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MICHIGAN TECHNOLOGICAL UNIVERSITY

Department of Chemistry & Chemical Engineering

C00-1712-7

FINAL PROGRESS REPORT

March 14, 1972

Fundamental Studies of Concentrated
Electrolyte Solutions

by

Leslie Leifer

AEC CONTRACT NO. AT(11-1)-1712

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Researches herein reported have been supported by the Atomic Energy Commission under Contract No. AT(11-1)-1712.

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SUMMARY AND ACKNOWLEDGMENT

The object of this research project, "to gain insight into the characterization of highly concentrated electrolyte systems," has certainly been fulfilled at least in part. We have measured the Hammett acidity function in acid-water systems over a wide range of temperature (25-80°C) and concentration, as well as in mixed acid-salt-water systems. We have combined these measurements with appropriate thermodynamic data in order to determine "species profiles" in these systems. We have used these "species profiles" in developing an entirely new approach to the study of the kinetics of acid catalyzed reactions in solution.

As part of our program we have set up both a gravimetric isopiestic apparatus and a thermoelectric osmometer in order to determine thermodynamic properties of a relatively new class of electrolytes - hydrophobic salts. In this we have determined osmotic coefficients, partial molal entropies, enthalpies and free energies of several tetraalkylammonium halides over a wide concentration and temperature range. This effort, we hope, will continue under new sponsorship.

Further, this contract has provided support for three theses at the M.S. level and two theses at the Ph.D. level, and partial

support for two additional Ph.D. theses. The support received has enabled us to establish an ongoing research program in Solution Physical Chemistry and our group has had an international flavor. This contact with students from abroad and from the U.S. has been of benefit to our undergraduate students, faculty and the entire community.

The Principal Investigator, Professor Leslie Leifer, expresses his gratitude for the support given to him and to the Michigan Technological University by the United States Atomic Energy Commission. We hope that our continued research efforts will demonstrate the desirability of such research support.

This is the Final Progress Report of the Department of Chemistry & Chemical Engineering at Michigan Technological University, Houghton, Michigan 49931, under U.S.A.E.C. Contract No. AT(11-1)-1712. Progress during the period March 1, 1970 and March 14, 1972 is recorded as well as an overall view of the progress and accomplishments made during the contract period.

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FUNDAMENTAL STUDIES OF CONCENTRATED ELECTROLYTE SOLUTIONS

A. Thermodynamic Properties of Tetraalkylammonium Halide Solutions

A detailed determination and analysis of the temperature dependence of the osmotic coefficients of dilute (0.01-1.0 molal) solutions of tetra-n-alkyl (methyl- through n-butyl) ammonium halides with respect to cation and anion size has been made. This study allowed us to determine the partial molal free energies, entropies and relative partial molal enthalpies of the solvent; and to evaluate more critically the Diamond theory of water enforced ion-pairing. In the temperature range 25-80°C the osmotic coefficients of the bromide and iodide salt solutions were in the order $\phi(\text{Me}_4\text{NX}) > \phi(\text{Et}_4\text{NX}) > \phi(\text{Pr}_4\text{NX}) > \phi(\text{Bu}_4\text{NX})$. For the fluoride salt solutions the inverse order was obtained and for the chlorides the relative order was the same as the fluorides below 45°C and the same as the bromide and iodides above 45°C. The conclusions drawn here involve both the Broadwater and Desnoyers models. The tendency toward cation-cation-anion triplet formation increases with increased hydrophobic character of the cation. Further, the mechanism of cation-cation-anion triplet formation is strongly influenced by the size of the anion.

For complete details of this work see Ph.D. Thesis,
"Thermodynamic Studies of Tetraalkylammonium Halides in Aqueous
Solutions as a Function of Temperature," T. Kanvanvongsa,
Michigan Technological University, April 1972.

(L. Leifer & T. Kangvanvongsa)

B. Ion-Solvent Interactions in Concentrated Electrolyte Solutions - Thermodynamic Studies of Concentrated Aqueous Tetraalkylammonium Halides Solutions as a Function of Temperature

Osmotic coefficients of tetramethyl, tetraethyl, tetra n-propyl and tetra n-butyl ammonium chloride and the latter three bromide salts were measured, using a gravimetric isopiestic technique, for concentrations 2 molal to saturation at temperatures of 25°C, 30°C, 40°C, 50°C, and 70°C. These data allowed us to calculate the relative apparent partial molal enthalpy, the excess partial molal entropy and the excess partial molal free energy. We found it possible to correlate the thermodynamic data by making use of the (T. L. Broadwater & D. F. Evans, J. Phys. Chem. 73 3985, 1969) formation of cation-cation-anion triple ions and the formation of micelles (S. Lindenbaum & G. E. Boyd, J. Phys. Chem., 68 911, 1964).

In Table (B-I) a comparison of the osmotic coefficients for the tetraalkylammonium halides in the low concentration range (0.1-1.0 molal) and in the high concentration range (3 molal-saturation) is given.

It should be noted that the excess partial molal free energy is a result of the difference between the relative apparent partial molal enthalpy and the excess partial molal entropy multiplied by the absolute temperature. Thus the use of $\overline{F}_1^E$ to indicate

structuring is not always correct and certainly should not be recommended.

TABLE B-I

Comparison of the Orders of the Osmotic Coefficients of
Tetraalkylammonium Halides

Reported by Kangvanvongsa

Chloride Salts

$.1 < m < 1.0, 25^\circ\text{C} < T < 45^\circ\text{C}$

$\phi\text{Bu}_4\text{N}^+ > \phi\text{Pr}_4\text{N}^+ > \phi\text{Et}_4\text{N}^+ > \phi\text{Me}_4\text{N}^+$

$.1 < m < 1.0, 45^\circ\text{C} < T < 80^\circ\text{C}$

$\phi\text{Me}_4\text{N}^+ > \phi\text{Et}_4\text{N}^+ > \phi\text{Pr}_4\text{N}^+ > \phi\text{Bu}_4\text{N}^+$

Bromide Salts

$.1 < m < 1.0, 25^\circ\text{C} < T < 80^\circ\text{C}$

$\phi\text{Me}_4\text{N}^+ > \phi\text{Et}_4\text{N}^+ > \phi\text{Pr}_4\text{N}^+ > \phi\text{Bu}_4\text{N}^+$

Reported Here

Chloride Salts

$3 < m < 6, 25^\circ\text{C} < T < 50^\circ\text{C}$

$\phi\text{Pr}_4\text{N}^+ > \phi\text{Et}_4\text{N}^+ > \phi\text{Me}_4\text{N}^+ > \phi\text{Bu}_4\text{N}^+$

$m > 6, 25^\circ\text{C} < T < 50^\circ\text{C}$

$m > 3, 50^\circ\text{C} < T < 80^\circ\text{C}$

$\phi\text{Et}_4\text{N}^+ > \phi\text{Pr}_4\text{N}^+ > \phi\text{Me}_4\text{N}^+ > \phi\text{Bu}_4\text{N}^+$

Bromide Salts

$3 < m < 6, 25^\circ\text{C} < T < 40^\circ\text{C}$

$\phi\text{Pr}_4\text{N}^+ > \phi\text{Et}_4\text{N}^+ > \phi\text{Bu}_4\text{N}^+$

$m > 6, 25^\circ\text{C} < T < 40^\circ\text{C}$

$m > 3, 40^\circ\text{C} < T < 80^\circ\text{C}$

$\phi\text{Et}_4\text{N}^+ > \phi\text{Pr}_4\text{N}^+ > \phi\text{Bu}_4\text{N}^+$

In Table (B-II) are given the signs of $\overline{L}_1^E$, $\overline{F}_1^E$, and $\overline{S}_1^E$.

TABLE B-II

Signs of $\bar{L}_1$, $\bar{F}_1^E$ and $\bar{S}_1^E$

Salt		$\bar{L}_1$	$\bar{F}_1^E$	$\bar{S}_1^E$
Me ₄ NCl		+	-	+
Et ₄ NCl	3-5 molal	+	-	+
	7-9 molal	-	-	-
Pr ₄ NCl		-	-	-
Et ₄ NBr	3-5 molal	+	+	-
	7-11 molal	-	-	-
Pr ₄ NBr		-	+	-
Bu ₄ NBr		-	+	-

For further details of these measurements, experimental procedure and discussion of results refer to Ph.D. Thesis, "Ion-Solvent Interactions in Concentrated Electrolyte Solutions," W. H. Streng, Michigan Technological University, December 1971).

(L. Leifer & W. H. Streng)

C. The Temperature Dependence of H_o , the Hammett Acidity Function in HCl-H₂O Systems

Measurements of the Hammett acidity function were completed during this period. These H_o values were determined over a wide range of temperature (25-80°C) and composition (0.01-11 Molar HCl). The results of these measurements are reported in Table (C-I). They constitute the most accurate H_o values determined to date. The H_o values determined here have been used in obtaining "species profiles" at various temperatures in acid-water and in mixed acid-salt systems.

Paul and Long (M. A. Paul and F. H. Long, Chem. Rev., 57 1, 1957) predicted that the Hammett acidity functions were almost independent of temperature. However, the results of this investigation showed H_o to be linearly dependent upon temperature in solutions above 5.0 Molal HCl.

For further details of this work refer to K. Inoue, M. S. Dissertation, "Temperature Variation of the Hammett Acidity Function in HCl-H₂O Solutions," Michigan Technological University, August 1970).

(K. Inoue & L. Leifer)

TABLE C-I

-Ho VALUES AT SELECTED ACID CONCENTRATIONS

Molarity (M)	Temperature (°C)					
	25°	35°	45°	55°	60°	65°
0.50	-0.189	-0.189	-0.189	-0.189	-0.189	-0.189
0.75	0.034	0.034	0.034	0.034	0.034	0.034
1.00	0.211	0.211	0.211	0.211	0.211	0.211
1.50	0.475	0.475	0.475	0.475	0.475	0.475
2.00	0.694	0.694	0.694	0.694	0.694	0.694
2.50	0.894	0.894	0.894	0.894	0.894	0.894
3.00	1.081	1.081	1.081	1.081	1.081	1.081
3.50	1.260	1.260	1.260	1.260	1.260	1.260
4.00	1.444	1.442	1.440	1.438	1.437	1.436
4.50	1.622	1.619	1.616	1.614	1.613	1.611
5.00	1.794	1.791	1.788	1.786	1.784	1.783
5.50	1.96	1.96	1.96	1.96	1.95	1.95
6.00	2.14	2.13	2.13	2.12	2.12	2.12
6.50	2.31	2.31	2.30	2.29	2.28	2.28
7.00	2.49	2.48	2.46	2.45	2.44	2.44
7.50	2.67	2.65	2.63	2.61	2.60	2.60
8.00	2.85	2.82	2.80	2.78	2.77	2.75
8.50	3.02	3.00	2.97	2.94	2.92	2.91
9.00	3.21	3.18	3.14	3.10	3.08	3.06
9.50	3.39	3.35	3.31	3.27	3.25	3.23
10.00	3.58	3.53	3.48	3.43	3.41	3.38
10.50	3.77	3.71	3.66	3.60	3.57	3.54
11.00	3.97	3.90	3.84	3.77	3.74	3.70

TABLE C-I cont.

Molarity (M)	Temperature (°C)		
	70°	75°	80°
0.50	-0.189	-0.189	-0.189
0.75	0.034	0.034	0.034
1.00	0.211	0.211	0.211
1.50	0.475	0.475	0.475
2.00	0.694	0.694	0.694
2.50	0.894	0.894	0.894
3.00	1.081	1.081	1.081
3.50	1.260	1.260	1.260
4.00	1.435	1.434	1.433
4.50	1.610	1.608	1.607
5.00	1.781	1.780	1.778
5.50	1.95	1.95	1.95
6.00	2.12	2.11	2.11
6.50	2.27	2.27	2.27
7.00	2.43	2.43	2.42
7.50	2.59	2.58	2.57
8.00	2.74	2.73	2.72
8.50	2.90	2.88	2.87
9.00	3.05	3.03	3.01
9.50	3.20	3.18	3.16
10.00	3.36	3.35	3.31
10.50	3.52	3.49	3.46
11.00	3.67	3.64	3.61

(K. Inoue & L. Leifer)

D. The Temperature Dependence of the "Anionic" Species Profiles in HCl-H₂O Solutions

By combining the Hammett acidity function values determined, as described in Section C, with the appropriate thermodynamic data, found in the literature (A. Cerquetti, et al. J. Chem. & Eng. Data 13 458 (1968) - G. Akerlof, et al. J. Chem. Soc. 59 1855(1937)) we were able to calculate the anionic species profiles and their temperature dependence.

The anion activity function has been shown to be given by:

$$\log \phi_o^{-1} a_{Cl^-} = H_o + \log a_{HCl} \quad (D-1)$$

ϕ_o = the molar activity coefficient ratio of base to acid form of the indicators used in the determination of the acidity function.
 a_{HCl} = the activity of HCl determined at various temperatures.

The ion activity coefficient function, $\log \phi_o^{-1} y_{Cl^-}$ was calculated using the following equation:

$$\log \phi_o^{-1} y_{Cl^-} = \log \phi_o^{-1} a_{Cl^-} - \log M_{Cl^-} \quad (D-2)$$

where M_{Cl^-} is taken to be the stoichiometric molarity of the HCl.

In considering the hydration equilibria of the Cl^-

the average degree of hydration is expressed as follows:

$$\bar{n}_{Cl^-} = - d[\log \phi_o^{-1} y_{Cl^-}] / d(\log a_{H_2O}) \quad (D-4)$$

where $a_{\text{H}_2\text{O}}$ is the water activity. At 25°C values for the water activity were obtained from osmotic coefficient data. At the higher temperatures water activities were obtained from the solute activities by using the integrated form of the Gibbs-Duhem equation.

Rearrangement and integration of equation (D-4) yields:

$$\log \phi_o^{-1} y_{\text{Cl}^-} = - n_{\text{Cl}} - \log a_{\text{H}_2\text{O}} + \log K_o \quad (\text{D-5})$$

In Figure D-I are shown plots of $\log \phi_o^{-1} y_{\text{Cl}^-}$ vs. $-\log a_{\text{H}_2\text{O}}$ at 25°C, 60°C and 80°C.

Following the "curve peeling" procedure described earlier (L. Leifer, U. S. Atomic Energy Commission Report COO-1712-3) the anionic species profiles were obtained. They are shown in Figures D-II, D-III and D-IV.

From the figures it can be seen that the predominant anionic species are the unhydrated chloride ion and the trihydrate, $\text{Cl}(\text{H}_2\text{O})_3^-$. With increase in temperature there is a decrease in concentration of the trihydrate and a corresponding increase in concentration of the free Cl^- . At 80°C the concentration of $\text{Cl}(\text{H}_2\text{O})_3^-$ decreases to about 50% of its concentration at 60°C. The decrease in $\text{Cl}(\text{H}_2\text{O})_3^-$ concentration at 60°C is about 20% of its concentration at 25°C.

(L. Leifer & K. Inoue)

E. Calculation of Species Profiles of Hydrogen Ion in
HCl-H₂O Solutions as a Function of Temperature

By a procedure similar to the one described in Section D of this report, we have determined the "species profiles" for the hydrogen ion at 25°C, 60°C, and 80°C. Three main species were found: H_3O^+ , H_9O_4^+ and $\text{H}_{21}\text{O}_{10}^+$. (See Figures E-I, E-II and E-III). In contrast to the behavior of the chloride ion it was found that there is essentially no temperature variation of the species profiles for the hydrogen ion. This result greatly simplifies the treatment of the kinetics of acid-catalyzed reactions. On the basis of these results one would now predict a simple temperature dependence of the reaction rate constant rather than one combined with a profile change.

(L. Leifer and K. Inoue)

PAPERS ACCEPTED FOR PRESENTATION

Leslie Leifer
and
Tongchai Kangvanvongsa

"THERMODYNAMIC STUDIES OF TETRAALKYL-
AMMONIUM HALIDES IN AQUEOUS SOLUTIONS
AS A FUNCTION OF TEMPERATURE" (Paper
to be presented at the 163rd National
Meeting of the American Chemical Soci-
ety, Boston, Mass., April 10-14, 1972)

PAPERS PRESENTED AT MEETINGS
DURING THE PERIOD
March 1, 1970 - March 14, 1972

D. H. Kenny,
L. Leifer and
H. J. Hallgren

"A MÖSSBAUER STUDY OF SUBSTITUTED PHENYLFERROCENES" (Presented at the Annual Meeting of the Physical Science Section of the Michigan Academy of Science, Detroit, Michigan, Apr. 3, 1970).

L. Leifer and
W. H. Streng

"SPECIES PROFILES IN AQUEOUS PERCHLORIC ACID SOLUTIONS" (Presented at the Great Lakes Meeting of the American Chemical Society, Fargo, North Dakota, June 18-19, 1970).

K. Inoue and
L. Leifer

"HAMMETT ACIDITY MEASUREMENTS IN HCl-H₂O SOLUTIONS IN THE TEMPERATURE RANGE 25°-80°C" (Presented at the Great Lakes Meeting of the American Chemical Society, Fargo, North Dakota, June 18-19, 1970).

T. Kangvanvongsa and
L. Leifer

"OSMOTIC COEFFICIENTS OF TETRAALKYLAMMONIUM HALIDES OVER THE TEMPERATURE RANGE 25°- 80°C" (Presented at the Great Lakes Meeting of the American Chemical Society, Fargo, North Dakota, June 18-19, 1970).

L. Leifer,
Kimio Inoue and
Paul A. Larson

"A SIMPLIFIED METHOD OF OBTAINING GROUND STATE ENERGIES OF POLYELECTRONIC ATOMS, UNKNOWN IONIZATION POTENTIALS AND REPULSION ENERGIES" (Presented at the Great Lakes Meeting of the American Chemical Society, Peoria, Illinois, June, 1971).

THESES

William H. Streng

"ION-SOLVENT INTERACTIONS IN CONCENTRATED ELECTROLYTE SOLUTIONS

Part I - Acidity Measurements
in Mixed Acid Salts

Part II - Thermodynamic Studies
of Concentrated Aqueous
Tetraalkylammonium Halide
Solutions as a Function
of Temperature"

(Ph.D. Thesis, Department of Chemistry
and Chemical Engineering, Michigan
Technological University, Dec. 1971)

Tongchai Kanvanvongsa

"THERMODYNAMIC STUDIES OF TETRALKYL-
AMMONIUM HALIDES IN AQUEOUS SOLUTIONS
AS A FUNCTION OF TEMPERATURE"

(Ph.D. Thesis, Department of Chemistry
and Chemical Engineering, Michigan
Technological University, April 1971)

Kimio Inoue

"TEMPERATURE VARIATION OF THE HAMMETT
ACIDITY FUNCTION IN HCl-H₂O SOLUTIONS"

(M.S. Thesis, Department of Chemistry
and Chemical Engineering, Michigan
Technological University, Aug. 1970)