

Thermodynamic Properties of Nonaqueous Solutions. III.

Heats of Solution of Some Electrolytes in N,N-Dimethylformamide¹

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Heats of solution of CsI, KBr, NaBr, NaI, LiCl, LiBr, MgCl₂, and GdCl₃ have been measured in N,N-dimethylformamide in the concentration range 1×10^{-4} to 4×10^{-3} *m*. The data for the alkali metal halides have been extrapolated to infinite dilution by use of the ρ function to obtain standard heats of solution. Salts having cations with high charge densities show limiting slopes many times greater than those predicted by theory, suggesting ionic association. This view is supported qualitatively by conductance measurements. Magnesium chloride is anomalous in that it dissolved in a two-stage process. A plot of solvation enthalpies for the alkali metal bromides *vs.* $1/(r + \delta)$ gives a linear relationship when $\delta = 0.8$ Å.

Introduction

In two recent papers,^{3,4} the thermodynamic properties of several electrolytes in N-methylformamide (NMF) (dielectric constant $D = 182.4$) were reported. In continuation of obtaining thermodynamic data for nonaqueous systems, results are presented for the heats of solution of a variety of electrolytes in N,N-dimethylformamide (DMF) ($D = 36.7$).

Experimental Section

Materials. N,N-Dimethylformamide was treated with CaH₂ accompanied by vigorous stirring and then distilled under reduced pressure through a 35-cm Vigreux column. The boiling point was 68° at 53 mm pressure. The reported value is 79° at 61–62 mm.⁵ The specific conductance was in the range 0.32 – 1.5×10^{-7} ohm⁻¹ cm⁻¹, which is in agreement with the lowest values reported in the literature (0.6 – 18.3×10^{-7} ohm⁻¹ cm⁻¹).^{6,7} There was no noticeable increase in conductivity with time. Karl Fischer titrations indicated the water content to be less than 0.002%. For methods used in the preparation of LiCl, NaBr, and NaI the reader is referred to the previous publications.^{3,4}

LiBr. Purified Li₂CO₃ was treated with excess concentrated reagent grade fuming HBr. The resulting LiBr was recrystallized and collected on a sintered-glass funnel. It was dried in a vacuum desiccator, then heated in an air oven to about 400°.

KBr. Reagent grade K₂CO₃ and excess reagent grade fuming HBr were allowed to react and the resulting KBr was recrystallized, collected, dried in a vacuum desiccator for 24 hr, and then heated at 400°.

MgCl₂. Reagent grade MgCl₂·6H₂O was doubly recrystallized from conductivity water, placed in a platinum crucible in a Vycor tube, and heated at about 400° under a fast stream of dry HCl gas. After evolution of water ceased, the temperature was raised over

(1) This paper was taken in part from the work submitted by R. P. Held to the Graduate School of the University of Vermont in partial fulfillment of the requirement for the Degree of Doctor of Philosophy.

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Table I: Integral Heats of Solution and ρ Values of Alkali Metal Halides in DMF at 25°

$m \times 10^4$, moles/kg of DMF	$m^{1/2}$	ΔH_s , kcal/mole	$\delta_H I^{1/2} \alpha$, kcal/mole	ρ , kcal/ mole
CsI				
3.75	0.0194	-4.210	0.022	-4.232
6.29	0.0251	-4.151	0.028	-4.179
9.35	0.0306	-4.158	0.034	-4.192
13.3	0.0365	-4.000	0.041	-4.041
18.6	0.0431	-3.958	0.049	-4.007
33.5	0.0579	-3.886	0.064	-3.950
KBr				
2.70	0.0164	-3.594	0.019	-3.613
3.10	0.0176	-3.784	0.020	-3.804
5.84	0.0242	-3.618	0.027	-3.645
9.42	0.0307	-3.633	0.035	-3.668
12.0	0.0346	-3.455	0.039	-3.494
17.5	0.0418	-3.214	0.047	-3.261
26.1	0.0511	-2.752	0.057	-2.809
NaBr				
2.15	0.0147	-7.303	0.017	-7.320
5.95	0.0244	-7.150	0.028	-7.178
13.0	0.0361	-7.117	0.041	-7.158
19.1	0.0437	-7.022	0.049	-7.071
25.2	0.0502	-6.818	0.056	-6.874
33.2	0.0576	-6.565	0.064	-6.629
NaI				
0.675	0.00822	-13.63	0.009	-13.64
1.61	0.0127	-13.97	0.015	-13.99
2.64	0.0162	-13.52	0.019	-13.54
3.46	0.0186	-12.95	0.021	-12.97
4.23	0.0206	-13.07	0.024	-13.09
8.84	0.0297	-12.63	0.033	-12.66
12.7	0.0356	-12.41	0.040	-12.45
16.4	0.0405	-12.59	0.046	-12.63
25.0	0.0500	-12.68	0.056	-12.74
LiCl				
1.42	0.0119	-14.11	0.014	-14.12
4.35	0.0209	-12.90	0.024	-12.93
7.50	0.0274	-12.13	0.031	-12.16
12.3	0.0351	-11.46	0.040	-11.50
15.3	0.0391	-11.17	0.045	-11.21
18.0	0.0424	-11.34	0.048	-11.39
21.1	0.0459	-11.33	0.052	-11.38
31.0	0.0557	-11.55	0.062	-11.61
LiBr				
0.714	0.00845	-20.70	0.010	-20.71
1.18	0.0109	-20.04	0.013	-20.05
1.55	0.0124	-19.54	0.014	-19.55
1.92	0.0139	-19.13	0.015	-19.14
2.72	0.0165	-18.89	0.019	-18.91
3.81	0.0195	-18.40	0.022	-18.42
4.50	0.0212	-18.49	0.024	-18.52
7.01	0.0265	-18.48	0.032	-18.51
12.9	0.0359	-18.53	0.041	-18.57
13.0	0.0360	-17.61	0.041	-17.65
19.3	0.0439	-17.93	0.049	-17.98

a period of a few hours to the fusion point of the salt (712°). Heating was ceased and the salt was subjected to vacuum to eliminate excess HCl. The anhydrous salt was transferred into ampoules in a vacuum drybox under an argon atmosphere. The salt was stored in the sealed ampoules until ready for use.

GdCl₃. GdCl₃ was prepared by the action of reagent grade concentrated HCl and Gd₂O₃ (Michigan Chemical Corp.; assayed at 99.55%). The six hydrate was recrystallized from conductivity water using HCl gas and the crystals were placed in a Pyrex tube. Dry HCl gas was passed over them at about 80° until no water was evident in the exit tube. The caked mass was pulverized, replaced in the tube, which had been equipped with a sulfuric acid trap to prevent entrance of water vapor, and dry HCl again passed over the crystals at 150, 250, and 375° for several hours at each temperature. Finally, excess HCl was removed from the crystals by heating the sample under vacuum. The final anhydrous GdCl₃ was transferred to ampoules under an argon atmosphere in a vacuum drybox. The salt was stored in the sealed ampoules until ready for use. All salts showed an absence of hydrolysis when treated with phenolphthalein solution. In addition, both the anhydrous MgCl₂ and GdCl₃ gave clear solutions in water, indicating the absence of hydrolysis.⁸

Apparatus and Procedure. The calorimeter, associated apparatus, experimental procedure, and treatment of primary data have been described previously.³ The only exception involved the experimental procedure for handling MgCl₂ and GdCl₃. Since water absorbed by these salts would cause hydrolysis upon heating, samples of these salts were never permitted to come into contact with the atmosphere during the weighing process but were kept under a dry argon atmosphere at all times. Each sample was weighed to 0.02 mg on a Mettler Model M5 microbalance.

Calculations and Results

Data for the 1:1 electrolytes were extrapolated to infinite dilution by means of the ρ function. The general treatment of data and definition of symbols have been given elsewhere.³ The theoretical Debye-Hückel limiting slope, δ_H , used in calculating ρ was calculated from a composite of the available density data^{5,9-11} and the dielectric constant data of Leader and Gormley.⁹ The resultant limiting slope is 1740 cal kg^{1/2} mole^{-1/2}. In aqueous solutions, a plot of ρ

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vs. m gives a linear relationship in dilute solutions, expediting extrapolation of the data to infinite dilution where $\rho = \Delta H_s^\circ$. For certain electrolytes in both NMF³ and DMF, a linear relationship appears to exist only for the most dilute solutions ($<1 \times 10^{-3} m$).

Results of the measurements for the alkali metal halides are summarized in Table I. The fourth column lists the theoretical values that must be subtracted from the measured integral heats of solution to obtain the ρ values. Although these values are small, they have been retained in order to be logically consistent with this technique of extrapolation. A plot of ρ *vs. m* is shown in Figure 1. The most striking feature about the data is the strong concentration effect upon the heats for electrolytes having high charge density cations. Because of this, the extrapolated heats for these electrolytes have a correspondingly greater uncertainty. The standard heats obtained from extrapolation of the ρ plots are listed in Table II.

Table II: Standard Heats of Solution and Heats of Solvation in DMF at 25°

Solute	ΔH_s° , kcal/mole	$\Delta H_{\text{solv}}^\circ$, kcal/mole
LiCl	-14.5	215.7
LiBr	-21.3	212.5
NaBr	-7.39	184.0
KBr	-3.89	165.3
CsI	-4.25	144.6
NaI	-13.95	178.5

Heats of solution for both gadolinium and magnesium chlorides also show strong concentration dependences much more pronounced than that for the lithium salts and, in the case of Gd, in the opposite direction. Furthermore, MgCl_2 evolved heat in a two-stage process. The first of these was rapid (about 5 min) and appeared to be a simple dissolution process. The second step took from 20 min to 2 hr, involved a much larger amount of heat, and its concentration dependence was in the opposite direction from the first step. The measurements are summarized in Table III and Figure 2. In view of the two-stage heat effect and long reaction time for MgCl_2 , there is considerably more error in the accuracy of these points. In addition, because of the very steep approaches of the curves to the heat of solution axis, no attempt has been made to extrapolate these data to infinite dilution.

The data for the salts having high charge density cations clearly suggest strong ionic association. This observation is supported by unpublished conductance

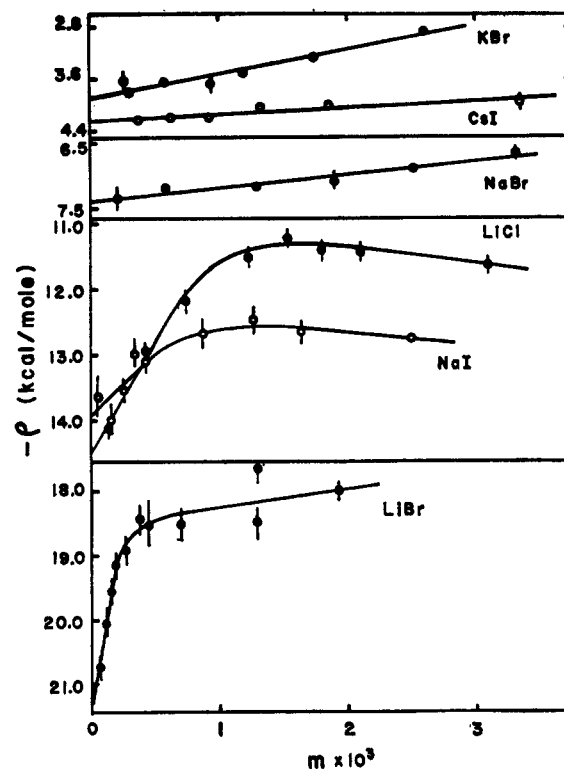


Figure 1. Plots of ρ *vs.* molality for alkali metal halides in DMF at 25°.

Table III: Integral Heats of Solution of MgCl_2 and GdCl_3 in DMF at 25°

$m \times 10^4$, moles/kg of DMF	$m^{1/2}$	Approximate ΔH_s initial reaction, kcal/mole	ΔH_s total reaction, kcal/mole
MgCl_2			
1.51	0.0123	-13.9	-172.06
3.86	0.0196	-26.6	-106.82
4.80	0.0219	-41.2	-103.03
14.3	0.0378	-37.0	-59.56
18.6	0.0431	-36.7	-50.13
39.0	0.0624	-37.1	-37.11
GdCl_3			
0.656	0.00810		-22.96
1.62	0.0127		-31.44
3.20	0.0179		-46.05
7.83	0.0280		-42.78
11.5	0.0339		-42.11
21.3	0.0462		-36.18
31.0	0.0557		-37.43

measurements in this laboratory which show GdCl_3 and MgCl_2 to be weak electrolytes in this solvent. The fact that the slopes for the heat data are in the opposite direction for GdCl_3 and LiCl is of no con-

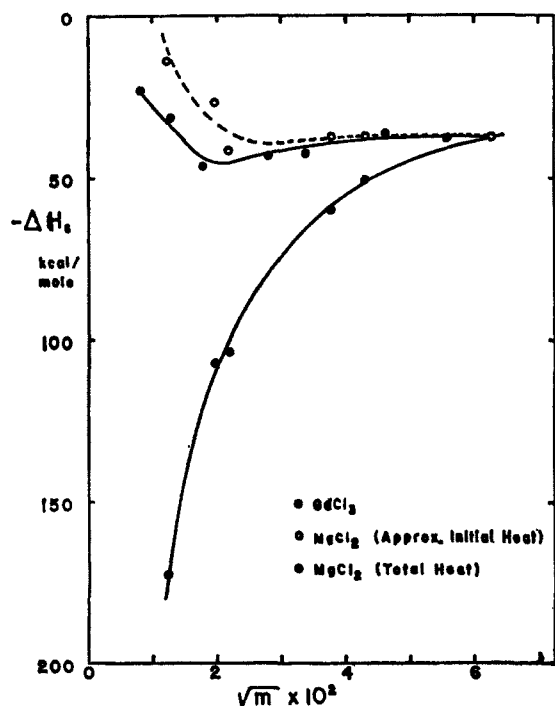


Figure 2. Integral heats of solution of MgCl_2 and GdCl_3 as a function of $m^{1/2}$ at 25° in DMF.

sequence, since whether heats become more positive or more negative with decreasing concentration is dependent upon the sign of the temperature derivative of the equilibrium constant for the association process. This derivative is generally quite temperature sensitive and it is not unusual for it to exhibit different signs for various weak electrolytes at a given temperature. Unfortunately, because of the complex equilibria involved, it is not possible to make a quantitative comparison between the degrees of dissociation obtained from conductance and heat data for GdCl_3 and MgCl_2 .

Conductance data for lithium chloride¹² also support the view that this electrolyte is associated in DMF. It is of interest to use the present heat data for LiCl to estimate quantitatively its dissociation constant and heat of dissociation of the complex. If we assume that the only association process occurring is the one to form ion pairs and if we further assume that in these dilute solutions the heats of dilution of the unassociated ions follow the simple Debye-Hückel theory, then the heat of solution at some concentration m is given by

$$\Delta H_m = \Delta H_s^\circ + \frac{2}{3}\delta_H\sqrt{m} + \left[\frac{-(K/m + \sqrt{K/m^2 + 4(K/m)})}{2} \right] \Delta H_{\text{dissoen}} - \Delta H_{\text{dissoen}}$$

where ΔH_s° is the standard heat of solution, K is the dissociation constant, and $\Delta H_{\text{dissoen}}$ is the heat of dissociation of the ion pairs. By using the ρ plots to fix ΔH_s° and computer techniques to vary the other parameters to obtain a best fit of the data, K and $\Delta H_{\text{dissoen}}$ for LiCl have been found to be 5×10^{-4} and -6000 cal/mole, respectively. The value of K evaluated from the conductance data is 0.024. The fact that agreement is not better is presumably due to the presence of equilibria involving ion-pair dimers or other larger associated species.

Solvation Enthalpies

Although the significance of solvation enthalpies cannot be fully interpreted until enthalpies are assigned to the individual ions, it is, nevertheless, possible and worthwhile to examine the functional relationship between the solvation enthalpies of a series of salts containing a common anion and the radii of the corresponding cations. The Born equation, modified by Latimer, Pitzer, and Slansky¹³ for the free energy of solvation of an ion, is

$$\Delta G_i = -e_i^2[1 - 1/\epsilon]/2[r_i + \delta] \quad (1)$$

where e_i and r_i are the charge and radius of the ion, respectively, ϵ is the dielectric constant of the solvent, and δ is a parameter which depends upon the sign of the charge on the ion and the solvent. Upon differentiation of eq 1 and combination with the Gibbs-Helmholtz equation, one obtains the corresponding enthalpy of solvation.

$$\Delta H_i = \Delta G_i \left[1 - \frac{T(\partial\epsilon/\partial T)}{\epsilon(\epsilon - 1)} + \frac{T}{r_i + \delta} \left(\frac{\partial\delta}{\partial T} \right) \right] \quad (2)$$

If we assume that $\partial\delta/\partial T$ is negligibly small, ΔH_i becomes a linear function of $1/(r_i + \delta)$.

Enthalpies of solvation of the salts investigated in this work have been calculated from the standard heats of solution listed in Table II and the crystal lattice enthalpies for the corresponding salts reported by Somsen.¹⁴ The enthalpies of solvation are also listed in Table II. A plot of these solvation enthalpies vs. $1/(r_i + \delta)$ for the bromide salts is shown in Figure 3. The value of δ is 0.8 Å. The solvation enthalpies of two alkali metal iodides also shown in Figure 3 give a line nearly parallel to that of the bromides. The point for CsBr was estimated from the average difference

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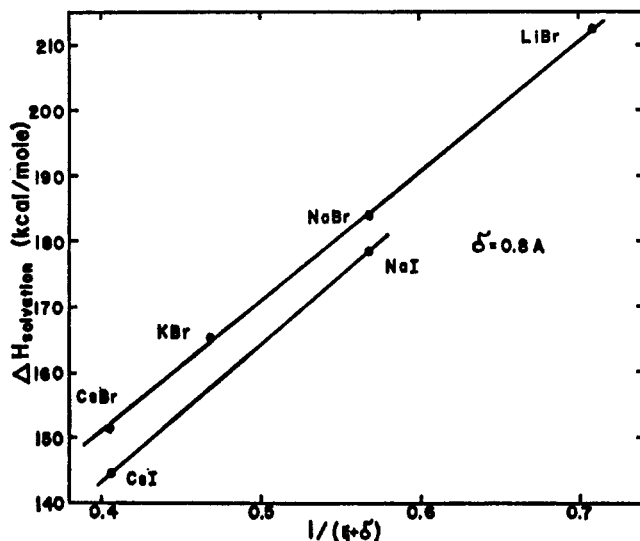


Figure 3. Solvation enthalpies vs. $1/(r_i + \delta)$. The value for CsBr was estimated from the average difference between the lines formed by the bromide and iodide salts and the measured solvation enthalpy for CsI.

between the two nearly parallel lines and the measured solvation enthalpy for CsI. The deviations from

linearity are comparable to the uncertainties of the solvation enthalpies. A similar treatment recently reported by Wu and Friedman¹⁵ for alkali metals in propylene carbonate yielded an identical value for δ in contrast to a value of 0.70 Å for the same ions in water. From this point of view, as one might expect, DMF resembles propylene carbonate more than water. The free energies of solvation and partial molal entropies should shed more light on the nature of these solutions. These are presently being examined and will be reported in a future communication.

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