 x 10^{-4} M.

c) T = 25.0°C, pH = 5.2, μ = 0.11 M, λ = 3920 Å,

d) Errors are standard deviations.

TABLE 3-30

Rate Constants for the Reactions of Ni(II) With the Ligand 4-(2-pyridylazo)-resorcinol in Dioxane-Water Mixtures [a], [b], [c].

% Dioxane (b/w)	k_{obs} [d] (sec^{-1})	k_{12} x 10^{-2} (sec^{-1} M^{-1})	# Runs
10.5	1.86 ± 0.06	3.01 ± 0.04	3
31.5	1.54 ± 0.08	2.50 ± 0.06	3
51.5	0.92 ± 0.04	1.50 ± 0.03	3
71.0	1.01 ± 0.04	1.63 ± 0.03	3
92.0	1.08 ± 0.08	1.75 ± 0.06	3

a) Concentration of PAR = 1.82 x 10^{-5} M.

b) Concentration of Ni(II) = 6.18 x 10^{-3} M.

c) T = 25.0°C, pH = 5.2, μ = 0.12 M, and λ = 3920 Å.

d) Errors are standard deviations.

TABLE 3-31

Rate Constants for the Reactions of Ni(II) With the Ligand 4-(2-pyridylazo)-resorcinol in Methanol-Water Mixtures [a, b, c].

% Methanol (b/w)	k_{obs}[d] (sec^{-1})	k_{12} x 10^{-2} (sec^{-1} M^{-1})	# Runs
9.4	1.65 ± 0.08	3.12 ± 0.1	3
26.8	1.38 ± 0.05	2.60 ± 0.06	3
45.9	0.89 ± 0.05	1.68 ± 0.05	3
65.8	0.96 ± 0.04	1.82 ± 0.06	4
96.1	0.98 ± 0.08	1.85 ± 0.1	3

a) Concentration of PAR = 7.03×10^{-5} M.

b) Concentration of Ni(II) = 5.31×10^{-3} M.

c) T = 25.0°C, pH = 5.2, and μ = 0.12 M.

d) Errors are standard deviations.

TABLE 3-32

Rate Constants for the Reactions of Zn(II) With the Ligand 4-(2-pyridylazo)-resorcinol in Methanol-Water Mixtures [a,b,c].

% Methanol (b/w)	k_{obs}^d (sec^{-1})	$k_{12} \times 10^{-5}$ (sec^{-1} M^{-1})	# Runs
0.0	54.7	2.41 ± 0.1	3
9.4	49.2 ± 0.4	2.17 ± 0.1	4
26.8	38.8 ± 0.2	1.71 ± 0.08	3
36.4	39.2 ± 0.2	1.73 ± 0.07	4
45.9	40.6 ± 0.2	1.79 ± 0.08	4
55.5	41.76 ± 0.4	1.84 ± 0.1	4
65.8	42.9 ± 0.4	1.89 ± 0.1	4
76.5	43.3 ± 0.4	1.91 ± 0.1	4
87.8	43.8 ± 0.5	1.93 ± 0.1	4

a) Concentration of PAR = 7.75 x 10^{-6} M.

b) Concentration of Ni(II) = 2.27 x 10^{-4} M.

c) T = 14.7°C, pH = 5.2, and μ = 0.12 M.

d) Errors are standard deviations.

TABLE 3-33

Rate Constants for the Reactions of Zn(II) With the Ligand 4-(2-pyridylazo)-
resorcinol in Dioxane-Water Mixtures [a, b, c].

% Dioxane (b/w)	k_{obs}[d] (sec^{-1})		$k_{12} \times 10^{-5}$ (sec^{-1} M^{-1})		# Runs
10.5	39.9	0.3	1.75	0.1	3
31.4	21.5	0.2	0.95	0.06	6
41.5	18.6	0.2	0.82	0.06	4
61.7	17.0	0.2	0.75	0.05	4
71.0	18.8	0.3	0.83	0.08	4
80.5	21.1	0.3	0.93	0.1	4
92.0	24.2	0.3	1.07	0.1	4

a) Concentration of PAR = 7.75 x 10^{-6} M.

b) Concentration of Zn(II) = 2.27 x 10^{-4} M.

c) T = 14.7°C, pH = 5.2, and μ = 0.12 M.

d) Errors are standard deviations.

TABLE 3-34

Rate Constants for the Reactions of Zn(II) With the Ligand 4-(2-pyridylazo)-resorcinol in Methanol-Water Mixtures [a, b, c].

% Methanol (b/w)	k_{obs} [d] (sec^{-1})	k_{12} x 10^{-5} (sec^{-1} M^{-1})	# Runs
9.4	75.0 ± 2.	2.39 ± 0.3	6
26.8	62.2 ± 1.	1.98 ± 0.1	3
36.4	59.3 ± 1.	1.89 ± 0.1	4
55.5	67.5 ± 1.	2.15 ± 0.1	3
76.5	69.0 ± 2.	2.20 ± 0.1	3
87.8	68.4 ± 2.	2.18 ± 0.1	4

a) Concentration of Zn(II) = 3.14 x 10^{-4} M.

b) Concentration of PAR = 7.75 x 10^{-6} M.

c) T = 25.0^{o}C, pH = 5.2, μ = 0.12 M, and λ = 3920 $\overset{o}{A}$.

d) Errors are standard deviations.

TABLE 3-35

Rate Constants for the Reactions of Ni(II) With the Ligand 4-(2-pyridylazo)-
resorcinol in Dioxane-Water Mixtures [a, b, c].

% Dioxane (b/w)	k_{obs} [d] (sec^{-1})	$k_{12} \times 10^{-2}$ (sec^{-1} M^{-1})	# Runs
10.5	1.29 ± 0.1	2.98 ± 0.2	3
31.5	1.11 ± 0.1	2.55 ± 0.2	3
51.5	0.64 ± 0.06	1.48 ± 0.1	6
71.0	0.69 ± 0.07	1.60 ± 0.1	4
92.0	0.75 ± 0.08	1.74 ± 0.1	3

a) Concentration of Ni(II) = 4.36 x 10^{-3} M.

b) Concentration of PAR = 7.75 x 10^{-5} M.

c) T = 25.0^{o}C, pH = 5.2, μ = 0.12 M, and λ = 3920 Å.

d) Errors are standard deviations.

TABLE 3-36

Rate Constants for the Reactions of Ni(II) With the Ligand 4-(2-pyridylazo)-
2-naphthol in Methanol Water Mixtures [a, b, c].

% Methanol (b/w)	k_{obs} [d] (sec^{-1})	k_{12} x 10^{-2} (sec^{-1} M^{-1})	# Runs
9.4	2.68 ± 0.1	3.11 ± 0.08	3
26.8	2.27 ± 0.1	2.63 ± 0.08	4
45.9	1.47 ± 0.1	1.71 ± 0.08	3
65.8	1.53 ± 0.08	1.78 ± 0.03	3
96.1	1.57 ± 0.08	1.83 ± 0.03	4

a) Concentration of PAR = 7.03 x 10^{-5} M.

b) Concentration of Ni(II) = 8.63 x 10^{-3} M.

c) T = 25.0°C, pH = 5.2, μ = 0.12 M, and λ = 3910 Å.

d) Errors are standard deviations.

TABLE 3-37

Rate Constants for the Reactions of Zn(II) With the Ligand 2,2'-bipyridine in Water [a, b].

Concentration of Bipy x 10^{+6}	Concentration of Zn^{+2} x 10^{+5}	k_{obs} [c] (sec^{-1})	k_{12} x 10^{-6} (sec^{-1} M^{-1})	# Runs
3.47 M	5.36 M	151.8 ± 3.3	2.83 ± 0.08	4
2.44 M	5.4 M	155.7 ± 6.3	2.88 ± 0.12	5
2.44 M	7.11 M	202.7 ± 4.1	2.85 ± 0.08	5

a) T = 25.0°C, pH = 5.8, μ = 5.7 x 10^{-3}M, and λ = 3080 Å.

b) Buffer 2,6 lutidine nitrate - 2.6 lutidine.

c) Errors are standard deviations.

TABLE 3-38

Rate Constants for the Reactions of Zn(II) With the Ligand 2,2'-bipyridine in Methanol-Water Mixtures [a, b, c].

% Methanol (b/w)	k_{obs} [d] (sec^{-1})	$k_{12} \times 10^{-6}$ (sec^{-1} M^{-1})	# Runs
9.4	147.2 ± 3.	2.71 ± 0.1	4
17.7	128.6 ± 5.	2.36 ± 0.2	4
26.8	119.1 ± 5	2.36 ± 0.2	4
36.4	111.2 ± 3.	2.04 ± 0.08	4
45.9	123.8 ± 2.	2.27 ± 0.05	4
55.5	120.3 ± 2.	2.21 ± 0.08	4
65.8	111.2 ± 3.	2.04 ± 0.1	4
76.5	109.3 ± 4.	2.01 ± 0.1	5
87.8	129.8 ± 3.	2.38 ± 0.1	4

a) Concentration of Bipy = 2.44 x 10^{-6} M.

b) Concentration of Zn(II) = 5.44 x 10^{-5} M.

c) T = 25.0°C, pH = 5.8, μ = 5.7 x 10^{-3} M, λ = 3080 Å.

d) Errors are standard deviations.

TABLE 3-39

Rate Constants for the Reactions of Zn(II) With the Ligand 2,2'-bipyridine in Methanol-Water Mixtures [a, b, c].

% Methanol (b/w)	k_{obs} [d] (sec^{-1})	$k_{12} \times 10^{-6}$ (sec^{-1} M^{-1})	# Runs
9.4	166.4	2.72 ± 0.1	3
17.7	142.5	2.33 ± 0.1	4
26.8	140.1	2.29 ± 0.1	3
36.4	121.7	1.99 ± 0.1	3
45.9	133.2	2.18 ± 0.1	4
55.5	123.0	2.01 ± 0.1	3
65.8	121.1	1.98 ± 0.1	3
76.5	128.5	2.10 ± 0.1	3
87.8	125.5	2.05 ± 0.1	3

a) Concentration of Bipy = 1.86 x 10^{-6} M.

b) Concentration of Zn(II) = 6.12 x 10^{-5} M.

c) T = 25.0°C, pH = 5.8, μ = 5.7 x 10^{-3}M, and λ = 3080 $\overset{o}{A}$.

d) Errors are standard deviations.

TABLE 3-40

Rate Constants for the Reactions of ZnS_6^{+2} With the Ligand 1-(2-pyridylazo)-2-naphthol at Different pH, in 50.5% (b/w) Dioxane in Water [a, b].

[PAN] x 10^5 (M)	[ZnS_6^{+2}] x 10^3 (M)	pH	k_{obs} (sec^{-1})	k_{12} x 10^{-3} (sec^{-1} M^{-1})
1.321	1.138	5.7	7.23	6.50
1.738	2.276	5.4	16.12	7.12
1.738	2.276	5.6	16.74	7.31
1.303	1.706	5.8	13.39	7.92
1.303	1.706	6.0	15.12	8.421

a) T = 25.0°C, μ = 0.12 M, and λ = 4600 Å.

b) Buffer 2,6 lutidine nitrate - 2,6 lutidine.

TABLE 3-41

Rate Constants for the Reactions of Zn(II) With the Ligand 1-(2-pyridylazo)-2-naphthol at Different pH, in 50.5% (b/w) Dioxane in Water [a].

[PAN] x 10^5 (M)	[Zn(II)] x 10^6 (M)	[b] pH	k_{obs} (sec^{-1})	k_{13} x 10^{-3} (sec^{-1} M^{-1})
13.21	1.138	5.2	0.411	3.10
17.38	2.276	5.4	0.619	3.56
17.38	2.276	5.6	0.645	3.71
13.03	1.706	5.8	0.510	3.90
13.03	1.706	6.0	0.557	4.26

a) T = 25.0°C, μ = 0.12 M, λ = 4600 Å.

b) Buffer 2,6 lutidine nitrate - 2,6 lutidine.

TABLE 3-42

Rate Constants for Reactions of Ni(II) With the Ligand 4-(2-pyridylazo)-resorcinol at Different pH
and Ionic Strength in Water.[a]

[PAR] x 10^6 (M)	[Ni(II)] x 10^{+3} (M)	pH	μ (M)	k_{obs} (sec^{-1})	k_{12} x 10^2 (sec^{-1} M^{-1})	# Runs
7.75	2.36	5.5	0.12	0.876	3.71	4
7.75	2.36	5.8	0.12	0.946	4.01	3
7.75	2.36	6.1	0.12	1.03	4.36	4
4.16	1.18	5.9	0.083	0.47	3.99	5
4.16	1.18	6.7	0.083	0.613	5.19	6

a) T = 25.0°C.

TABLE 3-43

Preliminary Rate Constants for the Reactions of M(II) With the Ligands PAR, β-PAN, and Bipy.

Ligand	Metal Ion	[Ligand] (M)	[Metal Ion] (M)	k_{obs} (sec^{-1})	k_{12} (sec^{-1}M^{-1})	Characteristics
PAR	Cu(II)	1.37×10^{-7}	1.95×10^{-6}	$56. \pm 8.$	$(2.8 \pm .5) \times 10^{7}$	a
β-PAN	Co(II)	1.303×10^{-5}	$7. \times 10^{-4}$	-	-	b
β-PAN	Zn(II)	1.303×10^{-5}	1.138×10^{-3}	9.00	7.92×10^{-3}	c
β-PAN	Zn(II)	1.303×10^{-5}	1.138×10^{-3}	9.71	8.53×10^{-3}	d
β-PAN	Zn(II)	1.303×10^{-5}	1.138×10^{-3}	≈ 9	$\approx 8.$	e
Bipy	Cu(II)	1.71×10^{-7}	1.95×10^{-6}	>100	$>6. \times 10^{7}$	f

a) $T = 25.0°C$, $\mu = 0.12$ M, $\lambda = 3920$ Å, pH = 5.2 in water.

b) $T = 25.0°C$, $\mu = 0.12$ M, $\lambda = 4600$ Å, pH = 5.8, the Guggenheim plot were not linear, in 50.5% Dioxane (b/w).

c) $T = 25.0°C$, $\mu = 0.02$ M, $\lambda = 4600$ Å, pH = 5.8 in 50.5% (b/w) of Dioxane.

d) $T = 25.0°C$, uncontrolled pH and μ in 50.5% (b/w) of Dioxane.

e) $T = 25.0°C$, "   " " " " "   " " "

f) $T = 25.0°C$, $\mu = 6.5 \times 10^{-4}$ M, $\lambda = 3080$, pH = 5.7 in water.

TABLE 3-44

Conductivities of $Zn(NO_3)_2$, $Ni(NO_3)_2$, and $Cu(NO_3)_2$ in the Solvent Mixtures Dioxane-Water [a].

% Dioxane (b/w)	$\Lambda(Zn(NO_3)_2)$ [b] $\times 10^4 (\Omega^{-1} M^{-1})$	$\Lambda(Ni(NO_3)_2)$ [c] $\times 10^4 (\Omega^{-1} M^{-1})$	$\Lambda(Cu(NO_3)_2)$ [d] $\times 10^4 (\Omega^{-1} M^{-1})$
0.0	1.12	0.95	1.17
10.5	1.10	0.94	——
21.0	0.89	0.75	0.93
31.4	0.68	0.58	——
41.5	0.62	0.53	0.65
51.5	0.61	0.52	——
61.3	0.67	0.57	0.70
71.0	0.70	0.59	——
80.5	0.81	0.68	0.8
92.0	0.97	0.82	——

a) $T = 25.0^\circ C$.

b) Concentration of $Zn(NO_3)_2 = 5.02 \times 10^{-3}$ M.

c) Concentration of $Ni(NO_3)_2 = 4.32 \times 10^{-3}$ M.

d) Concentration of $Cu(NO_3)_2 = 5.21 \times 10^{-3}$ M.

TABLE 3-45

Conductivities of $Zn(NO_3)_2$, $Ni(NO_3)_2$, and $Cu(NO_3)_2$ in the Solvent Mixtures Methanol-Water [a].

% Methanol (b/w)	$\Lambda(Zn(NO_3)_2)$[b] $\times 10^4 (\Omega^{-1} M^{-1})$	$\Lambda(Ni(NO_3)_2)$[c] $\times 10^4 (\Omega^{-1} M^{-1})$	$\Lambda(Cu(NO_3)_2)$[d] $\times 10^4 (\Omega^{-1} M^{-1})$
9.4	0.92	0.78	0.96
17.7	0.76	0.64	——
26.8	0.67	0.57	0.70
36.4	0.65	0.56	——
45.9	0.68	0.58	0.71
55.4	0.76	0.64	——
65.8	0.89	0.76	0.93
76.5	1.10	0.91	——
87.9	1.28	1.09	1.39

a) $T = 25.0^\circ C$.

b) Concentration of $Zn(NO_3)_2$ = 5.02×10^{-3} M.

c) Concentration of $Ni(NO_3)_2$ = 4.32×10^{-3} M.

d) Concentration of $Cu(NO_3)_2$ = 5.21×10^{-3} M.

TABLE 3-46

Conductivities of $Zn(NO_3)_2$ in the Solvent Mixtures Acetone-Water [a].

% Acetone (b/w)	$\Lambda(Zn(NO_3)_2)$ [b] $\times 10^4 (\Omega^{-1} M^{-1})$
8.8	1.25
17.6	1.10
27.1	0.92
36.3	0.91
44.9	0.94
55.5	1.07
65.8	1.30
76.2	1.81
87.7	——

a) $T = 25.0^{\circ}C$.

b) Concentration of $Zn(NO_3)_2 = 5.02 \times 10^{-3}$ M.

TABLE 3-47

Rate Constants and Activation Parameters of the Reactions of Zn(II) With the Ligand 1-(2-pyridylazo)-2 naphthol in Dioxane-Water Mixtures [a, b, c].

% Dioxane (b/w)	$k_{12} \times 10^{-4}$ (sec^{-1} M^{-1})				E^* kcal/mole	$\Delta H^{\neq}$ kcal/mole	$\Delta S^{\neq}$ cal/°K/mole	$\Delta G^{\neq}$ kcal/mole
	(40.0°C)	(35.0°C)	(30.0°C)	(25.0°C)				
10.5	9.92	7.78	6.06	4.65	9.3	8.7	8.	11.0
21.0	5.59	4.30	3.28	2.48	10.0	9.4	7.	11.3
31.4	3.40	2.57	1.92	1.40	10.7	10.1	5.	11.7
41.5	2.46	1.84	1.35	0.99	11.1	10.5	5.	11.9
51.5	1.87	1.40	1.00	0.74	11.5	10.9	4.	12.1
61.3	1.42	1.03	0.74	0.54	11.8	11.2	3.	12.2
71.0	1.35	0.97	0.71	0.50	11.9	11.3	3.	12.3
80.5	1.41	1.03	0.75	0.53	11.8	11.2	3.	12.4
92.0	2.21	1.64	1.20	0.90	11.2	10.6	4.	11.9

a)   Concentration of β-PAN = 8.5 x 10^{-6} M.

b)   Concentration of Zn(II) = 5.92 x 10^{-3} M.

c)   pH = 5.8, μ = 0.12 M, λ = 5600 Å.

TABLE 3-48

Rate Constants and Activation Parameters of the Reactions of Zn(II) With the Ligand 1-(2 pyridylazo)-2-naphthol in Methanol-Water Mixtures [a, b, c].

% Methanol (b/w)	$k_{12} \times 10^{-4}$ (sec^{-1} M^{-1})				E^* kcal/mole	$\Delta H^{\neq}$ kcal/mole	$\Delta S^{\neq}$ cal/°K/mole	$\Delta G^{\neq}$ kcal/mole
	(40.0°C)	(35.0°C)	(30.0°C)	(25.0°C)				
9.4	9.90	7.74	6.02	4.65	9.3	8.7	8	11.0
17.7	7.69	5.97	4.59	3.50	9.7	9.1	7	11.2
26.8	4.19	3.18	2.38	1.77	10.67	10.0	5	11.5
36.4	3.83	2.89	2.16	1.60	10.8	10.2	5	11.6
45.9	3.30	2.47	1.83	1.36	11.0	10.4	4	11.7
55.5	3.38	2.54	1.89	1.40	11.0	10.8	4	12.0
65.8	3.53	2.66	1.98	1.47	10.9	10.3	5	11.7
76.5	3.77	2.84	2.12	1.55	10.8	10.2	5	11.6
87.8	3.73	2.81	2.09	1.55	10.8	10.2	5	11.6

a) Concentration of β-PAN = 8.52 x 10^{-6} M.

b) Concentration of Zn(II) = 5.98 x 10^{-6} M.

c) pH = 5.8, μ = 0.12, λ = 4600 Å.

TABLE 3-49

Rate Constants and Activation Parameters of the Reactions of Zn(II) With the Ligand 1-(2-pyridylazo)-2-naphthol in Acetone-Water Mixtures [a, b, c]

% Acetone (b/w)	$k_{12} \times 10^{-4}$ $(sec^{-1} M^{-1})$				E^* kcal/mole	$\Delta H^{\neq}$ kcal/mole	$\Delta S^{\neq}$ cal/$^{\circ}$K/mole	$\Delta G^{\neq}$ kcal/mole
	(40.0°C)	(35.0°C)	(30.0°C)	(25.0°C)				
8.8	10.0	7.48	6.10	4.70	9.4	8.8	7	11.0
17.6	7.67	5.62	4.54	3.45	9.8	9.2	7	11.1
27.5	4.78	3.42	2.71	2.02	10.6	10.0	5	11.5
36.3	3.41	3.40	1.88	1.38	11.1	10.5	4	11.7
44.9	3.17	2.22	1.74	1.28	11.3	10.7	4	11.8
55.5	2.56	1.87	1.38	0.99	11.6	11.0	3	11.9
65.8	2.59	1.79	1.39	1.00	11.6	11.0	3	11.9
76.2	2.72	1.89	1.47	1.08	11.5	10.9	3	11.8
87.7	3.08	2.15	1.68	1.22	11.3	10.7	4	11.7

a) Concentration of β-PAN = 8.52 x 10^{-6} M.

b) Concentration of Zn(II) = 5.98 x 10^{-6} M.

c) pH = 5.8, μ = 0.12, λ = 4600 $\overset{o}{A}$.

TABLE 3-50

Rate Constants and Activation Parameters of the Reaction of Cu(II) With the Ligand 1-(2-pyridylazo)-2-naphthol in Acetone-Water Mixtures [a, b, c].

% Acetone (b/w)	$k_{12} \times 10^{-5}$ (sec^{-1} M^{-1})			E^* kcal/mole	$\Delta H^{\neq}$ kcal/mole	$\Delta S^{\neq}$ cal/$^\circ$K/mole	$\Delta G^{\neq}$ kcal/mole
	(30.0°C)	(25.0°C)	(14.6°C)				
8.8	14.5	11.5	6.9	8.3	7.7	5	9.1
27.5	4.7	3.6	1.9	10.0	9.4	1	9.8
36.3	3.6	2.7	1.4	10.4	9.8	0	10.1
44.9	2.8	2.1	1.1	10.7	10.1	3	10.1
55.5	2.4	1.8	0.91	11.0	10.4	0	10.2
65.8	3.3	2.5	1.3	10.5	9.4	0	10.0
87.7	5.6	4.3	2.3	9.7	9.1	1	9.7

a) Concentration of β-PAN = 7.58 x 10^{-7} M.

b) Concentration of Cu(II) = 1.67 x 10^{-5} M.

c) pH = 5.8, μ = 0.12 M, λ = 4600 $\overset{o}{A}$.

TABLE 3-51

Rate Constants and Activation Parameters of the Reaction of Cu(II) With the Ligand 1-(2-pyridylazo)-2-naphthol in Methanol-Water Mixtures [a, b, c].

% Methanol (b/w)	$k_{12} \times 10^{-5}$ (sec^{-1} M^{-1})			E* kcal/mole	$\Delta H^{\neq}$ kcal/mole	$\Delta S^{\neq}$ cal/°K/mole	$\Delta G^{\neq}$ kcal/mole
	(30.0°C)	(25.0°C)	(14.6°C)				
9.4	14.7	11.6	7.0	8.3	7.7	5	9.1
26.8	7.9	6.1	3.5	9.2	8.6	3	9.5
45.9	5.6	4.3	2.4	9.7	9.1	2	9.7
65.8	6.5	5.0	2.8	9.5	8.9	2	9.6
87.8	6.9	5.3	3.0	9.4	8.8	2	9.6

a) Concentration of β-PAN = 7.58 x 10^{-7} M.

b) Concentration of Cu(II) = 1.67 x 10^{-5} M.

c) pH = 5.8, μ = 0.12 M, λ = 4600 Å.

TABLE 3-52

Rate Constants and Activation Parameters of the Reactions of Cu(II) With the Ligand 1-(-2-pyridylazo)-
2-naphthol in Dioxane-Water Mixtures [a, b, c].

% Dioxane (b/w)	$k_{12} \times 10^{-5}$ (sec^{-1} M^{-1})			E* kcal/mole	$\Delta H^{\neq}$ kcal/mole	$\Delta S^{\neq}$ cal/°K/mole	$\Delta G^{\neq}$ kcal/mole
	(30.0°C)	(25.0°C)	(14.6°C)				
10.5	12.0	9.4	5.6	8.5	7.9	4	9.1
21.0	5.3	4.1	2.3	9.4	8.8	3	9.6
31.4	2.4	1.8	0.95	10.3	9.7	1	10.5
41.5	1.4	1.1	0.54	10.9	10.3	0	10.4
51.5	1.1	0.83	0.42	11.1	10.5	0	10.6
61.3	0.98	0.73	0.36	11.3	10.7	0	10.7
71.0	1.3	1.0	0.51	10.9	10.3	1	10.3
80.5	1.7	1.3	0.68	10.6	10.0	1	10.3
92.0	3.0	2.3	1.2	10.0	9.45	2	10.0

a) Concentration of β-PAN = 7.58×10^{-7} M.

b) Concentration of Cu(II) = 1.67×10^{-5} M.

c) pH = 5.8, μ = 0.12 M, λ = 4600 Å.

TABLE 3-53

Rate Constants and Activation Parameters of the Reactions of Ni(II) With the Ligand 1-(2-pyridylazo)-2-naphthol in Methanol-Water Mixtures [a, b, c].

% Methanol (b/w)	$k_{12} \times 10^{-1}$ (sec^{-1} M^{-1})				E* kcal/mole	$\Delta H^{\neq}$ kcal/mole	$\Delta S^{\neq}$ cal/°K/mole	$\Delta G^{\neq}$ kcal/mole
	(43.7°C)	(30.0°C)	(25.0°C)	(20.0°C)				
9.4	32.8	12.0	8.20	5.4	13.9	13.3	5	14.8
26.8	22.2	7.8	5.2	3.4	14.5	13.9	4	15.1
55.4	18.2	6.3	4.1	2.7	14.8	14.2	3	15.2
76.5	19.6	6.8	4.5	2.9	14.7	14.1	3	15.1

a) Concentration of β-PAN = 7.36 x 10^{-5} M.

b) Concentration of Ni(II) = 7.08 x 10^{-3} M.

c) pH = 5.8, μ = 0.12 M, λ = 4600 Å.

TABLE 3-54

Rate Constants and Activation Parameters of the Reactions of Ni(II) With the Ligand 1-(2-pyridylazo)-
2-naphthol in Dioxane Water [a, b, c].

% Dioxane (b/w)	$k_{12} \times 10^{-1}$ (sec^{-1} M^{-1})				E* kcal/mole	$\Delta H^{\neq}$ kcal/mole	$\Delta S^{\neq}$ cal/°K/mole	$\Delta G^{\neq}$ kcal/mole
	(43.7°C)	(30.0°C)	(25.0°C)	(20.0°C)				
10.5	27.5	9.9	6.8	4.5	14.1	13.5	5	14.9
31.4	14.2	4.9	3.2	2.1	15.0	14.3	3	15.4
51.5	8.5	2.8	1.8	1.1	15.6	15.0	2	15.7
71.0	9.7	3.2	2.0	1.3	15.5	14.8	2	15.6
92.0	14.0	4.8	3.1	2.0	15.0	14.4	3	15.4

a) Concentration of β-PAN = 7.36 x 10^{-5} M.

b) Concentration of Ni(II) = 7.08 x 10^{-3} M.

c) pH = 5.8, μ = 0.12 M, λ = 4600 Å.
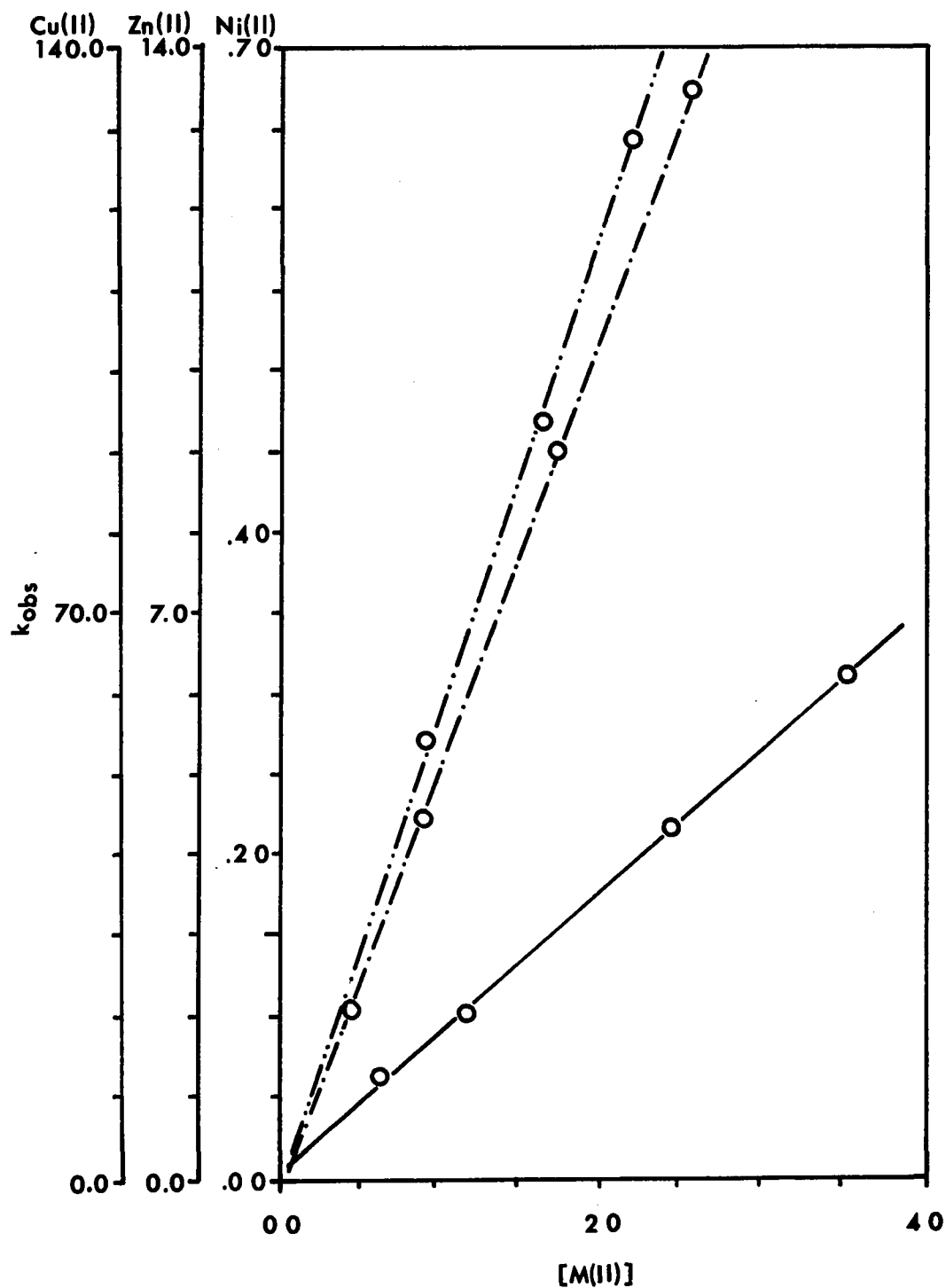
Figure 3-1. Functional Representation of $k_{obs} = k_{obs}([M(II)]_o)$ for the Ligand β-PAN in Water

Ni(II), $[Ni(II)] \times 10^{+3}$

Zn(II), $[Zn(II)] \times 10^{+4}$

Cu(II), $[Cu(II)] \times 10^{+5}$

Figure 3-2. Functional Representation of k_{obs}
$= k_{obs}([M(II)]_o)$ for the Ligand
β-PAN in Mixed Solvents

————————— Cu(II), [Cu(II)] x 10^{+5} in 31.5% b/w Dioxane/Water

—·——·—— · Cu(II), [Cu(II)] x 10^{+5} in 45.9% b/w Methanol/Water

—··——··—·· Zn(II), [Zn(II)] x 10^{+3} in 50.5% b/w Dioxane/Water

$$Zn + \beta\text{-PAN} \longrightarrow Zn(\beta\text{-PAN})_2^{+2}$$
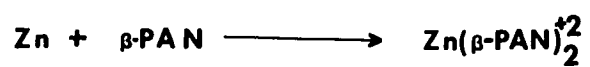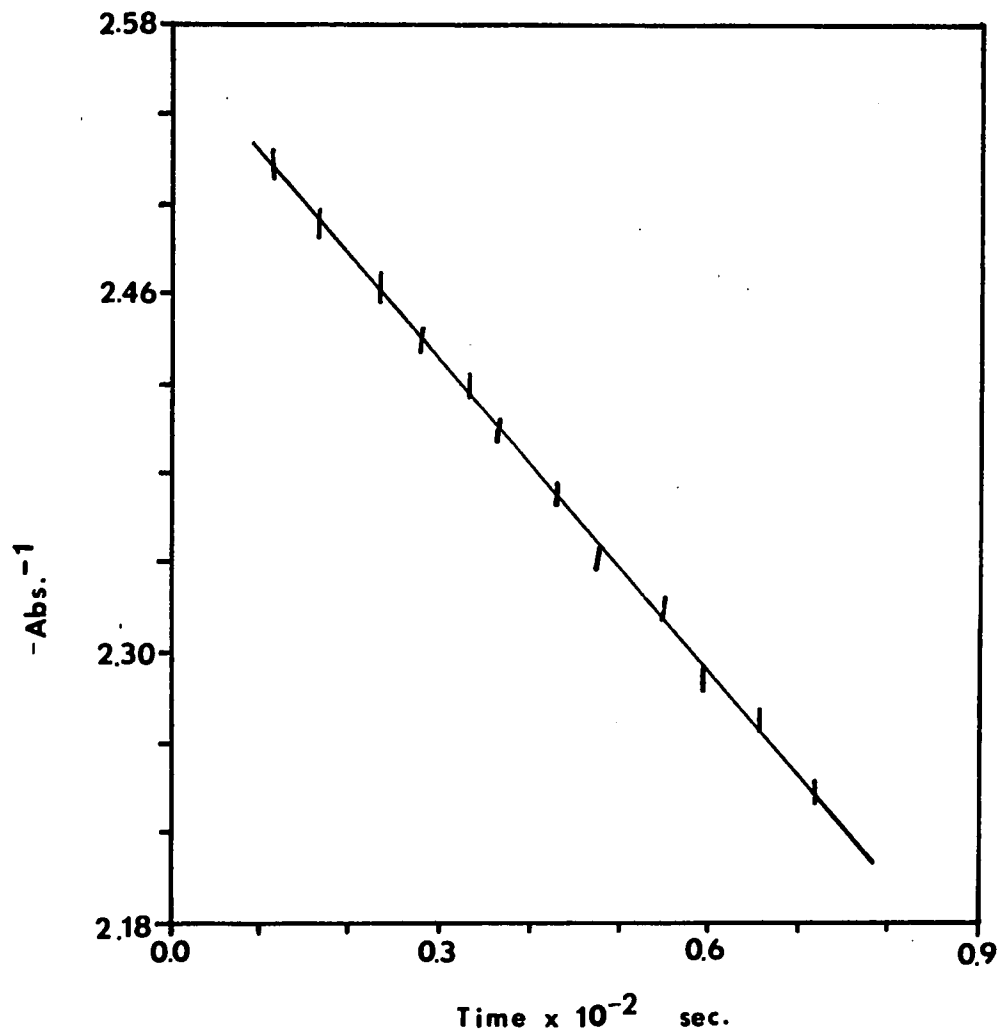
Figure 3-3. Typical Plot of [L] = [L](t)

for Experiment Type II
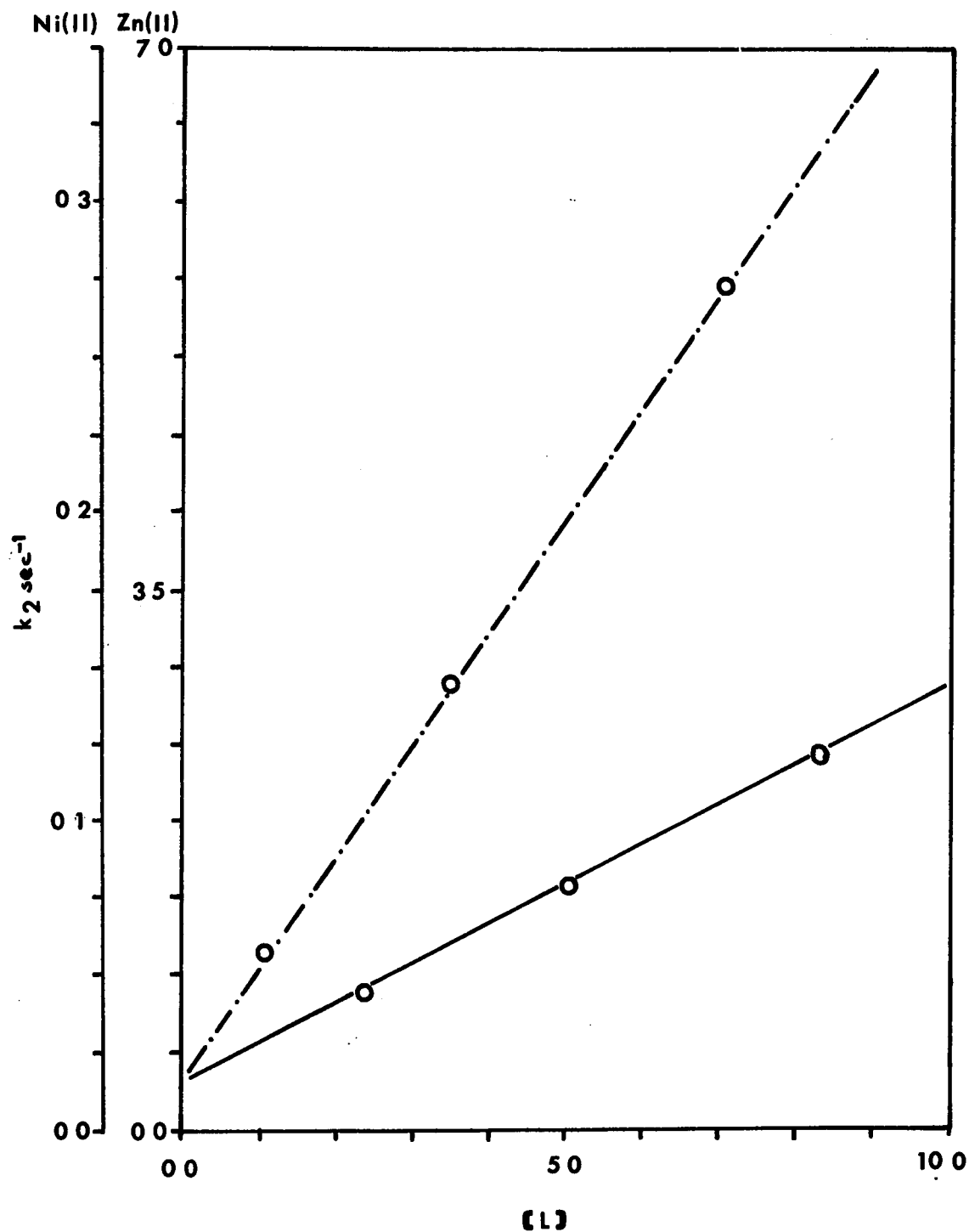
Figure 3-4. Functional Representation of $k_2 = k_2([L]_o)$ for the Ligand β-PAN in Dioxane-Water Mixtures

—————————— Zn(II), $[\beta\text{-PAN}] \times 10^{+5}$ in 31.4% Dioxane in Water

—·——·——··— Ni(II), $[\beta\text{-PAN}] \times 10^{+3}$ in 31.4% Dioxane in Water
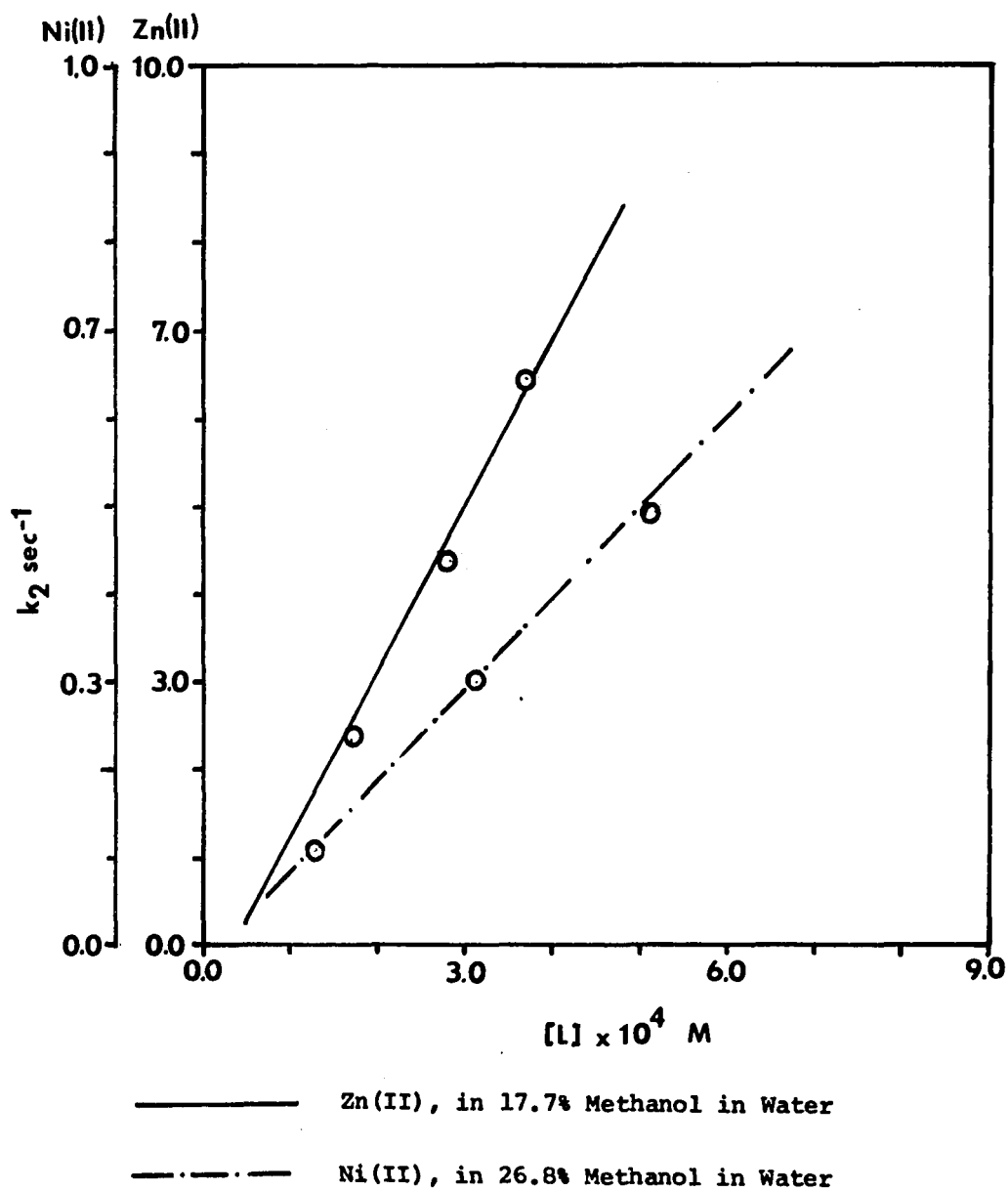
Figure 3-5. Functional Representation of

$$k_2 = k_2 ([L]_o) \text{ for the Ligand}$$

β-PAN in Methanol-Water Mixtures.
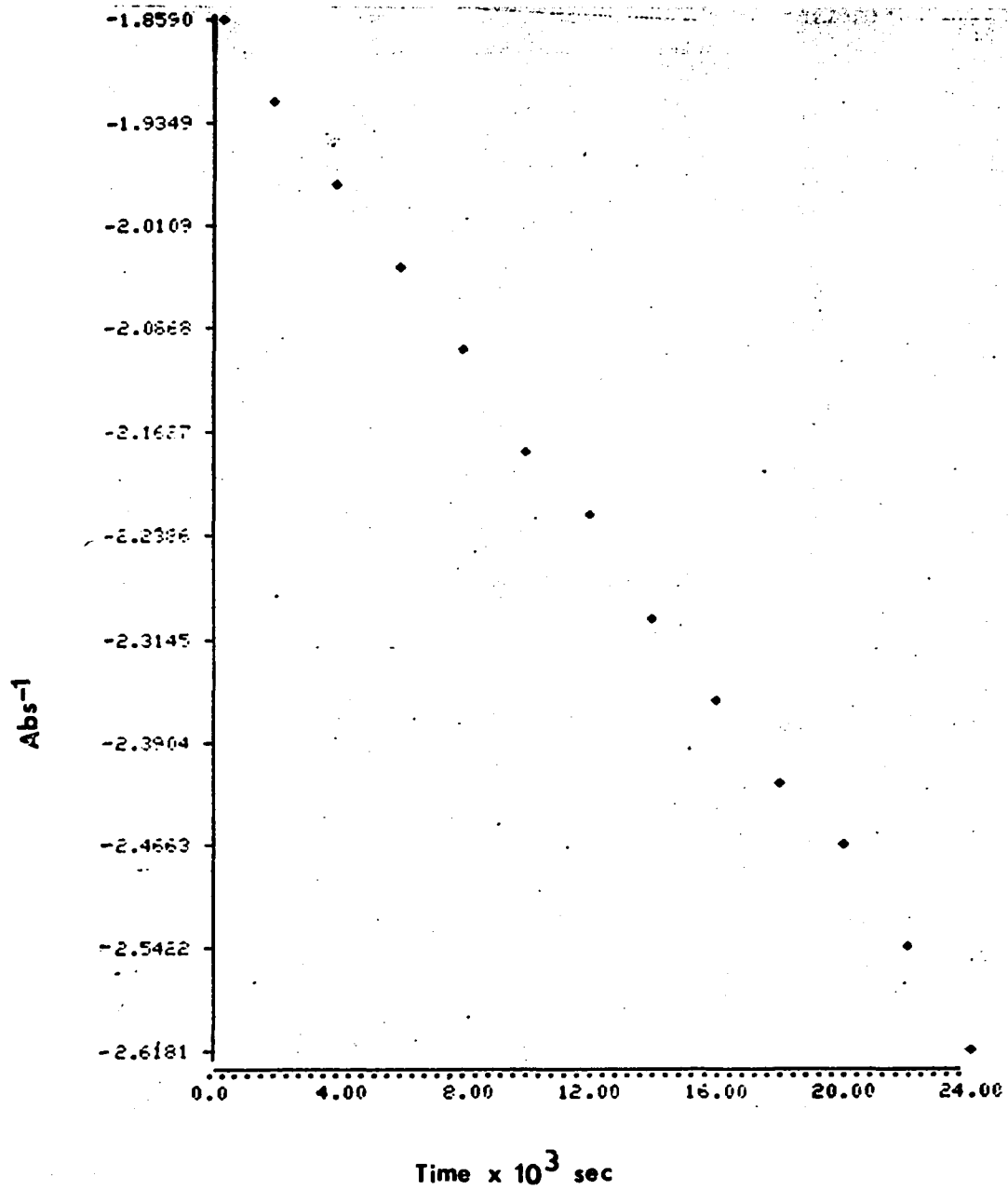
Figure 3-6. Typical Plot of [L] = [L](t)

for Experiment Type II
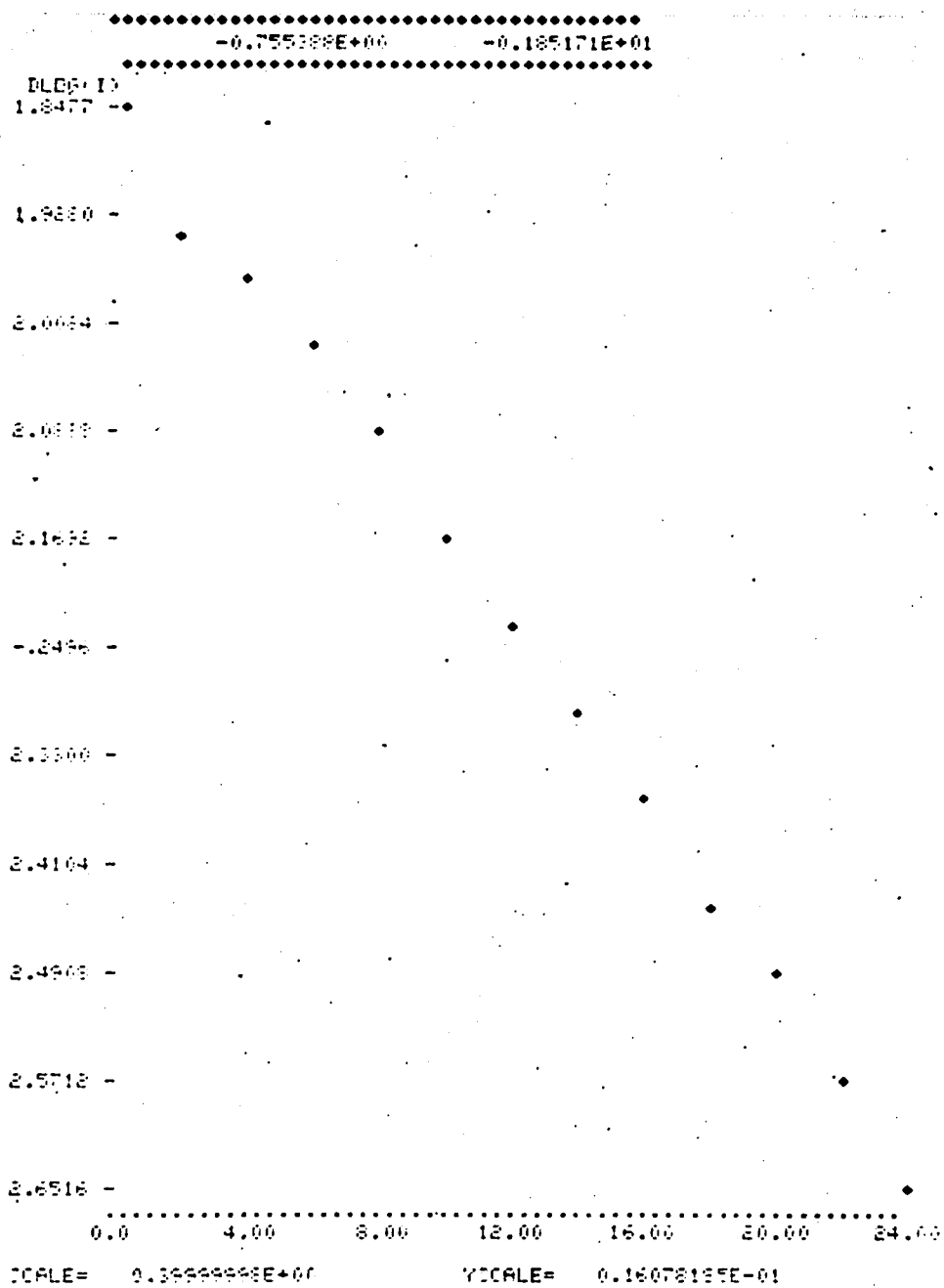
Figure 3-7. Typical Plot of [L] = [L](t)

for Experiment Type III.
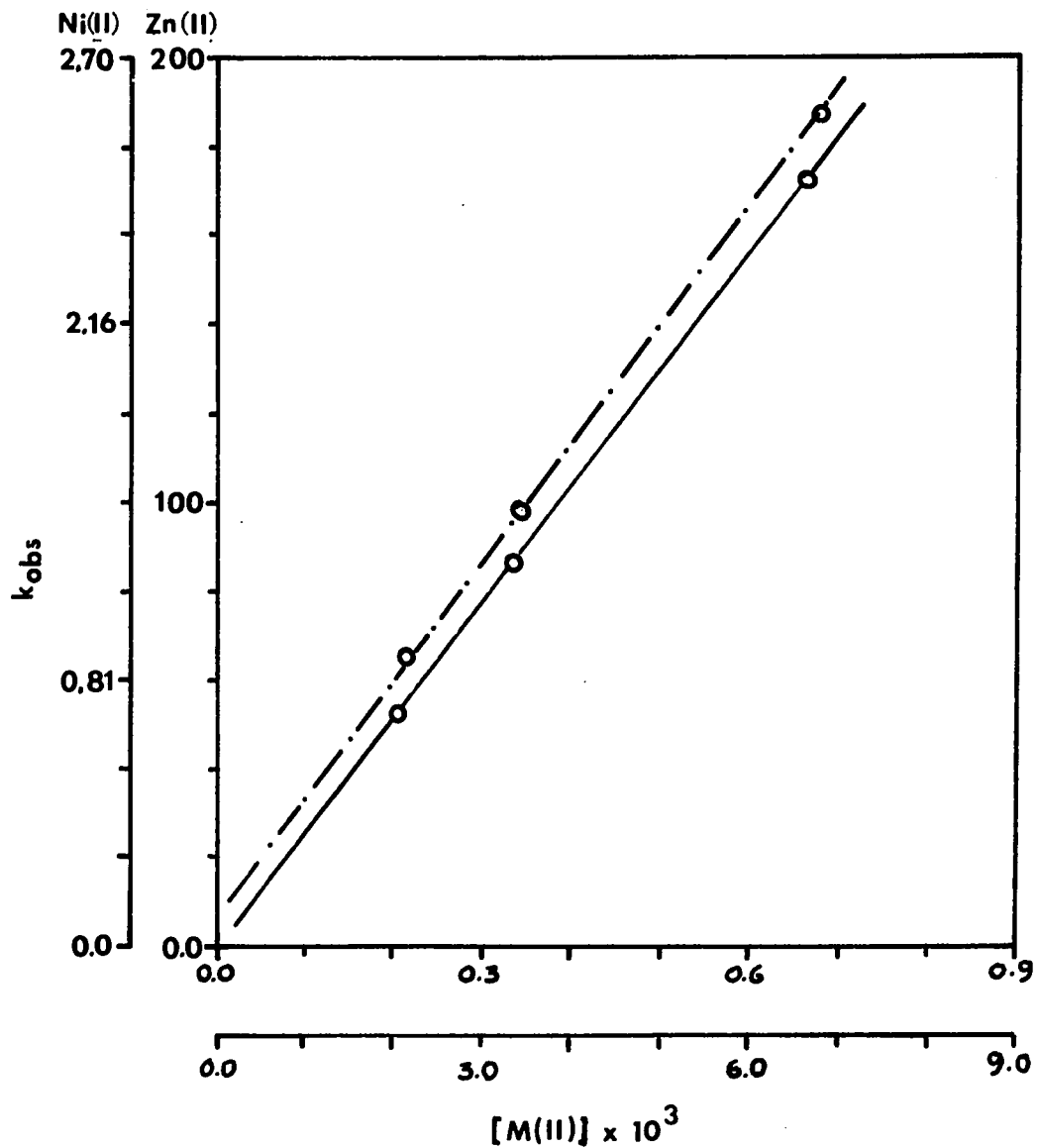
Figure 3-8. Functional Representation of
$k_{obs} = k_{obs}([M(II)]_o)$ for the
Ligand PAR in Water.

———————— For Zn(II)

—·—·—·—·— For Ni(II)
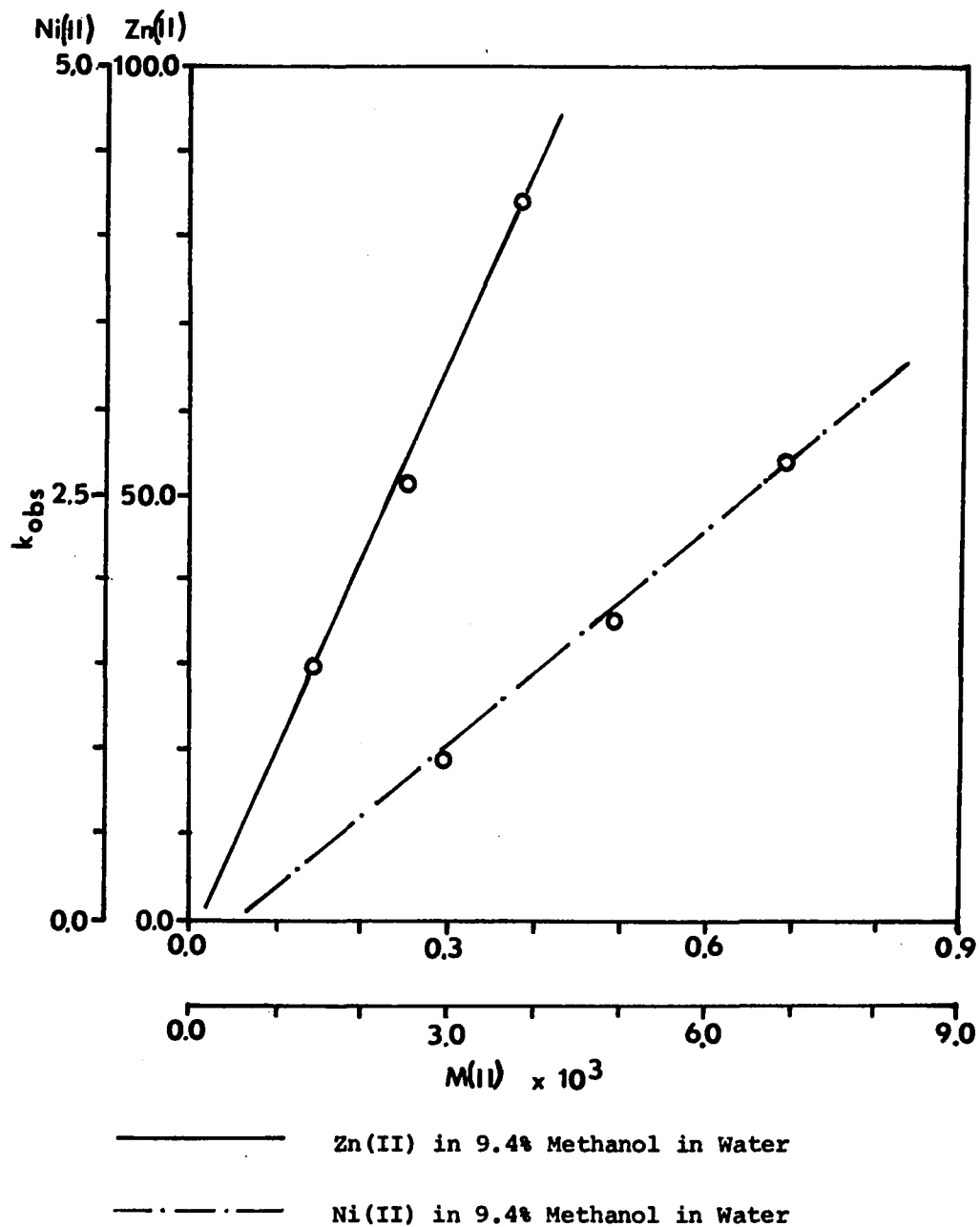
Figure 3-9. Functional Representation of $k_{obs} = k_{obs}([M(II)]_o)$ for the Ligand PAR in Mixed Solvents.
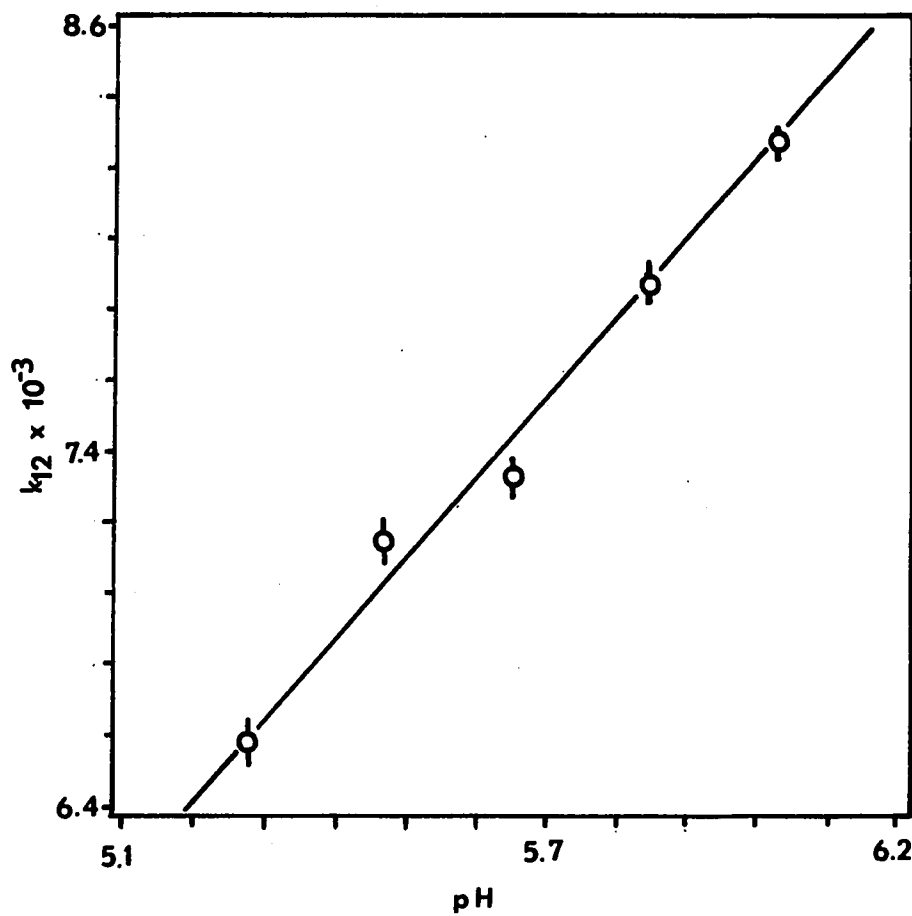
Figure 3-10. Functional Representation of $k_{12} = k_{12}(pH)$
for the Reactions of Zn(II) With β-PAN in
50.5% b/w of Dioxane in Water
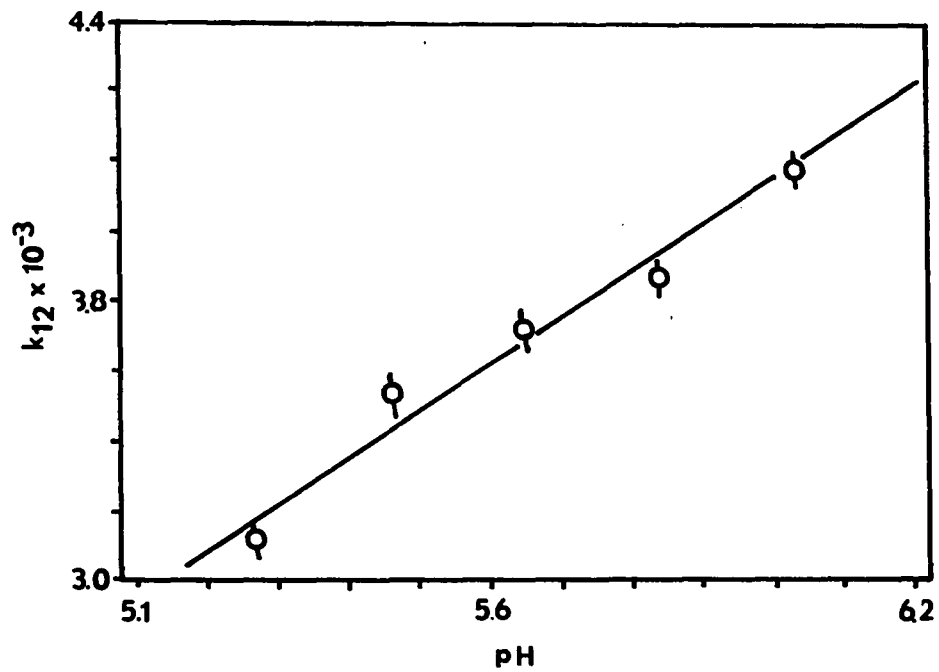
Figure 3-11. Functional Representation of $k_{13} = k_{13}(pH)$
for the Reactions of Zn(II) With β-PAN in
50.5% b/w of Dioxane in Water
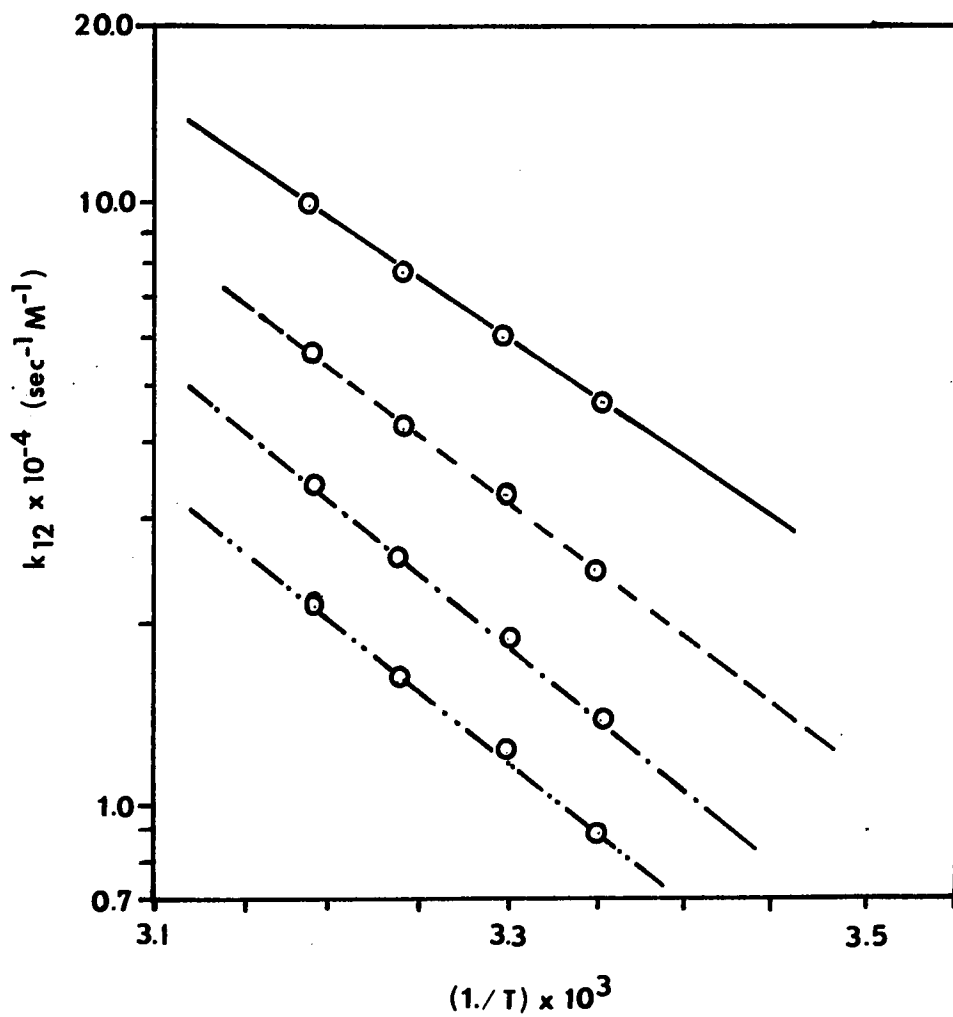
Figure 3-12. Functional Representation of $k_{12} = k_{12}(T)$ for the Reactions
of Zn(II) With the Ligand β-PAN in Dioxane-Water Mixtures

—————————— 10.5% Dioxane in Water

— — — — 21.0% Dioxane in Water

—·——·——·— 31.0% Dioxane in Water

—··——··——·· 92.0% Dioxane in Water
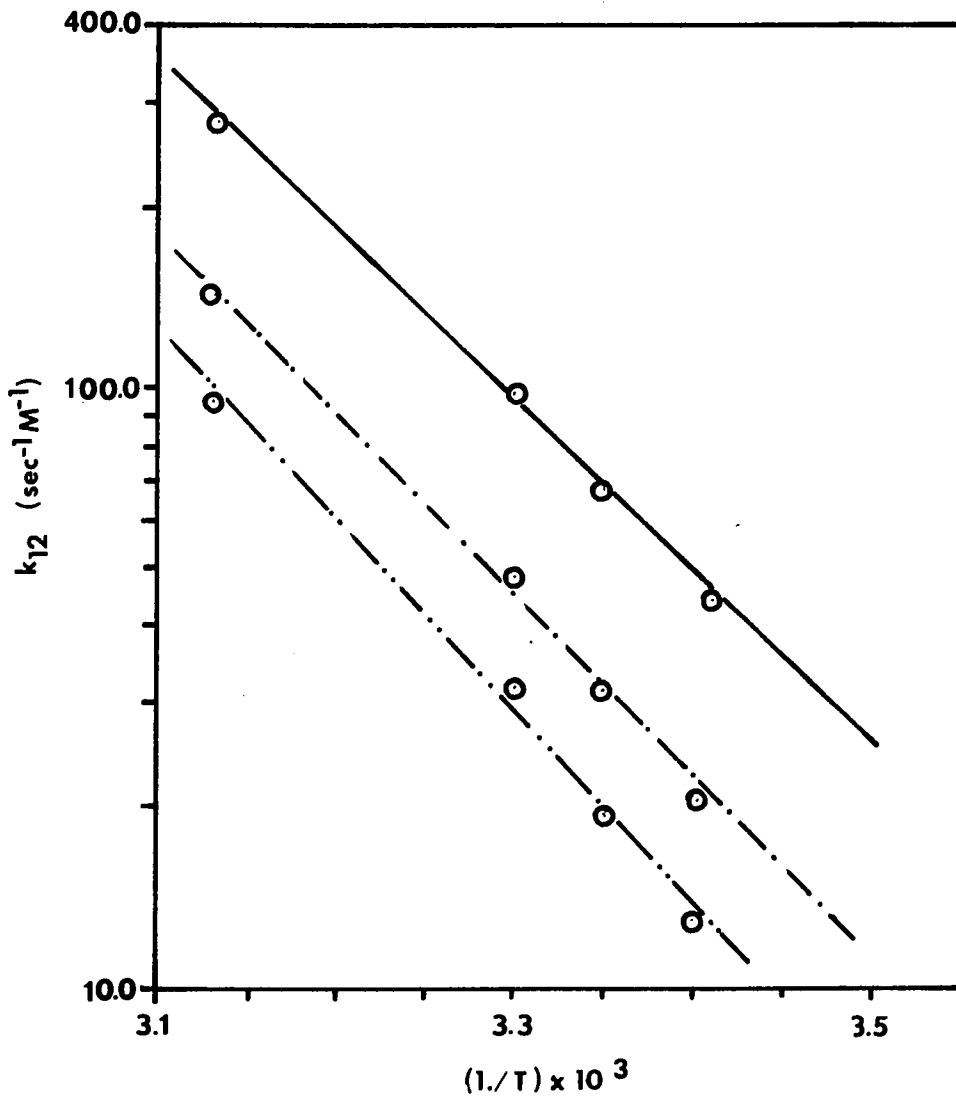
Figure 3-13. Functional Representation of $k_{12} = k_{12}(T)$ for the Reactions of Ni(II) With the Ligand β-PAN in Dioxane-Water Mixtures

———————— 10.5% Dioxane in Water

—·—·—· 31.4% Dioxane in Water

—··—··— 71.0% Dioxane in Water
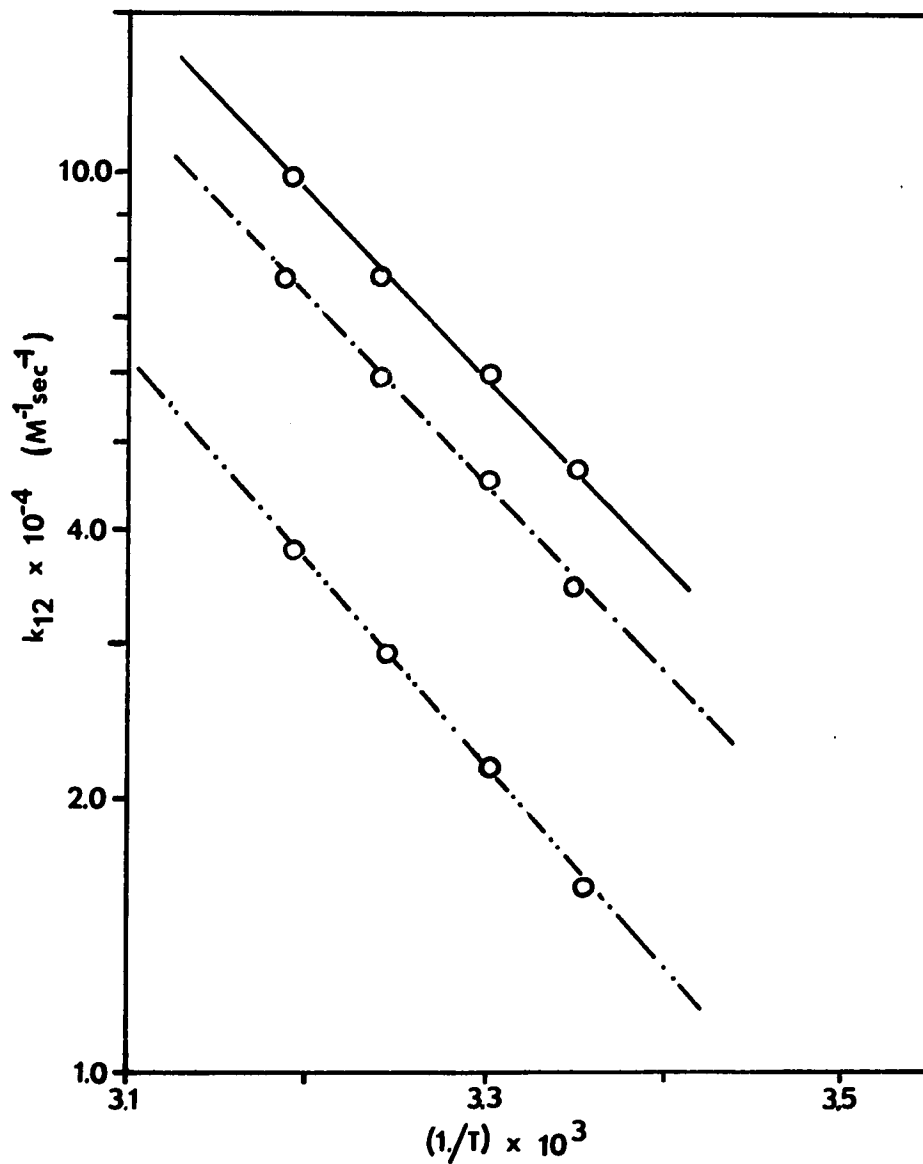
Figure 3-14. Functional Representation of $k_{12} = k_{12}(T)$ for the Reactions of Zn(II) With the Ligand β-PAN in Methanol-Water Mixtures

——————— 9.4% Methanol in Water

—·—·—·· 17.7% Methanol in Water

—··——··—·· 36.4% Methanol in Water
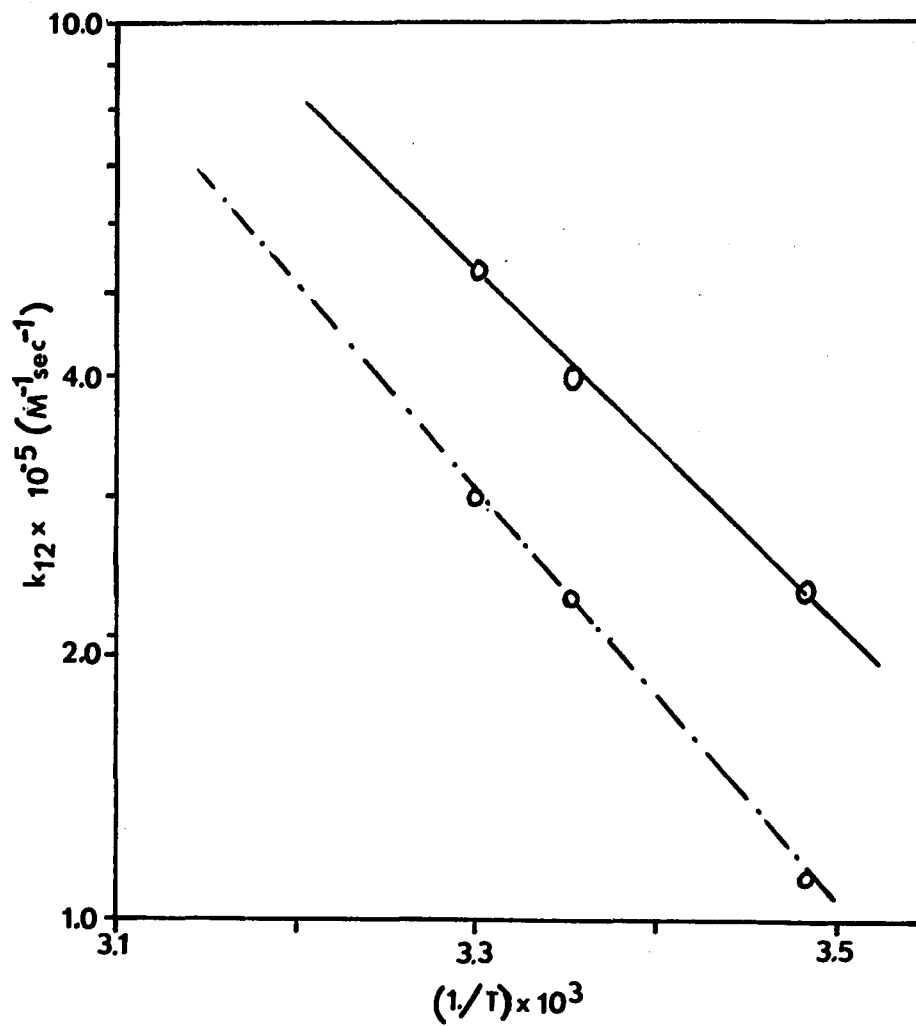
Figure 3-15. Functional Representation of $k_{12} = k_{12}(T)$
for the Reactions of Cu(II) With the
Ligand β-PAN in Dioxane-Water Mixtures

——— 21.0% in Dioxane-Water

—·—·— 92.0% in Dioxane-Water

DISCUSSION

Mechanistic Considerations. The results tabulated in Tables 3-1,

3-27, and 3-37 for the kinetic runs of the metal ions $Zn(aq)^{+2}$, $Ni(aq)^{+2}$,

and $Cu(aq)^{+2}$ with the ligands β-PAN, PAR and Bipy in water, yielding the

1:1 metal ion-ligand complexes, are in agreement with an empirical rate

law of the first order with respect to the concentration of each reactant.

This result implies that whatever mechanism is considered, it should be

possible to reduce the mathematical formulation of the empirical rate law

associated with such a mechanism to a second order empirical rate law.

When this condition is related to the theory considered in the introductory

section which dealt with the mechanism of substitution reactions of one

ligand by another in metal ion complexes, it seems logical to next con-

sider the Id mechanism. Extending Eigen's formulation (21) for the Id

mechanism to bidentate ligands (22), and tridentate ligands, we can write:

1. Id mechanism for bidentate ligands:

a) $M(aq)^{+2} + L-L \rightleftharpoons M(aq)^{+2} \cdot L-L$ k_o, k_{-o} or K_o

b) $M(aq)^{+2} \cdot L-L \rightleftharpoons M(aq)L-L^{+2} + H_2O$ k_2, k_{-2} or K_2 4-1

c) $M(aq)L-L^{+2} \rightleftharpoons M(aq)L_{(2)}^{+2} + H_2O$ k_3, k_{-3} or K_3
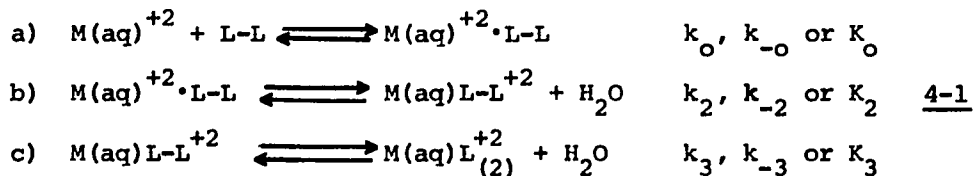
Assuming 4-1a is a very rapidly established equilibrium compared with 4-1b,

and 4-1c, and

$$\frac{d[M(aq)L-L^{+2}]}{dt} = 0 \qquad\qquad 4-2$$

The following equation is obtained:

$$\frac{d[L_{(2)}]}{dt} = \frac{d[M(aq)L_{(2)}^{+2}]}{dt} = \frac{K_o k_2 k_3}{k_{-2}+k_3} [M(aq)^{+2}][L_{(2)}] - \frac{k_{-2}k_{-3}}{k_{-2}+k_3} [ML_{(2)}^{+2}]$$

$$4-3$$

2. Id mechanism for tridentate ligands:

    a) $M(aq)^{+2} + L-L-L \rightleftharpoons M(aq)^{+2} \cdot L-L-L$ k_o, k_{-o} or K_o

    b) $M(aq)^{+2} \cdot L-L-L \rightleftharpoons M(aq)L-L-L^{+2} + H_2O$ k_2, k_{-2} or K_2 4-4

    c) $M(aq)L-L-L^{+2} \rightleftharpoons M(aq)L_{(2)}-L^{+2} + H_2O$ k_3, k_{-3} or K_3

    d) $M(aq)L_{(2)}-L^{+2} \rightleftharpoons M(aq)L_{(3)}^{+2} + H_2O$ k_4, k_{-4} or K_4
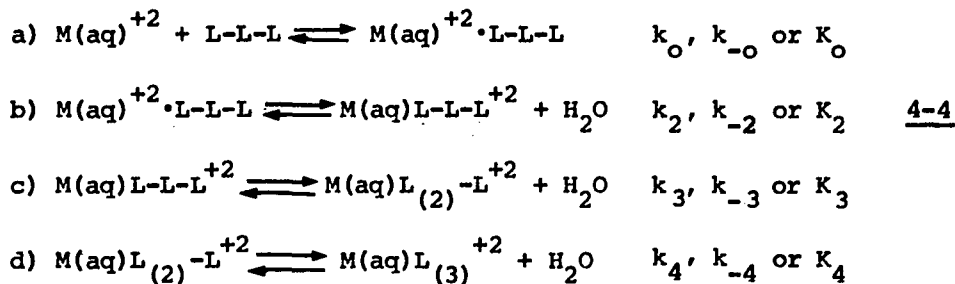
Assuming that 4-4a is a very rapidly established equilibrium compared with 4-4b, 4-4c, and 4-4d; and that:

    a) $\dfrac{d[M(aq)L-L-L^{+2}]}{dt} = 0$

                                                                        4-5

    b) $\dfrac{d[M(aq)L_{(2)}-L^{+2}]}{dt} = 0$

then the following rate equation is obtained:

$$\frac{d[ML_{(3)}^{+2}]}{dt} = \frac{K_o k_2 k_3 k_4 [M(aq)^{+2}][L_{(3)}] - k_{-2} k_{-3} k_{-4} [ML_{(3)}]}{k_2 k_{-3} + k_4 k_{-2} + k_4 k_3} \qquad \text{4-6}$$

From Equations 4-3 and 4-6 the constant of formation becomes:

    a) $k_{12} = \dfrac{K_o k_2 k_3}{k_{-2} + k_3}$

or   4-7

    b) $k_{12} = \dfrac{K_o k_2 k_3 k_4}{k_2 k_{-3} + k_4 k_{-2} + k_4 k_3}$

for bidentate and tridentate ligands respectively.

    Eigen (21) considered that the rate-determining step is the release of the water molecule from the first coordination sphere; therefore, the rate constant of formation becomes:

    $k_{12} = K_o k_2$ 4-8

for either 1 or 2 stoichiometry.

It becomes obvious that the above stoichiometric mechanisms (1 or 2) open the possibilities of different rate-determining steps. However, the reported literature shows the following facts in support of an Id mechanism:

a) For a particular metal ion, the rate constants for the formation of complexes with ligands of the same charge are very similar;

b) The activation parameters (for a particular metal ion) of the reactions that lead to the formation of the metal ion complexes for different ligands are similar;

c) $\Delta S^{\neq}$, which can be considered as a particular example of the activation parameters as described in b), is zero, within the experimental error.

d) Experimentally estimated or calculated K_o led to an estimation of k_2 (Equation 4-8) whose values can be equated with the water exchange rate constant (Table 4-1).

Table 4-1 shows typical examples by several authors of investigations of substitution reactions, where the above facts are specifically shown. In the same table, it is shown that K_o has general values larger than 1.0 M^{-1} for substitution reactions with negatively charged ligands, while for neutral ligands, the values of K_o are smaller than 0.2 M^{-1}. This behavior should be expected since the interactions between charged species are stronger than the interactions between dipolar and charged species.

Extension of the ideas mentioned above to the analysis of the results presented in Tables 3-1, 3-27, and 3-37, and a consideration of the Equation 4-8 concerning k_{12}, show that a rational choice of a value of K_o is 0.12 M^{-1} for the equilibrium between the reactants and the outer sphere complexes $M(aq)^{+2}$ (β-PAN), and using $k_{2(Zn)} = 3 \times 10^7$ sec^{-1}, $k_{2(Cu)} = 6 \times 10^8$ sec^{-1},

TABLE 4-1

Parametric Characterization of Id Mechanism in Metal Ion Substitution Reactions [a, b].

Ligand	Metal Ion	$k_{12} \times 10^{-4}$ $(sec^{-1} M^{-1})$	K_o (M^{-1})	$\Delta H^{\neq}$ (kcal/mole)	$\Delta S^{\neq}$ (e.u.)	Ref.
CH_3COO^{-1}	Ni(II)	10.	3.	—	—	22
$CH_3PO_4^{-2}$	Ni(II)	29.	40.	—	—	22
Bipy	Ni(II)	0.16	0.11	11.0	-3.3	78
Terpy	Ni(II)	0.15	0.11	11.7	-1.6	78
Phen	Ni(II)	0.29	0.15	10.3	-3.8	78
NH_3	Ni(II)	0.23	0.14	12.5	$+1.1^{d}$	58^{c}
Te[e]	Cu(II)	20000.	0.13	5.	0.0^{d}	79
PAD[f]	Zn(II)	400.	0.13	8.	-2.0^{d}	80

a) Solvent = water.

b) T = 25.0°C unless otherwise stated.

c) T = 11°C.

d) Estimated from Arrhenius factor A given.

e) C-Tetramethylethylenediamine.

f) pyridine-2-azodimethylaniline

and $k_{2(Ni)} = 3 \times 10^4 \text{ sec}^{-1}$ (k_2 for Cu(II) and Zn(II) were estimated by means of direct extrapolation of the values given in Tables 4-2 for k_2 at 11.0°C or 20.0°C to k_2 at 25.0°C using Equation 3-8 and assuming a rational value for E_e^* of 6 Kcal) for the water-exchange rate constants, led to the following <u>theoretical</u> values of k_{12}:

a) $k_{12(Cu(II))} \cong 7. \times 10^7 \text{ sec}^{-1} \text{ M}^{-1}$

b) $k_{12(Zn(II))} \cong 3. \times 10^6 \text{ sec}^{-1} \text{ M}^{-1}$ <u>4-9</u>

c) $k_{12(ni(II))} \cong 4. \times 10^3 \text{ sec}^{-1} \text{ M}^{-1}$

These values of k_{12} are approximately 55, 55, and 45 folds higher than our <u>experimental</u> results:

a) $k_{12(Cu(II))} = 1.3 \times 10^6 \text{ sec}^{-1} \text{ M}^{-1}$

b) $k_{12(Zn(II))} = 5.3 \times 10^4 \text{ sec}^{-1} \text{ M}^{-1}$ <u>4-10</u>

c) $k_{12(Ni(II))} = 94.9 \quad \text{ sec}^{-1} \text{ M}^{-1}$

Furthermore, it was found that $k_{12(Zn(II))}$ increases from $5.3 \times 10^4 \text{ sec}^{-1} \text{ M}^{-1}$ in the reaction with β-PAN to $2.5 \times 10^5 \text{ sec}^{-1} \text{ M}^{-1}$ in the reaction with PAR to $2.85 \times 10^6 \text{ sec}^{-1} \text{ M}^{-1}$ in the reaction with Bipy. Similar patterns of dependency of $k_{12(Zn(II))}$ on the ligands were found to be true for $k_{12(Ni(II))}$ (the value of $k_{12(Ni(II))}$ in the reaction with Bipy was taken from the literature (33)) and $k_{12(Cu(II))}$ ($k_{12(Cu(II))}$ of the reaction with Bipy was not estimated). Table 4-2 summarizes the comparative data.

In order to account for such dependencies, it is necessary to analyze all the different factors correlated with the system and the parametric assumptions present in the formulation of the Id mechanism. This

TABLE 4-2

Comparative Rate Constants for Reaction of M(II) With Ligand Bipy, PAR and β-PAN in Water With Respect to the Rate Constant of the Water Interchange [a].

Metal Ion	k_{12} ($sec^{-1} M^{-1}$) (β-PAN)	k_{12} ($sec^{-1} M^{-1}$) (PAR)	k_{12} ($sec^{-1} M^{-1}$) (Bipy)	k_2 (sec^{-1}) (Water Interchange)	(Theoretical)[g]
$Cu(aq)^{+2}$	1.33×10^6	2×10^7 [b]	-	$2. \times 10^8$ [d] (11.0°C)	$7. \times 10^7$
$Zn(aq)^{+2}$	5.35×10^4	2.52×10^5	2.85×10^6	$3. \times 10^7$ [e] (20.0°C)	$3. \times 10^6$
$Ni(aq)^{+2}$	94.9	3.50×10^2	1.6×10^3 [c]	$3. \times 10^4$ [f]	$4. \times 10^3$

a) T = 25.0°C unless otherwise stated.

b) Preliminary data from Table 3-43.

c) H. P. Bennetto and E. F. Caldin (33).

d) T. J. Swift and R. E. Connick (57).

e) M. Eigen and K. Tamm (21).

f) D. B. Rorabacher (58).

g) Equation 4-10.

analysis can be divided into the following categories:

a) Possibilities of different charge in the ligands;

b) Scaling of the values of K_o into characteristic boundaries;

c) Modification of the Id mechanism.

(Addendum: Very recently Kustin and Wolff (59) have reported a study of the substitution reactions of theophylline and caffeine at 25.0°C with the metal ion Ni(II). They found an abnormally low value of k_{12} for theophylline ($k_{12} = 1. \times 10^2$ sec^{-1} M^{-1}) and no substitution reaction occurring with caffeine suggesting that the hydrogen bonding of H at N_9 to the carbonyl group is responsible for such a low value of k_{12}. This interpretation is in contrast with the range of interpretations given by Johnson and Wilkins (60) of the relatively low values of k_{12} at 25.0°C ($k_{12(Q)} = 1.2 \times 10^3$ sec^{-1} M^{-1} at pH 6.0 for Ni(II); $k_{12(QR)} = 1.4 \times 10^3$ sec^{-1} M^{-1} at pH 5.5 for Ni(II); and $k_{12(Q)} = 7. \times 10^6$ sec^{-1} M^{-1} at pH $\cong$ 5.5 for Cu(II)) for the reactions of 8-hydroxyquinoline (Q) and 8-hydroxyquinoline-5-sulfonate (QR) with the metal ions Ni(II) and Cu(II) where the hydrogen bonding of H of OH at C_8 to N_1 has the same characteristics as in theophylline.)

Possibilities of Different Charges in the Ligands. In the experimental section concerning the Setting of the Experimental Conditions, it was indicated that the pH of the solutions were chosen on the basis of the values of the stability constants of the complexes and the acidic dissociation constants reported in Tables 2-2 and 2-3. In fact, specific simulation of the stoichiometry as a function of pH for the species $Zn(S)_3(\beta-PAN)^{+2}$ shows that it is present in more than 98% with respect to the initial concentration of β-PAN, assuming quantitative complexation. Using the same type of calculation for the free ligand, it was found that at pH 5.8, β-PAN was present in more than 99% with respect to the sum of the concentrations

of the species β-PAN$^-$, β-PAN$^+$, and β-PAN. Similarly, Bipy was present in more than 92% with respect to the sum of the concentration of the species Bipy$^+$ and Bipy at pH 5.8.

Assuming an Id mechanism and considering the contents of Table 4-1, it is expected that the species β-PAN$^-$ should be associated with a faster rate than does β-PAN. Similarly, Bipy should have a faster rate than Bipy$^+$. Therefore it becomes obvious that the different values of $k_{12(Bipy)}$ with respect to $k_{12(\beta-PAN)}$ cannot be explained in terms of the different charges of the ligands.

For the ligand PAR, however, an analysis based on pure stoichiometric consideration cannot be invoked as an exclusion of the presence of its anionic form. This observation becomes obvious from the uncertainty of K_{a3} (Table 2-3) related to the specific pH (pH = 5.2) in which the experiments reported in Table 3-27 were undertaken. Therefore, the relatively high values of $k_{12(PAR)}$ with respect to $k_{12(\beta-PAN)}$ (Table 4-2) may be considered as a result of the contribution of the anionic form of PAR as a ligand. However, on kinetic grounds, the idea implicit in Table 4-1 in relation to the different values of k_{12} depending on the charge of the ligands and taking into consideration the study reported by Funahashi and Tanaka (60) concerning the reaction of the anionic forms of PAR with the metal ion Ni(II), allow us to visualize the possibility of two different stoichiometries.

These two stoichiometries consider that the reaction of PAR with a metal ion may either react only as PAR$^-$ or as a competition between the PAR and PAR$^-$, provided that pH = $pK_{a3} \pm 2$, in which no other species of PAR are present in any significant amount. The two stoichiometries are:

1.

   a) $PAR \rightleftharpoons PAR^- + H^+$ K_{a3}

   b) $PAR^- + M(aq)^{+2} \rightleftharpoons M(aq)(PAR)^{+1}$ k_b **4-11**

   c) $M(aq)(PAR)^{+1} + H^+ \rightleftharpoons M(aq)(PAR)^{+2}$?
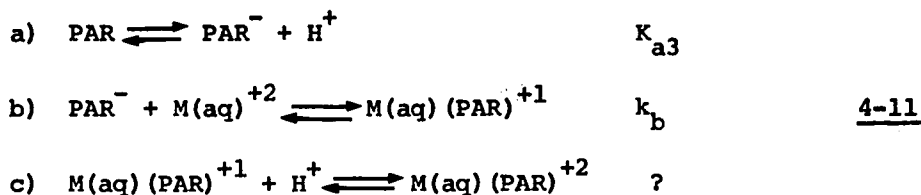
where the equilibrium 4-11c is not considered as part of the reaction rate. From this stoichiometry the following rate equation can be derived:

$$- \frac{d[PAR]}{dt} = \frac{d[M(aq)(PAR)^{+1}]}{dt} = \frac{K_{a3}\,k_b}{[H^+]}\,[PAR]\,[M(aq)^{+2}] \qquad \textbf{4-12}$$

where

$$\frac{K_{a3}\,k_b}{[H^+]} = k_{12} \qquad \textbf{4-13}$$

2.

$$PAR + M(aq)^{+2} \xrightarrow{k_b} M(aq)(PAR)^{+2}$$

a) $-H^+ \downarrow\uparrow +H^+$ K_{a3}

$$PAR^- + M(aq)^{+2} \xrightarrow{k_c} M(aq)(PAR)^{+1} \qquad \textbf{4-14}$$
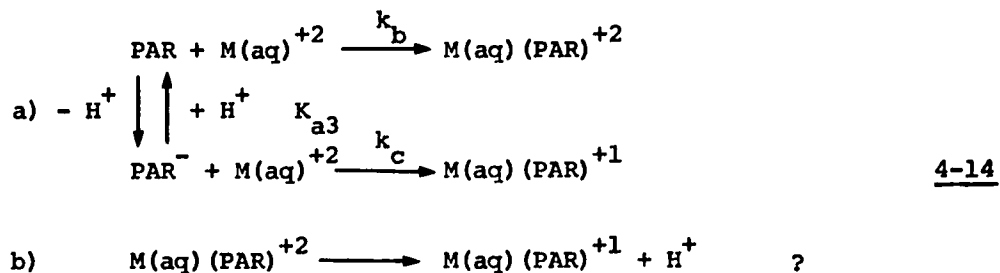
   b) $M(aq)(PAR)^{+2} \longrightarrow M(aq)(PAR)^{+1} + H^+$?

whereas in the previous stoichiometry the equilibrium 4-14b is not considered as part of the reaction rate. From this stoichiometry the following rate equation can be derived:

$$- \frac{d[PAR]}{dt} = \frac{d([M(aq)(PAR)^{+1}]+[M(aq)(PAR)^{+2}]}{dt} = k_b +$$

$$+ \frac{K_{a3}\,k_c}{[H^+]}\,[PAR]\,[M(aq)^{+2}] \qquad \textbf{4-15}$$

where

$$k_b + \frac{K_{a3}\,k_c}{[H^+]} = k_{12} \qquad \textbf{4-16}$$
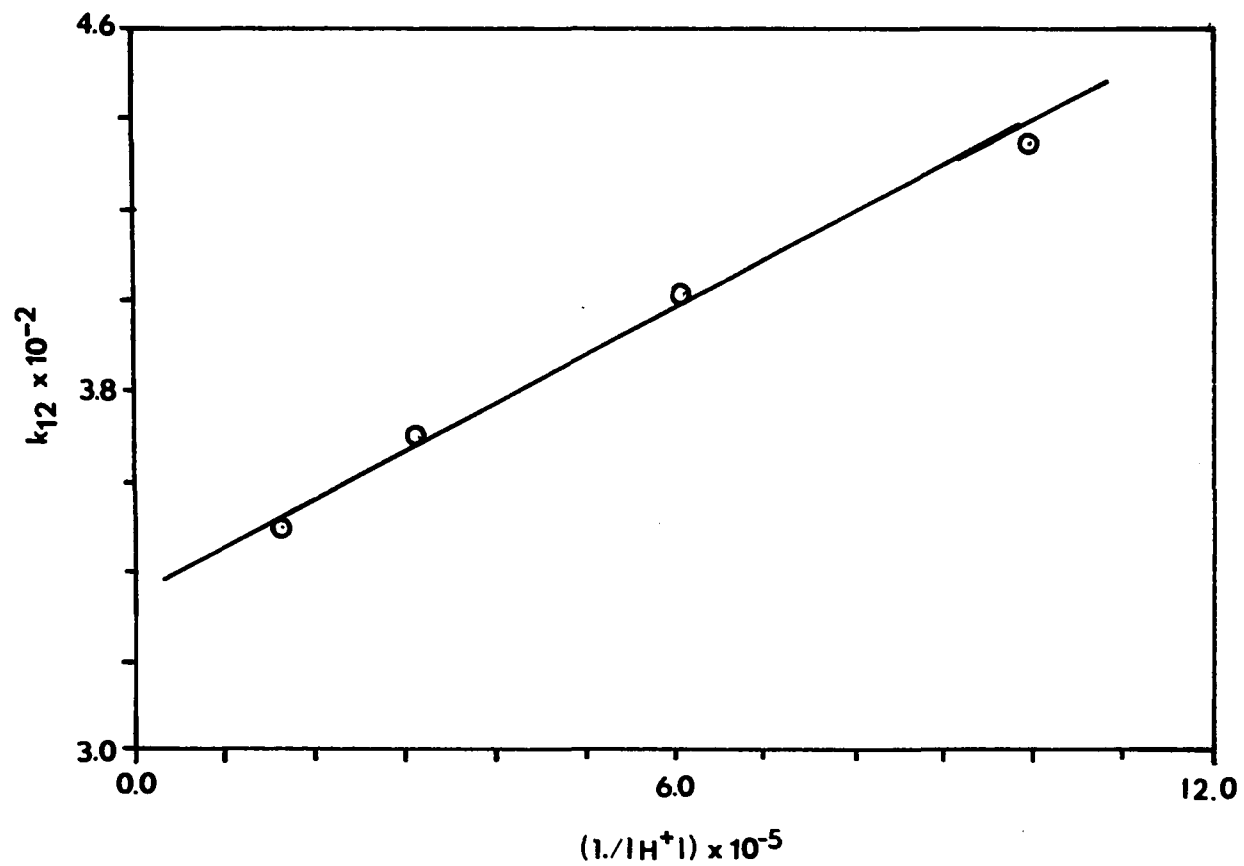
Figure 4-1. Functional Representation of $k_{12} = k_{12}([H^+])$ for the Reactions of Ni(II) With the Ligand PAR in Water

at the maximum of the charge density according to the Debye-Huckel theory (63, 64).

Qualitatively, Equation 4-17 can be divided into two different functions:

a) The pre-exponential factor which can be envisioned as an entropic factor and implies an increase of K_o as the distance a increases;

b) the exponential function which is the energy factor, and implies that the K_o decreases as distance a increases.

A function similar to Equation 4-7 has been suggested for neutral ligands by Rorabacher (58), namely:

$$K_o = (4/3)\pi Na^3 \cdot 10^{-3} \qquad \underline{4-19}$$

This is the pre-exponential factor of Equation 4-17. The justification for such a simplification of Equation 4-17 comes from the fact that evaluation of $U(a)/\overline{kT}$ (Equations 4-17 and 4-18) for charge-charge interaction using extreme values for a (5.0 to 8.0 x 10^{-8} cm), estimated from van der Waals radii (65) of the atoms, yield values smaller than 1. Therefore, evaluation of the same type of function for dipole-charge interactions for the same extreme values of a, should be smaller than 1. In fact, if the following dipole-charge interaction in a medium of dielectric constant ξ is considered:
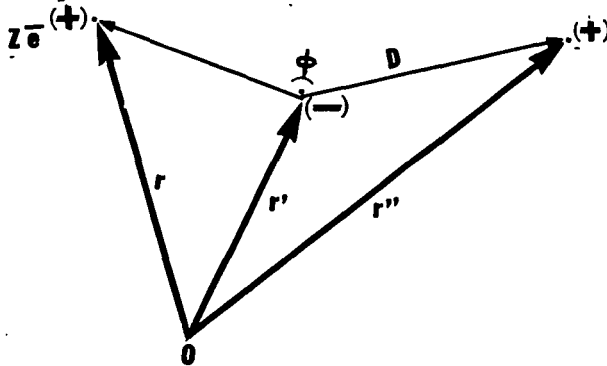
Figure 4-2 — Generalized dipole-charge interaction.

where, $\bar{r}-\bar{r}' = \bar{a}$, $\bar{D}$ the dipole moment, and | | implies the conventional

magnitude of the vectors, then it is possible to derive the following

equation for the potential energy U(a) for a dipole-charge interaction:

$$U(a) = D \cdot a/4\pi\xi|a|^3 - D \cdot a \ /4\pi\xi(1-\alpha|a|)$$ **4-20**

The evaluation of exp $(-U(a)/\bar{k}T)$ in the interval 5.0 to 8.0 x 10^{-8}cm

for a, assuming that $\phi=170$, yields values of approximately 1.

Evaluation of K_o from Equation 4-19 in the same interval of a

yields:

$$\frac{K_o(a_1)}{K_o(a_2)} = 2.55$$ **4-21**

This implies only a 2.5 fold increase in K_o that does not explain the dif-

ferences in k_{12} observed for β-PAN, PAR, and Bipy, unless the rate deter-

mining step is not the release of the water molecule, as required by an

unmodified Eigen (Id) mechanism. Furthermore, this increase in K_o predicts

values contradicting our experimental results.

Modification of the Id Mechanism.

At this point, it becomes obvious that the results presented in

this work cannot be analyzed in terms of an Id mechanism. Furthermore,

considerations of external interactions with the reacting system, such

as the steric effects on the reaction of $Ni(aq)^{+2}$ with alkyl amines, pro-

posed by Rorabacher and Melendez-Cepeda (36), raise questions about the

generalization of an Id mechanism of substitution reactions by polydentate

ligand of the solvated hexacoordinated metal ions.

Considerations of the steric effects extended into the systems of

concern in this study lead us to specific questions about the effects

that structure and configuration of the ligands β-PAN, PAR, and Bipy may

have upon the reaction rate.

Nakamoto (50) studied spectroscopically the conformational equilibrium of Bipy in solution, and found evidence for the conformation I (Figure 4-3) being predominant at pH values greater than 4.4. Evidence for the "cis" conformation in the corresponding metal complexes has been presented by Dothie et al. (66).

From a qualitative point of view, we should expect that the I structures (Figure 4-3) of β-PAN, and PAR predominate because:

1. The dipole moment of the ligand has the tendency to be a minimum in media of high dielectric constant. Or, it decreases as the dielectric constant increases.

2. The ligands have the tendency toward planarity due to the possible "double bond" character of the C_2-N_α bond and C_1-N_β bond, which is common in both ligands.

3. The ligands have a relatively more stable six-membered ring of the hydrogen bond to α nitrogen with respect to the stability of the five-membered ring of the hydrogen bond to the β nitrogen.

Betteridge et al. (43, 46) show spectroscopic evidences for the conformation (II) in the corresponding metal complexes with β-PAN and PAR.

It is possible to argue, then, that steric effects are perhaps a contributing factor in the differences in the rate constants observed. Indeed, qualitatively, they predict the rate constants to be in the following order, if it is acceptable that in solution the conformations I (Figure 4-3) are predominant with respect to the conformations II for the ligands Bipy, β-PAN, and PAR:

$$k_{12(Bipy)} > k_{12(PAR)} > k_{12(\beta-PAN)} \qquad \underline{4-22}$$

From other studies (67) it is known that there is a two-fold difference between the rate constants of the reaction of Phen and Bipy with
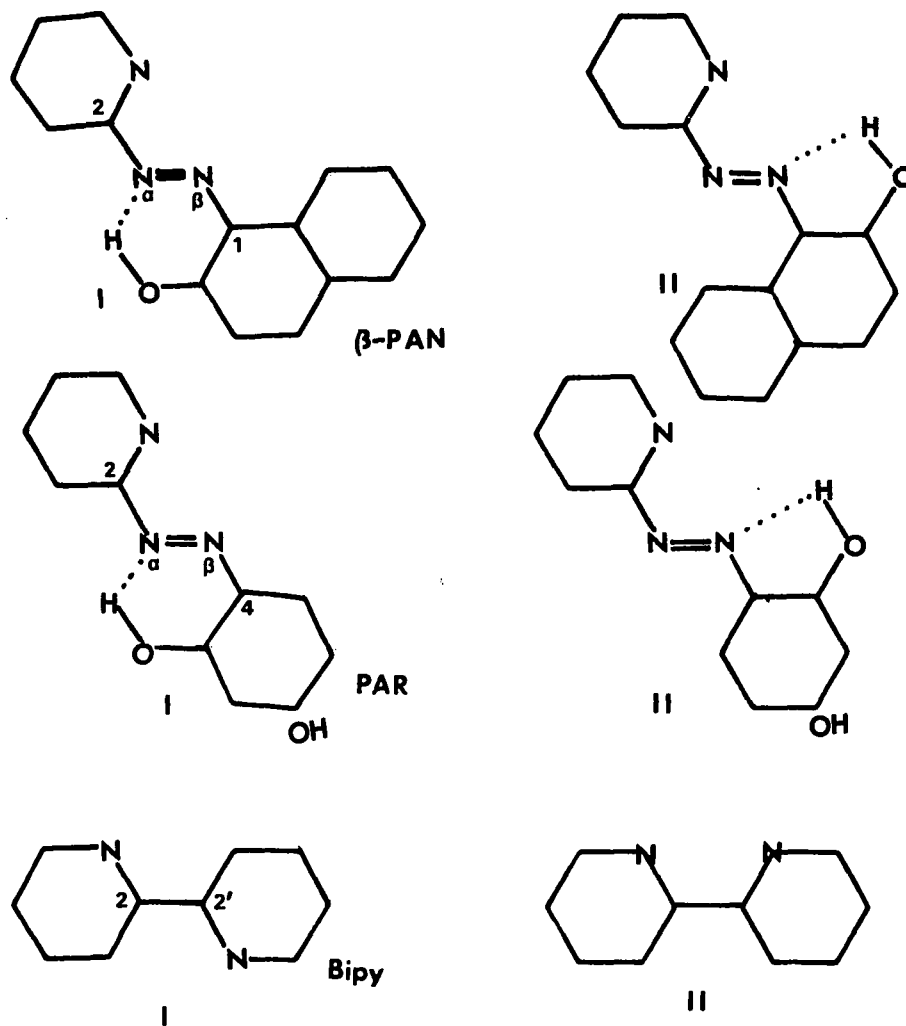
Figure 4-3. Conformational Equilibria of the Ligands β-PAN, PAR, and Bipy
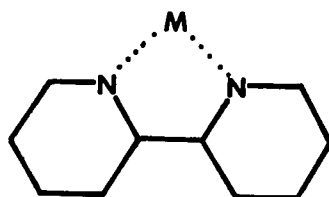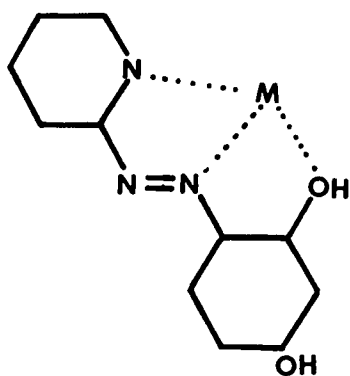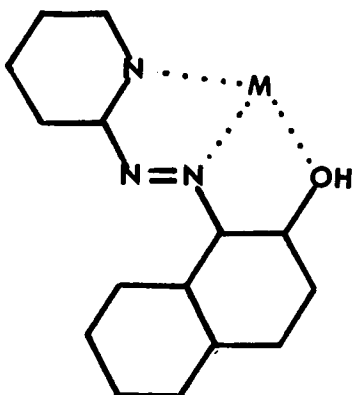
Figure 4-4. Structural Representation of ML for the
Complexes $M(\beta\text{-PAN})^{+2}$, $M(PAR)^{+2}$, and
$M(Bipy)^{+2}$

$Ni(aq)^{+2}$. Obviously, it becomes arbitrary to speculate about the justification of the differences in magnitude of the k_{12} in the present case.

If we consider the stoichiometry of the Id mechanism, it is possible to visualize a rate determining step other than the release of water molecules; Kustin et al. (68) studied the reaction of $Ni(aq)^{+2}$ and $Co(aq)^{+2}$ with the ligands α-alanine, β-alanine, α-aminobutyrate, and β-aminobutyrate. In considering the formation of the mono-complexes, it was found that in reactions of the β-forms, rates are slower than in the reactions of α-form. This was interpreted as indicative that in the stoichiometry of the Id mechanism, formulated by Eigen, the rate determining step may be the ring closure. The modified mechanism was named a sterically controlled substitution mechanism (SCS in the recalled work, and "Is" in this work).

Further evidence for the Is mechanism has been recently reported (69) in a study of the rates of formation of the complexes of Mn^{+2} with the ligands Phen, Bipy, and Terpy in anhydrous methanol. The following rate dependency at -22.0°C was found:

a) $k_{12}(Phen) \cong 8\ k_{12}(Bipy)$

                                                          4-23

b) $k_{12}(Phen) \cong 40\ k_{12}\ (Terpy)$

The Is mechanism seems to be critical in the interpretation of the present results because it accounts for the differences in the k_{12} of the ligands Bipy, PAR, and β-PAN, particularly due to the barrier of rotation of the $C_2-C_{2'}$ bond in Bipy, and the $C_{1'}-N_\beta$ bonds in PAR and β-PAN.

To the knowledge of the author of this work, no quantitative data are available for the rotation barriers of the above-mentioned bonds, nor for the internal rate process. Furthermore, considerations of the relative radii of rotation of the pyridine fragment and the pyridylazo fragment

(1.7 : 2.6 estimated from the Van der Waals atomic radii (65)) suggest that the formation of the B-ring (structures II in PAR and β-PAN, Figure 4-4) is the rate-determining step in the formation of the complexes. Perhaps the relatively large size of the naphthol fragment with respect to the resorcinol fragment is the steric factor that accounts for the differences in the reaction rate between PAR and β-PAN. Specifically, consideration of Equation 4-7 from which Equation 4-8 was derived led to new expressions for k_{12} as follows:

a) $k_{12} = K_o k_3$

b) $k_{12} = K_o k_4$

4-24

for the bidentate ligands and tridentate ligands respectively.

The assessment of Equation 4-24 implies that the order of coordination for the donating atoms of the ligands β-PAN and PAR are:

a) 1st the N_1 (-pyridyl group)

b) 2nd the N_β (-azo group)

These two groups may coordinate almost simultaneously.

c) 3rd the -OH (-hydroxyl group)

This order is in contrast to previous reports in the literature (58) concerning other ligands where hydroxy and amino groups are the donating centers. However, it is the view of the author of this work that the possibility of near-simultaneous coordination of N_1 and N_β are thermodynamically favored with respect to coordination with the monodentate hydroxyl group.

In conclusion, the relative rates of the water interchange with respect to the rate of the ring closing, namely:

a) $k_{-2} > k_3$

or

b) $k_3 > k_{12}$

4-25

for bidentate ligands, and

a) $(k_2k_{-3} + k_4k_{-2}) > k_4k_3$

or   4-26

b) $(k_2k_{-3} + k_4k_{-2}) < k_4k_3$

defines the Is or the Id mechanism.

<u>Solvent Effects</u>. - The profiles of the functional plots of k_{12}
versus the % b/w of the non-aqueous components of the solvent mixtures
dioxane-water, methanol-water, and acetone-water for the reaction of Zn(II)
with the ligand β-PAN at 25.0°C are presented in the Figure 4-5. In this
figure it is possible to observe that there is a distinctive minimum com-
mon to the three solvent mixtures. The values of k_{12} corresponding to the
functional minima $(k_{12 \, (min)})$ are approximately seven, nine and seventeen
fold lower than k_{12} in pure water $(k_{12(w)})$ for the solvent mixtures
methanol-water, acetone-water, and dioxane-water, respectively.

The similitude of the results obtained from the experiments per-
formed with the metal ions Ni(II), and Cu(II) with the ligand β-PAN led
to the general conclusion that the differences between $k_{12(w)}$ and $k_{12(min)}$
are independent of the metal ion in the reaction with the ligand β-PAN
and that these differences have the following order with respect to the
non-aqueous component of the solvent mixtures:

dioxane > acetone > methanol   4-27

Figures 4-6 and 4-7 show the profiles of the functional plots of
k_{12} versus the % b/w of the non-aqueous component of the solvent mixtures,
previously described, for the reaction of Zn(II) with the ligands PAR at
14.7°C and Bipy at 25.0°C respectively. (In Figure 4-7 the profile of
rate constants for the reaction of Zn(II) with Bipy in methanol-water is
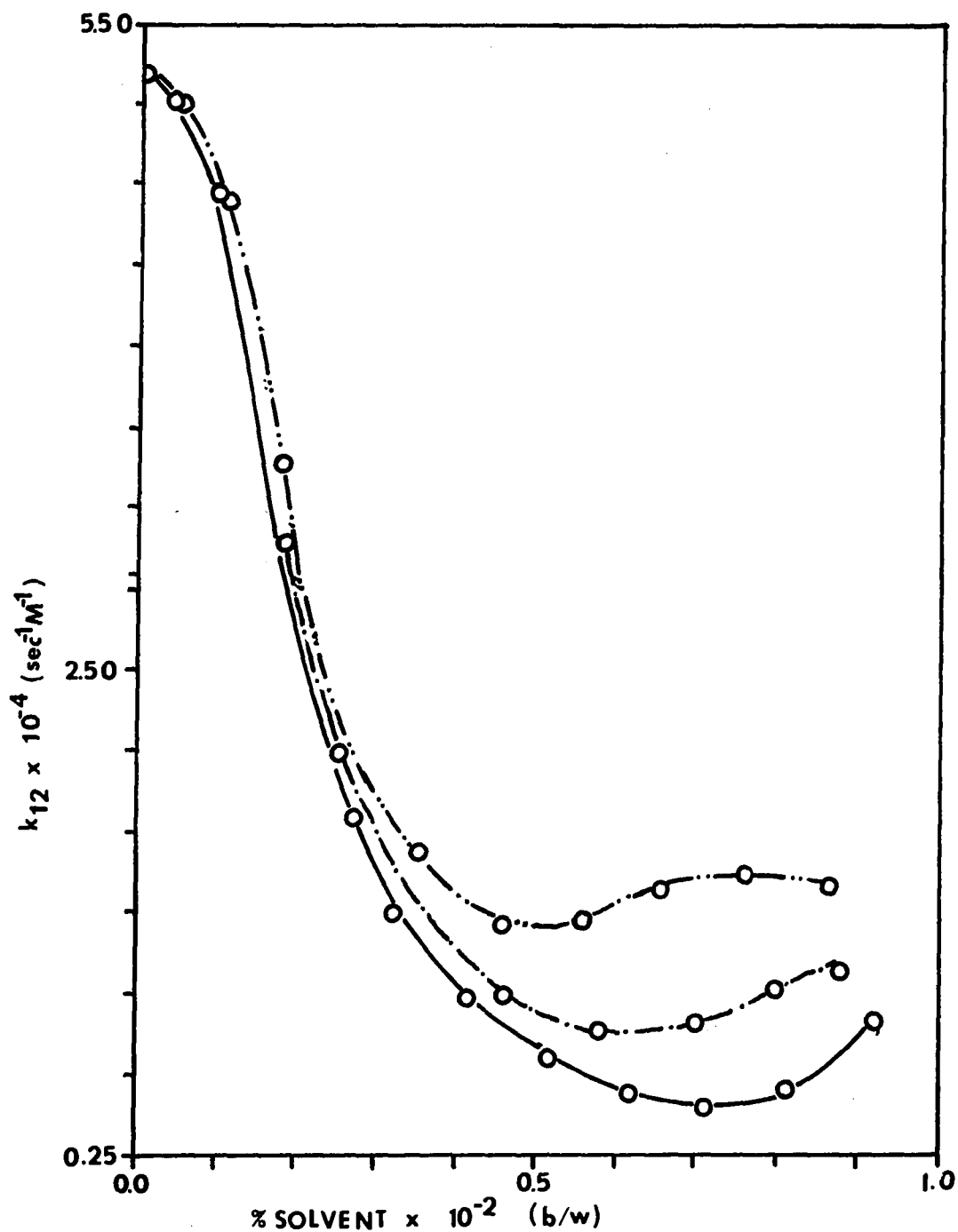
Figure 4-5. Representation of $k_{12} = k_{12}$(% b/w of the non Aqueous Component of the Solvent Mixtures) for the Reactions of M(II) With β-PAN

——————— Dioxane/Water

—·—·—·— Acetone/Water

—··—··—·· Methanol/Water
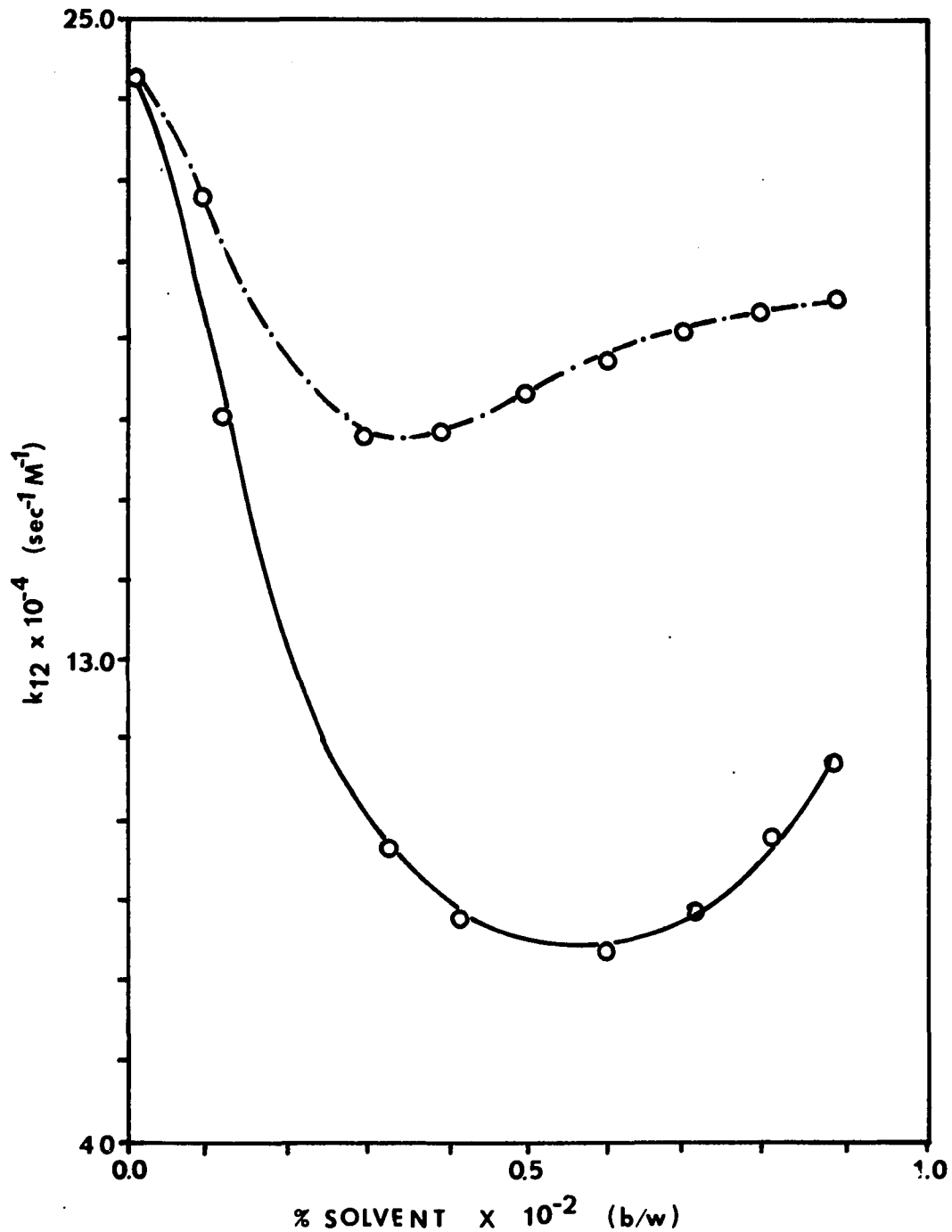
Figure 4-6. Representation of $k_{12} = k_{12}$(% b/w of the non
Aqueous Component of the Solvent Mixtures) for
the Reactions of M(II) With PAR

———————— Dioxane/Water

—·——·——·—— Methanol/Water
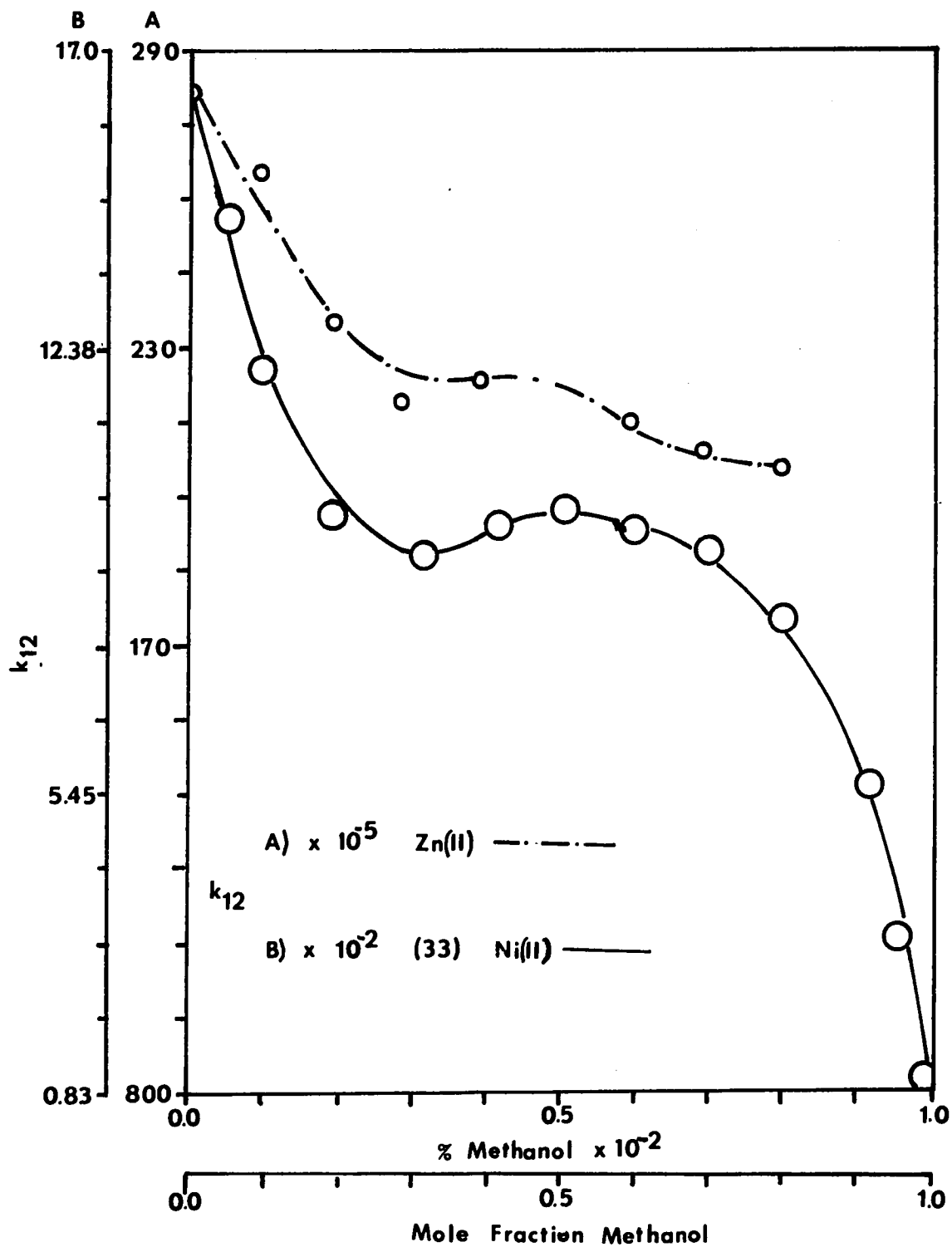
Figure 4-7. Representation of $k_{12} = k_{12}$(% b/w of the non-

Aqueous Component of the Solvent Mixtures) for

the Reactions of Zn(II) With Bipy

compared with the corresponding profile for the Ni(II) with Bipy in the
same solvent mixture as previously reported by Bennetto and Caldin (33).)
These figures show a distinctive minimum as previously described for the
ligand β-PAN. However, the differences between $k_{12(min)}$ and $k_{12(w)}$ for
each specific solvent mixture, are smaller for the ligand PAR than for
β-PAN and smaller for the ligand Bipy than for PAR.

Further experiments at temperatures other than 25.0°C for the
reactions of the metal ions Zn(II), Ni(II) and Cu(II) with the ligand
β-PAN were carried out in the solvent mixtures previously described at
25.0°C. The results of these experiments show the same patterns pre-
viously summarized concerning $k_{12(min)}$ and $k_{12(w)}$. These results were
used as data for estimation of the activation parameters reported in
Tables 3-47 to 3-54.

In the introduction, general ideas about the characteristics of
the solvent mixtures and their interactions with electrolyte and non-
electrolyte solutes were discussed. Also examples of kinetic studies
carried out in binary solvent mixtures were briefly reviewed. Combina-
tion of these ideas with the results previously summarized allow the
discussion to be subdivided as follows:

a) The effects of the structural properties of the
binary mixtures;

b) The dielectric effects upon the ion-dipole interactions
characteristic of the reactants;

c) The stoichiometry of both, the inner sphere coordination
and the outer sphere coordination;

d) The selective solvation of the metal ions, and

e) Activation parameters and their correlations.

The Effects of the Structural Properties in the Binary Mixtures. -

In terms of the absolute rate theory, the viscosity is the rate process
which better reflects the structure of the liquid state. This idea becomes
obvious if it is considered that the factors related to this dynamic pro-
cess in which direct interactions of elementary species (molecules in
general) characterize the magnitude of the rate process. In other words,
the size of the elementary species and the size of the short-term aggregates
of such elementary species define the magnitude of the rate process (4).

Therefore, it is expected that for solvent mixtures, where the com-
ponents have the possibility of hydrogen bonding (either homogeneously or
heterogeneously concerning the components), the structure of the solvents
characterized by both the elementary species and the relatively larger
short-term aggregates, were better reflected by the viscosity. In fact,
the functional dependence of the viscosity coefficient (η) on the solvent
composition usually shows a maximum value and the η_{max} is higher than the
value for either components. This fact has been confirmed for the methanol-
water, acetone-water, and dioxane-water mixtures as can be seen in the
Appendix A, where the physical properties of these solvents are summarized.

This behavior seems to be independent of the temperature and extra-
polation of the values of η to the critical temperature (T_c) of the non-
aqueous component (by means of an Arrhenius type of equation) supports
the conservation of the maximum. But the solvent composition where the
maximum occurs, shows that the maximum shifts at higher concentrations
of the non-aqueous component of the mixtures.

In the same line of thinking, the profile of the plot of k_{12} versus
the concentration of the solvent seems to be independent of the temperature
according to the experiments carried out with the ligand β-PAN and the metal

ions Cu(II), Ni(II), and Zn(II). The results are summarized in Tables
3-47 to 3-54 and are used in the estimation of the activation parameters.
However, extrapolation of $k_{12} = k_{12}(T)$ to the T_c of the non-aqueous com-
ponents of the solvent mixtures by means of the Arrhenius equation
(Equation 3-8) shows the interesting fact that k_{12} becomes constant
for all the solvent compositions at $T_c \pm 10°C$ for all the metal ions
reacting with the ligand β-PAN.

This was also reported by Bennetto and Caldin (33); they inter-
preted this as evidence for the structural effects of the solvent upon
the rate of the reaction. Although this interpretation may be qualitatively
correct, the following considerations should be presented:

a) Whichever mechanism is postulated (Id, Ia, or Is), k_{12} depends
upon two different quantities: K_o representing an equilibrium diffusion
controlled process, and k_2, k_3, or k_4, depending on the ligand and
specifically considered in Equations 4-3, 4-6 or more generally in
Equation 4-7; the rate constants are simple or complex functions of the
microproperties of the reacting system, namely: the solvent interchange
process on the ligand-metal ion bond formation whose values should not
depend on diffusion.

b) The experimental results of Rorabacher et al. (34-35) show
that the functional dependence of k_{12} on the solvent composition is
opposite to the results reported by Bennetto and Caldin (33). Further-
more, the results reported by Bennetto and Caldin are in general agreement
with our results.

c) The results summarized in the Inequality 4-27 concerning the
non-aqueous component of the mixed solvents reflect a dielectric constant
contribution, this is contrary to the expected order in terms of structural

properties characteristic of hydrogen bonded solvents.

The first consideration leads to the conclusion that K_o should reflect the structure of the solvent in terms of the diffusion of the reacting species. Since K_o is common to the mechanisms Ia, Is, and Id and case b) is concerned only with neutral ligands, an obvious contradiction arises between the considerations a) and b) because they imply that K_o should behave differently for each specific case. Furthermore, the idea of the effect of the relative size of the short-term order of the molecular aggregates with respect to the structure of the solvent discussed at the beginning of this subdivision predicts the opposite inequality of that found experimentally (Equation 4-27) as presented in case c).

In conclusion, it can be said that the structural properties of the solvent may have an effect upon the metal ions substitution reactions. However, this effect is not the most important compared with others produced by other factors to be considered subsequently.

The Dielectric Effects in the Ion-Dipole Interaction Characteristic of the Reactants. - A dependence of k_{12} on the solvent composition should be expected as a result of the effect of the dielectric constant of the medium in the dipole-charge interaction of the reactants. This type of dielectric interaction has been studied by Laidler and Eyring (70). They derived an equation based on statistical considerations in regard to the general reaction:

$$A^{ZA} + B^O \underset{\longleftarrow}{\overset{K}{\longrightarrow}} M^{\neq ZA} \overset{k}{\longrightarrow} X^{(ZA \text{ or } O)} \qquad \qquad \underline{4\text{-}28}$$
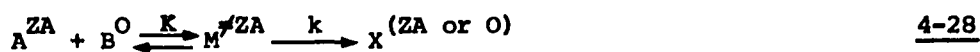
where A^{ZA} is a reaction species with charge ZA, B^O is a reacting species of charge zero and permanent dipole moment, $M^{\neq ZA}$ is a transition species of charge ZA, and $X^{(ZA \text{ or } O)}$ is a product with or without charge but with

permanent dipole moment; reacting in a medium of dielectric constant ξ

that can be varied with respect to a dielectric constant ξ_o (usually

water dielectric constant) and ionic strength μ that can be varied with

respect to a $\mu_o \rightarrow 0$ as reference. This equation can be written in the

following simplified expression:

$$\ln k = \alpha \left(\frac{1}{\xi} - 1\right) + \beta \frac{1}{\xi} + \gamma\mu \frac{1}{\xi} + \delta \qquad \text{4-29}$$

where α, β, γ, and δ are functions reflecting constants characteristic

of the system. LaMer (71) had pointed out that μ and ξ are not indepen-

dent variables; therefore, Equation 4-29 cannot be used unless $\mu = 0$

(usually by extrapolation to the ionic strength dependence of the reaction

to $\mu = 0$).

This became obvious in Figures 4-8 and 4-9 where a non-linear profile

of the functional plot of log k_{12} versus ξ^{-1} is shown. Obviously, the non-

linearity of $k_{12} = k_{12}$ (ξ) does not exclude any implicit functionality.

However, Equation 4-29 implies that a non-linear correlation may be due

to the following factors:

a) The dielectric effects upon the reaction rate may be of smaller

magnitude than the effects of the ionic strength upon the reaction rate.

b) The dielectric effects may be of smaller magnitude than the

effect of non-specific solvent-solute interactions due to structural

properties of the solvent, possible selective solvation of the reaction

and/or acid-base characteristics of the solvents.

The first consideration has a very precise mathematical meaning

in the analytical form of the general Equation 4-29. However, in the

introduction the concept of ionic strength was analyzed and specifically

stated as meaningless in the solvent mixtures of concern in this work.
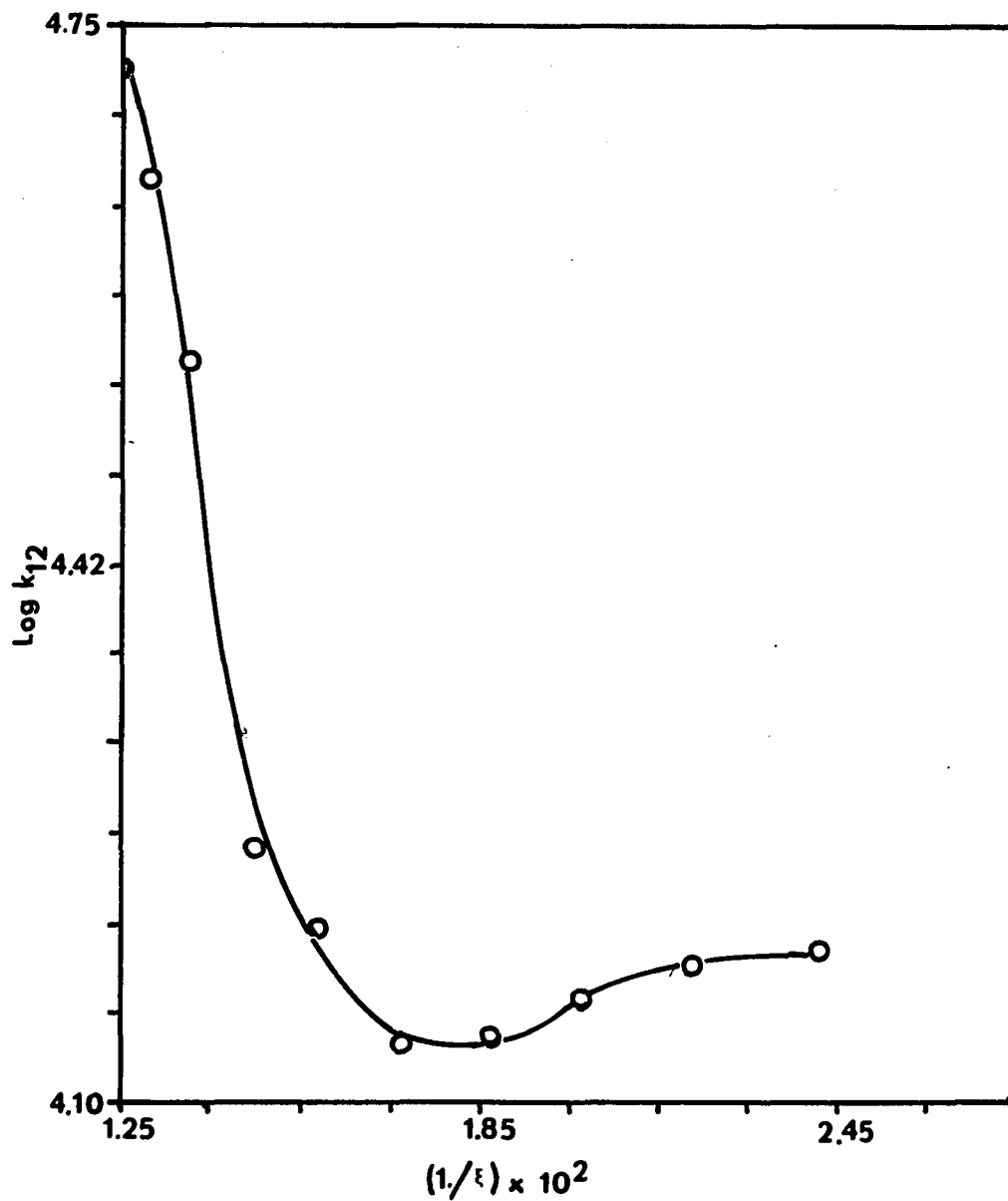
Figure 4-8. Functional Representation of $k_{12} = k_{12}(\xi)$ for the Reactions of Zn(II) With β-PAN in Methanol-Water Mixtures.
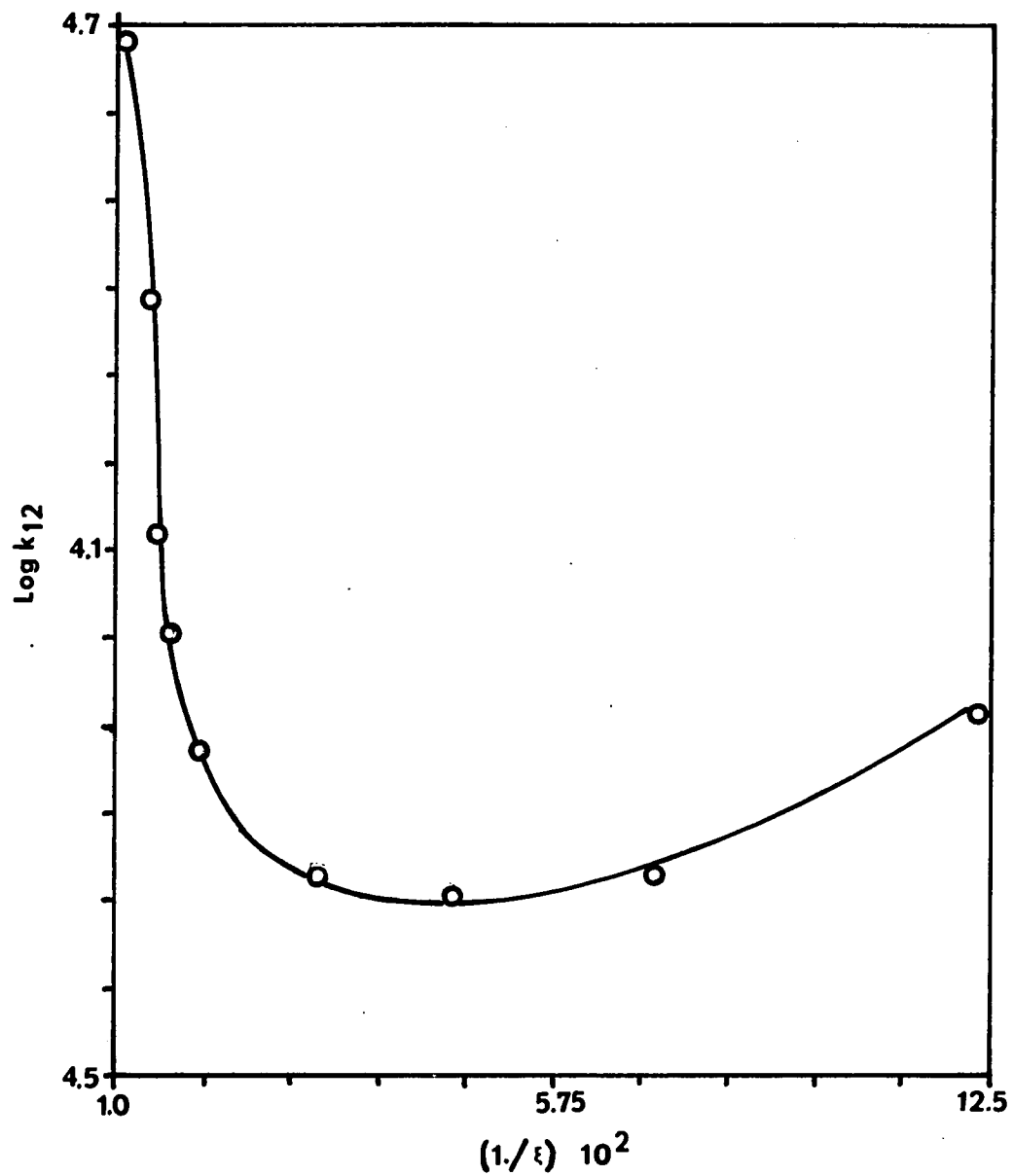
Figure 4-9. Functional Representation of $k_{12} = k_{12}(\xi)$
for the Reactions of Zn(II) With β-PAN
in Dioxane-Water Mixtures.

Nevertheless, the results presented in Table 3-43 of the experiments performed at 50.5% b/w of dioxane in water for the reaction of Zn(II) with the ligand β-PAN at different electrolyte concentrations (sodium nitrate) show no differences in k_{12} within the experimental error.

Evidence in the literature (30, 72) has been discussed in the introduction regarding acid-base characteristic of the solvents. In order to minimize this possible acid-base effect, all the experiments considered in this section were carried out at a constant pH, unless otherwise stated. These factors become critical if consideration of the experiments performed at different pH (Tables 3-40 to 3-42) show a noticeable dependency of k_{12} upon pH in the limited range of pH studied.

In conclusion, it is possible to state that the dielectric constant of the medium does not have an important effect upon the reaction rate compared with other factors to be analyzed.

Because of the implication of the consideration a) and b) of this subdivision, the stoichiometry of the inner sphere and the outer sphere coordination, and the selective solvation of the metal ions will be discussed in the next subdivision.

The Stoichiometry of Both the Inner Sphere of Coordination and the Outer Sphere of Coordination, and;

The Selective Solvation of the Metal Ions. The decrease of the conductivity (Λ) as the content of the non-aqueous component increases in solvent mixtures reported by Jones (73), was interpreted by Strehlow (27) as evidence of selective solvation in which the positive ions are solvated selectively by the solvent whose molecular units have the lower dipole moment.

The decrease in the conductivity has been confirmed for the nitrate
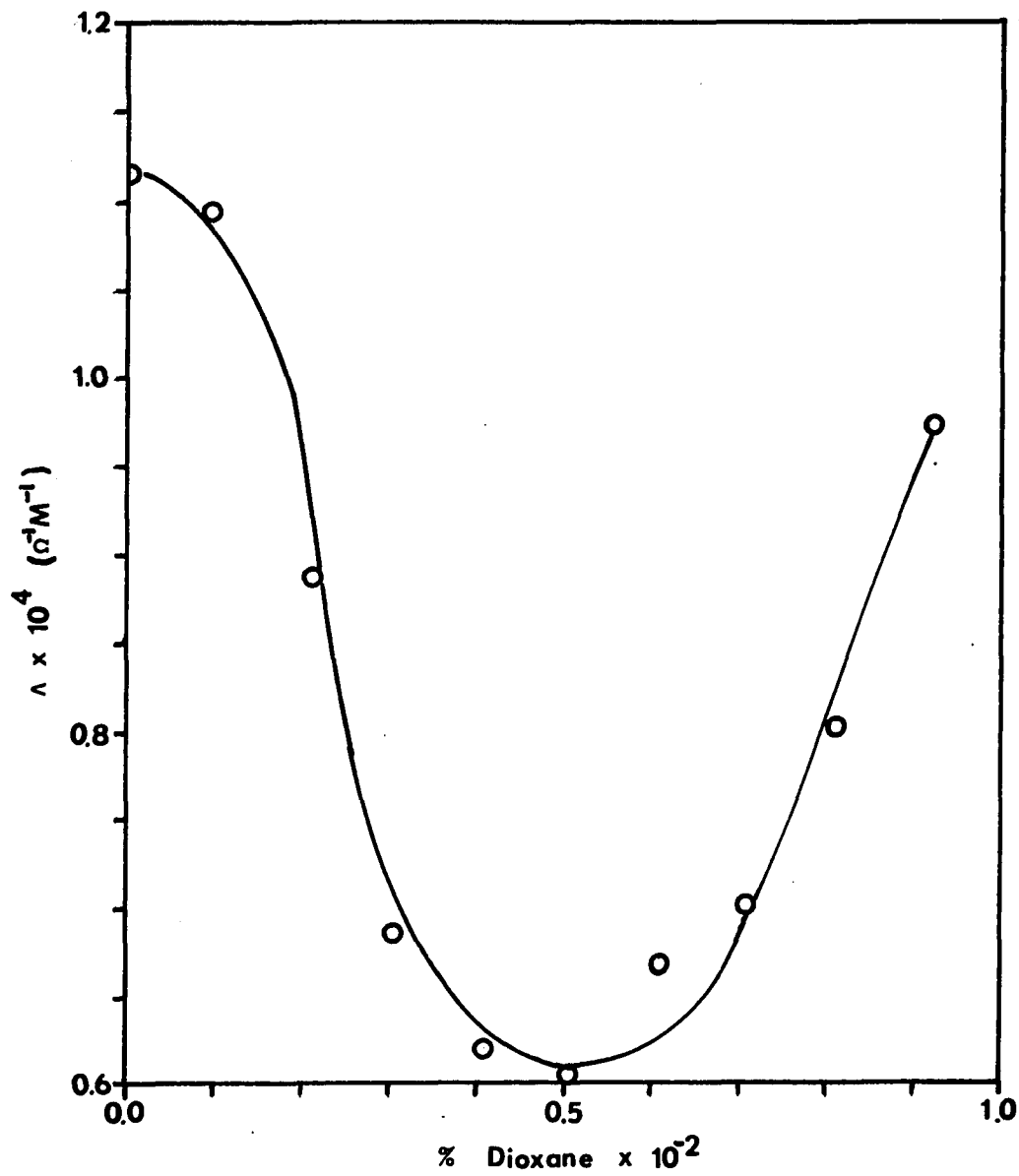
Figure 4-10. Functional Representation of $\Lambda = \Lambda$
(Solvent Composition) for $Zn(NO_3)_2$
in Solvent Mixtures.
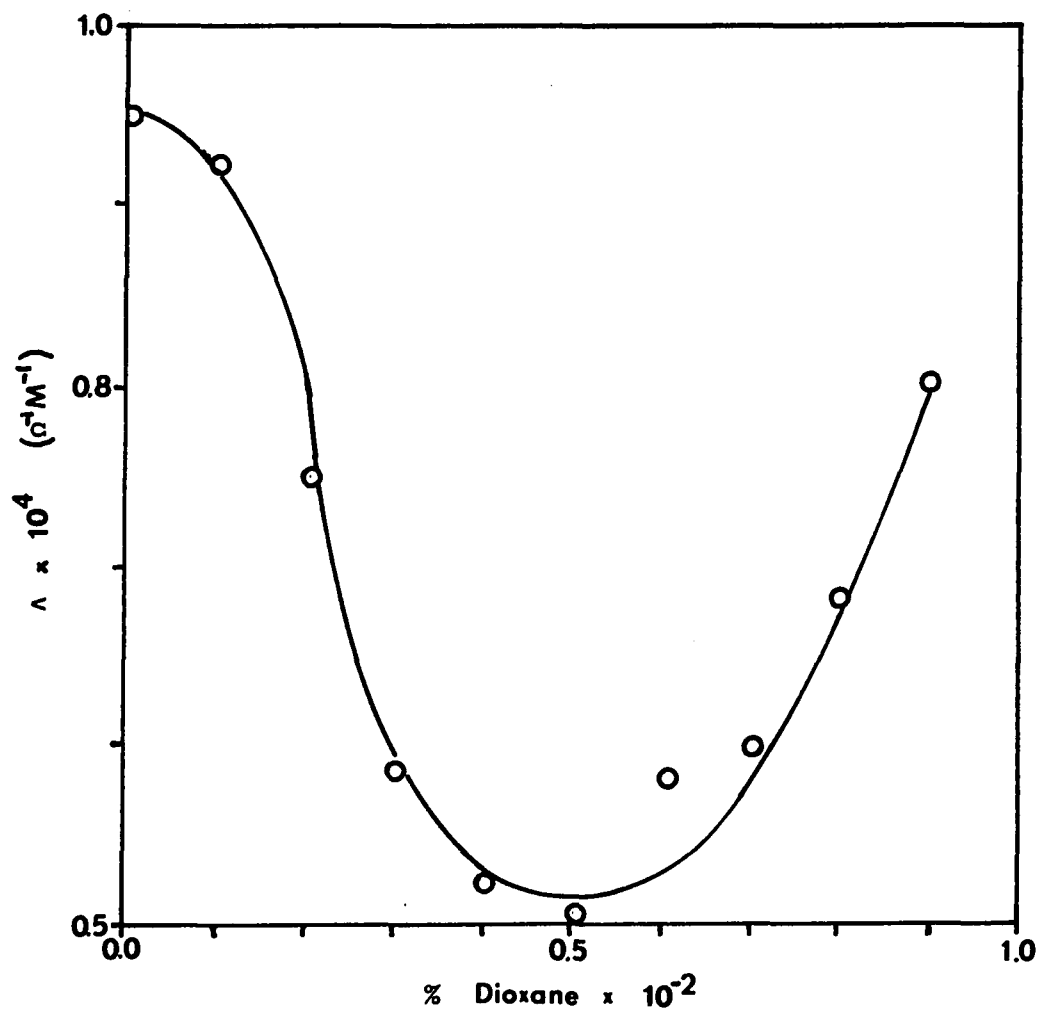
Figure 4-11. Functional Representation of

$\Lambda = \Lambda$(Solvent Composition) for

$Ni(NO_3)_2$ in Solvent Mixtures.
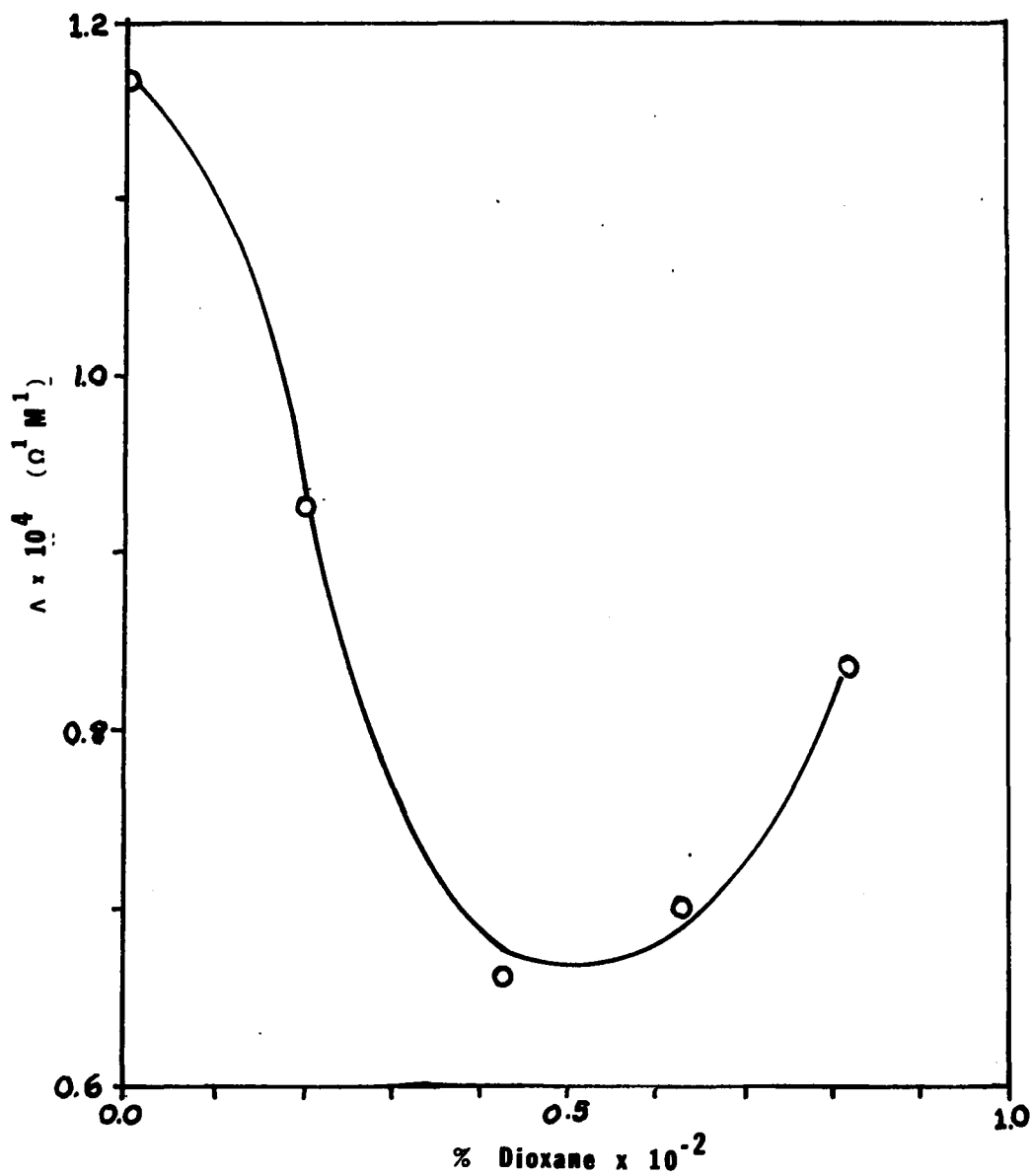
Figure 4-12. Functional Representation of

$\Lambda = \Lambda$(Solvent Composition) for

$Cu(NO_3)_2$ in Solvent Mixtures.

of the metal ions used in this work, and functional plots shown in Figures 4-10, 4-11, and 4-12 of the conductivity versus % b/w of the non-aqueous solvent show distinctive minima. This characteristic minimum, common to most electrolytes (73), was the main concern of Walden (74) who experimentally found the following relationship:

$$\Lambda_{oi}\ \eta \approx Constant \cdot Z_i \qquad\qquad \text{4-30}$$

where Λ_{oi} is the conductivity of the particular ion, η the viscosity of the medium and Z_i the charge of the ion. This relationship can be formally derived from basic equations of diffusion. The most important implication of this equation is the impossibility of separating the effect of selective solvation (reflected in the conductivity characteristics) and the structural properties of the solvent (reflected in the viscosity of the medium).

In mathematical terms, we can express the selective solvation as:

$$\frac{n_1/n_2}{n_1^o/n_2^o} = 10^{\alpha} \qquad\qquad \text{4-31}$$

where n_1/n_2 is the mole ratio of the component in the vicinity of the ion and n_1^o/n_2^o the initial molar ratio of the components of the mixture.

Padova (75) derived the following expression for the estimation of α

$$\alpha = \frac{\Delta \overline{G}_1 - \Delta \overline{G}_2}{2.303\ Z\ RT} \qquad\qquad \text{4-32}$$

where $\Delta \overline{G}_1$ is approximately the molar solvation free energy of the ion in the pure component i of the mixed solvent. He derived this formula using a thermodynamic approach with the following assumptions:

   a)   The electric field caused by the presence of the ions

        modified the short-term order of the solvents mixture;

b) The activity of the water approaches the molar fraction of water as the content of the non-aqueous solvent is increased;

c) the isobaric electrostatic work in a fluid is given by:

$$w = \frac{1}{4\pi} \int \int \overline{E} \, d \, \overline{\delta} \, d \, \nu \qquad \qquad \text{4-33}$$

where $\overline{E}$ and $\overline{\delta}$ are the electric field and electric displacement vectors, respectively, and $d \, \nu$ is the elementary volume.

Unfortunately, the values of the constant of the equilibrium for the following stoichiometric description

$$M^{+2} + 6S \rightleftharpoons MS_6^{+2} \qquad K \qquad \qquad \text{4-34}$$

for the metals Cu^{+2}, Zn^{+2}, and Ni^{+2} are not reported in the literature for the pure solvents methanol, acetone, and dioxane, but an estimation of K may be carried out using the values of K for other solvents given in tables of stability constants (76). With these values, we can obtain the following estimation of α:

dioxane-water	0.4 - 0.6
acetone-water	0.6 - 0.8
methanol-water	1.

4-35

These values correspond to Zn^{+2} as a typical example. Because of the crude approximation of α, the above values also hold for Cu^{+2} and Ni^{+2}.

This result suggests that in the mixtures methanol-water, acetone-water and dioxane-water, the metal ions are solvated by the non-aqueous component at a molar fraction of approximately 0.4 of the non-aqueous component, and at higher molar fractions of the non-aqueous component.

On kinetic grounds, early in this section it was indicated that the differences between $k_{12(w)}$ and $k_{12(min)}$ depend on both the solvents (Inequality 4-27) and on the ligands. These dependencies, compared with the results of the experiments carried out in pure water, summarized in Table 4-2, show the following common factors:

a) The magnitude of the differences between $k_{12(w)}$ and $k_{12(min)}$ are related to the ligands by the same inequality, namely:

Bipy > PAR > β-PAN   4-40

as $k_{12(w)}$ is:

b) The values of k_{12} are, in general, consistently lower with respect to the expected value for a typical Id mechanism as previously described in the mechanistic considerations. Therefore, it was concluded that the solvent effect observed is on the rate of the reaction and not in the Is mechanism previously postulated.

On the basis of the previous ideas it becomes obvious that there are three competitive factors to consider in relation to the observed solvent effects:

a) The stoichiometry of the spheres of solvation (both inner and outer);

b) The short-term interaction between the entering ligand and the solvents acting as ligands in the inner sphere of coordination, and

c) The combination of the previous two factors in relation to the considered mechanism itself.

As an indirect consequence of the discussion presented in the subdivision Effects of the Structure of the Binary Mixtures upon substitution reactions, it becomes clearer that the factor a) is to be considered only

in cases where an Id mechanism is applicable as it seems to be the case in the interpretation suggested by Rorabacher, et al. (34, 35) concerning the solvent effects observed in the reaction of Ni(II) with ammonia.

The short-range interactions refer to a series of interactions usually summarized under the name steric effects. These steric effects should be of minor importance in an Id mechanism, since such a mechanism has, as previously described, a dissociative mode of activation. However, it becomes critical in studying an Is mechanism.

Before extending the previous idea, let us make it clear that the steric factor associated with the stoichiometry of the inner sphere of coordination is not related to the stoichiometry of the Is mechanism.

For the Is mechanism, as previously described in this section, the ring closure of the complex formation is the rate-determining step of the reaction. Therefore, it is expected that different sizes of the molecular entities in the inner and outer sphere coordinations (specifically H_2O, CH_3OH, $(CH_3)_2CO$, and $O-(CH_2)_2-O-(CH_2)_2$ are in order of increasing relative size, 1:1.3:1.8:2.3, estimated from van der Waals radii) should constrict the ring closure by such an amount that direct correlation with the relative size of the molecular units and the size of the reacting ligands were in correlation with our experimental results summarized in the Inequalities 4-27 and 4-40. Furthermore, such an effect sustains the postulated Is mechanism in all the solvents studied.

The combination of the stoichiometric effects and the short-term interaction of the inner and outer sphere coordination led us to the consideration of Equations 4-31 and 4-32 whose implication, among others, is the thermodynamic control of the solvation of the metal ions, which obviously has a maximum, accounting for the minimum observed in $k_{12} = k_{12}$

(solvent composition) shown in Figures 4-5 to 4-7 concerning $k_{12} = k_{12}$(% non-aqueous components of the solvent mixtures).

In order to fulfill the relationship of the conductivity and viscosity (Equation 4-30), the behavior after the minimum observed (Figures 4-5 to 4-7) has to be explained in terms of the break of the short-term order of the solvent due to the molar increase of the non-aqueous components of the solvent mixtures, which are less polar.

In conclusion, the solvent effect observed upon k_{12} is primarily due to the selective solvation of the ions. This effect reaches a maximum depending upon the value of α in Equations 4-31 and 4-32. At concentrations of the non-aqueous component of the solvent mixtures higher than that characteristic of $k_{12(min)}$ this maximum effect of the selective solvation will be a competitive factor to be considered with respect to the structure of the solvent.

Figure 4-13 shows a comparison between k_{12} and k_{13} for the reactions of Zn(II) with β-PAN in the solvent mixtures dioxane-water and methanol-water leading to the 1:1 and 1:2 metal ion-ligand complexes respectively. The differences in magnitude between k_{12} and k_{13} are expected on statistical basis. Therefore, the similarity of the profiles probably reflects a conservation of the solvent effects previously described. However, the relatively faster increase of $k_{13} = k_{13}$(% non-aqueous components of the solvent mixtures) with respect to $k_{12} = k_{12}$(% non-aqueous components of the solvent mixtures) cannot be explained because of the lack of information in studies performed in other systems. Furthermore, the results summarized in Tables 3-8 to 3-12 concerning k_{13} should be accepted at this time as preliminary because the mathematical formulations (Appendix B) used for their estimation has not been fully tested since they are a novel

Estimated values of k_{13}. This is based upon a
model in which the mathematical formalism requires
further refinement (see Appendix D).

% SOLVENT x 10^{-2} (b/w)

Figure 4-13. Functional Representation of $k_{ij} = k_{ij}$ (Solvent
Composition) for Zn(II) With the Ligand β-PAN
in Solvent Mixtures

———————— k_{12} Methanol/Water   — —— —— — k_{12} Dioxane/Water

—·—— ·—— k_{13} Methanol/Water   —·· —— ··—— ·· k_{13} Dioxane/Water

approach to this type of study and should be further refined (Appendix D).

Activation Parameters and Their Correlation. - Because of the functional relationship between the different activation parameters considered in this work, listed in Tables 3-47 to 3-54, this subdivision will only consider $\Delta H^{\neq}$ in the temperature interval of 25.0 ± 15°C, and $\Delta S^{\neq}$ at 25.0°C.

At the beginning of this section, in the subdivision concerning Mechanistic Considerations, the meanings of the activation parameters and their general correlations regarding mechanisms were introduced. And, specifically, examples of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were listed in Tables 4-1 as additional characterization of an Id mechanism. In Table 4-3 the average values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ from the values summarized in Table 4-1 are presented.

TABLE 4-3

Average values for $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for the metal ions Zn(II), Cu(II), and Ni(II) using the examples given in Table 4-1.

Metal Ions	Solvent	$\Delta H^{\neq}$ (av) (kcal/mole)	$\Delta S^{\neq}$ (av) (cal/°K/mole)
Cu(II)	water	6. ± 1.	0. ± 1.
Zn(II)	water	8. ± 2.	0. ± 1.
Ni(II)	water	11. ± 2.	0. ± 1.

These average values for $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were equated with those estimated for the water interchange rate process (12, 22) and are considered to be in support of a mechanism for the ligand substitution reactions in metal ion complexes in which the rate of the water interchange is the rate-determining step. Furthermore, $\Delta S^{\neq}$, being equal to

zero within the experimental error, is considered to be in support of an outer sphere complex as an intermediate species in any I mechanism.

Although no experimental determination of the activation parameters for the reactions of the metal ions Zn(II), Cu(II), and Ni(II) with any of the ligands considered in this study in water as a solvent were conducted, the results tabulated in Tables 3-47 to 3-54 concerning the reactions of the above metal ions with the ligand β-PAN in different solvent mixtures, allow an estimation of such parameters. Two different approaches are possible for such an estimation:

a) By extrapolation to zero % of the non-aqueous component of the mixtures using the best cubic equation obtained from least squares curve fitting of $\Delta H^{\neq} = \Delta H^{\neq}$ (solvent composition) and/or $\Delta S^{\neq} = \Delta S^{\neq}$ (solvent composition) using the results reported in Tables 3-47 to 3-54.

b) By using the geometric mean between the highest and the lowest values of $\Delta H^{\neq}$ and/or $\Delta S^{\neq}$, using as before the results reported in Tables 3-47 to 3-54.

Mathematically, there is no necessity for justification of extrapolation by means of least squares curve fitting. However, the lack of physical meaning of the functions so obtained does not justify their use for extrapolation. On the other hand, a geometric mean becomes arbitrary in terms of mathematical treatment, but the values obtained in such a way are intuitively acceptable within an uncertainty of ±2 kcal/mole for $\Delta H^{\neq}$ and ±2 cal/°K/mole for $\Delta S^{\neq}$. Comparative data are listed in Table 4-4.

TABLE 4-4

Estimated values of the activation parameters for the reaction of M(II)

with the ligand β-PAN in water.

Metal Ions	$\Delta H^{\neq}$ (least square) kcal/mole	$\Delta H^{\neq}$ (geometric mean) kcal/mole	$\Delta S^{\neq}$ (least square) cal/°K/mole	$\Delta S^{\neq}$ (geometric mean) cal/°K/mole
Ni(II)	20.	15.	-9.	-7.
Zn(II)	15.	12.	-7.	-4.
Cu(II)	11.	8.	-6.	-3.

On the basis of the values listed in Table 4-4, and using the results

presented in Tables 3-47 to 3-54, the following summary can be stated:

1. In comparison with the averages of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ listed in

Table 4-3, the values of $\Delta H^{\neq}$, estimated for the same type of reactions

in pure water, are consistently higher for each metal ion than expected

in a normal Id mechanism. Similarly, the values of $\Delta S^{\neq}$ depart considerably

from zero, in contrast to a normal Id mechanism. Furthermore, neglecting

any solvent effect upon the rate of the substitution reactions of concern

(rate-determining step (Equation 4-8) expressed in terms of k_2 for an Id

mechanism) in this work the values of $\Delta H^{\neq}$ listed in the Tables 3-47 to

3-54 are higher than those listed in Table 4-3.

2. In specific terms concerning the geometric mean of $\Delta H^{\neq}$ and $\Delta S^{\neq}$

listed in Table 4-4 and considering the values listed in Tables 3-47 to

3-54, it is possible to observe that the profiles of the functional plots

of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ versus the solvent composition for the reaction of Zn(II)

with β-PAN in the solvent mixtures dioxane-water, methanol-water, and

acetone-water (Figure 4-14) show a marked dependence upon the solvent

composition. This dependency is characterized by a distinctive maximum

of $\Delta H^{\neq} = \Delta H^{\neq}$ (solvent composition) corresponding to the minimum observed

in k_{12} for the same reaction under the same conditions. Similarly,

$\Delta S^{\neq} = \Delta S^{\neq}$ (solvent composition) presents a distinctive minimum correspond-

ing to the minimum in k_{12} for the same reaction and the same conditions.

This pattern is observed for the reactions of Cu(II) and Ni(II)

with β-PAN in the solvent mixtures studied.

The first consideration is in agreement with a modified Id mechanism.

However, the fact that no studies concerning the internal rate processes of

the conformational equilibria of β-PAN, PAR, and Bipy (Figure 4-3) have been

reported in the literature, no basis of comparison can be claimed in order

to assess any agreement with an Is mechanism.

Nevertheless, in view of the solvent effect described in the second

case, it is possible to speculate that, on the hypothesis of "conservation

of mechanism" in all the solvents studied (discussion in the previous sub-

division), the presence of a maximum in $\Delta H^{\neq} = \Delta H^{\neq}$ (solvent composition) ,

presented in Figure 4-14, reflects the stoichiometry of the spheres of

coordination in the sense of increase of steric effect of the solvent

acting as a ligand. In addition, when the concentrations of the non-

aqueous component are higher than the concentration characteristic of

the maximum value of $\Delta H^{\neq}$, the break of the short-term order of the aggregates

of the solvent mixtures due to the increase in molar concentration of the

less polar solvent should be reflected by a decrease of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ as

observed in Figure 4-14.

In conclusion, the activation parameters are higher than expected

for a normal Id mechanism and are not inconsistent with the values which

might be expected in an Is mechanism and the postulated idea of the solvent

effect due to selective solvation of the metal ions. However, they are an

incomplete set of data from which no definite conclusions can be drawn
without unnecessary speculation.

Furthermore, as such, this incomplete set of data opens possibilities
of research for correlation of the activation processes of the rate processes
with the thermodynamic Equations 4-31 and 4-32.
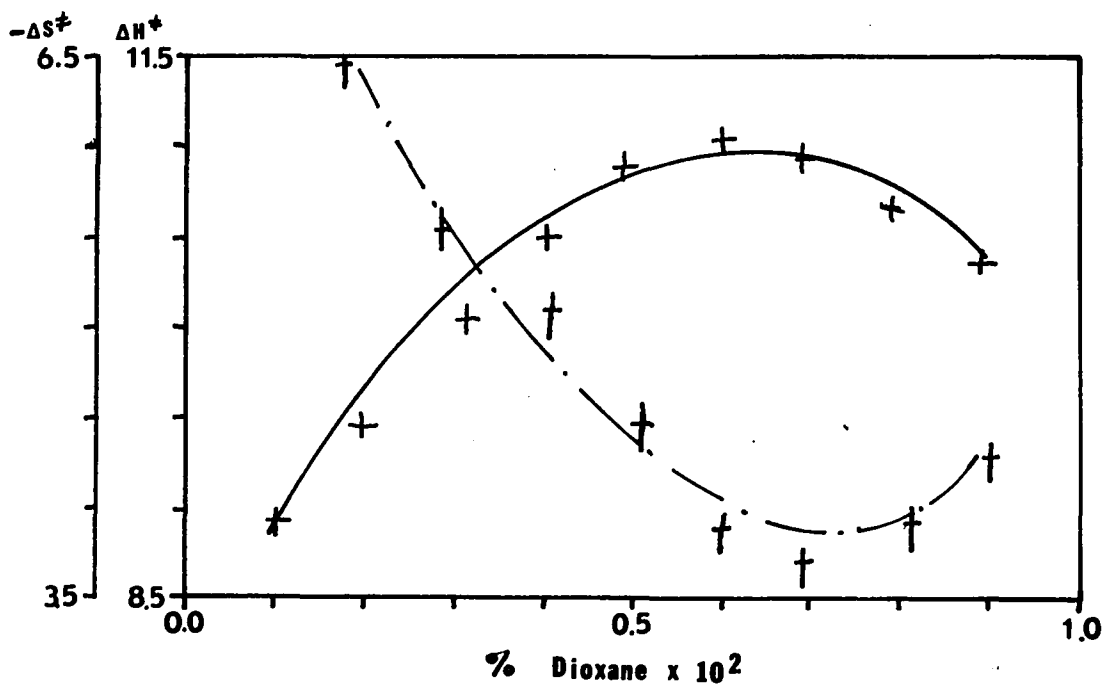
Figure 4-14. Functional Representation of $\Delta H^{\neq} = \Delta H^{\neq}$
(Solvent Composition) and $\Delta S^{\neq} = \Delta S^{\neq}$
(Solvent Composition in Solvent Mixtures.

SUMMARY AND CONCLUSION

The evidence presented in this work suggests that, for multiden-
tate ligands, an Id mechanism (as formulated by Eigen) does not properly
describe the differences in the rate of reaction among the polydentate
ligands in substitution reactions in metal ions. However, the stoichio-
metric description of the Id mechanism provides the possibility of
different rate-determining steps. By a process of elimination chelate
ring closure is postulated to be rate determining.

The B-ring closure as a rate-determining step provides a good
explanation of the possible steric effect observed. In qualitative terms
this should account for both, the variation of the rate constant with the
different ligands and the magnitude of such variation expressed in terms
of k_{12}. We have called this mechanism Is to distinguish it, at least
semantically, from the Id mechanisms.

The postulation of an Is mechanism was found to be in agreement
with the differences in k_{12} observed in the solvent mixtures methanol-
water, dioxane-water, and acetone-water.

The functional dependence of k_{12} on the solvents were interpreted
as a mutual and competitive effect of selective solvation and structural
properties of the solvents. These two competitive effects were separated
in two different regions of solvent composition. In the region of lower
concentration of the non-aqueous solvent, the selective solvation of the
metal ion by the less polar component of the mixture becomes predominant,
as a result of increasing steric hindrance which will be controlled by
the thermodynamic equilibrium of the solvolysis. The structural

characteristic of the solvent seems to predominate at higher concentrations of the non-aqueous component of the mixtures.

It is the hope of the author of this work that the observations presented will reopen the question of mechanisms of substitution reactions in metal ions.

This contribution in the studies of the solvent effects adds several controversial ideas to others previously presented by several authors, but these ideas will open basis for quantitative analysis by means of the thermodynamic characterization of the species present in solvent mixtures.

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APPENDIX A

A tabulation of the physical properties of the solvents used are presented in this appendix. These physical properties were either taken from the Critical Tables or estimated as described in the Experimental Section.

TABLE A-1

Physical Properties of Pure Solvents

Solvent	B.P. ($^\circ$C)	V.P. at 25.0°C (mm Hg)	ξ at 25.0 C	η at 25.0°C (centipoise)	D at 25.0°C (Debye)	ρ at 25.0°C (g/cm^3)	T_c ($^\circ$C)
Water	100.0	23.7	79.8	1.1	1.85	0.986	374
Methanol	64.0	120.0	32.7	0.54	1.68	0.791	240
Acetone	56.0	229.0	20.5	0.32	2.86	0.789	235
1-4 Dioxane	101.0	15.0	2.21	1.19	70.3	1.03	314

TABLE A-2

Physical Properties of the Binary Mixtures Methanol-Water

% Methanol b/w	ρ at 25.0 C (g/cm^3)	ξ at 25.0 C	η at 25.0 C (Centipoise)	E^*_{vis} (kcal)
9.4	0.981	77.0	1.33	4.40
17.7	0.970	73.0	1.62	4.75
26.8	0.959	67.0	1.83	5.66
36.4	0.945	63.0	1.87	5.58
45.9	0.924	58.0	1.80	5.33
55.5	0.906	54.0	1.62	5.12
65.8	0.886	50.0	1.37	4.98
76.5	0.854	45.0	1.14	4.70
87.9	0.824	39.0	0.96	4.50

TABLE A-3

Physical Properties of the Binary Mixtures Acetone-Water

% Acetone (b/w)	ρ at 25.0°C (g/cm^3)	ξ at 25.0°C	η at 25.0°C (centipoise)	E_{vis}^* (kcal)
8.81	0.988	76.0	0.97	-
17.6	0.975	72.0	1.13	-
27.1	0.960	66.0	1.33	-
36.3	0.944	59.0	1.35	-
44.	0.927	53.0	1.30	-
55.5	0.905	47.0	1.15	-
65.8	0.881	40.0	0.93	-
76.2	0.854	34.0	0.68	-
87.7	0.822	27.0	0.44	-

TABLE A-4

Physical Properties of the Binary Mixtures Dioxane Water

% Dioxane (b/w)	ρ at 25.0 C (g/cm^3)	ξ at 25.0 C	η at 25.0 C (centipoise)	E_{vis}^* (kcal)
5.52	0.990	78.0	0.93	3.82
10.5	0.990	76.5	1.60	3.92
21.0	0.989	65.0	1.38	4.21
31.4	0.988	48.0	1.79	4.31
41.5	0.986	40.0	1.97	4.32
51.5	0.987	23.0	1.99	3.84
61.3	0.987	25.0	1.83	3.41
71.0	0.988	18.0	1.76	3.12
80.5	0.990	12.0	1.52	3.00
92.0	0.993	8.0	1.27	2.86

APPENDIX B

The stoichiometric description of a consecutive and reversible reaction may be stated as follows:

a) $M + L \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} ML$

<div align="right">B-1</div>

b) $ML + L \underset{k_{31}}{\overset{k_{13}}{\rightleftharpoons}} ML_2$
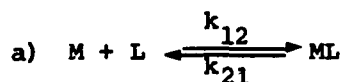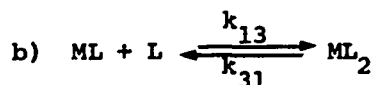
These equations are not univocally correlated to any specific rate law, therefore, it was assumed that first order kinetics, with respect to each species considered in the system (represented by Equation B-1), is important in the understanding of our study. The following equations represent the empirical rate law that fulfills such an assumption:

a) $\dfrac{d[M]}{dt} = - k_{12}[M][L] + k_{21}[ML]$

b) $\dfrac{d[L]}{dt} = - k_{12}[M][L] + k_{21}[ML] - k_{13}[ML][L] + k_{31}[ML_2]$

<div align="right">B-2</div>

c) $\dfrac{d[ML]}{dt} = k_{12}[M][L] - k_{21}[ML] - k_{13}[ML][L] + k_{31}[ML_2]$

d) $\dfrac{d[ML]_2}{dt} = k_{13}[ML][L] - k_{31}[ML_2]$

where the following boundary conditions are fulfilled:

a) $[M] = [M]_o$

b) $[L] = [L]_o$

at t = 0

<div align="right">B-3</div>

c) $[ML] = 0$

d) $[ML_2] = 0$

a) $[L] = [L]_o - [ML] - 2[ML_2]$

at t≠0

b) $[M] = [M]_o - [ML] - [ML_2]$

In Equation B-4, the cyclic conditions implied are:

a) $\dfrac{d[L]}{dt} = -\dfrac{d[ML]}{dt} - 2\dfrac{d[ML_2]}{dt}$

b) $\dfrac{d[M]}{dt} = -\dfrac{d[ML]}{dt} - \dfrac{d[ML_2]}{dt}$

In order to solve the systems of Equation B-2, several algebraic manipulations are necessary. The equation below represents an interesting step whereby mathematical representations can show possible simplifications, depending on the initial conditions:

a) $\dfrac{d[L]}{dt} = -k_{13}[L]^2 + (2k_{13}-k_{12})[L][M] + [L](k_{21}-k_{31}) +$

$- [M](2k_{21}-k_{31}) + ([L]_o - 2[M]_o)(k_{21}[L] - k_{21}) +$

$+ k_{13}([L]_o - [M]_o)$

b) $\dfrac{d[M]}{dt} = -k_{12}[M][L] + k_{21}([L] - 2[M]) - k_{21}([L]_o - [M]_o)$

c) $\dfrac{d[ML_2]}{dt} = -k_{13}[ML]^2 + k_{13}[L]_o[ML] - 2k_{13}[ML][ML_2] - k_{31}[ML_2]$

d) $\dfrac{d[ML]}{dt} = -k_{13}[L]^2 + (2k_{13} + k_{12})[M][L] - [L](k_{31} + k_{21}) +$

$+ [M](2k_{21} + k_{31}) + ([L]_o - 2[M]_o)(k_{21} + k_{13}[L]) +$

$+ k_{31}([L]_o - [M]_o)$

Let $d/dt = \mathscr{D}$, then Equations B-6b and B-6c can be rearranged as follows:

a) $\quad [M] = \dfrac{k_{21}[L] - k_{21}([L]_o - 2[M]_o)}{(\emptyset + k_{12}[L] + 2k_{21})}$

$\underline{B-7}$

b) $\quad [ML^2] = \dfrac{-k_{13}[ML]^2 + k_{13}[L]_o}{\emptyset + k_{31} + 2k_{13}[ML])}$

where the variables [M] and [ML_2] are explicitly written for substitutions in the Equations B-6a and B-6d. By substituting Equations B-7a and B-7b into B-6a and B-6d respectively, and rearranging all the terms, the following equations result:

a) $\quad \dfrac{d^3[ML]}{dt^3} + \phi([ML]) \dfrac{d^2[ML]}{dt^2} + \omega([ML]) \dfrac{d[ML]}{dt} + \Theta([ML]) = 0$

$\underline{B-8}$

b) $\quad \dfrac{d^2[L]}{dt^2} + \phi'([L]) \dfrac{d[L]}{dt} + \omega'([L]) = 0$

where $\phi[ML]$, $\omega([ML])$, and $\Theta([ML])$ are three real polynomials in [ML] whose coefficients are in general non-linear combinations of k_{ij} and the boundary conditions. $\phi'([L])$, and $\omega'([L])$ are two real polynomials in [L] whose coefficients present the same characteristics as above.

The general solutions are infinite series that are not particularly useful in analyzing our kinetic data because of the lack of precision of the stopped-flow technique. However, several particular solutions can be studied.

For the cases where β- PAN and PAR were used as ligands (Bipy is not considered in the general scope of this appendix, unless otherwise stated), the following boundary conditions are applied:

a) $\quad \dfrac{[ML]\infty}{[M]_\infty[L]_\infty} = K_1$

$\underline{B-9}$

b) $\quad \dfrac{[ML_2]\infty}{[ML]_\infty[L]_\infty} = K_2$

In Tables 2-2 and 2-3 of the experimental section, the values of K_1 and K_2 were listed for the specific conditions of the solvents, and for the pH for both β-PAN and PAR in their complexation reactions with the metals Zn^{+2}, Ni^{+2}, and Cu^{+2}.

The high magnitude of the stability constants (K_1 and K_2) for all the possible combinations of metal-ion ligand reactions justifies:

a) $k_{12} \gg k_{21}$

b) $k_{13} \gg k_{31}$

$\underline{\text{B-10}}$

Therefore, the stoichiometric description of the reaction can be simplified to:

a) $M + L \xrightarrow{k_{12}} ML$

b) $ML + L \xrightarrow{k_{13}} ML_2$
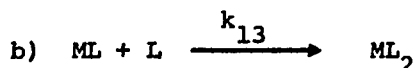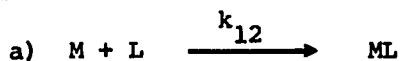
$\underline{\text{B-11}}$

The above simplification allows us to rewrite Equation B-6 as follows:

a) $\dfrac{d[M]}{dt} = -k_{12}[M][L]$

b) $\dfrac{d[L]}{dt} = -k_{13}[L]^2 + (2k_{13} - k_{12})[M][L] +$

$+ k_{13}[L]([L]_o - 2[M]_o)$

$\underline{\text{B-12}}$

c) $\dfrac{d[ML]}{dt} = -k_{13}[L]^2 + (2k_{13} + k_{12})[M][L] +$

$+ k_{13}[L]([L]_o - 2[M]_o)$

d) $\dfrac{d[ML_2]}{dt} = -k_{13}[ML]^2 + k_{13}[L]_o[ML] - 2k_{13}[ML_2][ML]$

This system might be analyzed by considering three particular cases where the initial conditions compelled specific mathematical treatment for

the kinetic data. These cases are:

I) $[M]_o \gg [L]_o$

II) $[M]_o = (1/2)[L]_o$ B-13

III) $[M]_o \ll [L]_o$

Case I. - ($[M]_o \gg [L]_o$)

Since $K_1 > K_2$, we expect that a significant quantity of ML_2, should not be formed (specific examples are shown in the experimental section), therefore, Equations B-2a and B-2c become:

$$- \frac{d[L]}{dt} = \frac{d[ML]}{dt} = k_{obs}[L]$$ B-14

where

$$k_{obs} = k_{12}[M]_o$$

with the general solution:

$$[L] = [L]_o \exp(-k_{obs}t)$$ B-15

A plot of $\ln[L]$ versus time, or $\ln[ML]$ versus time should have a slope $\pm k_{obs}$. This case was also used in analyzing the data obtained from the reaction of Bipy with Zn^{+2}.

Case II. - ($[L]_o = 2[M]_o$)

Equations B-12b and B-12c become:

a) $\frac{d[L]}{dt} = \frac{-k_{12}}{2}[L]^2 - (\frac{2k_{13} - k_{12}}{2})[L][ML]$

                                                              B-16

b) $\frac{d[ML]}{dt} = \frac{k_{12}}{2}[L]^2 + (\frac{2k_{13} + k_{12}}{2})[L][ML]$

Equation B-16b can be rewritten as:

$$\left(\mathscr{D} - \frac{2k_{13} + k_{12}}{2}[L]\right)[ML] = \frac{k_{12}}{2}[L]^2 \qquad \text{B-17}$$

Substitution of Equation B-17 into B-16a, and the simplification of the resulting equation gives:

$$\frac{d^2[L]}{dt^2} + 2k_{13}[L]\frac{d[L]}{dt} + (2k_{12}k_{13} - k_{12}^2)[L]^3 = 0 \qquad \text{B-18}$$

Equation B-18 has a very complex general solution from which the following particular solution can be derived:

$$\frac{1}{[L]}\Bigg|_{[L]_o}^{[L]_t} = (-k_{13} \pm \sqrt{k_{13}^2 + 8k_{12}k_{13} - k_{12}^2}\,)t \qquad \text{B-19}$$

for the condition where [L] << 1M. Therefore, a plot of 1/[L] versus time should yield a linear relationship with slope k_{obs}.

$$k_{obs} = (-k_{13} \pm \sqrt{k_{13}^2 + 8k_{12}k_{13} - k_{12}^2}\,) \qquad \text{B-20}$$

where k_{12} is known from Case I.

Case III. - ([M]$_o$ < < [L]$_o$)

Equations B-2a, B-2c, and B-2d can be simplified to:

a) $\dfrac{d[M]}{dt} = -k_1[M]$

b) $\dfrac{d[ML]}{dt} = k_1[M] - k_2[ML]$ $\qquad$ B-21

c) $\dfrac{d[ML_2]}{dt} = k_2[ML]$

where:

$$k_1 \cong k_{12}[L]_o; \qquad \text{and} \qquad k_2 \cong k_{13}[L]_o$$

Keeping in mind the balance of reactants and products given
by Equation B-4b, the general solution will be:

a) $[ML] = \dfrac{k_1 [M]_o}{k_2 - k_1} (\exp(-k_1 t) - \exp(-k_2 t))$

$$B-22$$

b) $[ML_2] = \dfrac{k_2 [M]_o}{k_2 - k_1} (\exp(-k_1 t)) - \dfrac{(2k_2 - k_1)[M]_o}{k_2 - k_1} \exp(-k_2 t) + [M]_o$

Experimentally, it was found that ML and ML_2 present very similar
visible spectra with extinction coefficients ξ equal within the experimental
error. Therefore, neither the absorption of ML nor that of ML_2 can be
observed individually, but their sum can be. If we add Equations B-22a
and B-22b after rearranging, we obtain:

$$\dfrac{[ML] + [ML_2]}{[M]_o} - 1 = \dfrac{k_1 + k_2}{k_2 - k_1} \exp(-k_1 t) - \dfrac{2k_2}{k_2 - k_1} \exp(-k_2 t) \qquad B-23$$

Let $k_1 = \alpha + k_2$, and substituting into Equation B-23:

$$\dfrac{[ML] + [ML_2]}{[M]_o} - 1 = (-\dfrac{2k_2 + \alpha}{\alpha} \exp(-\alpha t) + \dfrac{2k_2}{\alpha}) \exp(-k_2 t) \qquad B-24$$

Depending on the value of α, three possible cases may be discussed:

a) $\alpha = 0$; the problem becomes trivial in this case, since $k_1 = k_2$,
but it does not exclude the possibility of $k_2 < k_1$.

Providing that the absolute value of α does not differ by more
than one order of magnitude from either k_1 or k_2, the other two possibilities
are:

b) $\alpha < 0$; in Equation B-24 it is observed that:

$$(2k_2 + \alpha)\exp(-\alpha t) > 2k_2 \qquad B-25$$

therefore, the predominant function will be:

$$\frac{[ML] + [ML_2]}{[M]_o} - 1 = \frac{2k_2 + \alpha}{\alpha} \exp{-(\alpha + k_2)t} = \frac{2k_2 + \alpha}{\alpha} \exp(-k_1 t) \quad \underline{B\text{-}26}$$

c) $\alpha > 0$; in Equation B-24 it is observed that:

$$(2k_2 + \alpha) \exp(-\alpha t) < 2k_2 \qquad\qquad \underline{B\text{-}27}$$

therefore, the predominant function becomes:

$$\frac{[ML] + [ML_2]}{[M]_o} - 1 = \frac{2k_2 + \alpha}{\alpha} \exp(-k_2 t) \qquad \underline{B\text{-}28}$$

Equations B-26 and B-28 imply that a plot of $\ln\left(\dfrac{[ML] + [ML_2]}{[M]_o} - 1\right)$ versus time should have a linear profile for most of the reaction time, but the slope may be either k_1 or k_2; consequently, the estimation of k_2 becomes a heuristic problem which is complemented by the results discussed in Case II.

The general validity of the approximations presented above was confirmed by means of an analog-like simulation in a 360-50 IBM Computer, using the special program CSMP which is described in IBM publications (52 - 56). The stoichiometric Equation B-1 and its empirical rate law (Equation B-2) were used as the simulating system according to the analog symbolic representation shown in Figure B-1. The analog output is presented, case by case, in Figures B-2 through B-7.

$$-k_{12}[M][L] + k_{21}[ML]$$

$\mathscr{D}[M]$

$\rightarrow [M]$

$[M]_0$

k_{12}

$\mathscr{D}[L]$

$\rightarrow [L]$

$-k_{12}[M][L] + k_{21}[ML] - k_{13}[ML][L] + k_{31} \cdot [ML_2]$

$[L]_0$

k_{13}

$\mathscr{D}[ML]$

$\rightarrow [ML]$

k_{21}

$+k_{12}[M][L] - k_{21}[ML] - k_{13}[ML][L] + k_{31}[ML_2]$

$\mathscr{D}[ML_2]$

$\rightarrow [ML_2]$

k_{31}

$+k_{13}[ML][L] - k_{31}[ML]$
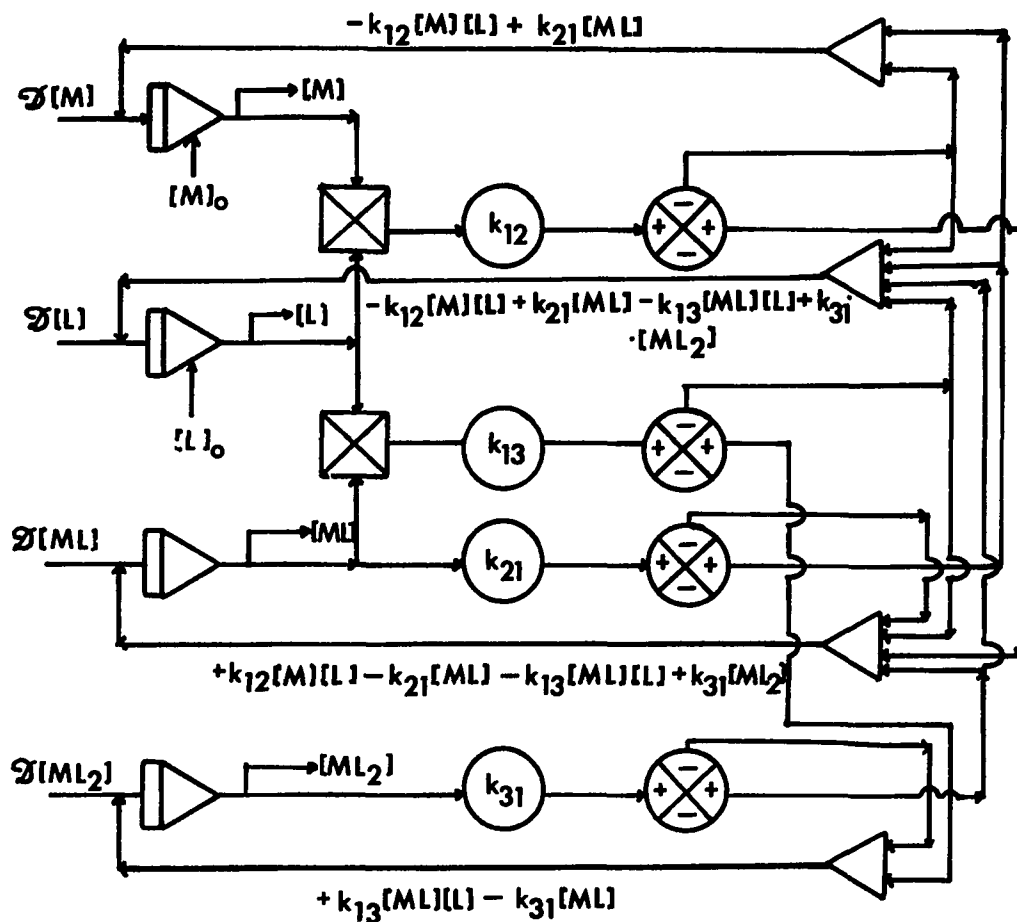
Figure B-1. Symbolic Representation of the Analog Simulation of the Stoichiometric System Formulated in Equation B-1 and Correlated to Equation B-2

Integrator

Function Adding

Function Multiplier

Constant Multiplier
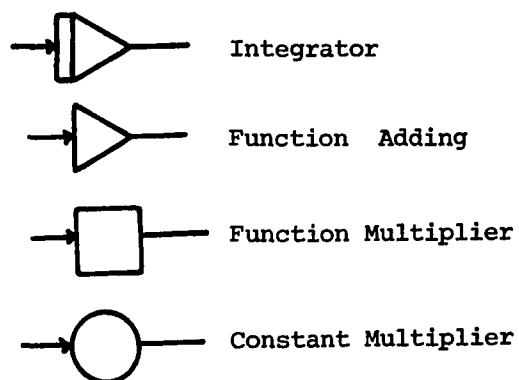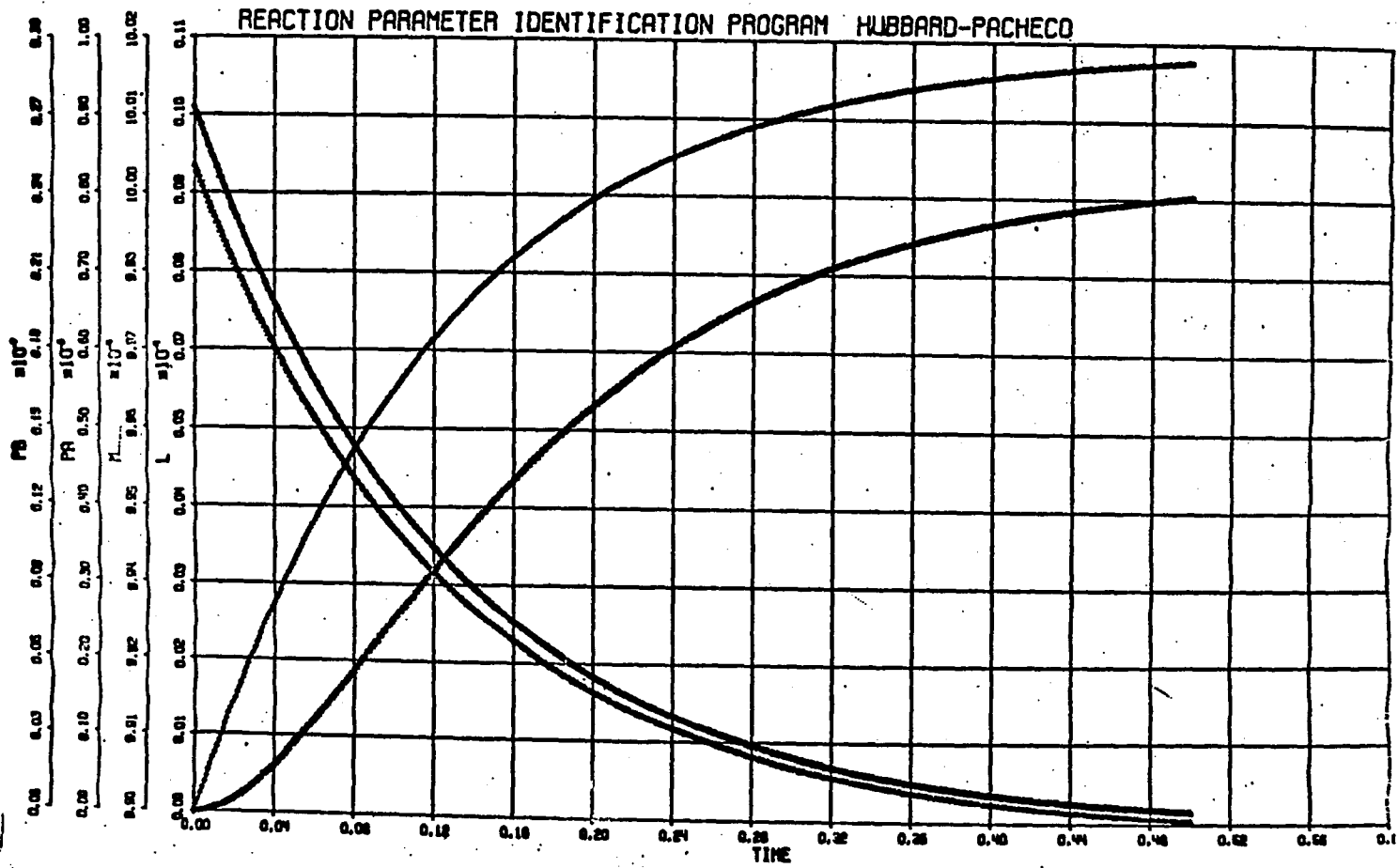
Figure B-2. Analog Representation of Equation B-2 for Experiment Type I

REACTION PARAMETER IDENTIFICATION PROGRAM   HUBBARD-PACHECO
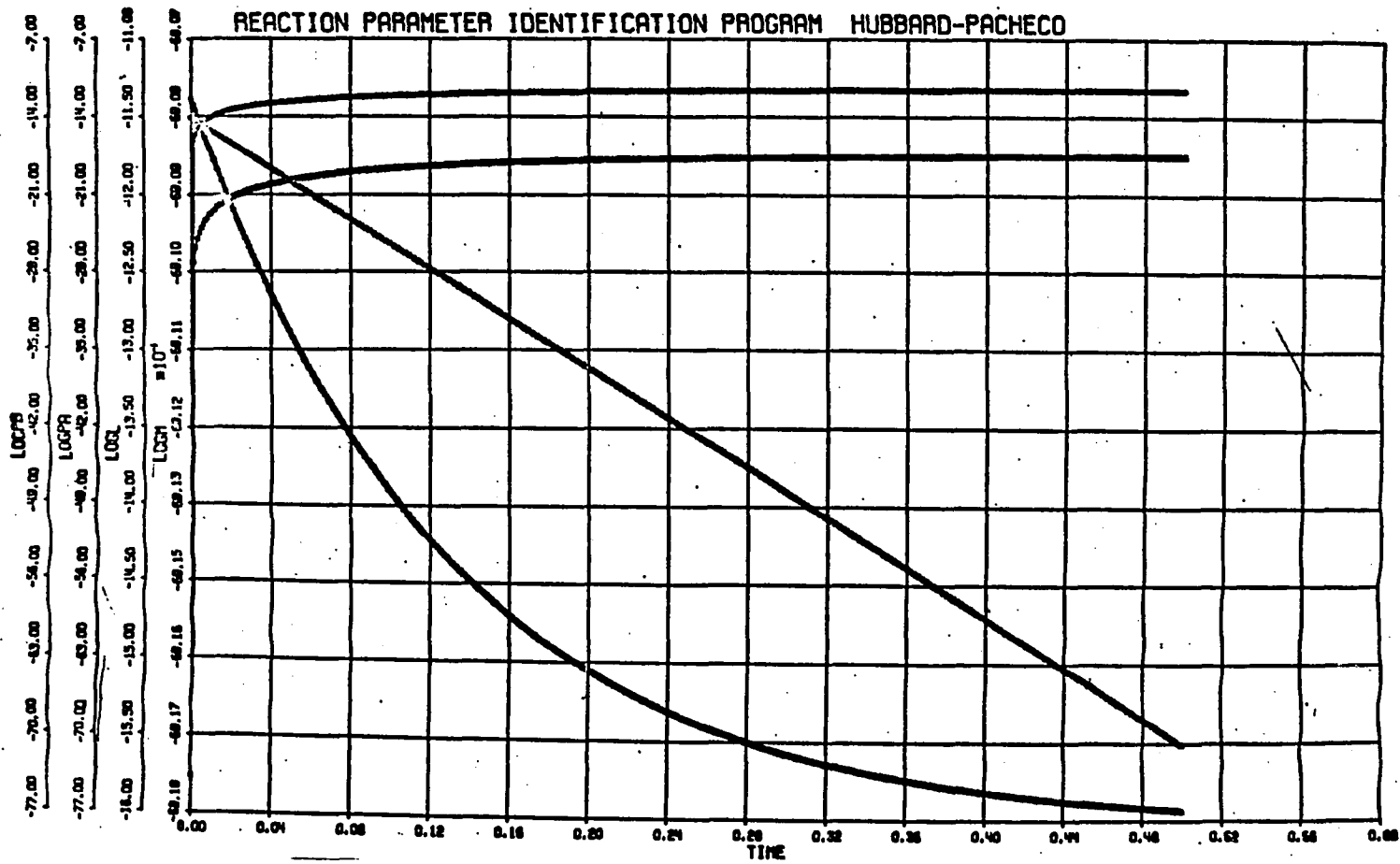
Figure B-3.   Analog Representation of Equation B-2 for Experiment Type I

REACTION PARAMETER IDENTIFICATION PROGRAM   HUBBARD-PACHECO
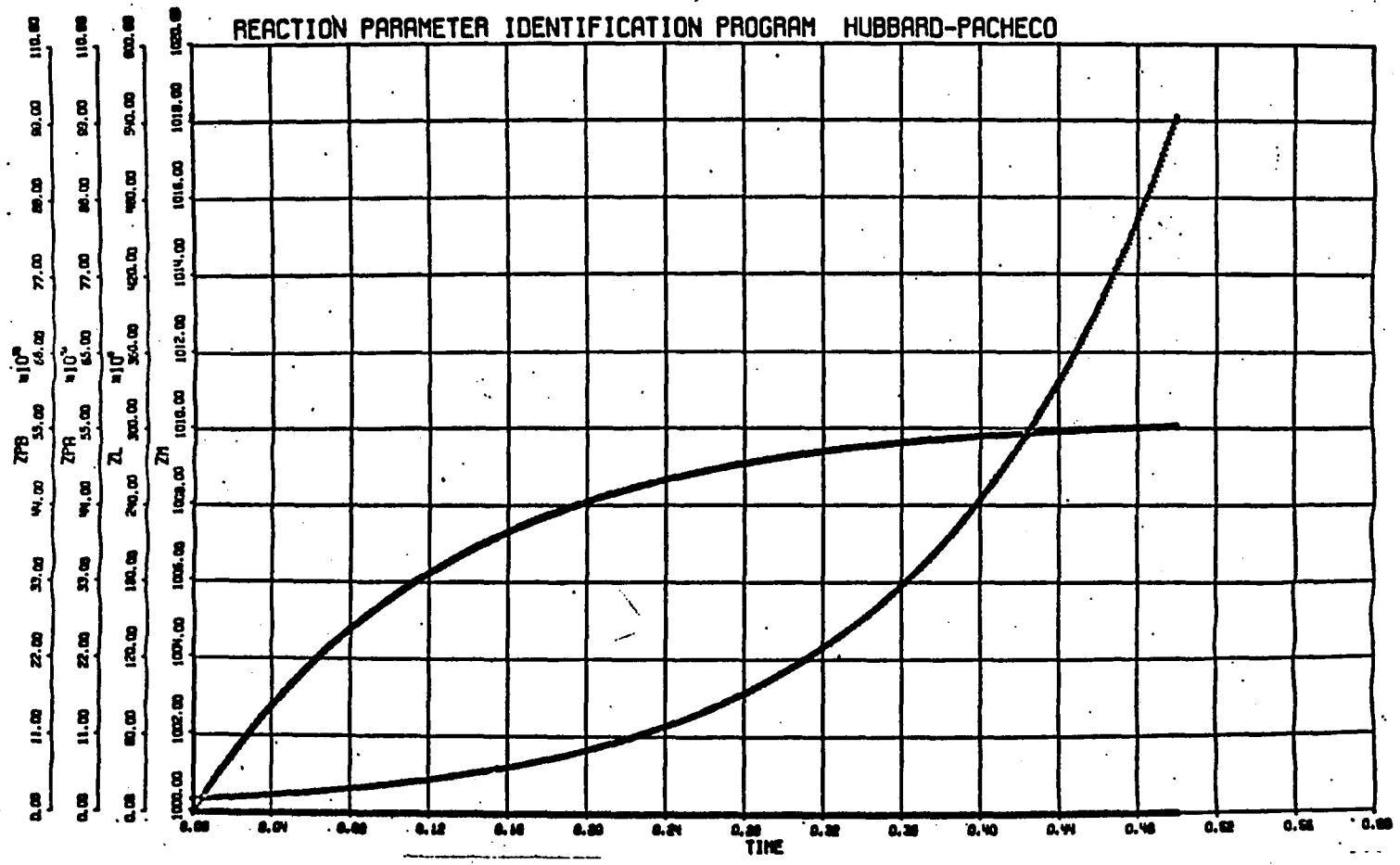
Figure B-4.   Analog Representation of Equation B-2 for Experiment Type II

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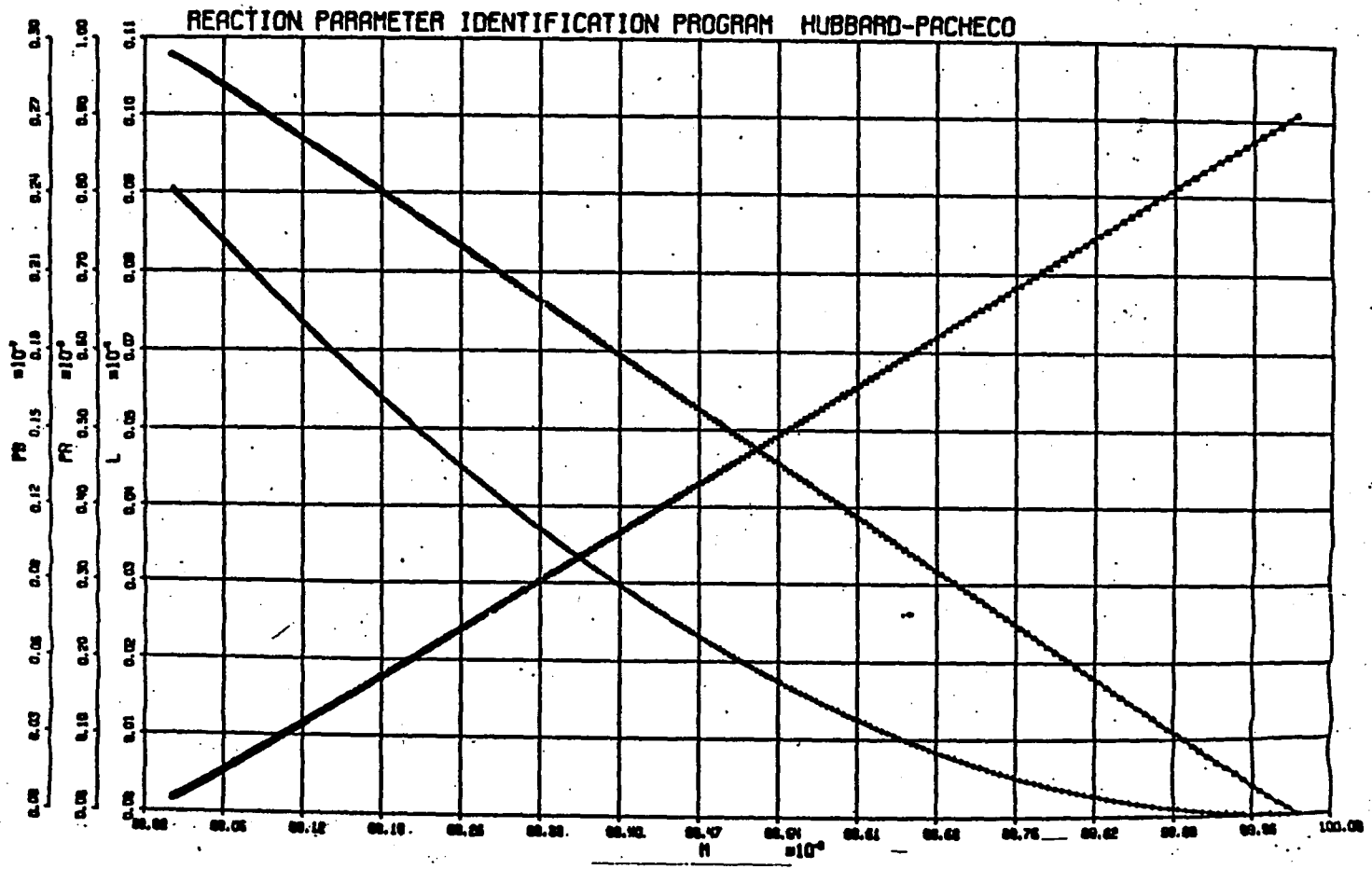
Figure B-5. Analog Representation of Eqation B-2 for Experiment Type II
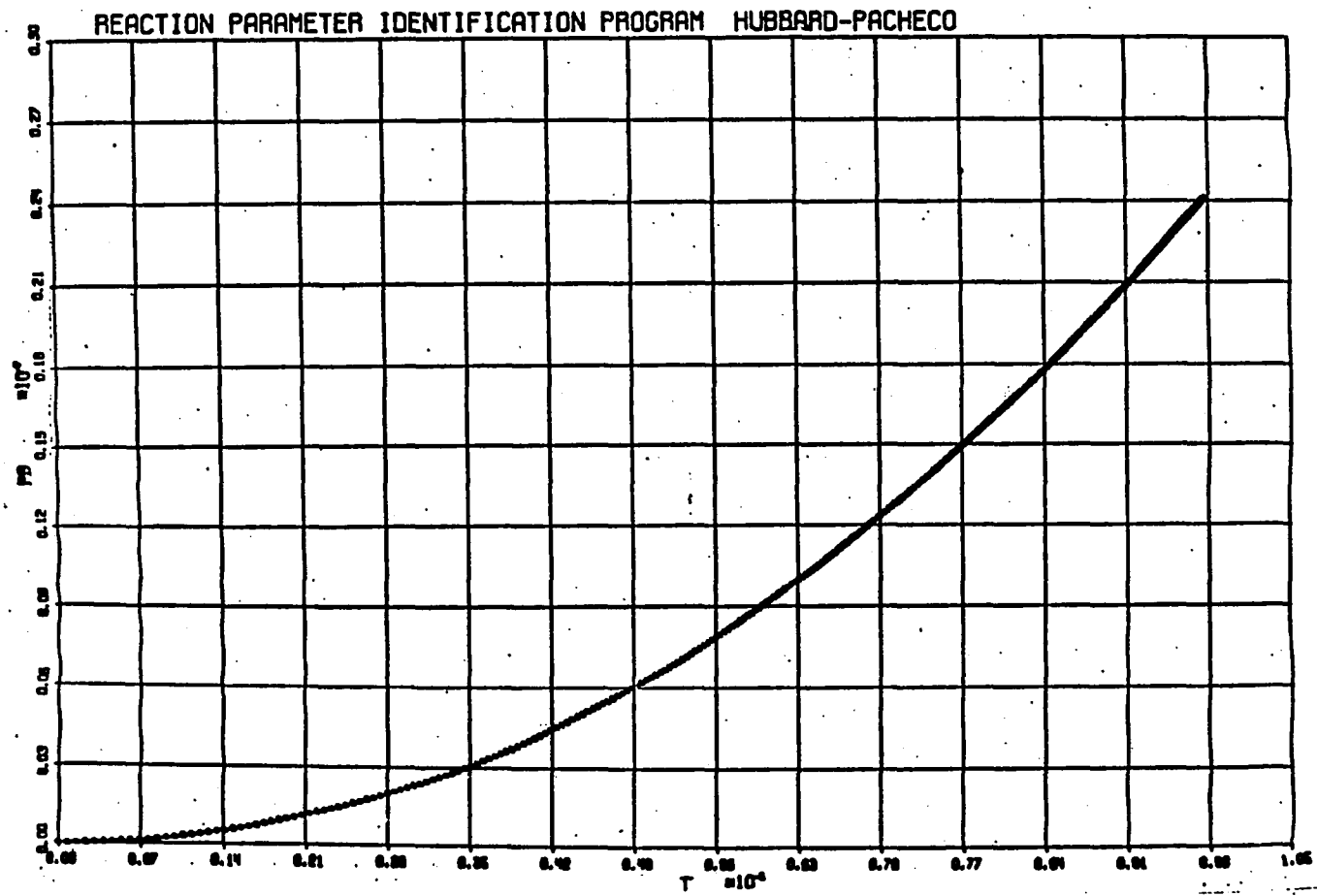
Figure B-6. Analog Representation of Equation B-2 for Experiment Type III
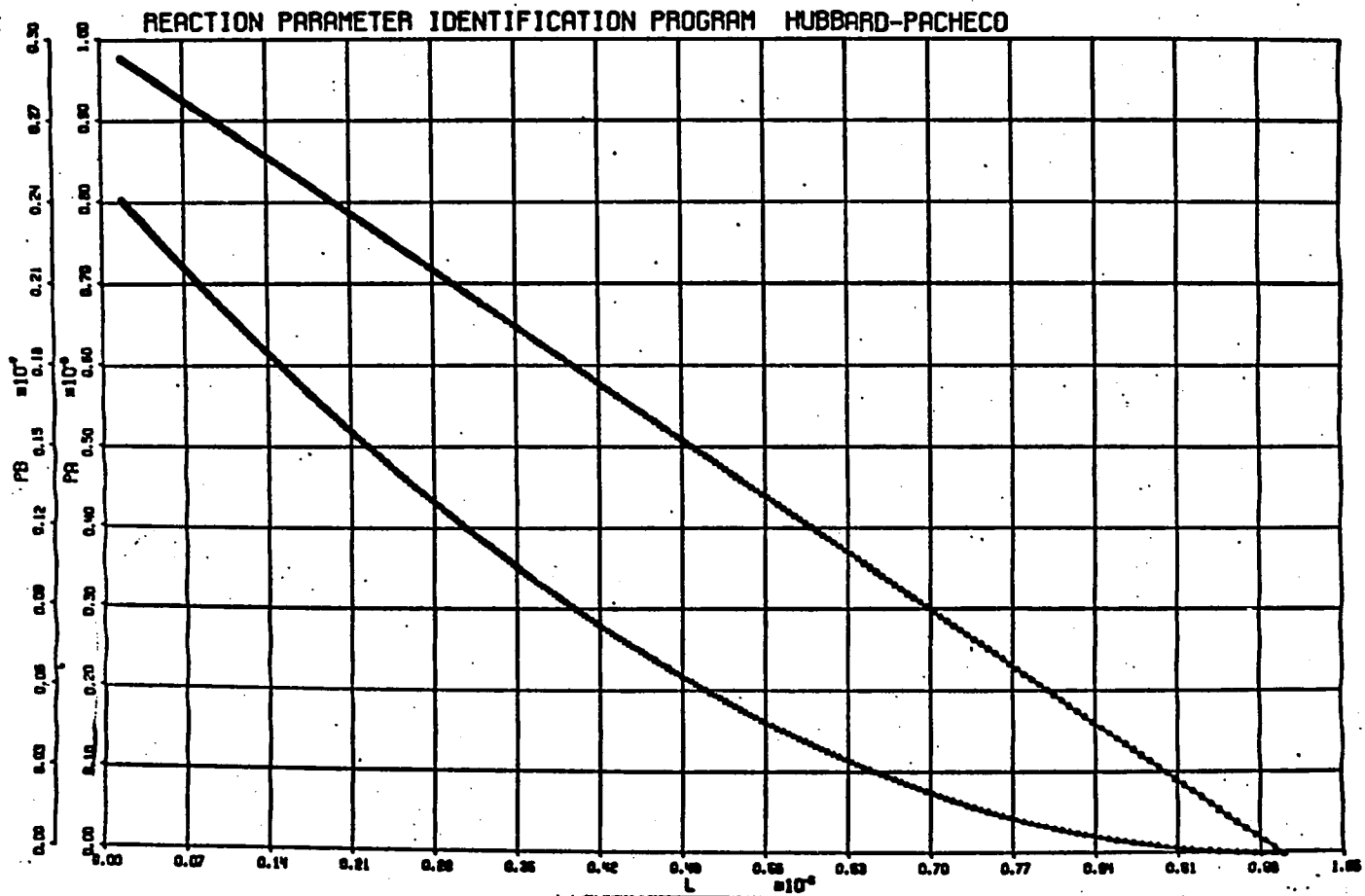
Figure B-7. Analog Representation of Equation B-2 for Experiment Type III

APPENDIX C

- DLOG%I< -

-1.2019 -*

-1.3019 -

-1.4019 -

-1.5019 -

-1.6019 -

-1.7019 -

-1.8019 -

-1.9019 -

-2.0019 -

-2.1019 -

-2.2019 -

TIME(MM)	TIME(SECONDS)	DEFLECTION
0.0	0.0	7.50
2.000	0.080	5.80
4.000	0.160	4.00
6.000	0.240	3.00
8.000	0.320	2.00
10.000	0.400	1.00
12.000	0.480	0.80
14.000	0.560	0.50
16.000	0.640	0.30

ADSORBANCE	LOG10(D(T)-D(INF))	D(T)-D(INF)
0.11394E 00	-0.11791E 01	0.66203E-01
0.99423E-01	-0.12867E 01	0.51682E-01
0.84559E-01	-0.14339E 01	0.36819E-01
0.76517E-01	-0.15410E 01	0.28776E-01
0.68620E-01	-0.16803E 01	0.20880E-01
0.60865E-01	-0.18819E 01	0.13124E-01
0.59330E-01	-0.19359E 01	0.11590E-01
0.57038E-01	-0.20316E 01	0.92980E-02
0.55517E-01	-0.21092E 01	0.77768E-02

0.0   0.0500   0.1000   0.1500   0.2000   0.2500   0.3000   0.3500   0.4000   0.4500   0.5000

XSCALE# 0.49999990E-02   YSCALE# 0.20000000E-01

Figure C-1. Computer Analysis of Experimental Data

```
IMPUT DEFL
192.71.55.5.42.0.31.5.25.5.19.5.15.11
..PPF PH.5.5 IN WATE     4
IMF =     0.32566E-01
 TIME    DEFLECTION   REFLECTANCE   LOG10(D(T)-D(INF)   D(T)-D(INF)
 0.0      92.00      0.4936E-01    -0.17775E+01        0.1669E-01
 3.00     71.00      0.4539E-01    -0.18920E+01        0.1282E-01
 6.00     55.50      0.4356E-01    -0.20003E+01        0.9992E-02
 9.00     42.00      0.4011E-01    -0.21266E+01        0.7540E-02
 12.00    31.50      0.3821E-01    -0.22485E+01        0.5643E-02
 15.00    25.50      0.3713E-01    -0.23409E+01        0.4562E-02
 18.00    19.50      0.3605E-01    -0.24578E+01        0.3485E-02
 21.00    15.00      0.3524E-01    -0.25722E+01        0.2678E-02
 24.00    11.00      0.3493E-01    -0.27073E+01        0.1962E-02
 **********************************************
            -0.881914E+00        -0.177590E+01
 **********************************************
 FLOG(I)
 1.7775 -*

 1.8705 -
              ◆

 1.9634 -
            ◆

 2.0564 -
                    ◆

 2.1494 -                                          ·

 2.2424 -                      ◆

 2.3354 -                              ◆

 2.4283 -                                    ◆

 2.5213 -                                  ◆

 2.6143 -

 2.7073 -                                              ◆
         .........................................
          0.0    4.00    8.00   12.00   16.00   20.00   24.00

XSCALE= -0.39999998E+00        YSCALE= 0.18595275E-01
```

Figure C-2. Computer Analysis of Experimental Data

ARE YOU FAMILIAR WITH THIS PROGRAM? IF YES WRITE 0, IF NO WRITE 1
?0
  INPUT: # RUNS WITH EQUAL CONDITIONS,
           # OF POINTS,
           IDEFL, 1 IF O.D. DECREASE, 0 OTHERWISE
           ITIME,0 IF TIME IS RANDOM, DELTA T OTHERWISE

?3,9,1,3
 INPUT TITLE 20 CHARACTERS ABSOLUTE
?..PAR PH 5.8 IN WATER......
  INPUT: P, O, Y, ICCIE, IFRE, TOTIME
?244,263,10,3+++20,3,0,5
  INPUT DEFL
?69.0,53,42-1,31,24,18,13.5,9.5,7.5
..PAR PH 5.8 IN WATE   1
INF =   0.32566E-01

TIME	DEFLECTION	ABSORRANCE	LOG1(D(T)-D(INF)	D(T)-D(INF)
0.0	69.00	0.5787E-01	-0.15971E+01	0.2588E-01
3.00	53.00	0.5129E-01	-0.17147E+01	0.1929E-01
6.00	41.00	0.4741E-01	-0.18284E+01	0.1437E-01
9.00	31.00	0.4374E-01	-0.19516E+01	0.1112E-01
12.00	24.00	0.4115E-01	-0.20541E+01	0.8628E-02
15.00	18.00	0.3907E-01	-0.21901E+01	0.6455E-02
18.00	13.50	0.3740E-01	-0.23156E+01	0.4872E-02
21.00	9.50	0.3594E-01	-0.24649E+01	0.3390E-02
24.00	7.50	0.3523E-01	-0.25772E+01	0.2673E-02

          -0.943832E+00   -0.158694E+01

·DLOG(I)
1.7450 -•

1.8432 -
            •

1.9415 -
               •

2.0397 -
                  •

2.1380 -

2.2362 -
                     •

2.3345 -
                        •

2.4327 -
                           •

2.5310 -

2.6292 -
                              •

2.7274 -   •
      ....
      0.0   4.00   8.00   12.00   16.00   20.00   24.00

SCALE= -0.39999996E+00   YSCALE= 0.19648654E-01

Figure C-3. Computer Analysis of Experimental Data

DINF #   -0.74288E 00

DLOG$I<

TIME	DEFLECTION	ABSORBANCE	LOG10(D(INF)-D(T))	D(INF)-D(T)
0.0	127.00	0.17442E 00	-0.24531E 00	0.56845E 00
2.000	95.00	0.26268E 00	-0.31859E 00	0.48019E 00
4.000	72.00	0.33943E 00	-0.39421E 00	0.40345E 00
6.000	56.00	0.40214E 00	-0.46758E 00	0.34074E 00
8.000	45.00	0.45119E 00	-0.53508E 00	0.29169E 00
10.000	36.00	0.49589E 00	-0.60734E 00	0.24698E 00
12.000	29.00	0.53416E 00	-0.68044E 00	0.20872E 00
14.000	23.00	0.56988E 00	-0.76195E 00	0.17300E 00
16.000	19.00	0.59543E 00	-0.83137E 00	0.14745E 00
18.000	16.00	0.61563E 00	-0.89537E 00	0.12724E 00
20.000	13.00	0.63682E 00	-0.97447E 00	0.10605E 00
22.000	11.00	0.65155E 00	-0.10394E 01	0.91330E-01
24.000	9.00	0.66679E 00	-0.11187E 01	0.76090E-01

****** APPARENT K = -0.417441E 00 INTERCEPTION = -0.247265E 00 ******

-0.1365
-0.2313
-0.3262
-0.4211
-0.5160
-0.6108
-0.7057
-0.8006
-0.8955
-0.9903
-1.0852

0.0   1.8000   3.6000   5.4000   7.2000   9.0000   10.8000   12.6000   14.4000   16.2000   18.0000

XSCALE# 0.17999995E 00   YSCALE# 0.18974960E-01

Figure C-4. Computer Analysis of Experimental Data

SOLUTIONS A3 & 5600

DINF #   0.12688E 01

DLOGSIK

TIME	DEFLECTION	ABSORBANCE	LOG10(D(INF)-D(T))	D(INF)-D(T)
0.0	132.00	0.25062E 00	0.78432E-02	0.1C182E 01
2.000	105.50	0.33761E 00	-0.30939E-01	0.93124E 00
4.000	84.00	0.42375E 00	-0.73093E-01	0.84510E 00
6.000	69.00	0.49589E 00	-0.11185E 00	0.77295E 00
8.000	58.00	0.55764E 00	-0.14801E 00	0.71120E 00
10.000	48.00	0.62258E 00	-0.18959E 00	0.64626E 00
12.000	41.00	0.67461E 00	-0.22604E 00	0.59423E 00
14.000	35.00	0.72478E 00	-0.26435E 00	0.54407E 00
16.000	31.50	0.75696E 00	-0.29083E 00	0.51188E 00
18.000	27.00	0.80219E 00	-0.33100E 00	0.46666E 00
20.000	24.00	0.83519E 00	-0.36286E 00	0.43366E 00
22.000	21.50	0.86475E 00	-0.39351E 00	0.40410E 00
24.000	19.00	0.89646E 00	-0.429C1E 00	0.37239E 00
26.000	17.00	0.92361E 00	-0.46189E 00	0.34523E 00
28.000	15.00	0.95258E 00	-0.49994E 00	0.31627E 00
30.000	14.00	0.96782E 00	-0.52139E 00	0.30103E 00

****** APPARENT K = -0.407987E 00 INTERCEPTION = -0.467159E-02 ******

0.42 sec^{-1}

YSCALE# 0.10584675E-01

KSCALE#   C.29999995E CO

Figure C-5. Computer Analysis of Experimental Data

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DINF #   -0.14267L 00

OLOGXI<
-0.7723

TIME	DEFLECTION	ABSCREANCE	LOG10DT<-D$INF<<	D$T<-D$INF<
0.0	15.50	0.326C6E 00	-0.73662E 00	0.18339E 00
2.000	11.50	0.27084E CC	-0.89222E 00	0.12817E 00
4.C00	9.00	0.23558E 00	-0.10136E 01	0.96910E-01
6.000	7.00	0.21C1CE CC	-0.11341E 01	0.73429E-01
8.000	5.50	0.19928E 00	-0.12471E 01	0.56615E-01
1C.000	4.00	0.18310E 00	-0.13933E 01	0.40429E-01
12.000	3.50	0.17783E 00	-0.14539E 01	0.35164E-01
14.000	2.50	0.16749E 00	-0.16051E 01	0.24824E-01
16.000	2.00	0.16241E CC	-0.17046E 01	0.19744E-01
18.000	1.50	0.15739E 00	-0.18320E 01	0.14723E-01
20.C00	1.00	0.15243E 00	-0.20106E 01	0.97598E-02

-0.9265 -

-1.0807 -

-1.2348 -

-1.3890 -

7.35 sec.^{-1} B X 3

-1.5432 -

8.5 "

-1.6973 -

-1.8515 -

-2.0057 -

-2.1599 -

-2.3140 -

| 0.0 | 1.8000 | 3.6000 | 5.4000 | 7.2000 | 9.0000 | 10.8000 | 12.6000 | 14.4000 | 16.2000 | 18.0000 |

XSCALE# 0.17999995E 00   YSCALE# 0.30833758E-01

Figure C-6.   Computer Analysis of Experimental Data

ERROR MINIMIZED - SCALAR IN ABSORBANCE   INPUT VARIABLE - ABSORBANCE

NO: OF ITERATIONS	K	AZO<	AZINF<
0	0.7965E 01	0.1912E 00	0.7918E-01
1	U.6953E 01	0.1912E 00	C.7131E-01
2	U.70C8E 01	0.1712E 00	0.7065E-01
3	U.7007E 01	0.1912E 00	0.7065E-01

- DLOGZI< -

STANDARD DEVIATION   0.2E-02   0.0   0.1E-04
STD. DEV. OF ABOVE PARAMETERS BASED ON STD. DEV. OF 0.10E-04 SCALAR IN ABSORBANCE
VALUE FOR THIS RUN 0.15E-02

TIME	PC. REACT.	A OBSD.	A CALC.	DELTA
0.2000E-01	13.08	0.1761	0.1754	0.0007
0.4000E-01	24.44	0.1615	0.1617	-0.0002
0.6000E-01	34.32	0.1521	0.1498	0.0023
0.8000E-01	42.91	0.1383	0.1394	-0.0011
0.1000E 00	50.38	0.1293	0.1304	-0.0011
0.1200E 00	56.87	0.1206	0.1226	-0.0021
0.14CCE 00	62.51	0.1163	0.1158	0.0004
0.1600E 00	67.41	0.1120	0.1099	0.0021
0.1800E 00	71.67	0.1061	0.1048	0.0013
0.2000E 00	75.38	0.1010	0.1003	0.0007
0.2200E 00	78.60	0.0953	0.0964	-0.0012
0.2400E 00	81.40	0.0912	0.0931	-0.0019
0.2600E 00	83.83	0.0896	0.0901	-0.0006
0.2800E 00	85.94	0.0871	0.0876	-0.0004
0.3000E 00	87.78	0.0871	0.0854	0.0018

-0.9256 -*

-1.0256 -

-1.1256 -

-1.2256 -

-1.3256 -

-1.4256 -

-1.5256 -

-1.6256 -

-1.7256 -

-1.8256 -

-1.9256 -
....
0.0   0.0300   0.0600   0.0900   0.1200   0.1500   0.1800   0.2100   0.2400   0.2700 C.3000

XSCALE# 0.29999998E-02   YSCALE# 0.20000000E-01
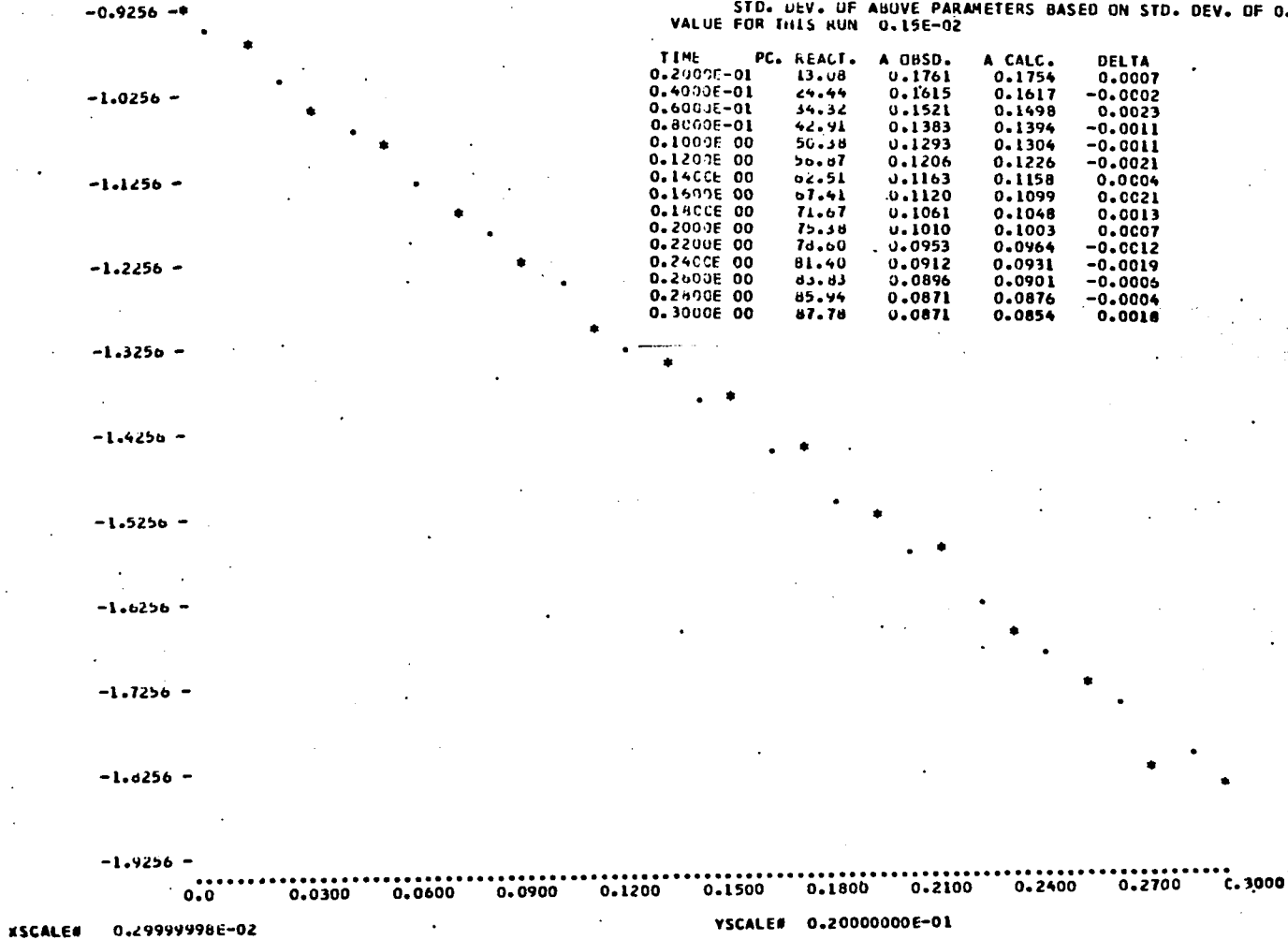
Figure C-7.   Computer Analysis of Experimental Data

SOLUTIONS C-Y # 4

INPUT VARIABLE - ABSORBANCE

ERROR MINIMIZED - SCALAR IN ABSORBANCE
NO. OF ITERATIONS

	K	AXOC	AXINFC
0	0.1223E 02	0.3882E 00	0.1861E 00
1	0.1091E 02	0.3882E 00	0.1751E 00
2	0.1092E 02	C.3882E 00	0.1739E 00

STANDARD DEVIATION   0.2E-02   0.0   0.2E-04
STD. DEV. OF ABOVE PARAMETERS BASED ON STD. DEV. OF 0.10E-04 SCALAR IN ABSORBANCE
VALUE FOR THIS RUN 0.24E-02

TIME	PC. REACT.	A OBSD.	A CALC.	DELTA
0.1200E-01	12.29	0.3571	0.3619	-0.0047
0.2400E-01	23.06	0.3352	0.3388	-0.0035
0.3600E-01	32.52	0.3212	0.3185	0.0027
0.4800E-01	40.81	0.3010	0.3007	0.0003
0.6000E-01	48.08	0.2817	0.2851	-0.0034
0.7200E-01	54.46	0.2730	0.2715	0.0015
0.8400E-01	60.05	0.2608	0.2595	0.0013
0.9600E-01	64.96	0.2490	0.2490	0.0000
0.1080E 00	69.27	0.2398	0.2397	0.0000
0.1200E 00	73.04	0.2341	0.2317	0.0024
0.1320E 00	76.35	0.2263	0.2246	0.0017
0.1440E 00	79.26	0.2175	0.2183	-0.0008
0.1560E 00	81.81	0.2142	0.2129	0.0014
0.1680E 00	84.04	0.2068	0.2081	-0.0013
0.1800E 00	86.00	0.2015	0.2039	-0.0024

- DLOG$IC -

-0.7581 -
-0.9081 -
-1.0581 -
-1.2081 -
-1.3581 -
-1.5081 -
-1.6581 -
-1.8081 -
-1.9581 -
-2.1081 -
-2.2581 -

```
      0.0    0.0300  0.0600  0.0900  0.1200  0.1500  0.1800  0.2100  0.2400  0.2700  0.3000
```

YSCALE$ 0.29999997E-01

XSCALE$ 0.2999999BE-02

Figure C-8. Computer Analysis of Experimental Data

SOLUTIONS D-2 # 3 5300 A

DLOG&I<

DINF #   0.70149E 00

TIME	:	DEFLECTION	ABSORBANCE	LOG10(D(INF)-D(T))	D(INF)-D(T)
0.0		73.00	0.32872E 00	-0.42856E 00	0.37277E 00
1.000		55.00	0.38595E 00	-0.50094E 00	0.31554E 00
2.000		45.00	0.42877E 00	-0.56428E 00	0.27272E 00
3.000		37.00	0.46636E 00	-0.62868E 00	0.23514E 00
4.000		30.00	0.50214E 00	-0.70038E 00	0.19935E 00
5.000		24.50	0.53249E 00	-0.77210E 00	0.16901E 00
6.000		20.00	0.55899E 00	-0.84619E 00	0.14250E 00
7.000		17.00	0.57761E 00	-0.90699E 00	0.12389E 00
8.000		14.50	0.59376E 00	-0.96764E 00	0.10774E 00
9.000		12.00	0.61053E 00	-0.10411E 01	0.90967E-01
10.000		10.00	0.62442E 00	-0.11131E 01	0.77068E-01
11.000		8.00	0.63878E 00	-0.12027E 01	0.62710E-01
12.000		7.00	0.64614E 00	-0.12569E 01	0.55349E-01
13.000		6.00	0.65363E 00	-0.13200E 01	0.47860E-01
14.000		5.00	0.66125E 00	-0.13953E 01	0.40241E-01
15.000		4.00	0.66901E 00	-0.14883E 01	0.32486E-01

****** APPARENT K = -0.160386E 02   INTERCEPTION = -0.423508E 00 ******

XSCALE# 0.149999998E 00   YSCALE# 0.21194875E-01

Figure C-9. Computer Analysis of Experimental Data

APPENDIX D

The values of k_{13} tabulated in Tables 3-8 to 3-12 and 3-23 to 3-26 were estimated by means of particular solutions to the system represented in Equation B-12 as named in Cases II and III.

The solutions presented in Case II assumes that the operator

$$(\frac{d}{dt} + \alpha(t)) \qquad \text{D-1}$$

is linear and $\alpha(t)$ is constant, such an assumption made the solution presented in Equation B-19 an approximation.

Similarly, the solution presented in Case III assumes that

$$[L]_o \gg [M]_o ; \qquad \text{D-2}$$

such an assumption is justified in view of the form of Equation B-12. However, the heuristic characteristics of the method bases its validity upon the solution presented in Equation B-19. Therefore, the estimated values of k_{13} should be accepted as <u>preliminaries in nature</u>.

By suggestions of Dr. L. D. Meeker, Professor of Applied Mathematics at the University of New Hampshire, the following scheme is proposed in order to analyze the validity of the assumptions implicit in Equations D-1 and D-2 and assess the values of k_{13}

$$\text{a)} \quad \text{solve} \quad \frac{d[ML]}{d[L]} = \frac{\frac{k_{12}}{2}[L] + (\frac{k_{12}}{2} - k_{13}) + C_1}{\frac{k_{12}}{2}[L] + (\frac{k_{12}}{2} + k_{13}) + C_2} \qquad \text{D-3}$$

for $\quad [ML] = [ML]([L]) \qquad \text{D-4}$

Assuming C_1 and C_2 constants depending upon the initial conditions:

from $\quad [L]_i = [L](t_i) \qquad \text{D-5}$

b) evaluate

$$\frac{d[ML](t_i)}{dt} = \frac{[ML]_{i+1} - [ML]_i}{\Delta t_i}$$ D-6

$$\frac{d[L](t_i)}{dt} = \frac{[L]_{i+1} - [L]_i}{\Delta t_i}$$

c) by means of least squares fit to Equation D-3 choose k_{12} and k_{13}.

It should be clear that this appendix does not invalidate the experimental results of k_2 or k_{obs}.