

MEDIUM EFFECTS ON THE EXTRACTION OF COPPER(II),  
AND NICKEL(II) PERCHLORATES BY 1-BUTANOL

By

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## CHAPTER I

### INTRODUCTION

#### Purpose and Scope of Investigation

This investigation represents part of a general research program at the Oklahoma State University initiated for the purpose of determining some of the factors influencing the extraction and separation of transition metal salts. Previous work in this program, as in this particular investigation, has been confined to systems in which extraction primarily depends upon solvation of the transition metal ions by the solvating solvent in the organic phase (19). For instance, Yates et al. (26) showed that it was possible to calculate hydration numbers for a number of salts from the dependence of solvating agent (water) concentration in the organic diluent (2-octanol) on the organic phase salt concentration. The ability to carry out successfully such a procedure, of course, is restricted to this particular type of distribution system (19).

In the water-octanol solvent pair, where the solvating solvent in the organic phase is also water, the concentration of water in the organic diluent cannot be varied at will. However, Yates et al. (26), found that at sufficiently low salt concentrations the solubility of water in octanol was almost unaffected by the presence of salt. The specific purpose of the present investigation is to investigate the concentration dependence of the distribution coefficients of copper and

nickel perchlorates in an analogous concentration range in the water-1-butanol solvent pair. It is assumed that for sufficiently low extracted salt concentration, the butanol-rich phase may be regarded as a mixed solvent of constant composition. Subject to this assumption, the distribution coefficients and their concentration dependence may then be analyzed in terms of Owen's medium effects (12).

The experimental part of the investigation includes the measurement of the concentration dependence of distribution coefficients of copper and nickel perchlorates at small concentrations and the calorimetric measurement of the heats of transfer of the metal salts from aqueous solutions to the equilibrium organic phase. The latter measurements are necessarily made indirectly, since the solid anhydrous perchlorate salts do not seem to be capable of preparation. From such distribution and calorimetric data it is possible by suitable extrapolation procedures to determine standard thermodynamic transfer properties.

#### Literature Survey

One of the mechanisms by which an inorganic salt may be extracted from aqueous solution is the solvation of the cation by the extracting solvent (4). This may occur by direct or "primary" solvation of the cation by a specific agent in the nonaqueous phase or by "secondary" solvation of a hydrated cation. An example of the former type is the extraction of transition metal salts by tri-n-butyl phosphate (TBP), while an example of the second type is the extraction of cobalt and nickel perchlorates by 2-octanol (19).

In most distribution studies involving TBP, the TBP is diluted by an inert organic solvent such as kerosene or cyclohexane, thus giving

the system two concentration degrees of freedom. That is, the distribution coefficient is a function of solvent concentration in the organic diluent and, for example, the aqueous phase salt molality. Under ideal conditions, i.e., tracer concentration of both metal salt and solvating agent, the dependence of the distribution coefficient on solvent concentration in the organic diluent may be used to determine solvation numbers and to identify the solute species (19).

Systems involving extraction of aqueous salt solutions by the higher alcohols have only one concentration degree of freedom and extraction is accomplished by secondary solvation of hydrated cationic species (19). An important factor in such systems is, of course, the amount of water soluble in the alcohol in the absence of extracted salt.

It was pointed out in the previous section, that the purpose of the investigation is to study the extraction of nickel and copper perchlorates by 1-butanol from the point of view that the organic phase consists of an electrolyte solution in a mixed solvent composed of a specific solvent (water) and an organic diluent (1-butanol). Thus, the system differs from the TBP-kerosene system only in that the system under consideration is univariant. In order to make the analogy complete and to provide a basis for future discussion of the behavior of the organic phase in terms of mixed solvent behavior, it is necessary to assume that the organic phase solvent composition is insensitive to the concentration of the extracted salt. This lends pseudo bivariance to the system and makes it possible to consider the water in the organic phase as a specific solvating agent in the organic diluent. This appears to be a reasonable assumption in the case of extracted salt concentrations in the water-1-butanol solvent pair which are small since 1-butanol



saturated with water constitutes a mixed solvent consisting of very nearly fifty mole per cent water (13).

At higher extracted salt concentrations, the co-extracted water becomes appreciable and the present treatment, in terms of a single mixed solvent, suffers in the following respects. First, the infinitely dilute solution standard state for the electrolyte in the organic phase depends on the equilibrium solvent composition; hence, it is a function of the single independent variable, e.g., the aqueous phase salt molality. Second, the concept of a distribution coefficient becomes ambiguous in the absence of a specific solvation model; i.e., it becomes necessary to assign definite hydration numbers and to consider the water of hydration as cosolute. Third, rather than the organic phase becoming saturated, as in the case of the TBP solvent mixtures, the system would most likely exhibit a plait point, becoming completely miscible.

The problem of the nature of electrolyte solutions in mixed solvents has been examined from two different points of view. Owen (12), has analyzed the effect of an added nonelectrolyte, e.g., a second solvent component, on the properties of an aqueous electrolyte. Owen's treatment refers the ionic activity coefficients in the mixed solvent to unity at infinite dilution in pure water solvent. This is accomplished by dividing the total medium effect of the added nonelectrolyte on the thermodynamic properties of the ionic solute into the "primary medium effect" and the "secondary medium effect." The primary medium effect is defined as the effect of the second solvent on the standard free energy of the electrolyte solute. This corresponds to the transfer of ions from one medium to another under conditions where interionic

actions are not present. The simplest model for the primary medium effect is that represented by the Born equation (4). This equation states that the free energy of transfer  $\Delta F_t^0$ , of a bare spherical ion of radius  $r$  and charge  $Ze$  from water (dielectric constant  $\epsilon_w$ ) to a mixed solvent (dielectric constant  $\epsilon_s$ ) is

$$\Delta F_t^0 = Z^2 e^2 / 2r (1/\epsilon_s - 1/\epsilon_w). \quad (1)$$

In the derivation of this equation, it is assumed that the solvent is a continuous medium of uniform dielectric constant, and that specific ion-solvent interaction can be ignored. Under these conditions, Owen's primary medium effect is represented by

$$\log \frac{s_f^0}{w_f^0} = (0.43) (\Delta F_t^0 / \nu RT), \quad (2)$$

where  $\frac{s_f^0}{w_f^0}$  is the activity coefficient of an infinitely dilute electrolyte in the mixed solvent referred to unity at infinite dilution in pure water. Although this is obviously a deficient model, it predicts qualitatively correct results. For instance, if  $\epsilon_s$  is less than  $\epsilon_w$ , then  $\Delta F_t^0$  is positive.

The secondary medium effect then accounts for the change in ionic interactions as a result of changes in composition of the medium. It corresponds to the transfer of ions from finite concentrations in one medium to infinite dilution and from the infinite dilute state to finite concentrations in the other. The Debye-Huckel theory adequately accounts for this effect only to the extent that it correctly predicts ionic activity coefficients in the individual solvents (23). If the Debye-Huckel limiting law applies, the secondary medium effect is given by

$$\log \left( \frac{s_f}{s_f} / \frac{w_f}{w_f} \right) = \frac{1.825 \times 10^{-6}}{T^{3/2}} \left( \frac{1}{\epsilon_w^{3/2}} - \frac{1}{\epsilon_s^{3/2}} \right) \sqrt{C_s} \quad (3)$$

Owen's equation for the total medium effect is then given by

$$\log \left( \frac{{}^S f}{w} / \frac{{}^W f}{w} \right) = \log {}^S f^0 + \log \left( \frac{{}^S f}{s} / \frac{{}^W f}{w} \right). \quad (4)$$

The notation is due to Robinson and Stokes (23), where the superscript indicates the solvent and the subscript indicates the reference state. That is,  $\frac{{}^S f}{w}$  means the activity coefficient of an electrolyte at concentration  $C_s$  in the mixed solvent referred to unity at infinite dilution in pure water.

Both effects are seen to be primarily dependent on the dielectric constant of the medium; however, the primary medium effect is obviously concentration independent; hence it is a solvation dependent property.

The effect of ionic concentration on the activity of nonelectrolytes in aqueous solution has been reviewed and analyzed by McDevit and Long (17). These workers showed that there is a general linear relationship between the logarithm of the nonelectrolyte activity coefficient and the salt concentration. The proportionality constant is termed the salting-in or salting-out coefficient depending upon whether the added salt decreases or increases the activity coefficient of the nonelectrolyte. The McDevit-Long equation is simply

$$\ln f_n = k_s C_s, \quad (5)$$

where  $k_s$  is the salting constant,  $C_s$  is the salt concentration and  $f_n$  is the activity coefficient of the nonelectrolyte in aqueous solution. Explanations of the salt effect have been given by Debye and McAulay (3), in terms of electrostatic effects and by Long and McDevit (16), in terms of internal pressure; however, neither theory is completely satisfactory. A good example of this effect is seen in the dependence of organic phase water concentration on extracted salt concentration in the

extraction of transition metal salts by the higher alcohols (18).

For a given solution, the medium effects of Owen and the general salt effect must, of course, be related by a Gibbs-Duhem type of equation. That is, at constant temperature and pressure, we have

$$\sum_i n_i d\mu_i = 0, \quad (6')$$

which, for an electrolyte solution in a mixture of water and an organic solvent may be written

$$x d \ln a_w + (1 - x) d \ln a_o = -m_o \bar{M} / 1000 d (\mu_o^0 / RT - \ln a_s), (6)$$

where  $x$  is the mole fraction of water in a pure mixed solvent of mean molecular weight  $\bar{M}$ ,  $m_o$  is the molality of the salt and  $\mu_o^0$  is the standard chemical potential of the electrolyte in the mixed solvent. Here  $\bar{M} = xM_w + (1 - x)M_o$ , where  $M_w$  is the molecular weight of water and  $M_o$  is the molecular weight of the organic solvent. If  $x$  is maintained constant, then the salt effect is given by the dependence of  $a_o$  on  $m_o$  whereas, if  $m_o$  is kept constant, the primary medium effect is given by the dependence of  $\mu_o^0$  on  $x$ .

*solvation*  
*discrimination* When the solvent composition is a variable, a slightly more convenient approach is desirable. For instance, Grunwald (10) has shown that the variation in the ratio of the activities of the two solvents can be used to determine the dependence of the standard state of the ionic solute on solvent composition. The treatment has been carried further by using the same criterion for determining the extent of selective solvation of the ionic species in solution. For instance, a decrease in the ratio  $a_w / a_o$  indicates that the electrolyte discriminates in favor of water in the solvation sphere.

The extent of solvent sorting by ionic species in solution has ✓

solvation  
isom

been considered from a theoretical point of view by Scatchard (24) and by Frank (8), in terms of electrostatic interactions of ions with nonelectrolytes. The practical effects of competitive solvation in extraction by mixed solvents have been reviewed by Marcus (19). In the systems under consideration, of course, the cations in solution are presumed to discriminate completely in favor of the "solvating agent" water in the organic phase, thus making possible the concept of a primary hydration number for the cation in the nonaqueous phase.

Perchlorate  
and perchlorate  
in  
the  
aqueous  
phase

In the case of extraction of transition metal salts by TBP in kerosene, TBP solvation numbers are found experimentally to be the difference between the maximum or characteristic coordination number of the cation and the ionic charge (19). That is, the extracted species is most likely a definite solvate of a neutral species. By contrast, the extraction of the same salts by the higher alcohols involves the salting-in of water into the organic phase in addition to specific hydration of the cations involved. This leads to nonintegral apparent hydration numbers which are generally higher than the coordination numbers for the cations (26), indicating that the salt in the organic phase is ionized, though only partially dissociated. According to Bockris (2), solvation should be divided into primary and secondary solvation where it is reasonable to assume that primary solvation of a transition metal cation is equivalent to aquo-complex formation but that the remainder of the salted-in water participates only in secondary solvation.

distribution  
coeff.

As can be seen from the Nernst partition law (4), the limiting distribution coefficient for a species distributed between a completely immiscible solvent-pair is directly related to the standard free energy

of transfer. Nernst's treatment gives the distribution coefficient as

$$D = m_0/m = \left(\frac{w_Y}{w_S} \frac{s_Y}{s_S}\right) \exp (\mu_0^0 - \mu_W^0) / \nu RT. \quad (7)$$

That standard free energy of transfer, i.e.,  $(\mu_0^0 - \mu_W^0)$ , of the salt from one phase to another is simply the difference in the free energies of solvation of the salt in the two phases. It is evident that the Nernst law applies equally well to distribution in a partially miscible solvent-pair if the presence by the distributed solute does not alter the degree of miscibility of the two solvents. Then  $(\mu_0^0 - \mu_W^0)$  is a constant characteristic of the mixed solvent composition. This is the basis for the most important simplifying assumption in the present treatment. This assumption is necessitated by the fact that the distribution of the perchlorate salts results in organic-phase solvent mixtures that do not exist in the absence of the salt, making calorimetric and other measurements in such mixtures impossible.

Heats of transfer for equilibrium distribution systems are simply the differences in the partial molal heats of solution of the distributed species in the two phases. Standard enthalpies of transfer are then equal to the corresponding differences in heats of solvation. Very little experimental data on heats of transfer are available, and one of the purposes of this investigation is to provide such data for the nickel and copper perchlorate salts in the water 1-butanol solvent pair. Since it seems not to be possible to prepare the anhydrous salts (27), it was evident that indirect methods would have to be resorted to in order to make the calorimetric measurements. The proposed method, as described in the experimental section, makes use of the assumption that the organic phase solvent composition remains constant at small extracted salt concentrations.

Very little work concerning the simple extraction of transition metal perchlorate salts by the higher alcohols is available in the literature and no measurements of heats of transfer are apparent. Heats of transfer for molecular systems have been measured (11), both calorimetrically and by the temperature dependence of distribution coefficients; however, the latter method is not applicable to the present study because of the dependence of the composition of the solvent in the two phases upon temperature.

The extraction of cobalt(II) and nickel(II) perchlorates by 2-octanol has been investigated at high concentrations. It was found that not only could  $\log D$  for both salts be represented by a single curve as a function of concentration but for the cobalt salt  $\log D$  was also a function of the total perchlorate and cobalt(II) perchlorate, alone or in mixtures with lithium, calcium, or aluminum perchlorates, shared a common isotherm. Furthermore, when an approximate correction was made for the variation in activity coefficients, the distribution could be described in terms of an equilibrium constant (21).

Goodrich (9) has recently studied the interaction of water with cobalt(II), copper(II) and nickel(II) perchlorates and 1-butanol. The shape and position of the absorption bands in the visible and near infrared are completely in agreement with an octahedral ligand field for all three ions in anhydrous solvent. Addition of small amounts of water shifts the bands slightly without altering their shapes significantly. The shift is only of the order of 10 - 15  $m\mu$  or less and indicates strongly that replacement of butanol molecules by water molecules is occurring in the coordination sphere of the nickel or copper ions. The magnitude of the shift further suggests that the perchlorate ions

are separated from the metal ions in the ion pairs by at least one solvent molecule (6). Saturation of the phase with water yields spectra identical to those obtained in aqueous solutions.



## CHAPTER II

### EXPERIMENTAL

#### Theoretical Basis of Experimental Design

##### Distribution Equilibria

The distribution systems under consideration are two liquid-phase three-component systems. Hence, according to the phase rule, at fixed temperature there is one compositional degree of freedom. If it can be assumed (1) that the presence of the alcohol in the aqueous phase can be ignored, (2) that the solvent composition of the alcohol-rich phase is unaffected by the presence of the salt at the small aqueous phase salt concentrations considered, and (3) that extraction results solely from hydration of the cation in the organic diluent, then the distribution equilibrium can be represented by the equation for the chemical potential

$$\mu(m_o, x) = \mu(m). \quad (8)$$

Here  $m_o$  and  $m$  are respectively, the organic and aqueous phase salt molality, and  $x$ , the mole fraction of water in the organic phase solvent, is included to emphasize the importance of the third of the above assumptions. It is convenient to choose  $m$ , the aqueous phase molality, as the single independent variable.

The distribution equilibrium is customarily represented by the concentration distribution coefficient  $D$ , defined by the ratio ( $m_o/m$ ).

In distribution systems such as the ones under consideration,  $D$  has a marked dependence on  $m$ ; however, the distribution isotherms, i.e., the plots of  $m_0$  against  $m$ , are sometimes found to become almost linear at small concentrations (19). In this case, the limiting slope of the isotherm then becomes equal to the thermodynamic distribution coefficient  $D^*$ .

Since  $m_0 = mD$  we have the following relation:

$$dm_0/dm = D + m dD/dm \quad (9)$$

and

$$\lim_{m \rightarrow 0} (dm_0/dm) = D^* \quad (10)$$

In view of these simple relations, the distribution data can be most conveniently analyzed in terms of a least squares fit.

### Thermodynamics of Transfer

The free energy of transfer for one mole of salt from concentration  $m$  in aqueous solution to concentration  $m_0$  in an aqueous alcohol solvent of composition  $x$  is given by

$$\begin{aligned} \Delta F_t &= \Delta F_t^0 + RT \ln (a_0/a) \\ &= \Delta F_t^0 + \nu RT \ln (m_0/m) + \nu RT \ln (S_Y^S/W_Y^W). \end{aligned} \quad (11)$$

(See Glossary for meaning of symbols.)

Two special applications of this equation are immediately evident.

The first is the case in which  $m$  and  $m_0$  are equal. The equation then becomes

$$\Delta F_t = \Delta F_t^0 + \nu RT \ln (S_Y^S/W_Y^W). \quad (12)$$

It can be seen that this is equivalent to Owen's equation (23) for the

total medium effect if

$$\Delta F_t = \nu RT \ln \left( \frac{S_Y}{W_Y} / \frac{W_Y}{W_Y} \right) \quad (13)$$

and

$$\Delta F_t^0 = \nu RT \ln \frac{S_Y^0}{W_Y^0}. \quad (14)$$

Owen's equation is derived in terms of rational activity coefficients.

The equation is identical, if  $\gamma$ 's are replaced by  $f$ 's however, the

numerical value of  $\Delta F_t^0$  will be different for the different scales. That

is,

$$\Delta F_t^0 (N) = \Delta F_t^0 (m) + \nu RT \ln (18/\bar{M}). \quad (15)$$

The other case of interest is the one for which  $(m_0/m)$  represents a

distribution equilibrium. Then  $\Delta F_t = 0$  and equation (11) becomes

$$-\Delta F_t^0 / \nu RT = \ln D + \ln \left( \frac{S_Y}{S} / \frac{W_Y}{W} \right). \quad (16)$$

Granted that the second assumption listed earlier is valid, extrapolation

to infinite dilution gives

$$\ln D^* = -\Delta F_t^0 / \nu RT = -\ln \frac{S_Y^0}{W_Y^0}. \quad (17)$$

In terms of rational activity coefficients

$$\log \frac{S_f^0}{W_f^0} = \log \frac{S_f^0}{W_f^0} + \log (18/\bar{M}). \quad (18)$$

This equation shows that the thermodynamic distribution coefficient is equivalent to Owen's primary medium effect, except for a constant depending upon solvent composition. It corresponds to the free energy change occurring when ions are transferred from water to the mixed solvent under conditions where the only interactions are ion-solvent and interionic interactions are absent.

The heat of transfer of one mole of salt at a sufficiently small molality  $m$  in aqueous solution to a correspondingly small molality of  $m_0$  in the mixed solvent of composition  $x$  is readily shown to be approximately equal to the difference in the integral heats of solution of the

salt in the two solvents. Likewise, the standard heat of transfer is equal to the difference in heats of solvation per mole at infinite dilution in the two solvents. If the two concentrations also correspond to equilibrium distribution concentrations, the free energy of transfer is zero and the entropy of transfer is, therefore, equal to the enthalpy of transfer divided by the absolute temperature.

As was previously mentioned, however, it has not proved possible to prepare solid anhydrous transitional metal perchlorate salts, so that the necessary calorimetric measurements must be made by indirect methods. One possible method is suggested which involves the introduction of a complexing agent. This method is illustrated by the following thermochemical design (Figure 1). In this design the heat of transfer of one mole of anhydrous salt B at concentration  $m$  in aqueous solution to concentration  $m_0$  in a mixed solvent of  $x$  mole fraction water is approximated by the difference in integral heats of solution of the salt B in the two solvents. It is understood that  $m_0$ ,  $m$  and  $x$  are compositions corresponding to equilibrium distribution so that the free energy change is zero.

In the thermochemical cycle (Figure 1),  $N$  is the maximum coordination for the cation,  $A$  is the complexing agent, and  $B$  is the transition metal perchlorate. The notation in parenthesis following  $B$  indicates its state; e.g.,  $B(C)$  denotes the hypothetical crystalline anhydrous salt. The integral heat of solution  $\Delta H'_S$  of  $B(c)$  is given by the equation

$$\Delta H'_S = \Delta H'_S - \Delta H'_R + \Delta H'_X, \quad (19)$$

where  $\Delta H'_S$  is the integral heat of solution of the complex  $BA_N$ ,  $\Delta H'_R$  is the heat of reaction of  $N$  moles of the complexing agent  $A$  with one mole

of B at concentration  $m$  in the solution and  $\Delta H_x$  is the (hypothetical) heat of reaction of  $N$  moles of A with one mole of the anhydrous salt B.  $\Delta H_x$  is, of course, not measurable; however, with the approximation

$$\Delta H_t = \Delta H_s(x) - \Delta H_s(\text{aq}), \quad (20)$$

it cancels out, and

$$\Delta H_t = (\Delta H'_s - \Delta H'_r)(x) - (\Delta H'_s - \Delta H'_r)(\text{aq}) \quad (21)$$

where the notation (x) and (aq) in the expression means that the indicated heat quantities are measured in solvents of composition x and in aqueous solution, respectively. In practice calorimetric measurements involve salt concentrations in the respective phases corresponding to phase equilibrium concentrations, and the heat of solution measurements must be made in solvents corresponding to the water-1-butanol distribution equilibrium. For the purposes of discussion, however, the aqueous phase will be assumed to be pure water.

The approximate heat of transfer is seen to involve measurements only of the heats of solution of the complex salt  $BA_N$  at small concentrations and of the heat of reaction of A with B in a solution of the same concentration. A suitable extrapolation procedure will then give a value for the standard heat of transfer.

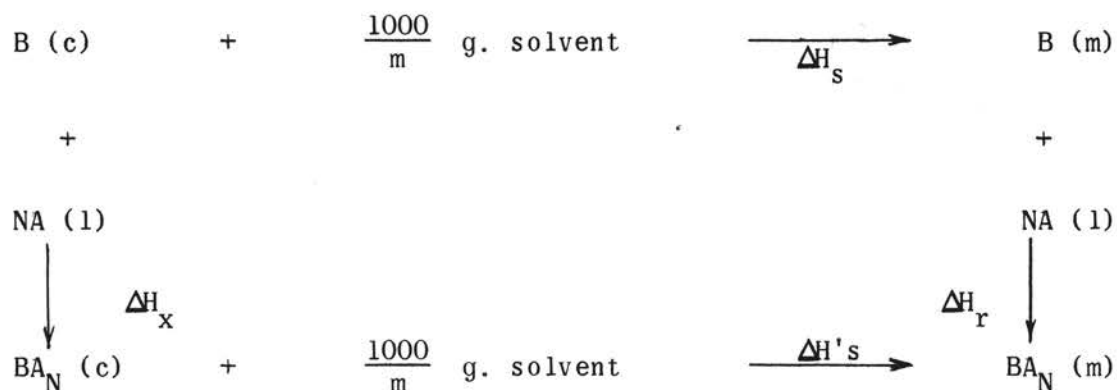


Figure 1. The Thermochemical Cycle.

## Chemicals

The chemicals used in this research were as follows:

Cupric perchlorate (hexahydrate); Nickel perchlorate (hexahydrate):

The G. Frederick Smith Chemical Co., Reagent. These chemicals were used without further purification.

1-Butanol: J. T. Baker Chemical Co., "Baker analyzed" reagent. Lot No. 28802. This compound was used without further purification.

Pyridine: J. T. Baker Chemical Co., "Baker analyzed" reagent. Lot No. 25238. This compound was used without further purification.

Distilled water was used throughout this experiment and is referred to as simply "water".

(Ethylenedinitrilo)tetraacetic acid Disodium salt: Eastman Organic Chemicals. Distillation Products Industries. This material was recrystallized by the method of Blaedel and Knight (1) before using.

Hexapyridinenickel(II) perchlorate; Tetrapyridinecopper(II) perchlorate: These compounds were prepared by dissolving the respective hexahydrates in 1-butanol and adding excess pyridine. The precipitated salts were filtered, washed with 1-butanol and sucked free of liquid in a Buchner funnel. The compounds were found to be stable in air and nonhygroscopic. The nickel salt was found, by EDTA titration, to have a formula weight of 734.7 corresponding to  $\text{Ni}(\text{ClO}_4)_2 \cdot 6.0 \text{ Py}$  and the copper complex, 570.4, corresponding to  $\text{Cu}(\text{ClO}_4)_2 \cdot 3.9 \text{ Py}$ .

## Analytical Methods

Solutions containing Cu(II) and Ni(II) salts, respectively, were analyzed for the metal ions by standard EDTA titrations using Murexide

indicator for the nickel titrations and Pan indicator for the copper titrations (7). Standard 0.05 and 0.10 molar solutions of the disodium salt of EDTA were prepared by accurately weighing the recrystallized EDTA and dissolving in water in a volumetric flask. Water concentration was determined by standard Karl Fischer titration (20).

### Experimental Procedures, Data and Confidence

#### Distribution Equilibrium

The distribution experiments were carried out by dissolving samples of the hexahydrates of copper and nickel perchlorates in 1-butanol and adding an equal volume of water. The mixtures were then shaken vigorously for several minutes. The shaking usually resulted in emulsions which were allowed to separate and come to final equilibrium in a water bath at  $25^{\circ} \pm 0.2^{\circ}$ . The mixtures were allowed to stand in the bath for two to three days. The phases were separated by drawing off the organic phase either with a pipette or by syphoning. The aqueous phase was then drained by means of a separatory funnel. In all cases, sufficient volumes of both phases were left in the separatory funnel to insure clean separations.

The separate phases were then analyzed for the metal ion by EDTA titration. Results of the determinations are reported in Table I as moles of anhydrous salt per 1,000 grams of solvent. Only two significant figures are reported because of the difficulty in reproducing duplicate analyses at the smaller concentrations. The data do, however, represent complete confidence to the accuracy reported.

TABLE I  
DISTRIBUTION DATA

Salt	m	$m_o$	D
$Ni(ClO_4)_2$	0.014	0.0008	0.0571
$Ni(ClO_4)_2$	0.023	0.0013	0.0565
$Ni(ClO_4)_2$	0.025	0.0016	0.0640
$Ni(ClO_4)_2$	0.035	0.0027	0.0771
$Ni(ClO_4)_2$	0.037	0.0029	0.0784
$Ni(ClO_4)_2$	0.055	0.0050	0.0909
$Ni(ClO_4)_2$	0.071	0.0069	0.0972
$Ni(ClO_4)_2$	0.072	0.0072	0.1000
$Ni(ClO_4)_2$	0.098	0.0115	0.1173
$Ni(ClO_4)_2$	0.102	0.0120	0.1176
$Cu(ClO_4)_2$	0.016	0.0009	0.0563
$Cu(ClO_4)_2$	0.021	0.0014	0.0667
$Cu(ClO_4)_2$	0.021	0.0018	0.0857
$Cu(ClO_4)_2$	0.032	0.0022	0.0688
$Cu(ClO_4)_2$	0.048	0.0040	0.0883
$Cu(ClO_4)_2$	0.065	0.0061	0.0938
$Cu(ClO_4)_2$	0.087	0.0097	0.1115
$Cu(ClO_4)_2$	0.111	0.0142	0.1279



Figure 2 presents the distribution isotherms and shows that both copper and nickel perchlorates fall on the same curve. The solid line is a quadratic least squares fit obtained by including all of the distribution data. The equation is

$$m_0 = 0.05 m + 6.84 m^2. \quad (22)$$

### Calorimetric Experiments

The calorimetric measurements were made by modifying the calorimeter of an American Instrument Company "Titrothermomat" (14). This instrument has, as a temperature measuring device, a 3,000 ohm thermister as one element of a Wheatstone bridge of variable input voltage. During a measurement the off-balance potential of the bridge was measured by means of a Sargent SRL 1 m.v. recording potentiometer. A preliminary experiment had established that the off-balance voltage across the thermister bridge was approximately linear in temperature for small enough temperature change.

Because the electrical calibration system supplied with the instrument was considered inadequate for the enthalpy measurements, the heater circuit shown in Figure 3 was designed and used.

The calorimeter vessel consisted of an especially designed 35 milliliter beaker which fit snugly into the insulated container forming part of the "adiabatic tower". The solvent or salt solution, according to the enthalpy measurement, was weighed directly into this vessel.

The heat of solution measurements were made by weighing out the desired amount of solid complex in a glass ampoule made from a 7 millimeter pyrex test tube. This was blown out thin on the bottom for greater ease of crushing. It was sawed off at the top to make a tube

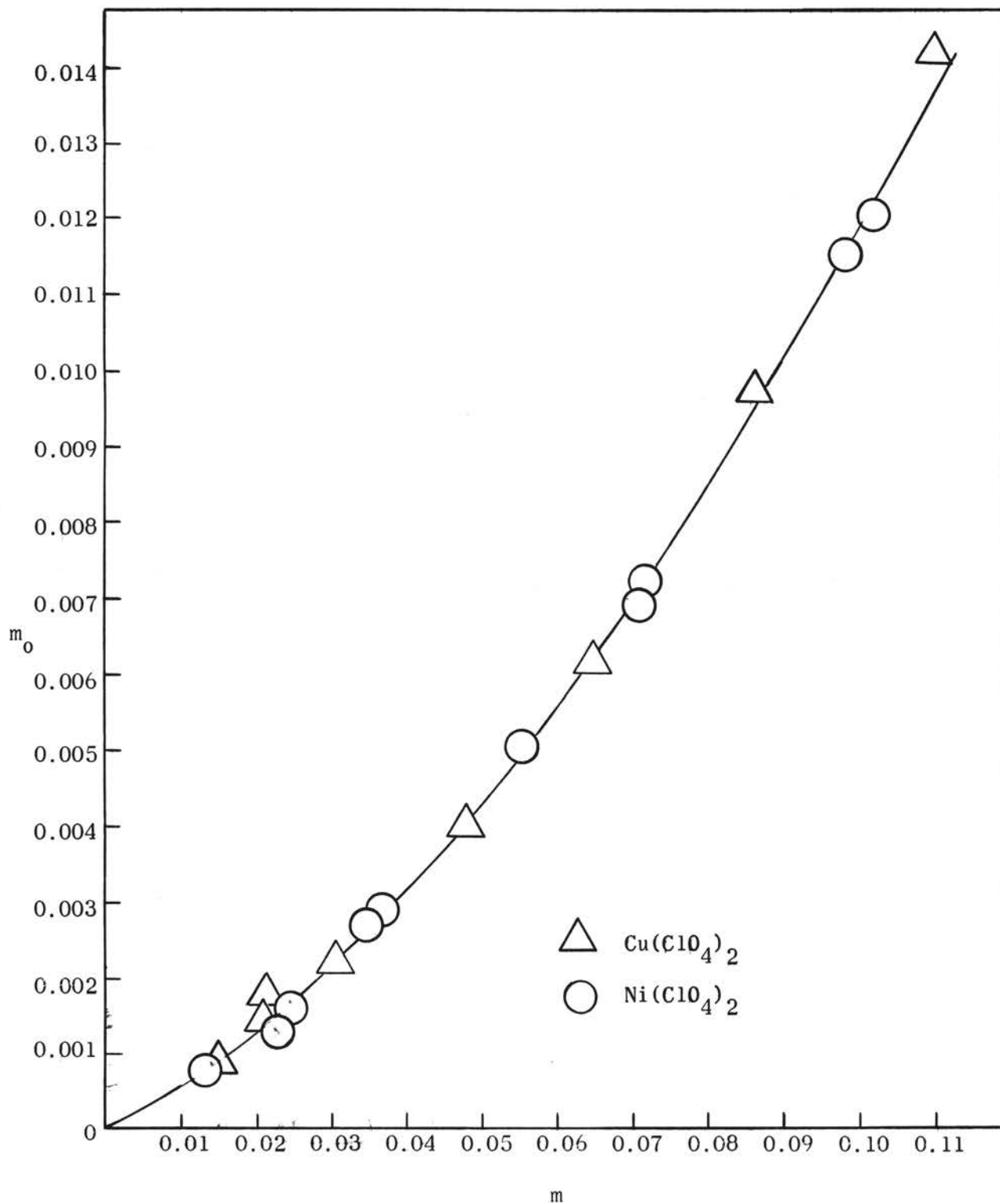


Figure 2. Distribution Isotherms for Nickel(II) and Copper(II) Perchlorates between 1-butanol and water.

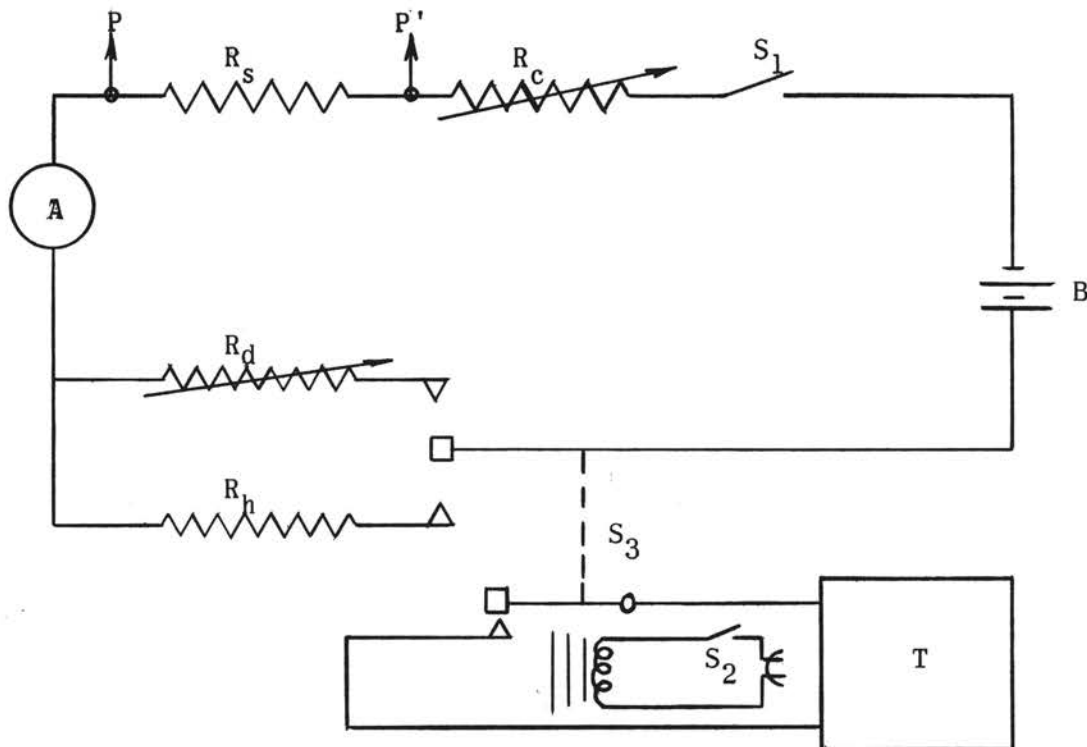


Figure 3. Electrical Calibration Circuit.

$R_h$  = 4.271 ohm manganin heater supplied with Titrathermomat

$R_d$  = General Radio Co. type 1432-F Decade Resistor

$R_s$  = General Radio Co., type 500-A, 1 ohm Resistor

$R_c$  = Current Control Resistor

B = 2.4 V Zinc-Cadmium Storage Battery

A = Ammeter

T = Electrical Timer, The Standard Electric Time Co. Model Special S-1

$S_1$  = Main Heater Circuit Switch

$S_2$  = Motor Driven X-ray Timer Switch

$S_3$  = Double Pole Relay

P, P' = Potentiometer Leads

approximately 25 millimeters long. The ampoule was fitted over a Teflon stopper attached to a thin Teflon rod. The ampoule was introduced into the calorimeter through the buret port in the top and suspended in the solvent until a constant calorimeter temperature drift was achieved. It was then crushed against the bottom of the calorimeter beaker.

The solvents used in the heat of solution determinations were the phases resulting from the water-1-butanol equilibrium at 25<sup>0</sup>. It was established in a preliminary experiment that the butanol phase corresponding to an extracted nickel perchlorate concentration of  $7 \times 10^{-3}$  molal had a composition of 51 mole per cent water. This compares with 50 mole per cent in the binary distribution used here. The heat of solution determinations were made by dissolving the necessary quantities of salt to produce solutions which corresponded as closely as possible to the salt concentrations in the respective phases of a distribution experiment.

The heats of reaction of pyridine with the respective equilibrium phases from a distribution experiment were measured by adding the calculated amount of pyridine to the solution from an American Instrument Company Automatic Microburet. This instrument has an accuracy of delivery of better than 0.001 milliliter. The actual volumes of pyridine added were small enough that any possible initial temperature differences between the pyridine and the solution could be ignored.

Each addition of reactant, solid complex or pyridine, to the calorimeter was followed by an electrical calibration over approximately the same temperature range as that resulting from the addition. In no case was it possible to exactly duplicate the reaction temperature change, however. Electrical calibrations were carried out by first

allowing the zinc-cadmium storage battery voltage (see Figure 3) to stabilize by passing current through the dummy heater,  $R_d$ , for two hours previous to measurement. The dummy heater was adjusted to approximately the same resistance as the heater,  $R_h$ . For calibration, the timer switch,  $S_2$ , was switched on, starting the electrical timer and the heater simultaneously. While the heater was in operation, the potential across the standard 1 ohm resistor,  $R_s$ , was measured. After a pre-set calibration time the heater and timer were automatically and simultaneously stopped.

Temperature changes, on an arbitrary scale, resulting from both reaction and calibration were determined directly on the recorder chart by the method of Dickenson (5). The heats of solution per mole of salt were calculated from the equation

$$\Delta H'_s = V_s^2 R_h \Delta T_r M / 4.186 \Delta T_c W R_s^2, \quad (23)$$

and the heat of reaction of pyridine, per mole of salt, with the salt solutions was calculated from the equation

$$\Delta H_r = V_s^2 R_h t \Delta T_r / 4.186 R_s^2 \Delta T_c mW. \quad (24)$$

Here  $\Delta T_r$  is the temperature change for the reaction;  $\Delta T_c$  is the temperature change on operating the heater for  $t$  seconds;  $W$  is the weight of the sample (solid complex or salt solution) in grams;  $M$  is the gram formula weight of the solid complex;  $m$  is the molality of the salt solution, and  $V_s$  is the potential drop across and 1 ohm standard resistor during calibration.  $V_s$  and  $t$  were adjusted so that  $\Delta T_c$  was roughly the same as  $\Delta T_r$ . The results of the individual calorimetric determinations are summarized in Appendix A. The heat values for the several steps in the thermochemical cycle are reported together with fifty per cent confidence limits (15) in Table II.

TABLE II  
HEAT VALUES FOR STEPS IN THE THERMOCHEMICAL CYCLE

Salt	Ni(C10 <sub>4</sub> ) <sub>2</sub>	Cu(C10 <sub>4</sub> ) <sub>2</sub>
m	0.023	0.021
m <sub>o</sub>	0.0013	0.0018
$\Delta H'_s$ (org)	22.8 $\pm$ 0.6	---
$\Delta H'_s$ (aq)	27.4 $\pm$ 0.1	---
$\Delta H_r$ (org)	- 5.4 $\pm$ 0.5	-6.3 $\pm$ 0.3
$\Delta H_r$ (aq)	-14.5 $\pm$ 0.4	-15.9 $\pm$ 0.2
$\Delta H_t$	-13.7 $\pm$ 1.6	---
$\Delta S_t$	-46.0 $\pm$ 5.3	---

Unfortunately, the physical limitations of the calorimeter and the mechanics for introducing solid samples restricted the measurement of heats of transfer to a single point on the distribution isotherm for each salt. To illustrate, the maximum capacity of a glass ampoule for the nickel complex was approximately 0.6 grams. This quantity makes an aqueous solution of concentration 0.0023 molal with 35 milliliters of water in the calorimeter. The corresponding equilibrium concentration in the nonaqueous phase is 0.0013 molal, requiring 0.0023 grams of complex in 35 milliliters of mixed solvent. Since the calorimeter would not accommodate larger ampoules for measurements at higher concentrations and the sensitivity of the calorimeter was inadequate for measurements at smaller nonaqueous phase concentrations, the experimental conditions used were optimum. Fortunately, these represent quite dilute solutions, where the results are of greatest significance.

Although preliminary tests with  $\text{NiPy}_6(\text{ClO}_4)_2$  and  $\text{CuPy}_4(\text{ClO}_4)_2$  had demonstrated that both salts were soluble in the solvents of the experiment, it was not until after the measurements of the heats of reaction of pyridine with the simple perchlorates had been completed that it was discovered that the copper salt, unlike the nickel salt, dissolved too slowly for calorimetric measurements. The rate of solution was also found to be little affected by the state of subdivision of the copper salt. As a result, it was not possible to obtain data for the heat of solution of  $\text{CuPy}_4(\text{ClO}_4)_2$  and hence the enthalpy of transfer of  $\text{Cu}(\text{ClO}_4)_2$ .

## CHAPTER III

### EXPERIMENTAL RESULTS AND CONCLUSIONS

It can be seen from Figure 1 that very little difference exists between the respective distribution isotherms for copper and nickel perchlorates. This, however, is not too surprising a result in view of the respective free energies of hydration (22), and similarity in ion size of copper(II) and nickel(II). A corresponding similarity has been found in the extraction behavior of nickel(II) and cobalt(II) perchlorates by 2-octanol (26).

The experimental data are rectified by an empirical equation of the form

$$\log D = a + b\sqrt{m}. \quad (25)$$

For nickel perchlorate the equation is

$$\log D = -1.45 + 1.67\sqrt{m}, \quad (26)$$

and for copper perchlorate

$$\log D = -1.38 + 1.42\sqrt{m}, \quad (27)$$

giving limiting distribution coefficients of 0.035 and 0.042, respectively on the molal concentration scale.

If the distribution data for both salts are incorporated in the same fit, the result is

$$\log D = -1.41 + 1.53\sqrt{m}, \quad (28)$$

This equation is represented graphically in Figure 4. Since complete calorimetric data were not obtained for the copper system, equation (28)



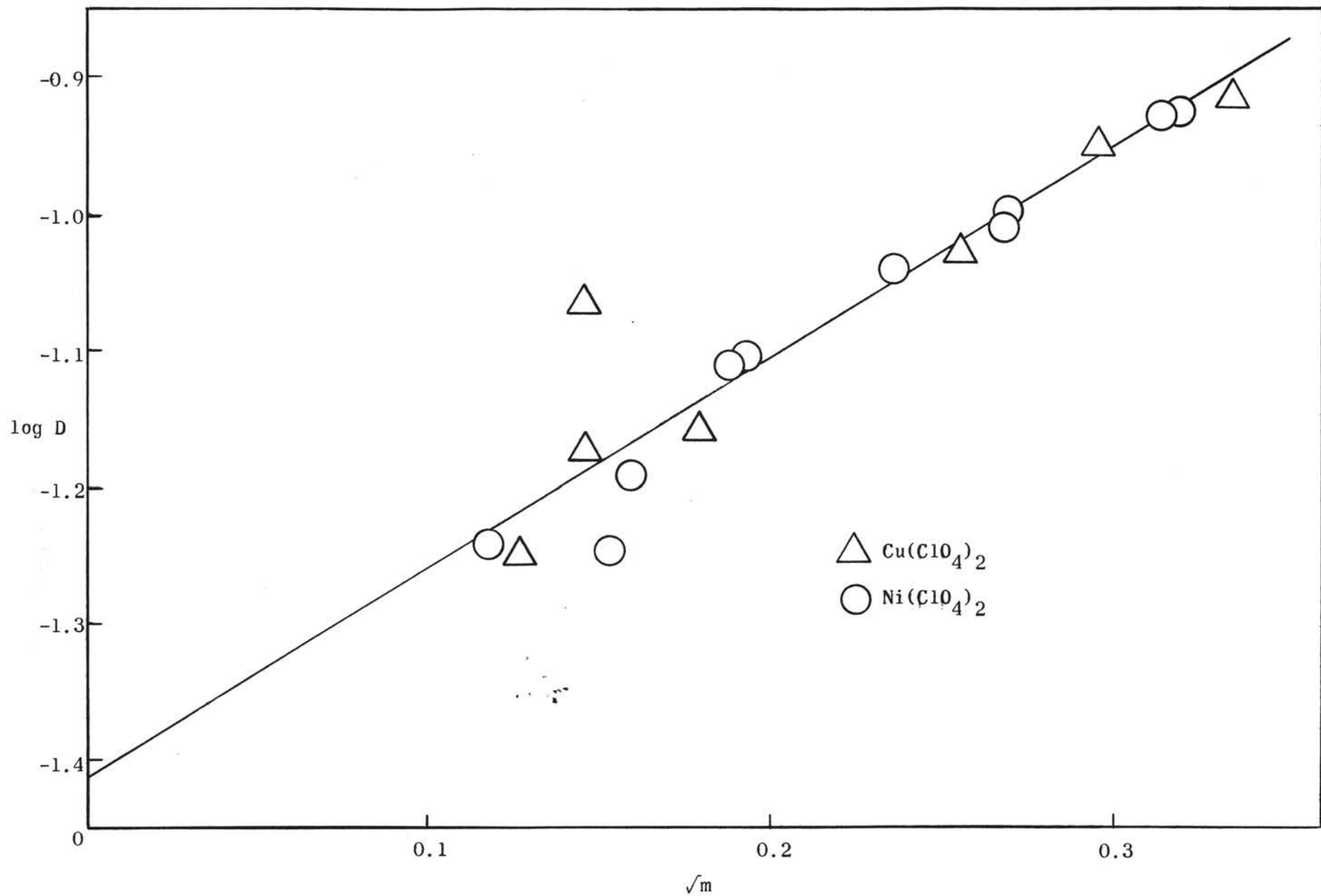


Figure 4. Rectified Distribution Data.

will be referred to in all future discussions.

From equation (17), the limiting distribution coefficient corresponds to a primary medium effect expressed by

$$\log \frac{s}{w} \gamma^0 = -\ln D^* = 1.41. \quad (29)$$

In terms of rational activity coefficients this becomes [equation (18)]

$$\log \frac{s}{w} f^0 = 1.10. \quad (30)$$

Although no experimental data for the primary medium effect of 1-butanol on aqueous transition metal salts have appeared in the literature, this is clearly of the correct order of magnitude. For example, (12), the primary medium effect on aqueous hydrochloric acid ranges from 0.115 for a solvent containing 20 weight per cent methanol to 2.23 for a solvent containing 82 weight per cent dioxane. The corresponding standard free energy of transfer for the transition metal perchlorates from water to the organic phase is +5.8 kcal. per mole of salt.

In order to examine the theoretical validity of the empirical extrapolation of the distribution data, the empirical  $\sqrt{m}$  dependence of the distribution coefficients can be considered from two points of view. Equation (16), upon rearrangement, gives

$$\begin{aligned} \log (D/D^*) &= -\log \left( \frac{s}{s} \gamma / \frac{w}{w} \gamma \right) \\ \text{or} \quad \log (D/D^*) &\cong -\log \left( \frac{s}{s} f / \frac{w}{w} f \right) - \log (\bar{M}/M). \end{aligned} \quad (31)$$

First if it is assumed that the Debye-Huckel limiting law applies to both phases, equation (3) may be rearranged to give

$$-\log \left( \frac{s}{w} f \right) = \frac{1.825 \times 10^6}{T^{3/2}} \left( \frac{\sqrt{\rho_0} \sqrt{D}}{\epsilon_s^{3/2}} - \frac{\sqrt{\rho}}{\epsilon_w^{3/2}} \right) \sqrt{m}. \quad (32)$$

Here,  $\rho_0$  and  $\rho$  are organic and aqueous phase densities, respectively. The dielectric constants for water-1-butanol mixtures have not been reported; however, the bulk dielectric constant for the butanol phase

solvent composition may be estimated (12) from the equation

$$\epsilon_s = \varphi_w \epsilon_w + \varphi_a \epsilon_a \quad (33)$$

to be approximately thirty. Here, the  $\varphi$ 's represent volume fractions of the solvent components. For  $T = 298^{\circ}\text{K}$ ,  $\rho_0 = 0.8$ ,  $\rho = 1.0$ .  $\epsilon_s = 30$  and  $\epsilon_w = 80$ , equation (32) becomes

$$-\log \left( \frac{S_f}{S} / \frac{W_f}{W} \right) \cong 0.33 (2/D-1)\sqrt{m}. \quad (34)$$

With the Debye-Huckel model, therefore, assuming complete dissociation of the electrolyte at extremely small concentrations, a negative coefficient for  $\sqrt{m}$  would be expected if  $2/D$  is less than unity. It is quite likely, however, that the effective dielectric constant of the organic phase is much less than thirty. This effect, together with a correction for ion-pairing in the nonaqueous phase could well bring equation (34) into reasonable agreement with the observed experimental fact of a positive slope.

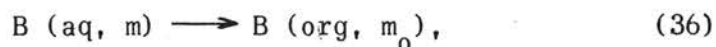
The effect of ion-pairing in the organic phase is given to the same degree of approximation (Debye-Huckel limiting law) by

$$\log (D/D^*) \cong 2 \log D^* + 2 \log m - 5.28\sqrt{m} + \log (K/4M^3). \quad (35)$$

In this equation,  $K$  is the dissociation constant for the ion triple on the mole fraction scale. Here it is assumed that, although the salt molality in the organic phase is small, the fraction of the complex dissociated is small compared with unity. The activity coefficient of the neutral complex is set equal to unity also. It would seem, then, that over the range of extensive ion association in the organic phase at small concentration,  $\log (D/D^*)$  should be an increasing function of  $m^{1/2}$ ; however, the observed linearity is not indicated by this equation. At an aqueous phase concentration of 0.8  $\log D$  falls a little below the value predicted by equation (28); again, however, the values for copper and nickel are the same.

At sufficiently low extracted salt concentrations, where ion-pairing is negligible, and where the Debye-Huckel limiting law is actually applicable, the slope probably becomes negative thus introducing some uncertainty in the extrapolation. A simple calculation based upon equation (35) gives a limiting slope of only -0.2. In the extraction of cobalt(II) and nickel(II) perchlorates by 2-octanol (21)  $\log D$  was found to be a linear function of the concentration with slope slightly greater than unity; however the lowest aqueous phase concentration investigated was about 0.5 molal.

The calorimetric data for the reaction



are reported in Table II. As was explained earlier, the calorimetric measurements for copper(II) perchlorate are necessarily incomplete; however, the available data indicate that the heat of transfer would not differ appreciably from that for nickel(II) perchlorate. For instance,  $\Delta H_r (org) - \Delta H_r (aq)$  for copper is  $9.6 \pm 0.5$  kcal, whereas the corresponding value for nickel is  $9.1 \pm 0.9$  kcal. Since a major part of the heat of transfer probably involves the heat of hydration of the cation, the measurements of Goodrich (9) for the reaction of water with anhydrous 1-butanol solutions of copper(II) and nickel(II) perchlorates seem relevant. Goodrich found that there was a difference in the heats of reaction for these salts of only  $1.2$  kcal per mole<sup>-1</sup> over the range of water-to-salt ratios of from 4 to 8.5, and the highest ratio studied. Although the salt concentration was much higher than that of the present investigation (0.1 molal compared with 0.001 molal), and the solvent composition was also different, the results do lend some support to the contention that the enthalpies of transfer for nickel(II) and

copper(II) perchlorates do not differ greatly.

The measurements for nickel perchlorate give an entropy of transfer of  $-46 \pm 5$  e. u. The major portion of this loss of entropy can be attributed to two principle factors, both resulting from the low dielectric constant of the organic phase solvent. The first is the translational entropy loss resulting from increased ion association. This association reaction probably occurs without loss of solvate water and corresponds to a decrease of two particles per mole. The magnitude of this effect is, of course, uncertain since little information is available concerning association constants for the perchlorate ion.

The second factor is the increased hydration resulting from the increase in ion-dipole interaction. For instance, Ulich (25) calculated hydration numbers for cations in aqueous solution by assuming that the entropy decrease upon hydration resulted entirely from the loss of translational degrees of freedom of water molecules entering the primary hydration sphere of the ion. He assumed further, that the entropy decrease per molecule was equal to that occurring during the formation of one molecule of water of crystallization in the solid state ( $-6$  e. u.). This value is considerably lower than that ( $-16.7$  e. u.) commonly used (21a). The magnitude of the measured entropy loss would then indicate an increase in hydration number for the cation in the organic phase in addition to ion association. If it is assumed that all  $-46$  e. u. result from this effect, the increase in the hydration number for the cation would be 6.7. This is necessarily an upper limit since part of the loss must be contributed by extensive ion association and an expected increase in water-anion interaction. That there could be an increase in the degree of ion hydration in the organic phase relative to the

aqueous phase in spite of an increase in ion association may seem surprising. Although from the long-range viewpoint there is a partial neutralization of charge as a result of ion association, the degree of order of the water in the organic phase solvent relative to that in the aqueous phase must certainly be less. This would lead to more favorable conditions for orientation and binding of water molecules in layers beyond first. This argument finds considerable support from the findings of Yates and co-workers (26), who reported the surprisingly high hydration numbers of 14.7 and 10.9 for cobalt(II) and nickel(II) perchlorates, respectively, in 2-octanol.

In contrast to the large hydration numbers for the transition metal perchlorates, are the results for the chlorides (26). Here it is expected that the chloride ions occupy coordination positions around the cation, thus, destroying the cationic charge in addition to displacing solvent molecules from the primary solvation sphere. It is also presumed that the neutralization of charge decreases the tendency of the salt toward secondary solvation.

This combination of results, then suggests the following conclusions:

First, in the extraction of transition metal perchlorates by the higher alcohols, the solute species found in the organic phase correspond to highly hydrated, largely associated salts. The large hydration probably results from the noncoordinating tendencies of the perchlorate ion.

Secondly, for low extracted salt concentrations, the Debye-Huckel theory accounts for the concentration dependence of the distribution coefficient only if ion association constants are calculated and a suitable "effective" dielectric constant is assigned to the organic

phase solvent.

Thirdly, in the extraction of transition metal perchlorates by the higher alcohols, the solvating solvent in the organic phase is water and the alcohol plays the part of an "inert" diluent whose principal role is that of providing a medium of lowered dielectric constant. The mechanism of the extraction can therefore, be profitably viewed in terms of Owen's primary and secondary medium effects, based on a solvation model for the general salt effect.

## SUMMARY

The distribution isotherms for copper(II) and nickel(II) perchlorates in the water-1-butanol solvent pair at 25<sup>0</sup> have been measured over the aqueous phase concentration range from 0.014 to 0.111 molal. It was found that both distribution isotherms were identical within experimental error and that the data were rectified by the equation

$$\log D = -1.41 + 1.53\sqrt{m}.$$

From this the primary medium effect of 1-butanol upon the activity of nickel(II) perchlorate was calculated to be  $\log \frac{s}{w} f^0 = 1.10$  corresponding to a value of the standard free energy of transfer of 5.8 kcal.

The heat of transfer, approximated by the difference in heats of solution of the anhydrous perchlorate salt in the two phases, for nickel perchlorate in distribution equilibrium at 25<sup>0</sup> has been measured. An indirect method was devised for this measurement since the anhydrous solid salts have never been isolated. This consisted of combining measurements of the heats of reaction of nickel perchlorate with pyridine in each phase with measurements of the heats of solution of the solid pyridine complexes. Attempts to make the same measurements for copper perchlorate failed; however, existing evidence indicates that the heat of transfer for copper perchlorate should not differ appreciably from that for nickel perchlorate. The measurement for nickel perchlorate gave an entropy of transfer of -46 e. u.

This combinations of results is interpreted to mean that the extracted species over the range of concentrations investigated is a



highly hydrated, largely associated salt. In fact, it is concluded that the salt is more highly hydrated in the alcohol rich phase than in the aqueous phase and that extensive ion association occurs without displacement of hydrate water.

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APPENDIX A

Heats of solution of  $\text{Ni(Py)}_6(\text{ClO}_4)_2$

Sample Wt.	Solv.	$\Delta H_s$ Kcal/mole
0.550	aq	27.12
0.6021	aq	27.44
0.5923	aq	27.60
0.0296	org	23.25
0.0270	org	22.41
0.0290	org	24.09
0.0276	org	21.69

Heats of reaction of pyridine with  $\text{Ni}(\text{ClO}_4)_2$  solutions

Wt. of Soln.	Phase	ml. Py	$\Delta H_r$ Kcal/mole salt
35.3620	aq	0.4017	-14.03
35.0162	aq	0.3948	-15.15
35.1092	aq	0.3906	-14.79
29.0430	org	0.0182	-6.35
29.4526	org	0.0185	-4.47
29.8330	org	0.0187	-5.41

Heats of reaction of pyridine with  $\text{Cu}(\text{ClO}_4)_2$  solutions

29.5070	org	0.0166	-6.47
29.3312	org	0.0165	-6.18
29.4547	org	0.0166	-5.70
33.5273	aq	0.2206	-16.52
34.0540	aq	0.2241	-15.39

## APPENDIX B

### Glossary of Symbols

Symbol	Page	Meaning
A(l)	16	Neutral complexing agent (liquid)
B(c)	16	Anhydrous transition metal perchlorate (crystalline)
B(m)	16	Transition metal perchlorate salt in solution (molality m)
$C_s$	6	Molar salt concentration
D	9	Molal distribution coefficient
D*	13	Thermodynamic distribution coefficient
$\Delta F_t$	13	Free energy of transfer
$\Delta F_t^0$	5	Standard free energy of transfer
$\Delta H_s$	16	Heat of solution of B(c)
$\Delta H'_s$	16	Heat of solution of $BA_N(c)$
$\Delta H_r$	16	Heat of reaction of N moles of A with one mole of B(m)
$\Delta H_x$	16	Heat of reaction of N moles of A with one mole of B(c)
$\Delta H_t$	16	Heat of transfer
K	30	Dissociation constant of ion associate
$\bar{M}$	7	Mean molecular weight of mixed solvent
$M_w$	7	Molecular weight of water
$M_o$	7	Molecular weight of organic solvent
M	24	Molecular weight of anhydrous perchlorate salt
N <sub>i</sub>	7	Mole fraction of component i in solution
N	16	Characteristic coordination number of cation
R	5	Gas constant

$R_h$	24	Heater resistance
$R_s$	24	Resistance of standard resistor
$\Delta S_t$	25	Entropy of transfer
$T$	5	Absolute temperature
$\Delta T_c$	24	Calorimeter temperature change on electrical calibration
$\Delta T_r$	24	Calorimeter temperature change on reaction
$V_s$	24	Voltage drop across standard resistor (volts)
$W$	24	Sample weight (grams)
$Z$	5	Ionic charge
$a$	13	Electrolyte activity in aqueous phase
$a$	27	Empirical constant
$a_o$	13	Electrolyte activity in organic phase
$a_w$	7	Water activity
$a_o$	7	Activity of organic solvent
$a_s$	7	Salt activity
$b$	27	Empirical constant
$e$	5	Electronic charge
$\frac{s_f}{s}$	6	Rational activity coefficient of electrolyte in mixed solvent
$\frac{w_f}{w}$	6	Rational activity coefficient of electrolyte in aqueous solution
$\frac{s_f^0}{s}$	5	Primary medium effect (rational scale)
$f_n$	6	Activity coefficient of aqueous nonelectrolyte
$k_s$	6	Salting constant
$m$	16, 24	Molality of salt
$m$	12	Aqueous phase salt molality
$m_o$	7	Organic phase salt molality

$r$	5	Ionic radius
$t$	24	Time (sec)
$x$	7	Mole fraction water in mixed solvent
$\epsilon_s$	5	Mixed solvent dielectric constant
$\epsilon_w$	5	Dielectric constant of water
$\mu_i$	7	Chemical potential of component $i$ in solution
$\mu_o^o$	7	Standard chemical potential of electrolyte in mixed solvent
$\mu_w^o$	9	Standard chemical potential of electrolyte in aqueous solution
$\nu$	5	Number of moles of ions produced by one mole of salt
$s_s^Y$	9	Molal activity coefficient of electrolyte in mixed solvent
$s_w^Y$	9	Molal activity coefficient of aqueous electrolyte
$s_w^{Y^o}$	14	Primary medium effect (molal scale)
$\rho$	29	Aqueous phase density
$\varphi_w$	29	Volume fraction of water in solvent mixture
$\varphi_s$	29	Volume fraction of organic component in solvent mixture
$\rho_s$	29	Organic phase density

VITA

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