Enthalpies of Solution of Some Electrolytes Having High-Charge Density Cations in *N*,*N*-Dimethylformamide

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Enthalpies of solution were measured for $GdCl_3$, $MgCl_2$, $BaBr_2$, LiBr, and KI at various concentrations in anhydrous *N,N*-dimethylformamide at 25°C, and the data extrapolated to infinite dilution to obtain standard enthalpies of solution. With the exception of $GdCl_3$, the limiting slopes were in agreement with the Debye-Hückel limiting slopes. The two-stage enthalpy effect previously observed for $MgCl_2$ was not observed when trace amounts of hydrolyzed salt were absent.

Although calorimetrically measured heats of solution of electrolytes in *N,N*-dimethylformamide (DMF) have been the subject of several recent studies (*1, 4–6, 8, 9, 11, 12*), only three of these (*5, 8*) have included higher valence-type salts. Furthermore, the low-concentration enthalpy data for electrolytes containing high-charge density cations have been in considerable doubt (*8, 11*), and in some cases it has not been possible to extrapolate the data to infinite dilution to obtain the standard enthalpies of solution. In addition, the enthalpy of solution of $MgCl_2$ in DMF at low concentrations was observed (*8*) to take place in two steps, indicating that a reaction other than the solution process was taking place. For these reasons, it appeared worthwhile to redetermine the enthalpies of solution of some previously measured electrolytes in DMF and to obtain new enthalpy data for $BaBr_2$ with the hope of obtaining more reliable standard enthalpies of solution for these electrolytes in DMF. Because of discrepancies in previously reported enthalpy data for KI (*6, 9, 12*), the enthalpy of solution of this salt was also redetermined.

Experimental

Materials. *N,N*-Dimethylformamide was prepared either by treatment with BaO, with subsequent vacuum distillation as previously described (*8*) or by treatment with molecular sieves (3 Å) with subsequent distillation. In both cases, the water content of the pure DMF after distillation, as determined by Karl Fischer titration, was about 0.003 wt % but generally rose to about 0.01% at the end of a calorimetric measurement.

LiBr was prepared by the method described previously (*8*), except that it was dried initially in vacuum over P_2O_5 and then in a vacuum oven for several hours at 100° and finally for 24 hr at 190°C.

KI (reagent grade) was recrystallized from deionized hot water under a nitrogen atmosphere. The crystals were washed with ethanol and dried in vacuum over P_2O_5 for 24 hr and then in a vacuum oven at 70–100°C for 12 hr.

Anhydrous $MgCl_2$ was prepared by reacting equimolar amounts of reagent-grade $MgCl_2 \cdot 6H_2O$ and NH_4Cl to form the double salt $NH_4Cl \cdot MgCl_2 \cdot 6H_2O$, from which the NH_4Cl was sublimed under a fast stream of dry HCl according to the method of Bryce-Smith and Hunt (*2*). The salt was then fused in platinum boats at 720°C. The purified salt gave a clear solution in water, and an aqueous solution showed no indication of hydrolysis when treated with phenolphthalene.

Reagent-grade $BaBr_2 \cdot 2H_2O$ was recrystallized from deionized water once and dried in a vacuum oven at 70°C. The crystals were then ground to a powder and heated under vacuum at 190°C for at least 24 hr.

$GdCl_3$ was prepared by the method of Spedding et al. (*10*) from Gd_2O_3 and HCl. Treatment with phenolphthalein indicated the absence of hydrolysis.

Apparatus and procedure. The calorimeter, calibrating procedure, and technique in weighing samples have been previously described (*7, 8, 11*). All measurements were at 25.0°C.

Results and Discussion

The results are listed in Table I. Within the limits of experimental error, all data are linear with $m^{1/2}$, and with

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

10^3m	$-\Delta H_s$, kcal/mol
LiBr	
1.849	18.52
2.802	18.46
4.041	18.50
6.327	18.49
6.711	18.48
8.600	18.52
KI	
0.0651	8.05
0.0665	8.04
0.0726	8.08
0.1131	8.03
0.1839	8.04
1.114	8.00
1.151	8.02
1.588	8.01
1.617	8.00
1.676	8.02
$MgCl_2$	
0.199	37.59
1.170	36.27
4.052	35.92
10.95	36.13
$BaBr_2$	
0.0924	23.41
0.2138	23.39
1.163	23.30
2.144	23.13
2.552	22.84
4.840	22.88
9.288	22.53
$GdCl_3$	
0.1508	42.54
0.2027	41.91
0.2444	42.86
0.2458	41.58
0.7041	40.83
2.204	39.75
4.433	38.24
7.800	37.48

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

	$\Delta H_s°$, kcal/mol		
	This work[a]	Other work[b]	
LiBr	-18.60 ± 0.04	-21.3	(*8*)
		-18.07[c]	(*8*)
		-18.4	(*6*)
		-18.52	(*12*)
		-18.48 ± 0.03	(*11*)
KI	-8.06 ± 0.02	-8.1	(*6*)
		-8.04	(*12*)
		-7.4	(*9*)
$MgCl_2$	-36.91 ± 0.50		
$BaBr_2$	-23.43 ± 0.11		
$GdCl_3$	-43.06 ± 0.43		

[a] With the exception of $GdCl_3$, these values are an average of the data in Table I, after they were corrected to infinite dilution by the equation $\Delta H_s° = \Delta H_s - {}^2/_3\, \delta_H \sqrt{m}$ where $\delta_H = 2281$ and 11852 cal kg$^{1/2}$ mol$^{-3/2}$ for 1:1 and 1:2 electrolytes, respectively. The data for $GdCl_3$ were extrapolated to infinite dilution with the above equation. The data exhibit a slope considerably greater than the theoretical slope of $\delta_H = 33524$ cal kg$^{1/2}$ mol$^{-3/2}$. [b] Numbers in parentheses identify the references. [c] Extrapolated from data at concentrations $>0.001m$.

the exception of $GdCl_3$, the slopes agree within experimental error with the theoretical Debye-Hückel limiting slope ($^2/_3\ \delta_H$, where δ_H = 2281, 11852, and 33524 cal kg$^{1/2}$ mol$^{-3/2}$ for 1:1, 1:2, and 1:3 electrolytes, respectively, see ref. 3). Consequently, for the 1:1 and 1:2 electrolytes, the simple Debye-Hückel equation has been employed to correct the enthalpies to infinite dilution. The average of these values is listed in Table II along with the standard deviations. The slope for $GdCl_3$ is about two and one-half times the theoretical, and for this electrolyte $\Delta H_s°$ was evaluated by a least-squares treatment of the data. The uncertainty is the standard deviation of the points from the line. A comparison with previously published data is also made in Table II.

Present data for LiBr are in fair agreement with most of the published results (*6, 8, 11, 12*). In a previous paper, Tsai and Criss (*11*) showed that the large enthalpy of dilution observed earlier (*8*) for LiBr solutions at concentrations $<0.001m$ probably was not real. However, the most concentrated solution studied was only $0.0018m$. The concentration range in the present measurements is extended to $0.009m$. Although the standard deviations do not quite overlap, the data presented here and that of Tsai and Criss (*11*) agree within 0.12 kcal, which we believe is about as good as one can expect, considering the difficulties of preparing the pure solvent and salt. These two values envelop the value reported by Weeda and Somsen (*12*). The present enthalpy data for KI are in satisfactory agreement with two (*6, 12*) of the three previously reported values.

In contrast with the results of Held and Criss (*8*), no unusually large enthalpy of dilution was observed with $MgCl_2$, nor was a two-stage enthalpy effect observed when the salt was completely free from hydrolysis. However, when the salt was dehydrated by passing HCl over $MgCl_2 \cdot 6H_2O$, rather than the double salt $NH_4Cl \cdot MgCl_2 \cdot 6H_2O$, a two-stage enthalpy effect was observed. This appears to be associated with small amounts of hydrolysis of the dehydrated salt.

The somewhat greater than theoretical limiting slope for $GdCl_3$ indicates some ion-pair formation in DMF. This is not unexpected for this low dielectric constant solvent, but the slope is not sufficiently large to lead to a significant error in the extrapolated standard enthalpy of solution.

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