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Fundamental Studies of Concentrated
Electrolyte Solutions

by

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FUNDAMENTAL STUDIES OF CONCENTRATED ELECTROLYTE SOLUTIONS

A. Hammett Acidity Measurements in Mixed Acid Salt Media

To determine the effect of a neutral salt on the Hammett acidity function and to broaden our attack on species present in mixed acid-salt media we began a series of measurements of the Hammett acidity function in HCl-LiCl-H₂O systems, both as a function of the total ionic strength and the ionic strength fraction of acid.

The experimental Hammett acidity function, H_0 , provides a measure of the activity, a_{H^+} , of unhydrated protons on concentrated solutions containing acids and is obtained from the acid-base equilibrium of an uncharged weak base indicator, B, in the following manner:

$$K_{BH^+} = a_B a_{H^+} / a_{BH^+} \quad (A-2)$$

$$-\log K_{BH^+} - \log C_{BH^+}/C_B - \log Y_B/Y_{BH^+} - \log a_{H^+} \quad (A-3)$$

or

$$pK_{BH^+} - \log C_{BH^+}/C_B = -\log \phi_0 a_{H^+} \equiv H_0 \quad (A-4)$$

The indicators used in determining H_0 are in general weak organic bases (those used in our work will be listed below). The spectral

measurements were made on a Beckman Model DU-2 spectrophotometer.

It can be seen from equation (A-4) that, involved in the experimental determination of H_0 is the evaluation of the concentration ratio of acid to base forms of the indicator used, C_{BH^+}/C_B and the determination of K_{BH^+} , the dissociation constant of the acid form of the indicator.

The determination of C_{BH^+}/C_B — the weak base indicators used in this work have absorption maxima of their acid and base forms in either the visible or UV region of the spectrum. After determining the absorption maximum of the indicator in the base form the absorption of the acid form was determined at the same wavelength. To find the extinction coefficients, $\epsilon_{BH^+}^\lambda$ and ϵ_B^λ , of acid and base forms of the indicator, the relationship

$$C = A/b\epsilon \quad (A-5)$$

was used. A is the absorbance, b is the path length of the cell used, and C is the concentration of the indicator. C , the extinction coefficient of the partially ionized indicator is found in an analogous manner and the concentration ratio C_{BH^+}/C_B is then obtained using the relationship

$$C_{BH^+}/C_B = \epsilon_B^\lambda - \epsilon^\lambda / \epsilon_{BH^+}^\lambda \quad (A-6)$$

By substitution of equation (A-5) into equation (A-6) the indicator concentration ratio may be expressed in terms of absorbance

$$C_{BH^+}/C_B = A_B - A/A - A_{BH^+} \quad (A-7)$$

The determination of pK_{BH^+} — pK_{BH^+} is defined by the equation:

$$pK_{BH^+} = \log C_{BH^+}/C_B C_{H^+} + \log f_{BH^+}/f_B f_{H^+} \quad (A-8)$$

in which f_{BH^+} , f_B and f_{H^+} are the activity coefficients on a molar scale. By keeping the indicator concentration small equation (A-8) becomes:

$$pK_{BH^+} = \lim_{C_A \rightarrow 0} \left[\log C_{BH^+}/C_B - \log C_{H^+} \right] \quad (A-9)$$

For a strong acid, C_{H^+} is obtained from the relation

$$C_A = C_{H^+} + C_{BH^+} \quad (A-10)$$

Thus, by extrapolation of a graph of the right hand side of equation (A-9) vs. C_A to $C_A = 0$ one obtains a value for pK_{BH^+} .

When an indicator is used such that the ionization ratio cannot be determined in dilute aqueous solution, a stepwise comparison must be made. For example, if we take two uncharged weak base indicators, denoted by R and S, one can obtain

the relation:

$$\begin{aligned} pK_{SH^+} - pK_{RH^+} = & \log C_{SH^+}/C_S - \log C_{RH^+}/C_R \\ & - \log \frac{f_S f_{RH^+}}{f_R f_{SH^+}} \end{aligned} \quad (A-11)$$

If R and S are structurally similar the last term in equation (A-11) may be neglected. Thus, if the pK for one of the indicators is known and the ionization ratios can be determined accurately at corresponding acid concentrations, the pK value of the second indicator can be obtained.

The results of H_0 measurements made on the system HCl-LiCl- H_2O at constant total ionic strengths of 0.01, 0.1, 1.0, 3.0 and 5.0 molal and at several ionic strength fractions of acid at each total ionic strength are reported in Table A-1. In column one the ionic strength fraction of HCl, denoted by X_A , is given and in columns two through six the experimentally determined H_0 values are given at each of the total ionic strengths, I_T , studied.

In Table A-2 we report a list of the indicators used in this work, their absorption maxima in millimicrons, and their useful ionic strength range.

TABLE A-1
H₀ Values in the System HCl-LiCl-H₂O

<u>X_A</u>	<u>I_T=0.0100,</u> <u>-H₀</u>	<u>0.100</u> <u>-H₀</u>	<u>1.000,</u> <u>-H₀</u>	<u>3.000,</u> <u>-H₀</u>	<u>5.00</u> <u>-H₀</u>
0.100	-2.96	-2.05 ₈	-0.75 ₅	0.188	1.02 ₀
0.200	-2.62	-1.70 ₈	-0.43 ₄	0.486	1.25 ₈
0.400	-2.34	-1.45 ₆	-0.18 ₂	0.72 ₈	1.46 ₆
0.600	-2.14	-1.27 ₈	-0.014	0.85 ₅	1.58 ₃
0.800	-2.01	-1.14 ₄	+0.098	0.91 ₈	1.65 ₈
0.900	-1.95	-1.09 ₃	+0.144	0.94 ₈	1.68 ₁
1.000	-1.91	-1.03 ₇	+0.192	0.97 ₃	1.69 ₈

TABLE A-2
Indicators Used in the Study of the HCl-LiCl-H₂O System

<u>Indicator</u>	<u>Absorption Maximum</u>	<u>Ionic</u> <u>Strength Range</u>
4-aminoazobenzene	376 mu	0.001-0.01
p-nitroaniline	383 mu	0.01-0.10
o-nitroaniline	413 mu	0.10-1.0
4-chloro-2-nitroaniline	425 mu	1.0-5.0

(W. H. Streng and L. Leifer)

B. The Ion Activity Function - An Approach to the Study of Electrolyte Behavior in Concentrated Solutions - Formal Species in the System HCl-H₂O

In electrolyte solutions where the mean activity coefficient shows a large increase with a corresponding decrease in water activity when approaching saturation, ion-solvent interactions are responsible for a large part of the variation of the excess free energy. Hydrochloric acid-water is an example of such a system. The principles of the ion activity function of ionic species $D^{\pm z}$ in concentrated aqueous media, defined as $\phi_o^{\pm z} a_{D^{\pm z}}$ (Högfeltdt and Leifer, Acta Chem. Scand. 17, 338 (1963)) and the ion activity coefficient function $\phi_o^{\pm z} \gamma_{D^{\pm z}}$ were used in examining the data for concentrated HCl-H₂O solutions. We have shown that over a substantial region of the water activity $\log \phi_o^{-1} \gamma_{Cl^-}$ is linear with $-\log a_{H_2O}$, with slope n . This is taken as evidence that only one term of the series $\sum_{m=0}^{m=n} Cl(H_2O)_m^-$, the n th one, is important. An analogous treatment for cationic species will be given. This picture of solvation properties of ions is quite definite, and thus subject to check by measurements of other properties of concentrated solutions. Applications to the study of the kinetics of acid catalyzed reactions are in progress.

(L. Leifer)

C. Thermodynamic Properties of Concentrated $\text{HClO}_4\text{-H}_2\text{O}$

A new method for the estimation of thermodynamic properties of concentrated electrolyte solutions is being developed.

In our work on the properties of concentrated electrolyte solutions it became necessary to obtain estimates of activity coefficients of perchloric acid in aqueous solutions at concentrations above 16 molal. Extrapolation of a graph of the ion activity function for H_3O^+ , $\log \phi_{\text{O}} a_{\text{H}_3\text{O}^+}$, vs. $-\log a_{\text{H}_2\text{O}}$ and subsequent combination of these results with the recent H_2O data for $\text{HClO}_4\text{-H}_2\text{O}$ obtained by Yates et al (K. Yates and H. Wai, J. Am. Chem. Soc., 86 5408 (1964)) yielded the acid molality as a function of the water activity up to acid concentrations of ~ 34 molal. Substitution of these results into the Gibbs-Duhem equation and performance of the necessary graphical integration yields the activity of HClO_4 . Thus knowing the activity and the molality of HClO_4 , it becomes a simple matter to calculate the activity coefficients. We have obtained these results over the extended concentration range, 16-34 molal and from these results, reported in Table C-1, is clear that there exist strong ion-solvent interactions in this systems.

TABLE C-1

Activity Coefficients of Perchloric Acid at High Concentrations

Molality of HClO_4 <u>M</u>	Mean Activity Coefficient <u>γ^+</u>
16.6	684
17.1	866
17.6	1.03×10^3
18.1	1.33×10^3
18.7	1.71×10^3
19.5	2.35×10^3
20.1	3.10×10^3
20.8	4.14×10^3
21.8	5.34×10^3
22.7	7.75×10^3
24.0	1.12×10^4
24.7	1.75×10^4
25.9	2.93×10^4
27.3	4.60×10^4
28.3	6.28×10^4
29.4	9.48×10^4
30.3	1.41×10^5
31.5	2.05×10^5
32.7	2.95×10^5
33.8	4.18×10^5

(L. Leifer and L. M. Julien)

D. Application of the Concepts of the Ion Activity Function to the Kinetics of Acid Catalyzed Reactions I. HCl Catalyzed Ester Hydrolyses (AC-2 Type Mechanisms).

As indicated in Section B, our concept of species formed in concentrated solutions is quite definite, and thus subject to check by measurements of other properties of concentrated solutions. We have used the concentration of the acid species in concentrated HCl solutions, as determined by combination of H_0 and thermodynamic measurements, of acid catalyzed ester hydrolyses.

This procedure has resulted in decidedly more linear relationships than heretofore reported when the pseudo-first-order rate constants were plotted against the particular species concentration. We studied the hydrolysis of γ -butyrolactone, ethyl acetate, methyl formate and several di-esters.

In addition we were able to kinetically separate two distinct ester hydrolysis reactions; one involving $H_9O_4^+$, the other involving H_3O^+ . The details of this study will be presented at the 155th meeting of the American Chemical Society and a preprint of our work is included with this report.

(L. Leifer and Fred D. Williams)

E. Application of the Concept of the Ion Activity
Function to the Kinetics of Acid Catalyzed Reactions II.
HCl-Catalyzed Ester Hydrolyses (Al-I Type Mechanisms).

We have established a criteria which is able to distinguish the two most common acid catalyzed ester hydrolysis reaction mechanisms -- bi-molecular acyl oxygen cleavage (Ac-2) and uni-molecular alkyl oxygen cleavage (Al-I). We have analyzed the data for the hydrolysis of tert-butyl acetate and methoxymethyl acetate utilizing the concentration profiles of H_9O_4^+ and H_3O^+ obtained from ion activity function data. Our results clearly indicate a linear relationship between the pseudo-first-order rate constant and the concentration of H_3O^+ . We have shown that for Ac-2 type mechanisms a linear relationship exists between the pseudo-first-order rate constant and the concentration of H_9O_4^+ . We have obtained data which indicate that the hydrolysis rate constant for several acetals, known to follow Al-I type mechanisms, are not linear with the concentration of H_9O_4^+ . In every case we have studied, wherein the reaction was H_3O^+ dependent, alkyl oxygen cleavage occurred. When the rate was H_9O_4^+ dependent, acyl oxygen or acyl nitrogen cleavage occurred.

(L. Leifer and Fred D. Williams)

F. Application of the Concept of the Ion Activity Function to the Kinetics of Acid Catalyzed Reactions III. HCl-Catalyzed Amide Hydrolyses.

A further test of the generality of the determination of mechanisms of acid catalyzed reactions utilizing species profiles obtained from calculations using the ion activity function concept is in the study of acid catalyzed amide hydrolysis. The kinetics of amide hydrolysis heretofore has presented the particularly difficult problem of explaining the existence of maxima in plots of pseudo-first-order rate constants vs. acid concentration. We have examined the data for the hydrolysis of formamide, acetamide, propionamide and benzamide, all of which exhibit maxima, and find that the rate increases with the concentration of H_9O_4^+ and decreases linearly with H_3O^+ concentration. We treat this as a hydrolysis reaction involving H_9O_4^+ and the formation of a relatively stable complex with H_3O^+ . In addition, we have worked out a detailed analysis of the kinetic scheme which successfully accounts for the maxima and the subsequent linear decrease of the rate of hydrolysis with H_3O^+ concentration. Previous schemes have predicted the attainment of a limiting rate for the hydrolysis of amides. This is not in accord with the experimental results.

(L. Leifer and F. D. Williams)

PAPERS ACCEPTED FOR PRESENTATION

- L. Leifer, "The Ion Activity Function-An Approach to the Study of Electrolyte Behavior in Concentrated Solutions IV. Formal Species in the System $\text{HCl-H}_2\text{O}$." (Paper to be presented at the 155th National Meeting of the American Chemical Society, San Francisco, California, March 31-April 5, 1968.)
- L. Leifer and F. D. Williams, "The Use of the Ion Activity Function in Solution Kinetics I. The Kinetics of Hydrochloric Acid Catalyzed Ester Hydrolyses (Ac-2 Type Mechanisms)." (Paper to be presented at the 155th National Meeting of the American Chemical Society, San Francisco, California, March 31-April 5, 1968.)
- F. D. Williams and L. Leifer, "The Use of the Ion Activity Function in Solution Kinetics II. Kinetics of Hydrochloric Acid Catalyzed Ester Hydrolyses (AL-1 Type Mechanisms)." (Paper to be presented at the Great Lakes Regional Meeting of the American Chemical Society, Milwaukee, Wisconsin, June 13-14, 1968.)
- F. D. Williams and L. Leifer, "The Use of the Ion Activity Function of Solution Kinetics III. The Kinetics of Hydrochloric Acid Catalyzed Amide Hydrolyses." (Paper to be presented at the Great Lakes Regional Meeting of the American Chemical Society, Milwaukee, Wisconsin, June 13-14, 1968.)
- L. Leifer and L. M. Julien, "A New Method for the Estimation of Thermodynamic Properties of Concentrated Electrolyte Solutions I. The Perchloric Acid-Water System." (Paper to be presented at the Great Lakes Regional Meeting of the American Chemical Society, Milwaukee, Wisconsin, June 13-14, 1968.)

ADDRESSES

L. Leifer, "Ion-Solvent Interactions in Concentrated Electrolyte Solutions", Department of Chemistry, Northern Michigan University, Marquette, Michigan, November 3, 1967.