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THOMAS GRADY CONALLY. Temperature Dependence of the Heats of Mixing of Tetrapropylammonium Chloride with some Alkali Metal Halides. (1972)
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Aqueous electrolyte solutions have been studied extensively in recent years with the result that several theories have evolved concerning the structure of the solvent and the properties of the ions involved. In aqueous solutions the solvent structure is usually different from that of pure water. Specific ion--solvent interactions are responsible for some of the structure changes. An excellent way of studying these interactions and their effect upon water structure is to measure the heats of mixing of aqueous electrolyte solutions. Several systems have been studied at 25 °C, but few studies have been made at higher temperatures. In order to obtain more information, further research at the higher temperatures is necessary.

The heats of mixing for the systems $\text{LiCl}--(\underline{n}\text{-C}_3\text{H}_7)_4\text{NCl}--\text{H}_2\text{O}$, $\text{KCl}--(\underline{n}\text{-C}_3\text{H}_7)_4\text{NCl}--\text{H}_2\text{O}$ and $\text{NaCl}--(\underline{n}\text{-C}_3\text{H}_7)_4\text{NCl}--\text{H}_2\text{O}$ were measured at 40-, 60-, and 80-°C. These mixings were carried out at 0.5 m and constant ionic strength. An adiabatic microcalorimeter was used to obtain these measurements.

The heats of mixing for these three systems show very little temperature dependence. The specific pairwise ion interaction parameter, \underline{RTh}_0 , is very large and relatively unchanged throughout the temperature range, possibly implying a large temperature-independent structure making influence. This probably involves the co-spheres of two $(\underline{n}\text{-C}_3\text{H}_7)_4\text{N}^+$ ions which can complete their hydration sheaths when they are separated in the mixing. The triplet interaction

parameter, RTh_1 likewise remains unchanged, but it is not as large as RTh_0 . The fact that the $(n-C_3H_7)_4N^+$ ions can still cause the structuring of water at 80 °C is very puzzling. It may be that the true interactions are not understood and that some other effect may account for the unexpected constancy of these parameters.

ROYAL SOCIETY

London, Great Britain

A Thesis Submitted to
the Faculty of the Graduate School of
the University of North Carolina at Charlotte
in Partial Fulfillment
of the Requirements for the Degree
Master of Science

Charlotte,
North Carolina

Approved by


TEMPERATURE DEPENDENCE OF THE HEATS OF MIXING OF
TETRAPROPYLAMMONIUM CHLORIDE
WITH SOME ALKALI
METAL HALIDES

by

Thomas Grady Conally

A Thesis Submitted to
the Faculty of the Graduate School at
The University of North Carolina at Greensboro
in Partial Fulfillment
of the Requirements for the Degree
Master of Science

Greensboro
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Approved by

John R. Jezorek

APPROVAL SHEET

This thesis has been approved by the following committee of the Faculty of the Graduate School at The University of North Carolina at Greensboro.

Thesis
Adviser

Henry L. Anderson, II

Oral Examination
Committee Members

John R. Jezurek
Walter H. Puterbaugh
John L. Graves

August 18, 1972
Date of Examination

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INTRODUCTION

In the last few years, much research effort has gone into the study of water, its structure and its unique capacity to form hydrogen bonds. These bonds are three dimensional in nature and rather strong in the liquid phase as well as in the solid phase of water. The research efforts have also included aqueous electrolyte solutions as a means of defining the very complex structural properties of water. This study does not imply, however, that nothing is known about the structure of water, because a great deal of research has been performed on the properties of water and aqueous solutions.¹ Some uncertainty remains concerning the structure of water and its interactions with the solute in aqueous solutions, and the subject invokes controversy.²

In these studies of water--solute and solute--water interactions, solutions of nonelectrolytes and organic salts are of significant interest since many of these compounds are known to increase or decrease the structure of water. Before we discuss these interactions, however, we must first investigate the existing theories of water structure.

DOCUMENTATION OF PREVIOUS WORK

Bulk Water. The earliest of these theories took into account the association of the molecules, but only in small polymers which contained a few water molecules. These theories could not adequately account for many of the observed properties of H_2O .³ Bernal and Fowler⁴ proposed that water was only ice with bent hydrogen bonds. They postulated that the hydrogen bond in water could be bent but not broken because of its electrostatic character which was a simple coulombic interaction between somewhat rigid charge distributions. This postulate was interpreted to mean that water was only a broken down ice lattice, joined completely by bonds which temperature and pressure could alter. Bernal and Fowler's model has been criticized because the bending of the hydrogen bonds results in significant strain. Their views are not completely wrong, however, as extensive regions of hydrogen bonding which break down with increased temperature have been shown to exist by x-ray scattering experiments.⁴ These indicate that low coordination exists in large amounts in liquid water. This low coordination is characteristic of tetrahedrally bonded structure. Cross, Burnham and Leighton⁵ estimated from Raman studies that at 25 °C, around 50% of the hydrogen bonds of ice are broken. The Raman spectra showed that there were extensive numbers of molecules with two, three, and four hydrogen bonds as would be expected in a broken down ice lattice. Lennard-Jones and Pople⁶ described a model in which very few bonds are broken at the melting point. Their model explained the

volume decrease upon melting by proposing that the first and second layer shells around a given molecule increased because of bond bending. Although the L-J. P. model had difficulties, the authors seemed to make the most of their good points.

Perhaps one of the more familiar of the theories is the Frank and Wen "flickering cluster" model.⁷ Water in the solid phase is tetra-hydrogen-bonded into an immobile, open (on a molecular scale) superstructure. As temperature is increased or the pressure reduced, some of these hydrogen bonds break and cause the immobile superstructure to partially melt, breaking some of the hydrogen bonds. This breaking leaves smaller structures which are liquid but retain a certain degree of similarity to ice. These smaller structures are interpreted to mean "ice-like" patches floating randomly in more liquid water. Frank and Wen interpret the hydrogen bond in water as a resonance structure:

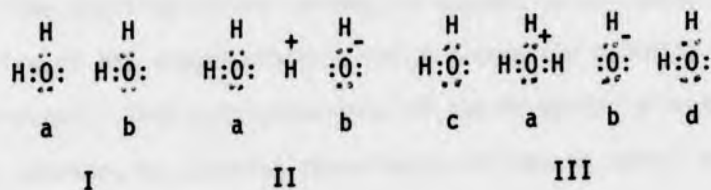


Figure 1. Resonance in Hydrogen-bonded Water Molecules.

The + and - represent formal charges; partial polarity of the O-H bond is represented by resonance of molecule "b" between I and II. A contribution from II constitutes the formation of a hydrogen bond. When "a" and "b" form a hydrogen bond, then "a" becomes more acidic and "b" more basic so that "a" can bond acidically with another water molecule

and "b" can bond more basically with another molecule of water; then the "a" - "b" bond is strengthened. This strengthening then is the driving force for "c" - "a" bonds and "b" - "d" bonds to form, which proliferates the structure in a cooperative type of way. The orbitals on oxygen will approximate sp^3 hybridization and increase the localization of the unbonded electrons, giving them a much greater tendency for bonding. This phenomenon seems to be, as said, a cooperative phenomenon: when one bond breaks, many will break, creating a group of water molecules which will associate themselves or melt into monomeric water molecules. This is a picture of many clusters of molecules suddenly forming and then melting, or as Frank and Wen say "Jumping to attention and relaxing at ease."⁷ The authors state that this process of hydrogen bonding also accounts for the change in H-O-H bond angle from $104^\circ 35'$ in water vapor to nearly $109^\circ 28'$ in the ice phase, and possibly for the high mobility of protons in both the liquid and ice phases. The mobility of the protons is thought to be caused by the hybridizing of the oxygen orbitals which lowers the potential barrier of the protons. This particular view of the structure of water was deduced, however, by studying the effects of ions on water structure.

Before delving into the effects of ions on water structure, however, we need to look further into these continuing studies of water structure. The main reason for so many different ideas of water structure is that no one theory answers all of the questions: *i.e.*, do the hydrogen bonds break or just bend; does monomeric water actually exist, or is every water molecule somehow associated with another?

It appears now that the most stable arrangement of atoms in two joined water molecules is close to the "trans" configuration of two neighboring molecules in ice. The "cis" configuration, which exists in ice and can be shown as lining up of dipole moments in parallel and in closed rings or double hydrogen bonds, at one time thought to be favorable, is actually less stable.⁸ The Frank and Wen cooperative reinforcement of hydrogen bonds seems to have been confirmed. The H₂O molecules joined in a chain trimer in the "chair" configuration are held together by an energy 2.4 times that of one hydrogen bond. As the chain length increases, the stabilization increases, at least to 5 molecules. When a particular molecule tries to donate either protons or electrons to both its neighbors, then destabilization occurs. Chains which have closed and formed ring systems are more stable than the same open-ended chain. The ring strain is overcome by the extra stabilization in the closed system.⁸

More insight into water structure may be gained by further examining what happens when ice melts. When water in the solid phase melts to the liquid phase, the following anomalies must be accounted for:

1. Shrinkage which occurs when ice melts
2. Maximum density phenomena
3. Increase of thermal expansibility when pressure is applied
4. The effect of increased pressure in lowering the viscosity of cold water

The structure of ice which is tetra-coordinated is an open structure which has voids regularly spaced in the lattice. When the ice melts

into water the density changes and the water is more dense than a corresponding weight of ice. The voids in the structure then must be nonexistent or either be filled with other free water molecules or be reduced in size by bond bending or reorganization. The above three views have been the basis for continuing discussions on the structure of water.⁸

The resonance scheme of Frank and Wen can account for experimentally observed data, such as density data, relaxation times, structural changes in solutions of non polar substances and changes in the thermodynamic quantities.

Another theory was initiated by Pauling⁹ and followed up by several other workers¹⁰⁻¹² in which it was proposed that the ice structure persisted in the liquid phase, and the cavities which existed were filled with nonbonded water molecules. This model, according to Pauling, was thermodynamically stable and its density was very close to that of liquid water. Pauling indicated it was a type of clathrate structure. Nemethy and Sheraga¹³ state that Pauling's model appears to result in too much rigidity for a liquid of low viscosity.

Jones and Dole¹² developed an equation which is used extensively in finding the concentration dependence of the viscosity of dilute electrolyte solutions:

$$\eta/\eta_0 = 1 + A\sqrt{C} + Bc$$

If the concentration is above 0.002 m and less than 0.1 m,

$$\eta/\eta_0 = 1 + Bc$$

and B is known as the viscosity B coefficient which is used to describe the viscosities of ions, molecules, etc.

η = viscosity of solution

η_0 = viscosity of pure solvent

A and B are constants specific for the given solvent--solute system. The magnitude of B shows the contribution to the viscosity of the system and the sign determines if the viscosity is greater or less than water.

Frank and Quist's¹⁵ analysis of Pauling's model by thermodynamic treatment shows that the model does not result in a good explanation for the thermodynamics of solutions of nonpolar substances.

Nemethy and Sheraga¹³ base their views of water structure on the theory of Frank and Wen⁷, the "flickering cluster" theory. These clusters are short lived, possibly 10^{-10} or 10^{-11} seconds as Frank and Wen suggested. However, this was long enough to be significant.⁷ The Nemethy and Sheraga model makes no assumption about the arrangement of molecules in a cluster except that the number of hydrogen bonds be the largest number that can be formed without any undue distortion arising from bond linearity being bent. The clusters should be compact, having as many tetrahedrally bonded molecules as possible, and without extended chains of molecules which are bonded bifunctionally. The model, therefore, postulates that interconnecting networks of five and six membered rings can fulfill the condition of a high degree of hydrogen bonding. In this model there are two main structures, clusters and unbonded water. There are five classes of molecules in the model:

1. Tetrahedrally hydrogen bonded molecules
- 2, 3, 4. Surface molecules with 3, 2 and 1 bonds respectively

5. Water in the space between the clusters with all four bonds broken

Nemethy and Sheraga¹³ based their views on Raman spectra, infrared spectra and various thermodynamic properties of water. Experimental results⁵ show that about 50% of bonds were broken at 25 °C. This evidence agrees with other experiments. They stated that the model lacks validity about 70 °C because the clusters reach such a small size that the calculations are no longer useful.

McCabe, Subramanian and Fisher¹⁶ in a near infrared spectroscopic investigation of water found that when the temperature is changed from 20 to 80 °C there is a shift of a peak in the 1.45 μ region. While there is no definite explanation of this shift, it is clear that a significant change has occurred in the structure of water. This change was proven by elimination of other causes and left only the structural change as the cause. This study more or less supports the "flickering cluster" theory with the exception that monomeric water is only a small fraction. The bulk of water molecules in liquid water must be engaged in H-bonding involving either one or both hydrogens. Water molecules with both hydrogens bonded will be found in the interior of clusters while those with only one hydrogen bonded will be at the periphery. A temperature rise causes a breakup of the clusters, thereby decreasing the ratio of low frequency species to high frequency species (low frequency species are cluster-bound in contrast to high frequency species which are probably monomeric or low polymeric species.) The production of more surface molecules at the expense of an interior one with temperature appears to proceed through an intermediate species

which has a constant spectral contribution in the temperature range 20 to 80 °C. Even with this evidence, chemical physicists⁸ seem to think that unbonded water doesn't exist. In fact, Bernal and Fowler's⁴ broken ice lattice model indicates to these researchers that no one molecule in liquid water has any greater ability to avoid the strong interactive forces than any other molecule. Now chemical physicists lean toward a uniformist model in which all molecules are equivalent.⁸

Aqueous Solutions. Our main interest is in the effects of solutes on water structure. Frank and Evans¹⁷ were two of the early researchers who looked at electrolyte solutions. Water structure for them was an "iceberg" picture, much like Frank and Wen's⁷ later "flickering cluster" theory which was probably born from this early model. The icebergs were patches of "frozen water" (hydrogen-bonded) which resulted from the influence of solute particles. Frank and Evans were researching the entropy of solutions when it was noticed in a specific calculation that the net change in entropy expected for dissolving ions into solutions was somewhat larger than the observed value. They pictured the ions as "freezing" the first layer of water molecules into a state of some sort of dielectric saturation. They then concluded that the entropy of the solution was too high. Their explanation was that around the ions, out beyond that first saturated layer of water molecules, there was a region or spherical shell in which the water structure is broken down or "melted" as one would say of ice. Depolymerized is probably a better term, for hydrogen bonds are probably broken. This description is compared with the structure

of bulk water, of course. As an example the Na^+ ion fits into the center of a tetrahedron of H_2O molecules. The strong ionic charge orients the polar water molecules with the hydrogen atoms out, which is not the pattern in the icebergs. The four-coordinated Na^+ ion then cannot fit into an iceberg, and disrupts the order of the molecules just outside the first four so as to prevent them from being icebergs. It seems as though it is a relatively long distance into the solution, away from the ionic charge, before that charge is negligible and water molecules begin to orient themselves as in bulk water. Frank and Evans called this effect "structural entropy".

Bernal and Fowler⁴ and Bingham¹⁸ have studied the fluidity or viscosity of ionic solutions. The ions which decrease the viscosity or increase the fluidity of water by "depolymerization" presumably are the ones to which Frank and Evans¹⁷ ascribe large, net structure-breaking effects. They also show that the large negative partial molal heat capacities can be explained by this structure-breaking effect. When cold water is warmed, a large part of the heat goes to melt the "icebergs", while in the ionic solution containing structure-breakers, the "icebergs" have been somewhat melted already and less heat is required to raise the temperature. The difference in the amount of heat needed is largest between pure water and solutions with the most structure-breaking ions. Al^{+3} , as revealed by viscosity data, is a structure-making ion which is associated with a large patch of frozen water surrounding it. Frank and Wen have delved into this problem and have come up with a very comprehensible model of structure modification caused by a small ion. See Figure 2.

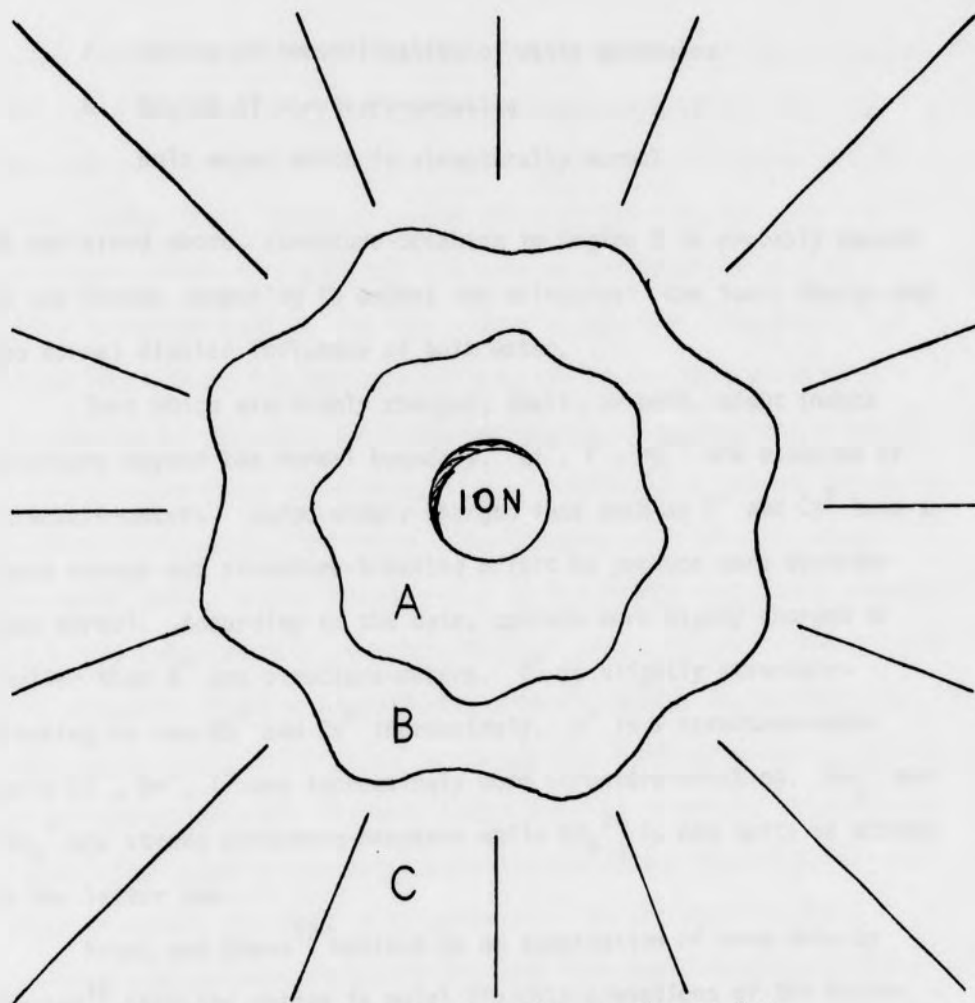


Figure 2. Structure of Water Surrounding an Ion

Region A: Electrostricted water with high orientation of water molecules

Region B: Structure - broken water

Region C: Bulk water

- A. Region of immobilization of water molecules
- B. Region of structure-breaking
- C. Bulk water which is structurally normal

As explained above, structure-breaking in Region B is probably caused by the forces competing to orient the molecules: the ionic charge and the normal dipolar influence of bulk water.

Ions which are highly charged, small, or both, might induce structure beyond the normal boundary. Li^+ , F^- , Mg^{++} are examples of structure-makers. Large singly charged ions such as I^- and Cs^+ have a large enough net structure-breaking effect to produce more disorder than normal. According to the data, cations more highly charged or smaller than K^+ are structure-makers. K^+ is slightly structure-breaking as are Rb^+ and Cs^+ increasingly. F^- is a structure-maker while Cl^- , Br^- , I^- are increasingly more structure-breaking. NO_3^- and ClO_4^- are strong structure-breakers while SO_4^{2-} is not quite as strong as the latter two.

Frank and Evans¹⁷ noticed in an examination of some data by Bingham¹⁸ that the change in molal fluidity elevations of the tetra-alkylammonium ions of the series tetramethyl-, tetraethyl-, tetrapropylammonium ions decreased too much to be accounted for by the Stokes law drag on a simple ion. They postulated from this observation that an ion which introduces large nonpolar groups into water causes iceberg formation much as the nonpolar groups would do in the absence of ionic charge. Large nonpolar solutes such as hydrocarbons are unhydrated. They cause a decrease in entropy upon dissolution in

water. This decrease is interpreted as a tightening of H_2O structure around the molecule. By analogy, it is expected that the large nonpolar quaternary ammonium ions will enforce the structure of H_2O around themselves. The more carbon atoms in the ion, the more hydrophobic these ions will be, the more water structure will be enforced and the greater the free energy of the ion. Therefore, the larger the cation, the greater the activity coefficient which is observed in the chloride salts of the tetra- n -alkylammonium series.¹⁹

Frank and Wen⁷ have proposed a mechanism for structure promotion by nonpolar solutes. The "flickering clusters" form when a volume element of suitable size loses energy to the extent that the disruptive forces are overcome and the volume freezes into a cluster. The element will melt when the disruptive forces transmit energy to overcome the force of the hydrogen bonds in the patch. If nonpolar solute particles are introduced into the solvent, they should be incapable of producing or harboring these disruptive forces because of the feeble electrostatic reactions for which they are known. In the solvent, they protect the boundaries of volume elements from the disruptive forces and thus the "ice-like" patches should be able to form more easily and last a longer time. If this extra "ice-likeness" is disrupted with increasing temperature at a rate proportional to that of normal bulk water "flickering clusters", then this would account for the excess apparent molal heat capacity noted by Frank and Wen.⁷

Tetraalkylammonium Solutions. A thorough review of previous work on electrolyte solutions has been compiled by Petree.²⁰ The documen-

tation in this thesis represents some of the previous work on the effects of solutes on solvent structure, specifically the quaternary ammonium ions, the R_4N^+ homologues where $R = -CH_3$, $-C_2H_5$, $-C_3H_7$, and $-C_4H_9$.

Desnoyers, et al.²¹ classify ions into two main types: hydrophobic and hydrophilic. These classifications have been used in many references but are explained very well here. Hydrophobic ions tend to stabilize the bulk structure of water. This structure may not be the same as ice, but it is still less dense and more structured than bulk water. The large tetraalkylammonium ions and surfactants are typically hydrophobic ions.

Hydrophilic ions tend to orient the water molecules radially with respect to their electrostatic field. This is known as electrostriction. In some cases this orienting influence may be sufficiently strong to cause an overall increase in the ordering of the solvent (Li^+ , F^-), but in most cases hydrophilic ions appear as overall electrostrictive structure-breakers (Br^- , I^-). An overall decrease in the structure of water implies a breakage of some hydrogen bonds; the melting of ice decreases its volume, increases the entropy and is endothermic.

By studies based on the Gurney Co-sphere model, Desnoyers, et al.²¹ have shown what happens between two different species of ions in solution. See Figure 3.

Situation I. Leads to attractive forces since hydrophobic hydration is unfavorable as the result of a repulsion of the water molecules from the ion surface. The sharing of two hydrophobic

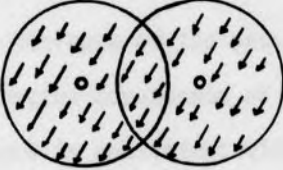
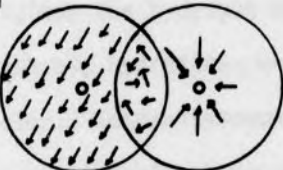
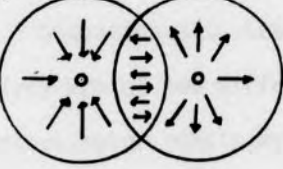
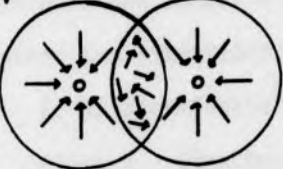
A	B	C			
I  Hb - Hb	Effect of overlap and resulting force	Contributions to excess functions			
	Less structure-forming.	\bar{G}^{ex}	\bar{V}^{ex}	\bar{H}^{ex}	\bar{S}^{ex}
	Attraction.	-	-	+	+
II  Hb - HI	More structure-breaking.				
	Repulsion.	+	-	+	+
III  + HI - HI -	Less structure-breaking.				
	Attraction.	-	+	-	-
IV  + HI - HI +	More structure-breaking.				
	Attraction.	+	-	+	+

Figure 3. Interaction Models

A. Interaction

B. Effect of overlap and resulting forces

C. Contributions to excess functions

Hb = Hydrophobic

HI = Hydrophilic

hydration co-spheres reduces the overall hydrophobic hydration by sharing some of the water molecules in the hydration spheres. This results in a decrease of the excess partial molal free energy, \bar{G}^{ex} . The concentration dependence of activity coefficients and apparent molal volumes is consistent with this model. Desnoyers, Arel, and Paul-Andre Leduc²² have shown that most large organic ions and molecules strengthen the hydrogen bonds of the neighboring water molecules by hydrophobic hydration, while intermediate size ions break the structure of water. Tetraalkylammonium salts are reasonably soluble in water and their hydrophobic character can be varied by changing the size and nature of the -R group.

Situation II. Leads to repulsive forces as the co-spheres involved are of two different modes of hydration. The electrostrictive structure-maker reacts by disordering some of the water molecules within the hydration sphere of the hydrophobic structure-maker. This is unfavorable and causes a positive contribution to the free energy. The other two situations are easily explained by Figure 3.

E. R. Nightingale²³ classifies hydration into 4 main classes:

Class I. Structure-ordering ions with peripheral hydration. This structure most nearly represents hydrated ions. The electric field at the surface of the ion is large enough to attract one or more layers of water molecules, thus forming a peripherally hydrated ion. The effective volume of these ions is large and the ions exhibit positive viscosity B coefficients. The effect decreases with rise in temperature.

Class II. Peripherally hydrated, structure ordering ions with anomalous temperature dependence. These ions act as Class I but exhibit negative activation energies for viscous flow with increasing temperature. The water molecules become more susceptible to orientation about the ion and the viscosity B coefficient appears to increase with a rise in temperature. The tetramethylammonium ion possesses a small degree of peripheral hydration which increases with temperature. This is unlike the other R_4N^+ ions.

Class III. Structure disordering ions with peripheral hydration. Only monatomic ions are in this class because the weak electric field about such species is only strong enough to reorient a limited number of solvent molecules. This acts as a disturbing center and collapses a region of ice-likeness about the ion to produce a net structure-disordering effect which is characterized by negative ionic B coefficients.

Class IV. Ions with a peripheral hydration. Very large ions such as the R_4N^+ ions, irrespective of charge, act in a manner exhibited by unhydrated Einstein solutes. They introduce extra ice-likeness into the solvent structure because the hydrophobic ionic surface cannot participate in the "flickering clusters". They exhibit positive activation energy for viscous flow which correlates with the melting of this extra ice-likeness with increased temperature.

Much interest has been generated about the anomalous behavior of the tetraalkylammonium ions in aqueous solutions. Their classification has been researched in various ways, which sometimes have been misleading.

Frank and Evans¹⁷ noted in their comparison of partial molal heat capacities of different ions that some had large negative partial molal heat capacities. To account for this, it was theorized that icebergs exist in cold water (this has been established in the introduction), and when this cold water is warmed, part of the heat introduced goes to melt the so called icebergs. In an ionic solution in which some of the icebergs had already been melted, the warming of the solution should take up less heat. This would contribute a negative term to the partial molal heat capacity and this term should be largest in the case where the ions had the greatest structure-breaking effect. Frank and Wen⁷ corroborated this theory and introduced measurements of the tetraalkylammonium salts to further show that structure promotion could be effected by large nonpolar ions. It was shown that $(n-C_4H_9)_4^- NBr$ was structure promoting, causing the water near the cation to be more ice-like than normal for bulk water. More energy was needed in heating this ionic solution than in pure water to cause this increased ice-likeness to melt. If there is extra ice-likeness around an ion then information should be derived from studying the effect of these ions on the viscosity of solutions.

Kay and Evans²⁴ have shown by comparing viscosity B coefficients that in aqueous as opposed to nonaqueous solution, the tetramethylammonium ion is a structure-breaker. Tetrabutylammonium ions and tetrapropylammonium ions are shown to be structure-makers. This seems to support the postulate that clathrate-like structures form about the hydrocarbon portions of these ions. Such an enforcement of the structure of water about the hydrophobic side chains of these ions

would tend to increase the viscosity as well as the size of the ion neighborhood this decreasing the mobility. Nightingale²⁵ noted an anomaly in the tetraalkylammonium homologues with respect to the viscosity that the B coefficient for the tetraalkylammonium ions other than tetramethylammonium ions decreased with temperature. Kay later explained this anomaly.

Kay, et al.²⁶ found that the tetraethylammonium ion showed no temperature dependence of viscosity B coefficient, presumably from a cancellation of the structure-making and structure-breaking effects. The mobility in D₂O relative to H₂O indicated a slight structure-breaking tendency while the dependence of viscosity B coefficient indicated that it was a slight structure-maker. This has shown that the tetraethylammonium ion has borderline tendencies in each of two slightly different ion-solvent interactions.

The tetramethylammonium ion has a negative temperature dependence of the viscosity B coefficient which is typical of a structure-breaking ion. As the temperature increases there is less structure available to be broken; therefore, the tetramethylammonium ion is much less effective in reduction of the local viscosity at higher temperature.

The tetrapropyl- and tetrabutylammonium ions both exhibit a positive temperature dependence of the viscosity B coefficient as would be expected of ions which form clathrate structures around their hydrocarbon side chains. As the temperature increases, these cages of water melt and produce a smaller and therefore faster moving entity.

Horne and Young²⁷ have investigated the electrical conductivities of some aqueous tetraalkylammonium halide solutions under hydrostatic pressure. They stated that the clathrate-like structure mentioned earlier seems to be a type of geodesic dome which forms very easily around the tetramethylammonium ion but awkwardly about the tetraethyl- or tetrapropylammonium ion. Within this shell, as it were, exists the cation and anion (halide, X^-), and upon application of hydrostatic pressure, a volume decrease occurs forcing the tetraalkylammonium ion and the halide ion together. The greater the hydrophobic character of the solute, the greater the above effect. It is also affected by the water structure-altering properties of the anion present. This effect offers some support for the cation-anion interaction in some of the tetraalkylammonium salt solutions, an ion pairing first discussed by R. M. Diamond.²⁸ He states that when two large hydrophobic ions are present, the stability of the solution is preserved by forming one cavity for an ion pair instead of one for each ion.

Wen and Saito²⁹ found in studies of partial and apparent molal volumes that in concentrated solutions of about 1 m, there is a type of clathrate structure around the tetrabutylammonium bromide ion pair which indicates slight structure-making effects. This association is thought to occur although the relationship is not clear cut as yet. At infinite dilution, however, it was found that the tetrabutylammonium ion enhances water structure while the bromide ion slightly breaks the water structure. Wen and Saito also postulate that the tetrapropylammonium ion is a structure-maker.

Based on some compressibility studies, Conway and Verrall³⁰ argue that the tetraethylammonium ion appears to promote structure slightly in comparison with the tetramethylammonium ion. This promotion acts to decrease the compressibility. The tetrapropyl- and tetrabutylammonium ions greatly increase the structure with a marked decrease in compressibility.

Wen and Saito²⁹ have observed that the partial molal volumes of the quaternary ammonium halides have a negative concentration dependence and eventually pass through a minimum. A very good explanation of this negative concentration dependence was given by Desnoyers and Arel.³¹ They postulate that when a hydrophobic solute is dissolved in water, mutual salting-in occurs. When the first molecule is dissolved, the increase of the structure of the water causes an increase in the nonideal free energy. This increase causes the solvent to be more ordered and less work must be done to introduce the second, third and subsequent molecules. Volumetrically, upon the addition of a hydrophobic molecule, there is an increase in the volume of the solvent due to the extra "ice-likeness", but in the introduction of subsequent molecules, the extra increase in volume is smaller. Conway, *et al.* observed that the partial molal volumes of the tetraalkylammonium salts are linear functions of their molecular weight. In studying the apparent molal volumes, it is important to remember that there are other contributions to \bar{V}° , the partial molal volume, than just structural ones.

$$\bar{V}^\circ (\text{ion}) = \bar{V}^\circ (\text{intrinsic}) + \bar{V}^\circ (\text{structural}) + \bar{V}^\circ (\text{electro-structure})$$

\bar{V}° (intrinsic) = intrinsic volume of the ion plus the volume due to void space

\bar{V}° (electrostriction) = decrease in volume due to electrostriction

\bar{V}° (structural) = for ions that have strong structural effects on water

The structural effects of the tetraalkylammonium salts are usually so large as to mask the other contributions.

Partial molal expansibilities, \bar{E}° have the same contributions as \bar{V}° . Millero and Drost-Hanson³³ found from studies of partial molal expansibilities, \bar{E}° , that tetrapropylammonium chloride and tetrabutylammonium chloride are structure-makers with a large \bar{E}° (structural) contribution, while the lower-molecular-weight tetraalkylammonium salts are not as strong contributing much less to \bar{E}° (structural). They also found that \bar{E}° (structural) decreases with temperature and increases as the molecular weight of the tetraalkylammonium salt is increased.

In a study of osmotic and activity coefficients, Lindenbaum and Boyd¹⁹ found that the osmotic coefficients for the tetraalkylammonium chlorides in dilute solutions increased with cation size; therefore, the larger the cation, they postulated, the larger the activity coefficient. This increase in activity coefficient gives the order in which these cations affect water structure, if not labelling them structure-makers or structure-breakers specifically. Lindenbaum, *et al.*³⁴ proved later with temperature dependence studies of the osmotic coefficients of the tetraalkylammonium halides that the earlier postulate was correct.

Lindenbaum found in his studies of the enthalpy and entropy of dilution of aqueous solutions of the tetraalkylammonium halides that the heats evolved on dilution of the tetrabutyl- and tetrapropylammonium chlorides and bromides are the largest of any 1--1 electrolytes previously reported. The order of heat evolved for a given halide is $(C_4H_9)_4N^+ > (C_3H_7)_4N^+ > (C_2H_5)_4N^+ > (CH_3)_4N^+$ over the entire concentration range. For any of the cations above the order of the heat evolved is $Cl^- > Br^- > I^-$. The entropy curves decrease in the same order as do the heats of dilution. Boyd, Chase and Vaslow³⁵ show in dilution studies that the tetramethylammonium ion appears to be a structure-breaking ion or the least effective structure-making tetraalkylammonium ion.

Wood and Anderson, et al.³⁶ found in their heat of dilution studies of aqueous tetraalkylammonium fluorides that those particular salts have higher apparent molal heat contents (Δ_L) than any other series. There is a regular increase in Δ_L going from tetramethyl- to tetrapropylammonium ion and from the iodide to the fluoride with the exception of tetraethylammonium bromide at low concentrations. This is explained in terms of changes in the overlap of cage-like structures around the tetraalkylammonium ions as the solution is diluted. The ions are moving farther apart and, therefore, there is more room around the ions and less competition for the water molecules. This allows more hydrogen bonding and thus an increase in structure. The increase in structure produces a heating of the solution and an increase in volume. The fluoride ion also contributes to the heat of dilution by causing some increased structure.

Heats of mixing involving the quaternary ammonium ions reveal a great deal about structure and thermodynamic functions. Wood and Anderson³⁷ have shown in a study of heats of mixing at 25 °C that the tetrapropylammonium ion is a strong hydrophobic structure-maker and that the tetraethylammonium ion is a transition ion between a structure-breaker and structure-maker. The tetramethylammonium ion has been said to be a structure-breaker.

Wen and Nara,³⁸ in their studies of volume changes on mixing solutions of potassium halides and symmetrical tetraalkylammonium halides, tried to obtain evidence of cation--cation interaction. They observed a positive excess molal volume change on mixing these species. According to them, the cation--cation overlap in tetraalkylammonium salt solutions resulted in structural stability by a linking up of the water cages around them. Upon mixing, the concentration of the tetraalkylammonium salt decreased despite constant ionic strength, yielding a decrease in the linkage of the water cages. This decreasing of the linkages permitted a larger cage to form around the tetraalkylammonium ions and an increase in the volume. This volume change cannot be explained in terms of ion sizes alone.

This prior work has fairly well characterized the properties of the large tetraalkylammonium ions at single temperatures. However, much insight can be gained from studying the temperature dependence of these properties, because as shown earlier, the structure of water itself is highly temperature dependent.

RESEARCH PROPOSAL

Anderson and Petree³⁹ examined the temperature dependence of heats of mixing of several aqueous electrolytes with a common anion. These heats of mixing were done at constant ionic strength to cancel the ionic atmosphere effects and with a common anion to cancel effects of oppositely-charged ion pairs. This was done in order to study conveniently the pairwise and triplet interactions of like-charged ions. It was noted that for three of the mixtures, LiCl--KCl--H₂O, LiCl--(CH₃)₄NCl--H₂O, and KCl--(CH₃)₄NCl--H₂O, the heats of mixing are constant up to 80 °C within experimental error. Using the Frank-Evans-Wen model of structure-breaking, structure-making ions, they explained this temperature independence by assuming that the specific interactions upon mixing involve ion--solvent interactions in the region of the primary hydration sphere. This temperature independence is based upon the insensitivity of the primary hydration sphere⁴⁰ to temperature. The interactions probably take place at the interface between the structure-made and structure-broken region. This is based on the mixings of HCl--NaCl--H₂O, LiCl--NaCl--H₂O and NaCl--KCl--H₂O, all three of which exhibit a temperature dependence. It was noticed that all three mixtures include the sodium ion which is classified as a borderline structure-maker, structure-breaker. The interface between the structure-making and structure-breaking is probably not very well defined and is affected by temperature changes which would make the heats of mixing containing the sodium ion temperature dependent.

Anderson, Wilson and Smith⁴¹ supported this view with a further study of heats of mixing. Some of these mixings were with common cations and some with common anions. This study revealed that the heat of mixing Cs^+ and Na^+ exhibited a temperature dependence, increasing with temperature. This was thought to be caused by the incompletely hydrated Cs^+ ion becoming hydrated as the Na^+ ion became more structure-breaking and provided more water molecules as temperature increased.

The tetrapropylammonium ion is a large hydrophobic structure promoting ion at 25 °C. It has been shown that when this ion is mixed with a different ion, the overlap of the hydration sheaths of the tetrapropylammonium ions is reduced. In close contact, tetrapropylammonium ions do not have their full hydration sheaths completed. On mixing, which is the same as diluting the tetrapropylammonium ions, the restriction on the hydration spheres is relieved, and the ions can complete their hydration spheres; this process results in more structure formation and consequent evolution of heat. Heats of dilution studies³⁶ support this. In addition, studies have been made at low temperatures³⁷ on the heats of mixing of the tetraalkylammonium chlorides. It is now proposed to expand the research on tetrapropylammonium chloride to higher temperatures, namely 40-, 60-, and 80-°C. A two-fold purpose is involved: first, to determine the temperature dependence of the heats of mixing of tetrapropylammonium chloride with Li^+ , Na^+ , and K^+ chlorides in order to better understand the solvent--solute structural relationship, and second, to further characterize the structure-making-breaking properties of these ions.

EXPERIMENTAL

Calorimeter Number One

Introduction. In this work two calorimeters were employed. The first one, because of its large size and therefore very long equilibration time, was abandoned for the smaller capacity calorimeter which will be described later. The large calorimeter was modified by Wilson⁴¹ and described by Vani.⁴² The major difference in the calorimeter as used here before modification was that the original set-up had no heater inside the pipet to cut down equilibration time.

Vessel. The vessel was a 700 ml Thermos⁴³ Dewar connected to brass fittings by silicone rubber cement (Figure 4). It was 19.5 cm in length and 9 cm in diameter. The brass collar was 12.5 cm in diameter. In the actual experiment, the vessel was secured to a matching collar on the superstructure by 4 screws and sealed by a rubber "O" ring. The "O" ring was seated in a groove on the lower collar which matched a groove on the upper collar.

Pipets. The pipets were mostly experimental in the early stages, but their construction evolved to elongated ovals blown from 18 mm glass tubing. Actually, a larger size tubing was used for the bulb and 18 mm tubing was fixed on each end to reduce and standardize the openings. The pipet was fitted with a plunger made of Teflon^R stoppers and glass shaft as described by Petree.²⁰ As several pipets

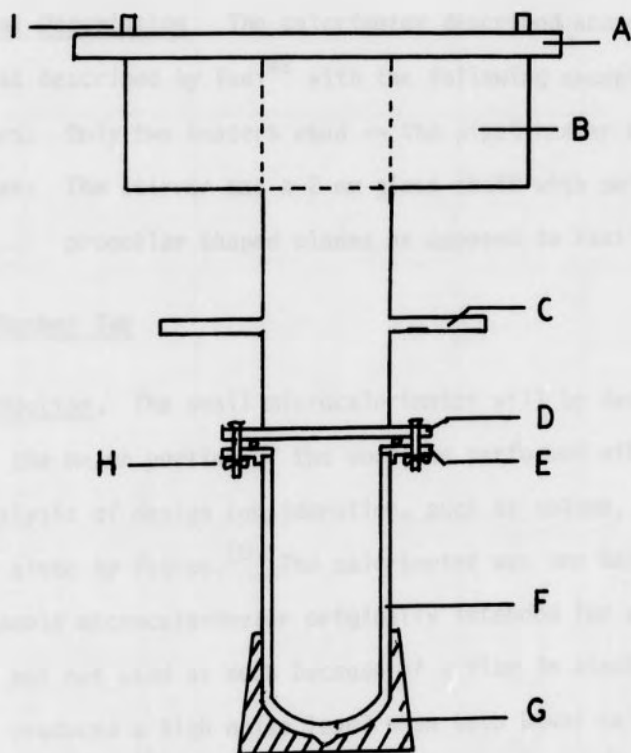


Figure 4. Large Calorimeter

- A. 5 X 30 X 0.64 cm plywood
- B. Styrofoam
- C. Brass plate for heat radiation
- D. Brass lid
- E. Brass collar
- F. Dewar vessel
- G. Tar base
- H. Brass wingnut
- I. Handle for lifting

were used, the volumes ranged from about 35 to 60 ml.

General Description. The calorimeter described above is exactly the same as described by Vani⁴² with the following exceptions.

Heaters: Only two heaters used -- the pipet heater was not used.

Stirrer: The stirrer was a 2 mm glass shaft with only 2 sets of propeller shaped blades as opposed to Vani's 4 sets.

Calorimeter Number Two

Introduction. The small microcalorimeter will be described in detail since the major portion of the work was performed with it. A very good analysis of design consideration, such as volume, size, and accuracy, is given by Petree.²⁰ The calorimeter was one half of an adiabatic, double microcalorimeter originally intended for a twin calorimeter, but not used as such because of a flaw in electronic design which produced a high noise level when both Dewar cells were being monitored simultaneously. The two calorimeters could be used, however, by two people to run two different experiments which did not require simultaneous monitoring. The advantage was that by heating each Dewar's contents with the same power supply, with the heaters inside the calorimeters in series, the heating times were lessened considerably.

Vessels. The vessels were Dewar cylinders⁴⁴ with internal capacity of approximately 240 ml. It was necessary to employ Dewar vessels to minimize radiation and conduction contributions to thermal

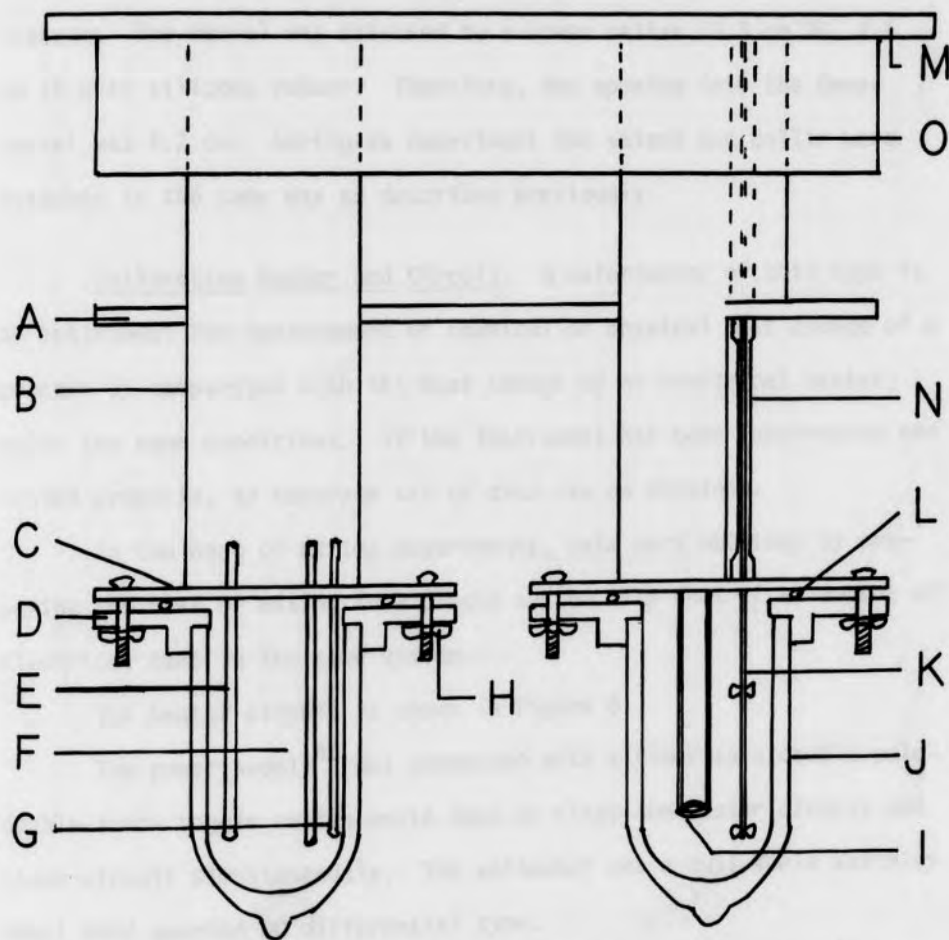


Figure 5. Double Micro-calorimeter

- A. 12 x 8 x 1/4 in brass plate
- B. Half-cylinder brass superstructure
- C. Brass lid
- D. Brass collar
- E. Thermistor
- F. Rough heater
- G. Calibration heater
- H. Brass wingnut

- I. Teflon^R pipet holder
- J. 10 oz Dewar flask
- K. Glass stirrer
- L. "O" rings
- M. 20 x 12 x 1/2 inch plywood
- N. 5 mm Trubore^R bearing
- O. Styrofoam

Note: Right calorimeter rotated 90°

leakage. The vessel was attached to a brass collar 13.3 cm OD, 4.7 cm ID with silicone rubber. Therefore, the opening into the Dewar vessel was 4.7 cm. During an experiment the vessel and collar were attached in the same way as described previously.

Calibration Heater and Circuit. A calorimeter of this type is an instrument for measurement of chemical or physical heat change of a process by comparison with the heat change of an electrical heater under the same conditions. If the instrument has been constructed and tested properly, an accurate set of data can be obtained.

In the heat of mixing experiments, data were obtained by comparing the heat of mixing in a closed system with that of an amount of electrical heat in the same system.

The heater circuit is shown in Figure 6.

The power supply⁴⁵ was connected with a timer so a double-pole-double-throw toggle switch would open or close the heater circuit and timer circuit simultaneously. The voltmeter was a null scale Keithley Model 660A guarded DC differential type.

The calibration heater was constructed of Evanohm^R wire⁴⁶ (126 ohm/ft) with #24 Teflon^R coated wire as leads. The leads were soldered with rosin core solder and low emf soldering paste to reduce resistance due to soldered joints. The heater wire was coiled around a 2 mm piece of pyrex tubing which was then inserted into a 5 mm pyrex glass well filled with silicone oil to facilitate even thermal conductance. The

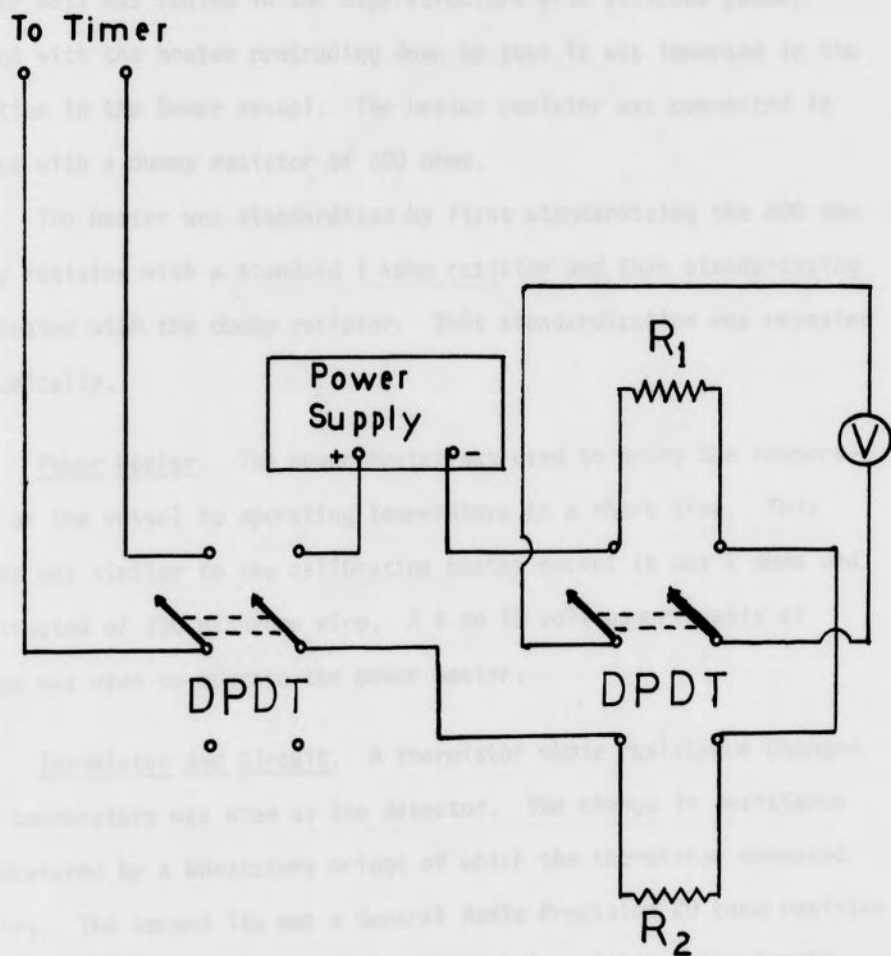


Figure 6. Calibration Heater Circuit

R_1 . Dummy resistor

R_2 . Calibration heater

heater well was sealed in the superstructure with silicone rubber cement with the heater protruding down so that it was immersed in the solution in the Dewar vessel. The heater resistor was connected in series with a dummy resistor of 500 ohms.

The heater was standardized by first standardizing the 500 ohm dummy resistor with a standard 1 kohm resistor and then standardizing the heater with the dummy resistor. This standardization was repeated periodically.

Power Heater. The power heater was used to bring the temperature of the vessel to operating temperature in a short time. This heater was similar to the calibration heater except it was 2 ohms and constructed of #30 nichrome wire. A 6 to 15 volt power supply at 3 amps was used to operate the power heater.

Thermistor and Circuit. A thermistor whose resistance changed with temperature was used as the detector. The change in resistance was measured by a Wheatstone bridge of which the thermistor composed one leg. The second leg was a General Radio Precision 20 kohm resistor. The third leg was an adjustable (1 - 10 kohm) resistor. The fourth leg was a precision decade resistor⁴⁷ adjustable to 0.1 ohm. It was set on approximately 20 kohm in these experiments. The thermistor used was a 10 kohm type imbedded in a glass bead and soldered to the lead wires with low emf solder (all solder joints in the thermistor circuit were low emf to prevent electrical noise). The solder joints of the thermistor were insulated with electrical spaghetti (heat shrinkable

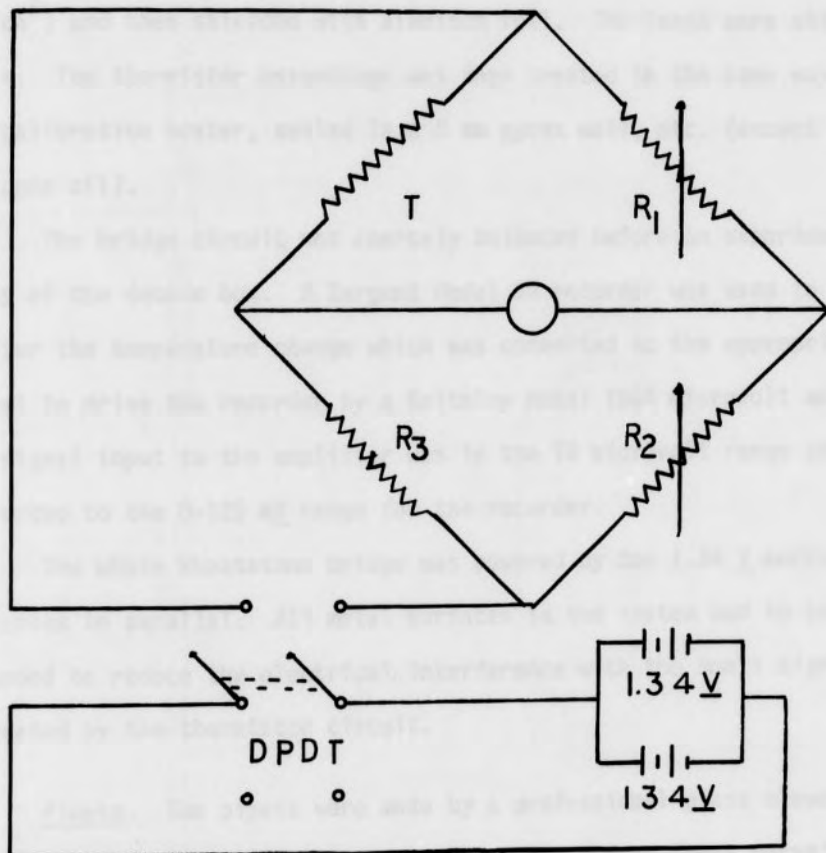


Figure 7. Thermistor Circuit

- R_1 . 1-10 kohm adjustable resistor
- R_2 . Decade resistor
- R_3 . 20 kohm standard resistor
- T. Thermistor
- A. Keithley Model 150A microvolt ammeter

Teflon^R) and then shielded with aluminum foil. The leads were shielded cable. The thermistor assemblage was then treated in the same way as the calibration heater, sealed in a 5 mm pyrex well, etc. (except for silicone oil).

The bridge circuit was coarsely balanced before an experiment by means of the decade box. A Sargent Model SR recorder was used to monitor the temperature change which was converted to the appropriate signal to drive the recorder by a Keithley Model 150A microvolt ammeter. The signal input to the amplifier was in the 10 microvolt range and was converted to the 0-125 mV range for the recorder.

The whole Wheatstone bridge was powered by two 1.34 V mercury batteries in parallel. All metal surfaces in the system had to be grounded to reduce the electrical interference with the small signal generated by the thermistor circuit.

Pipets. The pipets were made by a professional glass blower and were 65 mm long with 15 mm glass tubing on the ends. These weren't true pipets but open ended bottles fitted with Teflon^R rims and stoppers to match. The rims were epoxied to each end of the pipet and the stoppers were epoxied onto a 3 mm glass shaft. The rims and stoppers were shaped on a lathe and the stoppers had a groove around the circumference in which to place a small rubber "O" ring for sealing purposes. During the experiment the solution inside the pipet was sealed by silicone grease. The shaft of the pipet was cemented with ferrule cement to another larger (4 mm) shaft which contained a 5 mm Trubore^R bearing in its middle. The pipet was filled by a syringe

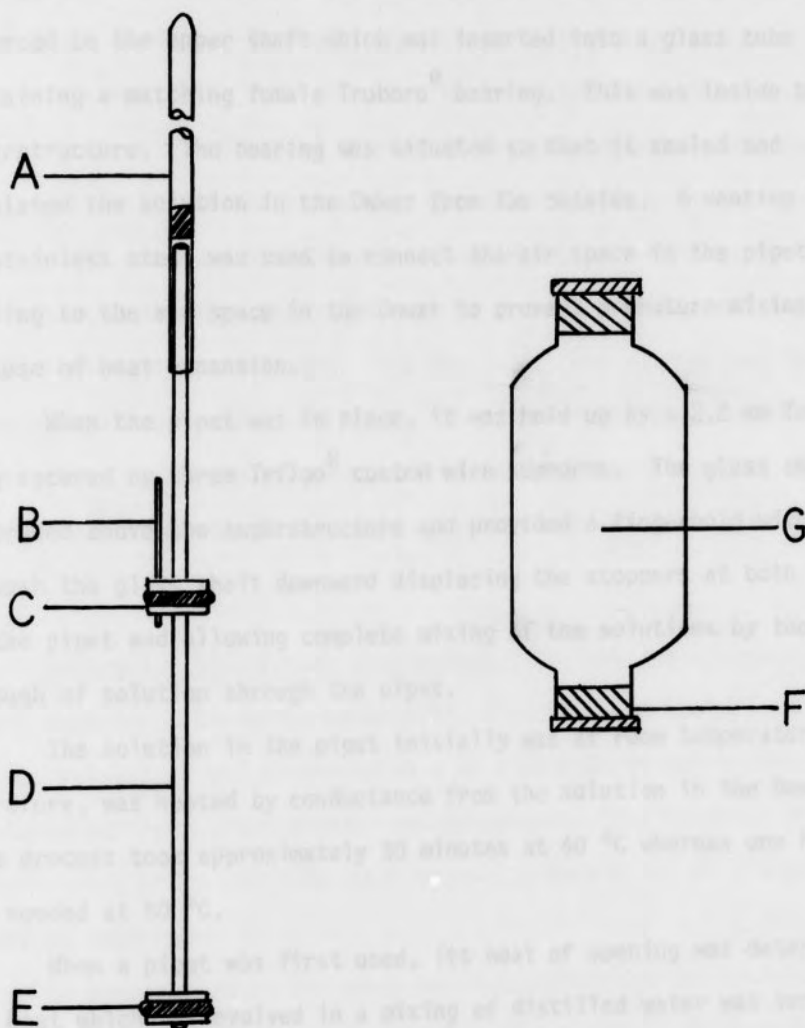


Figure 8. Pipet and Plunger

- | | |
|--------------------------------------|-------------------------------|
| A. 5 mm Trubore ^R bearing | D. 3mm glass tubing |
| B. Vent | E. "O" ring |
| C. Teflon ^R stopper | F. Teflon ^R sheath |

through a small hole in the Teflon^R stopper. This assembly was then cemented to the upper shaft which was inserted into a glass tube containing a matching female Trubore^R bearing. This was inside the superstructure. The bearing was situated so that it sealed and insulated the solution in the Dewar from the outside. A venting tube of stainless steel was used to connect the air space in the pipet after filling to the air space in the Dewar to prevent premature mixing because of heat expansion.

When the pipet was in place, it was held up by a 2.2 mm Teflon^R ring secured by three Teflon^R coated wire supports. The glass shaft protruded above the superstructure and provided a fingerhold with which to push the glass shaft downward displacing the stoppers at both ends of the pipet and allowing complete mixing of the solutions by the flow-through of solution through the pipet.

The solution in the pipet initially was at room temperature and, therefore, was heated by conductance from the solution in the Dewar. This process took approximately 30 minutes at 40 °C whereas one hour was needed at 80 °C.

When a pipet was first used, its heat of opening was determined. The heat which was evolved in a mixing of distilled water was very slight; nevertheless, a corrective factor was determined. The heats of opening ranged from 0.000 to 0.008 \pm 0.004 cal.

Stirrers. The solution must of necessity be stirred to promote thermal equilibrium with the surroundings and the pipet and to effect a complete and fast mixing when the pipet is opened. The stirrer was

constructed from 3 mm glass rod containing a short length of 5 mm Trubore^R glass bearing. Four glass paddles were attached to the end and 5 cm from the end. The stirrer exited the solution via a glass tunnel with a female glass Trubore^R bearing in the same manner as did the pipet shaft with the exception that the superstructure was so designed as to permit contact with the stirrer enclosure and water bath. This permitted any friction generated heat to be radiated into the bath rather than into the solution. The bearing of the stirrer was lubricated with glass bearing lubricant. The stirrer shaft protruded from the superstructure and was clasped by an arrangement of rubber tubing and gear wheel which allowed it to be rotated at 427.5 rpm by a small motor.⁴⁸

Controlled Temperature Environment. The controlled temperature environment was a 47 gallon water bath, a two ft in diameter, stainless steel, cylindrical vat contained in a 29 x 29 x 28 in wooden box, insulated by fiber glass padding and polystyrene foam blocks. Stirring was effected, using a 1/2 hp motor driving a double set of flanged blades at 1880 rpm.

The temperature of the water bath was controlled by a constant leak temperature control consisting of a Thermotrol,⁴⁹ which works on a short input heating cycle, and 25 feet of coiled copper tubing through which cooling water flowed to remove heat. A knife heater coupled with the Thermotrol supplied heat.

The calorimeter was standardized by Linda Petree²⁰ and confirmed by Danne Smith.²⁰

Solutions

Preparation, Standardization and Analysis. Water for all solutions was twice deionized to remove traces of chloride and other impurities. Solutions of NaCl and KCl were made from Mallinkrodt analytical reagent salts. LiCl used was from Research Inorganic Chemicals. The stock solutions were made about 4 m. The exact concentrations were determined by the silver gravimetric method. 0.5 m solutions were then made by dilution of the stock by the method of Vani.⁴²

Because of the cost of tetrapropylammonium chloride, the decision was made to prepare it from tetrapropylammonium iodide, a less expensive salt. Tetrapropylammonium iodide was obtained from Eastman Organic Chemicals. This tetrapropylammonium iodide was dried in vacuo at 60 to 80°C for three days. Gravimetric analyses were then performed, the precipitate being silver iodide. Results were 99.53% \pm 0.04% pure. Another test was run, drying the $(n-C_3H_7)_4NI$ in an Abterhalter drying pistol in vacuo and at a constant temperature of 63 °C by bathing the pistol in the vapors of boiling methyl alcohol. This was continued overnight and then the samples were analyzed as quickly as possible after being exposed to the air. This test gave a 99.90% purity which was deemed satisfactory. A pH titration was run on the sample after dissolving in H₂O and refluxing at 80 °C for 8 hours. The results showed no free ammine present.

An ion-exchange column on the Cl⁻ cycle was prepared to exchange the I⁻ in $(n-C_3H_7)_4NI$ to Cl⁻ giving the desired $(n-C_3H_7)_4NCl$. The

77 mm long column was constructed from 30 mm glass tubing. The resin used was Dowex 2-X4⁵⁰ of which the column held approximately 270 grams. The exchange capacity of the resin was 3.1 meq/g, giving a total exchange capacity for the column of approximately 0.83 eq. The solubility of $(n-C_3H_7)_4NI$ was such that less than a 1 m solution could be made. As this solution was run through the column, small samples were tested for the presence of iodide after each 100 ml of effluent by a 2% starch solution. At the first sign of iodide, the 100 ml of effluent preceding that fraction was reserved to be run a second time through the column, after regeneration. Regeneration was effected by backwashing the column with 3 m HCl (about 20 liters), then washing the column until the last traces of Cl^- were removed as shown by a $AgNO_3$ test. The very dilute $(n-C_3H_7)_4NCl$ was then put in vacuum desiccators to be concentrated isopiesticly, with CaCl as the hydrophilic agent. This process concentrates the salt solution in about 10 days to approximately 4 m. It was assumed that because of the precautions taken with the column (washing it free of Cl^- , rerunning the 100 ml fraction of the solution before the starch test became positive) that the $(n-C_3H_7)_4NCl$ was as pure as the $(n-C_3H_7)_4NI$ that was used to make it. The $(n-C_3H_7)_4NCl$ solution was then standardized by the $AgCl$ gravimetric procedure. As a precautionary measure, precipitation of the $(n-C_3H_7)_4N^+$ ion was effected with sodium tetraphenyl boron⁵¹ and found to be within 0.1% of the $AgCl$ value. Atomic absorption studies of possible impurities in the alkali metal chlorides were done by Petree²⁰ and since the salts used in the present study

were from the same company, it was decided not to repeat this test and to assume the impurities were approximately the same with no corrections necessary.

Since the heats of mixing took place at a temperature higher than ambient, a concentration check was made after each set of experiments at 40-, and 60-, and 80-°C by means of the Fajan's method of chloride ion analysis.⁵² The transfer method of Petree²⁰ was used at all temperatures to insure consistency. The only anomaly encountered in these analyses was that at 80 °C, each solution at the end of the set of experiments was found to be about 0.5% more concentrated. No reason could ever be found except the speculation that some evaporation did take place at this higher temperature.

Mixing Procedure. The pipet and Dewar vessel were filled with the proper solutions at room temperature. The pipet was first fitted with the stoppers and weighed, then filled with a syringe, reweighed, and fitted into the instrument as previously described. The contents of the Dewar vessel and pipet were weighed to approximately 0.1%. The air space in the pipet and vessel was minimized to reduce evaporation and heat leak by convection. A small air space was maintained to prevent the solution from touching the brass collar, which would affect the experiment because of severe heat conduction. After the initial pure solutions in both the pipet and vessel were mixed, a portion of the mixed solution was placed in the vessel with pure solution in the pipet again, and a second experiment performed. This procedure allowed heats of mixing to be determined in the mole fraction range of 0.0 to

0.2 and 0.8 to 1.0.

The calorimeter, complete with solutions, was immersed in the water bath and the contents were heated to the mixing temperature, about 0.02 °C below the water bath temperature. Equilibrium was complete when the recorder trace of thermistor resistance vs time was essentially straight. A foreslope was then recorded. If the foreslope was nearly linear and shallow with the amplifier on the 10 microvolt scale and recorder on the 125 mV scale, the pipet was opened. The sensitivity was reduced because mixing was rapid and the heat produced would cause the recorder to travel quickly off scale. After the initial heat change which usually occurred in 1 to 2 minutes, the decade resistance was changed to rebalance the bridge. The amplifier was then returned to the 10 microvolt scale and an afterslope was recorded. The change in resistance is, of course, related to the heat change. The foreslope and afterslope usually did not coincide and a correction factor was used. The correction was made at the point where 50% of the heat of mixing had been detected. The correction was calculated as the sensitivity of the recorder times the number of divisions of recorder paper between the foreslope and afterslope at that time (the horizontal distance between an extrapolation of the two lines). The total resistance change was the final resistance minus the initial resistance plus the correction term.

$$\underline{R}_D = \underline{R}_D^f - \underline{R}_D^i + C$$

The heat capacity of the calorimeter and contents was then obtained and used to convert the resistance readings into calories, using any

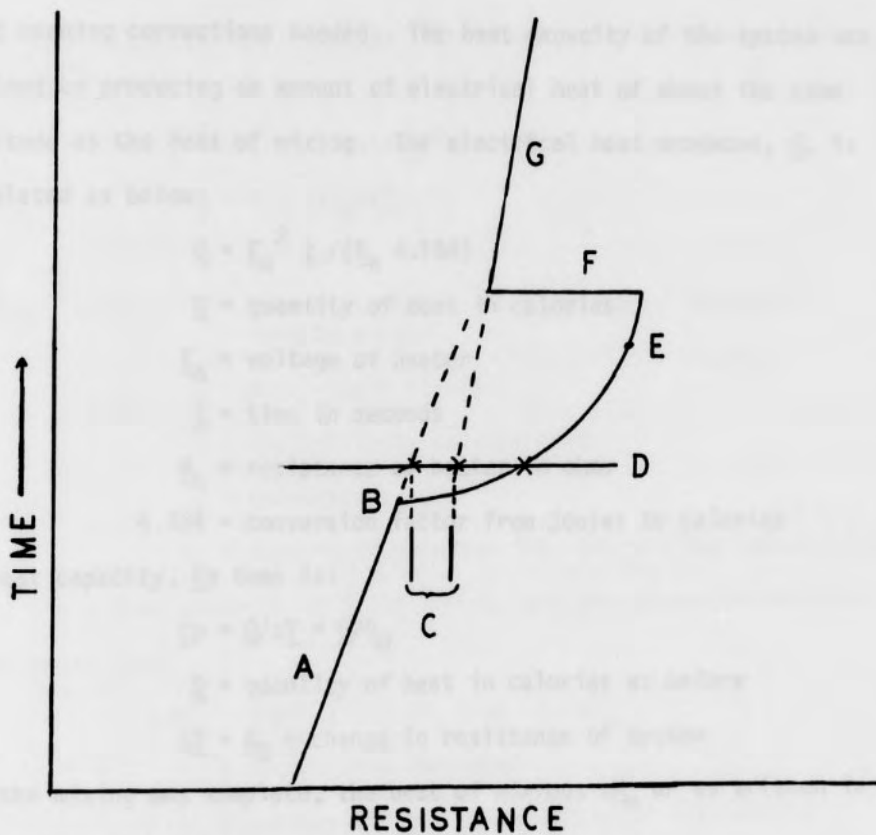


Figure 9. Resistance vs Time

(As in actual heat of mixing experiment)

- | | |
|---|------------------------|
| A. Foreslope | D. 50% of heat evolved |
| B. Pipet opening | E. 99% of heat evolved |
| C. Correction factor in scale divisions | F. Resistance change |
| | G. Afterslope |

pipet opening corrections needed. The heat capacity of the system was obtained by producing an amount of electrical heat of about the same magnitude as the heat of mixing. The electrical heat produced, Q , is calculated as below:

$$Q = \frac{E_h^2 t}{R_h} (4.184)$$

Q = quantity of heat in calories

E_h = voltage of heater

t = time in seconds

R_h = resistance of heater in ohms

4.184 = conversion factor from joules to calories

The heat capacity, C_p then is:

$$C_p = \frac{Q}{\Delta T} = \frac{Q}{R_D}$$

Q = quantity of heat in calories as before

$\Delta T = R_D$ = change in resistance of system

When the mixing was complete, the heat of mixing, ΔH_m or as written in the Fortran program DELH, was calculated as:

$$\text{DELH} = C_p \Delta T_m$$

C_p = heat capacity from the electrical calibration

ΔT_m = the change of resistance corrected for heat of opening of the pipet

DELH was then used in the Fortran least squares program. See Appendix B for sample experiment and Appendix C for symbols and units.

Each experiment was done in duplicate to give at least twelve mixing experiments at a given temperature. Vani⁴² gives a complete analysis of the mole fractions of salts in the vessel after each mixing.

Data Treatment and Results. The excess enthalpy of mixing is given by:⁵³

$$\Delta H_m^{\text{ex}} = \underline{I}^2 RT y(1-y) \sum h_p Y^p, \quad p = 0, 1, 2, \dots$$

$$h_p = - \underline{I} [\partial g_p / \partial \underline{I}]$$

$$Y = 1 - 2y$$

y = mole fraction of the salt having largest formula weight

\underline{I} = molal ionic strength

\underline{R} = gas constant, cal/deg mole

\underline{T} = temperature, °K

g_p = measure of pairwise like-charged ion interactions

The actual research data was fitted to a two parameter equation of the above type.

$$\Delta H_m = \underline{I}^2 RT X (1-X) [h_0 + h_1 (1-2X)]$$

h_0 = interaction parameter

h_1 = measure of skew or asymmetry of interaction

X = mole fraction of salt of the largest molecular weight

Rearranging and substituting:

$$A = \underline{I}^2 RT h_0$$

$$B = \underline{I}^2 RT h_1$$

We have:

$$\Delta H_m = X(1-X) [A+B(1-2X)]$$

yielding a simpler equation.

The experimental data obtained from actual heats of mixing were fitted to this equation by the method of least squares. The least

squares equation was programmed in Fortran and run on an IBM 360-75 computer. The Fortran program is treated in depth in Petree's thesis.²⁰ The experimental values of the heat of mixing were entered as DELH where:

$$\text{DELH} = X(1-X) [A+B(1-2X)]$$

for each experimental point. The least squares program calculated A and B and then calculated the equation for the parabola about $y = 0.5 \underline{m}$ and picked enthalpy values corresponding to the mole fractions used in the mixings. It then compared them with the experimental values of DELH. Since each mixing was a re-mix of the prior solution and pure solution, the calculated value, H_{CALC} had to account for the remixing.

$$\text{H}_{\text{CALC}} = \Delta \underline{H}(\text{WTSF}) - \Delta \underline{H}(\text{WTSI})$$

$$\text{H}_{\text{CALC}} = A(F_2) - B(F_3)$$

WTSF = final weight of solution

WTSI = initial weight of solution

$$F_2 = XF(1-XF) - XI(1-XI)(\text{WTSI})$$

$$F_3 = XF(1-SF)(1-2XF) - XI(1-XI)(1-2XI)(\text{WTSI})$$

I = initial condition

F = final condition

DELH = heat obtained by mixing

H_{CALC} = the least squares interpretation of the heat from the smoothed curve

The least squares program also evaluates the parameters \underline{RTh}_0 and \underline{RTh}_1 at $y = 0.5 \underline{m}$. By using Friedman's equation one can calculate the heat of mixing at $y = 0.5 \underline{m}$ of the salt pair involved. The actual parameters come out as $A = \underline{I}^2 \underline{RTh}_0$ and $B = \underline{I}^2 \underline{RTh}_1$ making it a simple

matter to substitute the values directly into the equation. The values, however, are not absolute because of the fact that they are extrapolations (the experimental heats of mixings are not in the actual vicinity of 0.5 m). See Table I for results.

The program tested each value of DELH for significance of RTh_0 , using a statistical "F" test at 95% confidence limits. When a point was wrong either intuitively or by a statistical test, it was rejected and the remaining data fitted to the least squares equation. Intuitive means the value was obviously off the standard enough that a statistical test was not needed to realize the error. The limits of error as listed in Table I are from the Student's "t" distribution.

Errors. The major sources of determinate error in this type of calorimetric work are the experimental limitations in measuring the heats of mixing, uncertainties of concentration which may arise either from stock solution dilutions or actual evaporations at the higher temperatures, and ion impurities. Most of these errors were negligible for the heats of mixing as calculated by least squares were accurate at most to 1 cal/mol.

Sources of random error were static electricity contributing electrical noise, shifts of air currents in the calorimeter laboratory and anything which affected the ambient temperature. The errors of the RTh_1 term are large and it is not known to what they are attributed. Most of the values are the same within experimental error. The major error in the experiments, however, arose from the inaccuracies in the slope extrapolations as they were not always ideal to measure.

DISCUSSION OF RESULTS

Upon examining the interaction parameters of the heats of mixing, it was noticed that the RTh_0 values were all large negative values of about the same magnitude and showed very slight temperature dependence. These large negative values are thought to be interactions between two large tetrapropylammonium ions which mask other effects in the solution.³⁷

Friedman⁵³ predicted that like-charged ions should have some specific interactions and that these interactions should be more important than triplet interactions for many systems. This must be true in the case of tetrapropylammonium ions for the RTh_0 parameter, which is a measure of the magnitude of pairwise interactions, is large and negative; and RTh_1 , which is a measure of asymmetry of the heat of mixing parabola about $y = 0.5$ m , is a significant negative number but not nearly as large as RTh_0 . RTh_1 is important as it shows that the triplet interactions are not insignificant. It is purely a measure of skew and does not contribute to the RTh_0 term because $X(1-X)$ is orthogonal to $X(1-X)(1-2X)$ in the Friedman equation.

Several reports^{29, 37, 54} have indicated that most of the heating effect, entropies, partial molal volumes, etc., could be explained by the overlap of the hydration sheaths of the tetraalkylammonium ions as explained in the introduction. If this is correct then both heats of mixing and heats of dilution are rough measures of the

heats of interactions of two tetrapropylammonium ions. Assuming this is correct, the large negative \underline{RTh}_0 values obtained justify the speculation that there is a large interaction of tetrapropylammonium ions at each temperature examined. Also, if the \underline{RTh}_1 value is a measure of triplet interactions, then the significant negative value of \underline{RTh}_1 indicates that triplet interactions are important in these heats of mixings.

The most striking feature of the heats of mixing obtained in this study is the fact that \underline{RTh}_0 values are of relatively the same magnitude and \underline{RTh}_1 values are even more identical with one another. Interchanging the cations used to mix with tetrapropylammonium ions changes \underline{RTh}_0 only about 50% and changes \underline{RTh}_1 very little. This implies that $\text{Pr}_4\text{N}^+ \text{--} \text{Pr}_4\text{N}^+$ interactions are somewhat dominant throughout [$\text{Pr}_4\text{N}^+ = (\text{n-C}_3\text{H}_7)_4\text{N}^+$]. The relative steadiness of \underline{RTh}_1 with respect to change of cation must mean that the $\text{Pr}_4\text{N}^+ \text{--} \text{Pr}_4\text{N}^+ \text{--} \text{Pr}_4\text{N}^+$ triplet interactions are dominant. These conclusions are thought to be correct because the difference in the size and charge density of the Li^+ , K^+ and Na^+ ions do not seem to cause a change of \underline{RTh}_0 in any pattern. The Li^+ ion is a small-sized structure-maker, the K^+ ion is a medium-sized structure-breaker, and the Na^+ ion is a borderline case whose structure-affecting tendencies seem to change with temperature.⁴¹ It appears to become a structure-breaker as temperature rises. There seems to be some correlation between the cation used and the \underline{RTh}_0 value. The $\text{Li}^+ \text{--} \text{Pr}_4\text{N}^+$ mixing has the largest negative \underline{RTh}_0 value. The $\text{K}^+ \text{--} \text{Pr}_4\text{N}^+$ mixing \underline{RTh}_0 value is next and the $\text{Na}^+ \text{--} \text{Pr}_4\text{N}^+$ value last

or smallest in value. This correlation does not fall into any discernible pattern because it does not increase or decrease with either molecular weight, ionic radius, or structure-enforcing ability (known). This change in RTh_0 may be the result of some pairwise interactions between the Na^+ , K^+ , or Li^+ and Pr_4N^+ ions. These interactions do not seem to be as strong as $Pr_4N^+--Pr_4N^+$ RTh_0 but strong enough to influence it noticeably. The most confusing results are that at 80 °C the heat of mixing and RTh_0 are still quite large and relatively unchanged for all three alkali ions. It was expected⁵⁵ that the structure of the solution would break down around 80 °C and give a much smaller heat of mixing. Ackermann⁵⁶ found that the partial molal heat capacities exhibit a maximum in the region 60 to 80 °C. This was postulated to be due to a degradation of the second hydration shell. Ackermann also found that the primary hydration shell of an ion is practically unaltered at 130 °C. From these observations and from the knowledge that Pr_4N^+ ions act to enforce the water structure (in introduction), and that bulk water structure probably breaks down around 80 °C, one is at a loss as to why so much structure seemingly remains at 80 °C. Also the $Pr_4N^+--Pr_4N^+$ interaction is still relatively the same with only a small decrease. Another basis for expecting the heat of mixing to decrease rapidly was the experiment reported by Eley⁵⁷ in 1939. He reported that when an inert gas molecule such as argon was dissolved in water at room temperature, the heat of solution was large but at 80 °C the heat of solution went to zero. The argon molecule was thought to structure the water about it at room temperature but at 80 °C the high temperature

prevented any water structure from being formed. The argon molecule was thought to be a large structure-forming ion, much like the large quaternary ammonium ions. This data shows that they apparently do not form structure in the same way.

It would appear that the heat of mixing (heat of dilution of the ions) of Pr_4N^+ is probably caused by the Pr_4N^+ ion completing its hydration shell. At 80 °C the Pr_4N^+ seems to complete that shell to about the same degree as at room temperature. The implication that any structuring is involved here may not be completely justified as interactions may exist that are not understood and some other effect may be causing the large \underline{RTh}_0 .

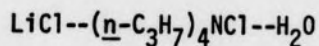
The relative stability of \underline{RTh}_1 supports the concept of $\text{Pr}_4\text{N}^+--\text{Pr}_4\text{N}^+--\text{Pr}_4\text{N}^+$ triplet interaction, for if pairwise interactions are unaffected by temperature it seems likely that the triplet interactions are also relatively unaffected, causing the major part of the skew. Reilly and Wood⁵⁸ show that triplet interactions such as $(\text{M}^+, \text{N}^+, \text{M}^+)$, $(\text{M}^+, \text{M}^+, \text{M}^+)$, $(\text{N}^+, \text{N}^+, \text{N}^+)$, and $(\text{N}^+, \text{M}^+, \text{N}^+)$, where N^+ is an alkali metal, contribute to the \underline{RTh}_1 parameter. We can eliminate $(\text{N}^+, \text{N}^+, \text{N}^+)$ by showing that \underline{RTh}_1 is insignificant for the cations used in this experiment (Li^+ , K^+ , Na^+)^{20, 58} other than the Pr_4N^+ cation. We can also eliminate $(\text{M}^+, \text{N}^+, \text{M}^+)$ by interchanging cations and showing that \underline{RTh}_1 is still relatively the same even though the cations are very different, as discussed above. This same analysis also eliminates the $(\text{N}^+, \text{M}^+, \text{N}^+)$ interaction leaving only the $(\text{M}^+, \text{M}^+, \text{M}^+)$ interaction to account for \underline{RTh}_1 . This evidence is not strong enough to say that these

interactions are the cause of the constancy of RTh_1 but it is evidence enough to justify more research on the matter.

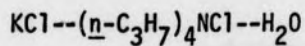
Solute-Solvent Relationships. For most common-ion heats of mixing that have been previously measured, a simple rule has been followed: the mixing of two structure-makers or two structure-breakers gave endothermic heats of mixing, while a structure-maker mixed with a structure-breaker gave an exothermic heat of mixing.³⁷ There are uncertainties and exceptions, such as the Na^+ ion. Under some conditions it is a structure-maker, and under others it is a structure-breaker.

This study does not throw any light on these classifications, for Pr_4N^+ ion is a large hydrophobic structure-maker and theoretically, upon mixing with Li^+ ion, the heat should be endothermic. It turns out that all the heats of mixing³⁷ of Pr_4N^+ and other ions have been large negative values at 25 °C. This again suggests that two large Pr_4N^+ ions are interacting to yield some or most of this large heat effect.

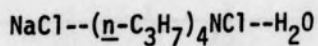
TABLE I

Heat of Mixing

<u>I</u>	Temp °C	<u>RTh</u> ₀	<u>RTh</u> ₁	<u>ΔH</u> _m
0.5	25	-693+3.8 ^a	-33.0+6.1 ^a	-43.3
0.5	40	-696+3	-31.2+4.4	-43.5
0.5	60	-668.2+4.3	-32.4+5.9	-41.8
0.5	80	-592+13	-19+18	-37.0



0.5	25	-348+4 ^a	-39+5 ^a	-21.8
0.5	40	-373+5	-20+8	-23.4
0.5	60	-354.4+3.5	-27+5	-22.2
0.5	80	-298+9	-23+12	-18.62



0.5	25	-	-	-
0.5	40	-294+2	-38+2.5	-18.4
0.5	60	-302.3+6	-9+9	-18.9
0.5	80	-252+3	-24+5	-15.8

^aR. H. Wood and H. L. Anderson, J. Phys. Chem., 71, 1871 (1967).

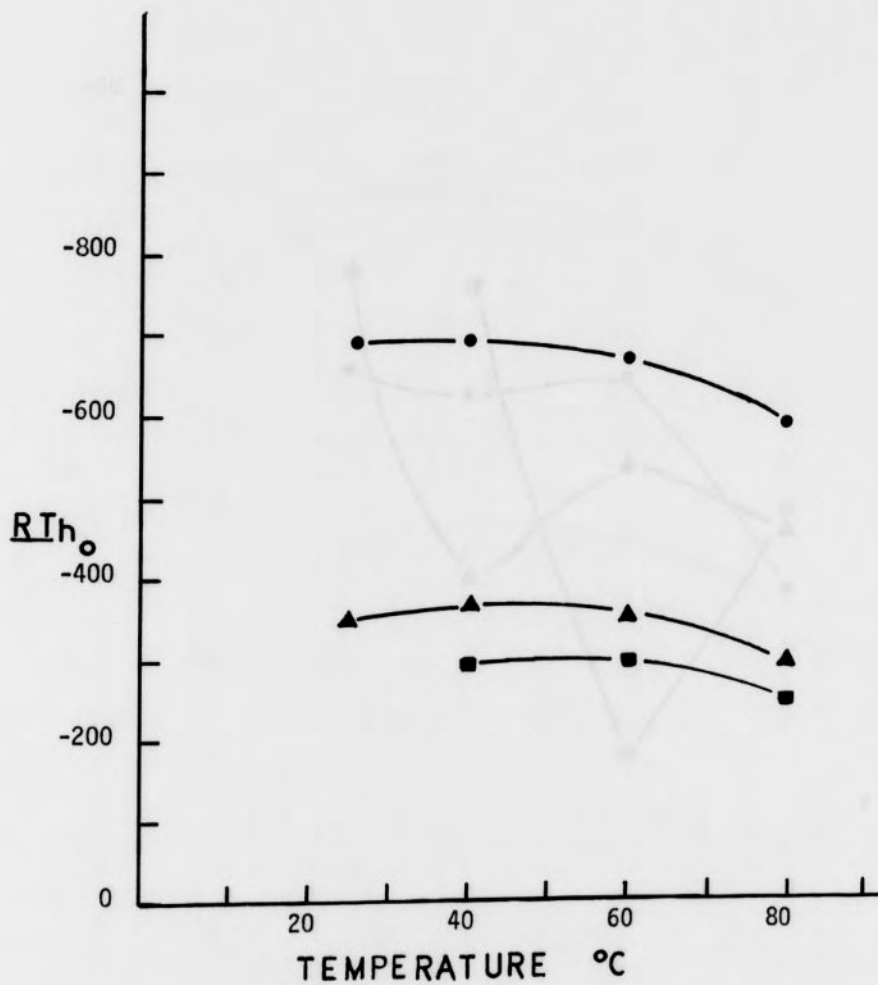


Figure 10. RTh_0 vs Temperature
 $y = 0.5 \text{ m}$

- = $LiCl--(n-C_3H_7)_4NC1$
- ▲ = $KCl--(n-C_3H_7)_4NC1$
- = $NaCl--(n-C_3H_7)_4NC1$

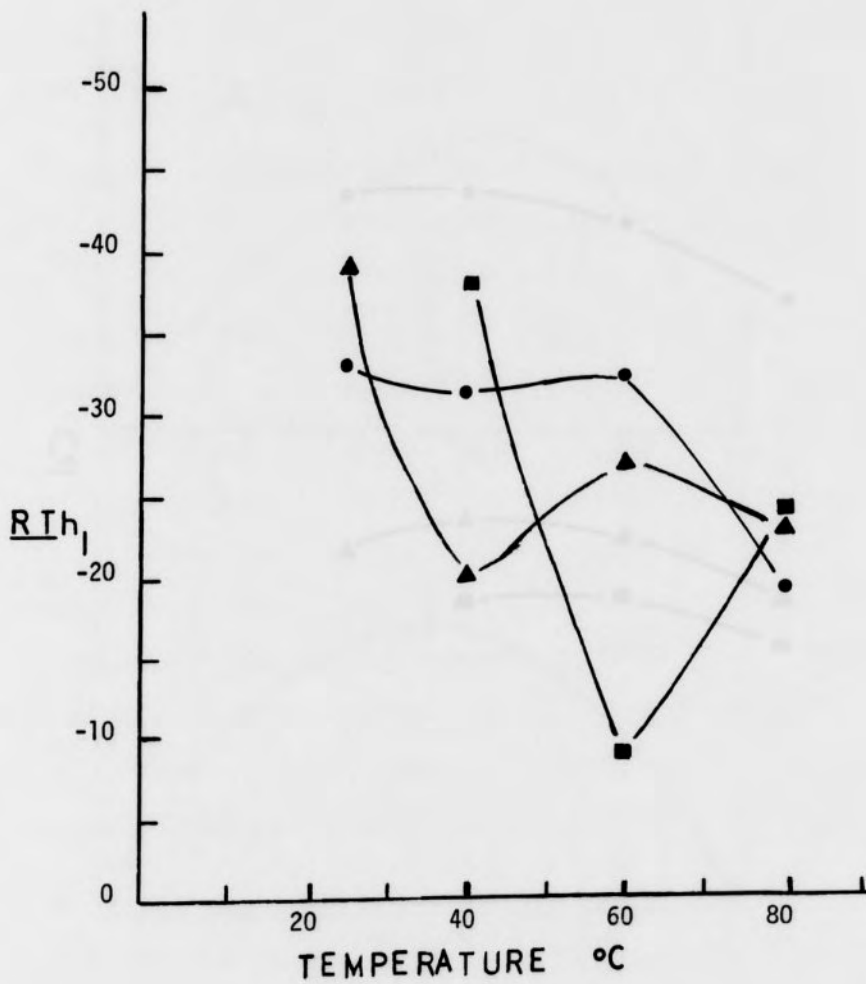


Figure 11. RTh_1 vs Temperature

$$y = 0.5 \underline{m}$$

- = LiCl--(n - C_3H_7) $_4NCl$
- ▲ = KCl--(n - C_3H_7) $_4NCl$
- = NaCl--(n - C_3H_7) $_4NCl$

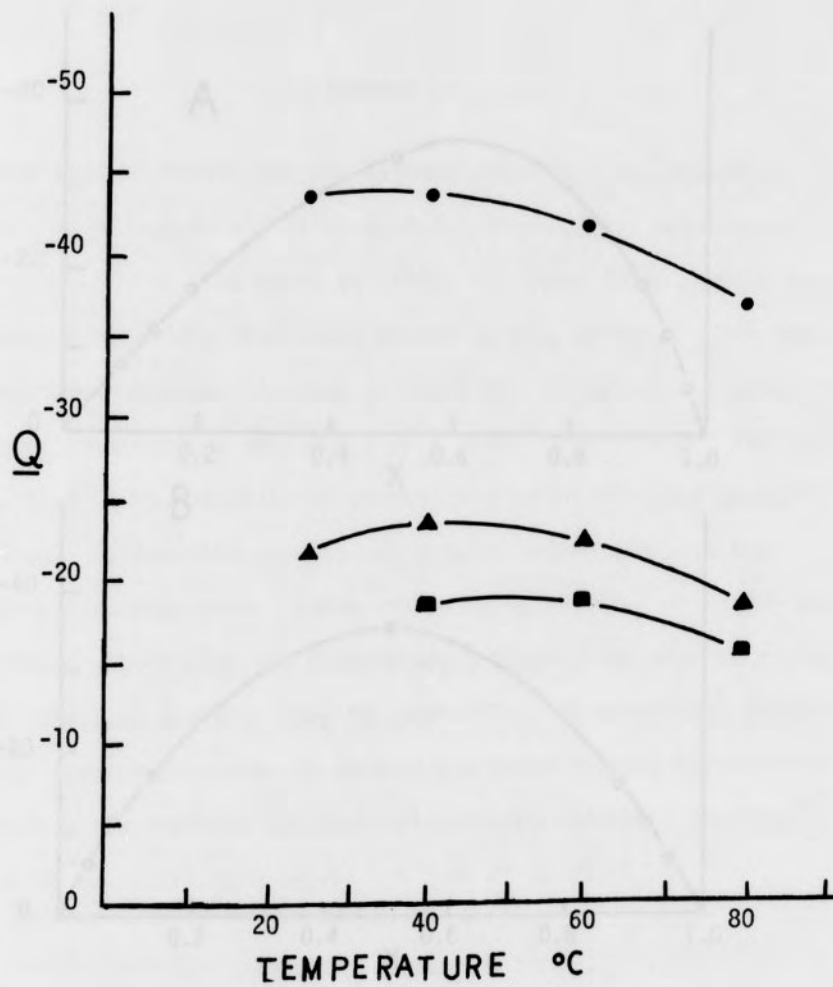
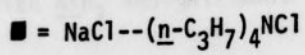
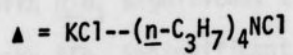
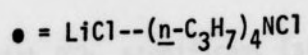


Figure 12. ΔH_m in Cal vs Temperature
 $y = 0.5 \underline{m}$



Q = ΔH_m in cal/mole

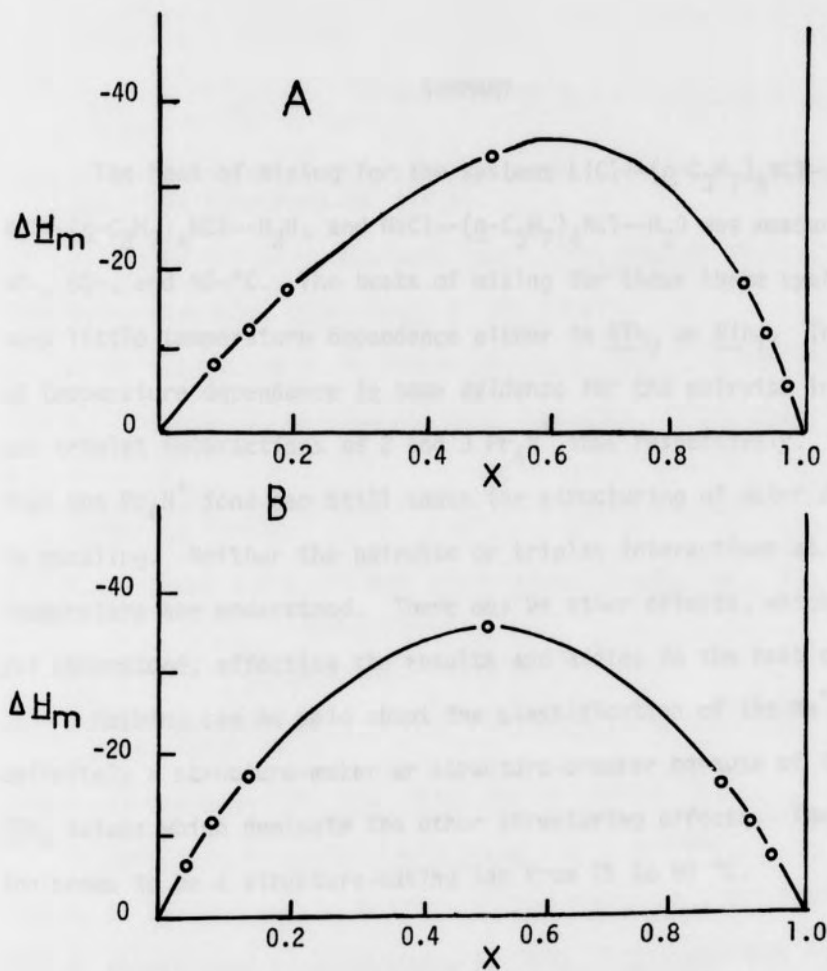


Figure 13. ΔH_m vs Mole Fraction

A = ΔH_m with RTh_1 significant (skewed curve).

B = ΔH_m with RTh_1 insignificant (symmetric curve).

SUMMARY

The heat of mixing for the systems $\text{LiCl}--(\underline{n}\text{-C}_3\text{H}_7)_4\text{NCl}--\text{H}_2\text{O}$, $\text{KCl}--(\underline{n}\text{-C}_3\text{H}_7)_4\text{NCl}--\text{H}_2\text{O}$, and $\text{NaCl}--(\underline{n}\text{-C}_3\text{H}_7)_4\text{NCl}--\text{H}_2\text{O}$ was measured at 40-, 60-, and 80-°C. The heats of mixing for these three systems show very little temperature dependence either in \underline{RTh}_0 or \underline{RTh}_1 . This lack of temperature dependence is some evidence for the pairwise interaction and triplet interactions of 2 and 3 Pr_4N^+ ions respectively. The fact that the Pr_4N^+ ions can still cause the structuring of water at 80 °C is puzzling. Neither the pairwise or triplet interactions at that temperature are understood. There may be other effects, which are not yet understood, affecting the results and adding to the heat of mixing.

Nothing can be said about the classification of the Na^+ ion as definitely a structure-maker or structure-breaker because of the large \underline{RTh}_0 values which dominate the other structuring effects. The Pr_4N^+ ion seems to be a structure-making ion from 25 to 80 °C.

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APPENDIX A

Heat of Mixing Data: Computer Fit

Symbols

DELH = Experimental heat of mixing

HCALC = Least squares calculation for heat of mixing

$$A = \frac{I^2 R T h_0}{\dots}$$

$$B = \frac{I^2 R T h_1}{\dots}$$

XI = Initial mole fraction of $(n-C_3H_7)_4NCI$ XF = Final mole fraction of $(n-C_3H_7)_4NCI$

TABLE A. I

LITHIUM CHLORIDE - TETRAPROPYLAMMONIUM CHLORIDE

MOLALITY = 0.5

X = TETRAPROPYLAMMONIUM CHLORIDE

TEMPERATURE = 40 °C

A = 174.1447; SA = 0.3427; B = 7.8229; SB = 0.5045; SYBC = 0.0166

DELH	HCALC	ERROR	XF	XI	W	F2	F3
2.77253	2.75473	0.01780	0.0638920	0.0000000	1.0000	0.0152222	0.0132771
2.39965	2.38174	0.01791	0.1237040	0.0638920	1.0000	0.0133034	0.0083121
2.06219	2.05898	0.00321	0.1798890	0.1237040	1.0000	0.0116184	0.0045639
2.76806	2.78569	-0.01763	0.0645340	0.0000000	1.0000	0.0153941	0.0134072
2.32458	2.34442	-0.01984	0.1235170	0.0645340	1.0000	0.0130954	0.0081702
2.06941	2.07366	-0.00425	0.1801760	0.1235170	1.0000	0.0117013	0.0045941
2.77416	2.77700	-0.00283	0.9243640	1.0000000	1.0000	0.0165786	-0.0140707
2.43755	2.41662	0.02092	0.8546260	0.9243640	1.0000	0.0142339	-0.0079422
2.11684	2.09627	0.02057	0.7905270	0.8546260	1.0000	0.0121967	-0.0035441
2.79655	2.80104	-0.00449	0.9235580	1.0000000	1.0000	0.0167209	-0.0141645
2.41508	2.42587	-0.01079	0.8537060	0.9235580	1.0000	0.0142866	-0.0079343
2.07627	2.09580	-0.01953	0.7893500	0.8537060	1.0000	0.0121915	-0.0034882

XM1 = 7.93155; XM2 = 0.48879; AO = 173.9801; SAO = 1.6343

TABLE A. I (contd.)

SUM ERRORS SQUARED = 0.690E-01; F = 240.4774; SYB = 0.0792

REGALTY = 3.3 X = TETRAHYDROFOLANOL TEMPERATURE = 66 °C

A = 167.2574; SA = 0.4525; B = 2.3386; SB = 0.5709; SYB = 0.4038

SELN	HCALC	ERROR	ST	ST	B	F2	F2
2.27070	2.27045	-0.00075	0.3614573	0.0000000	1.0000	0.0123044	0.0121325
2.28440	2.28405	-0.00035	0.3132100	0.0000000	1.0000	0.0120077	0.0088115
2.29230	2.29205	-0.00025	0.0644210	0.0000000	1.0000	0.0052807	0.0133153
2.30015	2.30030	0.00015	0.1207540	0.0000000	1.0000	0.0122853	0.0041175
2.30320	2.30145	-0.00175	0.9240070	1.0000000	1.0000	0.0165188	-0.0140096
2.30920	2.30622	-0.00298	0.5593020	0.3000000	1.0000	0.0141309	-0.0079023
2.32280	1.99873	-0.00407	0.7907200	0.0000000	1.0000	0.0121256	-0.0035004
2.30890	2.30835	-0.00055	0.3030320	1.0000000	1.0000	0.0157882	-0.0140001
2.28570	2.30541	-0.01971	0.8634750	0.5000000	1.0000	0.0141830	-0.0070100

XBT = 7.35306; YB2 = 0.46784; AD = 161.5009; SAD = 2.1367

SUM ERRORS SQUARED = 0.705E-01; F = 172.4176; SYB = 0.0937

TABLE A. II

LITHIUM CHLORIDE - TETRAPROPYLAMMONIUM CHLORIDE

MOLALITY = 0.5

X = TETRAPROPYLAMMONIUM CHLORIDE

TEMPERATURE = 60 °C

A = 167.0514; SA = 0.4525; B = 8.1398; SB = 0.6199; SYBC = 0.0198

DELH	HCALC	ERROR	XF	XI	W	F2	F3
2.61970	2.62045	-0.00075	0.0634670	0.0000000	1.0000	0.0150464	0.0131365
2.28440	2.28405	0.00035	0.1233100	0.0634670	1.0000	0.0132677	0.0083115
2.65350	2.66206	-0.00856	0.0644810	0.0000000	1.0000	0.0152867	0.0133153
2.30915	2.30533	0.00382	0.1251940	0.0644810	1.0000	0.0133950	0.0083136
2.63520	2.66146	-0.02626	0.9240870	1.0000000	1.0000	0.0166188	-0.0140956
2.30920	2.30662	0.00258	0.8543020	0.9240870	1.0000	0.0141929	-0.0079023
2.03280	1.99873	0.03407	0.7901250	0.8543020	1.0000	0.0121356	-0.0035054
2.70890	2.68835	0.02055	0.9232320	1.0000000	1.0000	0.0167852	-0.0142081
2.28620	2.30541	-0.01921	0.8534360	0.9232320	1.0000	0.0141830	-0.0078480

XM1 = 7.35306; XM2 = 0.48784; A0 = 166.5609; SA0 = 2.1357

SUM ERRORS SQUARED = 0.702E-01; F = 172.4176; SYB = 0.0937

TABLE A. III

LITHIUM CHLORIDE - TETRAPROPYLAMMONIUM CHLORIDE

MOLALITY = 0.5

X = TETRAPROPYLAMMONIUM CHLORIDE

TEMPERATURE = 80 °C

A = 147.9917; SA = 1.4207; B = 4.6989; SB = 1.8620; SYBC = 0.0459

DELH	HCALC	ERROR	XF	XI	W	F2	F3
1.71129	1.74402	-0.03273	0.0481430	0.0000000	1.0000	0.0114559	0.0103529
1.60143	1.56554	0.03589	0.0940220	0.0481430	1.0000	0.0103435	0.0074025
1.55090	1.56341	-0.01250	0.0936260	0.0478460	1.0000	0.0103290	0.0074065
1.41460	1.39977	0.01483	0.1371160	0.0936260	1.0000	0.0092995	0.0050079
1.70180	1.77793	-0.07613	0.9429000	1.0000000	1.0000	0.0123614	-0.0109497
1.64760	1.58949	0.05811	0.8893980	0.9429000	1.0000	0.0109719	-0.0072919
1.56740	1.59688	-0.02948	0.8879920	0.9418990	1.0000	0.0110214	-0.0072771
1.83380	1.79033	0.04347	0.9421443	1.0000000	1.0000	0.0124470	-0.0110067
1.61123	1.60377	0.00746	0.8877900	0.9421443	1.0000	0.0110688	-0.0073039

XM1 = 11.00627; XM2 = 0.49207; AO = 147.1606; SAO = 1.7863

SUM ERRORS SQUARED = 0.282E-01; F = 6.3639; SYB = 0.0593

TABLE A. III (contd.)

DELH	HOCAL	ERROR	XF	XI	W	WTSF	WTSI
1.71129	1.68586	0.02543	0.0481430	0.0000000	1.0000	0.2499910	0.2379550
1.60143	1.52216	0.07927	0.0940220	0.0481430	1.0000	0.2488500	0.2368560
1.55090	1.52002	0.03088	0.0936260	0.0478460	1.0000	0.2489280	0.2369590
1.41460	1.36851	0.04609	0.1371160	0.0936260	1.0000	0.2478070	0.2359160
1.70180	1.81911	-0.11731	0.9429000	1.0000000	1.0000	0.2295970	0.2164884
1.64760	1.61463	0.03297	0.8893980	0.9429000	1.0000	0.2305762	0.2174920
1.56740	1.62192	-0.05452	0.8879920	0.9418990	1.0000	0.2297400	0.2161530
1.83380	1.83171	0.00209	0.9421443	1.0000000	1.0000	0.2283500	0.2151380
1.66123	1.62889	-0.01766	0.8877900	0.9421443	1.0000	0.2293810	0.2161480

TABLE A. IV

POTASSIUM CHLORIDE - TETRAPROPYLAMMONIUM CHLORIDE

MOLALITY = 0.5

X = TETRAPROPYLAMMONIUM CHLORIDE

TEMPERATURE = 40 °C

A = 93.3896; SA = 0.5755; B = 5.0958; SB = 0.8822; SYBC = 0.0352

DELH	HCALC	ERROR	XF	XI	W	F2	F3
1.28381	1.28277	0.00104	0.8495990	0.9210430	1.0000	0.0141538	-0.0076612
1.10171	1.11705	-0.01534	0.7833866	0.8495993	1.0000	0.0121373	-0.0032282
1.49199	1.48689	0.00510	0.9217040	1.0000000	1.0000	0.0166894	-0.0140760
1.28524	1.29907	-0.01383	0.8495480	0.9217040	1.0000	0.0143346	-0.0077766
1.09642	1.07598	0.02044	0.7856960	0.8495480	1.0000	0.0116940	-0.0031631
3.30496	3.37491	-0.06995	0.0582430	0.0000000	1.0000	0.0344759	0.0304600
2.99569	2.97342	0.02227	0.1135380	0.0582430	1.0000	0.0307376	0.0201820
2.57809	2.57216	0.00593	0.1652815	0.1135380	1.0000	0.0268938	0.0118835
2.27037	2.27723	-0.00686	0.2145657	0.1652820	1.0000	0.0240686	0.0057838
3.42936	3.38708	0.04229	0.0584542	0.0000000	1.0000	0.0346010	0.0305558
3.01036	2.96508	0.04528	0.1136967	0.0584540	1.0000	0.0306528	0.0200990
2.61924	2.67443	-0.05519	0.1676453	0.1136967	1.0000	0.0279720	0.0121923
2.30661	2.28713	0.01958	0.2171920	0.1676453	1.0000	0.0241862	0.0055706

TABLE A. IV (contd.)

XM1 = 6.62260; XM2 = 0.48639; AO = 95.8042; SAO = 0.7604

SUM ERRORS SQUARED = 0.549E-01; F = 33.3627; SYB = 0.0676

A = 30.1902; SA = 0.3576; S = 6.8214; ZI = 0.3295; SYB = 0.0791

DELTA	HCALC	ERROR	XF	XI	X	F2	F3
1.23438	1.21475	-0.02963	0.3264370	0.0650470	1.0000	0.0130813	0.0000716
1.06405	1.09959	-0.02274	0.1874250	0.1264370	1.0000	0.0119571	0.0084202
1.43352	1.42804	0.00727	0.0550050	0.0000000	1.0000	0.0150853	0.0130975
1.44160	1.43509	0.00650	0.0651950	0.0000700	1.0000	0.0151817	0.0131719
1.25346	1.22075	0.03271	0.1879720	0.0651600	1.0000	0.0121572	0.0090401
1.02480	1.03624	-0.01144	0.1051070	0.1279720	1.0000	0.0113665	0.0062655
1.30631	1.30570	0.00061	0.0239720	1.0000000	1.0000	0.0164234	-0.0128635
1.16815	1.18976	-0.02161	0.0543250	0.2923720	1.0000	0.0140211	-0.0078096
1.05639	1.04385	0.01254	0.1053140	0.0543250	1.0000	0.0120466	-0.0034751
1.35615	1.35412	0.00203	0.0240250	1.0000000	1.0000	0.0163652	-0.0126881
1.20780	1.19059	0.01687	0.0540750	0.0144000	1.0000	0.0140400	-0.0070557
1.05267	1.05109	0.00158	0.0202100	0.0543720	1.0000	0.0121250	-0.0025194

SMI = 4.50042; SMI = 0.16080; AO = 95.8042; SAO = 0.7604

TABLE A. V

POTASSIUM CHLORIDE - TETRAPROPYLAMMONIUM CHLORIDE

MOLALITY = 0.5

X = TETRAPROPYLAMMONIUM CHLORIDE

TEMPERATURE = 60 °C

A = 88.5983; SA = 0.3976; B = 6.8344; SB = 0.5890; SYBC = 0.0191

DELH	HCALC	ERROR	XF	XI	W	F2	F3
1.18435	1.21415	-0.02980	0.1264370	0.0650470	1.0000	0.0130813	0.0080716
1.06685	1.08959	-0.02274	0.1874260	0.1264370	1.0000	0.0119571	0.0044202
1.43332	1.42604	0.00727	0.0658850	0.0000000	1.0000	0.0150853	0.0130975
1.44140	1.43509	0.00630	0.0661950	0.0000000	1.0000	0.0151817	0.0131718
1.25346	1.22075	0.03271	0.1279720	0.0661950	1.0000	0.0131577	0.0080481
1.02480	1.03624	-0.01144	0.1853070	0.1279720	1.0000	0.0113685	0.0042455
1.36631	1.36570	0.00061	0.9239720	1.0000000	1.0000	0.0164934	-0.0139855
1.16815	1.18976	-0.02161	0.8543250	0.2939720	1.0000	0.0140311	-0.0078096
1.05689	1.04355	0.01334	0.7899540	0.8543250	1.0000	0.0120466	-0.0034761
1.35615	1.35412	0.00203	0.9246090	1.0000000	1.0000	0.0163552	-0.0138891
1.20780	1.19099	0.01681	0.8549790	0.9246090	1.0000	0.0140486	-0.0078557
1.05267	1.05109	0.00158	0.7902490	0.8549790	1.0000	0.0121350	-0.0035194

XM1 = 4.84042; XM2 = 0.48080; AO = 88.4432; SAO = 1.4408

TABLE A. V (contd.)

SUM ERRORS SQUARED = 0.525E-01; F = 134.6279; SYB = 0.0691

RELATIVITY = 0.8

1 = 101340000PTLAFORUM CHLORINE

TEMPERATURE = 40 °C

A = 74.4049; SA = 0.9636; B = 5.7049; SB = 1.2429; SYB = 0.0224

WGT	WGT	WGT	WGT	WGT	WGT	WGT	WGT
0.90473	0.90473	0.90473	0.90473	0.90473	1.0000	0.90473	0.90473
0.80611	0.80611	-0.80611	0.80611	0.80611	1.0000	0.80611	0.80611
0.29503	0.29503	-0.29503	0.29503	0.29503	1.0000	0.29503	0.29503
0.90120	0.90120	-0.90120	0.90120	0.90120	1.0000	0.90120	0.90120
0.80104	0.80104	-0.80104	0.80104	0.80104	1.0000	0.80104	-0.80104
0.74529	0.74529	-0.74529	0.74529	0.74529	1.0000	0.74529	-0.74529
0.28382	0.28382	0.28382	0.28382	0.28382	1.0000	0.28382	-0.28382
0.80114	0.80114	0.80114	0.80114	0.80114	1.0000	0.80114	-0.80114
0.73055	0.73055	0.73055	0.73055	0.73055	1.0000	0.73055	-0.73055

SA = 0.9636; SB = 0.48094; AB = 74.5738; SA = 1.7882

SUM ERRORS SQUARED = 0.210E-01; F = 21.067; SYB = 0.0224

TABLE A. VI

POTASSIUM CHLORIDE - TETRAPROPYLAMMONIUM CHLORIDE

MOLALITY = 0.5

X = TETRAPROPYLAMMONIUM CHLORIDE

TEMPERATURE = 80 °C

A = 74.4949; SA = 0.9636; B = 5.7049; SB = 1.2420; SYBC = 0.0314

DELH	HCALC	ERROR	XF	XI	W	F2	F3
0.90477	0.89484	0.00993	0.0476000	0.0000000	1.0000	0.0112337	0.0101642
0.80611	0.80671	-0.00060	0.0934220	0.0476000	1.0000	0.0102647	0.0073696
0.69503	0.71770	-0.02267	0.1369523	0.0934220	1.0000	0.0092521	0.0049892
0.90180	0.90414	-0.00234	0.0480980	0.0000000	1.0000	0.0113512	0.0102593
0.80484	0.85487	-0.05003	0.9431330	1.0000000	1.0000	0.0123111	-0.0109109
0.74523	0.77178	-0.02655	0.8898660	0.9431330	1.0000	0.0109170	-0.0072707
0.88382	0.85452	0.02930	0.9428020	1.0000000	1.0000	0.0123055	-0.0108978
0.80114	0.77010	0.03104	0.8893080	0.9428020	1.0000	0.0108916	-0.0072344
0.73055	0.69560	0.03495	0.8391050	0.8893080	1.0000	0.0096761	-0.0044203

XM1 = 4.87178; XM2 = 0.48094; AO = 73.8775; SAO = 1.7882

SUM ERRORS SQUARED = 0.276E-01; F = 21.0967; SYB = 0.0588

TABLE A. VI (contd.)

DELH	HOCAL	ERROR	XF	XI	W	WTSF	WTSI
0.90477	0.82992	0.07485	0.0476000	0.0000000	1.0000	0.2477970	0.2360020
0.80611	0.75833	0.04778	0.0934220	0.0476000	1.0000	0.2470960	0.2352070
0.69503	0.68352	0.01151	0.1369523	0.0934220	1.0000	0.2462720	0.2344470
0.90180	0.83860	0.06319	0.0480980	0.0000000	1.0000	0.2479270	0.2360020
0.80484	0.90951	-0.10467	0.9431330	1.0000000	1.0000	0.2295420	0.2164880
0.74523	0.80652	-0.06129	0.8898660	0.9431330	1.0000	0.2303150	0.2173080
0.88382	0.90910	-0.02528	0.9428020	1.0000000	1.0000	0.2281900	0.2151380
0.80114	0.80465	-0.00351	0.8893080	0.9428020	1.0000	0.2289470	0.2159570
0.73055	0.71484	0.01571	0.8391050	0.8893080	1.0000	0.2296950	0.2167280

TABLE A. VII

SODIUM CHLORIDE - TETRAPROPYLAMMONIUM CHLORIDE

MOLALITY = 0.5

X = TETRAPROPYLAMMONIUM CHLORIDE

TEMPERATURE = 40 °C

A = 73.5744; SA = 0.2085; B = 9.5981; SB = 0.2805; SYBC = 0.0075

DELH	HCALC	ERROR	XF	XI	W	F2	F3
0.97008	0.98276	-0.01268	0.0520790	0.0000000	1.0000	0.0119596	0.0107139
0.73687	0.73539	0.00148	0.1397920	0.0960080	1.0000	0.0093506	0.0049409
0.94325	0.94276	0.00049	0.0477780	0.0000000	1.0000	0.0114614	0.0103662
0.83622	0.83272	0.00350	0.0932360	0.0477780	1.0000	0.0103488	0.0074301
0.75107	0.73966	0.01141	0.1367110	0.0932360	1.0000	0.0093916	0.0050724
0.79887	0.80973	-0.01086	0.9433840	1.0000000	1.0000	0.0124453	-0.0110361
0.74847	0.74967	-0.00120	0.8897720	0.9433840	1.0000	0.0111593	-0.0074356
0.68128	0.67986	0.00141	0.8399420	0.8897720	1.0000	0.0098296	-0.0045160
0.82164	0.82018	0.00146	0.9426190	1.0000000	1.0000	0.0126031	-0.0111567
0.73517	0.72698	0.00818	0.8905700	0.9426190	1.0000	0.0108217	-0.0072113
0.68770	0.68603	0.00167	0.8402540	0.8905700	1.0000	0.0099218	-0.0045804

XM1 = 3.08738; XM2 = 0.46779; A0 = 72.7587; SA0 = 2.2500

SUM ERRORS SQUARED = 0.662E-01; F = 1170.7460; SYB = 0.0814

TABLE A. VII (contd.)

DELH	HOCAL	ERROR	XF	XI	W	WTSF	WTSI
0.97008	0.87017	0.09991	0.0520790	0.0000000	1.0000	0.2422610	0.2302690
0.73687	0.68034	0.05653	0.1397920	0.0960080	1.0000	0.2482670	0.2362420
0.94325	0.83392	0.10933	0.0477780	0.0000000	1.0000	0.2519250	0.2398880
0.83622	0.75296	0.08326	0.0932360	0.0477780	1.0000	0.2510640	0.2390790
0.75107	0.68332	0.06775	0.1367110	0.0932360	1.0000	0.2502330	0.2382360
0.79887	0.90550	-0.10663	0.9433840	1.0000000	1.0000	0.2330110	0.2198190
0.74847	0.81194	-0.06347	0.8897720	0.9433840	1.0000	0.2339370	0.2206430
0.68128	0.71519	-0.03391	0.8399420	0.8897720	1.0000	0.2348518	0.2216990
0.82164	0.91698	-0.09534	0.9426190	1.0000000	1.0000	0.2330090	0.2196390
0.73517	0.78737	-0.05221	0.8905700	0.9426190	1.0000	0.2334610	0.2205700
0.68770	0.72190	-0.03420	0.8402540	0.8905700	1.0000	0.2346800	0.2214210

TABLE A. VIII

SODIUM CHLORIDE - TETRAPROPYLAMMONIUM CHLORIDE

MOLALITY = 0.5

X = TETRAPROPYLAMMONIUM CHLORIDE

TEMPERATURE = 60 °C

A = 75.5761; SA = 0.6688; B = 9.3309; SB = 0.9837; SYBC = 0.0321

DELH	HCALC	ERROR	XF	XI	W	F2	F3
1.22760	1.26277	-0.03517	0.0639160	0.0000000	1.0000	0.0150843	0.0131560
1.09990	1.08134	0.01856	0.1243330	0.0639160	1.0000	0.0132853	0.0082834
0.93595	0.91340	0.02255	0.1808680	0.1243330	1.0000	0.0115312	0.0044925
1.22600	1.26294	-0.03694	0.0638980	0.0000000	1.0000	0.0150863	0.0131583
1.10400	1.07454	0.02946	0.1239030	0.0638980	1.0000	0.0132004	0.0082423
0.98403	0.92304	0.06099	0.1805740	0.1239030	1.0000	0.0116509	0.0045560
1.14600	1.13325	0.01275	0.9234440	1.0000000	1.0000	0.0167458	-0.0141818
1.00160	1.00162	-0.00002	0.8534140	0.9234440	1.0000	0.0142256	-0.0078770
0.87731	0.87044	0.00687	0.7901390	0.8534140	1.0000	0.0119406	-0.0034282
1.10560	1.10468	0.00092	0.9253350	1.0000000	1.0000	0.0163321	-0.0138933
0.94529	0.98368	-0.03839	0.8565980	0.9253350	1.0000	0.0139897	-0.0078883
0.85280	0.87699	-0.02419	0.7929700	0.8565980	1.0000	0.0120490	-0.0036043

XM1 = 3.23037; XM2 = 0.46948; AO = 75.3720; SAO = 2.0154

TABLE A. VIII (contd.)

SUM ERRORS SQUARED = 0.103E-00; F = 89.9831; SYB = 0.0968

DELR	MOALC	ERROR	XF	XI	X	F2	F3
0.75225	0.77920	0.4022E	0.0010750	0.5000000	1.0000	0.0112744	0.0102829
0.69300	0.61121	-0.0748E1	0.1360270	0.0935600	1.0000	0.0092300	0.0049506
0.62040	0.59124	-0.1096E5	0.2820160	0.0470790	1.0000	0.0102703	0.5073682
0.53003	0.70220	0.0296E3	0.0432200	0.5000000	1.0000	0.0114252	0.0108330
0.56205	0.67783	-0.2072E	0.2523916	0.2032000	1.0000	0.0102501	0.0072186
0.71400	0.71007	0.20297E	0.2600200	1.0000000	1.0000	0.0123174	-0.0109152
0.62604	0.65473	-0.0170E	0.6890650	0.9430000	1.0000	0.0110200	-0.0073657
0.55006	0.59091	0.0000E	0.8322200	0.8390600	1.0000	0.0090000	-0.0080214
0.71429	0.71900	-0.0066E	0.9423970	1.0000000	1.0000	0.0120704	-0.0110337
0.69000	0.64677	0.0114E3	0.8687320	0.9423970	1.0000	0.0109850	-0.0072750
0.60490	0.60196	0.0570E	0.8321450	0.6087370	1.0000	0.0099140	-0.0044634

SRE = 4.01539; SRE = 0.47030; S0 = 62.6727; S40 = 1.4002

SUM ERRORS SQUARED = 0.283E-01; F = 172.4325; SYB = 0.0832

TABLE A. IX

SODIUM CHLORIDE - TETRAPROPYLAMMONIUM CHLORIDE

MOLALITY = 0.5

X = TETRAPROPYLAMMONIUM CHLORIDE

TEMPERATURE = 80 °C

A = 63.0461; SA = 0.4249; B = 6.0187; SB = 0.5651; SYBC = 0.0152

DELH	HCALC	ERROR	XF	XI	W	F2	F3
0.78225	0.77900	0.00325	0.0479790	0.0000000	1.0000	0.0113744	0.0102829
0.59300	0.61121	-0.01821	0.1368970	0.0936660	1.0000	0.0092203	0.0049686
0.68349	0.69194	-0.00845	0.0936660	0.0479790	1.0000	0.0102723	0.0073622
0.80883	0.78320	0.02563	0.0482200	0.0000000	1.0000	0.0114362	0.0103333
0.66026	0.67763	-0.01737	0.0929710	0.0482200	1.0000	0.0100591	0.0072186
0.71464	0.71087	0.00377	0.9430800	1.0000000	1.0000	0.0123174	-0.0109152
0.63684	0.65473	-0.01789	0.8890660	0.9430800	1.0000	0.0110880	-0.0073657
0.59086	0.58391	0.00695	0.8392270	0.8890660	1.0000	0.0096837	-0.0044214
0.71429	0.71980	-0.00551	0.9423970	1.0000000	1.0000	0.0124704	-0.0110337
0.66020	0.64877	0.01143	0.8887370	0.9423970	1.0000	0.0109850	-0.0072750
0.60490	0.59195	0.01295	0.8381450	0.8887370	1.0000	0.0098143	-0.0044534

XM1 = 4.01539; XM2 = 0.47630; A0 = 62.6227; SA0 = 1.4802

SUM ERRORS SQUARED = 0.283E-01; F = 113.4325; SYB = 0.0532

TABLE A. IX (contd.)

DELH	HOCAL	ERROR	XF	XI	W	WTSF	WTSI
0.78225	0.71230	0.06995	0.0479790	0.0000000	1.0000	0.2490180	0.2370700
0.59300	0.57740	0.01560	0.1368970	0.0936660	1.0000	0.2471080	0.2353210
0.68349	0.64328	0.04021	0.0936660	0.0479790	1.0000	0.2480760	0.2361710
0.80883	0.71617	0.09266	0.0482200	0.0000000	1.0000	0.2491830	0.2371680
0.66026	0.62993	0.03033	0.0929710	0.0482200	1.0000	0.2478190	0.2361670
0.71464	0.77135	-0.05671	0.9430800	1.0000000	1.0000	0.2294590	0.2163980
0.63684	0.69436	-0.05752	0.8890660	0.9430800	1.0000	0.2308940	0.2176690
0.59086	0.60642	-0.01556	0.8392270	0.8890660	1.0000	0.2315200	0.2185410
0.71429	0.78093	-0.06664	0.9423970	1.0000000	1.0000	0.2297210	0.2164890
0.66020	0.68791	-0.02771	0.8887370	0.9423970	1.0000	0.2303440	0.2172290
0.60490	0.61460	-0.00970	0.8381450	0.8887370	1.0000	0.2314500	0.2182740

APPENDIX B

SAMPLE EXPERIMENT

$(n\text{-C}_3\text{H}_7)_4\text{NCl} + \text{NaCl}$, 0.5 m, 80 °C. NaCl in pipet, 2nd point (2nd mixing in series.)

57.3660

weight of solution in vessel = 244.0g

-44.0981 Tare

13.2679g weight of NaCl in pipet

Open Pipet

$$\underline{I}_1 = 18568.4 \quad (\text{Initial resistance in ohms})$$

$$\underline{I}_2 = 18571.3 \quad (\text{Final resistance in ohms})$$

$$\Delta \underline{I} = 1.0 \text{ ohms} \quad (\Delta \underline{I} = \underline{I}_2 - \underline{I}_1)$$

Correction = -15 scale divisions

Sensitivity = 0.7 ohms/220 scale divisions

$$\Delta \underline{I} \text{ corr} = 1.0 + (-15)(0.7/220) = 1.85227 \text{ ohms}$$

 $\Delta \underline{I}$ opening = 1.85227 ohms Cp_1 (heat capacity number 1)

$$\underline{I}_1 = 18572.3 \quad \text{correction} = 0 \text{ division}$$

$$\underline{I}_2 = 18574.6 \quad \Delta \underline{I} \text{ corr} = \Delta \underline{I} = 2.3 \text{ (no correction necessary)}$$

$$q \text{ (heat added electrically)} = \frac{E^2 t}{4.184R}$$

$$4.184R = 2333.21 \quad (R = \text{value of calibration heater})$$

$$q = (10.303)^2 (20.03) / 2333.21$$

$$q = 0.914676$$

$$C_p = q / \Delta T \text{ corr} = 0.911286 / 2.3 = 0.396211$$

$$C_{p1} = 0.396211$$

C_{p2}

$$T_1 = 18575.3 \quad \text{corr} = 0$$

$$T_2 = 18577.6 \quad \Delta T \text{ corr} = 2.3$$

$$q = (10.319)^2 (20.05) / 2333.21$$

$$q = 0.914676 \quad C_{p2} = 0.397685$$

$$(C_{p1} + C_{p2}) / 2 = 0.396948 \pm 0.2\%$$

$$C_p \text{ ave} = 0.39695$$

$$Q \text{ opening} = C_p \text{ ave} \Delta T \text{ op} = (0.39695)(1.85227)$$

$$Q \text{ op} = 0.73517 \text{ cal}$$

no pipet correction necessary as

$$\Delta q \text{ pipet} = 0$$

Weight fraction (The weight fraction is simply the amount of solution from the previous mixing which is carried over to the next mixing, ie. In the first mixing in the series the amount of NaCl in the pipet was 13.7612 grams. The amount of $(n\text{-C}_3\text{H}_7)_4\text{NCl}$ in the vessel was 244.0 grams. Summing the two = 257.76 grams. The amount of that solution, after mixing, carried over for the second mixing was 244.0 grams. The weight

fraction becomes then $244/257.76$ grams = 0.946613

no of mmoles of NaCl in pipet = $(0.4858)(13.2679) = 6.4455$

(0.4858 = no of mmoles of NaCl per gram of 0.5m solution.)

13.2679 = grams of NaCl in pipet.

no of mmoles of NaCl in vessel = $(0.9466)(6.68519) = .63283$

(0.9466 = weight fraction)

6.68519 is simply the number of mmoles of NaCl which was mixed in the previous mixing.

no of mmoles of $(n-C_3H_7)_4NCl$ in vessel = $(0.9466)(109.819) = 103.9567$

109.8197 = no of mmoles of $(n-C_3H_7)_4NCl$ in the solution mixed previously.

Total no of mmoles of NaCl = 12.7738

Total no of mmoles of salts in solution = 116.7305

WTSF = 0.233461

WTSI = 0.220570

This is simply weight of solution after mixing (WTSF) and weight of solution before mixing (WTSI) in kilograms.

This is done for the computer program.

$$X_1 = \text{mole fraction of } (n-C_3H_7)_4NCl = \frac{\text{no of mmoles of } (n-C_3H_7)_4NCl}{\text{Total no of mmoles}}$$

$$= \frac{103.9567}{116.7305} = 0.89057$$

$$X_2 = 1 - X_1 = \text{mole fraction of NaCl}$$

$$= 0.10943$$

\underline{RTh}_0 for a single point = $\underline{Qop}/[X_1X_2I^2\text{WTSF-weight fraction}(X_1X_2I^2\text{WTSF}$
 from mixing prior to this one in series)].

$$\underline{RTh}_0 = 271.74$$

since exothermic heats are negative, $\underline{RTh}_0 = -271.74$

This is known from the fact that the resistance change for the electrical heat input and the heat of mixing had the same sign.

For the third mixing in this series, the parameters will again be carried over, this time being from the second heat of mixing rather than from the first.

APPENDIX C

The abbreviations, symbols, units, and style used in this thesis are recommended in "Handbook for Authors of Papers in the Journals of the American Chemical Society," American Chemical Society Publications, Washington, D. C. 1967. Below are some symbols not defined in the text.

Symbols and Units

\underline{m} = Molality

\underline{I} = Ionic strength

\underline{R} = The gas constant (1.987 cal/deg mole)

\underline{T} = Temperature (in degrees Kelvin)

\underline{G}^{ex} = Excess partial molal free energy

\underline{H}^{ex} = Excess partial molal enthalpy

\underline{S}^{ex} = Excess partial molal entropy

\underline{V}^{ex} = Excess partial molal volume

\underline{V} = Voltage

\underline{t} = Temperature (in degrees Celsius)

molality = moles/ kg solvent

ΔH_m = cal/ kg solvent

\underline{RTh}_0 = cal/ kg solvent

\underline{RTh}_1 = cal/ kg solvent