DISTRIBUTION AND ENTHALPY OF TRANSFER OF COBALT(II) PERCHLORATE FROM AQUEOUS TO 1-BUTANOL SOLUTIONS OF CALCIUM PERCHLORATE AT EXTRACTION EQUILIBRIUM

by

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CHAPTER I

INTRODUCTION

Alcohols have been extensively investigated as potential extractants for inorganic salts from aqueous solutions. In particular, immiscible alcohols have been applied to the extraction and separation of transition metals present as chlorides in concentrated hydrochloric acid. Alcohols such as 2-ethylhexanol (1) and 2-octanol (2) have been used to advantage in these applications. An important feature of such extraction systems is the ability of the metal to form ion-association complexes (chlorocomplexes). Metals which form complexes readily, appear to be more extractable than those which have little tendency to form chlorocomplexes. Thus, it is feasible to separate cobalt from nickel by extraction from chloride ion media with 2-octanol.

By contrast, with extractions from concentrated chloride solutions, 2-octanol will not separate nickel from cobalt when the metals are present as perchlorates. Although the distribution ratio (organic phase salt molality/aqueous phase salt molality) is at least an order of magnitude more favorable for the extraction of the perchlorates than for the extraction of the chlorides in the absence of excess chloride (3), there is little variation in this distribution ratio among the metals of the first transition series (4). Excess perchlorate ions in the aqueous phase will increase the distribution ratios but will not improve the separation factors (3).

The study described in this thesis was undertaken to gain a better understanding of the extraction of transition metal perchlorates by alcohols. n-Butanol was chosen for the extractant since this is the normal alcohol of smallest molecular weight which is partially immiscible with water at laboratory temperatures and which, because of its ability to dissolve relatively large amounts of water, results in an organic phase which is approximately aqueous in character, although of considerably smaller dielectric constant than the aqueous phase. It is believed that the investigation of such a relatively simple system might lead to a useful model for the extraction of other metal perchlorates by alcohols and, in particular, lead to a better understanding of the extraction-promoting effects of a second metal perchlorate upon the extractability of a given metal perchlorate. Cobalt(II) and calcium(II) perchlorates were selected for study in the n-butanol system, in part because of a prior study by Cheung (5) of the unpromoted extraction of cobalt perchlorate over a limited concentration range.

The physical chemistry of solvent extraction has recently been reviewed by Rozen (6) and Marcus and Kertes (7). At equilibrium the free energy of transfer is zero, requiring that the entropy of transfer be balanced by the enthalpy of transfer, and in the limit of zero metal perchlorate concentration the value of the distribution ratio measures the standard state free energy of transfer, while the enthalpy of transfer measures the standard state enthalpy of transfer. With increasing salt concentration, changes in the entropy of transfer from its limiting value reflect changes in the solvation and ionization. A study of the concentration dependence of the entropy of transfer was made in an effort to relate the concentration dependence of the distribution ratio to these variables through a model of the extraction process based on the selected perchlorate system.

CHAPTER II

GENERAL BACKGROUND

Properties and Structures of Solvents

Liquid water exhibits a number of unique structural properties which indicate that the structure is fundamentally different from the structures of most other liquids (8). Water has high melting and boiling points, an unusually high heat capacity, and exhibits a characteristic decrease in molar volume on melting and a subsequent contraction between 0 and 4°C, the maximum density of water occurring at about 4°C. Water is the most important of the ionizing solvents. A summary of the postulated structures of water and its properties which are relevant to the behavior of solutions of electrolytes is an essential preface to any discussion of extraction from aqueous solutions and solvation studies.

The water molecule itself has been thoroughly investigated. The H-O-H bond angle is very nearly 105°, the O-H internuclear distance is 0.97Å and the H-H internuclear distance is 1.54Å for the isolated gaseous molecule. This has been demonstrated by spectroscopic studies (9,10). The isolated gaseous water molecule has a dipole moment of 1.87×10^{-18} e.s.u., which acts along the bisector of the H-O-H angle with the negative end pointed toward the oxygen nucleus. In a classic early work, Bernal and Fowler (11) envisioned the aforementioned dipole moment as arising from an effective charge of $-e$ (e = protonic charge) which is positioned at 0.15Å from the oxygen nucleus, with $+0.5e$ situated at each of the hydrogen nuclei. From calculations based on this model, they determined that the value of kT at room temperature was small compared to the energy expenditure necessary to rotate a dipole through 90° or even 45°. This suggests that in liquid water at room temperature, each molecular dipole exerts some measure of influence upon the orientation of adjacent water molecules and is, in turn, influenced by its neighboring molecules. Verwey (12) has proposed a structural model in which a quadrapole charge arrangement replaced the tripolar charge distribution model of Bernal and Fowler. This quadrapole charge model has led to the prediction of acceptable values for the lattice energy of the ice crystal.

In liquid water, the volume per water molecule is almost $30 Å^3$ at room temperature. If water consisted of close-packed, rigid, spherical molecules, the diameter required to successfully yield this volume would be 3.48Å. However, x-ray analysis of liquid water indicates that the nearest-neighbor distance (O-O internuclear distance) is from 2.90 to 3.05Å in the temperature range 0-80°C (13). The reported values for the water molecule radius in the liquid state range from 1.35 to 1.39Å (10, 11, 12). It follows that the water molecules are not close-packed since the required volume per molecule would necessarily need to be much smaller. Instead of the twelve nearest neighbors which are characteristic of close-packing, the x-ray data show that the average number of nearest neighbors ranges from 4.4 to 4.9 in the temperature range 0-80°C. Moreover, x-ray evidence indicates a set of second nearest neighbors at the expected distance of 4.5Å from the central molecule, but this set becomes less clearly defined as the bulk solvent temperature increases (13).

Liquid water will retain, over short ranges and for short periods, the tetrahedrally coordinated structure of ice. This ice-like structure is believed to be maintained by 'hydrogen bonds', which are essentially electrostatic in nature and result from the favorable charge distribution and geometry of the water molecule. The fact that the bond angle of water (~105°) is close to the tetrahedral bonding angle (109° 28') and that Verwey's calculations lead to values within 1 kcal./mole of the experimental value (10.8 kcal./mole) for the vaporization energy of ice is strong evidence for the adequacy of a purely electrostatic picture of the intermolecular forces. Other evidence in favor of the tetrahedrally coordinated structure of water may be found in the Raman and infra-red spectra (9).

Liquid water is visualized as a rather loosely four-coordinated structure, held together by esstentially electrostatic forces which arise from the special charge distribution and shape of the water molecule. The period of association between a water molecule and its molecular neighbors is only temporary since the tetrahedral structure is constantly being regionally destroyed by thermal agitation; but it must be sufficiently stable to persist over small regions. These structures are stable for times of the order of 10^{-12} seconds, which are long when compared to x-ray or infra-red radiation.

Recently, Franks and Ives (14) authored a review article on the structures of liquid alcohols and alcohol-water mixtures. X-ray radial distribution curves (15-18) indicate that straight-chain alcohols tend to form linear polymers and do not exhibit the type of three-dimensional association which is dominant in the structure of liquid water. Since the oxygen atom of an alcohol molecule carries one proton and two lone pairs of electrons, it might be expected to form three hydrogen bonds with its neighbors. This could not, of course, be the case for every molecule of an assembly, but it is not obvious why there should not be a distribution of molecules forming one, two, or three bonds. All the experimental evidence shows, however, that no more than two bonds are formed, each oxygen acting once as a proton donor and once as a proton acceptor. This apparent degree of limitation to the equality of "give-and-take" is rationalized by the essentially co-operative nature of hydrogen bonding. Each oxygen atom (~sp^3 hybrid) can form four approximately tetrahedrally-disposed bonds; however, the formation of the hydrogen bonds is essentially a co-operative process because the mutual polarization of the participating alcohol molecules is not of a kind which strongly facilitates further bonding.

Coupled with the unfavorable steric effect of the organic groups, this limitation of two hydrogen bonds per alcohol molecule restricts the degree of ordered structure which can be established in liquid alcohols. This will preclude the three-dimensional association structure which is dominant in water and leads to linear polymer formation. For larger normal alcohols, linear polymeric groups tend to associate nonrandomly. The preferred oxygen atom positions lie in planes which are perpendicular to the parallel hydrocarbon chains (19). Normally, the type of association in liquid alcohols is well described in terms of equilibria between polymeric species. For such cases the formal thermodynamic treatment of "ideal associated solutions" is generally applicable (14, 20). These polymeric alcohol species do not generally exceed 5-7 molecules in length in the liquid alcohols. It is explicit that hydrogen bonding has a profound effect upon the properties of liquid alcohols but, unlike water, not in the sense of conferring openness of structure

(21). Water and alcohols resemble each other in hydrogen bonding facility, although the structures to which these bonds can give rise are known to be dissimilar in the case of water and alcohols and appear to be mutually exclusive (22-30).

Solvent systems of water and n-butanol have proven experimentally to have interesting features for solvent extractions. Water and n-butanol are not infinitely soluble in each other as are methanol and water, but at $20^{\circ}C$ water is soluble to the extent of 23.1% by weight in n-butanol (31). There are numerous literature references to the equilibrium distribution of organic and inorganic compounds between water and n-butanol and to the effect of these compounds upon the mutual solubilities of these solvents in each other.

Among aqueous solutions of organic compounds, hydroxy-derivatives are of interest because of their high solubility in water. However, their solutions often show abnormalities in properties such as viscosity-composition maxima or negative relative partial molar volumes. These phenomena are not yet completely understood. For monohydric alcohols in dilute aqueous solution, such peculiarities may be attributed, in a general way, to the bifunctional nature of the solute molecules. The hydrophobic hydrocarbon group is pictured as opposing the influence to be pulled into solution, which is exerted by the hydrophilic hydroxyl group. The hydroxyl group, which acts as either a proton donor or proton acceptor, can hydrogen-bond with the solvent molecules.

Monohydric alcohol-water mixtures are of maximum theoretical interest structurally. When studied over the whole range of alcohol-water compositions, even a simple single binary system of this type may present a variety of problems. In these mixtures, one component or the other might be present in excess and might possibly exert the major influence and control on such structures as are capable of existing in the liquid state. The fact that hydrogen bonding plays a primary role in the interaction of the components cannot alone account for the oddities in the properties which are observed for certain alcohol-water mixtures. Franks and Ives (14) picture these unusual properties as structural in origin and understandable in terms of the "structural behavior" of the components.

n-Butanol is the normal alcohol of smallest molecular weight which is partially immiscible with water at laboratory temperatures. The excess Gibbs free energy of mixing for monohydric alcohol-water mixtures is a consequence of negative and unsymmetrical enthalpy and excess entropy of mixing for most water-alcohol mixtures. An unusually large ratio of $T\Delta S^E$ to ΔH^M demonstrates clearly that it is $T\Delta S^E$ which is decisive in the determination of the exact nature of the deviations from Raoult's law, so that even mixtures which will evolve heat upon mixing show positive deviations from ideal behavior. This general disposition of the excess functions is always encountered in systems which separate, with rising temperature, into two liquid phases at a lower consolute temperature. Such a separation occurs as a result of a large negative ΔS^E, as opposed to separation with falling temperature, at an upper consolute temperature, which arises from energy effects (20). Each of the butyl alcohols, with the exception of t-butyl alcohol, forms a two-phase system with water which becomes homogeneous at the upper consolute temperature.

Incomplete miscibility and its frequent complex dependence upon temperature of the alcohol-water mixtures, could arise (14) from accentuation of "excess function behavior" similar to the closely related homogeneous alcohol-water systems. In such homogeneous systems, it is envisioned that at room temperature, entropy will dominate the energy-entropy balance which controls the excess free energy and, therefore, the overall deviations from ideal behavior. However, there is evidence that this behavior is strongly dependent upon temperature (32).

Interpretation of the thermodynamic excess functions is complicated by the overwhelming probability that these functions are, at the simplest, the resultants of opposite contributions. If, when the alcohol and water are mixed, hydrogen bonds are broken endothermically and new ones are made exothermically, ΔH^M will be the difference between two much larger thermal effects. Over the whole alcohol-water composition range, the relative magnitudes and even the origins of such contributions may vary widely, and a certain degree of uncertainty would accompany all "interpretations by inspection" of the excess functions.

In the case of the partially miscible mixtures of n-butanol and water, two distinct phases in equilibrium with each other are formed. One of these equilibrium phases is n-butanol-rich, while the other is water-rich. The structural problems associated with the n-butanol-water mixtures are significant in many respects. For example, low molecular weight alcohol-water solvents are frequently used in studies of chemical equilibria and reaction rates which can hardly be totally devoid of "solvent participation".

In a solution of water in n-butanol (X_2 ~ 75% by weight), each water molecule has a predominance of molecular alcohol neighbors. Thus, the water molecule has increased capability to hydrogen bond because of the greatly reduced proton concentration (compared to that in water), the somewhat greater abundance of lone electron pairs, and the reduced dielectric constant. Apart from questions concerning relative "basic strength", an alcohol molecule is statistically twice as likely to act as a proton acceptor than as a proton donor: by the water molecule acting as an 'acidic' proton donor, the chances will favor the formation of two hydrogen bonds with 'basic' alcohol neighbors. As a result, the basic function of the water molecule will be accentuated. It may form additional bonds, acting as an acceptor, with two more 'acidic' alcohol neighbors. Thus, it increases its co-ordination to four, in the absence of steric inhibition, and meets the requirement of equality of co-operative "give and take" for maximum hydrogen-bonding stability. It is certain from the exothermic contribution to ΔH^M that, in the region of large water mole fractions, strong alcohol-water bonds are formed. The stability of the suggested discrete, water-centered complexes is perhaps reflected in the proton magnetic resonance evidence for slow proton-exchange.

Two additional items of evidence for water-centered association in the n-butanol-rich phase may be mentioned. The Stokes-Einstein radius of the water molecule is greater when it is diffusing into low molecular weight alcohols than when the water molecule is diffusing in water (33). Addition of a little water to n-butanol increases its viscosity, at low temperatures, by an order of magnitude. Hydrous n-butanol solutions will supercool to form a type of "glass", as evidenced by the structures the n-butanol-water mixtures. Water molecules form junctions for cross-links between alcohol chains such that an amorphous silicate-like structure can be formed (34).

As the weight percentage of water increases in the n-butanol phase, the solution quickly becomes increasingly aqueous in character. Yet, in such a solution, molecular disorder is prevalent and structural order can only be very short-range in nature. It has been suggested (35) that in highly hydrous n-butanol solutions, the n-butanol is mainly interstitially dissolved (large volume loss--occupation of water cavities)--perhaps with some local change of structure (water clusters to gas-hydrate cages). From nuclear magnetic resonance studies, alcohol-water mixtures of low water content measured at low temperatures, give two discreet OH-proton signals indicating that the exchange of protons between oxygen atoms belonging to different molecular species is slow. Increase of water content leads to a merging of the signals, ultimately forming a single sharp peak.

In the n-butanol-water mixtures of low n-butanol content the mixtures are essentially aqueous in nature. Such a solution is one in which a resistance to depolymerization and a preservation of water structure is based upon the three-dimensional co-operative hydrogen bonding which is so fundamental to liquid water. Thus, water is able to act as host to molecules which, although alien, have a certain affinity for water. With progressively extensive invasion by the n-butanol molecules, however, rather sudden "cooperative failure" of structure retention is to be expected.

In a recently developed theory of the structure of liquid water (36-39), an equilibrium is envisioned between open, empty hydrogen-bonded clusters and a dense non-hydrogen-bonded fluid. n-Butanol added in small quantities to water is pictured as being distributed between two environmental situations--occupation of interstitial sites in the clusters of water molecules and the formation of a normal type of solution with the dense fluid.

Cheung (5) has reported the maximum solubility of n-butanol in water at 25°C to be 1.09 molal (~7% by weight n-butanol). This value is in good agreement with the experimental results of Kinoshita, Ishikawa and Shinoda (40), who determined the solubility of n-butanol in water to be 7.4% by weight.

The maximum solubility of water in n-butanol at 25°C, according to Cheung, was 13.6 molal (~50 mole percent and ~80% by weight alcohol). This value is in good agreement with the results reported by Rabinovich, et. al., (41).

Comparison of the experimental evidence for n-butanol-water mixtures at 16°C, reported by Beauvilain (42), with the work of Clark (43) on n-butanol-water mixtures at 25°C, reveals that the mutual solubilities of the two components in each other is temperature dependent. With decreasing temperature, the maximum solubility of n-butanol in water decreases and the solubility of water in n-butanol decreases. These decreases in maximum solubilities for the two components in each other results in an increase of the miscibility gap for the water-n-butanol mixtures. The region of the miscibility gap increases from the range of approximately 7 to 80% n-butanol by weight at 25°C to the range of approximately 6 to 88% n-butanol by weight at 16°C.

The static dielectric constants for n-butanol-water mixtures show no evident effects of structural complexity. There is, however, a miscibility gap in the n-butanol-water series at 25°C, extending in the region of mixtures from approximately 7 to 80% n-butanol by weight (42,44). The dielectric constants, at 25°C, in the water-rich end of the series decrease rapidly from that of pure water (78.5) to that for the aqueous solution of maximum n-butanol solubility (73.5) (44). The dielectric constants for the alcohol-rich end of the series of n-butanol-water mixtures should change only slightly. The estimated change in the dielectric constants for these mixtures would be less than three dielectric units in the region of mixtures containing 70 to 100% n-butanol by weight (42,45).

Lakhanpal and Conway (46) have studied the change in the activities of low molecular weight alcohol-water mixtures with increasing alcohol weight percentage, compared to the ideal Henry's law relation. Data from a modification of the Gibbs-Duhem relation for aqueous mixtures of certain alcohols at low temperatures, such as isopropanol, shows that the volatility of the alcohol, with increasing alcohol weight fraction, becomes larger than predicted on the basis of Henry's law. However, there is the opposite effect, or lower alcohol volatilities than predicted, at higher temperatures. This leads to activity-alcohol volume fraction curves which cross the reference line, giving rise to pseudo-ideal solutions. However, experimental evidence (14,46) reveals that, in the case of normal alcohols, the extent of this anomalous behavior decreases with successively larger molecular weight homologues. n-Butanol-water mixtures behave normally at all temperatures from -10°C to 30°C (46).

Ionic Solvation

The addition of electrolytes to water causes significant structural changes in the bulk liquid. One method of assessing such structural changes is to study the ionic entropies of solution. The entropy loss per mole of monoatomic ions upon solvation, due to increases in dielectric orientation, may be estimated by an emperical expression formulated by Latimer (47):

$$-\Delta S_D = \frac{22Z^2}{r_i + 2.8} \tag{2.1}$$

where Z is the valence of the ion, r_i is the radius of the bare ion expressed in Å, and 2.8Å is added to account for the first rigidly-held layer of water molecules which surround the ion as a result of hydration. Within the first layer of water molecules, the entropy loss is calculated in the model by assuming that the water molecules are rigidly held as in the structure of ice. Outside the first layer, the solvent is treated as a classical dielectric continuum with the expected bulk dielectric constant. Frank and Evans (48) define a term called the 'structure-breaking' entropy, ΔS^{st}, which corresponds to an increase of disorder beyond the first layer of oriented water molecules surrounding an ion. The region of solvent disorder, or structural breakdown, could arise, according to the authors, from the arrangement of the first water layer. For the case of a cation, the water molecules would be oriented with all of the hydrogens facing outward and could not, because of their orientation, all engage in normal, essentially tetrahedral, water bonding. For more highly charged monoatomic ions, not only does $|-\Delta S_D|$ greatly increase, as expected, but the ΔS^{st} term also increases, indicating that the region of structural breakdown is more extensive than in the case of singly charged cations, and that the region of 'rigidly-held' water may extend to solvent layers beyond the first layer. One could conclude from this that with increasing ionic concentration, the water structure would become more disordered; this has been experimentally demonstrated to be true (49,50).

The calculation of the thermodynamic properties of ionic solutions may be approached by utilization of the Born equation. The electrical contribution to the solvation free energy, E_S, for the transfer of an ion situated in vacuo to a large volume of structureless solvent is given by:

$$E_S = \frac{Z}{2r}\left(1 - \frac{1}{\varepsilon}\right) \tag{2.2}$$

where Z is the valency of the ion, ε is the bulk dielectric constant of the solvent and r is the radius of the bare ion, assumed to be a conducting sphere.

The total medium effect (51) on the transfer of an electrolyte from a finite concentration in one solvent to an identical concentration in a second solvent is a composite effect. The primary medium effect (52) is independent of ionic concentration and results from a difference in the ion-solvent interactions: it should be largely dependent upon the dielectric constants of the solvents. The secondary medium effect (52) results chiefly from a difference in ion-ion interactions in the two solvents and is also determined to a large degree by the dielectric constant of each medium. The simplest model for the primary medium effect is provided by the Born expression for the energy of transfer for an ion from one solvent medium to another:

$$\Delta\overline{G}^{o} = \frac{Z^2e^2}{2r}\left(\frac{1}{\varepsilon_1} - \frac{1}{\varepsilon_2}\right) \tag{2.3}$$

The Born treatment assumes that the ion is a rigid sphere of radius r with charge Z uniformly distributed over its surface, and that the ion is transferred from one continuous dielectric medium with bulk dielectric constant ε_1 to another medium of bulk dielectric constant ε_2. The free energy, per mole of salt, for the process involves the summation of the ion free energies since individual ion free energies are not measureable. The entropy of transfer may be calculated by the thermodynamic relationship:

$$\Delta\overline{G}_T = \Delta\overline{H}_T - T\Delta\overline{S}_T \tag{2.4}$$

Calculated results obtained from the Born equation are often incompatible with experimental results. Numerous explanations have been offered for the observed deviations (53,54):

(1) The "effective" radius of an ion is not constant, but is dependent upon the nature of the solvent.

(2) The derivation and nature of Born's approach ignores both the sign of the charge on the ion and the order-producing, order-destroying effect of the ions on the structure of the solvent.

(3) Bjerrum-type ion association occurs at finite molar or ionic concentrations.

(4) The Born calculation of the electrostatic energy needed to charge the ion treats the medium as being continuous and completely neglects its structure. Also, all forces which influence the ion, except electrostatic forces, are unaccounted for by the Born approach.

It is possible, in principle, to calculate thermodynamic functions for the transfer of a completely ionized electrolyte from one solvent to another at finite concentrations. Gladden and Fanning (55) envisioned the transfer process of a salt from one solvent medium to another as follows: Salt (aqueous solution) → Salt (ideal water solution) → Salt (ideal non-aqueous solution) → Salt (non-aqueous solution). If one could determine the free energy change for each step and then sum the terms, the following relation would result:

$$\Delta G_t = \Delta G_t^o + 2RT \ln (f_2/f_1) \qquad (2.5)$$

where f_1 and f_2 represent the activity coefficients of the salt in the nonaqueous solution and in the aqueous solution respectively. ΔG_t^o is the value of ΔG_t between standard states of the salt. The activity coefficients may be calculated by means of the Debye-Hückel expression provided that the solutions are sufficiently dilute. The resulting equation becomes the "limiting law" for the transfer process. However, this "limiting law" is unsatisfactory in that factors which are quite similar to those which cause deviations from Born's equation are ignored. ΔG_t^o must, therefore, be estimated theoretically.

The Born formula and most of its modifications are idealized models and are applicable only to essentially idealized systems and thus do not adequately detail the structure of electrolyte solutions. In order to gain a measure of insight into the structure of electrolyte solutions, one needs to know more concerning the nature of the solvent-solute bonding and the number of solvent molecules which are bound per ion.

Several theories and solvation models for aqueous systems have been presented (56-61). All of these theories and structural models have been shown to be inadequate in one way or another. Generally, such models have had one or more of the following assumptions incorporated into them: (1) a continuous dielectric solvent medium; (2) solely electrostatic forces and energies; (3) a classical model for the structure of water.

Numerous studies on ion hydration numbers of alkali metal and alkaline earth metal cations appear in the literature (62-72). The agreement of the experimental results obtained by the various techniques is not at all good. Typical results from the literature are included in the following table of ion hydration numbers for some alkaline earth metal ions (Table I):

TABLE I

EXPERIMENTAL HYDRATION NUMBERS OF IONS

Method	References	Mg^{++}	Ca^{++}	Ba^{++}
Mobility	59,60,63	10.5-13	7.5-10.5	5-9
Entropy	72	13	10	8
Compressibility	64	16	16	-
Cryoscopic	65	22.3	21.6	20.1
Cryoscopic	62	15	10.5	9
Dialysis	66	37.5	33.4	25.1
Partial Molar Volume	67	6.6	5.2	4
Solubility of Gases	68	13	14.6	16.8

Critical evaluation of the data on ion hydration numbers has led to the conclusion that the various experimental techniques measure different types and numbers of solvate water molecules (73-75). In spite of the abundance of experimental efforts made in the area of ionic hydration, the term "solvation number" and its significance remains obscure.

One classification scheme for solvation water in aqueous electrolytes has been proposed by Frank and Evans (48) from a critical analysis of the entropy of hydration. These authors picture a spherical ion surrounded by three concentric regions of solvation water molecules which are defined as: (1) the region of immobilized water molecules; (2) the normal water structure-destroyed region; (3) the structurally 'normal' water region displaying the expected continuous bulk dielectric constant of water. However, there is no agreement as to the boundaries of such regions.

Considering the formerly-held concepts of ionic solvation (56-61), coupled with the conclusions which were derived from his own treatment, Azzam (49,50,76) proposed a similar classification scheme with more precise definitions of the different types of solvate water molecules. His classification scheme is given as follows:

(1) Permanent Solvation - This term refers to solvent molecules which are firmly associated with the ion through the formation of chemical bonds. This type of solvation structure persists in the solid as well as in the liquid phases (e.g. co-ordinated water of crystallization).

(2) Primary Solvation - This term refers to solvent molecules which are firmly associated with the ion by electrostatic attraction. They have lost their translational degree of freedom and move as one entity with the ion during its Brownian motion. They cannot be dislodged by thermal motion.

(3) Secondary Solvation - This term refers to solvent molecules which undergo electrostatic attraction with the primary solvated ions. These molecules are much more weakly held, but the electrostatic attraction predominates over the separating action of thermal motion sufficiently to affect solvation-dependent quantities.

(4) Hydrodynamical Solvation - This term refers to solvent molecules which can be transferred hydrodynamically as the hydrated ion moves under the influence of an applied electrostatic field. This effect is due primarily to transfer of momentum between the solvated ion and the solvent molecules.

These several types of solvation molecules are influential to different degrees in the various experimental phenomena, depending upon the specific factor which is involved (11,50,76,77). However, the number of solvent molecules in the permanent and primary solvation sheets are conceived as having definite values, moving with the ion as a single entity without undergoing exchange with molecules of the bulk solvent. The number of solvent molecules in the secondary solvation sheath is variable depending upon the phenomena observed. Ions have been shown to continuously undergo exchange of solvent molecules as they migrate throughout the solution. Hydrodynamical solvation is relevant only in dynamic experiments such as the measurement of transport numbers. Hydrodynamical methods for the determination of ion solvation or ion hydration numbers give values which are far too large. This can be observed in the ion hydration number data presented earlier (Table I).

Azzam (76) has developed the basis for a statistical-mechanical approach to the calculation of the number of water molecules bound per ion and has derived the following relationship:

$$dS = 4 \pi \eta_o e^{-(\psi/kT)} r^2 dr \qquad (2.6)$$

dS = Number of solvent molecules associated with the ion in the spherical shell between r and r + dr from the center of the ion.

η_o = Number of solvent molecules per cubic centimeter in the bulk of the solution.

k = Boltzman's constant

T = Temperature, ^oK

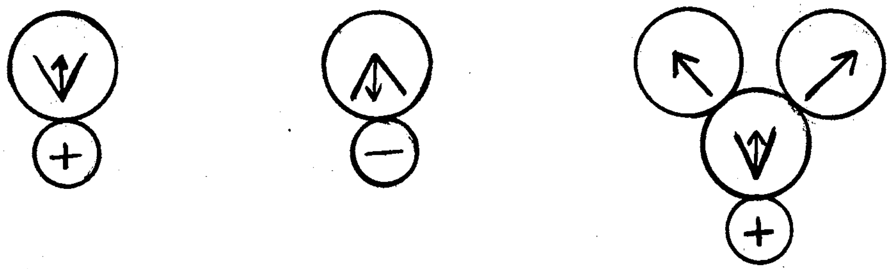
ω = Net potential energy of a solvent molecule in the solvation sheath. This energy is the algebraic sum of the energies of ion-dipole and dipole-dipole interactions.

ω may also be written as $\omega_r - \omega_o$, where:

ω_r = Net potential energy of a solvent dipole at a distance (r) from the ion.

ω_o = Potential of a water molecule in the bulk of the solution.

Azzam (76,78,79) has proposed the following models for the structures and polar orientation in hydrated ions (Figure 1):



Cation Anion Cation

Figure 1. Orientation of Water Molecules Near an Ion

By taking into account the specific factors on which the solvation number depends, together with the proposed structure of a solvated ion (see above), Azzam has evaluated the net interaction energy term (ω_r) from the following relationship:

$$\omega_r = (\mu_1 - \mu_2 - \mu_3)_r \qquad (2.7)$$

where μ_1 = The ion-dipole interaction energy.

μ_2 = The electrostatic potential due to the presence of the two water molecules attached to the dipole which is associated with the ion.

μ_3 = A term which accounts for the mutual effect on the coordinated water molecules.

By substituting values of the net interaction energy term, calculated by the foregoing expression, into Azzam's relationship for the calculation of the number of water molecules bound per ion, one obtains solvation numbers for both cations and anions which agree well with the solvation numbers calculated from an earlier model (76,77). This model was dependent upon the local effective dielectric constant of the ion and the bulk solution dielectric constant (76,77,80).

It is important, at this point, to emphasize that a knowledge of the local dielectric constant in the immediate vicinity of the ion is essential to understanding electrolyte behavior in solution; this dielectric constant will not be identical with the bulk solvent dielectric constant (11,80). Similarly, the solvation number is a quantity descriptive of only the immediate vicinity of an ion. Ion solvation numbers calculated by Azzam are based on Webb's theory (80), which predicts theoretically the local dielectric constant as a function of distance from the ion. Primary and permanent solvation numbers of selected bivalent metal ions have been presented by Azzam (49) and are compatible with those obtained by mutually self-consistent experiments. A recent paper by Azzam (79) has presented the theoretically evaluated maximum secondary solvation numbers based upon a treatment similar to that used for evaluating the primary solvation numbers.

It thus appears that Azzam's relatively simple model (presented earlier) for the structure of a solution immediately adjacent to a divalent ion is quite useful in envisioning a probable distribution of solvent dipoles around a divalent ion. The ionic heat of hydration for a divalent ion will then be the sum of four heat terms corresponding to the individual heat contributions of the four solvation zones around the ion. Thus, it follows that:

$$\Delta H_T = (\Delta H_1) + (\Delta H_2) + (\Delta H_3) + (\Delta H_4) \tag{2.8}$$

(ΔH_1) = The contribution of water dipoles in the catonium shell (permanent + inner primary solvation types).

(ΔH_2) = The contribution of water dipoles in the primary solvation shell (outer primary solvation types).

(ΔH_3) = The contribution of water dipoles in the secondary solvation sphere.

(ΔH_4) = The contribution of water dipoles beyond the previously mentioned solvation types (i.e. Born-Bjerrum term).

Calculations of the ionic heats of hydration have yielded results which are in good agreement with the most reliable ionic heats of solvation data available in the literature for bivalent metal ions (Table II).

The several bases for partitioning the values for the energy of hydration of salts into ionic contributions can be evaluated by comparing the corresponding solvation energies of the proton (86).

Ion-Association

Bjerrum type ion-association (or ion-pair formation) is an important factor which causes deviations from the Debye-Hückel approach, which assumes ions in solution to be totally independent of each other, Bjeruum (87) proposed that ions of opposite charge coming sufficiently close together would be bound together by their mutual electrostatic attractive forces and lose their thermodynamic independence. The ion-pairs formed are considered to be in equilibrium with the remainder of the ions in solution. The thermodynamic equilibrium constant K, for ion-association in the Bjerrum expression is given by (87):

$$K = 4\pi \int_a^q \exp. (Z_+ Z_- e^2/DkT_r) r^2 dr \qquad (2.9)$$

where r is the distance between the centers of the two ions, q is the critical distance of separation, a is the closest distance of approach, and D is the dielectric constant of the bulk solvent. Higher ionic charges and smaller dielectric constants are seen to favor ion-association or ion-pair formation.

Bjerrum's theory develops from consideration of the factors which will determine the extent of ionic association or, more specifically, the formation of ion pairs under the influence of Coulombic forces. The simplest possible model is assumed. The ions are assumed to be rigid unpolarizable spheres contained in a fixed macroscopic dielectric constant medium. Nonpolar bonds between ions and ion-solvent interactions are excluded. The theory is based upon purely electrostatic considerations and defines a distance q, between oppositely charged ions, within which the ions are considered to be associated into ion-pairs. This distance q, the ionic separation at which the mutual potential energy is equal to 2kT, represents the position of minimum probability of finding an ion of opposite charge anywhere on a spherical shell of radius

TABLE II

ENTHALPIES OF HYDRATION OF GASEOUS BIVALENT CATIONS

Ion	Noyes (85)	Azzam	Eley and Evans (81)	Latimer (82,83)	QuaGliano (84)
Zn^{+2}	530	524	485	485	491
Co^{+2}	505	506	488	—	497
Ni^{+2}	520	519	499	—	507
Ca^{+2}	395	385	428	—	395
Cu^{+2}	516	524	526	499	507
Ba^{+2}	326	321	347	—	305

Values in Kcal. $mole^{-1}$

r surrounding the central ion.

Bjerrum's equation predicts greater ion-pair formation the higher the valency of the ions and the smaller the dielectric constant of the medium: this is in qualitative agreement with experimental results (88). For 1:1 electrolytes in water at 18 °C, q equals 3.52Å and consequently, electrolytes of this type possessing values of the mean distance of approach of the ions, å, less than 3.5Å, will form short-range ion pairs. For 1:1 electrolytes having values of å greater than 3.5Å, the theory of Debye and Hückel is valid (89).

Bjerrum's theory is based entirely upon the range of validity of coulombic forces where the potential is given by $\Psi(r) = \frac{e_1 e_2}{Dr}$. However, for weak electrolytes $\Psi(r)$ is a much more complicated function of r than that which is postulated by Bjerrum. This theory will hold in media of low dielectric constants for electrolytes which have sufficiently large a values (52). However, this approach has been criticized because of the arbitrary cut-off distance q and thus has been largely replaced by the theory of Denison and Ramsey (90) and of Fouss and Kraus (91). These workers formulated a theory in which only those ions which are in actual contact are considered as forming ion-pairs. In this manner, they avoided the difficulty, which was encountered by Bjerrum, of considering ions not in physical contact as those constituting ion-pairs.

The interaction between a hydrated metal ion and an anion or neutral ligand may involve a number of partially solvated species. The ion-pairs formed in the solution need not be identical and thus, one can make a formal distinction between outer-and inner-sphere species. In the former case, one or at most two, solvent molecules are interposed between the interacting ions. In the latter case, the ions are immediately adjacent to each other. Most analytical methods for the determination of association constants do not adequately distinguish between these two alternatives. It is essential to recognize that different methods of investigation will respond to different types of associated species. Conductance and electromotive force (EMF) measurements will detect distant ion-pairs. Spectrophotometric methods, especially in the visible spectrum region, are expected to detect only those ion-pairs with the associating ions in close proximity. Spectral changes in the ultraviolet region may also reflect the presence of species formed in not-so-close interactions and so spectrophotometry is, in principle, capable of adequately distinguishing between outer- and inner-sphere ion pairs. A distinction for transition metal salts has been proposed by Smithson and Williams (92). They proposed that outer-sphere ion-pair formation would be expected to have little or no effect on the low-intensity absorption bands in the visible spectrum. These are due to forbidden d-d transitions, the wavelength depending upon the separation of the d-d states. This is, in turn, a function of the polarization of the cation by the associating anion as well as the symmetry of the polarizing field. Outer-sphere interaction would be expected to have little effect on the d-d splittings because of the large separation of the ions.

In place of the terms outer-sphere and inner-sphere, many workers have used "ion-pair" and "complex" respectively, to distinguish between the two types of species. It is preferable, however, to retain the terms outer-and inner-sphere to describe the type of association in question and to attach a broader meaning to the term "ion-pair". The latter is then defined as the association in which the bonding is almost exclusively due to long-range electrostatic forces between the oppositely charged ions. Under these circumstances, solvent molecules might possibly be interposed between the associated ions. In complexes, short-range or covalent forces will contribute to the stability of the species and such species will certainly involve inner-sphere interaction with the elimination of one or more solvent molecules from the co-spheres of the ions.

Nancollas (93) and others have pointed out that when two oppositely charged ions associate to form a single species, a moderately large and unfavorable negative entropy change which reflects the disappearance of a particle in the system would be expected. However, in many cases, there is, instead, a positive entropy change favoring ion-pair formation. This must result from the partial breakdown of the "iceberg" structure of coordinated water molecules around the ions. This leads to a decreased orientation of solvent molecules and thus, an increase in the total entropy of the system. Association reactions involving small, highly charged cations take place with relatively large positive values of ΔS. A large cation which has a comparatively high aqueous entropy value and which is not extensively hydrated, produces a small ΔS when it reacts to form ion-pairs. Although hydration effects are the most important factors governing the entropy of association, it is necessary to take into account other entropy contributions due to changes in configurational and rotational entropy which will accompany the association. Unless the unitary entropy changes (94) are calculated, direct comparison of ΔS values should be restricted to those reactions which will involve the same change in the number of solute species.

Liquid-Liquid Extraction

Marcus (7, 95) in his reviews on solvent extraction, calls attention to the mechanism for the extraction of both alkaline earth and transition metal perchlorates. Systems of this type consist of extraction by a solvating agent which directly solvates the metallic ion. In many of these systems, it is possible to assign a definite solvation number, which is the difference between the maximum coordination number of the cation and the ionic charge.

The extraction of the alkaline earth and transition metal perchlorates by a series of higher weight alcohols involves the salting-in of water molecules into the alcohol phase. These water molecules are in addition to the water molecules involved in the specific hydration of the cations in the system. This will lead to apparent non-integral hydration numbers in the organic phases, which are generally higher than the crystal coordination numbers for the cations (96). The hydration numbers obtained in this manner are probably best classified as being permanent + primary + some secondary.

The extraction of perchlorates by solvation of the cation does not require the complexing of the metal by the anion as required by the extraction of certain halo systems. Salts of anions which have little tendency to associate can be extracted. Cobalt and nickel (3, 4), zinc and cadmium (97), and other perchlorates (4) have been extracted, into a series of alcohols, with moderately high distribution coefficients.

The equilibrium extraction systems for nickel(II), cobalt(II) and copper(II) perchlorates, water, and n-butanol, have been studied by Libus and Libus (4) and more recently by Cheung (5). Nearly identical salt distribution coefficients and isotherms for the three transition metal perchlorates were obtained. It was found that the isotherms were linear in the square root of the salt molality for each salt at distribution equilibrium. At equilibrium, the free energy of transfer is equal to zero. Therefore, the enthalpy of transfer is equal to the product of the entropy of transfer and the temperature. The enthalpy of transfer is simply the difference in the partial molal heats of solution of the anhydrous salt in the two phases. In the limit of zero salt concentration, the distribution ratio becomes equal to $K_D^{1/3}$, the thermodynamic equilibrium constant for the transfer process. Similarly, the enthalpy of transfer becomes the enthalpy difference between the standard states for the solute in the equilibrium phase solvents. From these limiting values, the difference in the standard state entropies can be evaluated.

For extractions at finite concentrations and for the three transition metal perchlorates, cobalt, nickel and copper, Cheung (5) found that the enthalpy (and, of course, the entropy) of transfer varied linearly with aqueous phase salt concentration. Although a systematic error has been discovered in the values reported by Cheung, the linear dependence upon concentration is not affected by the error. Considering the scatter in the data, the values can be considered to vary linearly equally well with the square root of the aqueous phase molality. Linear variation of the heats of solution of alkali and alkaline earth metal perchlorates with the square root of the salt concentration, has been observed in dried n-butanol(98) and in water (99). From these data, it should be possible to estimate the heat of transfer at the same concentration in each phase. However, this quantity, which is the difference between two large quantities of about the same magnitude, is small, and its dependence upon concentration is correspondingly very uncertain. It appears, therefore, that existing data are not sufficiently precise to permit extrapolation (in the absence of any theoretical model) to the limit of zero concentration and the determination of the standard thermodynamic values.

The corrected experimental values for the partial molal heats of transfer for $Ni(ClO_4)_2$, $Cu(ClO_4)_2$ and $Co(ClO_4)_2$ from aqueous solutions into n-butanol are on the order of -14, -17, and -14 kcal. $mole^{-1}$ respectively, at an aqueous phase salt concentration of 0.02 molal, and -8.5, -12, and -8.5 kcal. $mole^{-1}$ respectively, at an aqueous phase salt concentration of 0.10 molal. The corresponding values for the entropy of transfer are on the order of -47, -57, and -47 e.u. per mole of salt and -28, -40, and -28 e.u. per mole of salt, respectively. A major portion of this gain of entropy at the higher concentration was attributed, by Cheung, to the net decrease of order in the solvent molecules resulting from the increased ion association in the butanol phase. The total entropy change of the system was explained in terms of several contributing factors, which were proposed from the solvation models and experimental evidence.

Physical Properties of Solvated Perchlorates in Solution

Transition metal perchlorates have been found to be highly dissociated in aqueous solutions (~100%); however, there is some evidence of a very small degree of ion-association in these solutions. For example, Ross (101) determined that the absorption maxima for $Ni(ClO_4)_2$ solutions intensified with $HClO_4$ addition.

Goodrich (102) studied the interaction of water with cobalt(II), copper(II) and nickel(II) perchlorates in n-butanol. The shape and position of the absorption bands in the visible and near infra-red spectra are completely in agreement with an octahedral ligand field for these ions in the anhydrous solvent. Addition of small quantities of water shifts the bands slightly without altering their shape significantly. The shift is of the order of 10-15 mμ or less and indicates strongly that replacement of butanol molecules by water molecules is occurring in the coordination sphere of the metal 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. Saturation of the n-butanol phase with water yields spectra which are almost identical to those obtained in aqueous solutions.

Salting Effects

Numerous solvent extraction systems are known in which a second salt is added to promote or enhance the extraction of a given salt from one solvent into a second solvent. This extraction promotion phenomena is familiarly known as the "salting-out" process. The addition of an extraction-promoting salt to the liquid-liquid extraction system, increases the distribution ratio of the first salt above the value which it had in the absence of the extraction-promoting salt.

The exact nature of the "salting-out" effect is extremely complicated and is not well defined. A complete and reliable theory of such effects has not been developed, but it can be demonstrated (52) that the order of magnitude of the experimental results can be computed theoretically from consideration of coulombic forces alone, exclusive of the inclusion of other factors or terms.

Many of the most important theoretical treatments have been reviewed by Marcus and Kertes (7). Among them is the electrostatic theory of Debye and McAulay (103). Debye and McAulay computed the partial free energy of a solute in solution with a nonelectrolyte, relative to its solution in the pure solvent, from the reversible electrical work of charging the ions. The theory assumes the ions formed, from dissociation of the salt, to be perfect rigid spheres. They based their theory of the causes of the "self-salting-out" upon the change in dielectric constant and the radii of the ions. They also developed an expression involving the contribution to the chemical potential of a nonelectrolyte, caused by the addition of an electrolyte. The resulting term, proportional to the ionic radii, expressing this contribution was designated as $\bar{\beta}$ (see ref. 52, 103). When $\bar{\beta}$ is positive, the macroscopic dielectric constant of the medium decreases, the activity increases and "salting-out" occurs. When $\bar{\beta}$ is negative, the bulk or macroscopic dielectric constant increases, the activity decreases and "salting-in" occurs.

Debye (104) developed a more refined theory of the causes of "salting-out" effects, which is based upon the influence of ions on the distribution of nonelectrolyte molecules, and derived an expression for the concentration of these molecules as a function of the distance from an ion. The salting-out effect was shown to increase very rapidly with decreasing separation distance between the ions and the nonelectrolyte molecule. This theory has been extended by Gross (105-107), who incorporated the effect of the ionic atmosphere.

Hückel (108) extended the scope of the Debye-Hückel theory by assuming that the dielectric constant of the medium varies linearly with the ionic concentration. According to this extended theory, there is added to the Debye-Hückel expression a term, Bc, which is linear in concentration. Bc thus represents the effect of the change of the dielectric constant with salt concentration. A lowering of D, produced by the addition of ions, has the effect of "salting-out" the ions as a consequence of an increase in the activity coefficient. The result corresponds formally to the effect of a repulsive force between the ions and is opposite in sign to the interionic attraction effect. If, on the other hand, the dielectric constant is increased by salt addition, the ions are "salted-in", Bc is negative and the activity coefficient is decreased. This type of behavior is also in accord with the theory of Debye and McAuley.

Moore, Laran and Yates (3) have illustrated that non-transition metal perchlorates can promote the extraction of a transition metal perchlorate by a higher weight monohydric alcohol. Specifically, they found that aqueous solutions of $LiClO_4$, $Ca(ClO_4)_2$ and $Al(ClO_4)_3$ will promote the extraction of $Co(ClO_4)_2$ by 2-octanol. For the $Co(ClO_4)_2$ alone and for its mixtures with $LiClO_4$, $Ca(ClO_4)_2$ and $Al(ClO_4)_3$, there resulted a common extraction isotherm. The distribution coefficient appears to be a function of only the total perchlorate molality over a wide concentration range and, thus, is independent of the charge type of the second or promoting perchlorate.

Gerlit and Spivakov (109) found that salting-out agents for ion-pair systems involving oxonium or pyridinium perrhenates followed an order paralleling the extent of hydration of the respective salting-out cation.

The relationship between such factors as the extent of hydration, molar volume and ionic forces in solutions of various nitrates used as promoting agents, has been discussed by Adamskii (110) and was utilized successfully to predict their effect on $UO_2(NO_3)$ extraction. The effectiveness of salting-out agents on uranyl nitrate extractions increases with increasing charge and decreasing cationic radius (111-115).

Moore, et. al. (116) have studied the effects of extraction-promoting chloride salts upon the distribution of $CoCl_2$ and also the effects of extraction-promoting bromide salts upon the distribution of $CoBr_2$ in a 2-octanol-water system. Whereas, the distribution coefficient of $CoCl_2$ showed a marked dependence upon the nature of the specific promoting salt, the extraction of $CoBr_2$, by comparison, did not greatly depend upon the charge type of the promoting salt.

CHAPTER III

EXPERIMENTAL METHOD AND PROCEDURE

Distribution Equilibria

For each of the individual salt and salt mixture concentrations studied, 200 milliliters of aqueous solution was prepared. The $Ca(ClO_4)_2$ solutions, made up in the range of 0.09 to 1.10 molal aqueous salt concentrations, were prepared by diluting a standard 2.42 molal $Ca(ClO_4)_2$ solution. The $Co(ClO_4)_2$ solutions, made up in the range of 0.15 to 1.05 molal aqueous salt concentrations, were prepared by diluting a standard 1.65 molal $Co(ClO_4)_2$ solution. The $Co(ClO_4)_2$ - $Ca(ClO_4)_2$ mixtures were each made up to 0.1 molal aqueous $Co(ClO_4)_2$ concentration, but ranged in aqueous $Ca(ClO_4)_2$ concentration from 0.1 to 1.0 molal, increasing in essentially 0.1 molal increments.

The distribution equilibrium experiments were conducted by equilibrating the aqueous metal perchlorate solutions with equal volumes of n-butanol. Mixtures were shaken vigorously on a "wrist-action" shaker for a minimum of three hours. The mixtures were then transferred into separatory funnels and allowed to equilibrate in a water bath at 25° ± 0.1°C. The standing time was at least ten days and sometimes longer for the more dilute salt concentration mixtures. The butanol phase was drawn off through a hypodermic syringe for analysis.

The individual phases were analyzed for their metal ion content. In the cases of either $Co(ClO_4)_2$ or $Ca(ClO_4)_2$ alone, the separate phases were analyzed by standard EDTA titrations (117). For $Co(ClO_4)_2$ - $Ca(ClO_4)_2$ mixtures, the total metal ion concentration was determined by back-titration of the excess added EDTA (excess above the amount necessary to complex all metal ions present) by a standard zinc chloride solution to an EBT (Eriochrome Black T) endpoint. The Co^{++} concentration in the mixtures was determined by the back-titration of excess added EDTA with a standard cupric nitrate solution to a PAN[1-(2-Pyridylazo)-2-naphthol] endpoint. The Ca^{++} concentration in the mixtures was obtained by taking the difference of the total metal ion concentration and the Co^{++} concentration for each mixture. Results of the metal ion determinations are presented in Tables III and IV as moles of anhydrous salt per 1,000 grams (kg.) of pure solvent. Reproducibilities were always better than 0.6%.

Water molality in the organic phase was determined by standard Karl Fischer direct titration employing a dead-stop endpoint determination with a Heathkit (#EAU 20-11) pH Recording Electrometer hooked into a basic pH meter setup (118-123). Results are tabulated in Table V. Reproducibilities were always better than 0.6%.

Since n-butanol and water form a minimum boiling azeotrope (b.p. 95°C), the quantity of n-butanol in the aqueous phases was determined at 25°C by measuring the densities of the distillates of the aqueous phase equilibrium solutions and comparing these densities with a previously prepared standard curve. The aqueous phase solutions were quantitatively distilled under atmospheric pressure at about 95°C until approximately 80% of the original solutions had been distilled. Deionized water was added to the distillate to redissolve all the n-butanol and the density of the distillates was compared with a standard curve, obtained by

TABLE III

DISTRIBUTION OF THE INDIVIDUAL PERCHLORATES AT 25°C

$Co(ClO_4)_2$[†]		$Ca(ClO_4)_2$[†]	
Maq. x 10	Morg. x 10	Maq. x 10	Morg. x 10
1.499	0.255	0.904	0.075
1.794	0.344	1.180	0.120
3.438	1.107	1.745	0.255
4.022	1.501	2.633	0.463
5.698	2.943	3.539	0.807
7.573	5.321	4.212	1.150
8.819	7.329	5.330	1.867
9.688	8.918	7.230	3.543
		9.510	6.461
		11.032	8.938

Maq. = aqueous phase salt molality, moles kg^{-1} water

Morg. = organic phase salt molality, moles kg^{-1} n-butanol

[†] The last figure on the right is not significant but is included for computational use.

TABLE IV

DISTRIBUTION OF THE PERCHLORATES IN A $Co(ClO_4)_2$ - $Ca(ClO_4)_2$ MIXTURE AT 25°C

$Co(ClO_4)_2$†		$Ca(ClO_4)_2$†	
Maq. x 10	Morg. x 10	Maq. x 10	Morg. x 10
1.008	0.223	1.316	0.221
0.961	0.307	2.517	0.572
0.934	0.373	3.697	1.086
0.894	0.467	4.858	1.770
0.874	0.556	6.091	2.628
0.851	0.643	7.257	3.796
0.834	0.736	8.386	5.244
0.827	0.844	9.682	7.111
0.777	0.807	9.809	7.379
0.771	0.883	10.917	9.113

Maq. = aqueous phase salt molality, moles kg^{-1} water

Morg. = organic phase salt molality, moles kg^{-1} n-butanol

† The last figure on the right is not significant but is included for computational use.

TABLE V

CONTENT OF N-BUTANOL IN THE AQUEOUS PHASES AT 25°C

$Co(ClO_4)_2$†		$Ca(ClO_4)_2$†		$Co(ClO_4)_2$ - $Ca(ClO_4)_2$†	
Maq. x 10	BuOH Molality*	Maq. x 10	BuOH Molality*	Maq. x 10	BuOH Molality*
1.499	1.055	0.904	1.086	2.324	1.083
1.794	1.029	1.180	1.081	3.478	1.085
3.438	1.143	1.745	1.093	4.631	1.070
4.022	1.168	2.633	1.106	5.752	1.066
5.698	1.336	3.539	1.151	6.965	1.080
7.573	1.520	4.212	1.159	8.108	1.094
8.819	1.700	5.330	1.184	9.220	1.176
9.688	1.795	7.230	1.220	10.509	1.309
		9.510	1.291	10.586	1.313
		11.032	1.402	11.688	1.469

*moles kg^{-1} water

†The last figure on the right is not significant but is included for computational use.

Cheung (5), showing the molality of n-butanol as a function of the weight of distillate solution per unit volume (density). Results are shown in Table VI. Reproducibilities were always better than 0.6%.

Thermochemical Measurements

Although the enthalpy of transfer of a salt at phase equilibrium is simply the difference in the heats of solution of the salt in the equilibrium phases, $Co(ClO_4)_2 \cdot 6\ H_2O$ is thermally unstable and efforts to remove the water of hydration invariably result in the contamination of the product by both the oxide and the chloride. Swartz (124) showed that this problem could be avoided by choosing, in place of the anhydrous salt, a stable, stoichiometrically reproducible solvate of the metal, determining its heat of solution in each equilibrium phase solvent, and correcting the result for the heat of solution of the solvating compound in each phase. This approach required that the salt solvate be easily soluble in both the organic and aqueous phase solvents. Simultaneously, the dissolution rate of the solvate had to be reasonably rapid. Such compound requirements pose numerous difficulties.

However, Cheung (5) showed that a "reference solution" of definite composition could be substituted into the cycle in place of the solid solvate compound. Examination of the experimental systems suggested the use of concentrated aqueous perchlorate solutions for use with n-butanol extractions: such concentrated aqueous perchlorate solutions were found to be completely miscible with the equilibrium solvents of both the aqueous and n-butanol-rich phases at the selected experimental temperature. Such reference solutions proved to be satisfactory over the entire range of cobalt perchlorate and calcium perchlorate concentrations

TABLE VI

CONTENT OF WATER IN THE ORGANIC PHASES AT 25°C

$Co(ClO_4)_2$†		$Ca(ClO_4)_2$†		$Co(ClO_4)_2$ - $Ca(ClO_4)_2$†	
Morg. x 10	H_2O Molality*	Morg. x 10	H_2O Molality*	Morg. x 10	H_2O Molality*
0.255	14.475	0.075	13.932	0.444	13.915
0.344	14.767	0.120	14.105	0.879	15.254
1.107	17.660	0.255	14.561	1.459	17.337
1.501	19.040	0.463	15.231	2.237	20.301
2.943	23.658	0.807	16.275	3.184	23.361
5.321	31.123	1.150	17.641	4.439	27.324
7.329	36.913	1.867	20.062	5.980	32.436
8.918	41.367	3.543	25.662	7.955	38.211
		6.461	34.572	8.186	39.135
		8.938	41.277	9.996	44.368

*moles kg^{-1} n-butanol

†The last figure on the right is not significant but is included for computational use.

studied.

Although $Ca(ClO_4)_2 \cdot 6\ H_2O$ can be thermally dehydrated, it was decided to use the <u>same</u> (cyclic) set of measurements to determine the enthalpy of transfer of this salt as was used in the case of the cobalt salt. This was due, in part, to the fact that the comparison of the results could be made more satisfactorily, but was done largely because the same calorimeter could be used for all measurements.

The modified thermodynamic cycle of Cheung is shown in Figure 2. The partial molal enthalpy of solution, $\Delta\bar{H}s$, of one mole of salt in an infinitely large quantity of equilibrium phase solution of salt molality m, is thermodynamically equivalent to the sum of the following enthalpy changes:

(a) $\Delta\bar{H}_s^*$ - The partial molal enthalpy change for dissolving one mole of the "reference solution" in an infinitely large quantity of equilibrium phase solution of salt molality m.

(b) ΔH_x - The enthalpy change for the process of dissolving the hypothetical anhydrous perchlorate salt in <u>x</u> moles of water to form a reference solution, $M(ClO_4)_2 \cdot (X\ H_2O)$.

(c) ΔH_r - The partial molal enthalpy change for the process of dissolving <u>x</u> moles of water in an infinitely large quantity of the equilibrium phase solution of salt molality M.

Thus, $\Delta\bar{H}_s = \Delta\bar{H}_x + (\Delta\bar{H}_s^* - \Delta H_r)$. (3.1)

The partial molal enthalpy of transfer of the perchlorate from the aqueous phase to the organic phase is represented by $\Delta\bar{H}_t = (\Delta\bar{H}_s)$org. - $(\Delta\bar{H}_s)$aq. The right hand side of this expression is equal to $(\Delta\bar{H}_s^* - \Delta\bar{H}_r)$ org. - $(\Delta\bar{H}_s^* - \Delta\bar{H}_r)$aq., since ΔH_x disappears upon subtraction.

$$\begin{tikzcd}
M(ClO_4)_2\ (S) + \begin{array}{c}\text{an infinitely large}\\ \text{quantity of equilibrium}\\ \text{phase solution}\\ \text{(molality M)}\end{array} \arrow[r, "\Delta\bar{H}_s"] & M(ClO_4)_2\ (M) \\
\begin{array}{c}+\\ \\ X\ H_2O\end{array} \arrow[d, "\Delta\bar{H}_x"] & \begin{array}{c}+\\ \\ X\ H_2O\end{array} \arrow[d, "\Delta\bar{H}_r"] \\
M(ClO_4)_2\cdot(x\ H_2O) + \begin{array}{c}\text{an infinitely large}\\ \text{quantity of equilibrium}\\ \text{phase solvent}\\ \text{(molality M)}\end{array} \arrow[r, "\Delta\bar{H}^*_s"] & M(ClO_4)_2\cdot(x\ H_2O)(M)
\end{tikzcd}$$

Figure 2. Modified Thermochemical Cycle

In order to transfer the salt from a finite quantity of one phase into a second phase without disturbing the extraction equilibrium, it is necessary that the amount transferred be infinitesimally small. Since there exists a state of equilibrium, the partial molal free energy change upon transfer is equal to zero, such that $\Delta\bar{H}_t = T\Delta\bar{S}_t$, where $T = 298.16^{\circ}K$, and $\Delta\bar{H}_t$ and $\Delta\bar{S}_t$ are, respectively, the partial molal enthalpy change and entropy change for the transfer. From examination of the cycles of Figure 2, it can be seen that the partial molal enthalpy of transfer is given by the sum of the differences in the experimental values of the partial molal heats of solution of water and the reference solution in the equilibrium phase mixtures.

Heats of solution were measured directly in a solution calorimeter at $25.0^{\circ}C$ and essentially at constant atmospheric pressure (such that the heat of solution can be equated to the enthalpy of solution). The calorimeter will be described later. To determine a value for $\Delta\bar{H}_s^*$ at a salt concentration corresponding to the extraction equilibrium, an aqueous "reference solution" of from 2.0 to 2.6 molal metal salt concentration was added incrementally from a micrometer syringe to approximately 60 milliliters of solvent in the calorimeter. The solvent consisted of a water-n-butanol mixture having a composition such that, with the continued addition of the reference salt solution, the equilibrium phase solution composition could be reached. Additions were continued until the concentration of metal salt in the calorimeter was slightly greater than the equilibrium value.

The integral heat of mixing was plotted against the number of moles of salt added, and the slope was evaluated graphically at the equilibrium phase composition, to obtain the partial molal quantity $\Delta\bar{H}_s^*$. It should be noted that plotting the integral heat change against the number of moles of salt added is equivalent to plotting the heat change against the number of moles of reference "compound" $M(ClO_4)_2 \cdot X\ H_2O$, since a mole of reference "compound" can be defined as the quantity of reference solution containing one mole of salt and <u>x</u> moles of water.

Values of $\Delta\bar{H}_r$ were obtained in a manner similar to that for $\Delta\bar{H}_s$. Water was added incrementally to the equilibrium phase solvent (equilibrium phase solution deficient in one mole of water per mole of salt) via a micrometer syringe, and the integral heat of mixing was plotted against the number of moles of water added. Since <u>x</u> moles of water were added for each mole of reference salt solution in the thermodynamic cycle, the values of the partial molal heat of solution of water, again obtained graphically from the slopes, were multiplied by <u>x</u> to find $\Delta\bar{H}_r$.

Thermochemical data are tabulated in Table VII. Except for the higher concentration cycles of $Co(ClO_4)_2$ and $Ca(ClO_4)_2$ alone, the values for $(\Delta\bar{H}_r)$org. were zero. This is reasonable since the organic phase solutions were already nearly saturated with water and the addition of a minute amount of water should not cause a significant change in the enthalpy. All values were recorded as the average of duplicate runs. The deviations (σ values) of the duplicates from their averages were doubled to statistically compensate for the fact that only two thermochemical determinations were made at each solution concentration. These doubled sigma values are reported in Table VII.

The Calorimeter

A sketch of the calorimeter assembly is shown in Figure 3. The calorimeter vessel consisted of a 120 ml. capacity silvered dewar flask (R), surrounded by a Pyrex water jacket. Through this Pyrex jacket was circulated water from a constant temperature water bath, regulated (± 0.05°C) with a Yellow Springs Instrument Company thermistemp temperature controller (Model 71). The calorimeter and jacket were suspended in a "dead-air" enclosure (G) of bakelite.

The silvered dewar (R), which composed the bottom portion of the calorimeter vessel, was coupled by a ground flange (H) to a glass solvent-tight lid (F). The lid was secured by a bakelite ring (C) and suspended from a bakelite disc (B) forming part of the top of the calorimeter jacket. The dewar flask was fastened to the lid by a bakelite ring (I) during the experiment. Through sealed ports in the glass top were inserted the liquid reagent delivery needle (E), thermistor (J) for temperature detection, acetone "cold-finger" (K) for internal tempera-

TABLE VII

HEAT VALUES FOR STEPS IN THE THERMOCHEMICAL CYCLE

$Co(ClO_4)_2$ Maq. x 10 Morg. x 10	$(\Delta \bar{H}^*_s)$org. Kcal/mole reference	$(\Delta \bar{H}_r)$org. Kcal/mole reference	$(\Delta \bar{H}_s)$org. Kcal/mole reference	(ΔH^*_s)aq. Kcal/mole reference	$(\Delta \bar{H}_r)$aq. Kcal/mole reference	$(\Delta \bar{H}_s)$aq. Kcal/mole reference	$(\Delta \bar{H}_t)$ Kcal/mole salt	$(\Delta \bar{S}_t)$ e.u./mole salt
$\frac{1.499}{0.255}$	-5.908±.030	0.000±.000	-5.908±.030	-.717±.012	-2.042±.019	+1.325±.031	-7.122±.061	-24.26±0.20
$\frac{1.794}{0.344}$	-5.650±.024	0.000±.000	-5.650±.024	-.636±.010	-1.965±.019	+1.329±.029	-6.979±.053	-23.41±0.18
$\frac{3.438}{1.107}$	-4.552±.022	0.000±.000	-4.552±.022	-.232±.008	-1.503±.019	+1.271±.027	-5.823±.049	-19.53±0.16
$\frac{4.022}{1.501}$	-4.256±.020	0.000±.000	-4.256±.020	-.136±.006	-1.195±.021	+1.059±.027	-5.315±.047	-17.83±0.16
$\frac{5.698}{2.943}$	-2.956±.032	0.000±.000	-2.956±.032	0.000±.000	-1.349±.020	+1.349±.020	-4.305±.052	-14.44±0.17
$\frac{7.573}{5.321}$	-2.228±.022	+.231±.019	-2.459±.041	0.000±.000	- .790±.019	+ .790±.019	-3.249±.060	-10.90±0.20
$\frac{9.688}{8.918}$	-1.203±.014	+.250±.019	-1.453±.033	0.000±.000	-1.098±.019	+1.098±.019	-2.551±.052	- 8.56±0.17

TABLE VII (Continued)

$Ca(ClO_4)_2$ Maq. x 10 / Morg. x 10	$(\Delta\bar{H}^*_s)$org. Kcal/mole reference	$(\Delta\bar{H}_r)$org. Kcal/mole reference	$(\Delta\bar{H}_s)$org. Kcal/mole reference	(ΔH^*_s)aq. Kcal/mole reference	$(\Delta\bar{H}_r)$aq. Kcal/mole reference	$(\Delta\bar{H}_s)$aq. Kcal/mole reference	$(\Delta\bar{H}_t)$ Kcal/mole salt	$(\Delta\bar{S}_t)$ e.u./mole salt
11.032 / 8.938	-1.426±.014	+.251±.019	-1.677±.033	0.000±.000	-.424±.019	+ .424±.019	-2.101±.052	- 7.05±0.17
9.510 / 6.461	-1.926±.020	+.231±.018	-2.157±.038	0.000±.000	-.482±.020	+ .482±.020	-2.639±.058	- 8.85±0.19
7.230 / 3.543	-2.670±.030	+.231±.019	-2.901±.049	+ .174±.006	-0.598±.018	+ .772±.024	-3.673±.073	-12.32±0.24
5.330 / 1.867	-3.431±.032	0.000±.000	-3.431±.032	+ .321±.008	- .733±.019	+1.054±.027	-4.485±.059	-15.04±0.20
3.539 / 0.807	-4.159±.016	0.000±.000	-4.159±.016	+ .403±.010	- .964±.021	+1.367±.031	-5.526±.047	-18.53±0.16
2.633 / 0.463	-4.631±.014	0.000±.000	-4.631±.014	+ .417±.006	-1.099±.019	+1.516±.025	-6.147±.039	-20.62±0.13
1.180 / 0.120	-5.767±.018	0.000±.000	-5.767±.018	+ .422±.004	-1.428±.021	+1.850±.025	-7.617±.043	-25.54±0.14
0.904 / 0.075	-6.164±.016	0.000±.000	-6.164±.016	+ .428±.006	-1.601±.020	+2.029±.026	-8.193±.042	-27.48±0.14

TABLE VII (Continued)

$Co(ClO_4)_2$ $\frac{Maq. \times 10}{Morg. \times 10}$	$Ca(ClO_4)_2$ $\frac{Maq. \times 10}{Morg. \times 10}$	$(\Delta\bar{H}^*_s)$org. kcal/mole reference	$(\Delta\bar{H}_r)$org. kcal/mole reference	$(\Delta\hat{\bar{H}}_s)$org. kcal/mole reference	$(\Delta\bar{H}_s)$aq. kcal/mole reference	$(\Delta\bar{H}_r)$aq. kcal/mole reference	$(\Delta\bar{H}_s)$aq. kcal/mole reference	(ΔH_t) kcal/mole salt	$(\Delta\bar{S}_t)$ e. u./mole salt
$\frac{1.008}{0.223}$	$\frac{1.316}{0.221}$	-5.686±.048	0.000±.000	-5.685±.048	0.000±.000	-1.056±.026	+1.056±.026	-6.741±.074	-22.61±0.25
$\frac{0.961}{0.307}$	$\frac{2.517}{0.572}$	-4.772±.014	0.000±.000	-4.772±.014	0.000±.000	- .977±.025	+ .977±.025	-5.749±.039	-19.28±0.13
$\frac{0.934}{0.373}$	$\frac{3.697}{1.086}$	-4.125±.018	0.000±.000	-4.125±.018	0.000±.000	- .924±.025	+ .924±.025	-5.049±.043	-16.93±0.15
$\frac{0.894}{0.467}$	$\frac{4.858}{1.770}$	-3.669±.012	0.000±.000	-3.669±.012	-.220±.010	- .872±.024	+ .652±.034	-4.321±.046	-14.49±0.15
$\frac{0.874}{0.556}$	$\frac{6.091}{2.628}$	-2.950±.014	0.000±.000	-2.950±.014	-.287±.012	- .792±.025	+ .505±.037	-3.455±.051	-11.59±0.17
$\frac{0.851}{0.643}$	$\frac{7.257}{3.796}$	-2.468±.018	0.000±.000	-2.468±.018	-.293±.012	- .740±.020	+ .447±.032	-2.915±.050	- 9.78±0.17
$\frac{0.834}{0.736}$	$\frac{8.386}{5.244}$	-2.168±.014	0.000±.000	-2.168±.014	-.292±.010	- .713±.021	+ .421±.031	-2.589±.045	- 8.68±0.15
$\frac{0.827}{0.844}$	$\frac{9.682}{7.111}$	-1.822±.012	0.000±.000	-1.822±.012	-.291±.010	- .713±.022	+ .422±.032	-2.244±.044	- 7.53±0.15
$\frac{0.777}{.807}$	$\frac{9.809}{7.379}$	-1.658±.020	0.000±.000	-1.658±.020	-.292±.008	- .740±.026	+ .448±.034	-2.106±.054	- 7.06±0.18
$\frac{0.771}{0.883}$	$\frac{10.917}{9.113}$	-1.472±.016	0.000±.000	-1.472±.016	-.294±.008	- .687±.000	+ .393±.008	-1.865±.024	- 6.27±0.08

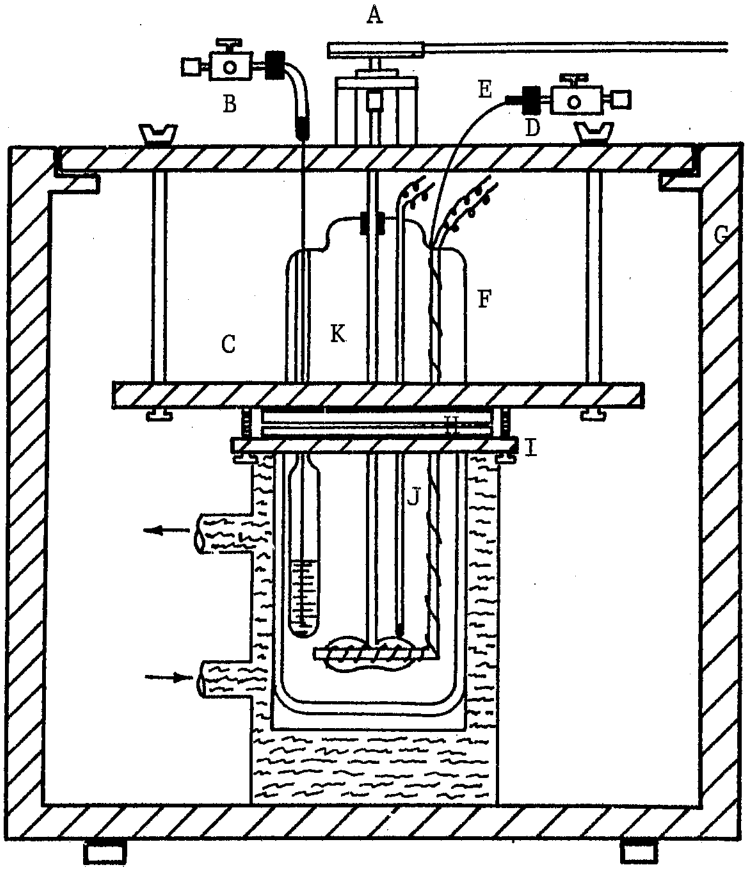


Figure 3. The Solution Calorimeter

ture variation and the leads from the internal heater (O). The heater was made from 40 gauge platinum wire, 32 ohms of which was wound around a one-inch high cylindrical, open glass form. The platinum wire was connected to heavy gauge copper leads through a mercury junction. A Fenwal (GA51PM12) 100,000-ohm thermistor probe constituted one arm of a shielded d.c. Wheatstone-bridge arrangement to monitor the changes in temperature (thermistor resistance) of the solution in the calorimeter. The bridge voltage was provided by a constant voltage Trygon Power Supply, 0-20 Volts D.C. (Model EAL 20-500). This circuit had as the detector of unbalanced current on the Wheatstone-bridge, a Sargent Model SRG recording potentiometer. The recorder, through variable range span adjustments, had several available sensitivity settings. A suitable compromise could be reached whereby the stirrer noise was minimized and, simultaneously, the high sensitivity of the 100,000-ohm thermistor fully utilized.

The stirrer (M) was made of Pyrex. It was connected through a plastic sleeve and ball bearing (Q) to the shaft of the metal pulley (A) on the outside of the calorimeter jacket by a latex sleeve joint. The latter greatly reduced any heat loss or gain by conduction through the stirrer to the calorimeter. The stirring rate was closely controlled with a Cole-Parmer, GT-21, thyratron controller.

The platinum heating element of the internal heater was totally immersed and completely exposed to the solution in the dewar. Thermal lags were made negligible in this manner. The mercury connection and copper leads from the calorimeter were made sufficiently large to assure that any resistance in leads external to the calorimeter would be very small compared to the resistance of the platinum heater. The heater circuit was powered by a very stable external power supply, which provided a constant current over the 120-second intervals used in measuring the heat capacity of the solution in the calorimeter.

When the circuit was closed to the internal heat by means of an X-ray timer switch, a Standard Time Company (Model SI) timer was activated through a relay. The timer was then deactivated when the timer switch opened the circuit at the end of each preset time interval. The elapsed time was determined to the nearest 0.01 second.

The current used in the measurement of the heat capacity of the solution in the dewar was approximately 40 milliamperes. The same potentiometer (Rubicon Instrument Company, Model 2730) could be used to measure, by switching, both the voltage drop across the heater and across a General Radio (Series 500) secondary laboratory standard 10-ohm (±0.05%) resistor in series with the heater. This was calibrated and found to agree with its nominal value within the 0.05% tolerance limit.

Liquid reagent was added through a teflon needle; throughout the additions of reagent the last portion of the curved needle (containing ~0.16 ml. of reagent) was kept beneath the level of liquid in the dewar. A manually operated 2.5 ml. Gilmont micrometer syringe (#7874) was connected to the teflon delivery needle. The smallest increment which could be read was 0.0001 milliliter. By calibration with water at 25°C, it was determined that the actual volume delivered from the micrometer syringe was 1.0014 times the volume indicated on the digital dial. However, this correction factor was found applicable for each experimental volume (0.03-0.06 ml) delivered.

A calibration of the 100,000-ohm thermistor gave a reproducible linear 0.011 degree ohm^{-1} relationship over the 23° - 27° C range. The individual runs made with the calorimeter were carried out within this temperature span. The thermistor showed excellent stability and reproducibility.

The 10^5 ohm thermistor which was used to measure the heats of solution and reaction had a manufacturer's rated temperature coefficient of resistance of 4.75% degree^{-1}. This is equivalent to -4750 ohms degree^{-1} at 25°C. When the recorder's five millivolt range setting was utilized, the sensitivity of the filled calorimeter was 0.262 cal. inch^{-1} of recorder pen movement for n-butanol solutions and 0.314 cal. inch^{-1} for aqueous solutions. The pen travel could easily be read to ±0.01 inch.

A 9-volt potential was impressed across the thermistor at all times to assure stability and uniformity of response.

The values of current, potential across the heater, and time were measured to four significant figures. The timer had 0.01 second divisions and the heating runs were approximately 120 seconds in duration. The method used in calculating the heat capacity of the calorimeter was to find the values of h from:

$$h = EIt/4.186d \tag{3.2}$$

where I = Current, amps

E = Potential across internal heater, volts

t = Time, seconds

d = Recorder deflection, inches

4.186 = Joules per calorie

This gave a value of h in calories inch^{-1} at a given experimental temperature. Any single measurement of the heat capacity raised the temperature of the solution less than 0.016°C and two successive heat capacity measurements could be made without significant increases in solution temperature. When corresponding heat capacity calibrations were compared, the results were always within 1% of each other.

The overall performance of the calorimeter was checked by measuring the endothermic heat of mixing of water with n-butanol at 25°C. The experimental value of 434 ± 2 cal. mole^{-1} of water added is in excellent agreement with the literature value of 432 ± 2 cal. mole^{-1} (125).

The calorimeter was designed to measure experimental heats of reaction of the order of one calorie or less with an accuracy of 1% or better. This seems to have been realized. The calorimeter was also designed to permit very small successive metered additions of reagents to be added and to include in the overall accuracy of 1% any volumetric errors in the addition of reagent.

Dielectric Constants

The dielectric constant, ε, of a liquid or solution is given by the ratio of the capacitance of a capacitor with the liquid or solution (an insulator or dielectric) between the plates to the capacitance of the empty capacitor in air.

$$\varepsilon = \frac{C}{C_o} \qquad (3.3)$$

C = Capacitance of the liquid or solution.

C_o = Capacitance in air.

The introduction of the sample into the capacitor results in a reduction of the field strength between the capacitance plates because of polarization of the dielectric sample. The force of attraction between two opposite charges (±q) separated by distance d is q^2/d^2 in a vacuum (air), but is equal to $q^2/\varepsilon d^2$ in a medium of dielectric constant ε. It is tacitly assumed that the sample is isotropic and homogeneous and that the sample completely fills the region in which the electric field exists and is effective.

An unsuccessful attempt was made to experimentally determine the dielectric constants of pure water, n-butanol and a series of homogeneous n-butanol-water mixtures at 25°C employing a General Radio Company Capacitance Measuring Assembly (Model 1610-B) with a Guard Circuit (#716-P4). From the results, it appeared that the conductivities of the simple monohydric alcohols, including methanol, n-butanol, hexanol and n-octanol were too large to allow the measurement of their respective dielectric constants with the available equipment. Therefore, it was not surprising that hydrous solutions of these alcohols also had conductivities too large to permit experimental ε determinations. Dielectric constants of substances with low conductivities such as benzene, chloroform, and 1,2-dichloroethane were easily measured with the Model 1610-B assembly.

Chemicals

The chemicals used in this research study were as follows:

Cobalt(II) and Calcium(II) Perchlorate hexahydrates: The G. Frederick Smith Chemical Company, Reagent. These chemicals were used without further purification.

n-Butanol: J. T. Baker Chemical Company "Baker Analyzed" reagent. This compound was dried over 4Å molecular sieve for a minimum of 60 hours, then removed from the sieve by dried nitrogen gas pressure and purified by distillation through a water-cooled condenser at about 118°C.

Only the middle portion of the distillate was collected for use.

Deionized water was used throughout the extraction equilibrium experiments and for thermodynamic measurements.

Disodium (ethylenedinitrilo) tetraacetate (EDTA): Eastman Organic Chemicals. Distillation Products Industries, Reagent. The material was used without further purification. Titrations with EDTA, for determination of $Co(ClO_4)_2$ in the $Co(ClO_4)_2$ - $Ca(ClO_4)_2$ mixtures, were made with PAN[1-(2-Pyridylazo)-2-naphthol] as the indicator. Titrations for $Co(ClO_4)_2$ alone, with EDTA, were made with Murexide as an indicator. Determinations of the total metal concentration in the $Co(ClO_4)_2$ - $Ca(ClO_4)_2$ mixtures and for $Ca(ClO_4)_2$ alone, employing EDTA, were made with EBT (Eriochrome Black T) as the indicator.

Karl Fischer Reagent: Eastman Organic Chemicals, Reagent. The reagent was diluted with three parts, by volume, of absolute methyl alcohol per part of reagent before use.

CHAPTER IV

A. EXPERIMENTAL RESULTS AND DISCUSSION

Distribution Isotherms

The isothermal distribution data for $Ca(ClO_4)_2$ and $Co(ClO_4)_2$ solutions at 25° C are tabulated in Table III and the isothermal distribution data for the $Ca(ClO_4)_2$ - $Co(ClO_4)_2$ mixtures at 25°C are tabulated in Table IV. Figure 4 shows a plot of the distribution coefficients, or stoichiometric distribution ratios, K_D, for both salts as a function of the TAPSM (total aqueous phase salt molality) for all series. There are clearly two distinct extraction isotherms. The cobalt extraction data at the smallest salt concentrations agree very well with the work of Cheung (5), while the calcium extraction data at lower salt concentrations are in good agreement with those obtained by Davis (126).

The plot of K_D as a function of TAPSM (Figure 4) for the extraction of cobalt from solutions containing only cobalt perchlorate and from solutions containing both calcium and cobalt perchlorates shows that the values fall on a common extraction isotherm. The distribution coefficient (organic phase salt molality/aqueous phase salt molality) for cobalt perchlorate is markedly dependent upon the TAPSM. There is exhibited, furthermore, a well defined synergistic effect of the calcium perchlorate on the extraction of cobalt perchlorate over the entire range of salt mixtures studied.

Similarly, the plot of K_D as a function of TAPSM for calcium per-

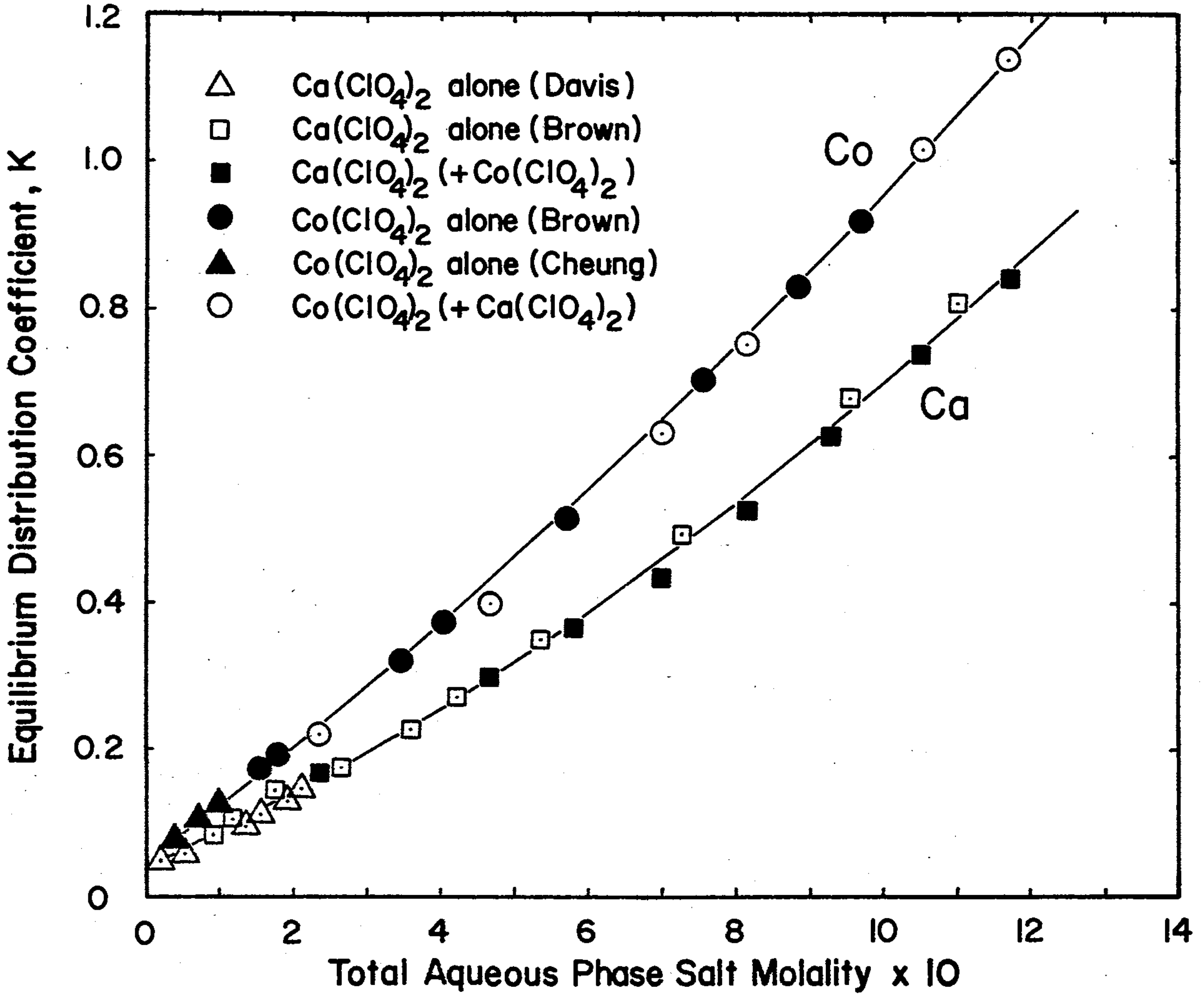


Figure 4. Equilibrium Distribution Coefficient of Perchlorates at 25.0°C

chlorate shows that the calcium perchlorate data fall on a common extraction isotherm. However, the calcium extraction isotherm is distinct from the cobalt extraction isotherm, and a well defined synergistic effect of cobalt perchlorate on the extraction of calcium perchlorate is observed.

These facts suggest a certain similarity in the extraction "mechanism" for both salts even though the cationic radii are not very close (0.99 Å for Ca^{++} and 0.74 Å for Co^{++}).

There is an increase in the values of K_D with increase in TAPSM for both salt extraction isotherms. As the TAPSM approaches the salt concentration of ~1.4 moles of salt per 1000 grams of solution, complete homogeneity of the two phases occurs at 25°C.

It is interesting, in this connection, to note that in the mixtures where homogeneity was observed, the calcium concentration was over ten times that of the cobalt. Solutions of calcium perchlorate remain two-phase, at least up to 4 molar, whereas solutions of cobalt perchlorate become homogeneous at about 1.3 molar at 25°C (127).

Values of the logarithm of the distribution coefficients as a function of the square root of the TAPSM are shown plotted in Figure 5. Except for the slight curvature at the high concentration end of the isotherms the plots are linear. At these higher salt concentrations the solutions are approaching homogeneity.

Table V lists the content of n-butanol in the equilibrium aqueous phases. In Figure 6, the molality of n-butanol as a function of TAPSM has been plotted. At low salt concentrations for both the individual salts and the salt mixtures, there is initially a salting-out of n-butanol from the aqueous phase. The degree to which n-butanol is salted-

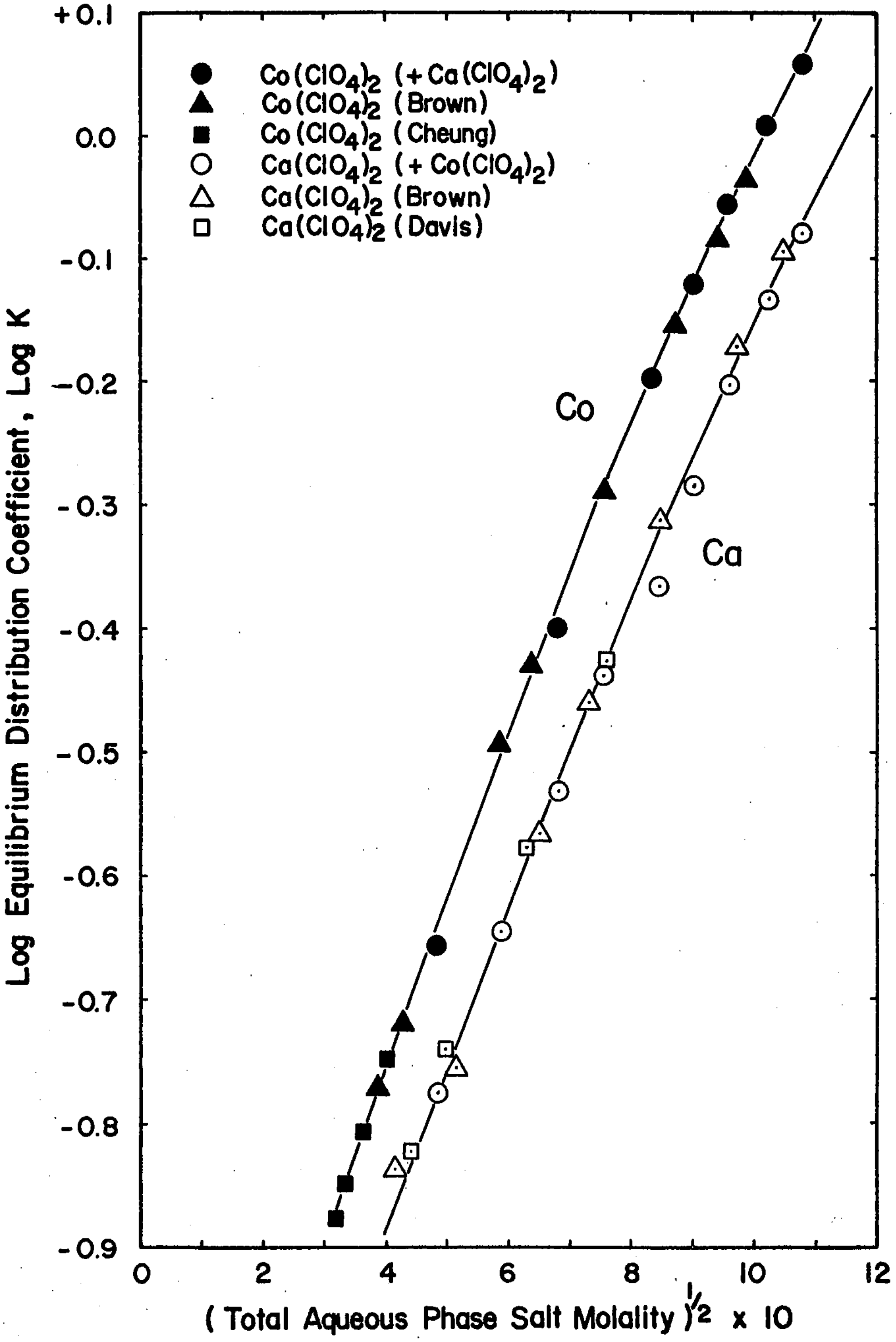


Figure 5. Log Equilibrium Distribution Coefficients Plotted Against Square Root of Total Aqueous Phase Salt Molality at 25.0°C

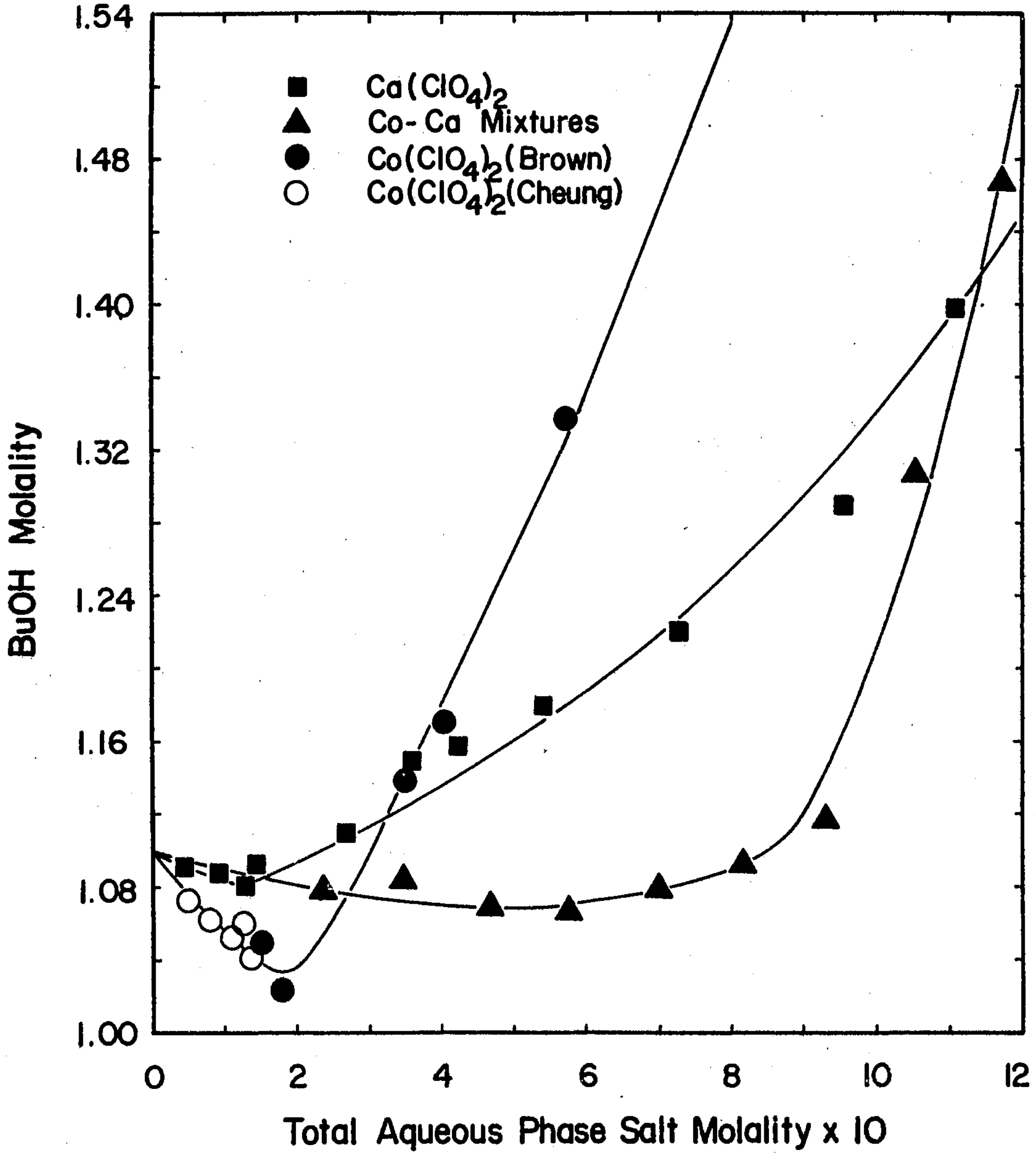


Figure 6. Content of n-Butanol in Equilibrium Aqueous Phases at 25.0°C

out from the aqueous phase depends upon whether the cation is calcium or cobalt or their mixtures. However, as pointed out earlier, with increasing total salt concentration there is a salting-in of n-butanol into the aqueous phase which continues until solution homogeneity of the phases results. This is observed to occur at high salt concentrations. In the mixtures, homogeneity of the phases occurs at a Ca^{++}: Co^{++} ratio of ~13:1 and a total salt concentration of ~1.4 molal. Cobalt perchlorate solutions undergo the salting-in of n-butanol at a lower aqueous phase salt concentration than do calcium perchlorate solutions.

According to the Debye-McAulay theory (103) of the salting effects of electrolytes on neutral molecules, Co^{++} would be expected to exhibit a greater salting-out effect on n-butanol than would Ca^{++}. This is due to the smaller bare ionic radius of the cobalt cation. The treatment of Debye-McAulay proposes that the salting effects should be of the same order as the sum of the reciprocals of the ionic radii involved in the salting effects. While the radius for the perchlorate anion should be identical for both salts, the crystallographic radius of the Co^{++} ion (0.74 Å) is considerably smaller than that for Ca^{++} (0.99 Å), giving Co^{++} a greater charge to radius ratio than Ca^{++}. This satisfies the requirements of the Debye-McAulay theory and predicts that Co^{++} will show larger salting-out effects upon neutral n-butanol molecules than will Ca^{++}. This is verified by the experimental results listed in Table V and shown in Figure 6.

In general, the results bear out the observations of Durand-Gasselin and Duclaux (127). The initial drop in the concentration of n-butanol in the aqueous phase, with increasing salt concentration, is expected on the basis of ion hydration and lowered solution dielectric constant.

However, the subsequent increase in n-butanol concentration is anomalous since n-butanol is less polar than water and is of lower dielectric constant. The more pronounced effect of the cobalt salt as compared with the calcium salt, both in salting-out and salting-in, is apparently related to the smaller size of the cationic radius of cobalt as compared with that of the calcium ion.

However, it is obvious that the n-butanol content in $Ca(ClO_4)_2$ - $Co(ClO_4)_2$ mixtures represents an even more complicated situation than it does in the individual salts. Evidently, a number of additional factors such as new ion-ion interactions and relative solvation of the ions are involved. The salting effects in the mixtures are complex, but perhaps can be rationalized in terms of conventional concepts.

Thus, it appears that the n-butanol molality in the aqueous phase is not solely determined by the total salt (or ClO_4^-) concentration, but is also dependent upon the specific nature of the cation or cation mixtures in both phases.

Hydration Numbers

The water content of the n-butanol phases is tabulated in Table VI. Figure 7 shows the distribution of water in the organic phases as a function of TBPSM (total butanol phase salt molality). There is an obvious similarity among the extraction systems for $Co(ClO_4)_2$, $Ca(ClO_4)_2$ and their mixtures, since the data for all three cases falls on a common isotherm. From the slope of the isotherm, apparent hydration numbers (excess moles of water per mole of extracted salt) of the order of 30 can be calculated. This value agrees with the apparent hydration number for cobalt perchlorate obtained by Cheung (5).

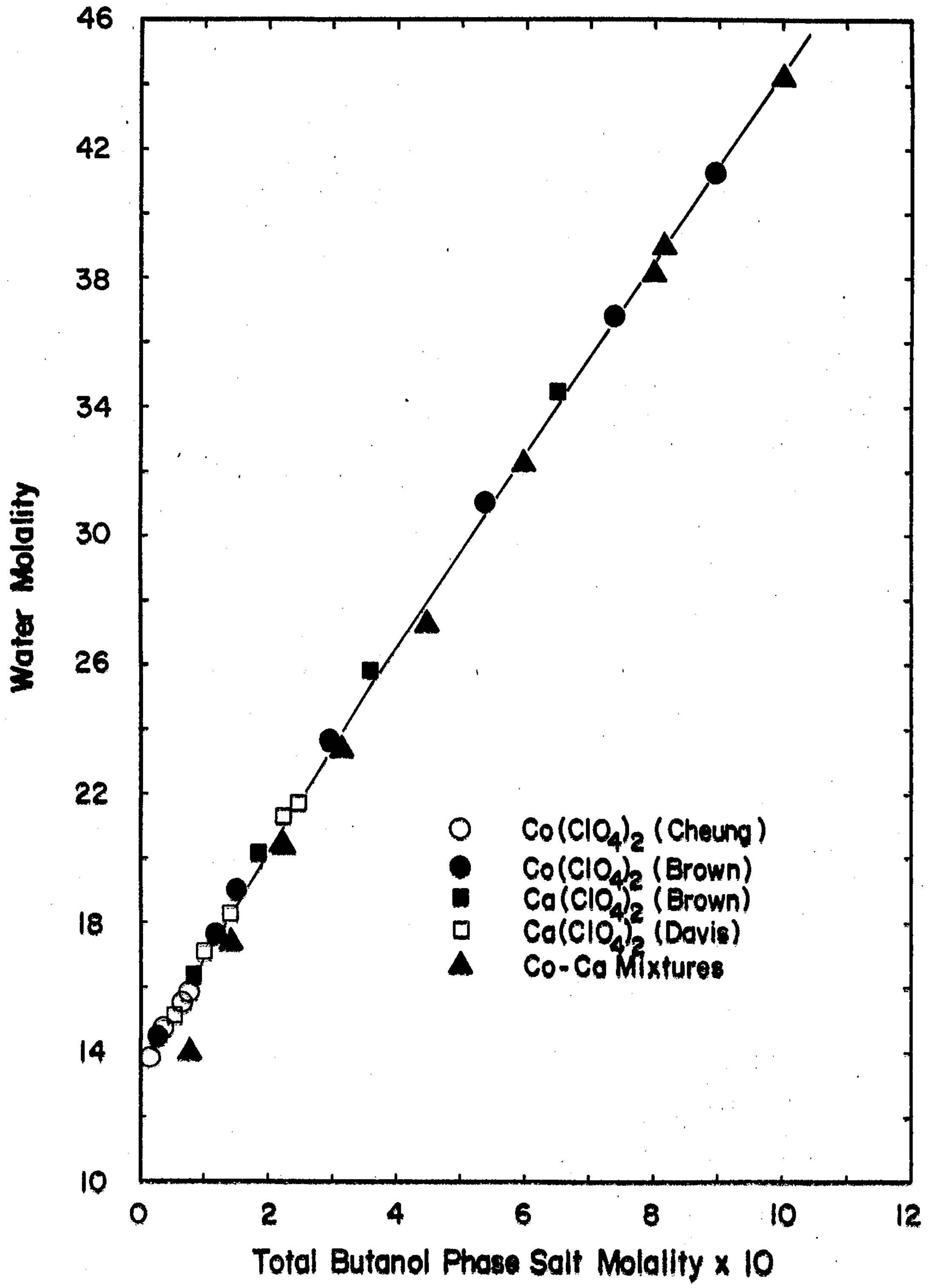


Figure 7. Content of Water in Equilibrium n-Butanol Phases at 25.0°C

According to Azzam's recent comprehensive analysis of hydration numbers of cations in aqueous solution (79), hydration numbers of the order of 50 for Ca^{++} and 60 for Co^{++} are to be expected when one considers the sum of the water molecules in the permanent, primary and secondary hydration sheaths. Since the butanol phase equilibrium solvents correspond to a minimum of 50 mole percent water by weight, there is ample water present for complete hydration of ions in the organic phase.

Because of the unusually large values of the hydration numbers and the fact that water is a stronger ligand than n-butanol (128), it seems likely that the immediate solvation sheaths surrounding the cations in both the aqueous and organic phases are occupied almost exclusively by water molecules; the hydration numbers for the calcium and cobalt salts, whether singly or in mixtures, being on the order of 30 for Ca^{++} and 30 for Co^{++} in both phases. Since the organic phase solutions contain adequate water for complete primary hydration of the ions, one can further suppose that the nature of solvation in the vicinity of the cations is similar in the two phases; i.e., there is a similar degree of ordering of water about the cations.

Enthalpy of Transfer

Partial molal enthalpies of transfer, $\Delta\bar{H}_t$, have been determined from the thermochemical cycle described in Chapter 3 (Figure 2). Calorimetric quantities for steps in the cycle, together with error estimates, are tabulated in Table VII. The measurements have been made for the range of aqueous salt concentrations between 0.09 molal and 1.17 molal. Errors in the determination of the partial heat of solution of the anhydrous salt involve deviations in the experimental measurement of the partial heat of solution of water in each phase solvent multiplied by the ratio X, the number of moles of water per mole of salt in the "reference" compound. Such errors are listed as errors in ΔH_x, and thus appear as values several times larger than the errors in the experimental measurements. All error estimates were arbitrarily doubled to account for any bias.

The results cannot be compared with literature values, as there have been no directly comparable measurements. Drakin and co-workers (98) have measured the heat of solution of calcium perchlorate in n-butanol (0.1% water) over a range of concentrations at 25°C. The extrapolated value of this quantity for an infinitely dilute solution is reported to be -16.6 kcal. mole^{-1}. Combining this with his value of -15.5 kcal. mole^{-1} for the heat of solution of this salt in water (99), gives about -1.1 kcal. mole^{-1} for the heat of transfer from water to n-butanol. Disregarding any uncertainties in the extrapolated values, the differences in the composition and structure of the phases compared to those of the pure solvents make comparisons between this result and the value -14.5 kcal. mole^{-1} of doubtful significance. To directly compare the values of the Russian workers (98,99) with those of this research would require additional data for the heats of solution of n-butanol in binary water-salt mixtures and of water in binary alcohol-salt mixtures; each of the mixtures being of the proper salt concentration.

Values for $\Delta\bar{H}_t$ and $\Delta\bar{S}_t$ are plotted in Figures 8 and 9 as functions of TAPSM. Within experimental error, data for both the calcium and cobalt solutions and their mixtures are represented by a common enthalpy isotherm so that $\Delta\bar{H}_t$ at any point on the curve is dependent <u>only</u> upon

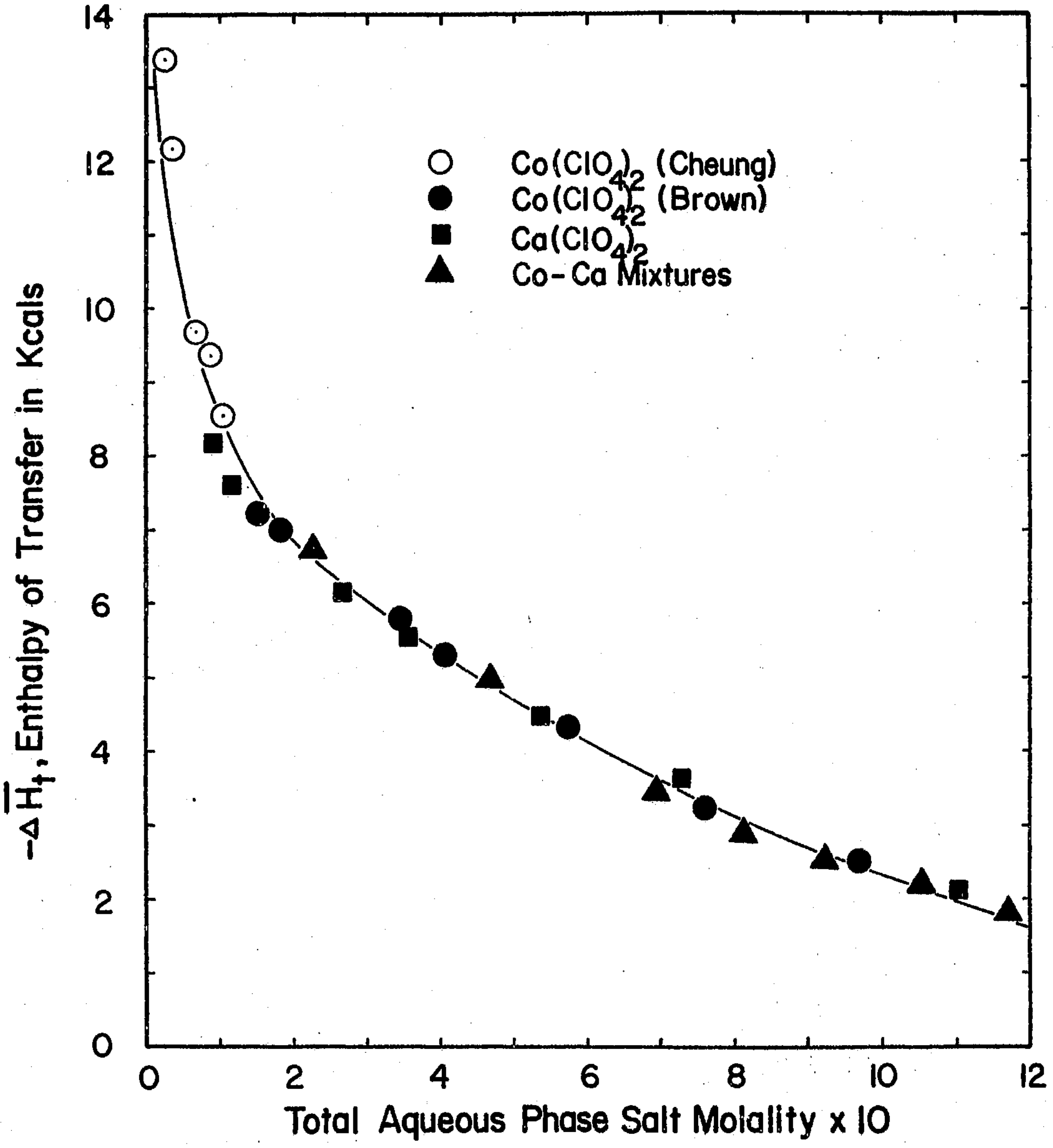


Figure 8. Enthalpy of Transfer at Equilibrium at 25.0°C

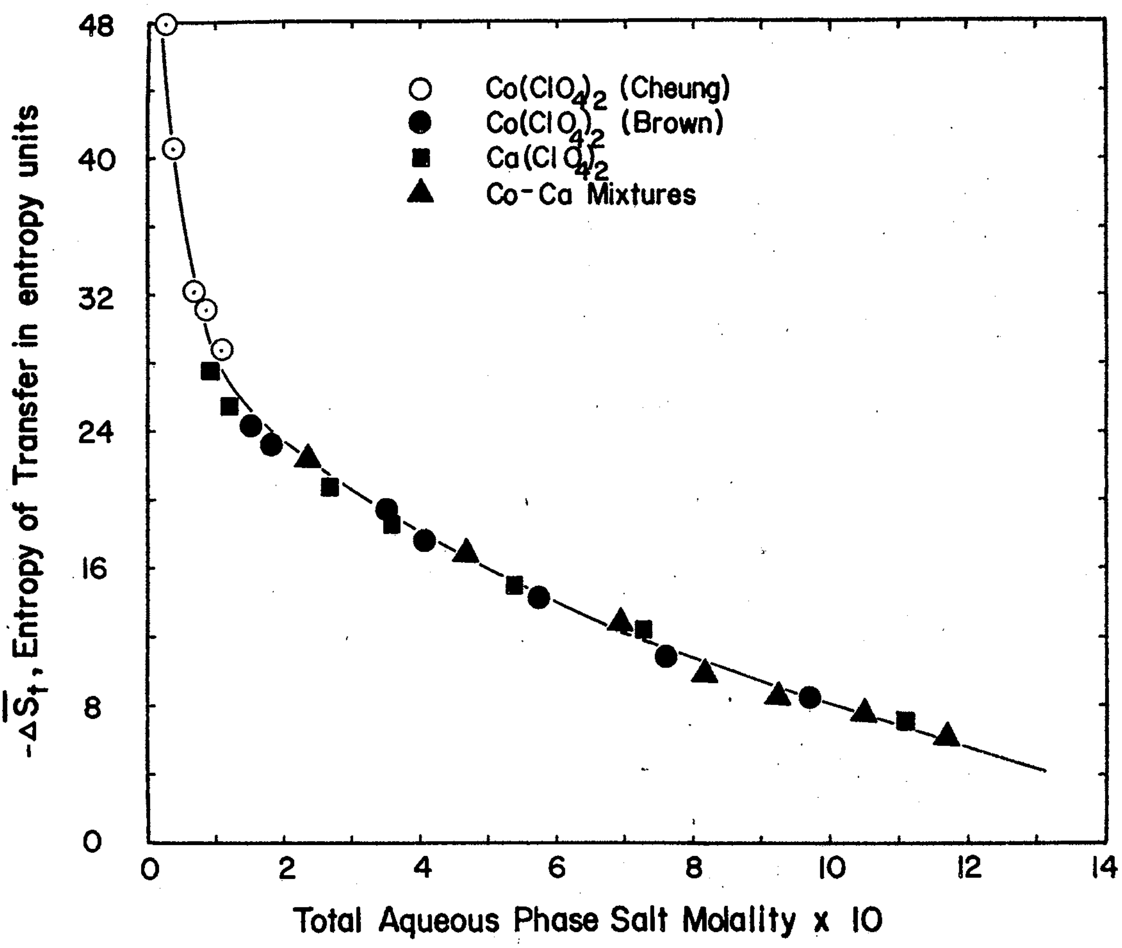


Figure 9. Entropy of Transfer at Equilibrium at 25.0°C

the total aqueous phase ClO_4^- (or salt) concentration and not upon the relative proportions of either cation in the salt mixture. This is significant in that it allows the perchlorate mixtures to be regarded (in some ways) as being thermodynamically equivalent to the individual salts at the same TAPSM. A single isotherm for the $\Delta\bar{H}_t$ values further emphasizes the probable similarity in the mechanism for the transfer of the salts.

The values of $\Delta\bar{H}_t$ and $\Delta\bar{S}_t$ are both negative, for the condition of equilibrium $\Delta G_t = 0$ requires that they be of the same sign. If both the isotherms are extrapolated to the point of infinite dilution, the value of the heat of transfer, $\Delta\bar{H}_t$, for $Co(ClO_4)_2$ or $Ca(ClO_4)_2$ is about -14.5 kcal. mole^{-1} and the entropy of transfer, $\Delta\bar{S}_t$ is about -48 e. u. mole^{-1} of salt transferred.

It should be noted from Figures 8 or 9 that there is a continuous increase in the values of $\Delta\bar{S}_t$ (or $\Delta\bar{H}_t$) with increasing salt concentration in the range from about 0.2 molal to 1.2 molal, but the slope of the curve is much more precipitous at concentrations below 0.2 molal. The possible significance of this is discussed in the following sections.

B. MODELS

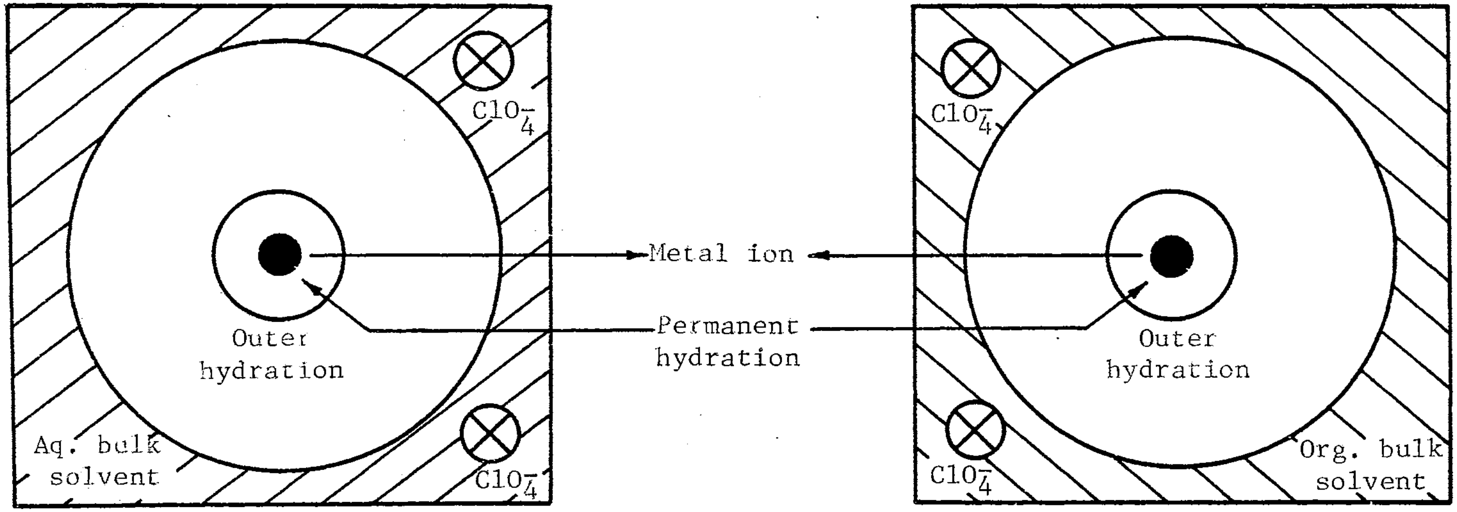
Solvation

A qualitative picture of the solvation of the individual salts and salt mixtures in both phases can be formulated by considering them to be fully hydrated in each phase. Evidence in support of this conclusion is found in the visible absorption spectra which prove to be almost indistinguishable from those of aqueous solutions. Such spectra are similar to, but distinguishably different from, spectra of the anhydrous n-butanol solutions, the maxima in the latter occurring at longer wavelengths.

Since all the butanol phases contain an abundance of water (in excess of 40 moles per mole of salt), an admittedly naive interpretation would be to ascribe the increase in coextracted water concentration in the butanol-rich phases entirely to the hydration of the extracted salts and their moieties. Successive, or step-wise, replacement of butanol by water from coordination with cobalt perchlorate in n-butanol has been demonstrated recently by Harris (129). From the magnitudes of the constants reported for the formation of aquocomplexes ($p\beta_1 = -1.76$, $p\beta_2 = -3.1$, $p\beta_3 = -4.1$) it seems reasonable to assume that the cations, both free and associated with anions, are preferentially hydrated in the organic phases. Whether one then is justified in interpreting the large values of the "apparent" hydration number (ca. 30 mole^{-1} salt) as support of Azzam's theory of total hydration (see p. 20), it is not possible to say. Certainly the assignment of "apparent" hydration numbers of the order of 30 to the individual salts raises the question of a reasonable structural arrangement of water molecules about the extracted entities and the possible significance of the consequent stoichiometry. A simple calculation shows that the number of water molecules which can be accommodated in a spherical shell one water molecule diameter thick (2.74 Å) about the hydrated Co^{++} of radius 3.46 Å is about 28, assuming the same packing as in liquid water. It is certainly true, however, that usually large apparent hydration numbers characterize the extraction of perchloric acid (7, 130, 131, 132) and perchlorate salts (3, 96) in other solvents, and this may be the result of the ability of perchlorates to bring about a degree of water-structure building in the solvents.

In the limit of infinite dilution, where dissociation is complete, a model for the solvation of the ions is that shown in Figure 10. The circle adjacent to the metal ion represents the outer boundary of the permanent hydration sheath occupied by six water molecules. Outside of this circle there is an outer hydration sheath which is assumed to be jointly occupied by water molecules and butanol. This is the region immediately adjacent to the permanent hydration sheath. It is assumed that the bulk dielectric constant of the extraction phase solvent is effective immediately outside the permanent hydration sheath. This corresponds to a model in which the hydrated cation is considered to be a sphere of effective radius equal to the ionic crystal radius plus one water molecule diameter. Perchlorate anions are not considered to be permanently hydrated in this mode.

At finite salt concentrations, ion-association would be expected to occur in the organic phase. From electrical conductance measurements on solutions of $Co(ClO_4)_2$ in the organic and aqueous equilibrium solvents at small concentrations, Cheung (5) concluded that for organic salt concentrations greater than 0.015 molal (0.12 molal salt concentration in the aqueous phase) second-order ion-association (neutral species formation) would also be important. From the Onsager limiting equation and Cheung's conductance data for concentrations less than 0.001 molar, a first-order (1:1) ion-association constant of the order of $1. \times 10^4$ can be obtained. Thus at the concentrations studied in this research second-order ion-association should be extensive for both metal perchlorates. The change in slope of the ΔH_t or ΔS_t isotherms referred to earlier, may be correlated with a change in the solute moiety to predominately neutral



Aqueous Phase

Butanol Phase

Figure 10. Solvation Model at Infinite Dilution

aggregates.

The organic-phase solvated species at finite salt concentrations in the model are represented by Figure 10 and either Figure 11a or 11b. Figure 11a represents first-order ion-association and Figure 11b represents second-order ion-association, with the positions of the perchlorate anions being unspecified.

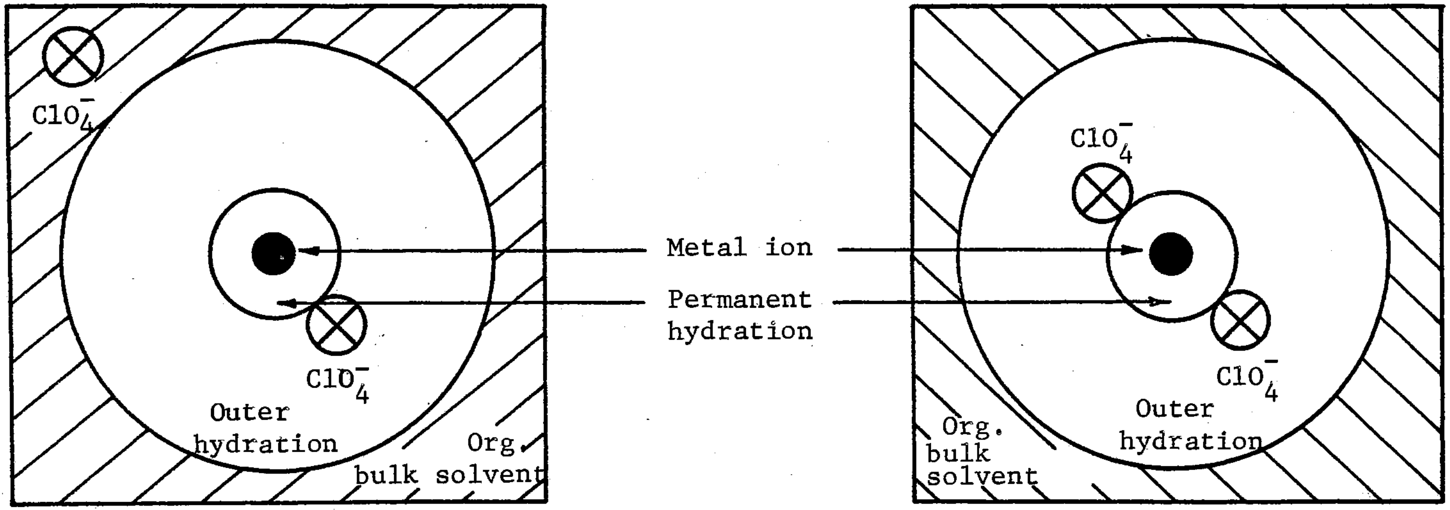
Infinitely Dilute Limit

All of the isotherms obtained in this study may be extrapolated to the limit of zero salt concentration. In this limit the values of ΔG^o_t, ΔH^o_t, and ΔS^o_t may be evaluated in principle. The Born model (described in Chapter II) predicts the electrical free energy of transfer of the ions of a salt from one continuum dielectric medium into a second continuum dielectric medium. By combining the thermodynamic equation for the temperature dependence of the free energy with an empirical value for the temperature dependence of the dielectric constant of the medium, the Born model also predicts the enthalpy of transfer of the ions.

The most important parameters in the Born model are the radii of the ions, the dielectric constants of the bulk media, and the temperature dependence of the dielectric constants. Of these perhaps the most critical is the dielectric constant and its temperature dependence. Since it was found to be impossible with existing facilities to measure the dielectric constants, reasonable estimates of these based on literature values were used to test the model against the experimental results.

A value for the aqueous phase solvent was obtained from the molar dielectric decrement defined by

$$(\Delta\varepsilon/\Delta\omega)(M/\rho) = 1000\ \delta \qquad (4.1)$$



(a) First Order Association (b) Second Order Association

Figure 11. Solvation Model of Organic Phase at Finite Salt Concentrations

The value for n-butanol was taken from the data of Lindenberg and Bien (44). At 25°C and an aqueous phase composition of 7.4% by weight butanol, the value of δ of 5.1 gives 73.5 for the dielectric constant. In the equation above, $\underline{M}$ is the molecular weight of the alcohol, $\underline{\rho}$ is the density of water, and $\underline{w}$ is the weight fraction of alcohol in the aqueous solution.

There is a pronounced paucity of data in the literature on the dielectric constant of butanol-water mixtures over a complete range of compositions. At 25°C the immiscibility gap extends from about 7% to 80% butanol by weight, and in order to estimate the dielectric constant of the butanol-rich solvent additional assumptions were necessary. Brown and Ives (133) have measured the dielectric constants of isobutanol-water mixtures in the alcohol-rich composition range. Since isobutanol is also a primary alcohol and is isomeric with n-butanol, the dielectric constants for isobutanol at 25°C (17.7) and n-butanol (17.1) are close. It was therefore assumed that mixtures of these alcohols with water would also be similar, and the dielectric constant of the organic phase at zero salt concentration was calculated to be about 19.3 at 25°C with an estimated error of no greater than 5%.

The concentration dependence of isobutanol-water mixtures has been determined by Ives and Brown (133) who found that there is little change in the dielectric constant in the range of alcohol mole fractions from about 0.6 to 1.0; i.e., the butanol-rich end of the composition range. Akerlof (45) has found similar results for the alcohols n-propanol and t-butanol, and it thus seemed reasonable that there should be only a small error in estimating the dielectric constant for the n-butanol-water solvent at a mole fraction of about 0.5 by using the isobutanol-water system as a guide. A value of 19.3 was obtained in this way.

Akerlof has also studied the temperature dependence of water-alcohol mixtures over a range of temperatures, including 25°C. For aqueous mixtures of all of the alcohols studied, including the propanols and t-butanol, the data are accurately represented by the equation

$$d\varepsilon/dt \;=\; -\,b\varepsilon \qquad (4.2)$$

where b is an empirical constant and T is the Kelvin temperature. Plots of bε as a function of the weight percent of alcohol are approximately linear for all of the alcohols, and it was assumed that a similar linear relation would hold satisfactorily for n-butanol-water mixtures at 25°C. Values of b were estimated at the compositions of the equilibrium phase solvents and the differential coefficients calculated. The values obtained are $-0.18\ \text{deg}^{-1}$ and $-0.36\ \text{deg}^{-1}$ for the organic and aqueous phase solvents, respectively. Using the value $-0.18\ \text{deg}^{-1}$ for the temperature coefficeint of the dielectric constant of a 82% butanol solution at 16°C, one calculates the dielectric constant to be 20.9. This compares with 20.9 reported by Beauvilain (42) at 16°C for the same solution.

Latimer, Pitzer and Slansky (82) showed that agreement with experimental data for the electrical free energy of hydration of many cations in water could be obtained by adding an empirical constant to the crystal radius of the cation in the Born equation. Since the Born model applied to the extraction process refers to the transfer of fully hydrated ions from one dielectric medium to another, an analogously corrected radius should include the addition of a water molecule diameter to the crystal radius of the ion. Thus the corrected radii would be $r_{Co^{++}} = 0.74\ \text{Å} + 2.74\ \text{Å}$ and $r_{Ca^{++}} = 0.99\ \text{Å} + 2.74\ \text{Å}$. No correction to $r_{ClO_4^-}$ is made.

Substitution of the values of the ion radii above, together with the estimated dielectric constants and temperature coefficients of dielectric constants of the equilibrium phase solvents into equations (A.4, Appendix B) and (2.3) yields calculated values of +12.8 kcal mole^{-1} for ΔG_t^o and -29.0 kcal mole^{-1} for ΔH_t^o for $Co(ClO_4)_2$. These compare only in sign with the extrapolated experimental values of +7.0 kcal mole^{-1} for ΔG_t^o and -14.5 kcal mole^{-1} for ΔH_t^o.. Correspondingly poor agreement is obtained for $Ca(ClO_4)_2$. Agreement (within about 10%) with the Born model would require that the free energy and enthalpy of transfer of the perchlorate ion were zero (corresponding to an infinite radius).

It is obvious that the Born model is inadequate and of little apparent use in interpreting the extraction behavior in the limit of zero concentration. It has been pointed out before, however, that not only is the model unrealistic in detail, but the extrapolated experimental values in the limit may be doubtful in view of the lack of any theoretical guide for the extrapolation. Any realistic model for the extraction behavior, however approximate, would certainly need to recognize the possibility of ion-association even at the smallest concentrations investigated in the organic phase. A change in solute moieties (and consequent properties) is not necessarily reflected in a linear extrapolation of properties from finite concentrations of significant ion-association to the limit of theoretically zero ion-association.

Although the use of trace quantities of metal might enable a study to be made of the system where ΔG_t^o could be obtained fairly reliably through activity coefficient corrections of the Debye-Hückel type, the sensitivity of our calorimeter would not permit measurement of the enthalpy of transfer at the great dilutions required.

Extraction

A common isotherm at finite concentrations for the distribution coefficient of $Ca(ClO_4)_2$ when alone and in mixtures with $Co(ClO_4)_2$ and also a common isotherm for $Co(ClO_4)_2$ when alone and in mixtures with $Ca(ClO_4)_2$ suggests a relatively simple and similar extraction model for the two salts. Consider the following equilibria in the system: (Overscored quantities refer to the organic phase, M to cation, X to anion.)

$$(M_T) = (M) + (MX) + (MX_2) \tag{4.3}$$

$$(\bar{M}_T) = (\bar{M}) + (\overline{MX}) + (\overline{MX}_2) \tag{4.4}$$

$$K_D = (\bar{M}_T)/(M_T) \tag{4.5}$$

Although in principle M, MX, MX_2 in each phase are related by partition coefficients P_j, there is no evidence for ion-association in 2:1 type metal perchlorates in aqueous solutions, and thus it seems unlikely that such association will occur to any significant extent in the aqueous phases during the extraction process. Therefore, $(M_T) = (M)$ should be a good approximation. For the organic phase the first-order ion-association constant found by Cheung ($\sim 10^4$) leads to the conclusion that little dissociated salt will be in that phase at the concentrations covered by the experimental measurements of this study. If, as seems reasonable, the second stage ion-association constant (β_2) for the formation of the neutral species in the organic phase, $(MX_2) = \beta_2(M)(X)^2$, is large then at sufficiently large concentrations in the organic phase $(\bar{M}_T) = (\overline{MX}_2)$ should be a good approximation also. Under these conditions the distribution coefficient K_D should vary with the square of the perchlorate ion concentration in the aqueous phase according to the law of mass action. This is most easily seen if one conceives of the mechanism involving the formation and partition of the complex MX_2, since in the aqueous phase the formation of MX_2 is, by the law of mass action, proportional to the product of the ion concentrations $(M)(X)^2$. If then $(\overline{MX}_2) = P_{MX_2}\,(MX_2)$ and $K_D = (\overline{MX}_2)/(M)$ it follows that K_D is proportional to $(X)^2$.

The distribution of a solute is determined entirely by free energy considerations and is independent of any non-thermodynamic assumptions regarding partition coefficients. It is for this reason that distribution coefficients are seldom informative about true extraction mechanisms, particularly at higher concentrations where activity coefficients are more difficult to evaluate.

The equilibrium constant for the extraction of a 2:1 type salt from aqueous solution by an organic extractant is related to the distribution coefficient K_D according to thermodynamics by

$$K_e = \bar{a}_{salt}/a_{salt} = \bar{m}_M\bar{m}_X^{2}\bar{\gamma}_\pm^{3}/m_M m_X^{2}\gamma_\pm^{3} = K_D\bar{m}_X^{2}\bar{\gamma}_\pm^{3}/m_X^{2}\gamma_\pm^{3} \qquad (4.6)$$

where molal concentrations are stoichiometric values and activity coefficients are mean (molal) values. If the salt in the organic phase is known to be essentially all in the form of the neutral complex MX_2 the above equation can be written as

$$K_e = K_D\bar{\gamma}_o/km_X^{2}\gamma_\pm^{3} \qquad (4.7)$$

Here $\bar{\gamma}_o$ is the activity coefficient of the neutral complex (which should be close to unity) and k is the formation constant for MX_2. From this equation one can see that if $\gamma_\pm$ is known, the concentration dependence of the distribution coefficient can be determined.

In fact, however, the observed dependence of K_D upon $\sqrt[3]{m_{M_T}}$ could not be predicted by a model requiring complete ion-association or dissociation in the organic phase and complete dissociation in the aqueous phase without a much greater understanding of the factors which determine the activity coefficients. Indeed, even the stoichiometric activity coefficient of $Co(ClO_4)_2$ in aqueous solution has not been measured, but the close similarity in the activity coefficients of $Mg(ClO_4)_2$ and $Zn(ClO_4)_2$ (134-139) suggest that the activity coefficients of $Co(ClO_4)_2$ and $Zn(ClO_4)_2$ should not be much different since the crystal radii of divalent zinc and cobalt ions have very nearly the same value. Also since the butanol content of the aqueous phases is comparatively small and does not change very much over the range of concentrations covered by the distribution isotherm, it seems reasonable to assume that the variation in the activity coefficients of $Co(ClO_4)_2$ or $Ca(ClO_4)_2$ with concentration would be quite similar to that for aqueous solutions of these salts. Substitution of the stoichiometric concentrations and the aqueous activity coefficients of $Zn(ClO_4)_2$ (for $Co(ClO_4)_2$) into Equation (4.7) for the aqueous phase and solving (4.7) for $\bar{\gamma}_o$ gives values of the "apparent" activity coefficient for $Co(ClO_4)_2$ under the assumption of no dissociation. The "apparent" values so obtained are, of course, proportional to the true values and are related to them through the (unknown) equilibrium constant K_e.

A plot of $\bar{\gamma}_o$ ("apparent") vs. butanol phase salt concentration shows an approximate linear increase in value with increase in concentration of $Co(ClO_4)_2$. If the model and other assumptions were entirely valid, $\bar{\gamma}_o$

would be expected to be almost independent of concentration, which it is not.

Equation (4.6) can be rewritten in the form

$$K_D = K_M(\bar{\gamma}_{\pm}^{3}/\gamma_{\pm}^{3}) \tag{4.8}$$

where K_M is the mass action concentration quotient $(\bar{m}_M \bar{m}_X^{2}/m_M m_X^{2})$ and concentrations are the stoichiometric values. A second salt having an anion X in common with the first salt will affect the extraction of the given salt through the concentration of the common anion and also through interactions which are reflected in the values of the activity coefficients. In the particular case of $Co(ClO_4)_2$--$Ca(ClO_4)_2$ mixtures investigated in this study, the second salt ($Ca(ClO_4)_2$) is coextracted and would be expected to interact with the first salt ($Co(ClO_4)_2$) in each phase. However, a common isotherm for the mixtures and the single salt points to the effect being primarily that due to the anion, in accord with Bronsted's principle of specific interaction of ions and the law of mass action. This was clearly demonstrated in a study of $Co(ClO_4)_2$ extractions from mixtures with $LiClO_4$, $Ca(ClO_4)_2$, and $Al(ClO_4)_3$ by 2-octanol (3).

By assuming that the values of the activity coefficients for $Co(ClO_4)_2$ and $Ca(ClO_4)_2$ in a mixture of 2:1 metal perchlorates are equal to those for pure $Co(ClO_4)_2$ alone and $Ca(ClO_4)_2$ alone, respectively, at the same total salt concentration as the mixtures, a pseudo equilibrium constant K'_e may be calculated analogous to K_e of Equation (4.6):

$$K'_e = \frac{K_D(\bar{m} + \bar{m}_x)^2 \, \bar{\gamma}'^{3}_{\pm}}{(m + m_x)^2 \, \gamma_{\pm}^{3}} \tag{4.9}$$

where m_x refers to the second salt in the mixtures at extraction equilibrium and the square terms in the numerator and denominator correspond to the total perchlorate (molal) concentrations in each phase. The organic phase activity coefficients are the "apparent" values, defined by $\bar{\gamma}_\pm/K_e^{1/3} = \bar{\gamma}'_\pm$. Thus K'_e will have a value of approximately 1 and be virtually independent of concentration if the assumptions regarding the activity coefficients are correct.

The "apparent" activity coefficients in the organic phase were obtained by plotting values of $\gamma_\pm/K_D$ against the organic phase perchlorate concentration, using aqueous $Zn(ClO_4)_2$ activity coefficient data and distribution coefficients obtained from extractions of $Co(ClO_4)_2$ alone, and then reading off the "apparent" activity coefficient at each perchlorate concentration in the organic phases of the mixtures.

The values of K'_e for $Ca(ClO_4)_2$-promoted extractions of $Co(ClO_4)_2$ are presented in Table VIII. In similar fashion, values of K'_e for $Co(ClO_4)_2$- promoted extraction of $Ca(ClO_4)_2$ were calculated, using the data of Robinson, Lim, and Ang (140) for the activity coefficients of $Ca(ClO_4)_2$ and the distribution coefficients of $Ca(ClO_4)_2$ alone from this work. Results are tabulated in Table IX.

Both sets of results are without systematic variation with concentration, and have an average deviation of about 10% from the average value. Comparison with the results of a similar calculation by Moore, et al. (3) for the $Ca(ClO_4)_2$-promoted extraction of $Co(ClO_4)_2$ by 2-octanol shows that the n-butanol pseudo constants conform even closer to the model than those in 2-octanol. The latter cover a wider range of concentrations, however.

TABLE VIII

EQUILIBRIUM CONSTANTS FOR THE $Ca(ClO_4)_2$—PROMOTED n-BUTANOL EXTRACTION OF $Co(ClO_4)_2$

TAPSM	$K_m \times 10$	K_e'
0.232	0.081	0.66
0.348	0.203	0.80
0.463	0.397	0.75
0.575	0.794	0.83
0.697	1.332	0.80
0.811	2.264	0.77
0.922	3.716	0.72
1.051	5.825	0.65
1.059	6.206	0.67
1.169	7.155	0.56

TABLE IX

EQUILIBRIUM CONSTANTS FOR THE $Co(ClO_4)_2$—PROMOTED n-BUTANOL EXTRACTION OF $Ca(ClO_4)_2$

TAPSM	$K_m \times 10$	K_e'
0.232	0.061	1.2
0.348	0.144	1.2
0.463	0.293	1.1
0.575	0.552	1.0
0.696	0.901	0.9
0.811	1.562	1.1
0.922	2.630	1.2

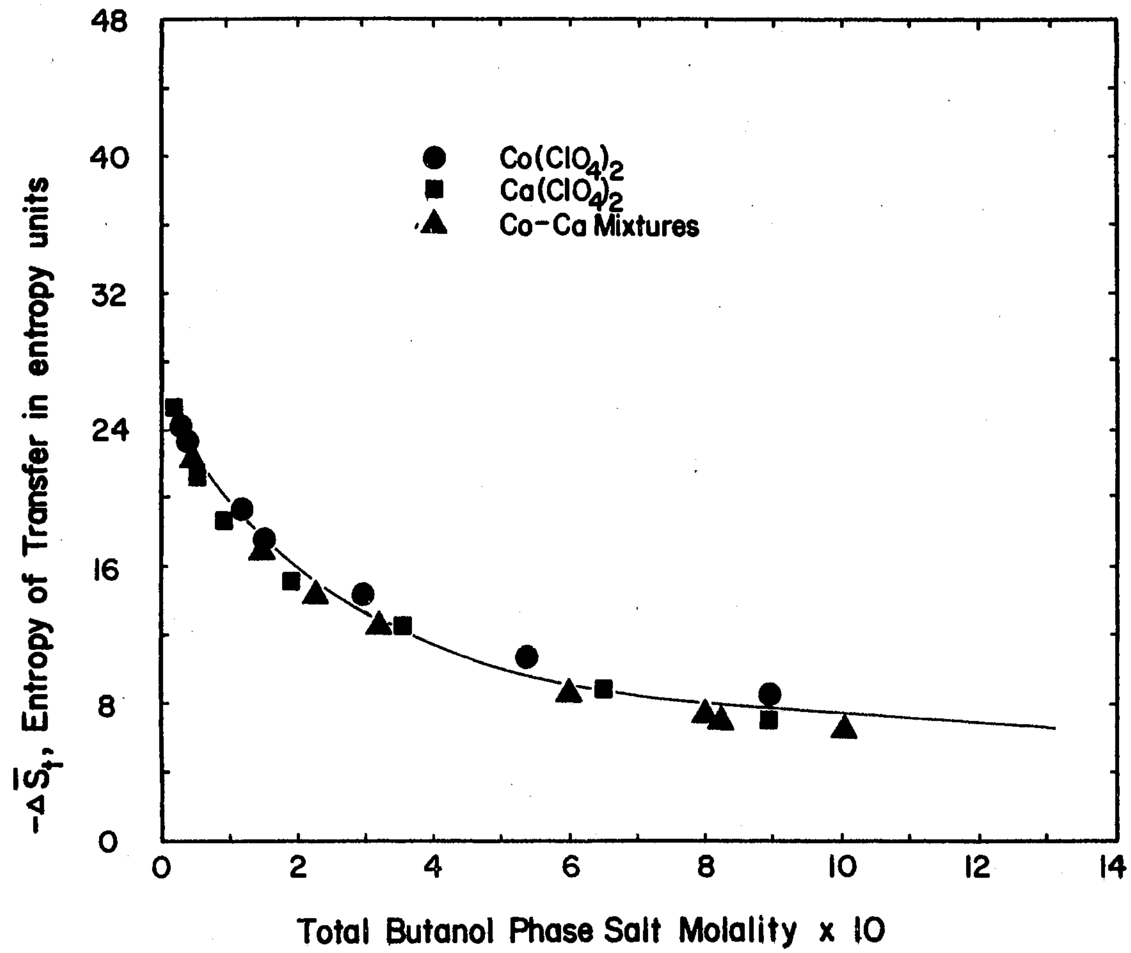


Figure 12. Partial Molal Entropy of Transfer Plotted Against Total Butanol Phase Salt Molality at 25.0°C

Synergism

The mutual extraction-promoting effects of cobalt and calcium perchlorates in the n-butanol extraction of these salts is graphically shown in Figure 13. This is an example of synergism. For example, the distribution coefficient of $Co(ClO_4)_2$ is approximately the same for an aqueous phase molal concentration of 0.344 as it is for a mixture of 0.0961 molal $Co(ClO_4)_2$ and 0.252 molal $Ca(ClO_4)_2$ having a total aqueous phase salt concentration of 0.348 molal. Similarly the distribution coefficient of $Ca(ClO_4)_2$ in the mixture is approximately the same as for the distribution of $Ca(ClO_4)_2$ alone where the aqueous phase concentration is 0.354 molal. That such synergy should occur and be effective over the entire range of salt concentrations studied was unexpected.

Thermodynamics places a restrictive requirement upon the activity coefficients for the two electrolyte components in the mixtures, viz.,

$$\nu_2(d\ln \gamma_{\pm_2}/dm_1)_{m_2} = \nu_1(d\ln \gamma_{\pm_1}/dm_2)_{m_1} \qquad (4.10)$$

and if Equation (4.10) is to be satisfied by the salts in the synergistic mixtures above, the activity coefficients must be expressible by proper functions of concentration. One such relation which has been found to hold for a number of systems is that known as "Harned's Rule" (141). This has been shown to be derivable from the Bronsted principle of "specific ion interactions" (142) and the Guggenheim (143) form of the approximate Debye-Hückel equation for the activity coefficient of an electrolyte (141). In a form suitable for use in the $Co(ClO_4)_2$ - $Ca(ClO_4)_2$ system as a representation of the aqueous phase activity coefficients at constant total molality m, it is

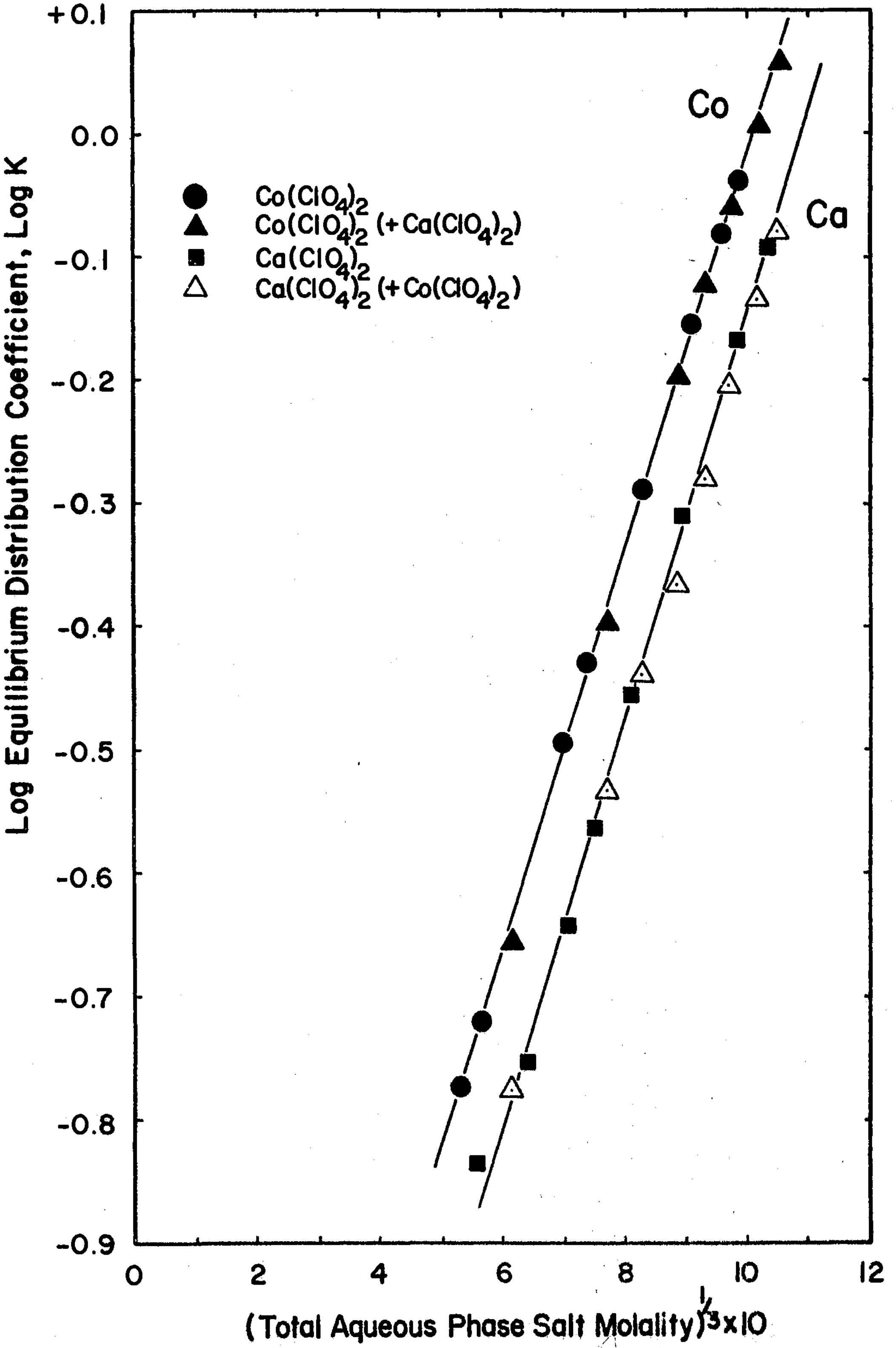


Figure 13. Log Equilibrium Distribution Coefficients Plotted Against Cube Root of Total Aqueous Phase Salt Molality at 25.0°C

$$\log \gamma_{\pm} = -A\sqrt{I}/(1+\sqrt{I}) + 2/3B_{Co-ClO_4}m + 2/3B_{Co-ClO_4}m_{Co} + 2/3B_{Ca-ClO_4}m_{Ca} \quad (4.11)$$

where the B's are the specific interaction coefficients of Bronsted and I is the molal ionic strength of the mixtures. Corresponding equations can be written

$$\log \gamma_{\pm} = -A\sqrt{I}/(1+\sqrt{I}) + 4/3B_{Co-ClO_4}m \quad (4.12)$$

and

$$\log \gamma_{\pm} = -A\sqrt{I}/(1+\sqrt{I}) + 4/3B_{Ca-ClO_4}m \quad (4.13)$$

for $Co(ClO_4)_2$ and $Ca(ClO_4)_2$, respectively, when alone at the same concentration m. Combination of Equations (4.11), (4.12), and (4.13) leads to Harned's form, which for $Co(ClO_4)_2$ is

$$\log \gamma_{\pm} = \log \gamma_{\pm}^{o} - k\, m_{Ca} \quad (4.14)$$

Here the term on the left is the activity coefficient of $Co(ClO_4)_2$ in the mixtures, the first term on the right is the coefficient for $Co(ClO_4)_2$ alone at the same total molality as in the mixtures, and the last term is the concentration of $Ca(ClO_4)_2$ in the mixtures.

If, as required on empirical grounds by Equation (4.9) the activity coefficient of each salt in the aqueous phases in the mixed extractions can be taken to be equal to its value in the unpromoted extractions at the same aqueous phase concentration as the total salt concentration in the mixtures, Equations (4.12) and (4.13) may be equated. It follows, therefore, that B_{Co-ClO_4} must equal B_{Ca-ClO_4} for this to be true. Values of the B-coefficients estimated from tables given by Pitzer and Brewer

(144) show, however, that the required equality does not hold very well. Again the B-coefficient for $Co(ClO_4)_2$ was taken as equal to that for $Zn(ClO_4)_2$ (or $Mg(ClO_4)_2$, which is identical).

When essentially no chemical interactions occur mixtures frequently follow Zdanovskii's rule (145, 146), which for a mixture of two electrolytes is simply

$$m_1/m_1^o + m_2/m_2^o = 1 \tag{4.15}$$

where $\underline{m}_1$ and $\underline{m}_2$ are the concentrations in the mixture and $\underline{m}_1^o$ and $\underline{m}_2^o$ are the concentrations of the pure salt solutions which are isopiestic with the mixture (147). Such mixtures have been termed "simple" mixtures (148, 149), and for them the activity coefficient of a component is given by

$$\gamma_{\pm 1} = \nu_1 m_1^o \gamma_{\pm 1}^o/(\nu_1 m_1 + \nu_2 m_2) \tag{4.16}$$

If one takes $m_1 + m_2 = m$ and $m_1^o = m_2^o = m$, Equation (4.16) above is satisfied, provided all solutions are isopiestic, or at least approximately so. A comparison of the osmotic coefficients of $Ca(ClO_4)_2$ and $Zn(ClO_4)_2$ shows that the water activities of solutions are within 10% of each other at the same concentration up to about one molal. If the mixtures are correspondingly isopiestic, and therefore simple, the empirical use of the activity coefficients of the single salts to represent those in the mixtures at the same total salt molality finds justification in Equation (4.16).

Ion-Association

In the earlier discussion of solvation it was emphasized that at finite concentrations in the organic phase solvent the extracted salts are believed to exist principally as associated hydrated ions. A considerable amount of water-structure building about the aggregates would then account for the observed large values of the "apparent" hydration numbers.

Since the organic phases contain from 50 to 75 mole percent water, the ion-solvent and ion-pair-solvent interaction energies in the immediate vicinity of the solute species should involve principally water molecules and be comparable to those in the aqueous phase. This means, according to the free volume theory of ion-pair dissociation of Gilkerson (150), that since specific solvent effects other than those due to dielectric polarization are the same in the two phases, any differences in the degree of ion-association in the phases must be dependent upon the bulk dielectric constant differences in the individual phase solvents.

Perhaps the best known and generally adequate model for outer sphere ion association is that due to Bjerrum (71, 87, 151). According to this model all pairs of oppositely charged ions within a spherical shell bounded by the distance of closest approach a of the ions and the Bjerrum critical distance q defined by

$$q = \frac{Z_+ Z_- e^2}{2\varepsilon kT} \qquad (4.17)$$

are to be regarded as associated. The model leads to the expression for the association constant K:

$$K_{ass} \approx \frac{4\pi N}{1000} \left(\frac{2e^2}{\varepsilon kT}\right)^3 Q(b) \qquad (4.18)$$

where N is Avogadro's number, e is the electronic charge, k is the Boltzmann constant, and ε is the dielectric constant. The quantity Q(b) is tabulated by Robinson and Stokes (10).

Substitution of the value 19 for the dielectric constant and a distance of closest approach equal to the sum of the ionic crystal radii plus the diameter of one water molecule, or 5.76 Å for Co^{++}, into Equation (4.18) gives a value of 9×10^3 for K_{ass}, comparing quite favorably with the value 1×10^4 calculated from the conductivity data of Cheung (5).

It is not possible to do much more than to speculate upon the second-order ion association of $Co(ClO_4)^+$ and $Ca(ClO_4)^+$ in the organic phases. Although models useful for the estimation of the thermodynamic properties of ion-pairs have been proposed (7, 90, 152-159), models for the further association of ions to give neutral aggregates such as $Co(ClO_4)_2$ or $Ca(ClO_4)_2$ of necessity must arbitrarily position the two perchlorate anions relative to one another and to the cation. From simple electrostatic considerations linear positioning on either side of the cation would be expected, for this minimizes the electrical potential energy. Fuoss and Kraus (160-163) have considered the analogous problem of ion-triplet formation in solutions of 1:1 electrolytes and have statistically averaged the positions of the ions on the basis of a Boltzmann distribution and electrostatic potential. Their theory following along the lines of that of Bjerrum for ion-pairs leads to an expression for the dissociation constant for the triple-ion to form the ion-pair.

A straight-forward modification of the equations of Fuoss and Kraus applicable to second-order ion association in 2:1 type electrolytes is possible. If $\underline{a}$ is the distance of closest approach of either anion to the cation and $\underline{r}$ is the distance of the approaching negative ion from the cation of the ion pair, a minimum in the radial part of the distribution function occurs when $r = R$ is the root of the equation

$$2/r = 2\varepsilon kT/e^2 + r/(r+a)^2 \tag{4.19}$$

In a manner analogous to that employed by Bjerrum for ion-pair formation it is assumed that triple-ions are formed when $r \leq R$ and θ, the angle between the position vector of the incoming ion and the axis of the ion-pair with the center of coordinates at the cation of the pair, is zero. The modified equation of Fuoss and Kraus then becomes ($\mu = e^2/\varepsilon kT$):

$$K_{ass} \approx \frac{2\pi N}{10^3} \int_a^R r^2 \exp\left[\mu\left(\frac{2}{r} - \frac{1}{r+a}\right)\right]dr \int_0^\pi \exp\left[\mu\left(\frac{1}{r+a} - \frac{}{\sqrt{r^2+a^2+2ra\cos\theta}}\right)\right]\sin\theta\, d\theta \tag{4.20}$$

Values of the second integral are tabulated by Fuoss and Kraus (160) as a function of $x = R/a$ and $b = |Z_+Z_-|e^2/2\varepsilon kT = 2\mu/a$ for $Co(ClO_4)_2$ or $Ca(ClO_4)_2$. Evaluation of the first integral was carried out graphically for $a = 5.76$ Å and $R = 3.57a = 20.57$ Å.

From the above considerations an order of magnitude value of 3×10^2 is obtained for the equilibrium constant of the reaction

$$Co(ClO_4)^+ + ClO_4^- \rightarrow Co(ClO_4)_2 \tag{4.21}$$

If one thus assumes the theoretical values of 9×10^3 and 3×10^2 for the first-order and second-order formation constants, respectively, it is easily shown that at a concentration of 10^{-2} molar and neglecting activity coefficients, the second-order association accounts for 20% of the cobalt in solution. A corresponding calculation for a 10^{-2}M solution of calcium perchlorate ($a = 6.01$ Å) for which the first and second-order constants are about 7×10^3 and 3×10^2, respectively, gives about 16%

second-order association. In either case the remaining non-associated metal ion is only of the order of a percent or two. The conclusion is that over the range of concentrations studied not only should almost all of the ions be associated, but the relative proportions of ion-pairs and ion-triples should not be very sensitive to the <u>proportions</u> of $Co(ClO_4)_2$ and $Ca(ClO_4)_2$ in mixtures of the two since there is no ion specificity aside from the size effect.

Energy of Transfer

From the point of view of thermodynamics the transfer of salt from aqueous solution where ionization is complete to some finite concentration in the nonaqueous phase where ion association has occurred can be considered as involving two steps: (1) the transfer of ions from one phase to the other and (2) the association of the ions in the organic phase. The sign and at least the magnitude of the energy effects for ion transfer are established by the Born equation and the dielectric properties of the phase solvents. Thus, a negative sign for the enthalpy (and entropy) of transfer from aqueous to butanol phases at small concentrations where ions predominate in both phases is in agreement with prior prediction, as pointed out earlier. Since the perchlorate salts can be assumed to remain ionized in the aqueous phases at finite concentrations, the variation in the enthalpy (or entropy) of transfer with concentration should be correlated with the degree of ion association in the butanol phases. This assumes that in the aqueous phase the small interionic (Debye-Hückel type) contributions to the heat of dilution may be disregarded.

In the butanol phase the partition of the solute salt into ions, ion-pairs, and triple-ions is not known from the experiment; however, the concentrations of these may be estimated on the basis of the Bjerrum and the Fuoss-Kraus theories of the preceding section. These theories lead to temperature dependent expressions for ΔS^o and ΔH^o which arise from the differentiation of the exponential $z_+z_-e^2/\varepsilon kT$ appearing in the equations for the association constant (c.f. Eq. (4.18)). Prue (164-166) has shown that the Bjerrrum equation for outer-ion (coulombic) association also can be derived from a simplified statistical model proposed by Guggenheim (156, 167), and by differentiation, this model yields theoretical equations for ΔS^o and ΔH^o. All of the models suffer from quantitative difficulties, however, and are most useful in identification of the significant factors.

If one can assume that the enthalpies of formation, $\bar{H}$, of paired-ions and triple-ions are constants over a range of concentrations, one has

$$\Delta H_t - \Delta H_t^o = \alpha \bar{H}_{M(ClO_4)+} + (1 - \alpha)\ \bar{H}_{M(ClO_4)_2} \qquad (4.22)$$

where $\underline{\Delta H}_t^o$ represents the medium effect, i.e., the molar enthalpy of transfer of ions from the infinitely dilute aqueous state to the infinitely dilute butanol state. Here α is the fraction of the solute as ion-pairs. It is assumed that the concentration of non-associated cations is insignificant (< 1%) and that heat of dilution effects in the aqueous phase may be ignored.

A plot of ΔH_t vs. α should then be linear under the assumptions above; however, subsequent substitution of the experimental values of ΔH_t for $Co(ClO_4)_2$ and the values of α calculated from Equations (4.17, 4.18) and (4.19, 4.20) into (4.22) results in a distinctly nonlinear

$\Delta H_t - \alpha$ curve. It is not possible to isolate any one cause for the departure from expectations: the $\bar{H}$'s may not be constants which are independent of concentration and changes in solvent composition as assumed, or the values of α may be incorrect, since they rest upon a model having simplifying assumptions concerning the nature of the dielectric medium and the distribution of ions in the medium. The model, furthermore, includes no activity coefficient corrections.

Qualitatively, the model seems plausible. Weaker forces between unipositive dipolar ions and anions relative to divalent cations and anions should result in the transfer becoming less exothermic as the proportion of triple-ions relative to ion-pairs increases. Correspondingly, the greatly decreased electric fields of triple-ions should lead to an increase in the solute entropy because of the increased freedom of water molecules in the solvation sheath.

Finally, it should be pointed out that the simple model above is even qualitatively unable to account for the common enthalpy (or entropy) of transfer curve for the mixtures when plotted against the aqueous phase salt (TAPSM) concentration. This follows from the result that $Co(ClO_4)_2$ and $Ca(ClO_4)_2$ have different distribution coefficients, and hence for the same aqueous phase concentration, the butanol phase concentration of the components will be different; i.e., there is a separation factor. Thus, the value of TBPSM will not be the same for mixtures as it is for either salt alone at equal TAPSM. The enthalpy or entropy of transfer of $Co(ClO_4)_2$ is experimentally the same, however, as if that component were alone at the same TAPSM. According to the model, this would require that the $\bar{H}$'s be independent of composition and concentration in Equation (4.22) and also that α be independent of composition and concentration. Even if this were true for $\bar{H}_{Co(ClO_4)^+}$ and $\bar{H}_{Co(ClO_4)_2}$, and the formation constants for ion-pairs and triple-ions were correct thermodynamic constants, α could not remain independent of $Co(ClO_4)_2$ concentration unless, fortuitously, the activity coefficients (which have not been taken into account) made it so.

CHAPTER V

CONCLUSION

Summary

For the transfer process from aqueous to n-butanol phases, the plots of the logarithm of the distribution coefficients for $Co(ClO_4)_2$ and $Ca(ClO_4)_2$ against the cube root of the total aqueous phase salt molality (TAPSM) are linear. This holds for the single salts and also for a series of their mixtures having initial aqueous phase concentrations of ~0.1 molar $Co(ClO_4)_2$ and from 0.1 to 1.0 molar $Ca(ClO_4)_2$. A common isotherm for each salt when alone or in mixtures with the other suggests that a mutual synergistic effect is operative for the salt mixtures such that the cobalt enhances the calcium transfer and the calcium enhances the cobalt transfer. The isotherm for the distribution of coextracted water is similarly nearly the same in the extraction of both salts and their mixtures. For all salts and mixtures, apparent molal hydration numbers of the order of 30 moles of coextracted water per mole of extracted salt have been determined.

Partial molal enthalpies of transfer, $\Delta\bar{H}_t$, for both the individual salts and salt mixtures at distribution equilibrium at 25°C have been measured over the ten-fold TAPSM range from ~0.1 to 1.0 molal. Corresponding molal entropies of transfer, $\Delta\bar{S}_t$, have been calculated from the requirement that $\Delta\bar{G}_t = 0$ at distribution equilibrium. For both the salts alone and in mixtures, a plot of $\Delta\bar{H}_t$ vs. TAPSM shows a common nonlinear isotherm and, consequently, a common $\Delta\bar{S}_t$ isotherm. Both $\Delta\bar{H}_t$ and $\Delta\bar{S}_t$ increase with increasing TAPSM. The increases in $\Delta\bar{H}_t$ (and $\Delta\bar{S}_t$) are initially steep at low TAPSM. This is believed to be due primarily to the relatively larger enthalpy changes occurring as a result of decreasing ion-pair formation in the n-butanol phase relative to neutral species formation. This is then followed by a modest increase at higher TAPSM, due principally to the smaller relative enthalpy increases as a result of the decreasing rate of neutral species formation in the organic phase at still higher concentrations. It is self-evident that corresponding changes occur in the ΔS_t curves since $\Delta S_t = \Delta H_t/T$. Extrapolation of the common enthalpy and entropy isotherms to infinite dilution yields -14.5 kcal. mole^{-1} as the limiting enthalpy of transfer, $\Delta\bar{H}^o_t$, and -48 e.u. mole^{-1} for the limiting entropy of transfer, $\Delta\bar{S}^o_t$.

A modified Born model, which incorporates solvated ionic radii and estimated values for the solvent dielectric constants and their temperature dependence predicts the correct sign and magnitude for the enthalpy and entropy of transfer, but gives poor numerical agreement with experiment unless seemingly unreasonable ionic radii are employed.

Use of the Bjerrum model for the extent of outer ion-association and the Fuoss-Kraus model for triple-ion-association in the n-butanol phase demonstrates that virtually all ions should be considered as associated, with the relative proportions of neutral species increasing with increasing salt concentration. Furthermore, the relative proportion of ion-pairs and ion-triples should not be sensitive to the proportions of $Co(ClO_4)_2$ and $Ca(ClO_4)_2$ in the mixtures, but should depend principally upon the total salt concentration.

It is found that activity coefficients estimated for the salts in the n-butanol phase from distribution data on the single salts can be used to calculate stoichiometric distribution equilibrium constants which are true "constants" (~10%) for the salts in their mixtures. This assumes that at the same TAPSM the butanol phase salt activity coefficients are those of the pure salts alone. This is interpreted to mean that the salt-promoted transfer from perchlorate mixtures is dependent upon the total perchlorate salt concentration rather than upon the specific cations or cation ratio in the salt mixtures.

The extraction system studied should be useful as a model for the extraction of other metal perchlorates by monohydric aliphatic alcohols. The fact that this study has shown mutual transfer promotion, common enthalpy and entropy of transfer isotherms and a transfer process apparently dependent upon total salt concentration rather than the proportions of the specific cations indicates a certain degree of simplicity in the extraction mechanism, even for a system of this complexity.

Suggestions for Further Work

In a study of any extraction system the number of components is at least three in each phase. Consequently, the number of unknown physical parameters needed to interpret the behavior of any one component is usually much larger than the number of known parameters.

Thus, for example, it would have been useful in this study to have had the experimentally - determined dielectric constants of n-butanol-water mixtures at 25°C. However, not only were the values unavailable in the literature, but the instrumentation required for their determination was not currently accessible to the investigator. Thus, it is suggested that a study might be undertaken of the dielectric properties of immiscible solvent mixtures, such as n-butanol-water mixtures, over the whole range of solution compositions. The study should be made at several temperatures.

If the energetics of transfer of perchlorate salts are principally determined by coulombic interactions, as indicated by this study, the ionic parameters of size and charge rather than electronic structure should be of paramount importance.

Thus it would be of interest to determine the analytical and thermodynamic promotion effects of different electronic types of transition metal perchlorates upon the transfer of a particular transition metal perchlorate from aqueous solution into n-butanol. A similar study should be carried out using only alkaline earth metal perchlorates in place of transition metal perchlorates. Such studies should provide a further test of the dependence of perchlorate-promoted extractions upon the factors of cation size as well as electronic structure.

The effect of perchlorate concentration requires further study. If, as has been shown for extractions by 2-octanol, the promotion effect of other perchlorates is not dependent on cation charge type, but apparently depends on the total perchlorate ion concentration, this should be studied by employing mixtures containing 1:1 and 3:1 type perchlorates as promoting agents. A three-salt system would embody a greater number of possible interactions between solvents and ions, but would enormously increase the complexity of the system.

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APPENDIX A

GLOSSARY

a = closest distance of ionic approach from Bjerrum's treatment

D, ε = dielectric constant

e = electronic charge

E_s = electrical contribution to ion solvation free energy

f = salt activity coefficient

ΔG^o, ΔH^o, ΔS^o = Born's free energy, enthalpy and entropy changes for the transfer of a mole of an ion from vacuum to a medium with dielectric constant ε

ΔG_t, ΔH_t, ΔS_t = integral free energy, enthalpy and entropy of transfer of a mole of a salt from aqueous to n-butanol phases at extraction equilibrium

$\Delta \bar{G}^o_t$, $\Delta \bar{H}^o_t$, $\Delta \bar{S}^o_t$ = partial molal free energy, enthalpy and entropy of transfer of a mole of a salt from aqueous to n-butanol phases at infinite dilution of salt, and at extraction equilibrium

$\Delta \bar{G}_t$, $\Delta \bar{H}_t$, $\Delta \bar{S}_t$ = partial molal free energy, enthalpy and entropy of transfer of a mole of a salt from aqueous to n-butanol phases at extraction equilibrium

ΔH^M = excess free enthalpy of mixing

I = molar ionic strength

K = thermodynamic equilibrium constant

K_{ass} = ion association constant

K_D = distribution ratio of salts between two separate phases

K_e = equilibrium constant fro the extraction of 2:1 salts from aqueous to organic phases

K_M = mass action concentration quotient

N_o = Avogadro's number

q = critical distance of approach from Bjerrum's treatment

r_α = radius of ion α

ΔS^E = excess free entropy of mixing

ΔS_D = entropy of solvation due to changes in dielectric orientation

ΔS^{st} = structure-breaking entropy

Z_α = charge on ion α

density of aqueous solvent at 25°C = 0.9870 gm.cm.^{-3}

density of organic solvent at 25°C = 0.8344 gm.cm.^{-3}

APPENDIX B

ENTHALPY OF TRANSFER, BORN'S MODEL

From the requirements of Born's model, the free energy change for the transfer of a mole of an ion of radius r and charge Ze, from a vacuum to a medium with dielectric constant D, is given by

$$\Delta G^{o} = -\frac{N_{o}Z^{2}e^{2}}{2r}(1 - 1/D) \qquad (A.1)$$

where N_o represents the Avogadro's number and e the electronic charge.

From the Gibbs-Helmholtz equation the corresponding enthalpy change is given by

$$\begin{aligned} \Delta H^{o} &= -T^{2}\frac{\partial(\Delta G^{o}/T)_{P}}{\partial T} \\ &= -T^{2}\frac{\partial}{\partial T}\left[(-N_{o}Z^{2}e^{2}/2rT)(1 - 1/D)\right] \qquad (A.2) \\ &= -(N_{o}Z^{2}e^{2}/2r)\ \{1 - (1/D)[1 + (T/D)(dD/dT)]\} \end{aligned}$$

If the species transferred is a mole of salt, then

$$\Delta H^{o} = (-N_{o}e^{2}/2)\ (\Sigma_{\alpha}\nu_{\alpha}Z_{\alpha}^{2}/r_{\alpha})\ \{1 - (1/D)[1 + (T/D)(dD/dT)]\} \qquad (A.3)$$

where Z_α and r_α represent, respectively, the charge and radius of ion α and ν_α represents the number of ions α in the molecular formula of the salt.

The transfer of a mole of salt from the aqueous phase to the n-butanol phase will result in an enthalpy change ΔH_t^o, which is given by

$$\Delta H_t^o = (\Delta H^o)_{org.} - (\Delta H^o)_{aq.}$$

$$= (N_o e^2/2)(\sum_\alpha \nu_\alpha Z_\alpha^2/r_\alpha)\ \{(1/D)[1 + (T/D)(dD/dT)]\}_{org.} - \{(1/D)[1 + (T/D)(dD/dT)]\}_{aq.} \qquad (A.4)$$

Substituting

$e = 4.80 \times 10^{-10}$ e.s.u.

$N_o = 6.02 \times 10^{23}$ mole^{-1}

$(\frac{dD}{dT})_{aq.} = -0.357$ per degree Kelvin

$(\frac{dD}{dT})_{org.} = -0.180$ per degree Kelvin

$T = 298.16\ ^oK$

$D_{aq.} = 73.5$

$D_{org.} = 19.3$

and after conversions of units

$$(\Delta H_t^o) = -14.30\ (\sum_\alpha \nu_\alpha Z_\alpha^2/r_\alpha)\ \text{kcal. mole}^{-1} \qquad (A.5)$$

providing r_α is in $\mathring{A}$.

Since ΔH_t^o refers to infinite dilution of the salt, $\Delta H_t^o = \Delta\bar{H}_t^o$. (It should be noted that $\Delta\bar{H}_t^o$ is the partial molal enthalpy of transfer at extraction equilibrium.)

Thus, at 25.0°C,

$$\Delta\bar{H}_t^o = -14.30\ (\sum_\alpha \nu_\alpha Z_\alpha^2/r_\alpha)\ \text{kcal. mole}^{-1} \qquad (A.6)$$

The ionic radii to be used are as follows:

$r_{Co^{+2}} = 0.74\ \mathring{A}$

$r_{ClO_4^-} \cong 2.28\ \mathring{A}$

$r_{Ca^{+2}} = 0.99\ \mathring{A}$

VITA

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Candidate for the Degree of

Doctor of Philosophy

Thesis: DISTRIBUTION AND ENTHALPY OF TRANSFER OF COBALT(II) PERCHLORATE FROM AQUEOUS TO 1-BUTANOL SOLUTIONS OF CALCIUM PERCHLORATE AT EXTRACTION EQUILIBRIUM

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