phate at high pH, it is necessary to change both the activation energy and the frequency factor to explain the temperature dependence of the hydrolysis. These results agree with a recent publication (*24*) that shows the interdependence of the Arrhenius parameters at pH values ≤2.5 for sodium pyro- and tripolyphosphate. The reasons for this anomalous behavior are not apparent.

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Supplementary Material Available. Complete data for Tables I, III, and IV will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number JCED-75-276.

Salt Effects on Vapor-Liquid Equilibrium of Tetrahydrofuran-Water System

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Vapor-liquid equilibrium data at atmospheric pressure for the systems tetrahydrofuran (THF)–water, THF–water–LiCl, THF–water–NaCl, and THF–water–$CaCl_2$ were obtained by use of a modified Othmer still. THF was salted out from the aqueous solution by addition of these salts, and the salting out of THF caused separation into two liquid phases. The order of the salting out effect was LiCl > $CaCl_2$ > NaCl.

The system tetrahydrofuran (THF) and water is of theoretical and industrial importance. A good deal of information on this system is already available. Matous et al. (*4*) found that this system has a closed loop region of limited miscibility (71.8° ∼ 137.1°C). Cigna and Sebastiani (*1*) and Shnitko and Kogan (*9*) measured the isobaric vapor-liquid equilibrium at 760 mm Hg and found that THF forms a homogeneous positive azeotrope with water, boiling at 63.52°C and containing 18.28 mol % of water. Matous et al. (*5*) measured the isothermal vapor-liquid equilibria at 50° and 70°C, and Signa et al. (*10*) at 25°C. Fukala and Kopechy (*2*) and Yoshioka et al. (*11*) proposed methods for dehydration of THF solution by salting out, but no data for the vapor-liquid equilibrium are given.

In this paper, the effects of addition of LiCl, NaCl, or $CaCl_2$ on the vapor-liquid equilibrium of the THF-water solution are measured at fixed solvent composition and atmospheric pressure. Furthermore, the equilibrium data saturated with each salt are also obtained.

Experimental

All vapor-liquid equilibrium data were obtained by use of a modified Othmer still (Figure 1). The total volume of the still was about 500 cc, of which about 300 cc was occupied by liquid. The holdup in the condensate receiver was about 7 cc. To heat the boiling chamber of the still, an external electric heater regulated by a variable rheostat was used. The liquid in the boiling chamber was stirred by a magnetic stirrer. To avoid the partial condensation of vapor on the inside still wall, an electric heater was wound around the upper portion.

The boiling point temperature was measured within an accuracy of ±0.05°C by using a mercury-in-glass thermometer (0° ∼ 100°C, 0.1°C divisions) calibrated against a standard thermometer certified by the National Research Laboratory. Atmospheric pressure was measured with a mercury column barometer. Equilibrium vapor condensate was analyzed by means of density measurement at 25.00° ± 0.02°C. An Ostwald pycnometer (capacity ca. 5 cc) was used. Liquid-phase composition was calculated by taking a material balance (*6*). The accuracies of both compositions were ±0.001 mole fraction.

In this work, since all measurements were made under atmospheric pressure, the boiling points should be corrected to those at 760 mm Hg. As all vapor-phase compositions were over 75 mol % of THF and boiling point temperatures were nearly equal to that of pure THF, we assumed that the value of (dt/dP) for the mixture is equal to that of THF at the normal boiling point, that is, 0.044°C/mm Hg (*7*). The correction of the vapor-phase composition with respect to the small change in pressure

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was neglected. Actual measurements were made after about 2 hr circulation. For the system saturated with salt, the saturation was definitely established by always having a slight amount of solid salt present.

Distilled water was used in all experimental work. THF, LiCl, NaCl, and $CaCl_2$ were of guaranteed reagent grade from Wako Pure Chemicals Co. and were used without further purification as almost all impurities were water. Before use, the purity of THF was checked by gas chromatography with Porapak Q as the column packing and was over 99.9%. The water content of each salt was checked by heating to constant weight at a temperature above the transition point to anhydrous salt. The water content of NaCl was below 0.1 wt %, LiCl about 0.1 wt %, and $CaCl_2$ about 0.2 wt %. The physical properties of pure solvents are compared with the literature values in Table I.

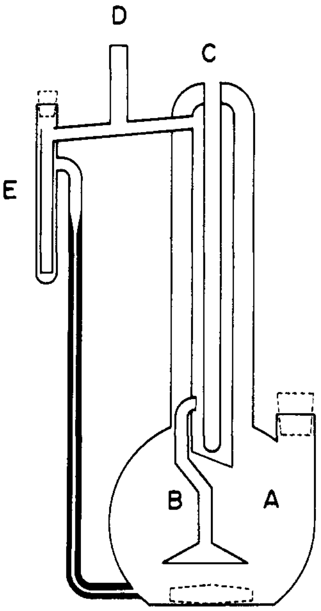

Figure 1. Equilibrium still

A: Boiling chamber
B: Cottrell pump
C: Thermometer well
D: To condenser
E: Condensate receiver

Results and Discussion

Isobaric vapor-liquid equilibrium data at 760 mm Hg for the THF-water system are shown in Table II and Figure 2 and are compared with those measured by Shnitko and Kogan (*9*). The agreement is very good and shows that the apparatus used in this work may give consistent data. As shown in Figure 2, THF forms a homogeneous positive azeotrope with water outside the composition range of immiscibility (ca. 10 ~ 40 mol % of THF). Thus, the boiling point-composition curve has two points of inflection. The activities of THF and water are shown in columns 4 and 5 of Table II. The activities were calculated by the following equation:

$$a_i = f_i/f_i^\circ \simeq P_i/P_i^\circ \qquad (1)$$

where the superscript ° denotes the pure component. The saturation vapor pressures of THF and water were calculated from the Antoine equation with constants in the literature (*5*, *9*).

$$\log P_1^\circ = 7.0922 - 1245.5/(t + 230) \qquad (2)$$

$$\log P_2^\circ = 7.9668 - 1668.2/(t + 228) \qquad (3)$$

The activities were calculated, not by the fugacity, but by the pressure. Therefore, the values of a_2 apparently show the erroneous behavior ($a_2 > 1$) in the water-rich region.

The effects of addition of LiCl, NaCl, or $CaCl_2$ on phase equilibrium of the THF-water system are shown in Tables III-V and Figure 3. As shown in Figure 3, THF is remarkably salted out from the aqueous solution by the addition of these salts, and even at low salt concentration, the salting out of THF causes separation into two liquid phases. The azeotrope of this system, however, cannot be eliminated by the salt addition, because in the systems saturated with each salt, the normal boiling point in the immiscible region is lower than that for THF or water.

Table I. Physical Properties of Materials

Material	Bp, °C	Density, 25°C	Refractive index, 25°C
THF	65.75	0.8820	1.4049
	65.93 (*5*)	0.8822 (*5*)	1.4051 (*5*)
	65.72 (*9*)	0.8821 (*10*)	1.4048 (*10*)
Water	100.01	...	1.3325
	100.00 (*7*)	0.99705 (*7*)	1.3325 (*7*)

Table II. Vapor-Liquid Equilibrium Data for THF-Water System at 760 mm Hg

x_1	y_1	t, °C	a_1	a_2
0.127	0.758	64.55	0.788	1.000
0.163	0.760	64.4	0.794	0.999
0.245	0.761	64.25	0.799	1.001
0.254	0.761	64.25	0.799	1.001
0.278	0.761	64.25	0.799	1.001
0.356	0.762	64.2	0.801	0.999
0.365	0.762	64.2	0.801	0.999
0.428	0.763	64.1	0.806	1.000
0.439	0.763	64.1	0.806	1.000
0.622	0.774	63.8	0.825	0.966
0.793	0.806	63.55	0.866	0.843
0.950	0.916	64.3	0.961	0.351

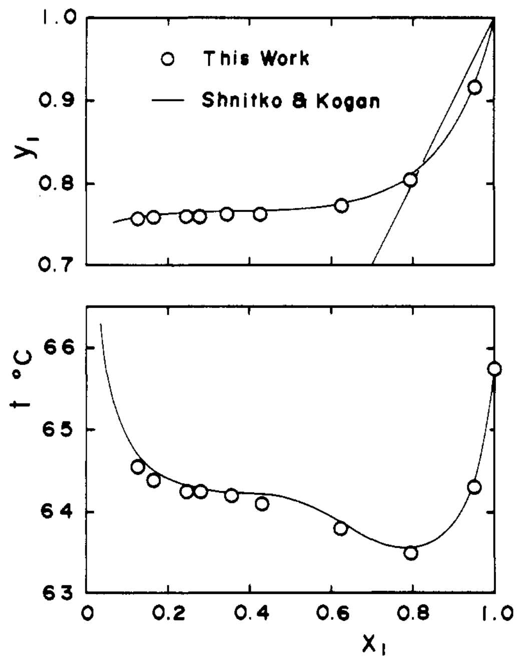

Figure 2. Vapor-liquid equilibrium for THF-water system at 760 mm Hg

From columns 5 and 6 of Tables III–V and Figure 4 for LiCl, the activity of THF increases with increasing salt concentration, and the activity of water decreases remarkably. The changes of each activity show that each ion of these salts in the mixed solvent of THF–water is preferentially hydrated because the activity (thermodynamic effective concentration) of water decreases regularly and rapidly with increasing salt concentration. THF is thus dehydrated and enriched in the vapor phase, that is, salted out. The salting out of THF may cause the boiling point decrease of the mixed solvent.

The extent of the salt effect on a mixed solvent should be measured, not by the change of the activity of nonelectrolyte caused by the salt addition, but by the relative change of the chemical potentials of each solvent:

$$[\partial(\mu_1 - \mu_2)/\partial N_3]_{T,P,z_1} \gtrless 0 \qquad (4)$$

To conveniently compare the salt effects, we will introduce the relative change of both chemical potentials in the same way as that by Johnson and Furter (*3, 8*) instead of Equation 4, that is,

$$\Delta\mu = [(\mu_1 - \mu_2)/RT] - [(\mu_1 - \mu_2)/RT]_0 \qquad (5)$$

where the subscript 0 denotes the system without salt. Equation 5 can be rewritten as

$$\Delta\mu = \ln (f_1 f_{20}/f_2 f_{10}) - \int_{T_0}^{T} (dT/RT^2) \int_{T_0}^{T} (C_{P1} - C_{P2}) dT \qquad (6)$$

As the second term is entirely negligible at low pressures compared with the first term,

$$\Delta\mu \simeq \ln (P_1 P_{20}/P_2 P_{10}) = \ln (\alpha/\alpha_0) \qquad (7)$$

where α is the relative volatility of THF with respect to water. The changes of relative volatility are shown in column 7 of Tables III–V. In Figure 5 the dependency of the relative volatility on the concentration of LiCl is shown; also those for the other salts show similar characteristics. Figure 5 shows that a linear relation between the value of $\Delta\mu$ and the salt concentration assumed by Johnson and Furter (*3*), $\Delta\mu = k_0 N_3$, is held only in very low salt concentration. The salt effect parameter k_0 at infinite dilution depends remarkably on the solvent composition.

The variation of k_0 for each salt with solvent composition is shown in Figure 6. The values of k_0 increase with increasing concentration of THF, and the order of salting out effect at infinite dilution is LiCl > $CaCl_2$ > NaCl. The salt effect can no longer be treated as a colligative function of the ionic strength.

Table III. Vapor-Liquid Equilibrium Data for THF–Water–LiCl System at 760 mm Hg

z_1	x_3	y_1	t, °C	a_1	a_2	$\Delta\mu$
0.127	0	0.758	64.55	0.788	1.000	0
0.126	0.030	0.781	63.65	0.837	0.943	0.130
0.126	0.050	0.799	63.55	0.859	0.869	0.238
0.126	0.070	0.823	63.55	0.885	0.765	0.395
0.126	0.100	0.862	63.8	0.919	0.590	0.690
0.126	0.150	0.923	64.6	0.958	0.318	1.342
0.125	0.200	0.964	65.35	0.977	0.144	2.146
0.125	Sat.	0.980	65.65	0.983	0.079	2.750
0.278	0	0.761	64.25	0.799	1.001	0
0.278	0.029	0.789	63.65	0.846	0.908	0.161
0.278	0.050	0.816	63.55	0.877	0.796	0.331
0.278	0.070	0.842	63.65	0.902	0.680	0.515
0.278	0.100	0.888	64.1	0.937	0.472	0.912
0.277	0.150	0.950	64.95	0.975	0.194	1.786
0.277	0.200	0.978	65.6	0.983	0.087	2.636
0.277	Sat.	0.979	65.7	0.980	0.082	2.684
0.428	0	0.763	64.1	0.807	1.000	0
0.428	0.030	0.804	63.7	0.860	0.842	0.242
0.427	0.050	0.837	63.7	0.895	0.700	0.467
0.427	0.070	0.877	64.0	0.929	0.521	0.795
0.427	0.100	0.922	64.65	0.956	0.321	1.301
0.426	0.150	0.970	65.45	0.979	0.119	2.307
0.426	Sat.	0.979	65.7	0.980	0.082	2.673
1	Sat.	1	66.25	0.984		

Table IV. Vapor-Liquid Equilibrium Data for THF–Water–NaCl System at 760 mm Hg

z_1	x_3	y_1	t, °C	a_1	a_2	$\Delta\mu$
0.254	0	0.761	64.25	0.799	1.001	0
0.254	0.010	0.765	64.0	0.816	0.996	0.022
0.253	0.020	0.770	63.75	0.822	0.985	0.052
0.252	0.029	0.779	63.65	0.835	0.951	0.100
0.251	0.038	0.789	63.7	0.844	0.906	0.162
0.251	0.047	0.800	63.6	0.859	0.863	0.229
0.251	Sat.	0.821	63.55	0.883	0.774	0.365
0.365	0	0.762	64.2	0.801	0.999	0
0.365	0.010	0.768	63.95	0.815	0.985	0.033
0.365	0.020	0.776	63.75	0.829	0.960	0.076
0.364	0.029	0.783	63.7	0.838	0.931	0.119
0.363	0.038	0.794	63.65	0.852	0.889	0.185
0.363	0.047	0.805	63.65	0.863	0.839	0.254
0.362	Sat.	0.821	63.6	0.881	0.772	0.359
0.120	Sat.	0.820	63.6	0.880	0.776	
0.540	Sat.	0.821	63.55	0.883	0.774	
0.681	Sat.	0.821	63.55	0.883	0.774	
0.754	Sat.	0.820	63.55	0.881	0.778	
0.852	Sat.	0.833	63.5	0.897	0.724	
0.935	Sat.	0.895	64.2	0.942	0.441	
1	Sat.	1	65.75	1.000		

Table V. Vapor-Liquid Equilibrium Data for THF–Water–$CaCl_2$ System at 760 mm Hg

z_1	x_3	y_1	t, °C	a_1	a_2	$\Delta\mu$
0.245	0	0.761	64.25	0.799	1.001	0
0.244	0.010	0.770	63.85	0.820	0.981	0.050
0.244	0.030	0.804	63.65	0.862	0.844	0.253
0.244	0.051	0.854	63.8	0.911	0.624	0.608
0.244	0.071	0.900	64.2	0.947	0.420	1.039
0.243	0.101	0.943	64.9	0.970	0.232	1.648
0.243	Sat.	0.957	65.25	0.973	0.172	1.945
0.356	0	0.762	64.2	0.801	0.999	0
0.356	0.010	0.777	63.75	0.830	0.955	0.084
0.356	0.030	0.821	63.75	0.877	0.767	0.359
0.355	0.050	0.876	63.95	0.929	0.527	0.791
0.355	0.071	0.919	64.5	0.957	0.336	1.265
0.355	0.101	0.954	65.2	0.971	0.185	1.868
0.354	Sat.	0.958	65.3	0.972	0.168	1.963
0.439	0	0.763	64.1	0.806	1.000	0
0.438	0.011	0.784	63.8	0.836	0.923	0.120
0.438	0.031	0.837	63.65	0.897	0.702	0.467
0.437	0.051	0.889	64.0	0.942	0.470	0.912
0.437	0.071	0.929	64.65	0.963	0.292	1.402
0.437	Sat.	0.957	65.3	0.971	0.172	1.934
0.199	Sat.	0.957	65.3	0.978	0.172	
0.792	Sat.	0.957	65.2	0.974	0.173	
0.922	Sat.	0.958	65.25	0.974	0.168	
0.948	Sat.	0.958	65.25	0.974	0.168	
1	Sat.	1	65.95	0.993		

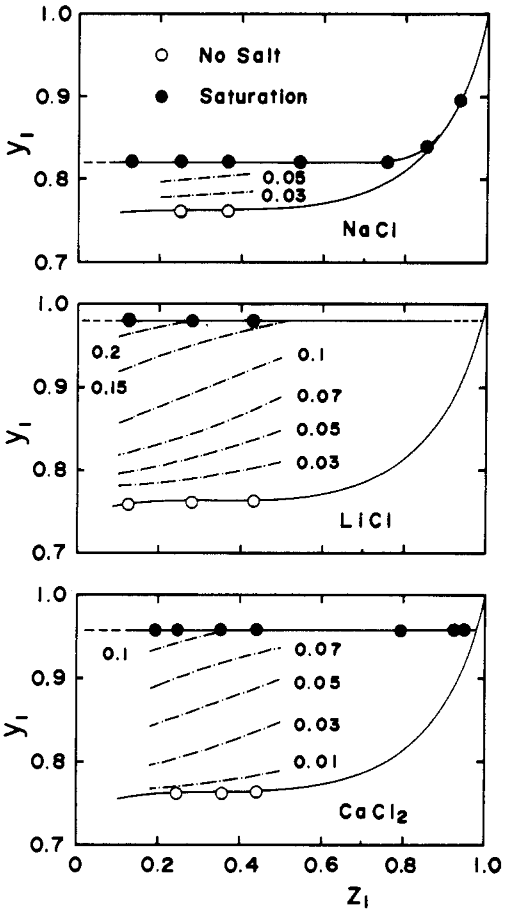

Figure 3. Vapor-liquid equilibria for THF-water-salt system at 760 mm Hg

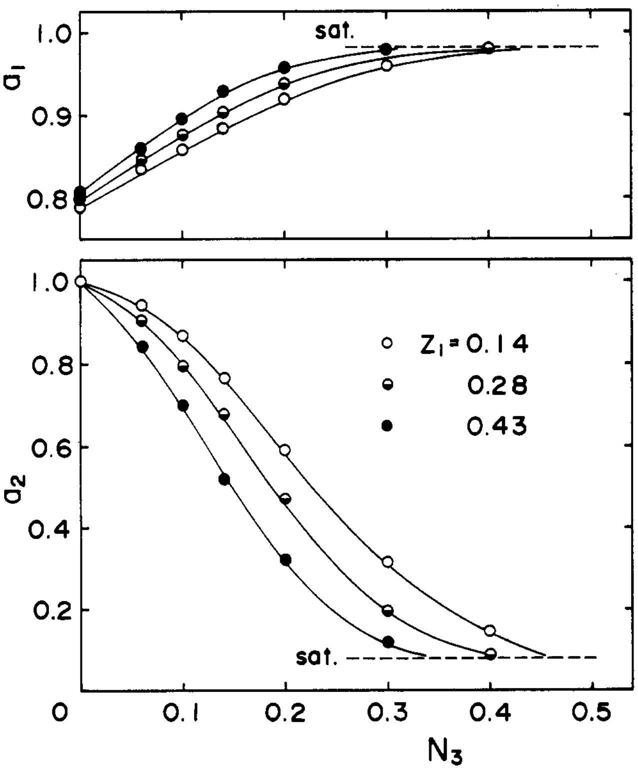

Figure 4. Activities of each solvent for THF-water-LiCl system at 760 mm Hg

Nomenclature

a_i = activity of solvent i
C_p = heat capacity at constant pressure in ideal gas state, cal/mol K
f_i = fugacity of solvent i, mm Hg
k_0 = salt effect parameter
N_3 = mole fraction of both ions, i.e., νx_3
n_j = number of moles of component j, mol
P = pressure, mm Hg
P_i = partial pressure of solvent i, mm Hg
R = gas constant, cal/mol K
T = absolute temperature, K
t = temperature, °C
x_j = mole fraction of component j in liquid phase, i.e., $n_j/(n_1 + n_2 + \nu n_3)$
y_i = mole fraction of solvent i in vapor phase, i.e., $n_i'/(n_1' + n_2')$
z_i = mole fraction of solvent i in mixed solvent, i.e., $n_i/(n_1 + n_2) = x_i/(1 - N_3)$
α = relative volatility of THF to water
μ_i = chemical potential of solvent i, cal/mol

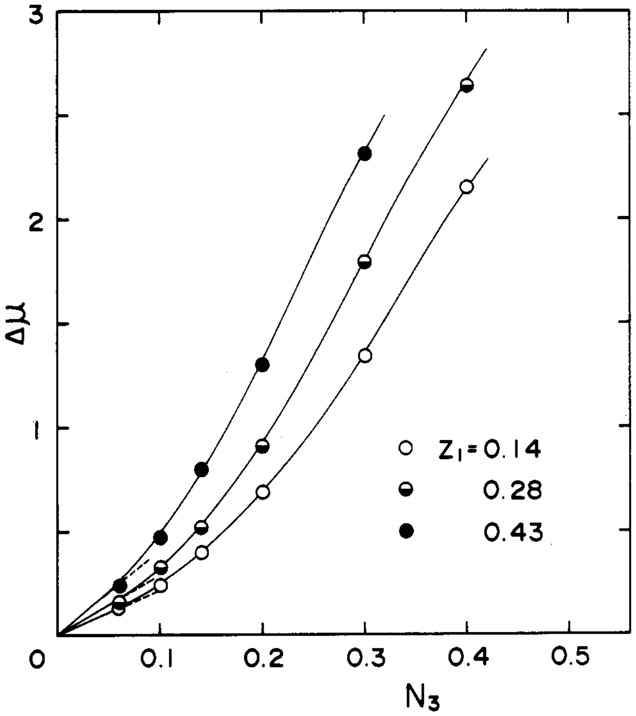

Figure 5. Salt effect of LiCl on THF-water system at 760 mm Hg

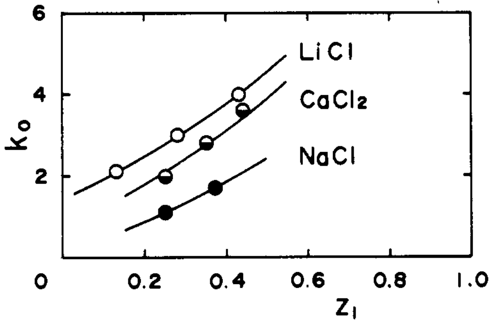

Figure 6. Variation of salt effect parameter k_0 with mixed solvent composition

$\Delta\mu$ = salt effect defined by Equation 5
ν = number of moles of both ions dissociated from 1 mole of salt, mol

Subscripts

0 = no salt
1 = THF
2 = water
3 = salt

Superscripts

$'$ = vapor phase
$^\circ$ = pure component

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Heats of Dilution of Aqueous Electrolytes: Temperature Dependence

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The heats of dilution of KCl, $MgCl_2$, Na_2SO_4, and $MgSO_4$ were measured over a concentration range of 0.005–2.0*m* at temperatures between 40–80°C. The data were extrapolated to infinite dilution by use of the Debye-Hückel limiting law to obtain relative apparent molal heat contents (ϕ_L). The heats of dilution of $MgCl_2$ and $MgSO_4$ were measured at 25°C and combined with the low concentration work of Lange and Streeck to yield values of ϕ_L. The relative partial molal heat content of solvent and solute was calculated from the experimental values. The heat content data were then used to calculate activity and osmotic coefficients in the temperature range 40–80°C.

The thermodynamic properties of aqueous electrolytes have been under investigation for many years. Extensive data exist for a wide variety of aqueous electrolytes at or near 25°C. A need for thermodynamic data at temperatures above 25°C has developed in recent years, owing mainly to the interest in desalination processes. Several electrolytes have been studied by different investigators (*3, 9, 15*) at temperatures between 100–300°C. However, very few precise data exist for aqueous electrolytes above 25° and below 100°C.

Ensor and Anderson (*2*) have shown that the measurement of heats of dilution as a function of temperature and concentration is an efficient way of obtaining accurate heat content data. These data were then used to extend existing thermodynamic data at 25°C to the experimental temperature range 40–80°C. The activity and osmotic coefficients of NaCl derived by Ensor and Anderson were in excellent agreement with existing data. The purpose of the present research was to extend this treatment to other electrolytes important in seawater (KCl, $MgCl_2$, $MgSO_4$, and Na_2SO_4).

Experimental

Solutions. Near saturated stock solutions of Baker analyzed reagent Na_2SO_4, $MgCl_2$, and KCl and Fisher certified $MgSO_4$ were prepared using distilled deionized water and stored in polyethylene bottles. The molalities of the KCl and $MgCl_2$ stock solutions were determined by AgCl gravimetric analysis. The $MgSO_4$ stock solution was analyzed by EDTA titration. $BaSO_4$ gravimetric analysis was used to determine the molality of the Na_2SO_4 stock solution. All less concentrated solutions were made by diluting a known weight of stock solution with a known weight of deionized water.

Table I. Extrapolation Coefficients for Equation 2

Temp, °C	*B*	C	SD, cal/mol
	KCl		
40	−782.99	1378.78	2.1
60	−158.55	−353.71	1.7
80	−1006.82	2094.86	2.3
	$MgCl_2$		
40	−377.80	633.22	5.4
50	−231.76	326.67	4.4
60	621.17	−1263.68	4.4
70	1738.3	−4575.8	5.5
80	679.29	−1949.08	5.1
	$MgSO_4$		
40	2125.02	−2988.20	9.6
60	19594.8	−43115.7	6.8
80	7307.60	−11066.9	10.5
	Na_2SO_4		
40	−402.38	−1177.90	2.2
60	611.79	−2849.73	3.2
80	7789.30	−20777.09	5.1

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