

SPECTROPHOTOMETRIC STUDIES OF NICKEL(II)

AQUOCOMPLEXES IN 1-BUTANOL

By

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CHAPTER I

INTRODUCTION AND LITERATURE SURVEY

Statement of Problem and Introduction

The butanol-rich phases in the extraction of aqueous $\text{Ni}(\text{ClO}_4)_2$ by 1-butanol contain approximately 50 mole percent water. In such a hydrous environment it would be expected that water would compete with the alcohol for coordination sites about the solute. This work was undertaken to learn more about the complexes present in 1-butanol solutions of $\text{Ni}(\text{ClO}_4)_2$ and water. It was desired to determine what complexes were present and, hopefully, their formation constants by a spectrophotometric method.

Investigation of spectra indicated that the changes observed in the visible region when water was added to 1-butanol solutions of $\text{Ni}(\text{ClO}_4)_2$ were too small to be of apparent use in a spectrophotometric study. However, addition of pyridine to the solutions as an auxiliary ligand produced complexes exhibiting an absorbance band in the 600 m μ region. Thus, it was hoped that pyridine could be used as a ligand to compete with water and 1-butanol for coordination sites on the nickel (II). However, application of the corresponding solutions treatment to the absorbance data failed to give meaningful results when applied to the 1-butanol- $\text{Ni}(\text{ClO}_4)_2$ -water-pyridine system. (See Chapter III for more details.)

Two absorption bands of water in the near infrared showed promise

of differentiating between free water and at least part of the bound water. Both bands decreased in intensity with increases in the metal/water ratio at constant water concentration. After preliminary experimentation at wavelengths of 1450 μ and 1940 μ , which were approximately the locations of the peaks of these two bands, it was decided to study in detail the absorbance at 1940 μ . (See Chapters III and IV.)

The problem posed for the principal study involved (1) hypothesizing a reaction or process model consistent with observations, (2) deriving a method, or extending or adapting an existing method, for data treatment consistent with the model, and (3) obtaining data and treating it by that method. Three models (with two being special cases of the other) are postulated. A method is derived for use with one specific model, and an existing method is modified and shown to be appropriate for the more general model. (See Chapter II.) Data treatment is reported in Chapter V, and the most general of the models is shown to be preferable to the ~~two~~ more restricted ones.

Literature Survey

Selected Computational and Graphical Methods

Several methods exist for determining formation constants from measurement of physical properties of a system in which several complexes are formed. Most of these have been critically reviewed by Rossotti and Rossotti (51).

According to a computational method given by Poe (46), one may successively approximate each β_n value by calculating, for each data point $([L], \bar{n})$ whose \bar{n} value is between approximately $n-1$ and $n-\frac{1}{2}$ or slightly less than $n-1$,

$$\beta_n = \frac{\bar{n}}{(n-\bar{n})[L]^n} \left\{ 1 + \frac{n-1}{\sum_{p=1}^{n-1} (\bar{n}-p)[L]^p \beta_p} + \frac{N}{\sum_{q=n+1}^N \frac{(\bar{n}-q)[L]^q \beta_q}{\bar{n}}} \right\}, \quad (1-1)$$

where β_n is an approximation to the overall (concentration) formation

constant defined by $\frac{[ML_n]}{[M][L]^n}$ (in which $[M]$ represents the free metal

concentration and $[ML_n]$ represents the concentration of the complex ML_n),

\bar{n} is the average number of bound ligands L per metal atom M (12) (thus,

$$\bar{n} = \frac{C_L - [L]}{C_M}), \quad [L] \text{ is the concentration of free ligand L, } N \text{ is the}$$

maximum value of n, β_p and β_q are previously determined approximations of the formation constants β_p and β_q . (Charges are omitted for simplicity.)

Bjerrum (9) gives Equations (1-3 and 1-4) with which successive approximation can be used to estimate each stepwise stability constant,

$$k_n = \frac{\beta_n}{\beta_{n-1}} = \frac{[ML_n]}{[ML_{n-1}][L]} : \quad (1-2)$$

$$k_n = \frac{1}{[L]} \cdot \frac{\sum_{t=0}^{n-1} \frac{\bar{n} - n + 1 + t}{[L]^t k_1 k_2 k_3 \dots k_t}}{\sum_{t=0}^{N-n} (n-\bar{n}+t) [L]^t k_{n+1} k_{n+2} \dots k_{n+t}}. \quad (1-3)$$

Bjerrum (9) substitutes $\bar{n} = n - \frac{1}{2}$ into (1-3) to obtain

$$k_n = \frac{\left(\frac{1}{[L]}\right)_{\bar{n} = n - \frac{1}{2}}}{1 + \frac{\sum_{t=1}^{n-1} (1+2t)[L]^t k_{n+1} k_{n+2} \dots k_{n+t}}{1 + \sum_{t=1}^{n-1} \frac{1+2t}{[L]^t k_1 k_2 k_3 \dots k_t}}}. \quad (1-4)$$

Use of only Equation (1-4) ("half \bar{n} " method) requires a smooth curve, interpolation, or N data points for which $\bar{n} = \frac{1}{2}, \frac{3}{2}, \dots, N - \frac{1}{2}$

(with other data points being disregarded). Any number of data points can be used with Equation (1-3).

Schröder (53) gives an "extended \bar{n} method". From the determinant¹

$$D_0 = \begin{vmatrix} + [L]_{\bar{n}=1/2} & +3[L]_{\bar{n}=1/2}^2 & +5[L]_{\bar{n}=1/2}^3 \dots \\ - [L]_{\bar{n}=3/2} & + [L]_{\bar{n}=3/2}^2 & +2[L]_{\bar{n}=3/2}^3 \dots \\ -3[L]_{\bar{n}=5/2} & - [L]_{\bar{n}=5/2}^2 & + [L]_{\bar{n}=5/2}^3 \dots \\ \dots & \dots & \dots \dots \end{vmatrix}, \quad (1-5)$$

the determinant D_i can be made by substituting the numbers 1, 3, 5, 7, ..., (2N-1) into column number i. Then the step stability constant k_i is given by

$$k_i = \frac{D_i}{D_i - 1} \quad (1-6)$$

It is desirable to recalculate constants by using [L] values equal to $\frac{1}{k_i}$ and the corresponding experimental \bar{n} values. Schröder (53) gives a computer program (in Gier Algol) "for correction of preliminary step stability constants and recalculation at optimal experimental conditions."

Irving and Rossotti (36) give the following equation to use for successive approximation:

$$\log k_{\bar{n}} = p[L]_{\bar{n}} + \log \left\{ \frac{\sum_{t=0}^{\bar{n}-1} (\bar{n}-t) \beta_t [L]^t}{\sum_{t=n}^N \frac{(t-\bar{n}) \beta_t [L]^{t-1}}{k_n}} \right\} \quad (1-7)$$

¹The term in the second row and third column is given as indicated by Schröder (53) although it is suspected that the coefficient "2" should be "3".

It is believed that (1) $k_{\bar{n}}$ refers to the value of k_n calculated by using the point $([L]_{\bar{n}}, \bar{n})$ and that (2) k_n on the right side of Equation (1-7) refers to the approximation for k_n obtained from the previous cycle but that (3) $[L]_{\bar{n}}$ and $[L]$ refer to the same thing.

It is reported that when the ratio of the two successive formation constants (presumably the two step constants in a system for which $N=2$) of an acid is $10^{0.8}$ or less the method of successive approximation cannot be applied with success (7).

According to Bjerrum's (10) "corresponding solutions" principle,

$$\bar{n} = \frac{C'_L - [L]}{C'_M} = \frac{C''_L - [L]}{C''_M}, \quad (1-8)$$

where C'_L and C''_L are the total ligand concentrations of "corresponding solutions", i.e., solutions having equal values of \bar{n} (and therefore the same percentage distribution of complexes), and C'_M and C''_M are the respective total metal concentrations. Since \bar{n} is a strictly increasing function of only constants and $[L]$, "corresponding solutions" also have equal values of $[L]$. Often the correspondence of solutions can be established by equality of absorptivities of total metal ($\bar{\epsilon}_M$), but the free ligand must not absorb significantly at the wavelength used.

It can be seen from Equation (1-8) that for any solution in a set of "corresponding solutions"

$$C_L = \bar{n} C_M + [L], \quad (1-9)$$

where C_L and C_M are the total concentrations of ligand and metal, respectively. This equation suggests the widely-used graphical method of plotting C_L vs. C_M for each set of "corresponding solutions" and ob-

taining \bar{n} as the slope of the line and $[L]$ as the intercept (at $C_M = 0$).

Nazarova and Ablov (45) assert that all the successive stability constants can be calculated using spectrophotometric data and the method of "corresponding solutions" only "when the light absorption increases continuously with the number of ligands." (However, this is perhaps an overly strict restriction. See Chapter II of this work.)

Fronaeus' (23) "method of ligand displacement" requires the use of a ligand B that forms sufficiently strong complexes with M to completely displace the ligand L from M when $[B]$ is sufficiently high. In a series of measurements, C_L is kept constant, C_M is either kept constant or is a known function of C_B , and C_B is varied. $[B]$ and \bar{n}_B , which is defined by

$$\bar{n}_B = \frac{C_B - [B]}{C_M}, \quad (1-10)$$

are determined. The quantity $\frac{\bar{n}_B}{[B]}$ can be plotted against $[B]$, with C_M (or the initial C_M) and C_L as parameters. This procedure is repeated for different values of C_M (or initial C_M), while C_L is kept at the same value as before. By extrapolation to $C_M = 0$, the limiting function

$$\frac{\bar{n}_B([L],[B])}{[B]}, \text{ defined by } \frac{\bar{n}_B([L],[B])}{[B]} = \left(\frac{\bar{n}_B}{[B]}\right)_{C_M=0}, \quad (1-11)$$

can be obtained. Since $[L] = C_L$ when $C_M = 0$, the function $\frac{\bar{n}_B(0,[B])}{[B]}$

can be obtained in the same way by setting $C_L = 0$. $\left(\frac{\Delta\bar{n}_B}{[B]}\right)_{C_M=0}$ is de-

fined by

$$\left(\frac{\Delta\bar{n}_B}{[B]}\right)_{C_M=0} = \frac{\bar{n}_B([L],[B])}{[B]} - \frac{\bar{n}_B(0,[B])}{[B]}. \quad (1-12)$$

If graphical integration is done from a plot of $\left(\frac{\Delta\bar{n}_B}{[B]}\right)_{C_M=0}$ vs. $[B]$, then a pair of values, one for $[L]$ and one for $(1 + \sum_{j=1}^N \beta_j [L]^j)$, can be obtained according to the equation

$$\ln(1 + \sum_{j=1}^N \beta_j [L]^j) = \int_0^{[B]'} \left(\frac{\Delta\bar{n}_B}{[B]}\right)_{C_M=0} \cdot d[B], \quad (1-13)$$

where $[B]'$ is a value such that $\left(\frac{\Delta\bar{n}_B}{[B]}\right)_{C_M=0}$ is 0 whenever $[B] \geq [B]'$.

If this procedure is repeated a sufficient number of times, each time with a different C_L value, then enough $([L], \{1 + \sum_{j=1}^N \beta_j [L]^j\})$ points can be obtained to determine the formation constants $\beta_j = \frac{[ML_j]}{[M][L]^j}$.

The method is one requiring a large amount of data, however.

Various computer-oriented methods are reported in the literature. These methods emphasize the importance of weighting data according to probable experimental errors. One method uses an iterative procedure to successively refine the estimates of the weights (which depend on the β_n values) and the β_n values (58). Another uses spectrophotometric data at more than one wavelength, a nondiagonal weight matrix, and the Gaussian method of least squares (40).

Brown (14) has given a computer algorithm for solution of simultaneous non-linear equations. In a typical step, variables for which linear representations have been found in previous steps are replaced by those representations in one of the remaining equations. That equation is "linearized" by expanding in a Taylor series and retaining only linear terms. This "linearized" equation is used to find a linear re-

presentation for another variable. When one equation in one unknown is left, a single Newton step is performed, followed by back-substitution in the triangularized linear system that has been generated. This is a general procedure.

A related procedure, which involves solving for k_1 and k_2 by finding values to satisfy

$$\frac{\partial S}{\partial k_1} = 0 \quad (1-14a)$$

and

$$\frac{\partial S}{\partial k_2} = 0, \quad (1-14b)$$

where S is a sum of squares to be minimized, is mentioned by Unwin, Beimer, and Fernando (57). If T_i is the linear (Taylor) approximation of

$\frac{k_1[L]_i + 2k_1k_2[L]_i^2}{1 + k_1[L]_i + k_1k_2[L]_i^2}$ about an estimate of (k_1, k_2) , the S to be minimized

is

$$S = \sum_{i=1}^K [\bar{n}_i - T_i]^2, \quad (1-15)$$

where K is the number of data points. A warning is given that the system (1-14) may have many solutions. The new estimate found for (k_1, k_2) is used when the process is repeated, and so on. Analogous procedures can be used with systems of higher complexity.

Rossotti and Rossotti (50) have proposed a graphical treatment based largely on the equation

$$\sum_{n=0}^{t-1} \left(\frac{\bar{n} - n}{t - \bar{n}} \right) \beta_n [L]^{n-t} = \beta_t + \sum_{n=t+1}^N \left(\frac{n - \bar{n}}{t - \bar{n}} \right) \beta_n [L]^{n-t} . \quad (1-16)$$

If the values of $\beta_1, \beta_2, \dots, \beta_{t-1}$ have already been found, the left-hand side of Equation (1-16) can be calculated and plotted against

$\frac{(t+1 - \bar{n})[L]}{(t - \bar{n})}$. The plot gives β_t as the intercept and an approximate

value of β_{t+1} as the limiting slope as $[L] \rightarrow 0$.

Fomin and Maiorova (21) have used

$$\lim_{[L] \rightarrow 0} G_1 = \beta_1, \quad (1-17)$$

where G_1 is defined as $\frac{\bar{n}}{[L]}$, to find β_1 for Th NO_3^{++} in aqueous solution by extrapolating a plot of G_1 vs. $[L]$ to $[L] = 0$, where L represents NO_3^- . Values for β_2, β_3 , and β_4 were similarly found by extrapolating plots of G_2, G_3 , and G_4 vs. $[L]$ to $[L] = 0$ and using previously-determined β_n values and:

$$\lim_{[L] \rightarrow 0} G_2 = 2\beta_2 - \beta_1^2, \quad (1-18)$$

where G_2 is defined by

$$G_2 = \frac{G_1 - \beta_1}{[L]}; \quad (1-19)$$

$$\lim_{[L] \rightarrow 0} G_3 = 3\beta_3 - 3\beta_1\beta_2 + \beta_1^3, \quad (1-20)$$

where G_3 is defined by

$$G_3 = \frac{G_2 - (2\beta_2 - \beta_1^2)}{[L]}; \quad (1-21)$$

and

$$\lim_{[L] \rightarrow 0} G_4 = 4\beta_4 - 4\beta_1\beta_3 + 4\beta_1^2\beta_2 - 2\beta_2^2 - \beta_1^4, \quad (1-22)$$

where G_4 is defined by

$$G_4 = \frac{G_3 - (3\beta_3 - 3\beta_1\beta_2 + \beta_1^3)}{[L]}. \quad (1-23)$$

An extrapolation method useful for spectrophotometric measurements is given by Yatsimirskii (60). If $\bar{\epsilon}_M$ is the mean molar absorptivity of total metal and ϵ_0 is the molar absorptivity of free metal, then a simple auxiliary function f_1 can be defined by

$$f_1 = \frac{(\bar{\epsilon}_M - \epsilon_0)}{[L]}. \quad (1-24)$$

Extrapolation yields

$$\lim_{[L] \rightarrow 0} f_1 = (\epsilon_{ML} - \epsilon_0) \beta_1, \quad (1-25)$$

where ϵ_{ML} is the molar absorptivity of the complex species ML. In general, f_i for $i > 1$ is constructed by

$$f_i = \frac{f_{i-1} - \lim_{[L] \rightarrow 0} f_{i-1}}{[L]}, \quad (1-26)$$

and extrapolation yields

$$\lim_{[L] \rightarrow 0} f_i = (\epsilon_{ML_i} - \epsilon_0) \beta_i - (\epsilon_{ML} - \epsilon_0) \beta_1^i, \quad (1-27)$$

where ϵ_{ML_i} is the molar absorptivity of the complex species ML_i . If y

is defined by

$$y = \frac{1}{[L]}, \quad (1-28)$$

another set of extrapolations, each as y approaches zero, can be performed.

$$\text{First, } \lim_{y \rightarrow 0} (\bar{\epsilon}_M - \epsilon_0) = \epsilon_{ML_N} - \epsilon_0. \quad (1-29)$$

If γ_1 is defined by

$$\gamma_1 = \frac{(\bar{\epsilon}_M - \epsilon_0) - \lim_{y \rightarrow 0} (\bar{\epsilon}_M - \epsilon_0)}{y}, \quad (1-30)$$

then

$$\lim_{y \rightarrow 0} \gamma_1 = [(\epsilon_{ML_{N-1}} - \epsilon_0) - (\epsilon_{ML_N} - \epsilon_0)] \frac{\beta_{N-1}}{\beta_N}. \quad (1-31)$$

Obviously, Equation (1-31) can be written as

$$\lim_{y \rightarrow 0} \gamma_1 = (\epsilon_{ML_{N-1}} - \epsilon_{ML_N}) \frac{\beta_{N-1}}{\beta_N}. \quad (1-32)$$

The functions $\gamma_2, \gamma_3, \dots, \gamma_{N-1}$ can be similarly constructed and extrapolated to $y = 0$. Jasinski and Kwiatkowski (37) propose the use of the reciprocal of f_1 for plotting against $[L]$.

Rose and Drago (47) have, for each experimental "point" used in a certain one-complex problem, calculated k_1^{-1} as a function of $\epsilon_{\text{complex}}$, an unknown for which various values were assigned. The resulting values were used to plot k_1^{-1} vs. $\epsilon_{\text{complex}}$, with one line resulting from each experimental "point". Both k_1^{-1} and $\epsilon_{\text{complex}}$ were then determined by a cluster of intersections on that plot.

The quantity $\left\{ \frac{N}{Z} \log \bar{k} + \log 55 \right\}$ is an expression for the mean affinity for the exchange of bound water molecules for a particular ligand (11). Here N_v is the number of "uniformly bound" ligands, Z is the characteristic coordination number (which is 6 or 4 for Ni(II)) de-

terminated by the number of the first more firmly and uniformly bound ligands, \bar{k} is the mean complexity constant, i.e.,

$$\log \bar{k} = \frac{1}{N_V} \log (k_1 k_2 \dots k_N) , \quad (1-33)$$

and 55 is the total concentration of water molecules in moles per liter.

A similar and useful quantity, the average formation constant \bar{k}' , can be determined when a ligand L competes rather successfully with the solvent for coordination sites on the metal (or central group) M.

Jørgensen (38) has found \bar{k}' from the relation

$$\bar{k}' = \left(\frac{1}{[L]} \right) \bar{n} = \frac{N}{2} . \quad (1-34)$$

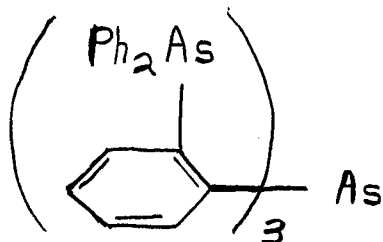
Multiplying \bar{k}' by the molar concentration of the solvent gives a value for the relative tendency of M to be bound to L rather than to the solvent.

Perchlorate Coordination

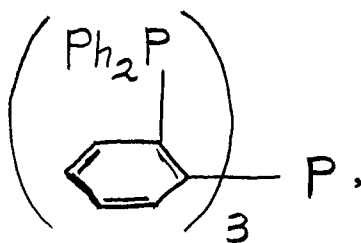
The perchlorate anion has been widely regarded as non-coordinating or weakly coordinating in aqueous solutions. Therefore, perchlorate salts have often been used (as in this work) when the ligands of primary interest are uncharged. However, there have been recent reports of perchlorate coordination in a variety of systems, particularly in nonaqueous media.

A perchlorato complex of nickel reportedly forms in nitrobenzene solution and has been isolated as the compound $[\text{Ni}\{\text{o-C}_6\text{H}_4(\text{AsMe}_2)_2\}_2 \text{ClO}_4] \text{PF}_6$ (27). In addition, conductometric measurements have established the existence of perchlorate coordination to nickel in nitrobenzene when

2,2'-bipyridyl or 1,10-phenanthroline (each denoted by "chelate") also serves as a ligand (28, 29). The Ni(II) species with coordinated perchlorate are interpreted to be $[\text{Ni}(\text{chelate})_2(\text{nitrobenzene})(\text{ClO}_4)]^+$. The complexes $[\text{Ni}(\text{ClO}_4)(\text{QAS})](\text{ClO}_4)$ and $[\text{Ni}(\text{ClO}_4)(\text{QP})](\text{ClO}_4)$, where QAS represents



and QP represents



are 1:1 electrolytes in nitrobenzene, thus indicating yet another instance of perchlorate coordination to nickel(II) in solution (19).

Perchlorate coordination has also been observed in dichloromethane, with a species formulated as $\text{Ni}(\text{py})_4(\text{ClO}_4)_2$ existing in that solvent (48).

There is presumably some degree of perchlorate coordination even in aqueous solutions when the perchlorate concentration is extremely high, as evidence has indicated the existence of $[\text{Ni}(\text{H}_2\text{O})_5\text{ClO}_4]^+$ in concentrated (~10.8 molar) perchloric acid solutions (49). Bidentate perchlorate has been identified in the solid $\text{Ni}(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ (34).

Coordination Numbers of Nickel(II)

The maximum coordination number of nickel(II) is generally considered to be 6. Complexes in which nickel(II) exhibits coordination numbers of 4 and 5 have been reported (30, 52). However, nickel (II) re-

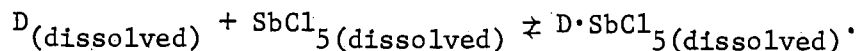
portedly has seven-coordination in the $[\text{Ni}(\text{N}(\text{CH}_2\text{CH}_2\text{N}=\text{CH}-\text{C}_6\text{H}_5)_3)]^{++}$ complex (8). The distance between the nickel and the unique nitrogen in that "capped octahedron" complex is the large value of 3.25 angstroms. It would appear, however, that in the absence of stereospecific ligands, six coordination is the usual maximum for nickel (II).

Measures of Donor Ability

Several empirical measures of the donor ability of a solvent have been suggested. Among these, donor number $\text{DN}_{\text{SbCl}_5}$ for a donor "solvent" D has been defined by

$$\text{DN}_{\text{SbCl}_5} = -\Delta H_{\text{D}\cdot\text{SbCl}_5}, \quad (1-35)$$

where $-\Delta H_{\text{D}\cdot\text{SbCl}_5}$ is associated with the reaction



The evaluation of $-\Delta H_{\text{D}\cdot\text{SbCl}_5}$ is actually done in a "highly dilute" solution in 1,2-dichloroethane (26).

One is $D_{\text{II,I}}$, an empirical spectrophotometric shift caused by interaction between vanadylbisacetylacetonate $[\text{VO}(\text{acac})_2]$, which has one ligand site available, and a solvent (26). The $D_{\text{II,I}}$ values have been found to be proportional to the respective donor numbers ($\text{DN}_{\text{SbCl}_5}$) as long as hydrogen bonding is absent. With the occurrence of hydrogen bonding, the actual solvent - $\text{VO}(\text{acac})_2$ interaction is increased.

A solvent of low donor number acts as a leveling solvent for the stabilities of analogous complex species containing competitive ligands

of different donor properties (26).

Some donor and physical properties as reported by Gutmann (26) for the liquids used in this study are given in Table I.

TABLE I
SELECTED PROPERTIES OF LIQUIDS

	1-Butanol	Water	Pyridine
DN_{SbCl_5}		18.0	33.1
$D_{II,I}$	4.10	5.49	4.40
Dielectric constant	17.7^{20°	81.0	12.3
Molecular volume at 20°	91.08		
Dipole moment (Debye)	1.66		

Spectra Related to This Work

According to Moiseev and Vinnik (43), the spectrum of bound water in the region of 6900 cm^{-1} (1450 μ) and 5150 cm^{-1} (1940 μ) does not differ appreciably from that of free water for aqueous solutions of NaCl and LiCl. However, differences were noted for aqueous solutions of the acids HCl and H_2SO_4 and the bases LiOH, NaOH, KOH, and CsOH. For the same or identical solutions of the salts or acids, the water concentrations calculated from the peak absorbances at or near 6900 cm^{-1} (1450 μ) tends to be lower than those calculated from the peak absorbances at or near 5150 cm^{-1} (1940 μ). However, for the alkali solutions, the calculated water concentrations tends to be equal at the two peaks (and in the

reverse order for 15 molar solutions of NaOH and KOH). (When salt solutions behave as indicated here, higher \bar{n} values under the "nothing" model would be calculated from 1450 μ data than from 1940 μ data. Correspondingly, in this work (see Chapters III and V), the highest supposed \bar{n} values were indeed calculated from 1450 μ data.)

Absorption of radiation in the 1450 μ region by water has been variously attributed to the $\nu_1 + \nu_3$, $2\nu_3$, $2\nu_2 + \nu_3$, or $2\nu_1$ vibrational mode, while absorption in the 1940 μ region has been attributed to the $\nu_2 + \nu_3$ or $\nu_1 + \nu_2$ vibrational mode of water (6, 16, 24, 39, 43). No complete agreement seems to have been reached.

Work with Related Systems Involving Pyridine in Nonaqueous Solvents

Studies involving systems with 1-butanol as the solvent, pyridine as a ligand, and nickel (II) as the metal have been reported. For one such system, with $\text{Ni}(\text{ClO}_4)_2$ salt supplying the nickel and with water also present to the extent that the ratio $C_{\text{H}_2\text{O}}/C_{\text{M}}$ (where $C_{\text{H}_2\text{O}}$ is the total concentration of water and C_{M} is the total concentration of nickel) was 18, \bar{n}_{py} (the average number of bound pyridine molecules per nickel atom) seemed to approach a limiting value of 2 as the pyridine concentration was increased (44).

An instability constant (k_1^{-1}) of 6.5×10^{-4} has been reported for NiPy^{++} in 1-butanol when the nickel was supplied by $\text{Ni}(\text{NO}_3)_2$ salt (2). This corresponds to a stability constant k_1 equal to 1.5×10^3 . Solvents used, in the order of increasing stability of the monopyridine complex dissolved in them, were water, methanol, ethanol, 1-butanol, and acetone. For the aqueous and alcoholic solutions, a near-linear relationship was

demonstrated between $\log k_1$ and the reciprocal of the dielectric constant of the solvent.

Although there is evidence for the existence of $\text{Ni}(\text{py})_4(\text{H}_2\text{O})_2^{++}$ in hydrous pyridine solution (13), there is evidence also for the existence of $\text{Ni}(\text{py})_6^{++}$ in nitromethane solution (48). Solid $\text{Ni}(\text{py})_6(\text{ClO}_4)_2$ crystallizes from dried 1-butanol solutions of $\text{Ni}(\text{ClO}_4)_2$ and pyridine (44).

Work with Related Systems Involving Pyridine in Aqueous Solutions

Several investigators have studied pyridine complexes of nickel (II) in aqueous solutions. The results are not all in agreement, however. When NiCl_2 or NiSO_4 was used as the source of nickel, the metal is reported to coordinate up to three, and perhaps more, pyridine molecules per nickel atom; however, when $\text{Ni}(\text{ClO}_4)_2$ was used as the source of nickel, only a monopyridine complex was observed to form in aqueous solution during the same study by Timofeeva, Knyazeva, and Kalinichenko (56). Instability constants were estimated at "half \bar{n} " values on the formation curves for the NiCl_2 -py- H_2O and NiSO_4 -py- H_2O systems.

Atkinson and Bauman had observed earlier that not only was a monopyridine complex of nickel (II) formed in aqueous solutions containing 1 F NaClO_4 at 25° , but evidence also indicated the existence of complexes containing up to 4 bound pyridine molecules per nickel atom (5). Moreover, these complexes were comparatively (see Table II) stable in the presence of perchlorate ions. This is in contradiction to the results reported by Timofeeva and his co-workers. Potentiometric titrations were used in determining the following values:

$$\begin{aligned} \log \beta_1 &= 2.13, & \log \beta_2 &= 3.79, \\ \log \beta_3 &= 4.91, & \text{and} & \log \beta_4 &= 5.56. \end{aligned}$$

Fridman, Levina, and Sorochan (22) have determined formation constants for pyridine complexes of nickel in aqueous solutions containing 1 M total NH_4NO_3 , nickel(II) introduced as the nitrate, and pyridine. The values reported are: $\log \beta_1 = 1.98$, $\log \beta_2 = 3.02$, $\log \beta_3 = 3.42$, and $\log \beta_4 = 3.44$. Potentiometric and distribution methods were used.

In still another study formation constants were determined for nickel (II)-pyridine complexes in aqueous (deaerated distilled water) solutions of $0.01 \text{ F Ni}(\text{NO}_3)_2 + 0.1 \text{ F (Hpy)}^+ \text{NO}_3^- + 0.5 \text{ F KNO}_3$ + varied concentrations of pyridine at $25.0 \pm 0.1^\circ\text{C}$ (54). Measurement of pH and an equation derived from Bjerrum's (9) model were used to find:

$$\log \beta_1 = 1.91 \pm 0.02, \log \beta_2 = 3.19 \pm 0.06, \text{ and } \log \beta_3 = 3.71 \pm 0.26.$$

A spectrophotometric study of the $\text{Ni}(\text{NO}_3)_2$ -pyridine-water system yielded the following instability constants for nickel (II)-pyridine complexes $\text{Ni}(\text{py})_n^{++}$ in aqueous solutions (1): $k_1^{-1} = 0.012$, $k_2^{-1} = 0.14$, $k_3^{-1} = 0.25$, and $k_4^{-1} = 0.76$. These correspond to k_n values of 83, 7, 4.0, and 1.3, respectively, and yield β_n values of: $\beta_1 = 83$, $\beta_2 = 6 \times 10^2$, $\beta_3 = 2.4 \times 10^3$, and $\beta_4 = 3 \times 10^3$. Under conditions when pyridine was considered to be bound chiefly as $\text{Ni}(\text{py})^{++}$, the instability constant k_1^{-1} was redetermined and this time was found to be $(8.6 \pm 0.4) \times 10^{-3}$, which corresponds to $k_1 = \beta_1 = (1.16 \pm 0.5) \times 10^2$. The effect of adding KNO_3 on the middle part of the formation curve was also studied. The slight shift that was observed in the curve in the presence of 1 F KNO_3 was considered to be insignificant, with the change in instability constants not exceeding the limits of experimental error.

Table II summarizes some of the $\log \beta_n$ values found in the literature for pyridine complexes of nickel(II) in aqueous solutions. It should be noted that although the values of $\log \beta_1$ are all close together, the values of the other $\log \beta_j$'s are significantly larger when ClO_4^- is the anion than when it is NO_3^- .

TABLE II
FORMATION CONSTANTS OF NICKEL(II)-PYRIDINE
COMPLEXES IN AQUEOUS SOLUTIONS

Chief anion present	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	$\log \beta_4$	Reference
ClO_4^-	2.13	3.79	4.91	5.56	(5)
NO_3^-	1.98	3.02	3.42	3.44	(22)
NO_3^-	1.91 ± 0.02	3.19 ± 0.06	3.71 ± 0.26		(54)
NO_3^-	1.92	2.77	3.38	3.50	(1)
NO_3^-	2.06 ± 0.02				(1)

For nickel (II) and pyridine in aqueous solutions at room temperature, the quantity $\left\{ \frac{N}{Z} \log \bar{k} + \log 55 \right\}$ (see page 11) was found to be 1.7 (11).

The 1-Butanol-Ni(ClO₄)₂-Water System

Harris and Moore (32) have reported values for β_1 through β_5 of aquocomplexes of nickel(II) in 1-butanol. The nickel(II) was intro-

duced as $\text{Ni}(\text{ClO}_4)_2$, and calorimetric data were obtained at 25° . These data were treated using Bjerrum's (10) principle of "corresponding solutions". The formation function thus obtained was utilized to determine formation constants by Poe's (46) method. Varga (58) has used the same data to recalculate a set of β_n values by his computer method. However, although β_6 was used by Varga (58), β_4 and β_5 were omitted for the sake of gaining a better fit. The $\log \beta_n$ values of both sets are given in Table III.

TABLE III
LOG β_n VALUES FOR AQUO COMPLEXES OF
NICKEL (II) IN 1-BUTANOL AT 25°

Reference	(32)	(58)
$\log \beta_1$	1.80 ± 0.05	1.81 ± 0.01
$\log \beta_2$	3.23 ± 0.05	3.13 ± 0.03
$\log \beta_3$	4.36 ± 0.05	4.60 ± 0.02
$\log \beta_4$	5.20 ± 0.08	-----
$\log \beta_5$	5.8 ± 0.1	-----
$\log \beta_6$	-----	7.38 ± 0.02

Swartz (55) obtained data for the distribution of $\text{Ni}(\text{ClO}_4)_2$ between water and 1-butanol. He interpreted results to signify that the species in the 1-butanol phase was a "highly hydrated, largely associated salt" over the concentration range investigated ($0.0008 \text{ molal} \leq C_M \leq 0.0120$

molal in the 1-butanol phase for the distribution study). The conductance measurements of Cheung (18) reported by Harris and Moore (32) support this hypothesis.

It has been reported that the shape and position of the absorption bands in the visible and near infrared agreed with the hypothesis of an octahedral ligand field for nickel (II) (introduced as $\text{Ni}(\text{ClO}_4)_2$) in hydrous butanol solution (25). The magnitude of band shift resulting from adding small amounts of water to dried solutions of $\text{Ni}(\text{ClO}_4)_2$ has been interpreted to suggest "that the perchlorate ions are separated from the metal ions in the ion pairs by at least one solvent molecule."

Other Related Systems

The average formation constant \bar{k}' for nickel (II) aquocomplexes in ethanol at 25°C was found to be 0.82 liter/mole by taking the reciprocal of the free water concentration at which the aquocomplex formation was half completed (38). Multiplying by the ethanol concentration gave a value of 13 for the relative tendency of nickel (II) to be bound to a water molecule rather than to an ethanol molecule.

Investigation of the heats of solution of crystalline hexahydrates $[\text{M}(\text{H}_2\text{O})_6] (\text{ClO}_4)_2$ (where M = Fe, Co, Ni, or Cu) in water showed that the stable hydrate environment of the M^{++} ions is completed by the attachment of about 26 water molecules to the $[\text{M}(\text{H}_2\text{O})_6]^{++}$ ion (3). The stable hydrate environment of Fe^{++} , Ni^{++} , Co^{++} , and Cu^{++} ions in aqueous solution is considered to consist of two monomolecular layers and can be formulated as $[\text{M}(\text{H}_2\text{O})_6] (\text{H}_2\text{O})_{-26}^{++}$. The average strengths of the bonds between the water molecules in these layers and the central atom are about 42 kcal (first layer) and about 10 kcal (second layer). Strong

bonding of first and second layer water molecules accounts qualitatively for the large "apparent" hydration numbers of about 30-50 reported by Cheung (18) for $\text{Ni}(\text{ClO}_4)_2$ in the 1-butanol phases from solvent extraction.

CHAPTER II

THEORY AND METHODS

"All or Nothing" Model

Basis of the Model

In this model it is postulated that some bound water would not absorb 1940- μ radiation at all while other bound water would absorb with the same absorptivity as that of free water. A simple representation of a complex is $MA_{\ell}B_m^{++}$, where M represents nickel(II), A represents non-absorbing coordinated water, ℓ is the number of non-absorbing molecules of water in the complex, B represents absorbing coordinated water, and m is the number of absorbing water molecules in the complex, and coordinated solvent and perchlorate molecules (if any) are ignored. Assuming that the absorptivities of nickel(II), perchlorate, and 1-butanol in 1-butanol solution remain the same in any environment, one can conclude that the molar absorptivity of the complex $MA_{\ell}B_m^{++}$ is $m\epsilon_L$ greater than the molar absorptivity of an anhydrous solution with identical concentrations of anhydrous solutes, where ϵ_L is the molar absorptivity of free water. Also, one can conclude that the absorbance due to water is LESSENERD by the amount $\ell\epsilon_L b[MA_{\ell}B_m^{++}]$ through a path of b centimeters by the complex $MA_{\ell}B_m^{++}$ at a concentration of $[MA_{\ell}B_m^{++}]$ when compared with the absorbance of a solution of uncoordinated water at the same total concentration in 1-butanol.

Twenty-seven different overall formation constants $\beta_{\ell,m}^*$ are required for a general treatment by this model if a maximum of six water molecules can be coordinated to a single nickel(II) atom. The constant $\beta_{\ell,m}^*$ is defined by

$$\beta_{\ell,m}^* = \frac{[MA_{\ell}B_m^{++}]}{[M^{++}][L]^{(\ell+m)}}, \quad (2-1)$$

where $[L]$ represents the concentration of free water. The traditional, singly-subscripted β_n is defined by

$$\beta_n = \frac{[ML_n^{++}]}{[M^{++}][L]^n}, \quad (2-2)$$

where coordinated water molecules are not distinguished from any other coordinated water molecules. The β_n and $\beta_{\ell,m}^*$ are related by

$$\beta_n = \sum \{ \beta_{\ell,m}^* \mid \text{where } (\ell+m) = n \}. \quad (2-3)$$

The average number of bound ligands per central metal ion has been denoted by \bar{n} (12). One can define $\bar{\ell}$ and \bar{m} analogous to \bar{n} . The average number of non-absorbing water molecules coordinated to each nickel atom is denoted by $\bar{\ell}$. The average number of absorbing water molecules coordinated to each nickel atom is denoted by \bar{m} . Thus,

$$\bar{\ell} = \frac{\sum_{\ell=0}^6 \sum_{m=0}^{6-\ell} \text{if } \ell > 0 \quad \ell \beta_{\ell,m}^* [L]^{\ell+m}}{1 + \sum_{\ell=0}^6 \sum_{m=0}^{6-\ell} \text{if } \ell > 0 \quad \beta_{\ell,m}^* [L]^{\ell+m}} \quad (2-4)$$

and

$$\bar{m} = \frac{\sum_{l=0}^6 \sum_{m=0}^{6-l} \beta_{l,m}^* [L]^{\lambda+m}}{1 + \sum_{l=0}^6 \sum_{m=0}^{6-l} \beta_{l,m}^* [L]^{\lambda+m}} \quad (2-5)$$

Method for Obtaining [L], $\bar{\lambda}$, and \bar{m}

The concentration of total absorbing water is

$$C_L - \bar{\lambda}C_M = [L] + \bar{m}C_M, \quad (2-6)$$

where C_M is the total metal concentration and C_L is the total water concentration. At a constant absorbance and path length, the concentration of total absorbing water is constant. Thus,

$$C_L - \bar{\lambda}C_M = C_L' - \bar{\lambda}'C_M'. \quad (2-7)$$

Letting $C_M' = 0$ yields

$$C_L - C_L' = \bar{\lambda}C_M, \quad (2-8)$$

where C_L' is the concentration of a water in 1-butanol solution that has no nickel present but has the same absorbance as a solution of C_M total $\text{Ni}(\text{ClO}_4)_2$ plus C_L total water in 1-butanol. Solving Equation (2-8) for $\bar{\lambda}$ gives

$$\bar{\lambda} = \frac{C_L - C_L'}{C_M}. \quad (2-9)$$

Substituting Equation (2-9) into Equation (2-6) produces

$$C_L - \left(\frac{C_L - C_L'}{C_M} \right) C_M = [L] + \bar{m}C_M, \quad (2-10)$$

which can be simplified to

$$C_L' = [L] + \bar{m}C_M \quad (2-11)$$

or

$$[L] = C_L' - \bar{m}C_M. \quad (2-12)$$

Referring to Equations (2-4) and (2-5), one can see that $\bar{\ell}$ and \bar{m} are strictly increasing functions of $[L]$ for all defined (zero or positive) $[L]$. Thus, equality of any two $\bar{\ell}$ values ($\bar{\ell}_1 = \bar{\ell}_2$) implies the equality of the two corresponding \bar{m} and $[L]$ values ($\bar{m}_1 = \bar{m}_2$ and $[L]_1 = [L]_2$).

If one of the two absorbance values in Figure 1 is chosen so that $\bar{\ell}_1 = \bar{\ell}_2$, i.e.

$$\frac{(C_L)_1 - (C_L')_1}{(C_M)_1} = \frac{(C_L)_2 - (C_L')_2}{(C_M)_2}, \quad (2-13)$$

one has two equations in two unknowns:

$$[L] = (C_L')_1 - \bar{m}(C_M)_1 \quad (2-12a)$$

$$[L] = (C_L')_2 - \bar{m}(C_M)_2 \quad (2-12b)$$

These yield

$$\bar{m} = \frac{(C_L')_1 - (C_L')_2}{(C_M)_1 - (C_M)_2} \quad (2-14)$$

and

$$[L] = (C_L')_i - \bar{m}(C_M)_i \quad (2-12c)$$

in which i may be either one or two.

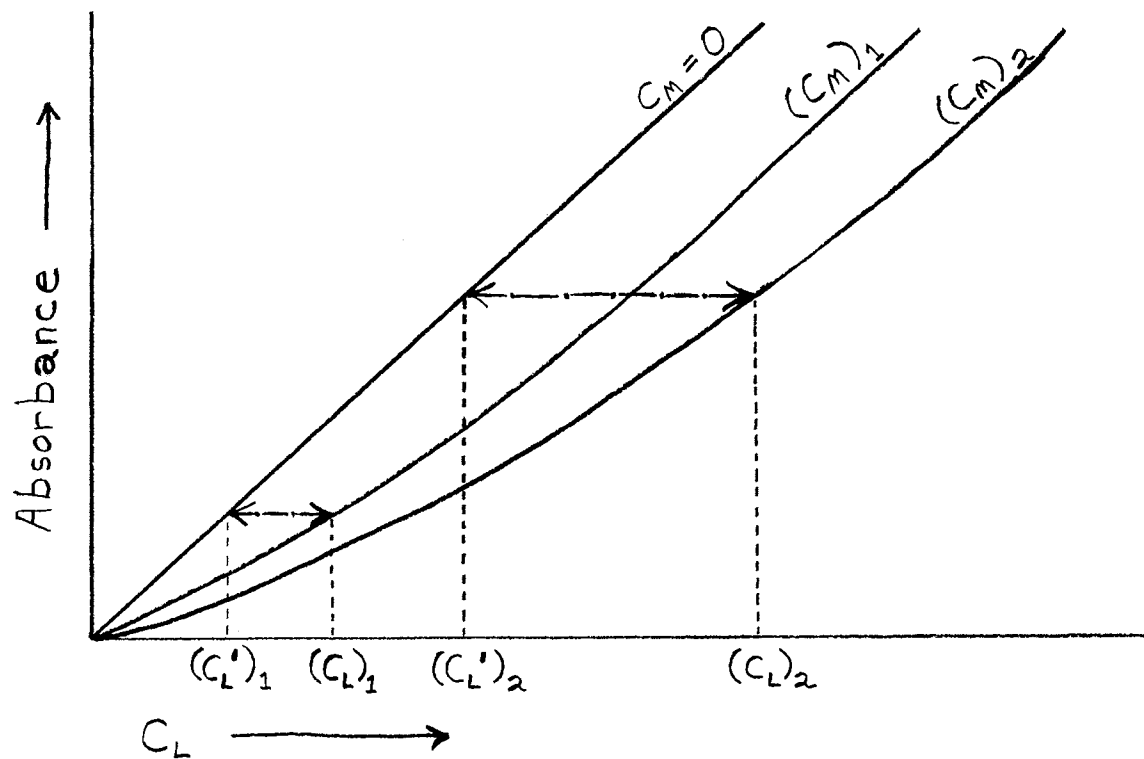


Figure 1. Illustration of Method

In the absence of conclusive evidence that some coordinated water molecules absorb with the same ϵ_L as free water and some coordinated water molecules do not absorb, this model must be used with care. In this work, \bar{n} vs. $\log[L]$ points obtained using this model are given for comparison with a plot obtained by treating the same experimental data

by a theoretically more general method--an extension of Bjerrum's (10) method of corresponding solutions.

Method for Further Treatment of Data

Under the "all or nothing" model, there are twenty-seven $\beta_{\ell,m}^*$ formation constants to be determined if the maximum ($\ell+m$) value is six. One way to approach this problem is to try to minimize the sum of squares (S) of differences between experimental and calculated values:

$$S = \sum_{k=1}^K (\bar{\ell}_{k,CALC} - \bar{\ell}_k)^2 + \sum_{k=1}^K (\bar{m}_{k,CALC} - \bar{m}_k)^2, \quad (2-15)$$

where $\bar{\ell}_{k,CALC}$ and $\bar{m}_{k,CALC}$ are calculated values for the $\bar{\ell}$ and \bar{m} , respectively, of data point k; $\bar{\ell}_k$ and \bar{m}_k are the experimental values of $\bar{\ell}$ and \bar{m} , respectively, of data point k; and K is the number of data points.

If S_M is the minimum sum of squares S, then

$$\left(\frac{\partial S}{\partial \beta_{\ell,m}^*} \right) = 0 \quad \text{at } S = S_M \quad (2-16)$$

for every $\beta_{\ell,m}^*$. However, even if there is only one absolute minimum S_M , the set of equations (2-16) may have non-unique solutions. Such equations for a much simpler system, one with only two formation constants to be determined, reportedly "may have many solutions, e.g., local minima, maxima, and saddle points" (57).

Equations (2-16) are made linear by temporarily holding the denominator of $\bar{\ell}$ and \bar{m} constant. The temporary constant W_k for data point k is defined by

$$W_k = \left(1 + \sum_{\ell=0}^6 \sum_{m=0}^{\ell} \beta_{\ell,m}^* [L]_k^{(\ell+m)}\right)^{-2} \quad (2-17)$$

Although a unique solution to the whole problem is still not guaranteed, Equations (2-16) become linear. The $\beta_{\ell,m}^*$ values obtained as solutions to "linearized" equations (2-16) can be used to calculate new W_k values, and the process of setting up Equations (2-16) and solving can be repeated.

From Equations (2-4), (2-5), (2-15), and (2-17) and the notational identity $\beta_{i,j}^* = \beta_{\ell,m}^*$ if $i = \ell$ and $j = m$, one obtains:

$$S = \sum_{k=1}^K W_k \left\{ \left[\sum_{i=0}^6 \sum_{j=0}^i \beta_{i,j}^* [L]_k^{(i+j)} \right]_{\bar{\ell}_k}^2 + \left[\sum_{i=0}^6 \sum_{j=0}^i \beta_{i,j}^* [L]_k^{(i+j)} \right]_{\bar{m}_k}^2 \right\} \quad (2-18)$$

Using Equation (2-18), finding $\partial S / \partial \beta_{p,q}^*$, and setting $\frac{\partial S}{\partial \beta_{p,q}^*}$ equal to

zero leads to twenty-seven equations (2-19), one equation for each combination of p and q such that $1 \leq (p+q) \leq 6$, with the twenty-seven $\beta_{i,j}^*$ unknowns appearing in each equation:

$$\sum_{i=0}^6 \sum_{j=0}^i \beta_{i,j}^* \left\{ \sum_{k=1}^K W_k [L]_k^{(i+j+p+q)} [(i-\bar{\ell}_k)(p-\bar{\ell}_k) + (j-\bar{m}_k)(q-\bar{m}_k)] \right\} \quad (2-19)$$

An IBM 360 digital computer and simulated "data" without "experimental error" were used to test a computer program based on this method. In this testing, the "maximum coordination number" used much of the time was three, instead of six, in order to conserve computer time. It was found that $\beta_{0,1}^*$ and $\beta_{1,0}^*$ became constant or essentially so but that the other $\beta_{i,j}^*$ values varied widely from cycle to cycle with no apparent hope of convergence. However, it was observed that values for each β_n , which is defined in Equation (2-3), became constant or essentially so. With real, badly-scattered data, convergence was not observed in a reasonable length of time.

Modified "Corresponding Solutions" Treatment

Basis of the Model

A model less restrictive than the "all or nothing" model also postulates one coordinated ligand having two different molar absorptivities. However, the molar absorptivity ϵ_1 of A, which is the lesser-absorbing coordinated ligand L, is not necessarily zero. Also the molar absorptivity ϵ_2 of B, which is the greater-absorbing coordinated ligand L, is not necessarily the same as the molar absorptivity ϵ_L of free ligand L. Like the "all or nothing" model, this model assumes that the absorptivities of the central atom or group M (such as nickel(II)), any non-coordinating species (such as ClO_4^- is assumed to approximate) present, and solvent (such as 1-butanol) remain unchanged in any environment in the system being studied. Hence, the absorbance due to free ligand L is $\epsilon_L [L]$ per cm of path length. Also, the absorbance due to the complex MA_iB_j is $(i\epsilon_1 + j\epsilon_2) [\text{MA}_i\text{B}_j]$ per cm of path length. (The charges on M and MA_iB_j are omitted for simplicity and generality.) If ϕ is the total

absorbance minus the absorbance of a solution that is identical in total composition except for no L being present, if b is the path length in cm, and if M has a maximum coordination number of six,

$$\frac{\phi}{b} = \epsilon_L [L] + \sum_{i=0}^6 \sum_{j=0}^{6-i} (i\epsilon_1 + j\epsilon_2) [MA_i B_j] . \quad (2-20)$$

Method for Obtaining $[L]$ and \bar{n}

In the usual corresponding solutions treatment, corresponding solutions would be those with equal ϕ/b values (10). However, one requirement for success with that method is an insignificant absorptivity of the free ligand. In the model being considered here, the value of ϕ/b is provided entirely by the ligand in its various moieties (A, B, and L), and equal ϕ/b values would not imply corresponding solutions. If ϕ_L is defined as the absorbance of a solution of C_L molar ligand in solvent (with nothing else present and the absorbance of the solvent being nullified by using solvent in a matched cell as reference) and δ is defined by

$$\delta = \frac{(\phi_L - \phi)}{bC_M} , \quad (2-21)$$

it is asserted that equal values of δ on corresponding parts of a δ vs. C_L curve signify corresponding solutions. This assertion will be demonstrated by examining the nature of δ .

By the Beer-Lambert law,

$$\frac{\phi_L}{b} = \epsilon_L C_L . \quad (2-22)$$

From Equation (2-22) and the definition of C_L ,

$$\frac{\phi_L}{b} = \epsilon_L \left\{ [L] + \sum_{i=0}^6 \sum_{\substack{j=0 \text{ if } i>0 \\ j=1 \text{ if } i=0}}^{6-i} (i+j) [MA_{iB_j}] \right\} . \quad (2-23)$$

By the definition of C_M ,

$$C_M = [M] + \sum_{i=0}^6 \sum_{\substack{j=0 \text{ if } i>0 \\ j=1 \text{ if } i=0}}^{6-i} [MA_{iB_j}] . \quad (2-24)$$

Equation (2-21) can be written as

$$\delta = \frac{\left(\frac{\phi_L}{b} - \frac{\phi}{b} \right)}{C_M} . \quad (2-25)$$

Substituting (2-20), (2-23), and (2-24) into (2-25) and simplifying yields

$$\delta = \frac{\sum_{i=0}^6 \sum_{\substack{j=0 \text{ if } i>0 \\ j=1 \text{ if } i=0}}^{6-i} [i(\epsilon_L - \epsilon_1) + j(\epsilon_L - \epsilon_2)] [MA_{iB_j}]}{[M] + \sum_{i=0}^6 \sum_{\substack{j=0 \text{ if } i>0 \\ j=1 \text{ if } i=0}}^{6-i} [MA_{iB_j}]} . \quad (2-26)$$

As in Equation (2-1), $\beta_{i,j}^*$ is defined by

$$\beta_{i,j}^* = \frac{[MA_{iB_j}]}{[M][L]^{i+j}} , \quad (2-27)$$

from which

$$[MA_{iB_j}] = \beta_{i,j}^* [M][L]^{(i+j)} . \quad (2-28)$$

Substituting (2-28) into (2-26) and dividing both numerator and denominator by $[M]$ gives

$$\delta = \frac{\sum_{i=0}^6 \sum_{j=0}^{6-i} [i(\epsilon_L - \epsilon_1) + j(\epsilon_L - \epsilon_2)] \beta_{i,j}^* [L]^{(i+j)}}{1 + \sum_{i=0}^6 \sum_{j=0}^{6-i} \beta_{i,j}^* [L]^{(i+j)}} \quad (2-29)$$

Thus, δ is a continuous function of only constants and $[L]$. Therefore, equality of δ values in a δ vs. $[L]$ curve portion that contains no zero value for $\frac{d\delta}{d[L]}$ implies equality of $[L]$ values.

Now $\frac{d\delta}{d[L]}$ may be considered to be the differential $d\delta$ divided by the differential $d[L]$. Likewise, $\frac{d\delta}{dC_L}$ may be considered to be the differential $d\delta$ divided by the differential dC_L . $\frac{d\delta}{d[L]} = 0$ implies that $d\delta = 0$. This condition ($d\delta = 0$) and the additional assumption $dC_L \neq 0$ imply that $\frac{d\delta}{dC_L} = 0$. Therefore, given the assumption $dC_L \neq 0$, equality of δ values in a δ vs. C_L curve portion that contains no zero value for $\frac{d\delta}{dC_L}$ implies equality of $[L]$ values. One can tell directly from the δ vs. C_L plot if or when $\frac{d\delta}{dC_L} = 0$.

A Method Used in Further Treatment of Data

One method followed in further treatment of data uses a computer program that refines one β_n value while the other β_n values are held constant. A flow diagram for this program is given in Figure 2, and the program itself, as used in the last step, is given in Table IV. The particular β_n being refined is denoted by β_c . Interpolation can be used to further refine β_c from the two "best" values given in the output. After a refined value for β_c is obtained, the program is changed slightly

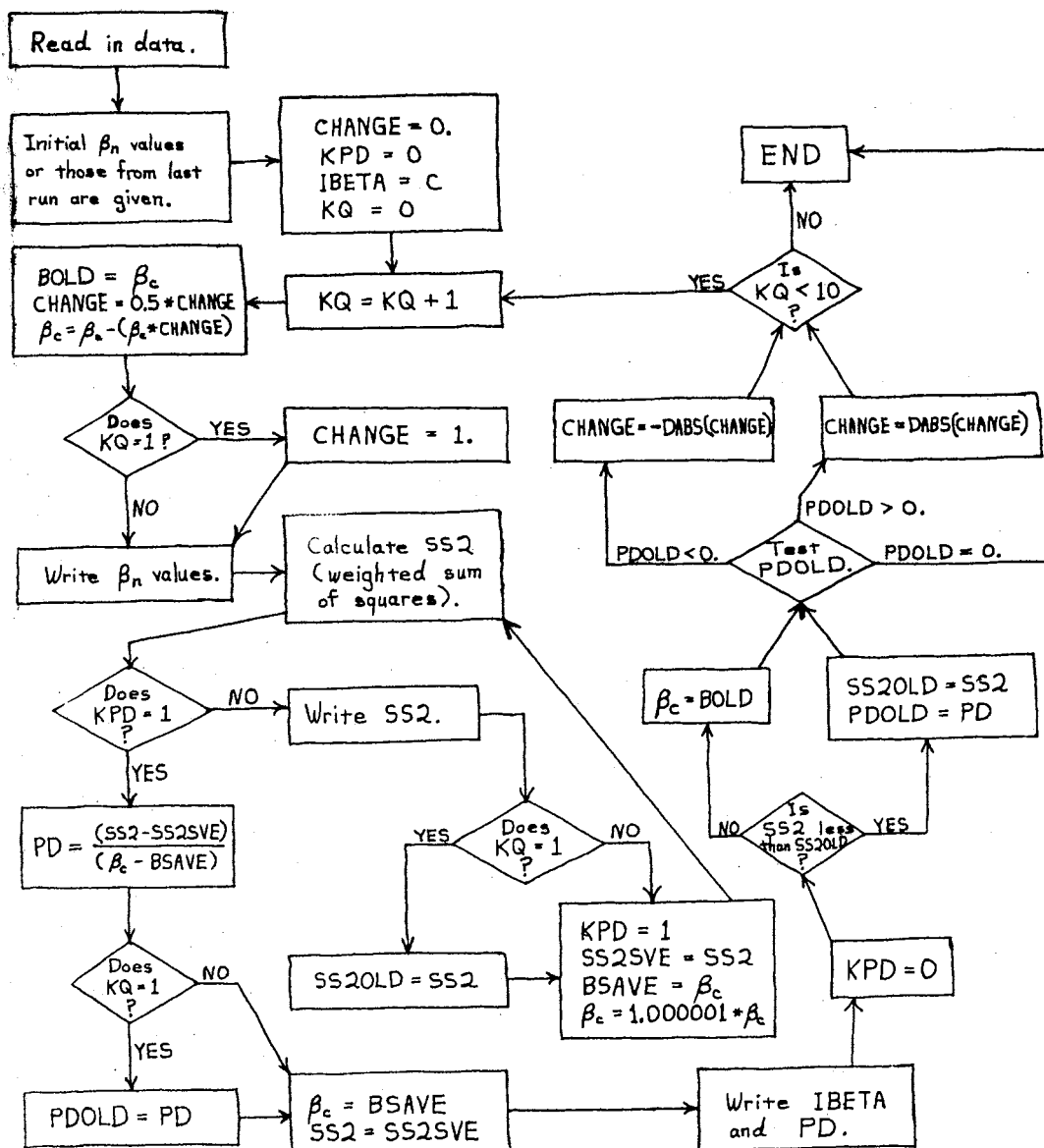


Figure 2. Flow Diagram of a Computer Program for Refining one β_c Value When the Other β_n Values are Held Constant. In a square or rectangle of this diagram, as in computer programming, an equals sign means that the quantity on the right-hand side of the equals sign is to be taken and stored as the value of the single variable on the left-hand side.

TABLE IV

THE COMPUTER PROGRAM WHOSE FLOW DIAGRAM IS GIVEN IN FIGURE 2

80/80 LIST

000000000111111112222222223333333334444444455555555666666667777777778
 1234567890123456789012345678901234567890123456789012345678901234567890

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CARD
0001      IMPLICIT REAL*8 (A-H,O-Y)
0002      DIMENSION FREEL(28),CALCNB(28),EXPNB(28),ERROR(28),Z(3,28)
0003      1 FORMAT (E11.5,2E12.5)
0004      2 FORMAT ( 48X,'NICKEL(II) AQUOCOMPLEXES IN 1-BUTANOL'//28X,'TREA
0005      ATMENT OF COMBINED SPRING SEMESTER, 1969, AND FALL SEMESTER, 1969-7
0006      70, DATA'///16X,1HL,12X,'1',15X,'2',15X,'3',15X,'4',15X,'5',15X,'6'
0007      6//13X,'BETA(L)',1P6D16.6//
0008      6      19X,'FREE WATER',15X,'CALCULATED N BAR',11X,'EXPERIMENT
0009      TAL N BAR',5X,'DEVIATION (CALC-EXPERIMENTAL)'/)
0010      3 FORMAT (4F28.5)
0011      4 FORMAT (//31X,'SUM OF DEVIATIONS',1PD54.9/)
0012      5 FORMAT (31X,'SUM OF DEVIATIONS WEIGHTED BY 1/ERROR',1PD34.9/)
0013      6 FORMAT (31X,'SUM OF SQUARES OF DEVIATIONS',1PD43.9/)
0014      7 FORMAT (31X,'SUM OF SQUARES WEIGHTED BY 1/ERROR',1PD37.9/)
0015      8 FORMAT (31X,'SUM OF SQUARES WEIGHTED BY 1/(ERROR**2)',1PD32.9/)
0016      11 FORMAT (1HL,62X,15/)
0017      29 FORMAT (31X,'APPROXIMATE PARTIAL DERIV. OF SS2 WITH RESPECT TO BET
0018      TA(',11,') =',1PD12.4/)
0019      100 FORMAT (48X,'NICKEL(II) AQUOCOMPLEXES IN 1-BUTANOL'//28X,'TREA
0020      ATMENT OF COMBINED SPRING SEMESTER, 1969, AND FALL SEMESTER, 1969-7
0021      70, DATA'///16X,1HL,12X,'1',15X,'2',15X,'3',15X,'4',15X,'5',15X,'6'
0022      6//13X,'BETA(L)',1P6D16.6//)
0023      101 FORMAT (/62X,15/)
0024      102 FORMAT (/1X,'*****')
0025      X*****')
0026      X*****')
0027      DO 9 K = 1,28
0028      READ (5,1) Z(1,K),Z(2,K),Z(3,K)
0029      FREEL(K) = DBLE(Z(1,K))
0030      EXPNB(K) = DBLE(Z(2,K))
0031      9 ERROR(K) = DBLE(Z(3,K))
0032 C      ONE BETA VALUE AND EVERY STATEMENT IDENTIFIED BY 'CHANGE' SHOULD
0033 C      BE CHANGED BEFORE EACH NEW RUN.
0034      BETA1 = 1.4D 02
0035      BETA2 = 3.0D 04
0036      BETA3 = 5.2D 05
0037      BETA4 = 4.3D 06
0038      BETA5 = 2.2D 08
0039      BETA6 = 3.2D 08
0040      CHANGE = 0.0D 00
0041      KPD = 0
0042      IBETA = 6
0043      KQ = 0
0044      12 KQ = KQ + 1
0045      KKQ = KQ + 0
0046      BOLD = BETA6
0047      CHANGE = 0.5D00 * CHANGE
0048      BETA6 = BETA6 - BETA6 * CHANGE
0049      IF (KQ.EQ.1) CHANGE = 1.0D 00
0050      FORMF(X) = ( BETA1*X + 2.000*BETA2*X**2 + 3.000*BETA3*X**3
0051      F + 4.000*BETA4*X**4 + 5.000*BETA5*X**5 + 6.000*BETA6*X**6 ) /
0052      F ( 1.000 + BETA1*X + BETA2*X**2 + BETA3*X**3
0053      F + BETA4*X**4 + BETA5*X**5 + BETA6*X**6 )
0054      K110 = (KQ-1) * (KQ-10)

```

CHANGE

CHANGE

CHANGE

CHANGE

TABLE IV (Continued)

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                                80/80 LIST
0000000001111111112222222222333333333344444444445555555555666666666677777777778
12345678901234567890123456789012345678901234567890123456789012345678901234567890
CARD
0055      IF (K110.EQ.0) WRITE (6,11) KKQ
0056      IF (K110.NE.0) WRITE (6,101) KKQ
0057      IF (KQ.NE.10) WRITE (6,100) BETA1,BETA2,BETA3,BETA4,BETA5,BETA6
0058      IF (KQ.EQ.10) WRITE (6,2) BETA1,BETA2,BETA3,BETA4,BETA5,BETA6
0059      IF (KQ.LT.10) GO TO 31
0060      S = 0.D 00
0061      S1 = 0.D 00
0062      SS = 0.D 00
0063      SS1 = 0.D 00
0064      31 SS2 = 0.D 00
0065      DO 10 K = 1,28
0066      H20 = FREEL(K)
0067      CALCNB(K) = FORMF(H20)
0068      DEV = CALCNB(K) - EXPNB(K)
0069      SS2 = SS2 + DEV*DEV/(ERROR(K)*ERROR(K))
0070      IF (KQ.LT.10) GO TO 10
0071      IF (KPD.EQ.1) GO TO 10
0072      S = S + DEV
0073      S1 = S1 + DEV/ERROR(K)
0074      SS = SS + DEV*DEV
0075      SS1 = SS1 + DEV*DEV/ERROR(K)
0076      WRITE (6,3) FREEL(K),CALCNB(K),EXPNB(K),DEV
0077      10 CONTINUE
0078      IF (KPD.EQ.1) GO TO 32
0079      IF (KQ.LT.10) GO TO 38
0080      WRITE (6,4) S
0081      WRITE (6,5) S1
0082      WRITE (6,6) SS
0083      WRITE (6,7) SS1
0084      38 WRITE (6,8) SS2
0085      IF (KQ.EQ.1) SS2OLD = SS2
0086      KPD = 1
0087      SS2SVF = SS2
0088      BSAVE = BETA6
0089      BETA6 = 1.000001 * BETA6
0090      GO TO 31
0091      32 PD = (SS2-SS2SVE) / (BETA6-BSAVE)
0092      IF (KQ.EQ.1) PDOLD = PD
0093      BETA6 = BSAVE
0094      SS2 = SS2SVE
0095      WRITE (6,29) IBETA,PD
0096      IF (KQ.LT.10) WRITE (6,102)
0097      KPD = 0
0098      IF (SS2-SS2OLD) 26,27,27
0099      26 SS2OLD = SS2
0100      PDOLD = PD
0101      GO TO 37
0102      27 BETA6 = BOLD
0103      37 IF (PDOLD) 34,36,35
0104      34 CHANGE = -DABS(CHANGE)
0105      GO TO 28
0106      35 CHANGE = DABS(CHANGE)
0107      28 IF (KQ.LT.10) GO TO 12
0108      36 STOP

```

CHANGE
CHANGE

CHANGE
CHANGE

CHANGE

80/80 LIST

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0000000001111111112222222222333333333344444444445555555555666666666677777777778
12345678901234567890123456789012345678901234567890123456789012345678901234567890

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CARD
0109 END

to use this refined value and to refine one of the other β_n . It is expected that the six β_n values would eventually become reasonably constant after sufficient iterations.

CHAPTER III

PRELIMINARY EXPERIMENTS

The addition of water to dried solutions of $\text{Ni}(\text{ClO}_4)_2$ in 1-butanol results in slight changes in color arising from shifts in the visible absorption bands. Such shifts in d-d transition bands in transition metals are usually interpreted as indicative of changes in solvation and complexing. Spectrophotometric investigation of changes in solvation occurring upon the addition of water conceivably could be carried out in several ways. These include (1) study of the change in the absorption of radiation by the water in solution as a function of water and salt concentration, (2) study of the d-d transition bands of the metal with changes in concentration of water and salt, and (3) study of the formation of a suitably characterized ligand complex of the metal as a function of the water concentration in the 1-butanol. Preliminary experiments were done to explore the feasibility of each of these approaches.

Near Infrared Spectra of Water as a Solute in 1-Butanol

1-Butanol absorbs strongly enough in the near infrared to make dilution effects significant at some wavelengths. This absorbance (which is greater than 1.9 through a 2 cm path at 1450 and 1940 $\text{m}\mu$) places an added demand on a spectrophotometer to yield significant readings of solute absorbance against such a strong "background" absorbance.

Water as a solute in 1-butanol has an absorbance peak near 1450 $\text{m}\mu$

and has a molar absorptivity of approximately 0.25 at 1450 μ . An absorbance peak near 1940 μ is also exhibited, with water having a molar absorptivity of approximately 1.1 at 1940 μ .

Integrated Intensity Measurements

Some measurements were undertaken to determine whether the water absorbance in hydrous 1-butanol at a wavelength of 1450 μ is reasonably proportional to the area of the water absorbance band that peaks at or near this wavelength. (Similar measurements for the water absorbance band that peaks at or near 1940 μ were not undertaken because the longer wavelength end of the band was obscured, seemingly by an overlapping band but possibly owing to instrument limitation. The corresponding band in published water spectra, although not symmetrical, is only slightly obscured on the longer-wavelength side (6,41).)

The product of an empirical constant and the area enclosed by the absorbance line and by the zero line between the wavelength limits of 1350 μ and 1650 μ on a spectrogram seemed to be a good estimator of the absorbance (i.e., absorbance minus the zero line absorbance) at 1450 μ in the two systems with which this experiment was done. (For the system containing no nickel, the absorbance peak was actually closer to 1430 μ or 1440 μ . For the system containing 0.06 molar total $\text{Ni}(\text{ClO}_4)_2$, the peak was very close to, if not exactly at, 1450 μ . In both cases, the absorbances used and estimated were at 1450 μ , not necessarily exactly at the peak.) The average fractional error of the estimator for sixteen measurements on solutions of water, ranging from 0.09 to 2.22 molar, in 1-butanol was 0.015. Dried 1-butanol was used in obtaining the zero absorbance line. The average fractional error of a similar estimator for

sixteen measurements on solutions of water, ranging from 0.09 to 3.47 molar, and containing also 0.06 molar $\text{Ni}(\text{ClO}_4)_2$, in 1-butanol was 0.080, with more than half of that error resulting from only the smallest pair of values. A dried 0.060 molar $\text{Ni}(\text{ClO}_4)_2$ solution in 1-butanol was used in obtaining the zero line. The constant appropriate to the first set of measurements was 0.0328864, whereas it was 0.0316473 for the second set. (Non-significant digits, which were used in calculations, are included in those constants. Using only significant digits would make the constants 0.033 and 0.032, respectively.)

1-Butanol- $\text{Ni}(\text{ClO}_4)_2$ -Water-Pyridine System

Kinetic Experiments

Since it had been found by Swartz (55) in an earlier study that the salt hexapyridinenickel perchlorate was soluble in dried 1-butanol, it was thought that a study of the visible spectra during nickel-pyridine complex formation in both anhydrous and in hydrous 1-butanol would be informative concerning the state of solvation of nickel perchlorate in 1-butanol solutions containing small quantities of water. It was noticed, however, that precipitation and lowering of absorbance eventually occurred in 1-butanol solutions containing the three components $\text{Ni}(\text{ClO}_4)_2$, water, and pyridine. A study of this phenomenon was made using two starting solutions as indicated in Figure 3. Each solution, in a 2-cm cell, was placed in the "sample" light beam of a Beckman DK-1 spectro-

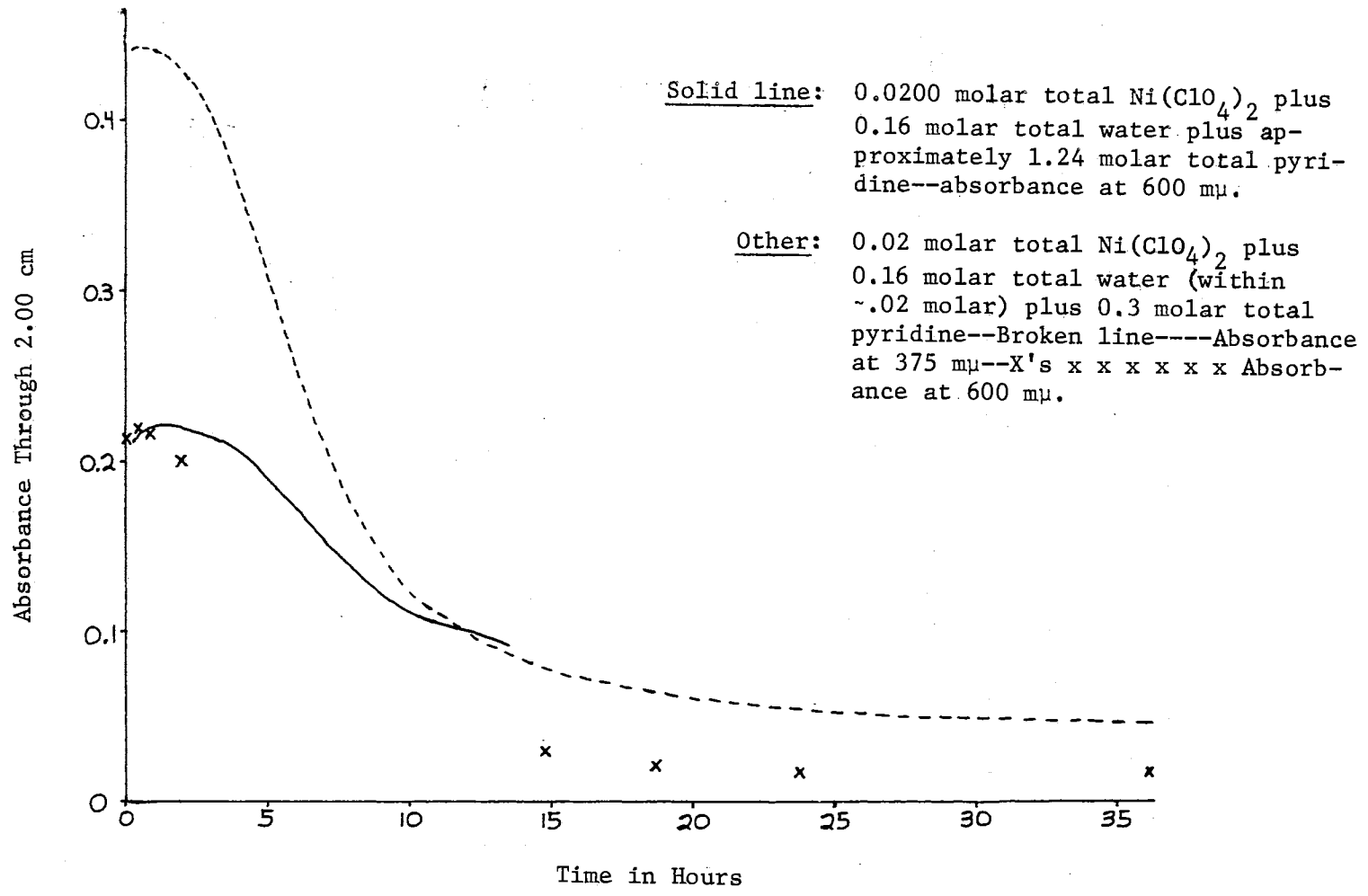


Figure 3. Partial Results of Kinetic Experiments

photometer, which was kept turned "on" continuously throughout the respective run. The length of an observation was extended up to 36 hours. Thus, it could not be safely assumed that either sample remained at its original temperature throughout the entire time-period.

It appeared that equilibrium absorbances (not zero) were being approached. This result, plus the presence of an "induction period", hampered determination of a reaction order with respect to absorbing nickel (II)-pyridine and/or absorbing nickel(II)-pyridine-aquo complexes.

The results did indicate the possibility of a study of the initial reaction occurring within a time period of up to two or three hours.

Corresponding Solutions Treatment

A study of the formation of nickel(II)-pyridine and/or nickel(II)-pyridine-aquo complexes in 1-butanol by Bjerrum's (10) method of corresponding solutions was attempted. Absorbance measurements were taken at 580, 600, 610, and 620 m μ within 2.1 hours after the addition of pyridine.

In application of this method plots of total (analytical) concentrations of ligand (C_L) are plotted against total concentrations of metal (C_M) for solutions having the same molar absorptivity ($\bar{\epsilon}_M$) of the metal. Such plots theoretically should give lines whose slope is the average number of bound ligand molecules per metal atom (\bar{n}) and whose intercept on the C_L axis is the concentration of free ligand $[L]$ in each such corresponding solution. Thus, $C_L = \bar{n}C_M + [L]$ for each set of corresponding solutions.

Unfortunately, the pyridine-containing complexes were apparently

too stable for a good corresponding solutions treatment under the experimental conditions used (C_M values of .02, .04, and .08 molar nickel perchlorate; a water/nickel(II) mole ratio of roughly 36 to one; and a 2-cm light path). Most of the "corresponding solutions" (C_L vs. C_M) lines converged in the region of small free pyridine concentration, causing the fractional errors for the resulting free pyridine values to be magnified. Experimental error was especially noticeable on the C_L vs. C_M plots for higher equal $\bar{\epsilon}_M$ (molar absorptivity of total nickel) values at the shorter wavelengths. At each wavelength, at least one doubtful \bar{n} value greater than six was indicated. The data yielded one \bar{n} approaching what appears to be the incredible value of 13 at each of the two shortest wavelengths, 580 and 600 μ . Therefore, this series of experiments was discounted, and the use of pyridine was abandoned. (However, if the stable environment of Ni(II) consists of two layers, and if both layers are included in defining \bar{n} , then 13 could be a quite reasonable value for \bar{n} . See reference 3.)

1-Butanol--Ni(ClO₄)₂--Water System

Precipitation

Precipitates have been noticed in samples containing no pyridine at sufficiently high water/nickel ratios during some spectrophotometer runs. Addition of a small amount of water to some 0.094 molar Ni(ClO₄)₂ stock solution caused a slight precipitate to form. Such precipitates, as in the case of the butanol-Ni(ClO₄)₂-pyridine-water system, are indicative of slow hydrolytic reactions at high water/butanol ratios. Since most of the subsequent work with this system was concerned with study at smaller ratios, precipitation presented no serious problem. However, during the principal study, very small amounts of threadlike solid matter were often

observed in sample solutions, as reported in Chapter IV.

Studies in Visible Region

Increments of water were added to a solution of 0.02 molar $\text{Ni}(\text{ClO}_4)_2$ in 1-butanol. At 394 $\text{m}\mu$, the molar absorptivity for total nickel(II) remained practically constant at 8, although a slight decrease was apparent by the time the water/total nickel(II) mole ratio reached 100. At 401 $\text{m}\mu$, the molar absorptivity started at 9 but had decreased to 7.4 by the time a water/total nickel(II) mole ratio of 160 was reached. A path-length of 2-cm was used in all these measurements, and the wavelength was scanned at a rate of -150 $\text{m}\mu$ per minute.

Increments of water were added to two other series of solutions containing 0.04 molar and 0.08 molar $\text{Ni}(\text{ClO}_4)_2$ in 1-butanol. At 665 $\text{m}\mu$, the molar absorptivity remained in the 2.2-2.5 range for both. At 713 $\text{m}\mu$ and 735 $\text{m}\mu$, small decreases in the molar absorptivity of total nickel(II) were observed as the water/total nickel(II) mole ratio became sufficiently high. However, at these wavelengths, as well as at 401 $\text{m}\mu$, the decreases appeared to be too gradual to be of much value in determining the composition of the complexes or formation constants.

Studies at 1450 Millimicrons

For a study using absorbance measurements for water at a wavelength of 1450 $\text{m}\mu$ and with 1-butanol as the solvent, it was initially assumed that equal "corrected" absorbance (i.e., absorbance minus absorbance of the practically anhydrous starting solution) values indicated equal free water concentrations. Under this assumption, the maximum \bar{n} (i.e., the average number of bound water molecules per nickel(II) atom) calculated

exceeded the unlikely value of nine for a C_M (i.e., total nickel(II) perchlorate concentration) of 0.04 molar and exceeded the value of eleven for a C_M of 0.02 molar.

However, plots showed deviations from the Beer-Lambert law at 1450 μ for 1-butanol-water mixtures. Using data obtained by means of a Beckman DK-1 recording spectrophotometer, an even more disturbing observation was made: Treatment of absorbance data for water in 1-butanol solutions with one- and two-cm light paths indicated that the hypothesis

$$\text{Absorbance} = \epsilon[f(c)]b, \quad (3-1)$$

where ϵ = molar absorptivity, $f(c)$ = some function of water concentration in moles per liter (total water equals free water in these solutions), and b = light path through solution, can be REJECTED at the 99% confidence level. There appeared to be a slight dependence upon path-length of the light which may have had its origin in a failure of the instrumentation to adequately compensate for the background absorption from the solvent. Both a different spectrophotometer (a Cary 14) and a different wavelength (1940 μ) were eventually used for the principal study.

Experiment With Perchloric Acid

It was hoped that an absorbance band due only to free pyridine existed in the near infrared region and that such a band could be detected by its disappearance when pyridine was protonated. The following experiment was performed to try to find such a band. Although unsuccessful in this respect, the experiment did produce some interesting results.

A solution of 0.08 or 0.09 molar total $\text{Ni}(\text{ClO}_4)_2$ plus 3 molar total

water plus 0.5 molar total pyridine in 1-butanol was prepared. When the water was added to a $\text{Ni}(\text{ClO}_4)_2$ solution (a portion of a 0.094 molar stock solution), almost no precipitate formed, with only a very few black specks being present. The addition of pyridine caused no apparent precipitation. With some of this solution as the sample, a spectrogram was made. Then a few drops of $\text{HClO}_4 \cdot 2\text{H}_2\text{O}$ were added to the 10 ml. of solution, and a water-soluble white precipitate formed. With some of the supernatant liquid as the sample, a spectrogram was again made. The two spectra showed small but definite differences, as if the addition of $\text{HClO}_4 \cdot 2\text{H}_2\text{O}$ had caused the water concentration to decrease and the concentration of pyridine-containing nickel complex(es) to increase. No identification of the white precipitate was attempted.

CHAPTER IV

PROCEDURES AND DETERMINATIONS USED

IN THE PRINCIPAL STUDY

Preparation of $\text{Ni}(\text{ClO}_4)_2$ in 1-Butanol Stock Solution

G. F. Smith Chemical Co. hydrated nickel(II) perchlorate and reagent grade 1-butanol were used without further purification for preparing the $\text{Ni}(\text{ClO}_4)_2$ in 1-butanol stock solution. Portions of the stock were used in solution preparation for the principal study. Following preliminary water removal by distillation of a 1-butanol-water azeotrope, which is reported (18) to have a b.p. of 95° , approximately 400 ml of the $\text{Ni}(\text{ClO}_4)_2$ stock solution was further dried by refluxing at 15 mm Hg over a bed of type 3A Linde Molecular Sieve in a modified Soxhlet apparatus, basically following a procedure given by Harris (31) and Harris and Moore (32). This procedure was a modification of that given by Arthur, Haynes, and Varga (4).

The solution was stored in 500 ml. pyrex round-bottomed flask, which is pictured in Figure 4. Portions of solution were removed through a syringe needle inserted through the serum rubber cap. On widely separated occasions, the ground glass stopper was loosened for an instant to relieve the partial vacuum in the container.

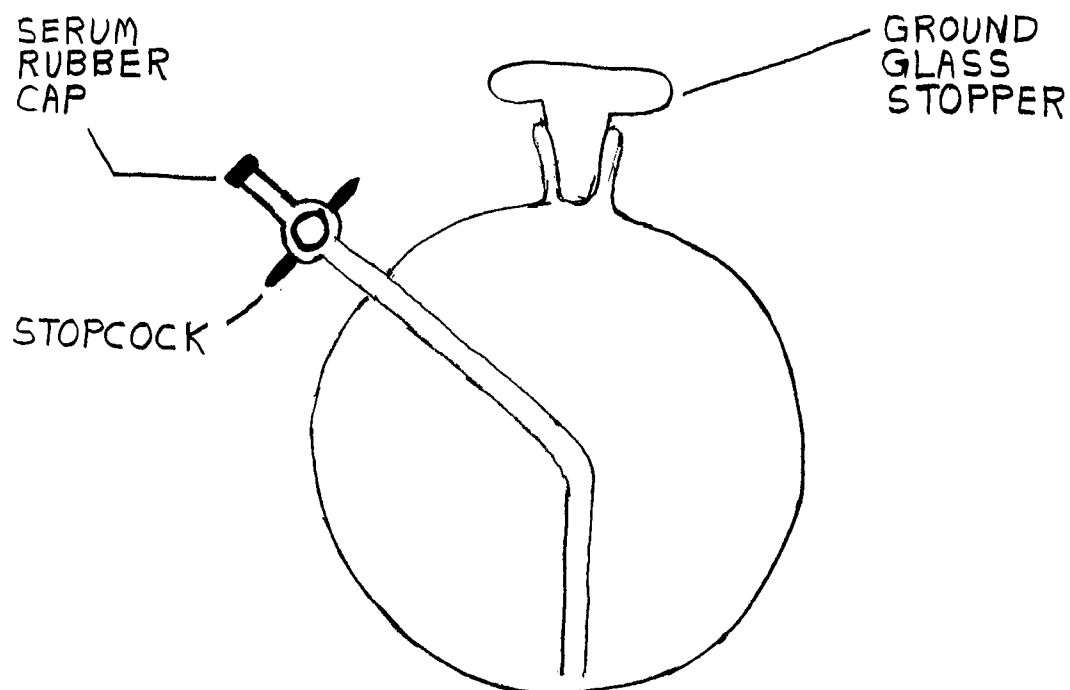


Figure 4. The Container Used for Storing Stock Solution Used in the Principal Study

Apparent Reaction with Serum Rubber Caps

Apparently, some of the 0.315 molar $\text{Ni}(\text{ClO}_4)_2$ in 1-butanol stock solution reacted with part of a serum rubber cap used on the container in which that stock solution was stored. A color change was noticed in a quite small portion of the stock solution between the stopcock and the serum cap. This apparent reaction seemed to occur whenever some of the stock solution contacted a serum rubber cap for an extended period of time. However, it is thought that the closed stopcock of that container virtually isolated the contaminated portion of the solution. Virtually all of the obviously affected portion of the solution was routinely discarded.

Determination of Water

Water concentrations were determined by the Karl Fischer method (42). Polarized electrodes were used, and a Beckman Expanded Scale pH meter served as a null-point detector. Water was used to standardize the Karl Fischer reagent. Each time, the standardization and the determination were performed the same day or within three hours of the same day.

The Karl Fischer method is reported to be generally applicable for the determination of water in alcohols (42). The number of moles of water reportedly found per mole of salt for $\text{Ni}(\text{OOCCH}_3)_2 \cdot 4\text{H}_2\text{O}$ by Karl Fischer titration was 3.97 ± 0.01 (42). Also, the number of moles of water reportedly found per mole of salt for $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ by Karl Fischer titration was 6.11 ± 0.03 (15). These results imply that the Karl Fischer method can yield valid results in the presence of nickel(II).

It was found that water seemed to be slowly escaping from the Karl Fischer reaction mixture. Stirring seemed to enhance this escape. It is suspected that the desiccant in two drying tubes, while functioning to prevent water vapor from entering the titration setup from the outside, actually was somewhat desiccating the reaction mixture. Although there was visual evidence that water had reacted with Karl Fischer reagent below the stopcock in the buret, the amount of Karl Fischer reagent involved was insufficient to account for the water deficiency observed. On another occasion, when the desiccant in one drying tube appeared to be spent, the reaction mixture seemed to gain water.

The 0.315 molar $\text{Ni}(\text{ClO}_4)_2$ in 1-butanol stock solution was found to contain less than .015 molar water at the 99.5% confidence level. The mean value obtained was .010 molar water.

The 1-butanol used for dilution when preparing solutions in the sample cell for the principal study was obtained through the courtesy of Gordon F. Wallace. This 1-butanol had been dried by contact with Linde 4-A molecular sieve and was reported to contain .005% or less water by weight (59). Exactly .005% water would correspond to a concentration of .0022 molar total water.

The use of "dried" or "dry" in this work is not intended to preclude the presence of slight amounts of water as an impurity. For the principal study, these slight amounts were as indicated in the preceding two paragraphs.

Determination of Nickel(II)

For each titration, a small amount of $\text{Ni}(\text{ClO}_4)_2$ in 1-butanol stock solution was pipetted into a flask. A comparatively large amount of water was added. The warmed and buffered (pH = 10) aqueous solution, to which a very small amount of murexide indicator powder had been added, was titrated with standard EDTA solution, essentially according to a procedure given by Flaschka (20).

The $\text{Ni}(\text{ClO}_4)_2$ in 1-butanol stock solution that was used in the principal series of absorbance measurements was originally determined to contain $0.315 \pm .001$ (standard deviation) molar total nickel(II) ($0.315 \pm .004$ molar total nickel (II) at the 95% confidence level) if the concentration of the EDTA titrant was assumed to be known exactly. Much later, by making the same assumption about a different EDTA titrant, the remaining stock solution was redetermined and found to be 0.3128 ± 0.0005 (standard deviation) molar in total nickel(II) ($0.313 \pm .001$ molar in total nickel(II) at the 95% confidence level). This was after

the last absorbance measurement for this study had been taken. A "t" test indicated significance at the 80% confidence level, but not at the 90% confidence level, in the difference between the two means. Actually, the hypothesis rejected at the 80% confidence level, but not at the 90% confidence level, was that $\mu_1 R_1 = \mu_2 R_2$; where μ_1 and μ_2 represent the actual total nickel(II) concentrations at the time of the first and second determinations, respectively; R_1 represents the ratio of (1) the stated stoichiometric concentration of standard EDTA solution used in estimating μ_1 to (2) the actual stoichiometric EDTA concentration of that titrant; and R_2 represents an analogous ratio for the EDTA titrant used in estimating μ_2 .

One can consider the possibility that a reaction of nickel(II) with serum rubber and a possible slight stopcock leak (not observed) might have led to migration of nickel(II) to the serum rubber cap being used on the stock solution container and resulting decrease in nickel(II) concentration of the stock solution. Also, one can consider the possibility of a nickel(II) concentration gradient, with the concentration being less in the vicinity of the serum rubber stopper. These considerations, plus significance (at the 80% confidence level) of the difference in two determinations of nickel(II) in the stock solution, plus the fact that the nickel(II) concentration value (0.315 molar) determined earlier was used in this work, prompted an analysis of the effect of overestimating the nickel(II) concentration of the stock solution by something in the order of 1% on the results of the modified "corresponding solutions" treatment used. Overestimating the nickel(II) concentration by 1% would not affect the $[L]$ values obtained but would cause the \bar{n} values obtained to be 1% lower than they would be if the

correct nickel(II) concentration were used (see Appendix). The effects of not using one or more sets of measurements and the deviations of some points from a smooth curve were both relatively large. Hence, the data obtained by accepting the 0.315 molar value for the $\text{Ni}(\text{ClO}_4)_2$ stock solution were retained without adjustment.

Procedural Difficulties and Experiments

Procedures Affecting Accuracy of Water Addition

Since the incremental volumes of water added to the spectrophotometer cell were of the order of 5 microliters, precautions had to be taken to insure reasonable accuracy in the volume measurement. Care had to be taken to exclude all air bubbles from the syringe used for adding small increments of water. Experience showed that the presence of any air bubbles caused, or helped to cause, erratic delivery of water (probably owing to the compressibility of air). Also, some of the unwanted ejections of water from the syringe after removal of the syringe needle from the sample cell were thought to be caused by the combination of (1) one or more air bubbles in the syringe, (2) the compressibility of air, and (3) a buildup of pressure in the sample cell. The final procedure adapted (described later) dealt with factors (1) and (3).

Use of a glass syringe barrel that was much larger than the plunger of the syringe used for adding small increments of water was highly unsatisfactory. The extremely high ratio of water contained in the syringe barrel to the water delivered made the amount of water delivered extremely sensitive to temperature. The heat of a human hand alone would often cause one or more extra drops to be ejected. A glass barrel that fit the plunger of the syringe was used for each series from which

final data were taken in the principal study.

There was conclusive evidence that significant amounts of water were evaporating and escaping through the tip of the syringe needle between incremental additions of water. This water loss caused the measurement of amounts of water added to be unreliable. For the ten series that yielded acceptable data, a little water was ejected and the needle tip was wiped with glassine powder paper immediately before each increment of water was added, thus insuring that water would extend almost exactly to the tip of the needle at the beginning of each incremental water addition.

Pressure in Cells

At one time (but not for the principal study), increments of water were added to the solution in a capped 2 cm sample cell by a syringe whose needle was inserted through the serum rubber cap on that cell. However, eventually the volume of liquid increased to the point that the resulting increase in the pressure inside the cell forced some solution out of the cell through one or more holes in the cap. To relieve the pressure inside the cell, a hollow needle was occasionally inserted through the cap. Later in the study, when one cm cells with silicone rubber stoppers were used (including the ten series yielding acceptable data for the principal study), a similar procedure for relief of gas pressure was followed.

Solid Matter in Solutions

During the principal study, very small amounts of threadlike solid matter were often observed in sample solutions, even at very small water

concentrations and even when no nickel was present. Since these quantities of solid were so minute, they were not expected to cause an increase in the order of magnitude of experimental error, and data related to these solutions were used as if no solid matter were present.

Temperature Dependence of Absorbance

Temperature dependence was exhibited at 1450 μ . The 1450 μ absorbance decreased noticeably as the sample (and reference) remained in the cell compartment of a spectrophotometer. It was concluded that the beam radiation probably was causing the sample temperature to rise. The 1940 μ absorbance was observed not to be nearly as temperature dependent, but there was some indication that rising temperature shifted the peak to slightly higher wavelengths.

It was found that adding 0.1% of water to a dilute 1-butanol solution of water at approximately room temperature in a 2 cm cell and shaking vigorously for 30 seconds raised the solution temperature by roughly 1° C. However, directing a small fan at the cell and its contents for one minute lowered the temperature of the contents to reasonably near room temperature. In view of the observation that the temperature dependence of the 1940 μ absorbance was so small and that the temperature could be rapidly restored to the controlled ambient temperature of the room, further temperature control was not attempted.

Spectrophotometers and Wavelengths

In the first part of the study, absorbance values were obtained (either directly or by subtracting the base 10 logarithm of the transmittance from the base 10 logarithm of the transmittance of the initial

or reference solution) by means of a Beckman DK-1 recording spectrophotometer. However, disturbing deviations from the Beer-Lambert law were observed at a wavelength of 1450 m μ when this instrument was used (as reported in Chapter II). Later, a Cary 14 recording spectrophotometer and a wavelength of 1940 m μ were used. The final absorbance data used in the principal study were obtained directly (from chart paper used) with the latter-mentioned instrument and stated wavelength.

One advantage of using the wavelength of 1940 m μ rather than that of 1450 m μ was that the ratio $\epsilon_{[L]}/\epsilon_M$, where $\epsilon_{[L]}$ is the molar absorptivity of free ligand and ϵ_M is the molar absorptivity of total nickel in dried starting solutions, was much larger at 1940 m μ than at 1450 m μ . Typical values of ϵ_M at 1940 m μ were in the 0.3 - 0.5 range, and typical values of ϵ_M at 1450 m μ were in the 1.0 - 1.5 range. With the $\epsilon_{[L]}$ values given on page 39, it is apparent that the ratio $\epsilon_{[L]}/\epsilon_M$ is more than 8 times as great at 1940 m μ as at 1450 m μ .

Using approximately one molar water in 1-butanol as the sample, a scan was run by means of the Cary 14 recording spectrophotometer, and the location of an absorbance peak at or within 3.5 m μ of 1940 m μ was verified.

Method for Taking Absorbance Readings

At one time, the absorbance readings were taken directly from the pointer and scale on the Cary 14 recording spectrophotometer. However, it was thought that the statistical mean values of fluctuating absorbance readings could be estimated more accurately if the absorbances were recorded on chart paper. The absorbance data used for the principal study were read from chart paper.

Reference Solutions

In the first stages of the study, the reference solutions routinely used in the spectrophotometer were identical to the initial sample solutions (i.e., the dry sample solutions before any water was added to them). This meant that reference solutions with different total metal concentrations were used for different series. There were definite, although not extremely large, absorbance differences in these reference solutions for different series. One could suspect that some factor, such as a difference in band widths necessary to obtain an equal reference energy for each series, might have led to slight differences in instrument performance. If such differences existed, subsequent data treatment probably would have magnified them.

Since (1) the effect of using different reference solutions was not studied and (2) the absorbances of reference solutions, even without any nickel in them, were quite high in the near infrared; dried 1-butanol, containing no nickel in any case, was used as the reference solution in each of the ten series from which final data were taken in the principal study.

Final Procedure Adopted for Principal Study

Cells, nonaqueous solutions, silicone rubber stoppers, and syringes and needles not used for water addition were stored in desiccators.

A total of 3.00 ml of 1-butanol and/or 0.315 molar $\text{Ni}(\text{ClO}_4)_2$ in 1-butanol stock solution was transferred by means of one, or possibly two, 2 ml syringes into a stoppered one cm spectrophotometer cell (designated as the sample cell). Each transfer from a syringe into a cell was accomplished through a hollow needle inserted through the silicone

rubber stopper. While 1-butanol or $\text{Ni}(\text{ClO}_4)_2$ in 1-butanol stock solution was being injected into a cell, another hollow needle inserted through the stopper allowed displaced air to escape. If both 1-butanol and the $\text{Ni}(\text{ClO}_4)_2$ stock solution in 1-butanol were used, the sample cell was shaken vigorously to obtain a homogeneous solution. 1-Butanol was similarly injected into a matched reference cell and an unmatched "zeroing" sample cell if the 1-butanol in them from a previous series of measurements had not been saved. The chief purpose of this was to check for instrumental drift and to compensate, if necessary, by readjusting the electrical balance. This procedure could also provide a ready reference for detection of instrument malfunctioning.

After being taken to the room in which the absorbance measurements were to be recorded, the three one cm cells were fanned together for 4 minutes with a small electric fan to bring them to ambient temperature. The room temperature remained constant within $\pm 0.9^\circ$ for the entire ten series. The outside optical surfaces of the cells were wiped with a Kimwipe disposable tissue. The "zeroing" sample cell and contents and the reference cell and contents (dried 1-butanol) were used in adjusting the electrical balance of a Cary 14 recording spectrophotometer so that the recording pen would mark at an absorbance of 0.000 on the chart paper. An absorbance measurement was taken using the sample cell and contents against its matched reference cell and contents (1-butanol). The recording pen was allowed to mark on the chart paper to give data to be treated later.

The syringe used for addition of water was a 0.2 ml micrometer syringe with a precision bore glass barrel and a Teflon plunger and was manufactured by Roger Gilmont Instruments, Inc. The best method found

for filling the 0.2 ml syringe with water was to add the water through the larger hole (through which the plunger would enter) in the glass barrel before completing assembly of the syringe. Attempts to fill the assembled syringe through the needle usually resulted in air bubbles being introduced into the syringe. Distilled water was used as it came from a distilled water tap.

The following procedure was repeated for each incremental water addition and subsequent absorbance measurement. A small amount of water was ejected from the syringe. The tip of the needle was wiped with glassine powder paper to remove excess water without drawing any more out of the syringe. Without undue delay, 0.0050 ml of water (according to syringe markings) was added to the contents of the sample cell. This cell was shaken vigorously for 30 seconds. The three cells together were fanned with a small electric fan for 2 minutes. The outside optical surfaces of the cells were wiped with a Kimwipe disposable tissue. After the electrical balance of the Cary 14 recording spectrophotometer was checked and, if necessary, readjusted, an absorbance measurement was made as described previously. Usually after each absorbance measurement immediately following the second, fourth, sixth, etc., water increment addition in a series, a hollow needle was inserted through the stopper of the sample cell to prevent pressure build-up in that cell by allowing a small quantity of air to escape.

Calculation of Water Concentrations

According to the literature (35), the density at 20°C can be calculated to within 0.0005 g/ml for any solution of only water in 1-butanol in a range of water concentrations that more than covers the range used

in this study. The formula given for such a calculation is

$$d = 0.8097 + .002103 p_w - .0000113 p_w^2, \quad (4-1)$$

where d is density in g/ml and p_w is weight percent of water. However, most of the solutions used in this study also contained $\text{Ni}(\text{ClO}_4)_2$. Experiments were conducted to determine whether (1) formula (4-1) with the density of 0.315 molar $\text{Ni}(\text{ClO}_4)_2$ solution in 1-butanol replacing the constant term or (2) assuming additivity of volumes would lead to more accurate estimation of densities of solutions prepared by adding small amounts of water to portions of the 0.315 molar $\text{Ni}(\text{ClO}_4)_2$ stock solution. The results indicated that the assumption of the additivity of volumes was better than the other option. Thus, volumes were assumed to be additive in calculating water concentrations.

The 0.2 ml micrometer syringe used for adding increments of water was calibrated by (1) ejecting increments of water and reweighing the syringe and contents and (2) ejecting increments of water into a stoppered cell and weighing the stopper, cell, and its contents. The factor, 0.977 ± 0.004 (standard deviation) g of water per ml according to syringe markings, was the mean of the factors obtained by methods (1) and (2).

The 2 ml micrometer syringe used throughout most of the principal study for introducing 1-butanol into the cells and $\text{Ni}(\text{ClO}_4)_2$ stock solution (in 1-butanol) into the sample cell was similarly calibrated, without the cell used in method (2) being stoppered. By averaging the factor from method (1) and that from method (2), the factor for this 2 ml syringe was determined to be 0.990 ± 0.003 g of water per ml according to syringe markings.

The ratio of calibration factors ($0.977/0.990$) was 0.987 ± 0.005 .

During absorbance measurements for the ten series yielding the final data, the overall temperature range in the room in which those measurements were being taken was approximately $23.6^{\circ} \pm 0.9^{\circ}$ C. Interpolating from published data gave the value of 0.9974 ± 0.0002 g/ml as the density of water at $23.6^{\circ} \pm 0.9^{\circ}$ C (17).

Using the values previously indicated for the ratio of calibration factors and density of water at 23.6° C and using 18.015 as the molecular weight of water, the following equation is obtained:

$$C_L = \frac{(0.987)(0.9974) \chi / 0.018015}{3.0000 + (0.987) \chi} (\pm 0.55\%) \quad (4-2)$$

Here, C_L is the molar concentration of total water, and χ is the ml of water added to 3.0000 ml of starting solution according to markings on syringes. Equation (4-2) simplifies to:

$$C_L = \frac{54.65 \chi}{3.0000 + 0.987 \chi} (\pm 0.55\%) \quad (4-3)$$

(In the actual calculations, two extra digits were usually carried to avoid possible introduction of bias in the last significant digit of C_L by rounding off too soon.)

CHAPTER V

EXPERIMENTAL DATA AND ITS TREATMENT

Experimental Data

The data eventually used with concentration values were absorbance values for solutions of $\text{Ni}(\text{ClO}_4)_2$ and/or water in 1-butanol at a wavelength of 1940 m μ , measured with a Cary 14 recording spectrophotometer. Dried 1-butanol was used in the 1-cm reference cell. For each nearly-constant total $\text{Ni}(\text{ClO}_4)_2$ concentration, the absorbance of the initial (dried) $\text{Ni}(\text{ClO}_4)_2$ in 1-butanol solution was subtracted from the absorbance measured after each successive increment of water had been added. Because of the procedure used, one would expect the total $\text{Ni}(\text{ClO}_4)_2$ concentration C_M to become slightly less after each increment, owing to dilution caused by adding water. The method used to (approximately) correct for this dilution was based upon the assumption of volume additivity and an average (constant) temperature of 23.6° C, at which the reported (17) density of water is 0.99742 g/ml. The correction formula used was

$$\text{Corrected } C_M = \frac{\text{Initial } C_M}{1 + \frac{.018015}{0.99742} C_L}, \quad (5-1)$$

where C_L is total water concentration in moles per liter of solution. However, this correction was not considered when subtracting initial solution absorbance from the absorbance measured after addition of each

increment of water. Each initial (dried) solution had a relatively small absorbance; thus the decrease in that absorbance due to dilution by water was regarded as insignificant compared to each total solution absorbance, which included relatively large absorbance due to water when sufficient water was present to make dilution effects on C_M significant.

Experimental data are given in Table V. Absorbance vs. C_L plots are presented in Figures 5 and 6. Each "starting solution" used in obtaining this data consisted of (1) $Ni(ClO_4)_2$ at the formal (total molar) concentration indicated as "initial C_M " plus (2) a minute amount of water present as an impurity (see Chapter IV) (but considered in subsequent data treatment not to be present at a significant concentration) in (3) 1-butanol. Each "wet solution" used consisted of (1) $Ni(ClO_4)_2$ at the same formal concentration as "initial C_M " except for the dilution effect plus (2) water at a formal concentration of C_L ($\pm 0.55\%$) in excess of the total water concentration of the "starting solution" in (3) 1-butanol.

Unsuitability of "Nothing" Model

The simplest model postulated is one that assumes that coordinated water simply does not absorb any 1940-m μ radiation. If this were true, the expected value of each \bar{m} (average number of absorbing bound water molecules per nickel(II) atom) in the "all or nothing" model would have been zero. One would have expected a single \bar{m} value to have a probability of no more than $\frac{1}{2}$ of being positive (owing to random error). However, in data treatment, only 4 of the 71 \bar{m} values were negative or zero.

The cumulative binomial probability distribution gives a proba-

TABLE V

ABSORBANCE AT 1940 MILLIMICRONS MINUS ABSORBANCE OF "STARTING SOLUTION"

<u>Measurements were made on month/day in 1969.</u>										
	2/9-10	3/21	10/8	3/16	10/15	9/19	3/19	4/5	10/13	10/27
	<u>Initial C_M</u>									
C _L	.000	.020	.040	.060	.080	0.100	0.150	0.200	0.315	.000
.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000
.091	.105	.087	.078	.066	.063	.061	.055	.053	.056	.105
.182	.207	.181	.170	.144	.142	.133	.114	.120	.116	.212
.272	.304	.279	.264	.228	.225	.215	.181	.180	.178	.315
.362	.405	.377	.361	.316	.313	.300	.254	.248	.241	.418
.452	.505	.473	.462	.409	.403	.386	.337	.318	.307	.525
.541	.596	.576	.564	.501	.495	.478	.416	.392	.377	.625
.630	.694	.673	.664	.591	.584	.568	.499	.468	.448	.726
.719	.789	.767	.760	.681	.679	.658	.583	.545	.518	.818
.808	.888	.859	.855	.773	.770	.748	.667	.621	.594	.919
.896	.980	.956	.954	.864	.863	.840	.751	.702	.670	1.009
.984	1.079			.955	.958	.927	.837	.781	.747	1.115
1.072	1.172						.919	.860	.826	1.211
1.159	1.262							.944	.901	1.315
1.247	1.351									

TABLE V (Continued)

		Measurements were made on month/day in 1969.									
		2/9-10	3/21	10/8	3/16	10/15	9/19	3/19	4/5	10/13	10/27
		Initial C_M									
C_L		.000	.020	.040	.060	.080	0.100	0.150	0.200	0.315	.000
1.333	1.439										
1.420	1.528										

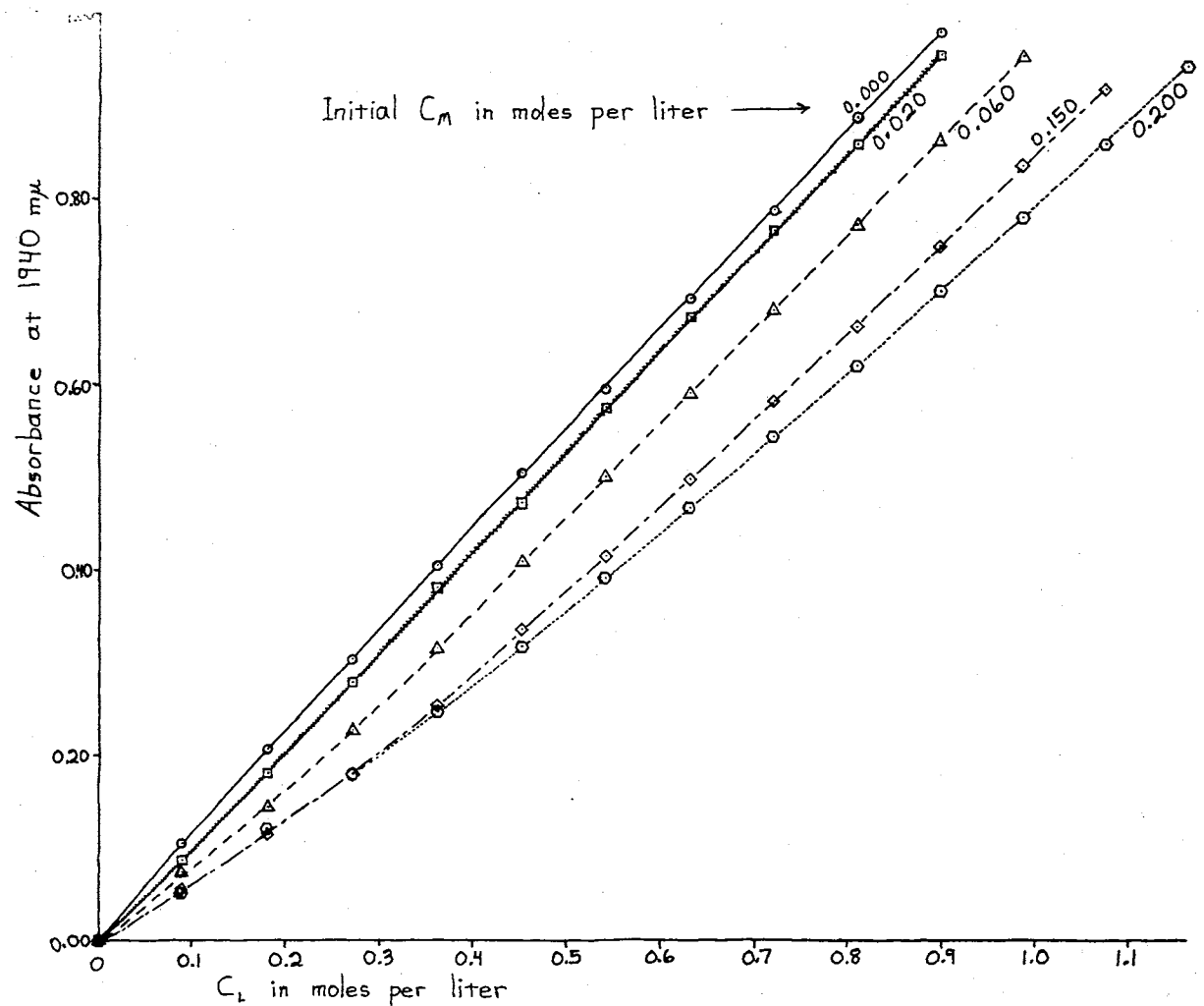


Figure 5. Absorbance Vs. C_L for $Ni(ClO_4)_2 + Water$ in 1-Butanol--Plot of Spring Semester, 1969, Data

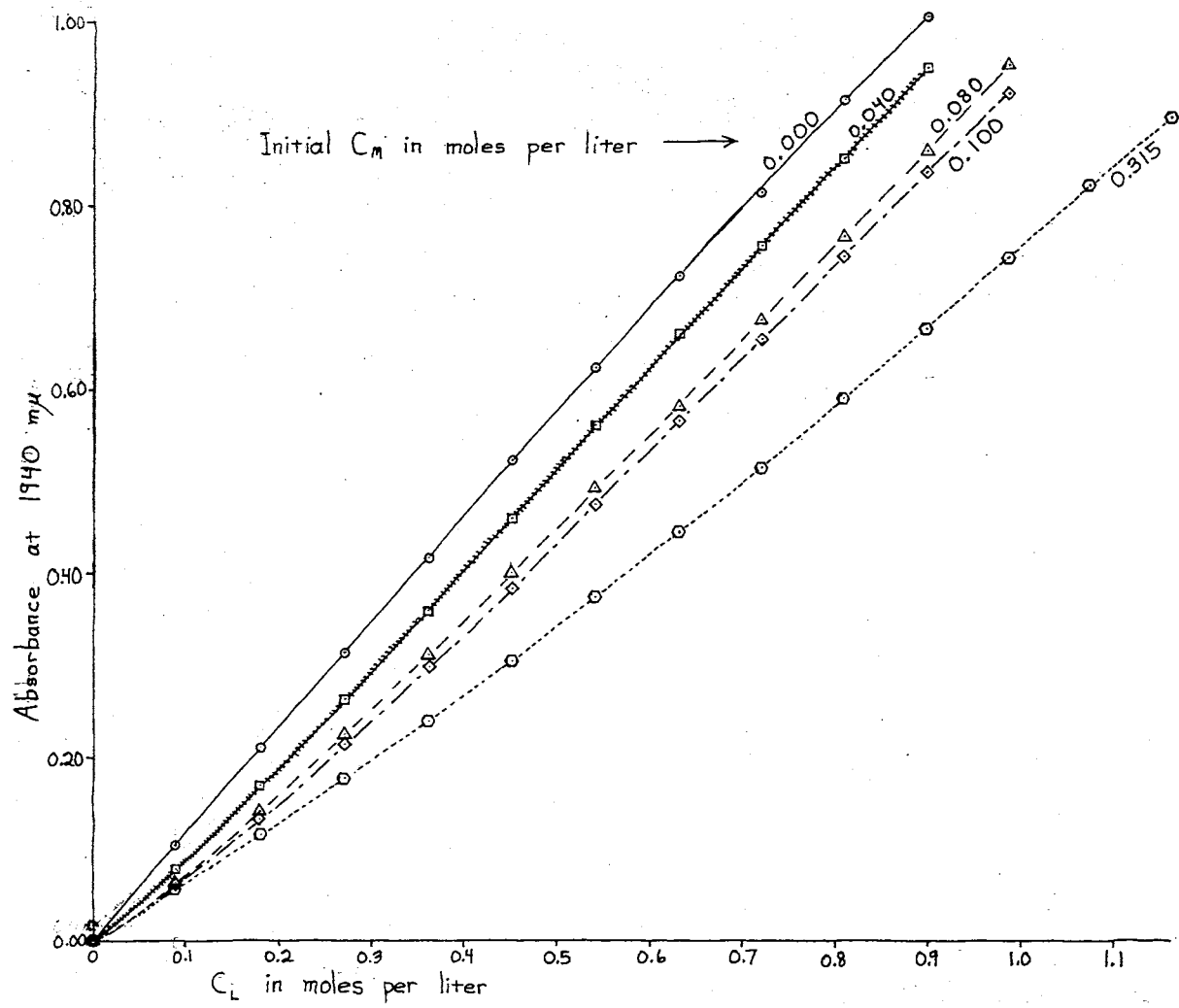


Figure 6. Absorbance Vs. C_L for $Ni(ClO_4)_2$ + Water in 1-Butanol--Plot of Fall Semester, 1969, Data

bility of 1.00000 (with an uncertainty of 0.0000051 or less) of at least 17 successes in 70 independent trials when the probability of success for a single trial is 0.50 (33). Thus this simplest model could be rejected at the 99.999% confidence level if independence of all the experimental \bar{m} values could be assumed.

The assumption of independence seems highly questionable owing to the use of smooth curves in obtaining \bar{m} values and the addition of several increments of water to each starting solution to obtain several original data points. However, the evidence for rejecting this simple "nothing" model still seems quite adequate.

Unsuitability of "All or Nothing" Model

If the "all or nothing" model were correct for this system, one would expect a single ($[L], \bar{n}$) point (where $[L]$ is the molar concentration of free water) not on the calculated

$$\bar{n} = \frac{\sum_{n=1}^6 n\beta_n [L]^n}{1 + \sum_{n=1}^6 \beta_n [L]^n} \quad (5-2)$$

(with the β_n values being correct) vs. $\log [L]$ curve to have a probability of $\frac{1}{2}$ of being above that line and the same probability of being below that line. However, only 14 of the 71 points obtained by a data treatment under this model were found to lie above a line determined by Equation (5-2) and the β_n values given for Figure 10, and 57 of the points lie below the line, in an \bar{n} vs. $[L]$ plot (see Figure 10).

It should be pointed out again that the probability of at least 17 successes in 70 independent trials, when each trial alone has a probability of success of 0.50, is 1.00000 (with an uncertainty of

.0000051 or less) (33). If it is assumed that the \bar{n} line is sufficiently close to being correct, that no more than two points are incorrectly assigned as being below the correct line, and that all the data points are independent, then the "all or nothing" model could be rejected at the 99.998% (two-tailed) confidence level for this system. Although the \bar{n} line does not seem to warrant that much confidence and the assumption of independence again seems highly questionable, Figure 10 shows that it is still highly likely that the "all or nothing" model leads to significantly underestimating \bar{n} .

Examination of Figure 10 reveals another serious deficiency of the "all or nothing" model treatment. The points are so badly scattered that any curve fit to them would have very questionable meaning. The scatter may be partly due to error magnification caused by trying to find the equal-absorbance points for a certain $\bar{\lambda}$ value on two nearly parallel lines (see Figure 1). This is roughly equivalent to trying to find the point on each of two nearly-parallel lines at which the horizontal distance between the two lines is a specified value.

Data Treatment Using Modified "Corresponding Solutions" Method

Experimental data were finally and most successfully treated by the modified "corresponding solutions" method as indicated in Chapter II. Results of this treatment are shown in Figures 7 through 11. The points for initial $C_M = 0.150$ molar seemed somewhat irregular (see Figure 9). These points were included in calculating the $[L]$ and \bar{n} values plotted as x's in Figure 10 and used in subsequent data treatment. However, they were not included in calculating the $[L]$ and \bar{n} values plotted in Figure 11.

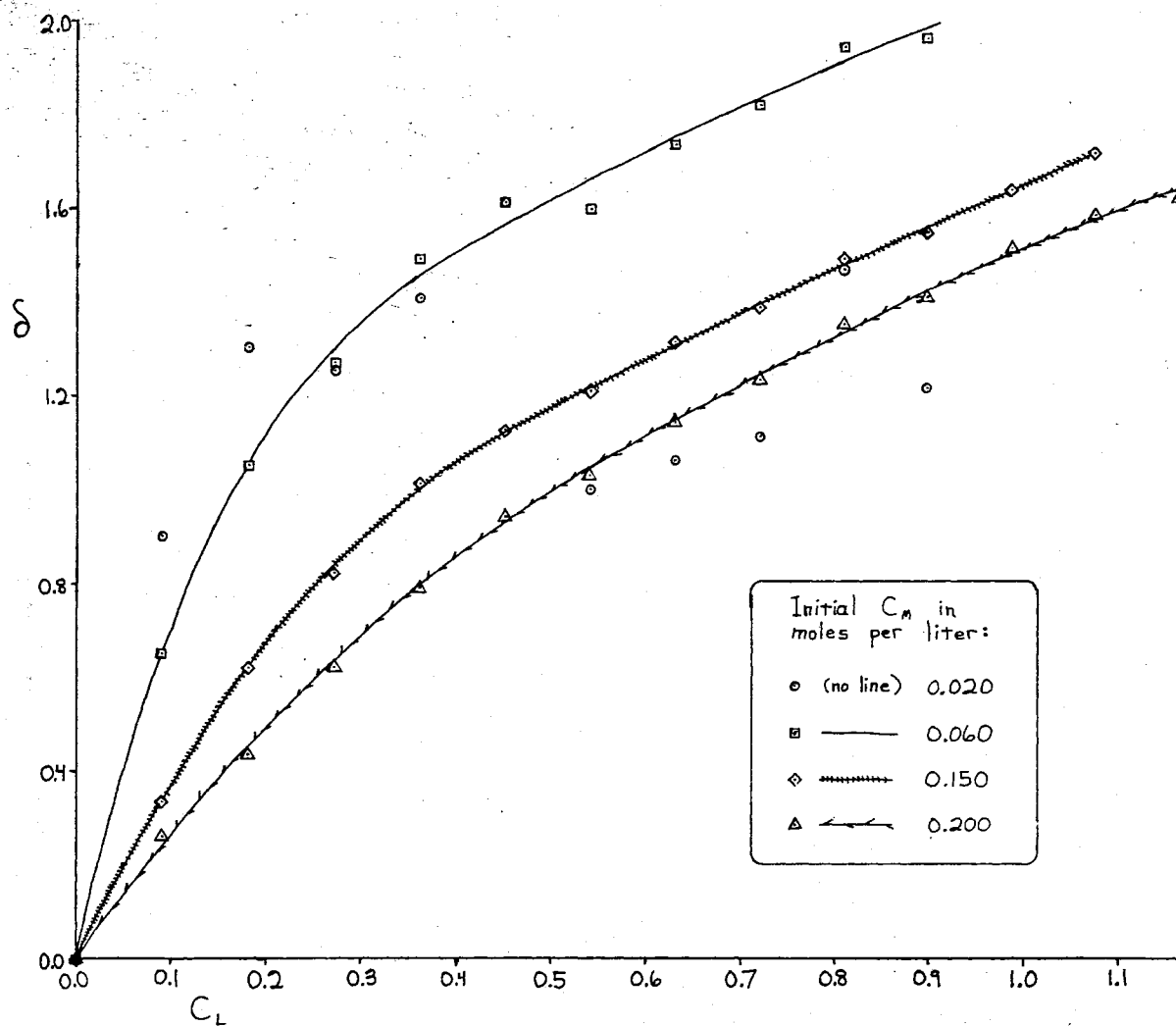


Figure 7. Plot of δ Vs. C_L for $\text{Ni}(\text{ClO}_4)_2$ + Water in 1-Butanol--From Spring Semester, 1969, 1940- μ Absorbance Data

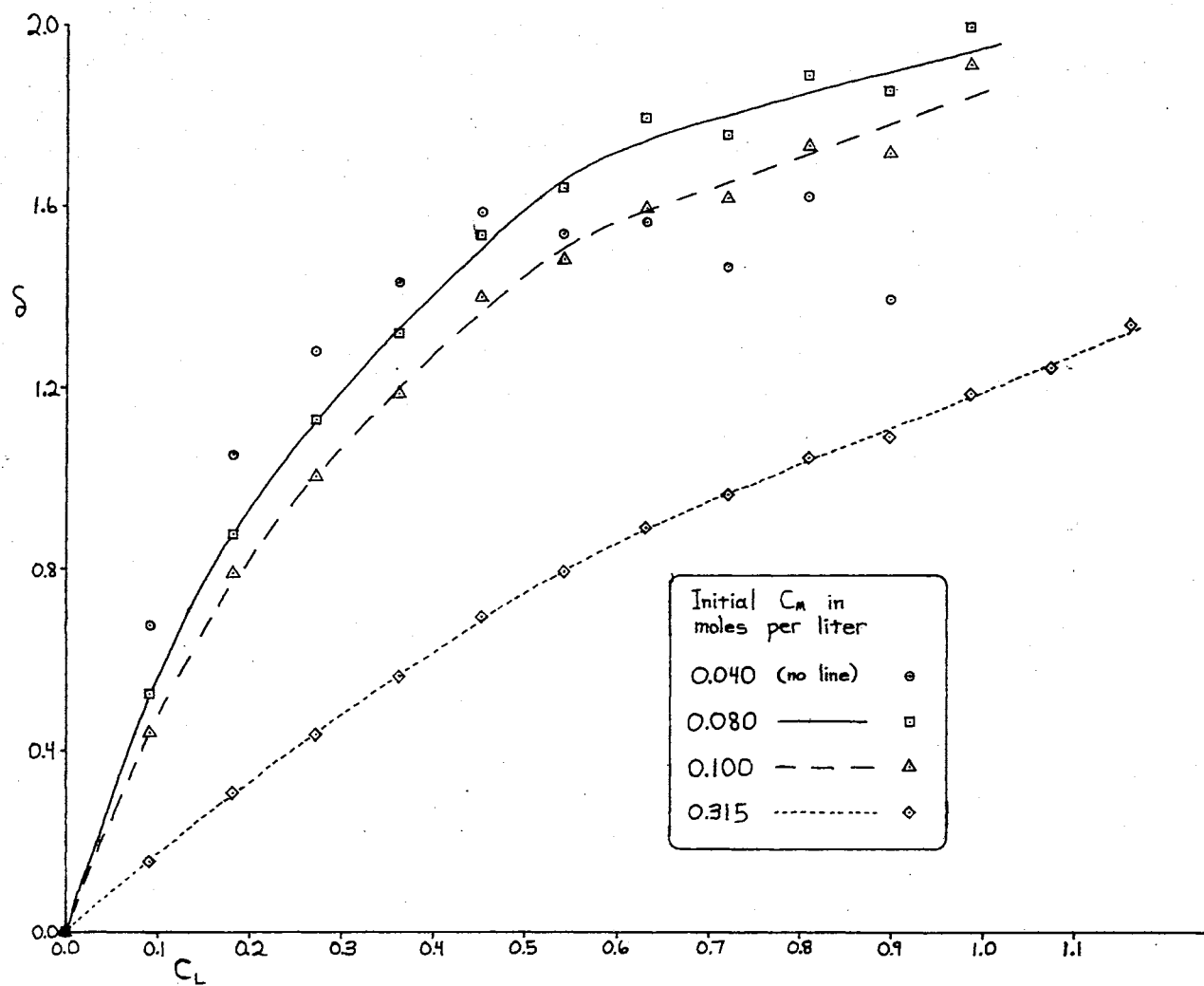


Figure 8. Plot of δ Vs. C_L for $\text{Ni}(\text{ClO}_4)_2$ + Water in 1-Butanol--From Fall Semester, 1969, 1940- μ Absorbance Data

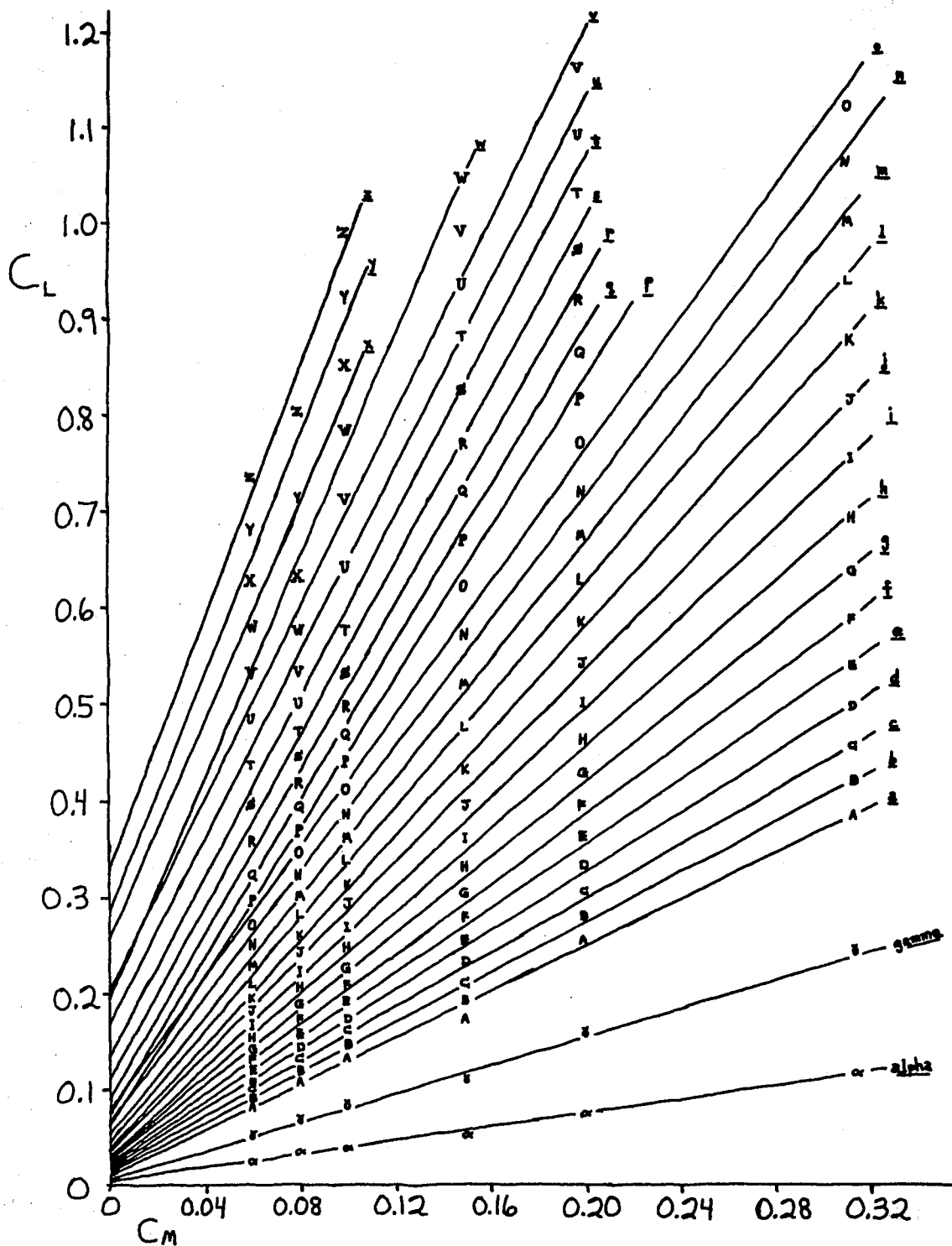


Figure 9. Nickel(II) Aquocomplexes in 1-Butanol--Combined 1969 Data--Modified "Corresponding Solutions" Plot. (Each capital or Greek letter represents a point. Designations of lines are underlined.)

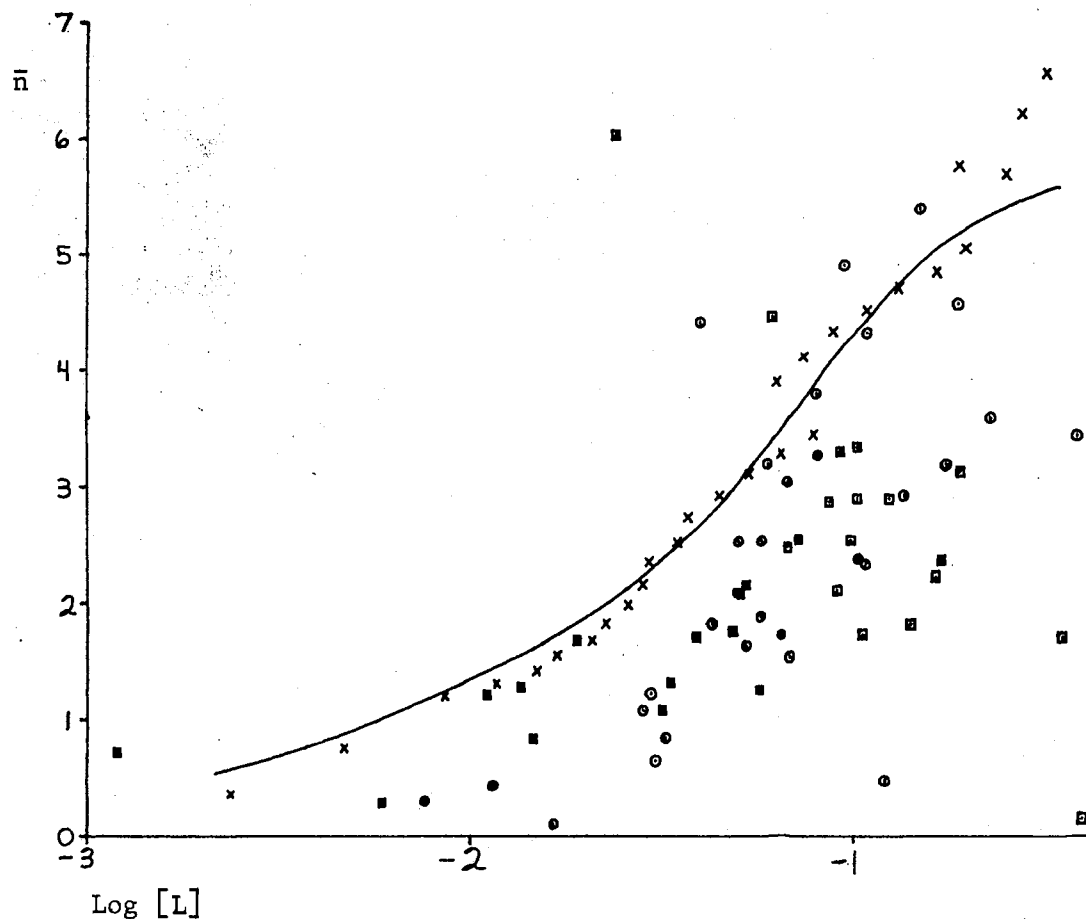
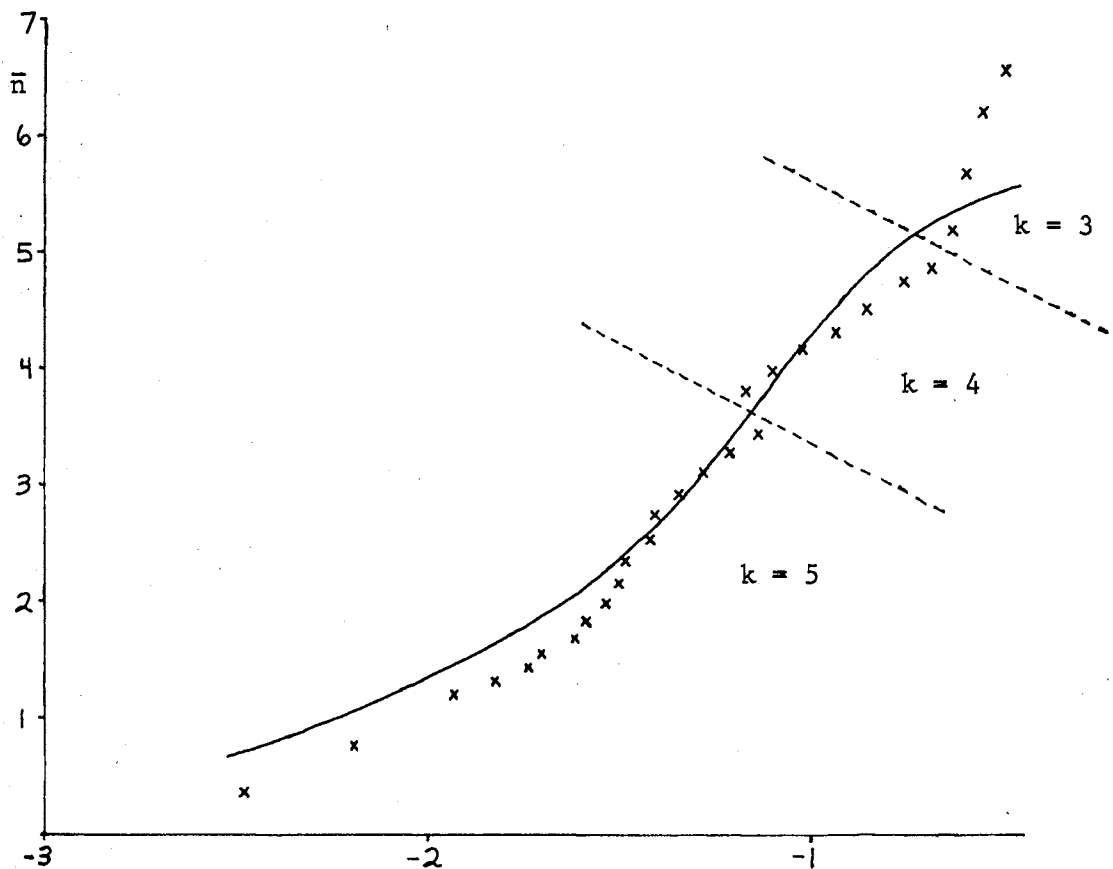


Figure 10. Nickel(II) Aquo complexes in 1-Butanol-- \bar{n} Vs. $[L]$ Plot from 1940-m μ Absorbance Data

Points are from modified "corresponding solutions" (x) treatment of both spring semester, 1969, and fall semester, 1969, data and "all or nothing" model treatment of spring semester, 1969, (\circ) and fall semester, 1969, (\square) data. The line represents values calculated by using $\beta_1 = 3.5 \times 10^2$, $\beta_2 = 2.3 \times 10^4$, $\beta_3 = 5.2 \times 10^5$, $\beta_4 = 4.3 \times 10^6$, $\beta_5 = 7.7 \times 10^7$, and $\beta_6 = 5.5 \times 10^8$. These points were excluded:

- | | |
|--|---|
| 1 \bar{n} negative | \circ |
| 6 $[L]$ negative and $0 \leq \bar{n} \leq 7$ | $\circ \circ \square \square \square \square$ |
| 1 $[L]$ negative and $\bar{n} > 7$ | \square |
| 1 $[L]$ positive and $\bar{n} > 7$ | \square |



Log [L]

Figure 11. Nickel(II) Aquo complexes in 1-Butanol-- \bar{n} Vs. [L] Plot from 1940-m μ Absorbance Data, with Data for Initial $C_M = 0.150$ Molar Omitted.

Points are from modified "corresponding solutions" treatment of both spring semester, 1969, and fall semester, 1969, data with the indicated omission. Each of these ([L], \bar{n}) points is determined by k (C_M, C_L) points. The line is the same as that in Figure 10.

Figure 11 illustrates the effect of losing (i.e., either (1) not having, owing to the associated absorbance being above the absorbance range used, or (2) discarding) the use of a point from the set of (C_M, C_L) points used to determine $[L]$ and \bar{n} by linear least squares calculation, when the lost point is associated with a relatively high C_M . The transition from 5 points to 4 points was accompanied by an apparent marked discontinuity in the formation curve. Moreover, the transition from 4 points to 3 points was accompanied by an obvious increase of slope in the formation curve. This is the kind of behavior that one might expect from a system containing polynuclear complexes. However, the theory used in this work has considered only mononuclear complexes. Thus, the results obtained should be cautiously interpreted.

Treatment of $([L], \bar{n})$ Data Obtained

Attempts were made to use an existing computer method (58) and assume that all complexes of the type $Ni(H_2O)_n^{++}$ from $n = 1$ to $n = 6$ were formed. However, the model assuming formation of six complexes was not acceptable under the rejection criteria of the computer program. Formation constants β_1 , β_3 , and β_5 would have been negative, even if the last four data points were omitted or if only the spring semester, 1969, data were used.

The three positive β_n values were used as initial values and an attempt was made to use Poe's (46) computational method (without use of "pseudo-constants"). When all $([L], \bar{n})$ points were used, the resulting β_n values eventually included some negative numbers. An adjustment was made to use only points that would contribute positive values from whose weighted mean a given β_n was found. However, such an adjustment would

be expected to introduce bias, so the β_n values were refined by further treatment.

Further treatment included the computer method mentioned in Chapter II and illustrated by Figure 2 and Table IV. Results are given in Figure 12.

Attempts were also made to find β_n values by graphical methods. Rossotti and Rossotti's (50) method yielded values of about 95 for β_1 and about 2×10^4 for β_2 , but a negative value appeared for β_3 . Fomin and Maiorova's (21) method indicated that β_1 was around 1.4×10^2 .

Another graphical method tried was similar to Poe's (46) computational method. However, instead of calculating one β_c value from five fixed β_n values and each suitable data point ($[L], \bar{n}$), β_d was calculated as the dependent variable while β_1 was varied as the independent variable. The other four β_n values were fixed and used with each suitable (i.e., \bar{n} not too widely separated from both i and d) data point ($[L], \bar{n}$) as parameters. A line was thus obtained from each suitable data point. Ideally, a compact cluster of intersections of these lines on a β_d vs. β_1 graph could yield β_1 and β_d values to be used in the next iteration. However, the experimental data from this study produced intersections so widely scattered that they defined interpretation.

A brief calculation, similar to a method used by Jørgensen (38) was performed. The calculation using the reported (26) value of 91.08 for the molecular volume of 1-butanol (at 20°) and 4.8×10^{-2} molar as the approximate value of $[L]$ when \bar{n} equals exactly 3 (corresponding to an assumed equal average number of water and 1-butanol molecules bound per nickel(II) atom) led to the expression $\frac{1000}{.048 \times 91.08} = 2.3 \times 10^2$. Thus, the relative tendency of a nickel(II) atom to be coordinated to a

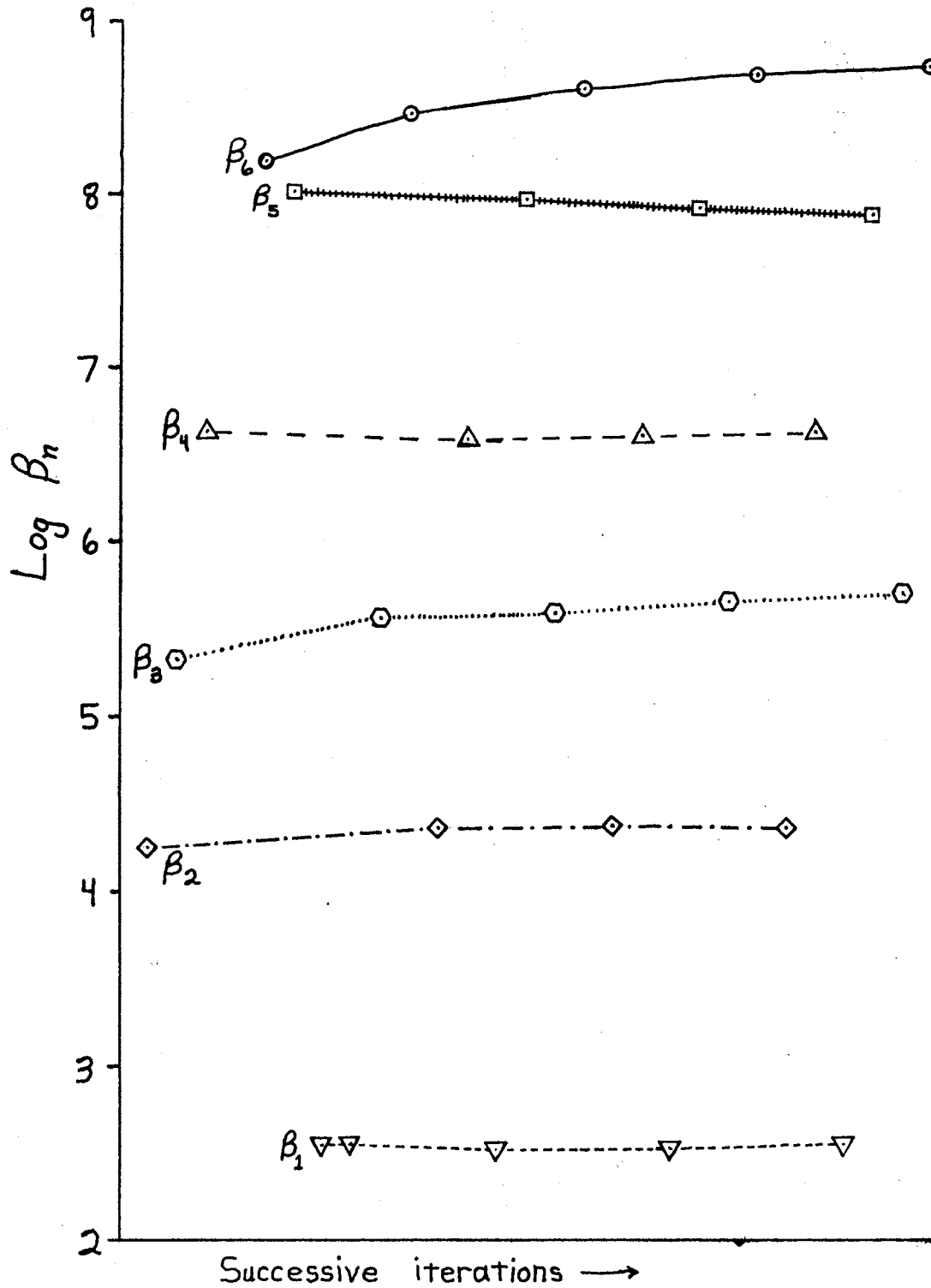


Figure 12. Variation of the $\text{Log } \beta_n$ Values With Successive Iterations of the Computer Method Illustrated by Figure 2 and Table IV

water molecule rather than to a 1-butanol molecule was estimated to be 2.3×10^2 . (This may be compared to a corresponding value of 13 reported (38) when ethanol, rather than 1-butanol, competes with water.) Assumptions that are made in this calculation include (1) the absence of appreciable concentrations of polynuclear complexes and (2) only water and 1-butanol being bound at an average of 6 coordination sites per nickel(II) atom when \bar{n} is exactly 3.

CHAPTER VI

SUMMARY AND CONCLUSIONS

The absorption spectra of nickel(II) perchlorate solutions in 1-butanol containing varying amounts of water have been examined with the view of studying the formation of aquocomplexes spectrophotometrically. Metal ion ligand field bands in the visible region of the spectra are not considered very useful because of the small changes in the values of the molar absorptivities with added water. Also, the attempted use of pyridine as an auxiliary ligand has failed to yield useful results under the experimental conditions used. However, the ligand (water) bands centered at about 1450 and 1940 $m\mu$ decrease in intensity with increase in metal concentration at constant total water concentration. Careful investigation of the shorter wavelength band showed that the peak height was proportional to the integrated intensity.

Experiments were conducted in which small increments of water were added to solutions of practically constant salt concentration and the absorbances at 1940 $m\mu$ were measured. Concentrations of "free" water can be found from the decrease in the absorbance of the solutions relative to that of the solvent, if it can be assumed that none of the coordinated water molecules absorb. If, however, it is assumed that some of the coordinated water molecules do not absorb while other positionally nonequivalent water molecules do absorb with an absorptivity the same as that for the "free" water, the interpretation is more complicated.

Three models have been examined in interpreting the experimental results. These are (1) the "nothing" model in which it is assumed that water coordinated to nickel(II) does not absorb radiation at the wavelength studied; (2) the "all or nothing" model in which it is postulated that all water molecules coordinated to nickel(II) fall in two groups, (A) water molecules not absorbing radiation at the wavelength being studied and (B) water molecules absorbing with the same absorptivity as that of "free" water at that wavelength; and (3) a model in which it is postulated that all ligand molecules L coordinated to metal or central group M fall in two groups, each exhibiting a different molar absorptivity, with the smaller absorptivity not necessarily being zero and the larger absorptivity not necessarily being equal to that of free L, and for which a modification of Bjerrum's (10) principle of "corresponding solutions" has been shown to apply. For 1-butanol solutions containing $\text{Ni}(\text{ClO}_4)_2$ and water studied at 1940 $\text{m}\mu$, the first two of these have been rejected on statistical arguments while a modified "corresponding solutions" treatment based on the third has been applied to the data with only limited success. Attempts to determine a set of formation constants by methods given in the literature (46, 50, 58) have not yielded a set of values which are all positive and give a good fit to the \bar{n} vs. $\log [L]$ formation curve.

A method of data treatment is proposed for use (1) when the "all or nothing" model can safely be assumed to apply or (2) in testing the validity of the "all or nothing" model for a given system by comparison of results with those obtained by a more general method. The results of treating experimental data by using this method have been used in rejecting the "all or nothing" model. A graphical method patterned largely

after Poe's (46) computational method has been tried without success. A common fault of these two methods and the modified "corresponding solutions" method is that they tend to magnify experimental error. A simple computer program is also given, although convergence has not resulted from its use with a limited number of iterations.

Despite the scantiness of success in this work, the modified "corresponding solutions" method is expected to be useful in a number of systems in which the average decrease in absorptivity of the ligand upon being bound is sufficiently large compared with the absorptivity of free ligand. Data resulting from the use of this method have been used to estimate the relative tendency of a nickel(II) atom to be bound to a water molecule rather than to a 1-butanol molecule to be 2.3×10^2 .

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APPENDIX

EFFECT OF A CONSTANT FRACTIONAL ERROR IN C_M ON THE RESULTS OF A MODIFIED "CORRE- SPONDING SOLUTIONS" TREATMENT

If an erroneous total metal concentration is used in the modified "corresponding solutions" treatment described in Chapter II of this thesis, and if no other errors are considered, then the designated total metal concentration of each solution can be represented by $h C_M$, where C_M is the true total metal concentration and h is a nonzero value given by

$$h = \frac{\text{Value used as } C_M \text{ of stock solution}}{\text{True value of } C_M \text{ of stock solution}} \quad (\text{A-1})$$

If h is sufficiently close to being exactly one, the total volume produced by mixing x ml of stock solution and $(y-x)$ ml of solvent is essentially the same as the total volume produced by mixing $\frac{x}{h}$ ml of stock solution and $(y - \frac{x}{h})$ ml of solvent, and the designated total metal concentration can be taken essentially as equal to $h C_M$.

Substituting $h C_M$ for C_M in Equation (2-21) and designating the left-hand member as δ' gives

$$\delta' = \frac{(\phi_L - \phi)}{bh C_M} \quad (\text{A-2})$$

Since h is constant throughout the study, one can multiply both sides of Equation (A-2) by h , compare the resulting equation with Equation (2-21),

and see that equality of values for δ' implies equality of values for $h\delta'$. The latter implies equality of values for δ . This is the "corresponding solutions" criterion. (Note that it is essential that h have the same value throughout the entire study, since "corresponding" solutions generally might include one for every approximate C_M used.)

With the validity of the modified "corresponding solutions" treatment established so far despite the hypothesized error, the C_L values should be linearly plotted against the true C_M values for each set of corresponding solutions. However, it is hypothesized that it is the $h C_M$ values, rather than the true C_M values, that are used. Since the "corresponding solutions" equation,

$$C_L = \bar{n} C_M + [L], \quad (A-3)$$

is valid, the equivalent relation

$$C_L = \left(\frac{\bar{n}}{h}\right) (hC_M) + [L] \quad (A-4)$$

is also valid. Thus, a true $[L]$ value can be obtained from each intercept in spite of the postulated error; however, a $\left(\frac{\bar{n}}{h}\right)$ value, instead of the desired \bar{n} , is obtained from each slope.

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