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February 28, 1970

Fundamental Studies of Concentrated  
Electrolyte Solutions

by

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This is the third Progress Report of the Department of Chemistry and Chemical Engineering at Michigan Technological University, Houghton, Michigan 49931. Progress during the period March 1, 1969 through February 28, 1970 is recorded.

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FUNDAMENTAL STUDIES OF CONCENTRATED  
ELECTROLYTE SOLUTIONS

A. Hammett Acidity Measurements and Determination of  
Ion Activity Functions in the System HCl-LiCl-H<sub>2</sub>O

The spectrophotometric determination of  $H_o$ , the Hammett acidity function, for the mixed acid-salt system HCl-LiCl-H<sub>2</sub>O has been obtained up to a total ionic strength of 16 molal, and at seven values of the ionic strength fractions of acid.

The details of the experimental procedure have been given (W. H. Streng "Hammett Acidity Function Measurements in Mixed Acid-Salt Media," M.S. Thesis, Michigan Technological University 1968). The  $pK_{BH^+}$  of the indicators used in this study, and their range of validity (i.e. the range over which Beer's Law is followed) are given in Table A-1.

The smoothed values of  $H_{om}$ , the Hammett acidity function in HCl-LiCl-H<sub>2</sub>O (tabulated as  $-H_{om}$ ) for total ionic strengths 1.0-16 molal and at several ionic strength fractions of acid are reported in Table A-2.

TABLE A-1

Indicators Used for the Determination of  $H_{om}$   
in the System HCl-LiCl-H<sub>2</sub>O

Indicator	$I_T$ Range (molality)	$pK_{BH^+}$
4-aminoazobenzene	0.001 - 0.01	2.77
p-nitroaniline	0.01 - 0.1	0.99
o-nitroaniline	0.1 - 1.0	-0.29
4-chloro-2-nitroaniline	1.0 - 5.0	-1.03
p-nitro-diphenylamine	5.0 - 12.0	-2.47
2,4-dinitroaniline	12.0 - 16.0	-4.26

TABLE A-2

 $H_{om}$  Values for the System HCl-LiCl-H<sub>2</sub>O

$I_T$	(Tabulated as $-H_{om}$ )				
	$X_A=0.10$	$X_A=0.20$	$X_A=0.30$	$X_A=0.40$	$X_A=0.50$
1.00	-0.75	-0.43	-0.292	-0.15	-0.098
2.00	-0.19	0.04	0.213	0.29	0.394
3.00	0.26	0.44	0.590	0.68	0.764
4.00	0.64	0.79	0.913	1.02	1.083
5.00	0.97	1.11	1.239	1.32	1.387
6.00	1.26	1.41	1.547	1.61	1.683
7.00	1.54	1.68	1.828	1.91	1.968
8.00	1.79	1.94	2.087	2.16	2.232
9.00	2.02	2.20	2.323	2.42	2.478
10.00	2.26	2.44	2.549	2.66	2.713
11.00	2.48	2.68	2.772	2.86	2.948
12.00	2.73	2.92	2.983	3.09	3.181
13.00	2.97	3.12	3.202	3.32	3.420
14.00	3.23	3.32	3.423	3.58	3.672
15.00	3.50	3.58	3.654	3.81	3.932
16.00	3.79	3.86	3.924	4.06	4.198

TABLE A-2  
(cont.)

$-H_{om}$  Values for the System HCl-LiCl-H<sub>2</sub>O

$I_T$	$X_A=0.60$	$X_A=0.70$	$X_A=0.80$	$X_A=0.90$	$X_A=1.00$
1.00	0.01	0.042	0.10	0.141	0.188
2.00	0.45	0.532	0.57	0.621	0.653
3.00	0.82	0.883	0.92	0.979	0.991
4.00	1.14	1.191	1.24	1.273	1.309
5.00	1.46	1.498	1.55	1.572	1.588
6.00	1.73	1.787	1.84	1.864	1.881
7.00	2.03	2.071	2.12	2.151	2.184
8.00	2.30	2.344	2.38	2.427	2.465
9.00	2.55	2.597	2.62	2.691	2.729
10.00	2.79	2.843	2.87	2.938	2.981
11.00	3.02	3.089	3.10	3.174	3.211
12.00	3.27	3.338	3.38	3.411	3.442
13.00	3.51	3.579	3.59	3.638	3.677
14.00	3.74	3.810	3.82	3.874	3.914
15.00	3.98	4.044	4.08	4.120	4.159
16.00	4.24	4.281	4.31	4.364	4.410



To determine the species present in HCl-LiCl-H<sub>2</sub>O mixtures we must combine the measured H<sub>Om</sub> values (determined spectroscopically) with the appropriate thermodynamic values (water activities and solute activities in the acid-salt mixtures) determined by procedures outlined below. The osmotic coefficient in the mixed solution,  $\phi$ , is given by:

$$\phi = \phi_{\text{HCl}} + (\phi_{\text{LiCl}} - \phi_{\text{HCl}}) X_{\text{LiCl}} \quad (\text{A-1})$$

where  $\phi_{\text{HCl}}$  and  $\phi_{\text{LiCl}}$  are the osmotic coefficients in the pure salt and acid solutions at the same total ionic strength as in the mixed solution, and  $X_{\text{LiCl}}$  is the ionic strength fraction of LiCl. It has been shown that Harned's Rule is obeyed in HCl-LiCl-H<sub>2</sub>O solutions up to a total ionic strength of 6 molal (Robinson and Stokes' "Electrolyte Solutions" - 2nd Ed. Butterworth's Scientific Publications, 1959, p. 439). Since the Harned Rule is even more accurate the higher the total ionic strength (Harned and Gary. J. Am. Chem. Soc. 76, 5924, 1954), we have assumed linear behavior for the solute activity coefficients up to 16 molal. Thus:

$$\log \gamma_{\pm \text{HCl}} = \log \gamma_{\pm \text{HCl}}(0) - \alpha_{12} (1-X) I \quad (\text{A-2})$$

and

$$\log \gamma_{\pm \text{LiCl}} = \log \gamma_{\pm \text{LiCl}(o)} - \alpha_{21} \text{XI} \quad (\text{A-3})$$

$\gamma_{\pm \text{HCl}}$  and  $\gamma_{\pm \text{LiCl}}$  are the stoichiometric mean ionic molal activity coefficients of acid and salt in solutions of total ionic strength I, and ionic strength fraction of acid, X.

$\gamma_{\pm \text{HCl}(o)}$  and  $\gamma_{\pm \text{LiCl}(o)}$  are the molal activity coefficients of acid and salt in their separate pure solutions and the same total ionic strength as the mixture.

The " $\alpha$ " values are determined by using the equation:

$$\frac{0.8686 \phi - \phi_{\text{LiCl}}}{\text{XI}} = X (\alpha_{12} + \alpha_{21}) - 2\alpha_{21} \quad (\text{A-4})$$

and plotting the left side vs. the ionic strength fraction of acid, X. The intercept will be  $-2\alpha_{21}$  and the slope  $(\alpha_{12} + \alpha_{21})$ .

Knowing the solute activities and the water activity (as determined from the osmotic coefficient in the mixtures) we can construct the ion activity functions in the mixed solute system.

They are:

$$\log \phi_o a_{\text{H}_3\text{O}^+} = -H_{\text{om}} + \log a_{\text{H}_2\text{O}} \quad (\text{A-5})$$

$$\log \phi_o^{-1} a_{Cl^-} = H_{om} + \log a_{HCl} \quad (A-6)$$

$$\log \phi_o a_{Li^+} = -H_{om} + \log a_{LiCl} - \log a_{HCl} \quad (A-7)$$

Thus in a mixed system the anion activity function is given by

$$\log \phi_o^{-1} a_{Cl^-} = H_{om} + \log X I^2 d_o^2 + 2 \log \gamma_{\pm} HCl(o) - 2\alpha_{12} (1-X)I \quad (A-8)$$

and the cation activity functions are:

$$\log \phi a_{H_3O^+} = -H_{om} + \log a_{H_2O} \quad (A-9a)$$

$$\log \phi a_{Li^+} = -H_{om} + \log (1-X)/X \quad (A-9b)$$

$$+ 2 (\log \gamma_{\pm} LiCl(o) - \log \gamma_{\pm} HCl(o)) - 2\alpha_{12} XI + 2\alpha_{12} (1-X)I$$

In Table A-3 are given the calculated values of the anion activity function ( $\log \phi_o^{-1} a_{Cl^-}$ ) in the HCl-LiCl-H<sub>2</sub>O system.

The anion activity coefficient is then calculated from equation (A-10) below:

$$\log \phi_o^{-1} a_{Cl^-} - \log M_{Cl^-} = \log \phi_o^{-1} \gamma_{Cl^-} \quad (A-10)$$

and the average hydration of the chloride ion is given by:

$$\frac{-d \log \phi_o^{-1} \gamma_{Cl^-}}{d \log a_{H_2O}} = \bar{\eta}_{Cl^-} \quad (A-11)$$

TABLE A-3

The Anion Activity Function in the System HCl-LiCl-H<sub>2</sub>O

$I_T$	$X_A=0.30$	$X_A=0.50$	$X_A=0.70$	$X_A=0.90$	$X_A=1.00$
1.00	-0.429	-0.399	-0.389	-0.376	-0.375
2.00	-0.156	-0.107	-0.091	-0.064	-0.045
3.00	0.039	0.099	0.136	0.160	0.198
4.00	0.216	0.280	0.330	0.403	0.383
5.00	0.350	0.434	0.481	0.525	0.561
6.00	0.468	0.562	0.614	0.656	0.689
7.00	0.591	0.679	0.732	0.768	0.785
8.00	0.724	0.803	0.841	0.870	0.880
9.00	0.857	0.925	0.953	0.969	0.977
10.00	0.976	1.030	1.042	1.053	1.054
11.00	1.096	1.114	1.111	1.126	1.131
12.00	1.164	1.176	1.155	1.179	1.187
13.00	1.221	1.213	1.188	1.225	1.225
14.00	1.254	1.217	1.213	1.247	1.248
15.00	1.259	1.197	1.225	1.251	1.256
16.00	1.219	1.167	1.228	1.251	1.250

TABLE A-4

Anion Activity Coefficient Function  
for the System HCl-LiCl-H<sub>2</sub>O

$I_T$	$X_A=0.3$	$X_A=0.5$	$X_A=0.7$	$X_A=0.9$	$X_A=1.0$
1.0	-0.420	-0.390	-0.379	-0.366	-0.365
2.0	-0.429	-0.390	-0.374	-0.347	-0.328
3.0	-0.412	-0.352	-0.315	-0.291	-0.253
4.0	-0.352	-0.288	-0.238	-0.165	-0.185
5.0	-0.306	-0.222	-0.175	-0.131	-0.096
6.0	-0.259	-0.165	-0.113	-0.072	-0.039
7.0	-0.195	-0.107	-0.054	-0.019	-0.002
8.0	-0.112	-0.033	0.005	0.033	0.043
9.0	-0.022	0.046	0.073	0.089	0.097
10.0	0.059	0.112	0.124	0.135	0.136
11.0	0.145	0.163	0.160	0.174	0.179
12.0	0.183	0.195	0.173	0.197	0.205
13.0	0.212	0.204	0.179	0.216	0.216
14.0	0.221	0.184	0.180	0.213	0.214
15.0	0.203	0.141	0.169	0.195	0.200
16.0	0.142	0.090	0.151	0.174	0.174

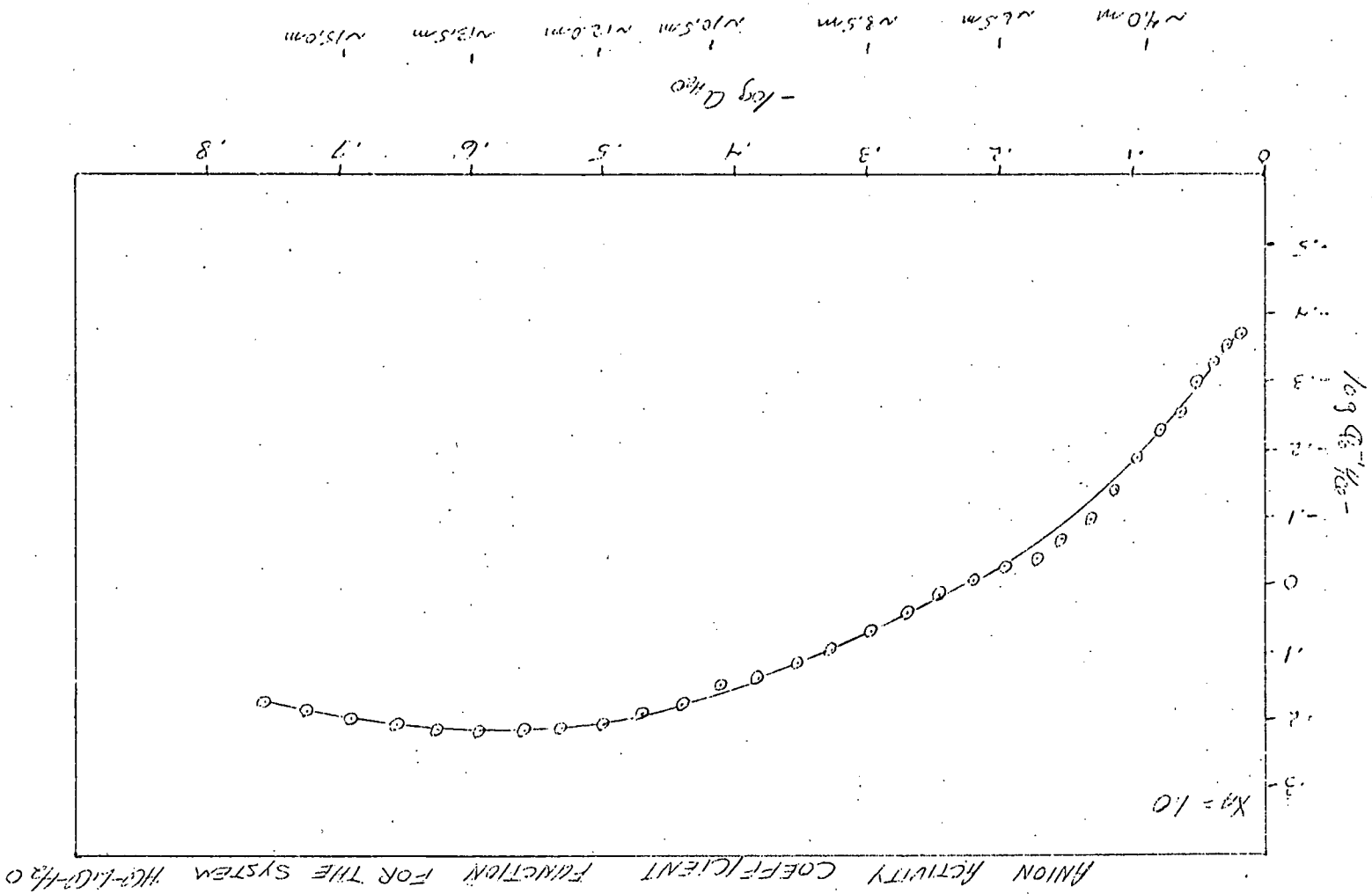


FIGURE (A-1)

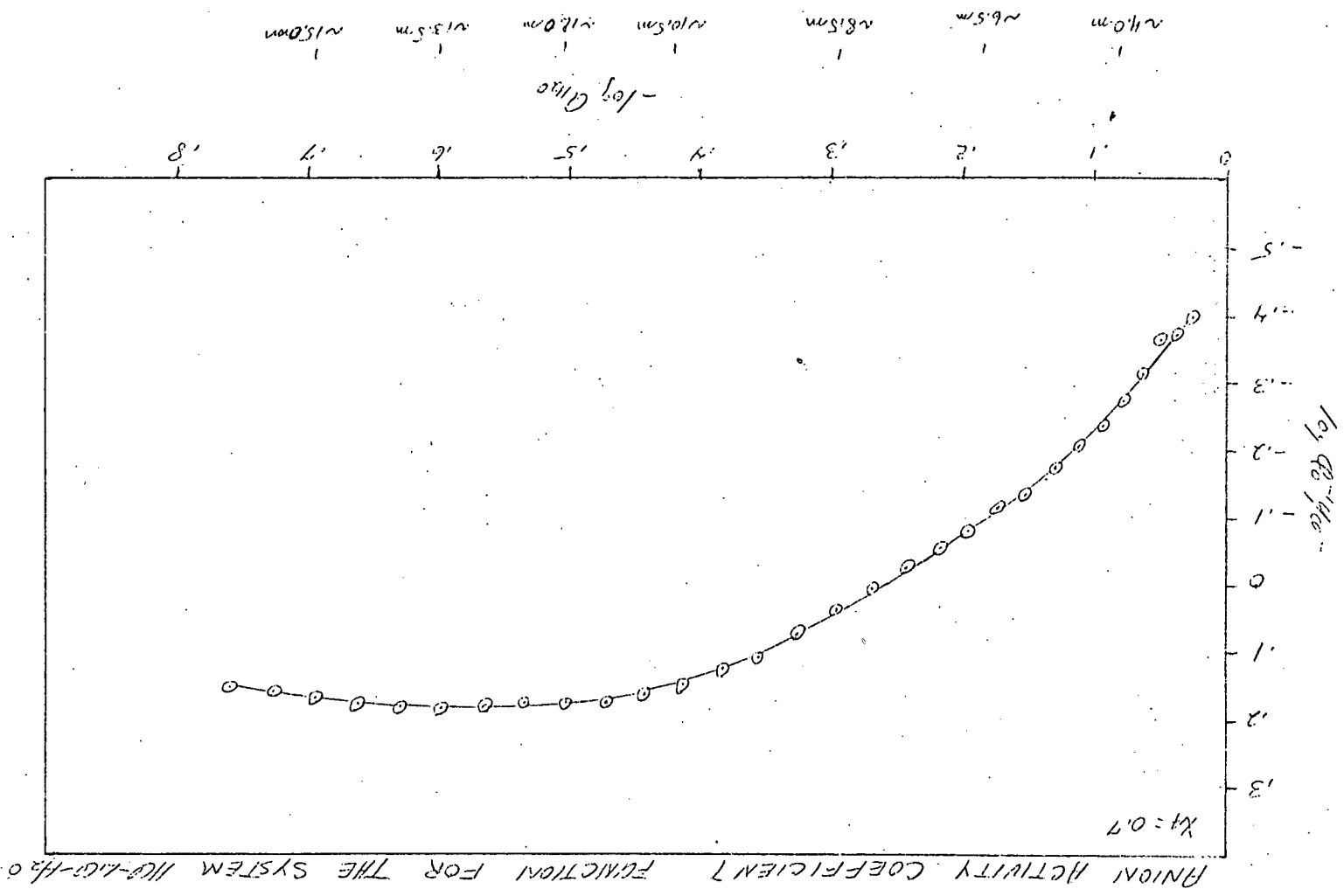


FIGURE (A-2)

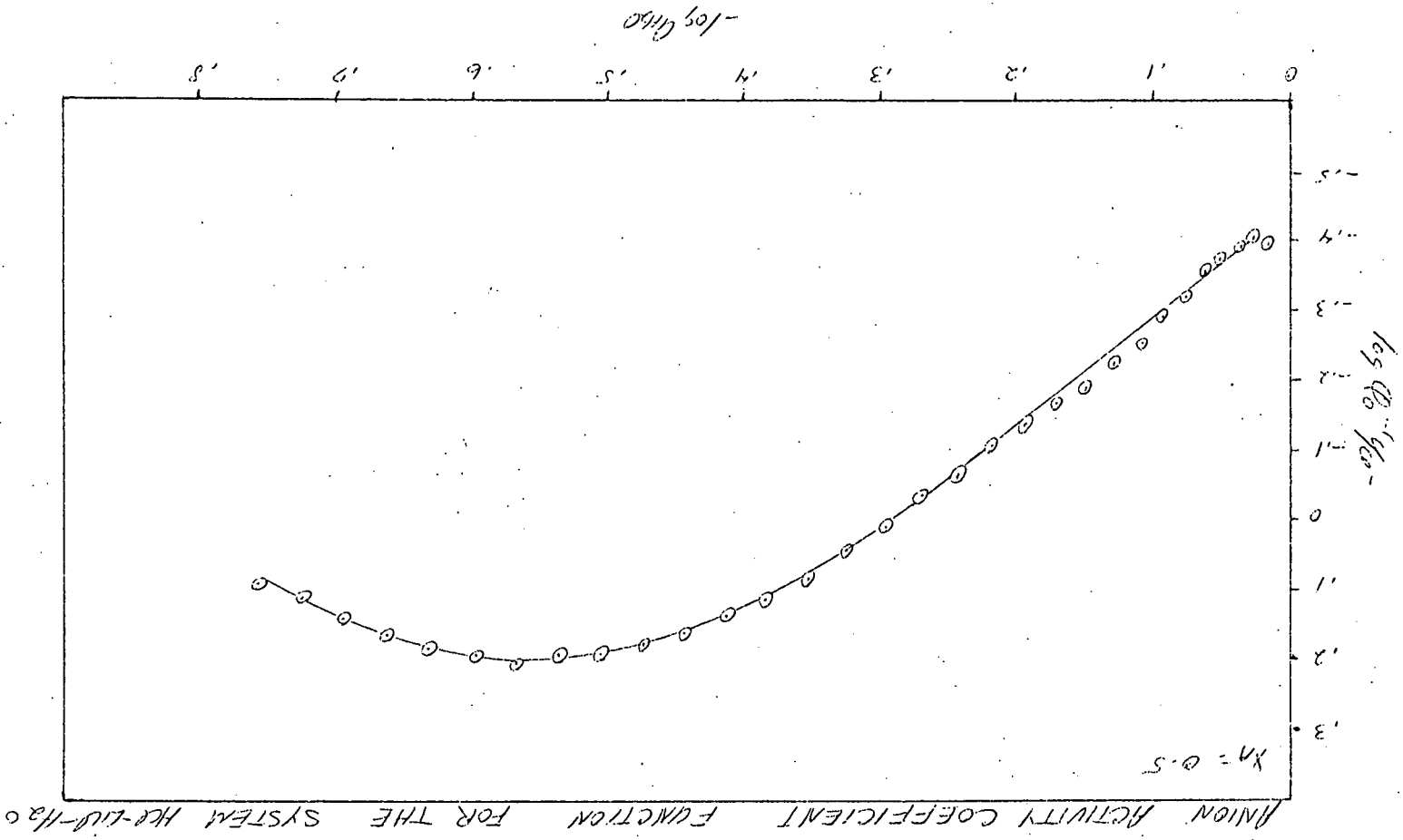


FIGURE (A-3)



Table A-4 and figures (A-1), (A-2) and (A-3) give the anion activity coefficient function in the mixed solutions for several ionic strength fractions of acid at total ionic strengths from 1 through 16 molal. From the figures it can be seen that the anion profiles are likely to contain the same species, indicating very definite ionic structures exist in the liquid state. We will now be able to obtain the detailed "species profile" in the mixed acid-salt solutions.

(L. Leifer and W. H. Streng)

### B. Thermodynamic Studies and Species Profiles in HClO<sub>4</sub>-H<sub>2</sub>O

Recently the water activity was determined in concentrated solutions ( $\approx$  16-28 molal) of HClO<sub>4</sub> in water (H. Wai and K Yates, Can. J. Chem. 47 2326 (1969) ). We obtained a linear relationship by plotting the acid molality vs. the negative logarithm of the water activity, and linearly extrapolated the curve to acid concentrations of approximately 36 molal. Using the Gibbs-equation (Eqn. B-1 below), we calculated the solute activity, by graphical integration, and then the mean activity coefficients for HClO<sub>4</sub>. The results are given in Table B-1.

$$\int d \log a_{\text{HClO}_4} = - \int \frac{55.51}{m} d \log a_{\text{H}_2\text{O}} \quad (\text{B-1})$$

We then combined the values of the Hammett acidity function determined in HClO<sub>4</sub>-H<sub>2</sub>O (K. Yates and H. Wai, J. Am. Chem. Soc. 86 5408 (1964) ) with the thermodynamic results calculated above in order to determine the formal species profile in concentrated HClO<sub>4</sub>-H<sub>2</sub>O solutions.

The anion activity function, the anion activity coefficient function and the average anionic hydration are determined by use of the equations given below.

$$\log \phi_o^{-1} a_{\text{ClO}_4^-} = H_o + \log a_{\text{HClO}_4} \quad (\text{B-2})$$

$$\log \phi_o^{-1} Y_{\text{ClO}_4^-} = \log \phi_o^{-1} a_{\text{ClO}_4^-} - \log M_{\text{ClO}_4^-} \quad (\text{B-3})$$

$$\frac{-d \log \phi_o^{-1} Y_{\text{ClO}_4^-}}{d \log a_{\text{H}_2\text{O}}} = \bar{n} \quad (\text{B-4})$$

A graph showing  $\log \phi_o^{-1} Y_{\text{ClO}_4^-}$  as a function of  $-\log a_{\text{H}_2\text{O}}$  Fig. (B-1) shows a zero hydrate species as the predominant one in the most concentrated  $\text{HClO}_4\text{-H}_2\text{O}$  solutions.

Integration of Eqn. (B-4) using " $\bar{n}$ " values of 0, 1, and 4 yielded the same constant value over a substantial region of the water activity. We take this as evidence that only one term in series  $\sum_{m=0}^{m=n} \text{ClO}_4(\text{H}_2\text{O})_m^-$ , the  $\bar{n}$ <sup>th</sup> one, is important. This procedure enables us to obtain the species profile for perchlorate ion shown in Fig. (B-2).

An analogous procedure for the proton yields the species profiles given in Fig. (B-3). Thus, in the  $\text{HClO}_4\text{-H}_2\text{O}$  system the main cationic species are  $\text{H}_3\text{O}^+$ ,  $\text{H}_5\text{O}_2^+$ ,  $\text{H}_7\text{O}_3^+$ ,  $\text{H}_9\text{O}_4^+$  and  $\text{H}_{21}\text{O}_{10}^+$  and the main anionic species are  $\text{ClO}_4^-$ ,  $\text{ClO}_4(\text{H}_2\text{O})^-$ , and  $\text{ClO}_4(\text{H}_2\text{O})_4^-$ . An attempt to correlate these results with

FIGURE (B-1)

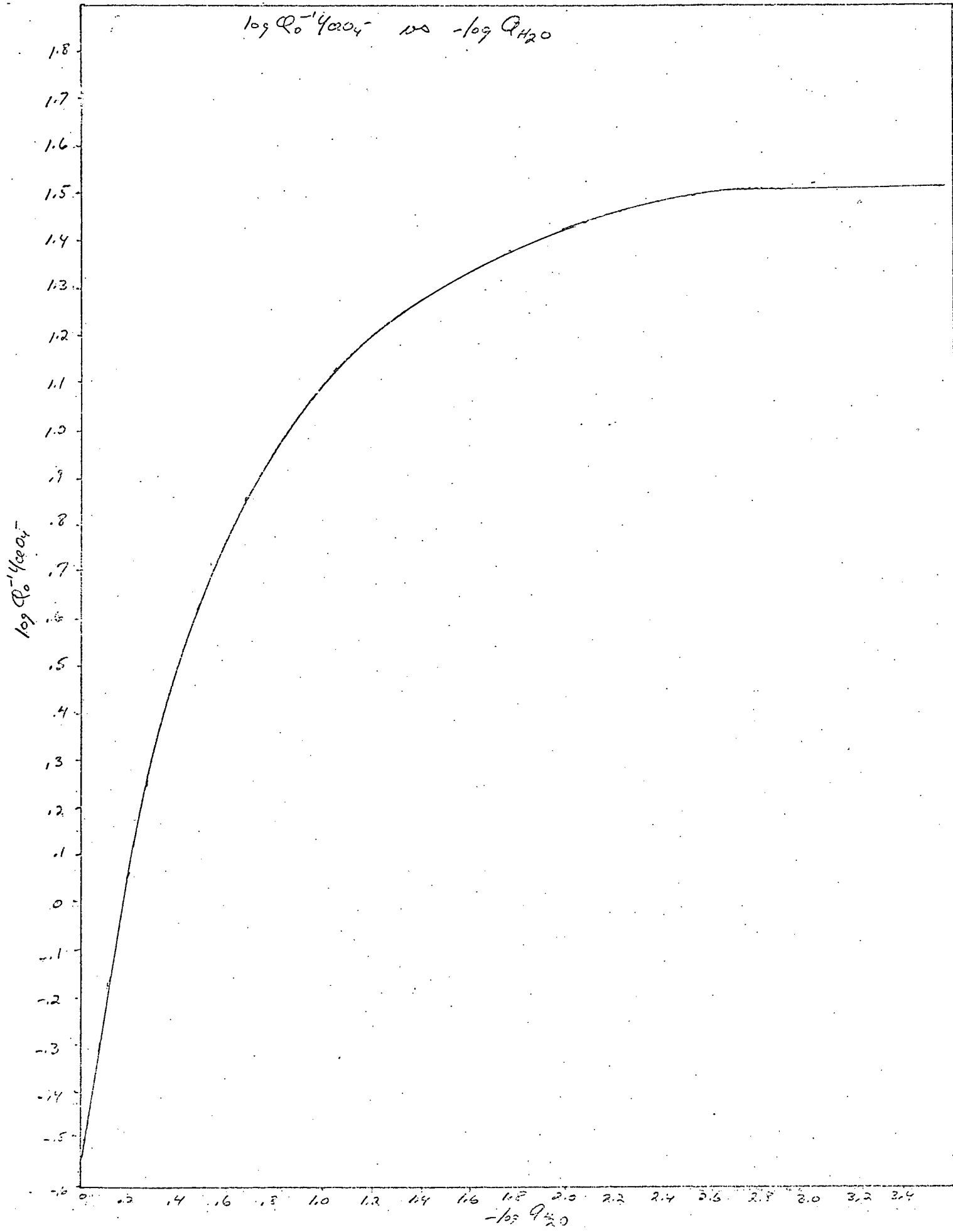


FIGURE (B-2)

FIG II  $[\text{ClO}_4^-]$  SPECIES PROFILE IN SYSTEM  $\text{HClO}_4 - \text{H}_2\text{O}$

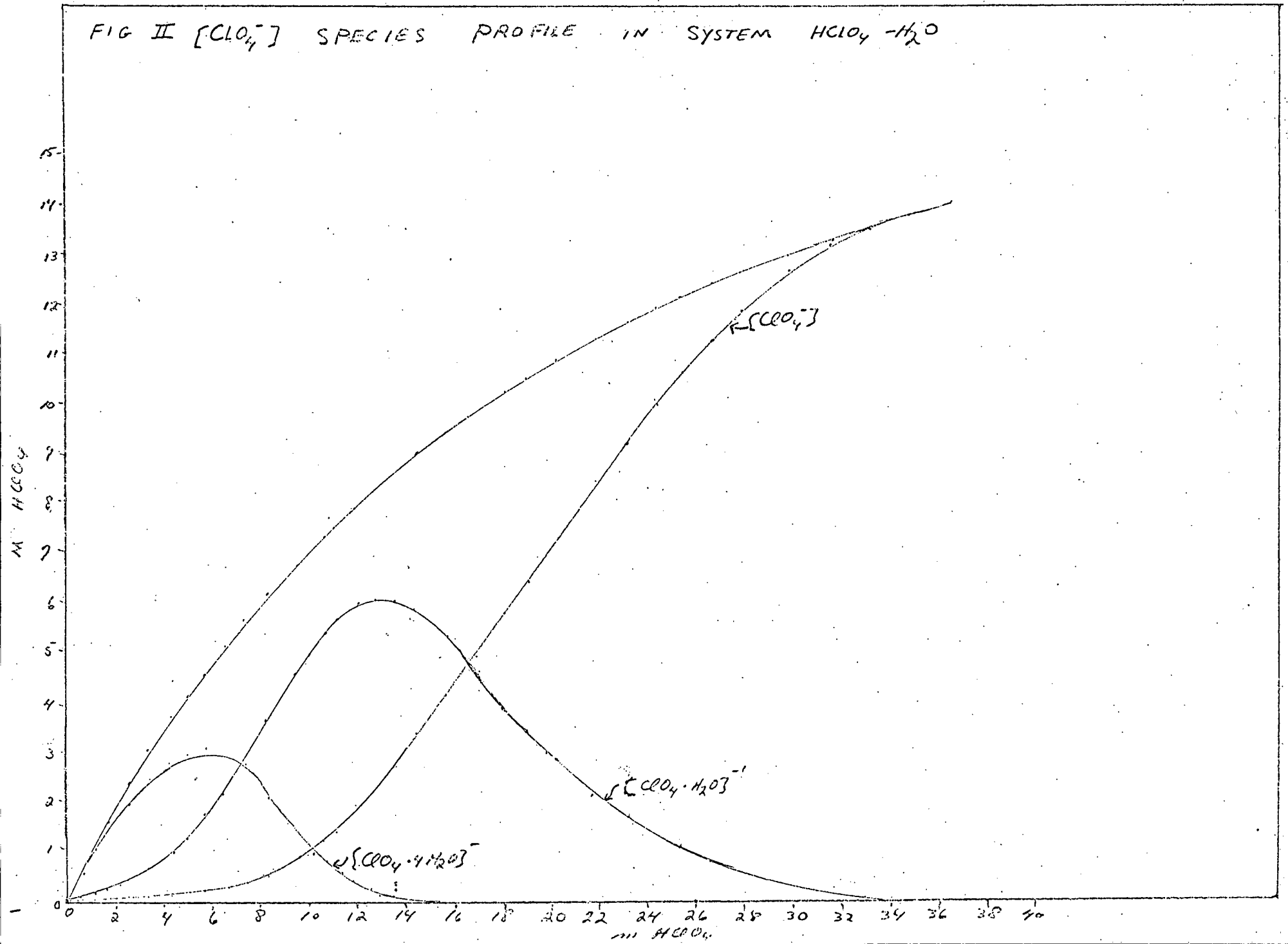


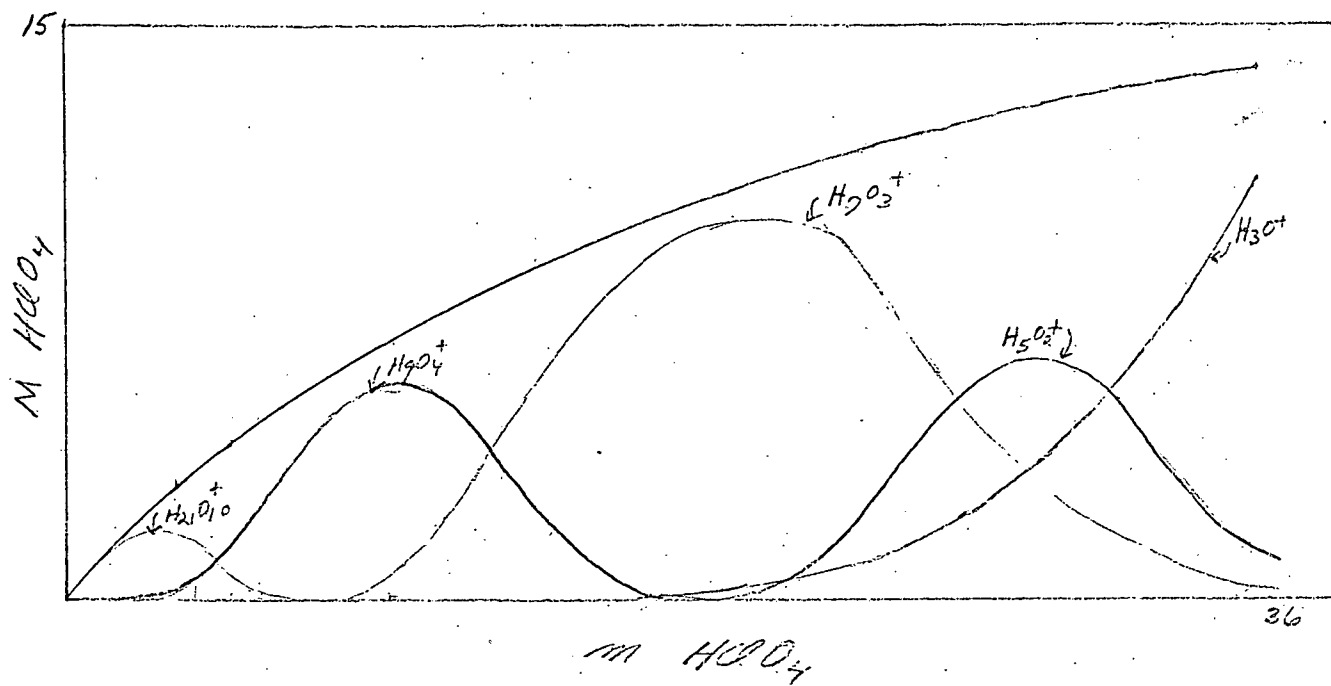
FIGURE (B-3)  $[H^+]$  Species Profile in  $HClO_4-H_2O$  System

TABLE B-1

Values of  $a_{\text{H}_2\text{O}}$  and  $\gamma_{\pm}$  Calculated for  $\text{HClO}_4$   
in the Range 13 m to 36 m

m	$-\log a_{\text{H}_2\text{O}}$	$\log a_{\text{HClO}_4}$	$\gamma_{\pm}$
13.58	0.867	6.721	$1.70 \times 10^2$
14.44	0.966	7.112	$2.50 \times 10^2$
15.70	1.113	7.652	$4.29 \times 10^2$
16.58	1.238	7.986	$5.97 \times 10^2$
16.95	1.251	8.162	$7.13 \times 10^2$
18.08	1.385	8.596	$1.102 \times 10^3$
19.07	1.492	8.946	$1.563 \times 10^3$
20.30	1.636	9.349	$2.37 \times 10^3$
21.85	1.817	9.842	$3.83 \times 10^3$
23.22	1.970	10.247	$5.73 \times 10^3$
24.49	2.112	10.582	$8.02 \times 10^3$
25.47	2.222	10.834	$1.030 \times 10^4$
26.77	2.368	11.160	$1.426 \times 10^4$
27.89	2.497	11.426	$1.858 \times 10^4$
29.86	2.713	11.854	$2.84 \times 10^4$
31.69	2.923	12.231	$4.13 \times 10^4$
33.32	3.107	12.556	$5.70 \times 10^4$
34.68	3.262	12.801	$7.28 \times 10^4$
36.56	3.475	13.137	$1.016 \times 10^5$

the NMR and Raman measurements of Hood et al (G. C. Hood, O. Redlich, and C. A. Reilly, J. Chem. Phys. 22 2067 (1954); G. C. Hood and C. A. Reilly *ibid* 32 127 (1960)) and Weston (K. Heinzinger and R. E. Weston, Jr., J. Chem. Phys. 42 272 1965) ) is underway.

(W. H. Streng and L. Leifer)



C. Temperature Dependence of the Hammett Acidity Function in HCl-H<sub>2</sub>O

To gain insight into the temperature dependence of electrolyte-solvent interactions and to study the kinetics of acid catalyzed reactions as a function of temperature, we have determined the Hammett acidity function,  $H_0$ , in HCl-H<sub>2</sub>O solutions over the temperature range 25 - 80°C.

The measurements reported below are probably the most precise  $H_0$  measurements reported to date.

For the reaction:



the  $H_0$  acidity function is defined as

$$H_0 \equiv pK_{BH^+} - \log (c_{BH^+}/c_B) \quad (C-1b)$$

$$\begin{aligned} \text{where } c_{BH^+}/c_B &= (\epsilon_B^\lambda - \epsilon^\lambda) / (\epsilon^\lambda - \epsilon_{BH^+}^\lambda) \\ &= (A_B - A) / (A - A_{BH^+}) \end{aligned}$$

$\epsilon_B^\lambda$ ,  $\epsilon_{BH^+}^\lambda$  and  $\epsilon^\lambda$  represents the extinction coefficients at a given wavelength,  $\lambda$ , of the base, acid and partially ionized forms of the indicators used. In accordance with Beer's law,  $\epsilon = A/lc$ ;  $A$  being the absorbance of the solution;  $l$ , the path length and  $c$ , the indicator concentration. The experimental conditions are

set so that  $\ell$  and  $c$  will be constant. Thus, the extinction coefficient is directly proportional to the absorbance which is measured with a Beckman Model DV-2 spectrophotometer.

$pK_{BH^+}$  is defined by the equation:

$$pK_{BH^+} = \log \left( \frac{C_{BH^+}}{C_B C_{H^+}} \right) + \log \left( \frac{f_{BH^+}}{f_B f_{H^+}} \right) \quad (C-2)$$

the  $f$  values being the activity coefficients on a molar scale. The indicator concentrations are small enough so that the activity coefficients can be taken as their value in the reference state (i.e. unity) and for the indicator o-nitroaniline the  $pK_{BH^+}$  is obtained by extrapolation to zero acid concentration, i.e.:

$$pK_{BH^+} = \lim_{C_{H^+} \rightarrow 0} \log \left( \frac{C_{BH^+}}{C_B C_{H^+}} \right) \quad (C-3)$$

For the indicators 4-chloro-2-nitroaniline and 4-nitrodiphenylamine the comparison method (illustrated by equation (C-4)) was used to obtain  $pK_{BH^+}$  values.

$$pK_{CH^+} - pK_{BH^+} = \log \left( \frac{C_{CH^+}}{C_C} \right) - \log \left( \frac{C_{BH^+}}{C_B} \right) \quad (C-4)$$

The indicator concentration used in these measurements was  $2.25 \times 10^{-4} M$ . No temperature effect on the  $\lambda_{max}$  was observed

TABLE C-1

$pK_{BH^+}$  Values for Indicators Used in the  
Determination of  $H_0$  in  $HCl-H_2O$  Solutions

$T(^{\circ}C)$	o-nitroaniline	4-chloro-2-nitro- aniline	4-nitrodiphenyl- aniline
25	-0.292	-1.052	-2.48
35	-0.325	-1.071	-2.47
45	-0.359	-1.091	-2.45
55	-0.392	-1.111	-2.43
60	-0.409	-1.121	-2.43
65	-0.425	-1.131	-2.42
70	-0.442	-1.141	-2.41
75	-0.459	-1.151	-2.40
80	-0.475	-1.160	

in the interval 25 - 80°C.  $\lambda_{\max}$  for o-nitroaniline and 4-chloro-2-nitroaniline was found to be 413 and 425 *mμ*, respectively.

The  $pK_{\text{BH}^+}$  values for the indicators used as a function of temperature are given in Table C-1. The  $H_0$  values at selected temperatures 25°C, 45°C, 60°C, 70°C, and 80°C are given in Table C-2.

It will be noted that the  $H_0$  values are almost constant up to 60°C at acid concentrations below 5M and increase slightly with temperature in the region 6-8M HCl.

These results, when combined with the appropriate thermodynamic data will yield "species profile" in HCl-H<sub>2</sub>O over a wide temperature and composition range. Further, the small variation in  $H_0$  over the temperature range 25 - 80°C indicates clearly that the concern of Deno and Taft regarding hydration of the indicators is unfounded and that  $H_0$  can indeed be used to indicate ion-solvent interactions in concentrated electrolyte solutions.

(K. Inoue and L. Leifer)

TABLE C-2

Ho Values at Different Temperatures  
for 0.5-8.0 M HCl Solutions

Conc'n. HCl (M)	25°	45°	60°	70°	80°
0.5	+0.175	+0.185	+0.195	+0.195	+0.200
0.75	-0.035	-0.035	-0.030	-0.035	-0.025
1.0	-0.210	-0.200	-0.200	-0.200	-0.195
1.5	-0.485	-0.480	-0.470	-0.480	-0.475
2.0	-0.700	-0.690	-0.700	-0.695	-0.695
2.5	-0.895	-0.885	-0.900	-0.890	-0.890
3.0	-1.085	-1.075	-1.080	-1.080	-1.070
3.5	-1.270	-1.260	-1.253	-1.250	-1.250
4.0	-1.445	-1.43	-1.435	-1.425	-1.425
4.5	-1.62	-1.60	-1.615	-1.595	-1.600
5.0	-1.80	-1.77	-1.79	-1.77	-1.78
5.5	-1.98	-1.95	-1.98	-1.94	-1.97
6.0	-2.19	-2.16	-2.18	-2.13	-2.17
6.5	-2.40	-2.36	-2.38	-2.33	-2.37
7.0	-2.62	-2.56	-2.58	-2.53	-2.58
7.5	-2.86	-2.78	-2.78	-2.74	-2.81
8.0	-3.10	-3.00	-3.00	-2.94	-3.03

D. Thermodynamic Properties of Aqueous Tetra n-alkyl Ammonium Halides

In this study of thermodynamic properties of a very interesting class of compounds was undertaken. These compounds, the tetra n-alkylammonium halides interact with  $H_2O$  to form clathrate hydrates. To determine the relative apparent partial molal heat content  $L$  and the relative apparent molal entropies ( $S - S^0$ ) of the solvent ( $H_2O$ ) we measured the osmotic coefficients, in the concentration range 0-1 molal, and at temperatures of  $25^\circ$  to  $80^\circ C$ .

The experimental results reported below were obtained by use of a Hewlett Packard Model 302B Vapor Pressure Osmometer. The technique of thermoelectric osmometry was described in a previous report (T. Kangvanvongsa and L. Leifer, Michigan Technological University Technical Progress Report COO-1712-3, March 1969, pp. 24-27). The instrument constant was determined by means of equation (D-1) using NaCl as the reference salt.

$$\Delta R = K (\nu m \phi) \quad (D-1)$$

$\Delta R$  = observed resistance change between the reference solution (NaCl) and pure water for the determination of K; or between the tetra n-alkyl ammonium salt and pure water to determine the osmotic coefficient.

K = the instrument constant

$\nu$  = the number of ions into which 1 mole of salt dissociates

m = molality

$\phi$  - osmotic coefficient.

TABLE D-1

The Osmotic Coefficients of Tetramethylammonium Chloride

m (molal)	<u>25°C</u>	<u>30°C</u>	<u>35°C</u>	<u>40°C</u>	<u>50°C</u>	<u>60°C</u>	<u>70°C</u>	<u>80°C</u>
.01	0.950	0.935	0.917	0.900	0.888	0.900	0.915	0.930
.05	0.936	0.920	0.898	0.890	0.877	0.910	0.938	0.944
.10	0.915	0.902	0.880	0.875	0.875	0.899	0.927	0.926
.20	0.890	0.871	0.850	0.840	0.847	0.870	0.897	0.894
.30	0.878	0.847	0.825	0.816	0.825	0.850	0.876	0.876
.40	0.873	0.834	0.812	0.801	0.807	0.833	0.866	0.867
.50	0.866	0.826	0.804	0.793	0.805	0.821	0.852	0.864
.60	0.863	0.824	0.801	0.791	0.795	0.816	0.848	0.865
.70	0.861	0.829	0.802	0.792	0.790	0.808	0.847	0.870
.80	0.850	0.824	0.802	0.795	0.791	0.812	0.847	0.878
.90	0.851	0.825	0.806	0.795	0.795	0.817	0.849	0.890
1.0	0.851	0.830	0.806	0.802	0.802	0.822	0.858	0.907

TABLE D-2

The Osmotic Coefficients of Tetraethylammonium Chloride

m (molal)	<u>25°C</u>	<u>30°C</u>	<u>35°C</u>	<u>40°C</u>	<u>50°C</u>	<u>60°C</u>	<u>70°C</u>	<u>80°C</u>
.01	0.951	0.936	0.920	0.908	0.889	0.896	0.911	0.922
.05	0.937	0.922	0.902	0.899	0.880	0.902	0.928	0.937
.10	0.917	0.906	0.886	0.881	0.870	0.889	0.918	0.920
.20	0.902	0.877	0.854	0.843	0.837	0.863	0.887	0.880
.30	0.884	0.858	0.835	0.824	0.818	0.838	0.862	0.862
.40	0.877	0.845	0.825	0.809	0.805	0.821	0.845	0.849
.50	0.872	0.839	0.811	0.799	0.795	0.811	0.836	0.841
.60	0.870	0.835	0.809	0.798	0.791	0.807	0.831	0.840
.70	0.869	0.835	0.812	0.799	0.788	0.800	0.828	0.840
.80	0.870	0.838	0.814	0.800	0.789	0.801	0.829	0.862
.90	0.873	0.842	0.817	0.808	0.792	0.802	0.832	0.860
1.0	0.875	0.847	0.822	0.816	0.801	0.803	0.839	0.877



TABLE D-3

The Osmotic Coefficients of Tetrapropylammonium Chloride

m (molal)	<u>25°C</u>	<u>30°C</u>	<u>35°C</u>	<u>40°C</u>	<u>50°C</u>	<u>60°C</u>	<u>70°C</u>	<u>80°C</u>
.01	0.952	0.938	0.923	0.911	0.894	0.890	0.900	0.915
.05	0.938	0.927	0.908	0.900	0.883	0.895	0.919	0.925
.10	0.918	0.907	0.890	0.883	0.865	0.881	0.909	0.905
.20	0.903	0.881	0.859	0.849	0.830	0.844	0.877	0.867
.30	0.889	0.864	0.837	0.830	0.812	0.820	0.851	0.845
.40	0.882	0.853	0.825	0.814	0.798	0.808	0.830	0.830
.50	0.882	0.848	0.820	0.802	0.790	0.798	0.820	0.821
.60	0.888	0.847	0.816	0.802	0.788	0.791	0.814	0.816
.70	0.896	0.850	0.821	0.802	0.786	0.788	0.810	0.815
.80	0.902	0.855	0.828	0.805	0.786	0.778	0.810	0.819
.90	0.912	0.862	0.837	0.815	0.786	0.788	0.812	0.827
1.0	0.925	0.872	0.850	0.830	0.792	0.790	0.815	0.840

TABLE D-4

The Osmotic Coefficients of Tetrabutylammonium Chloride

m (molal)	<u>25°C</u>	<u>30°C</u>	<u>35°C</u>	<u>40°C</u>	<u>50°C</u>	<u>60°C</u>	<u>70°C</u>	<u>80°C</u>
.01	0.952	0.940	0.920	0.919	0.898	0.885	0.897	0.910
.05	0.938	0.930	0.910	0.905	0.886	0.893	0.910	0.917
.10	0.919	0.912	0.897	0.886	0.865	0.875	0.893	0.897
.20	0.910	0.888	0.868	0.851	0.825	0.837	0.857	0.859
.30	0.899	0.871	0.848	0.835	0.807	0.803	0.830	0.834
.40	0.900	0.862	0.840	0.820	0.791	0.791	0.811	0.814
.50	0.903	0.860	0.826	0.811	0.784	0.782	0.798	0.800
.60	0.906	0.862	0.826	0.809	0.780	0.775	0.791	0.792
.70	0.916	0.867	0.833	0.809	0.780	0.774	0.788	0.790
.80	0.923	0.881	0.844	0.810	0.783	0.769	0.790	0.790
.90	0.934	0.894	0.859	0.820	0.775	0.769	0.790	0.793
1.0	0.942	0.914	0.881	0.839	0.784	0.773	0.792	0.805

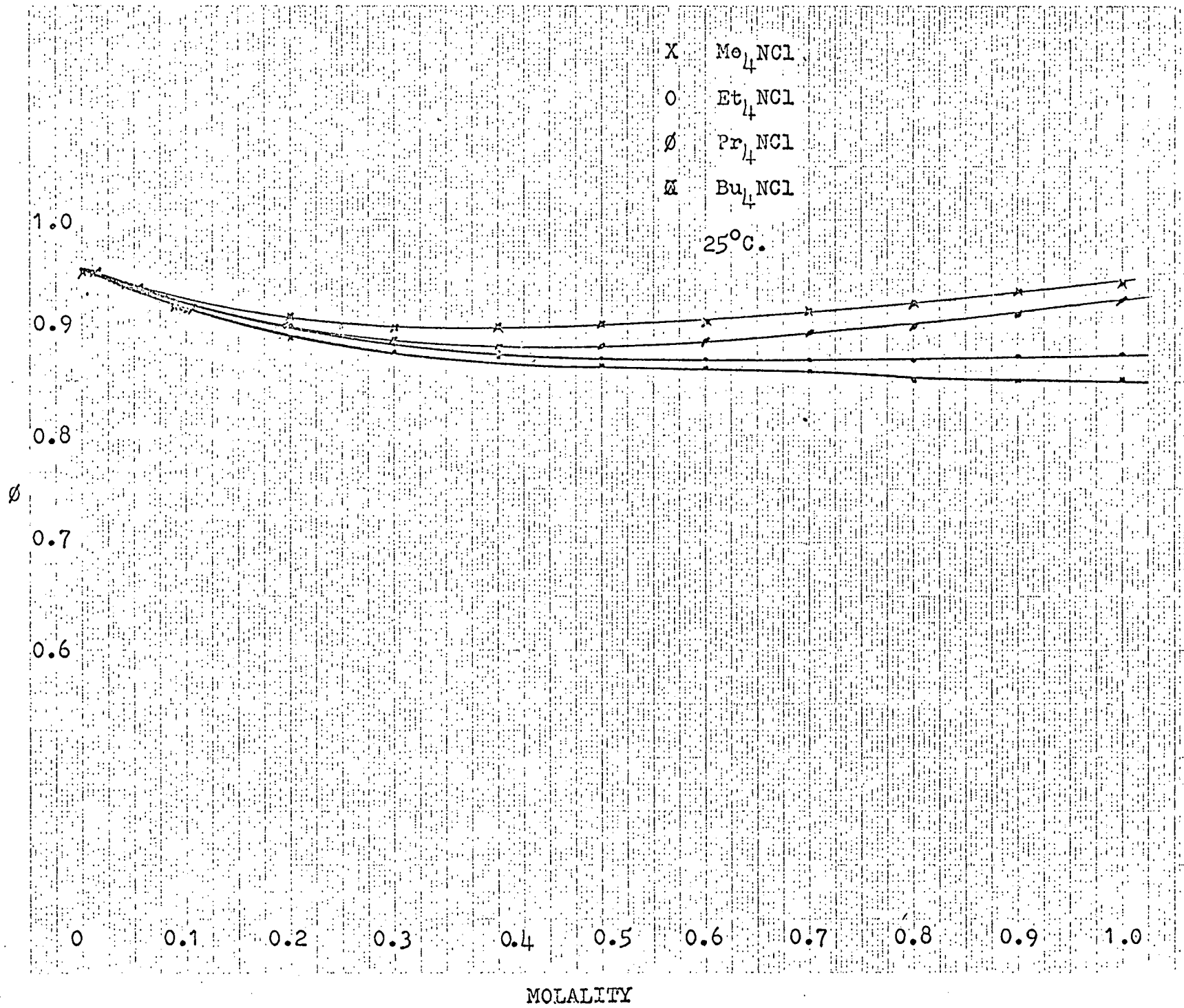


Figure D-1.

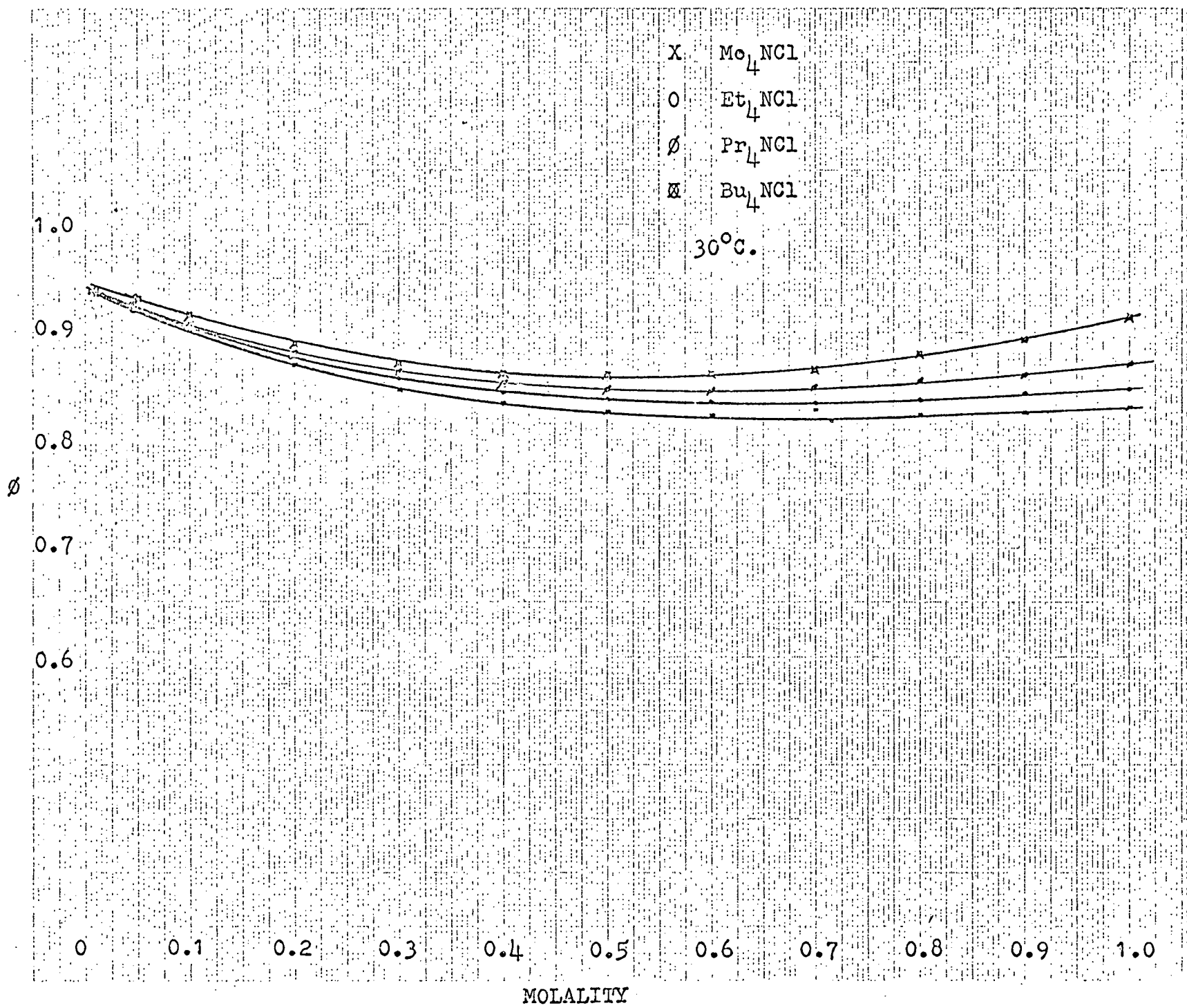


Figure D-2.

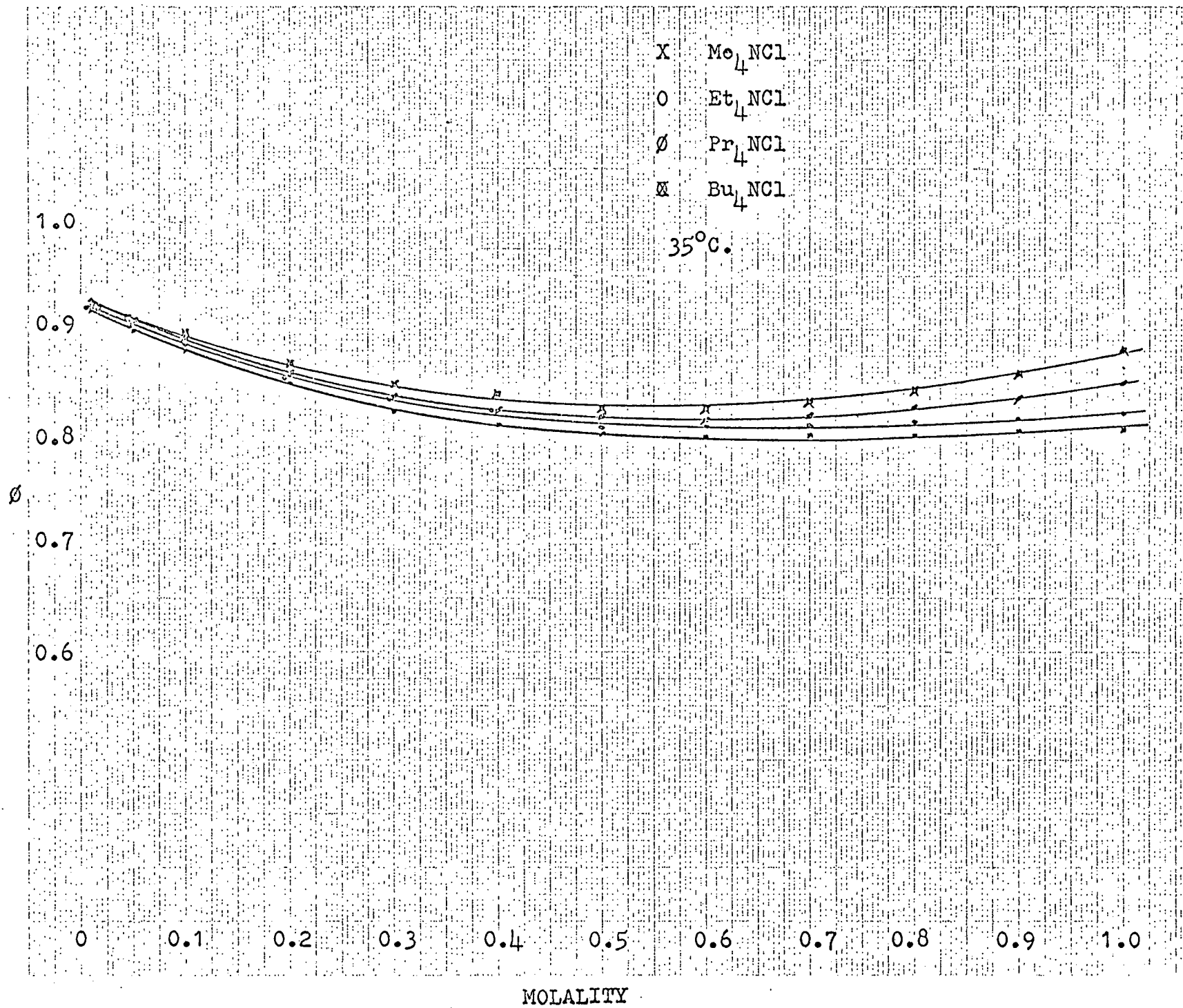


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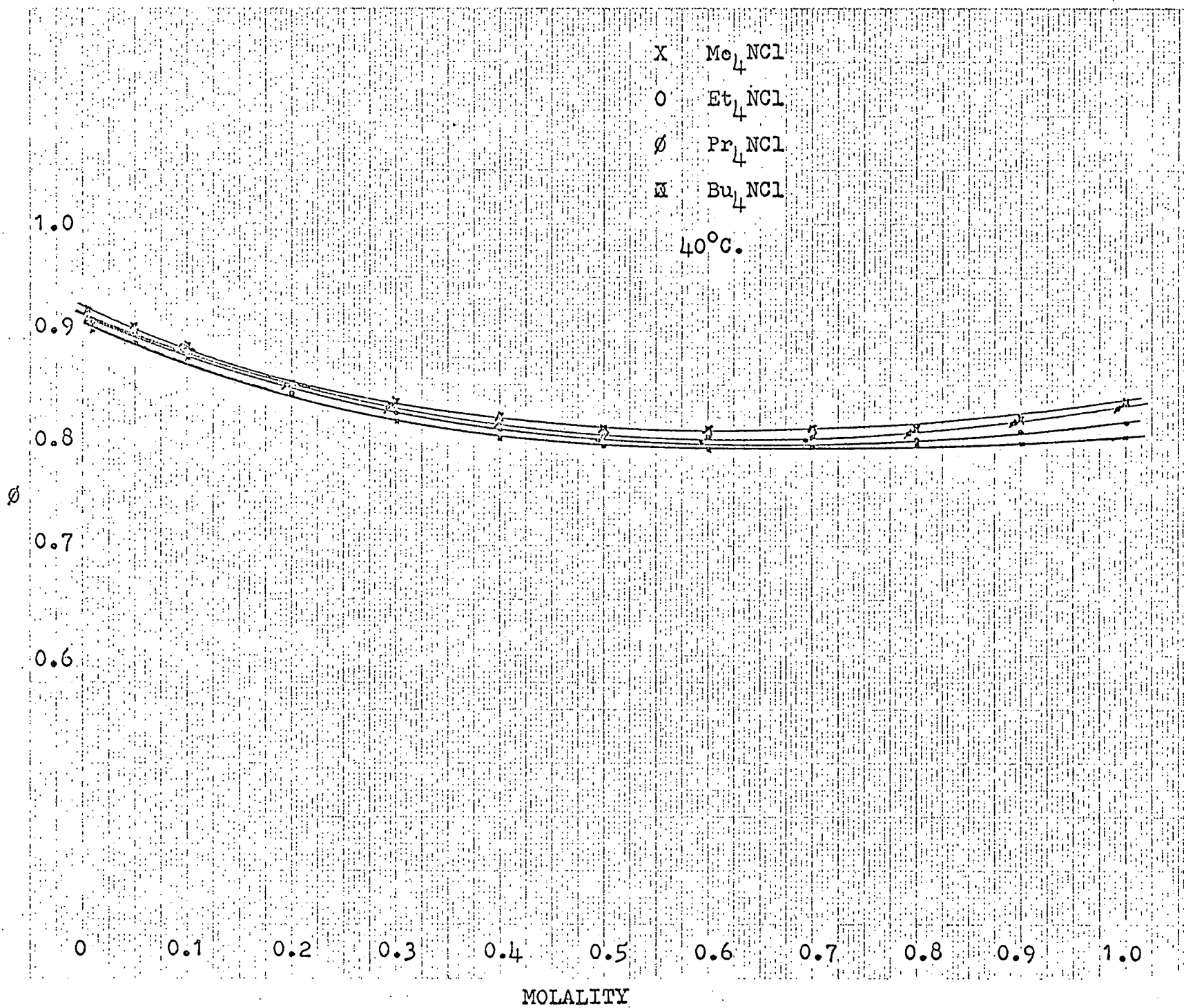


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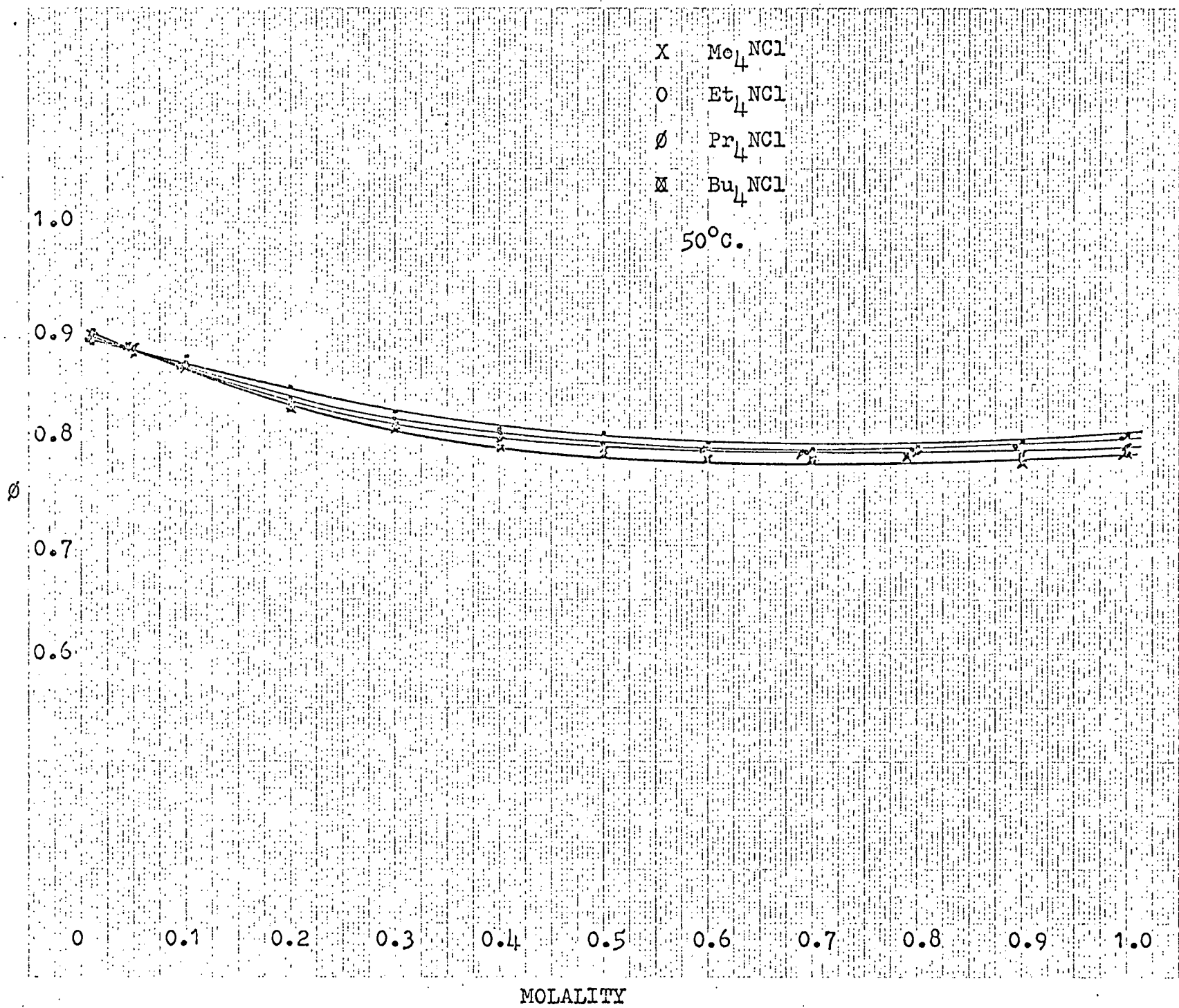


Figure D-5.

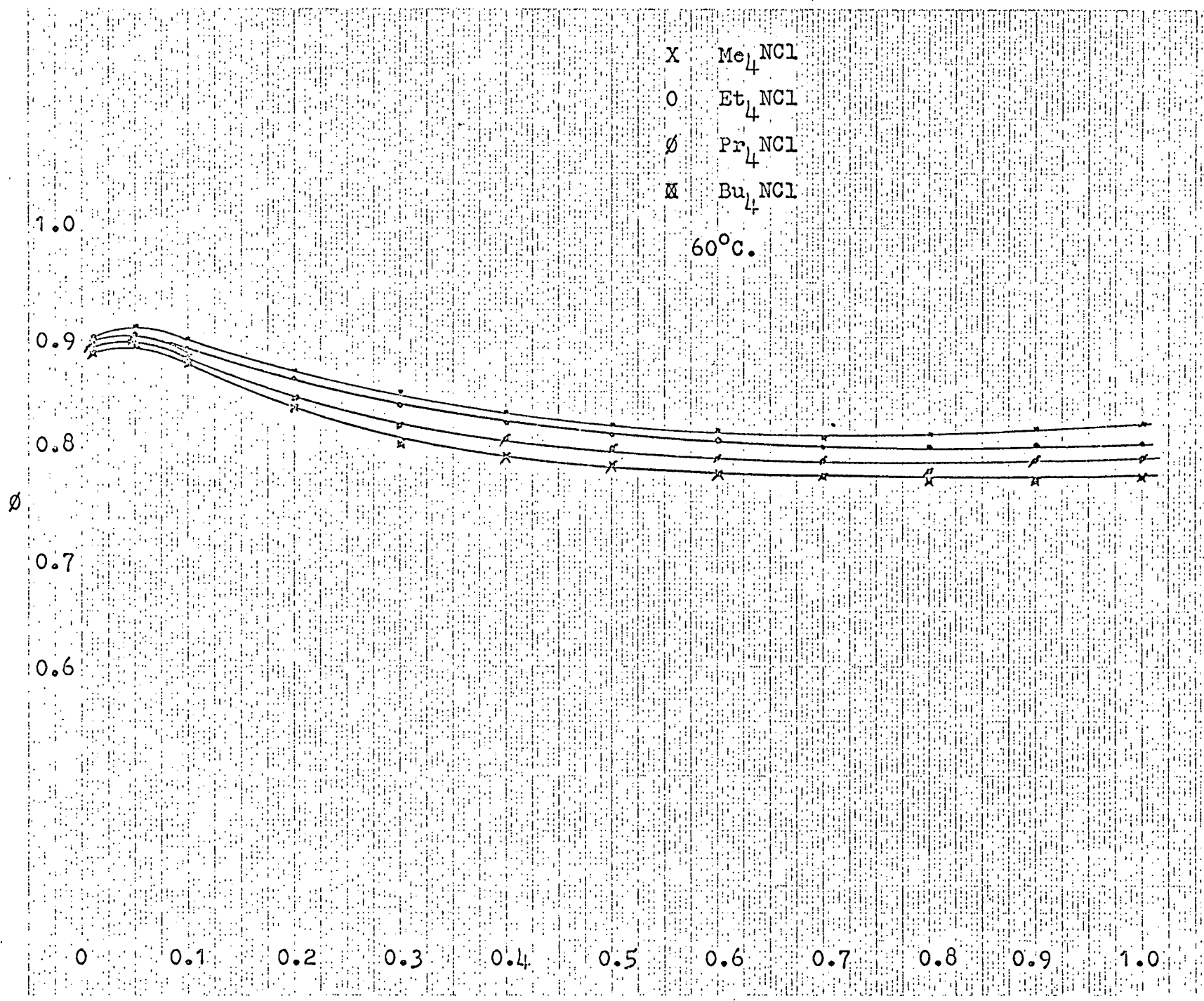


Figure D-6.



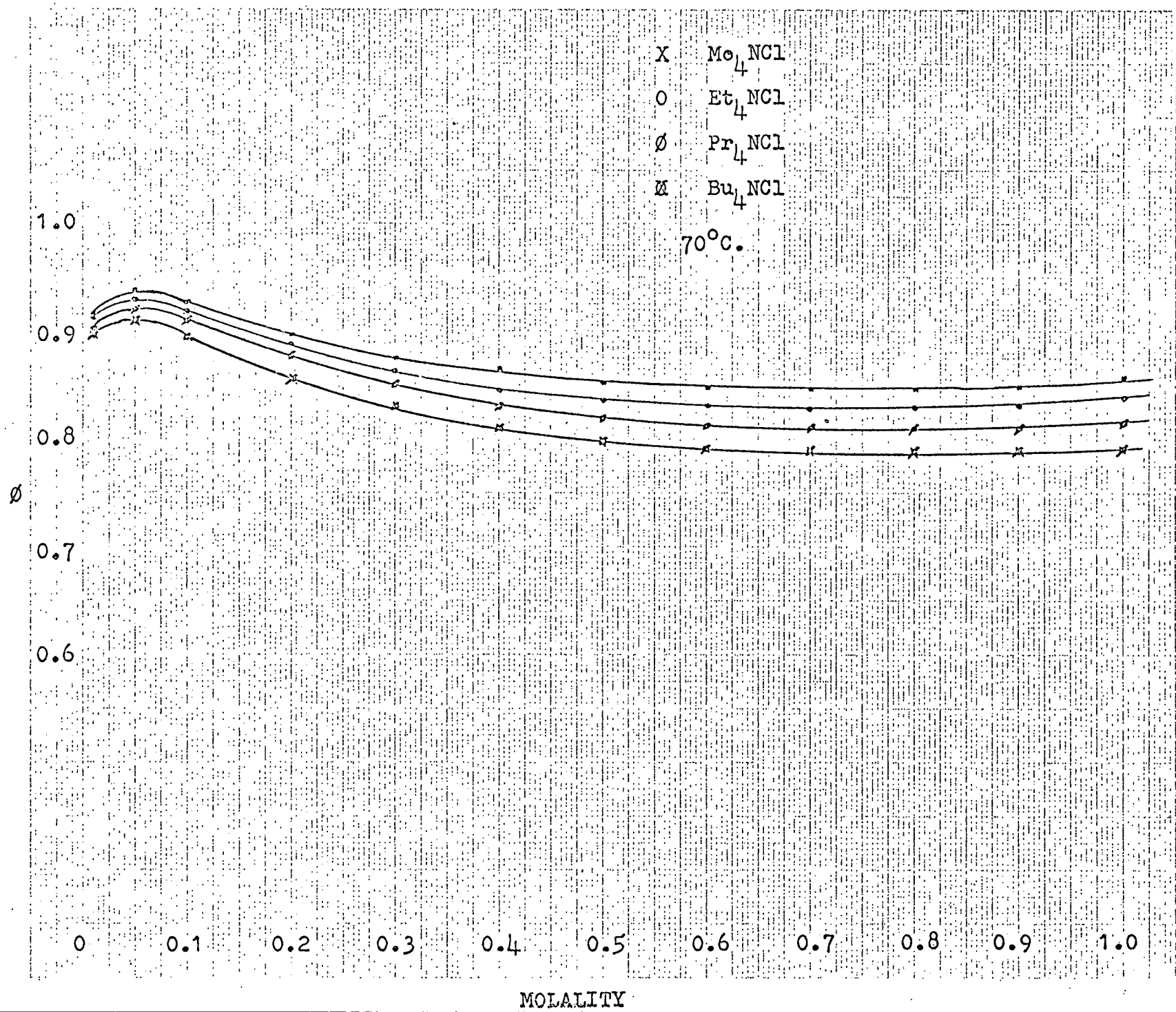


Figure D-7.

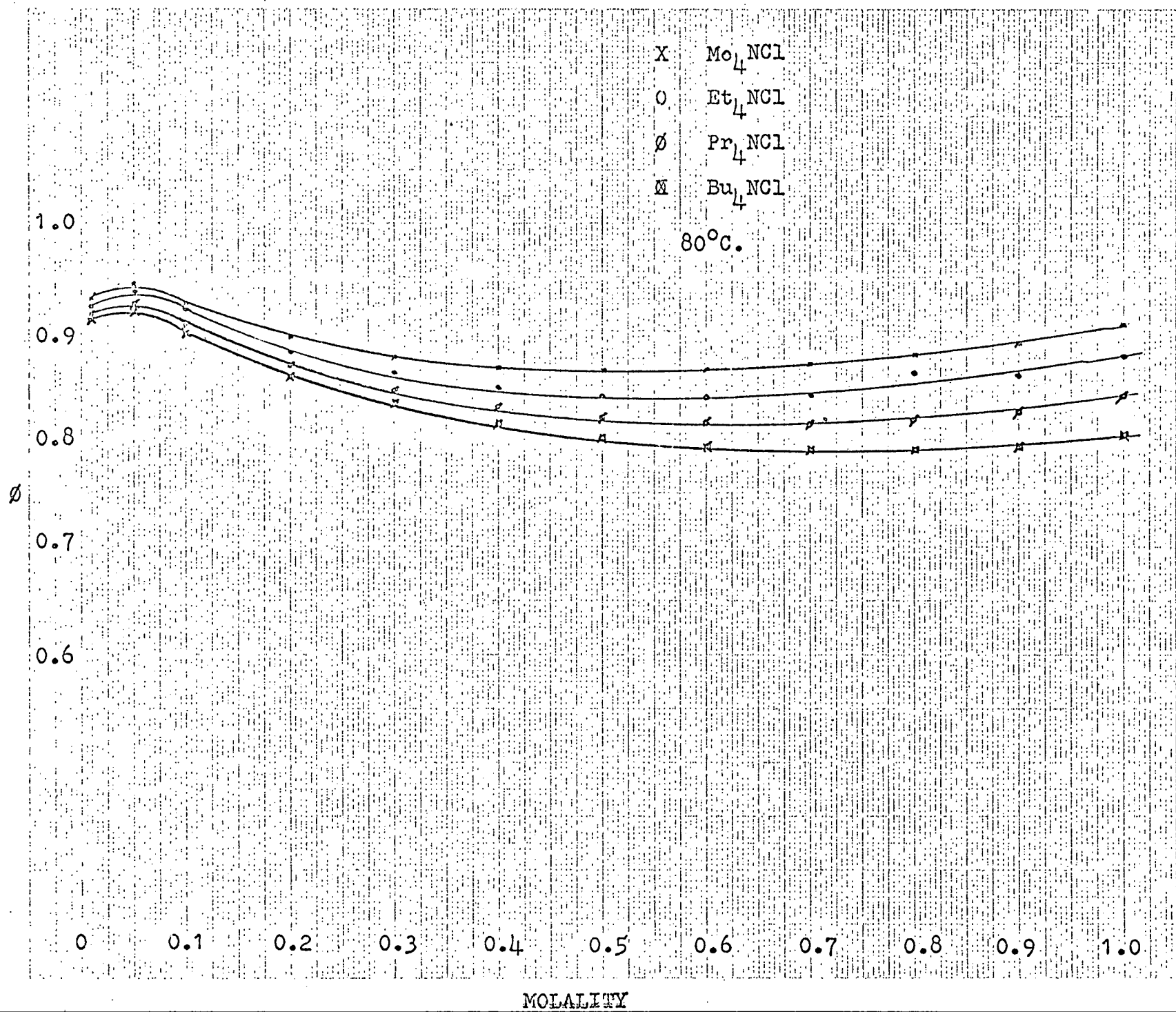
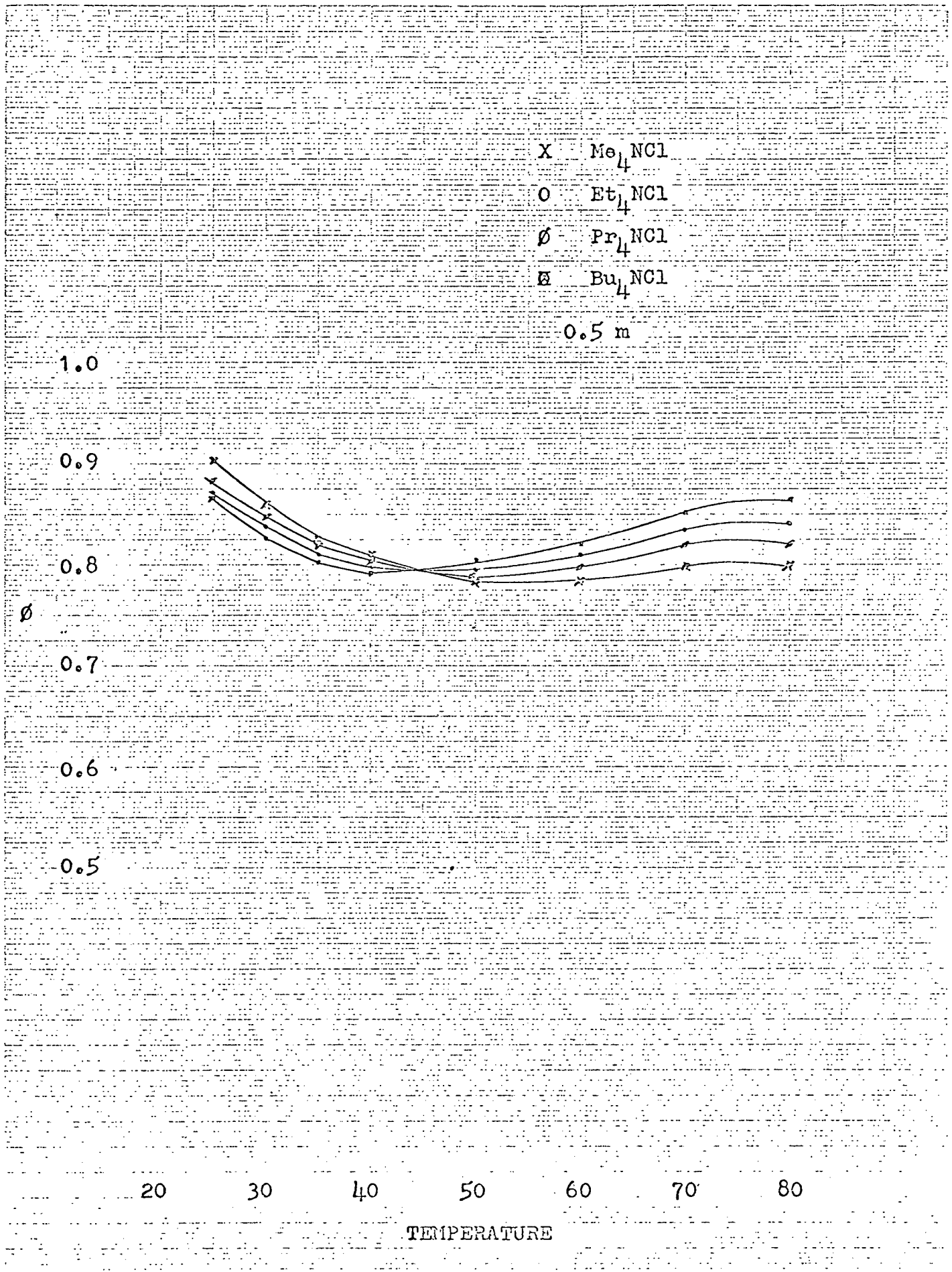


Figure D-8.



The results reported below are for the tetra n-methyl, ethyl, propyl and butyl ammonium chloride.

The methyl salt ( $\text{Me}_4\text{NCl}$ ) was recrystallized from a methanol-ether solution, the  $\text{Et}_4\text{NCl}$  from chloroform-ether solution, the  $\text{Pr}_4\text{NCl}$  and  $\text{Bu}_4\text{NCl}$  from acetone-ether solution. In general the procedures reported by R. L. Kay and by A. K. R. Unni were followed (R. L. Kay et al., J. Phys. Chem., 69 4028 (1965) ); A. K. R. Unni et al. ibid 67 1216 (1963) ). The solutions were prepared by weight and the observed osmotic coefficients are reported for each of the salts listed above in Tables D-1 to D-4 and are shown graphically in Figures D-1 to D-8.

It can be seen that the effect of temperature on the chloride salts is to reverse the normal order (i.e.  $\phi_{\text{Bu}_4\text{N}^+} > \phi_{\text{Pr}_4\text{N}^+} > \phi_{\text{Et}_4\text{N}^+} > \phi_{\text{Me}_4\text{N}^+}$ ) of osmotic coefficients. Indeed, Figure D-9 shows the osmotic coefficients as a function of temperature for 0.5 molal solutions. The inversion temperature is seen to be approximately  $45^\circ\text{C}$ . Thus increasing temperature causes disruption of the short-range order in the water and offsets the water structure promoting ability of the tetra-alkylammonium ions.

(T. Kangvanvongsa and L. Leifer)

## PAPERS ACCEPTED FOR PRESENTATION

- D. H. Kenny, L. Leifer and J. E. 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, April 3, 1970. To be published in the transactions of the Michigan Academy of Science.
- L. Leifer and W. H. Streng, "Species Profiles in Aqueous Perchloric Acid Solutions." (Paper to be 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-H<sub>2</sub>O Solutions in the Temperature Range 25°-80°C." (Paper to be 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." (Paper to be presented at the Great Lakes Meeting of the American Chemical Society Fargo, North Dakota, June 18-19, 1970.)

PAPERS PRESENTED AT MEETINGS DURING THE PERIOD  
March 1, 1969-February 28, 1970

- A. P. Craig, L. Leifer and F. D. Williams, "The Use of the Ion Activity Function in Solution Kinetics V. The Kinetics of Acid Catalyzed Hydrolyses of Amides Containing a Basic Amine Nitrogen." (Paper presented at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 14-18, 1969. Paper #87 Physical Chemistry Division Abstracts.)
- D. Foss, L. Leifer, and F. D. Williams, "The Use of the Ion Activity Function in Solution Kinetics VI. The Kinetics of the Acid Catalyzed Hydrolysis of 4-Butyrolactone." (Paper presented at the Great Lakes Regional Meeting of the American Chemical Society, DeKalb, Illinois, June 4-5, 1969.)
- W. H. Streng and L. Leifer, "Hammett Acidity Measurements in Mixed Acid-Salt Media," (Paper presented at the Great Lakes Regional Meeting of the American Chemical Society, DeKalb, Illinois, June 4-5, 1969.)

## PAPERS PUBLISHED

- S. Lindenbaum, L. Leifer, G. E. Boyd and J. W. Chase,  
"Variation of Osmotic Coefficients of Aqueous Solutions  
of Tetraalkylammonium Halides with Temperature. Thermal  
and Solute Effects on Solvent Hydrogen Bonding."  
J. Phys. Chem. 74 761 (1970).

## THESES

David A. Foss "The Concentration and Temperature Dependence of the Acid Catalyzed Hydrolysis of 4-Butyrolactone." (M.S. Thesis, Department of Chemistry and Chemical Engineering, Michigan Technological University, August 1969)