Thermochemical Studies and Ion Solvation Enthalpies in Formamide, *N*-Methylformamide, and *NN*-Dimethylformamide

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Heats of solution of alkali-metal and ammonium perchlorates, thiocyanates, and halides have been measured in the concentration range 0·003—0·25 mol l^{-1} in formamide, (F), *N*-methylformamide, (NMF), and *NN*-dimethylformamide (DMF) at 26·9°. In some cases, the plots of heats of solution *vs.* the square root of concentration are linear and have been extrapolated to obtain standard heats of solution. In other cases, where the change in heat of solution with concentration is very small, standard heats of solution have been taken as the mean of four to six observations. Lattice energies of the salts which are not available have been calculated from Kapustinskii's equation. The combined ion-solvation enthalpies have been calculated by using the relation: $\Delta H^\circ_{solv} = U + \Delta H^\circ_s$. A method for obtaining ion-solvation enthalpies of the electrolytes has been suggested based on the modified Born model. Ion-solvation enthalpies of various ions have been evaluated in F, NMF, and DMF by this method. These values in F are in good agreement with absolute ion-solvation enthalpies obtained by an independent approach.

Although conductance and transference number measurements of some electrolytes have been carried out in amide solvents [1-4] in order to study ion–solvent interactions, their thermochemistry is not yet well understood. Somsen and his co-workers have measured heats of solution of alkali-metal halides in formamide,[5] (F), *N*-methylformamide [6] (NMF), and *N*-methylacetamide [7] (NMA) in order to evaluate the ion-solvation enthalpies. Held and Criss have measured heats of solution of some electrolytes in NMF [8] and *NN*-dimethylformamide [9] (DMF), while Finch and his co-workers [10] have measured heats of solution of some alkaline-earth metal chlorates and bromates in F, NMF, and DMF. It has been shown that the simple Born model [11] is insufficient to predict the correct ion-solvation enthalpies for electrolytes in these solvents. A modified Born model [12] has been successfully applied for obtaining correct ion-solvation enthalpies for a few electrolytes in aqueous solutions. However, this model has not yet been applied in non-aqueous media probably due to lack of sufficient heat of solution data. Here heats of solution of alkali-metal and ammonium perchlorates, thiocyanates, and some halides have been measured in F, NMF, and DMF and the ion-solvation enthalpies have been calculated, using the modified Born model.

EXPERIMENTAL

N-Methylformamide and *NN*-dimethylformamide were purified by methods already reported.[2,13] Formamide (Riedel Pure) was thrice distilled at 80—90° and 2 mmHg and then treated with sodamide (0·5—10 g l^{-1}) in order to neutralize the free acid and to remove traces of water. Final distillation was carried out under reduced pressure in the dark with a dry nitrogen atmosphere. The fraction (b.p. 77—78° at 0·5 mmHg; κ 1·0—2·5 × 10^{-6} Ω^{-1} cm^{-1}) was collected. Fractional crystallization (m.p. 2·57°) of this gave a purer sample, and a further distillation under reduced pressure gave a sample (κ 5·0 × 10^{-7} Ω^{-1} cm^{-1}, *d* 1·1298). It was stored in the dark and its physical constants were checked before use.

The electrolytes were prepared and purified and dehydrated by the usual methods reported earlier.[1,2,8,13]

Heats of solution of various electrolytes were measured in an isothermal phase-change calorimeter after the design of Dainton *et al.*[14] using diphenyl ether (m.p. 26·9°) as the dilatometric fluid. Details of the experimental procedure are essentially the same as reported earlier.[13]

RESULTS AND DISCUSSION

Heats of solution of various electrolytes have been measured in the concentration range 0·003—0·25 mol l^{-1}. Plots of heat of solution (ΔH_S) *vs.* square root of concentration for some of the electrolytes are linear † and have been extrapolated to zero concentration for evaluation of ΔH°_s. In other cases where the change in heats of solution is very small, standard heats of solution have been taken as the mean of four to six observations.

The combined ion-solvation enthalpies (ΔH°_{solv}) for all the electrolytes have been calculated from the standard heats of solutions (ΔH°_s) and lattice energies (U), using the relation [13] $\Delta H^\circ_{solv} = U + \Delta H^\circ_s$. The lattice energies for alkali-metal and ammonium perchlorates, thiocyanates, and ammonium halides are not available in the literature. These were calculated from

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† The plots of lithium salts in DMF only are slightly curved. These plots, and those of heat of solvation *vs.* $1/(r_i + \delta)$ are given in Supplementary Publication No. SUP 20277 (7 pp., 1 microfiche).

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Kapustinskii's equation[15] which is applicable to all types of electrolytes. The equation can be written as:

$$U = 287{\cdot}2\left[\frac{v_{z_+z_-}}{r_1 + r_2}\right]\left[1 - \frac{0{\cdot}345}{r_1 + r_2}\right]$$

where v is the number of ions, z is the charge on the ions, and r_1 and r_2 are the radii of anion and cation. The lattice energies of alkali-metal halides have been taken from the literature.[5] All the relevant data are in Table 1.

Examination of Table 1 reveals that, with the exception of the ammonium ion, heats of solution of electrolytes having a common anion decrease with increase in the size of the cation. The reverse order of heats of solution for salts having a common cation may be due to Lewis acid–base type interaction between the anions and the solvent.[16] However, lower heats of solution for thiocyanates and perchlorates may be due to the lack of such interactions.

TABLE 1

Lattice energies, heats of solution, and heats of solvation of some electrolytes in formamide, NMF, and DMF

Electrolyte	Lattice energies $(-U)$	Heats of solution $(+\Delta H^\circ_s)$ F	NMF	DMF	Heats of solvation $(-\Delta H^\circ_{solv})$ F	NMF	DMF
LiCl	201·20	−9·40 †	−13·10	−14·40 *	210·60	214·30	215·60
LiBr	191·20	−13·40 †	−16·14 *	−19·30 *	204·60	207·34	210·50
LiCNS	182·70 *	−8·50 *	−11·80 *	−16·80 *	191·20	194·50	199·50
$LiClO_4$	169·40 *	−10·80 *	−13·80 *	−22·00 *	180·20	183·20	191·40
NaCl	185·80	−2·10 †	−1·95		187·90	187·75	
NaBr	176·60	−4·40 †	−4·39 *	−7·50 *	181·00	180·99	184·10
NaI	164·50	−7·40 †	−7·50 *	−13·30 *	171·90	172·00	177·80
NaCNS	163·40 *	−3·70 *	−4·78 *	−8·63 *	167·10	168·18	172·03
$NaClO_4$	153·80 *	−1·70 *	−3·35 *	−7·85 *	155·50	157·15	161·65
KCl	168·90	+0·80 †	+0·30 *		168·10	168·60	
KBr	161·40	+0·20 †	−0·80 *	−3·75 *	161·20	162·20	165·15
KI	151·10	−1·00 †	−3·20 *	−7·60 *	152·10	154·30	158·70
KCNS	148·70 *	−0·75 *	−1·05 *	− 5·95 *	149·45	149·75	154·65
$KClO_4$	139·70 *	+3·50 *	+1·50 *	−2·30 *	136·20	138·20	142·00
RbCl	162·80	+0·70 †	+0·80 *		162·10	162·00	
RbBr	155·90	+0·70 †			155·20		
RbI	147·30	+1·00 †	+1·50	−6·64	146·30	145·80	153·94
$RbClO_4$	134·90 *	+4·05 *	+2·70 *	−1·95 *	130·85	132·20	136·85
CsCl	155·20	+0·90 †	+0·55 *		154·30	154·65	
CsBr	149·30	+2·10 †			147·20		
CsI	140·30	+2·20	+1·00	−4·25	138·10	139·30	144·55
$CsClO_4$	128·60 *	+4·60 *	+3·10 *	−1·77 *	124·00	125·50	130·37
NH_4Cl	158·00 *	−4·40 *	−5·80 *		162·40	163·80	
NH_4Br	152·20 *	−5·40 *	−6·00 *	−7·70 *	157·60	158·20	159·90
NH_4I	144·30 *	−5·90 *	−6·30 *	−10·15 *	150·20	150·60	154·45
NH_4CNS	144·60 *	+0·60 *	−0·80 *	−5·20 *	144·00	145·40	149·80
NH_4ClO_4	136·10 *	+0·80 *	−1·55 *	−8·50 *	135·30	137·46	144·60

* The values obtained from the present work. † Taken from G. Somsen, *Rec. Trav. chim.*, 1966, **85**, 517, 526.

Heats of solution of electrolytes in ammonia[17] and ethanol[18] are higher than those in water, which reflects the stronger hydrogen bonding present in aqueous solutions.[19] In agreement with the work of Finch *et al.*,[10] the heats of solution for electrolytes decrease, for the solvents used, in the order DMF > NMF > F, *i.e.* in order of their increasing association due to hydrogen bonding.

Ion-solvation Enthalpies.—The simple Born model gave only qualitative ion-solvation enthalpy values and this model was, therefore, modified to predict the correct ion-solvation enthalpy values in aqueous solutions.[12] Somsen,[5] after modifying Verway's method,[20] has obtained such values for a few ions in formamide. He has further corrected these values by taking into consideration factors accounted for in the Buckingham model[21] of solvation. Gourary and Adrian[22] have arrived at a new set of ionic radii on the basis of electron-density maps obtained by Witte and Wolfel[23] for sodium chloride. The ionic radii have been equated to the distance between the point of zero electron density and the centre of the ion. These ionic radii have been used to estimate ion-solvation enthalpies in water[24] and amide solvents.[25] However, in the present studies, plots of ΔH°_{solv} *vs.* the reciprocal of these ionic radii have not been found to be linear. Thus the use of these radii was not considered worthwhile.

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The modified Born equation for the ion-solvation enthalpy can be written as:

$$\Delta H_{\text{i solv}} = \Delta G_{\text{i solv}} \left[1 - \frac{T(\partial D/\partial T)}{D(D-1)} + \frac{T}{(r_{\text{i}} + \delta)} (\partial\delta/\partial T) \right]$$

where

$$\Delta G_{\text{i solv}} = -\frac{Ne^2 z^2}{2(r_{\text{i}} + \delta)} \left[1 - \frac{1}{D} \right]$$

where the terms T, D, N, e, and z have their usual meanings and δ is the additional ion-size parameter, which depends upon the nature of the solvent and the sign of the charge on the ion.[12] If we assume that $\partial\delta/\partial T$ is negligibly small, $\Delta H^{\circ}_{\text{solv}}$ becomes a linear function of $1/(r_{\text{i}} + \delta)$.

The plots of combined ion-solvation enthalpies for a series of salts having common anion *vs.* the reciprocal of Pauling radii of cations were not linear for the electrolytes in F, NMF, and DMF. We have tried to find the correction required to obtain linear plots. On adding the ion-size parameters $\delta = 0{\cdot}75$, $0{\cdot}75$, and $0{\cdot}70$ Å to the crystallographic radii of the cations in F, NMF, and DMF respectively, the plots of heats of solvation *vs.* $1/(r_{\text{i}} + \delta)$ in these solvents have been found to become linear and parallel to each other. The experimental slopes of the plots are in good agreement with the slope predicted by the modified Born equation. The extrapolation of these plots gives the values of solvation enthalpies of the common anions. Using these values of anion-solvation enthalpies, the enthalpies of solvation of various cations have been computed. The ion-solvation enthalpies in F obtained here are in very good agreement with the absolute values reported by Somsen.[5] A comparison of the ion-solvation enthalpy data in the amide solvents and water (Table 2) reveals that these values decrease with increase of hydrogen bonding in these solvents. This is supported by partial molal entropy data of some electrolytes in various solvents.[19]

The plots of combined ion-solvation enthalpies for a series of salts having common cations *vs.* the reciprocal radii of the anions are also not linear. However, with $\delta = 0{\cdot}1$ Å for the anions, such plots of heat of solvation of the salt *vs.* $1/(r_{\text{a}} + \delta)$ have been found to become linear. The extrapolation of these plots to $1/(r_{\text{a}} + \delta) = 0$ for halide ions, gives values which are in close agreement with ion-solvation enthalpy values computed and recorded in Table 2. However, if thiocyanate and perchlorate ions are included along with the halide ions in the plots, the extrapolation gives solvation enthalpy of the cation which is slightly different from the values recorded above. This variation may be due to the uncertainty in the size of thiocyanate and perchlorate ions.[26,27]

TABLE 2

Ion-solvation enthalpies of various ions in F, NMF, DMF, and water in kcal mol^{-1} $(-\Delta H^{\circ}_{\text{solv}\,\pm})$

Ion	Formamide	NMF	DMF	Water [a]
Li^+	123·56	126·30	129·20	121·20
Na^+	99·78	100·01	101·76	94·60
K^+	80·51	81·41	82·95	75·80
NH_4^+	76·60	77·73	80·06	
Rb^+	74·50	74·50	77·25	69·20
Cs^+	66·96	67·81	69·71	62·00
Cl^-	87·50	87·00	85·70	88·70
Br^-	81·00	81·00	82·00	81·40
I^-	72·00	72·00	74·50	72·10
CNS^-	68·00	68·50	71·00	
ClO_4^-	56·00	57·50	61·00	

[a] From W. M. Latimer, K. S. Pitzer, and C. M. Slansky, *J. Chem. Phys.*, 1939, **7**, 108.

In a recent publication Criss and Luksha [28] have reported a value of $\delta = 1{\cdot}00$ Å for the anions in DMF which gives a linear relationship between the free energies of solvation of alkali-metal and halide ions *vs.* $1/(r_{\text{a}} + \delta)$. Using this value of δ for the anions in our results, the plots obtained are not linear. On re-checking the results reported by the authors, the value $\delta = 1{\cdot}00$ for the anions has been found to be erroneous.

From the present studies it can be concluded that (*a*) the method used for evaluating ion-solvation enthalpy by the extrapolation of the plots of heats of solvation *vs.* $1/(r_{\text{i}} + \delta)$ is much simpler than the methods already reported as it avoids all the cumbersome calculations; (*b*) F, NMF, and DMF have a tendency to approach nearer the anions than the cations. This behaviour of the amide solvents is similar to that of water.[12]

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