Effect of Water on Enthalpies of Solution of Electrolytes in *N*, *N*-Dimethylformamide

Yung A. Tsai and Cecil M. Criss[1]
Department of Chemistry, University of Miami, Coral Gables, Fla. 33124

Enthalpies of solution of LiCl, LiBr, LiI, and NaBr have been determined calorimetrically at 25.0°C in dry *N,N*-dimethylformamide (DMF) and in DMF to which small amounts of water have been added in order to measure the effect of water on the enthalpies of solution of these salts in DMF. The results, analyzed in terms of the mole ratio of water to salt, show that up to a mole ratio of 200–300 there is very little influence on the enthalpies of solution of LiBr and LiI, but for LiCl the enthalpy of solution varies by about 0.7 kcal/mol. In the solvent containing trace amounts of water, only LiCl shows a strong heat effect with concentration. This heat effect cannot be explained in terms of the mole ratio of water to salt. New values for the standard enthalpies of solution of these salts in DMF are evaluated.

The effect of water on thermodynamic properties of nonaqueous solutions of electrolytes is generally considered to be sufficiently significant to warrant precautions in keeping the solvent as dry as possible. For the evaluation of standard enthalpies of solution of electrolytes in nonaqueous solvents it is desirable to make measurements at low concentrations to minimize ion-pair formation and deviations from theoretical relationships used for extrapolation. However, it is in these dilute solutions in which trace quantities of water may be particularly troublesome. Even for a water content of 0.001 wt % the ratio of moles of water to electrolyte is 0.5 for a 0.001*m* solution of electrolyte. During the course of a calorimetric measurement it is not infrequent that the water content will increase to 0.01 wt % with the result that the water content is significantly larger than the salt concentration.

In two publications (*1*, *2*), Held and Criss observed that certain salts containing high-charge density ions exhibited extremely large enthalpies of dilution at concentrations below 0.001*m* in the solvents *N,N*-dimethylformamide (DMF) and *N*-methylformamide (NMF). It was suggested (*2*) that the heat effects in DMF were the result of ionic association, although the association constants calculated from the data for DMF solutions were significantly larger than those derived from conductance measurements for the same salts. Extrapolation of the low concentration data (<0.001*m*) gave standard enthalpies of solution up to 3 kcal/mol different from the extrapolation of data from higher concentrations.

An examination of more recent data suggests that the unusually large heat effects are probably not the result of ionic association, but rather the result of trace impurities in the solvent. Since water is always present in trace amounts, this investigation was undertaken to examine the effect of water on heats of solution of electrolytes in DMF.

Experimental

Materials. *N,N*-Dimethylformamide and water were purified by the method described previously (*2*). The water content of the pure DMF immediately after distillation, as determined by Karl Fischer titration, was about 0.003 wt % but at the end of a calorimetric measurement the water content had increased to about 0.01%. The composition of the DMF–water mixtures did not change significantly during the course of a measurement. LiCl, LiBr, and NaBr were also prepared by methods previously used in this laboratory (*2*). Reagent grade LiI (Research Organic/Inorganic Chemical Co.) was recrystallized from hot water twice under a nitrogen atmosphere and the crystals were collected on a sintered-glass funnel. The salt was dried in a vacuum desiccator over P_2O_5 for 24 hr, and then dried under vacuum for 1 hr at 60° and then at 120°C. The salt was cooled to room temperature and kept under a nitrogen atmosphere. To avoid decomposition, it is necessary to keep air away from the hot LiI.

Apparatus and procedure. The calorimeter was identical to that used by Held and Criss (*1*, *2*), and the same general procedures in calibrating the calorimeter and sample handling were employed except for weighing the samples. In the present work all samples were weighed under anhydrous conditions in a dry box on an electric microbalance (Cahn, Model G-2), having an accuracy of 0.1%, even for the smallest samples investigated (0.4 mg). This procedure eliminates the inherent weighing error of the previous work (*1*, *2*), caused by difference weighing external to the dry box. All measurements were made at 25.00° ± 0.05°C. To test the suitability of the salts for calorimetric measurement, especially LiI, which has a tendency to decompose, enthalpies of solutions of the salts were first measured in pure water at concentrations of approximately 0.001–0.002*m*. The infinitely dilute values at 25°C (average of two or more measurements) for the three lithium salts are: LiCl, −8.844 ± 0.025; LiBr, −11.638 ± 0.006; and LiI, −14.988 ± 0.079 kcal/mol. Within the limits of error these agree with the "best" values tabulated by Parker (*3*).

Results and Discussion

Two sets of measurements were made—those in which the water content of the solvent was kept as low as possible (~0.01 wt %) and the salt concentration varied, and those in which water was added to the solvent in varying amounts up to approximately 1.0 wt % while the electrolyte concentration was kept constant at about 0.0015–0.002*m*. For one series of measurements with LiCl solutions, the salt concentration was kept constant at about 0.009*m* and the water content of the solvent varied to a maximum of 3.7 wt %. Table I lists enthalpies of solution of electrolytes in the "dry" solvent. Even though the water content is minimal (<0.01%), it becomes significant at the lower salt concentrations; consequently, the mole ratio of water to salt is listed in the table. These data are also shown in Figure 1, along with data from other investigations.

Except for LiCl, there is no unusual heat effect at low concentration, in spite of the fact that the water content reaches several times the salt concentration. For LiCl, the increased exothermicity is much less than that re-

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[1] To whom correspondence should be addressed.

Table I. Enthalpies of Solution of Selected Electrolytes at 25°C in "Dry" *N,N*-Dimethylformamide

$m \times 10^4$	$m^{1/2} \times 10^2$	$-\Delta H_s$, kcal/mol	Mol H_2O^a/mol salt
		LiCl	
0.974	0.987	12.10	57
1.372	1.17	12.04	41
1.867	1.37	11.65	30
2.081	1.44	12.16	27
2.688	1.64	12.14	21
9.718	3.12	11.34	5.7
10.97	3.31	11.30	5.1
11.12	3.33	11.44	5.0
11.39	3.38	11.44	4.9
11.84	3.44	11.33	4.7
15.85	3.98	11.39	3.5
16.63	4.08	11.31	3.3
17.96^b	4.24	11.35	3.1
18.35^b	4.28	11.30	3.0
19.01^b	4.36	11.38	2.9
19.56	4.42	11.38	2.8
19.74	4.44	11.34	2.8
31.40	5.60	11.33	1.8
93.27^b	9.66	11.36	0.6
97.72^b	9.89	11.36	0.6
		LiBr	
1.199	1.10	18.37	46
1.587	1.26	18.38	35
2.429	1.56	18.42	23
15.242^b	3.90	18.42	3.6
15.752^b	3.97	18.44	3.5
16.612	4.08	18.47	3.3
18.095	4.25	18.49	3.1
18.169	4.26	18.51	3.1
		LiI	
2.749	1.66	26.18	20
3.264	1.81	26.10	17
3.861	1.97	26.14	14
11.469	3.39	25.95	4.8
18.190^b	4.27	25.97	3.1
19.856	4.46	26.08	2.8
24.421	4.94	26.04	2.3
		NaBr	
12.417	3.52	7.10	4.5
14.817^b	3.85	7.09	3.8
18.967^b	4.36	7.11	2.9

[a] Based on a water content at end of measurement of 0.01 wt %. [b] Data used in Figure 2 for the enthalpies of solution in DMF containing 0.01% water.

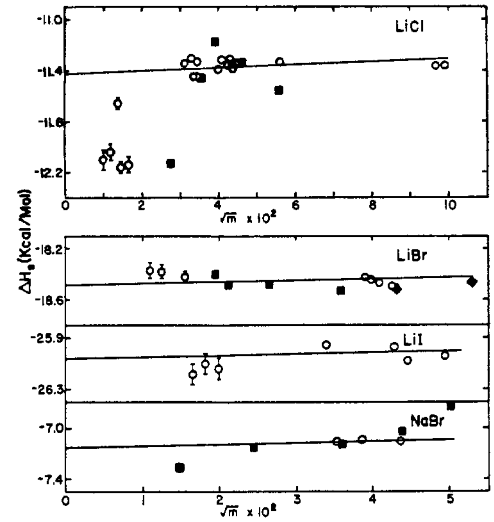

Figure 1. Concentration dependence of enthalpies of solution of electrolytes in *N,N*-dimethylformamide. The curves are drawn with a slope equal to the theoretical Debye-Hückel limiting slope
○ This work, ■ Held and Criss (*2*), ◆Wong-Tso and Criss (*4*)

Table II. Integral Enthalpies of Solution of Electrolytes at 25°C in *N,N*-Dimethylformamide to Which Water Has Been Added

$m \times 10^4$	$m^{1/2} \times 10^2$	$-\Delta H_s$ (kcal/mol)	m (H_2O)/ m (salt)
		LiCl (low salt concn)	
19.373	4.40	11.34	8.6
19.417	4.41	11.43	19
18.310	4.28	11.60	62
16.654	4.08	11.73	172
16.664	4.08	12.01	267
17.551	4.19	12.07	280
		LiCl (high salt concn)	
88.858	9.43	11.42	11
87.437	9.35	11.64	33
90.269	9.50	11.89	130
		LiBr	
14.080	3.75	18.40	26
15.436	3.93	18.34	73
14.202	3.77	18.33	240
		LiI	
16.896	4.11	26.21	67
16.154	4.02	26.27	211
15.810	3.98	26.29	311
		NaBr	
17.656	4.20	7.11	21
14.474	3.80	7.16	78
16.754	4.09	7.24	203
14.968	3.87	7.27	328

ported earlier (*2*), being on the order of 0.7 kcal/mol rather than 3.0 kcal/mol. In contrast to the earlier work, no large concentration effect was observed for LiBr at the low concentrations.

Table II lists the enthalpy measurements for the same electrolytes in DMF containing added amounts of water. The effect of water, as a function of mole ratio of water to salt, on the enthalpies of solution of the electrolyte is shown in Figure 2. With the exception of LiCl, which exhibits a relatively large heat effect with an increase in water content of the solvent, the change in the enthalpies of solution of the various electrolytes is small, not exceeding at most 0.3 kcal/mol as the mole ratio of water to salt is increased from approximately 3 to 200 or 300. Variation in the enthalpies of solution of LiCl over the same range for the ratio of water to salt is about 0.7 kcal/mol, considerably smaller than the deviations reported previously (*2*) at low concentrations in dry solvent, but about the same as the low-concentration deviations in the present work. However, the mole ratio of water to salt is about 250, whereas in the dry solvent this deviation is obtained for low-concentration salts when the mole ratio of water to salt is only 57. This would imply that the effect of mole ratio on enthalpies is most significant when the quantities of both water and salt are small. On the other hand, enthalpies of solution for the more concentrated series of LiCl solutions vary more rapidly with the mole ratio of water to salt, and if one plots enthalpies of solution for both the dilute and concentrated series of LiCl solutions vs. the wt % of water in the solvent (see insert in Figure 2), the variation appears to be the same for both concentrations of salts, and linear with water concentration up to about 1 wt %. This indicates that for water concentrations up to about 1%, enthalpies of solution are more dependent on the abso-

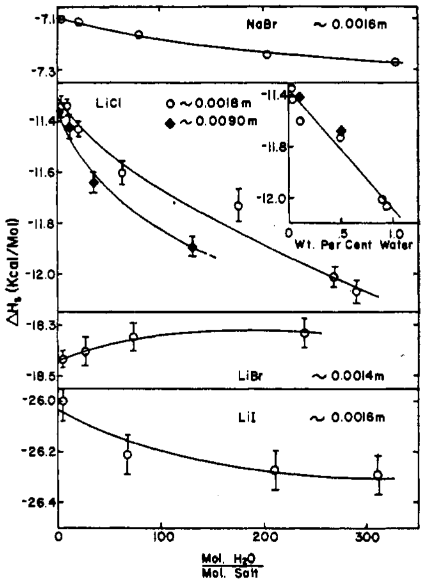

Figure 2. Effect of ratio of water to salt concentration on enthalpies of solution of electrolytes in *N,N*-dimethylformamide
Data at lowest mole ratio are from Table I

lute amount of water present than on the mole ratio of water to salt.

The above results imply that the large change in the enthalpy of solution of LiCl at low concentration is caused by factors other than water content of the solvent. In view of the nonreproducibility of the LiCl data below 0.001*m*, it also seems unlikely that the phenomenon is caused by ionic association, as suggested earlier (2). In the earlier measurements it is possible that the weighing technique introduced systematic errors in the measurements at low concentrations for which the sample weights varied down to 0.6 mg, but in the present measurements no significant weighing errors, even at the lowest concentration, should exist. We conclude therefore that the large heat effects observed at the lower concentrations are experimental artifacts, probably the result of trace impurities other than water and that in general, calorimetric measurements in this solvent should be confined to concentrations >0.001*m*.

Table III. Standard Enthalpies of Solution of Some Electrolytes in *N,N*-Dimethylformamide at 25°C

	$\Delta H^\circ_{\text{soln}}$, kcal/mol	
Electrolyte	This work	Held & Criss[a]
LiCl	−11.42 ± 0.02	−14.5 (−11.42)
LiBr	−18.48 ± 0.03	−21.3 (−18.07)
LiI	−26.06 ± 0.04	
NaBr	−7.150 ± 0.003	−7.39

[a] Ref. 2. Values in parentheses are derived from extrapolation of data from higher concentrations.

On the basis of the above discussion, the data for LiCl at very low concentrations were not used in the extrapolations shown in Figure 1. All data were extrapolated with the help of the simple Debye-Hückel equation, and the curves in Figure 1 represent the theoretical limiting slope of 1740 cal $\text{kg}^{1/2}$ $\text{mol}^{3/2}$. The resultant standard enthalpies of solution are listed in Table III, along with the standard deviations of the points from the lines. For comparison, the results of the previous work are also listed. The agreement is, in general, satisfactory only if data above 0.001*m* are used for evaluating $\Delta H^\circ_{\text{soln}}$.

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