

# Physicochemical Studies in Non-aqueous Solvents: Part XI—Thermochemical Studies of Some 1:1 Electrolytes in Hexamethylphosphotriamide

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Heats of solution of alkali metal, silver, ammonium and substituted ammonium perchlorates, lithium chloride and potassium thiocyanate have been measured in the concentration range  $1.26-61.2 \times 10^{-3}$  mole litre<sup>-1</sup> in hexamethylphosphotriamide (HMPT) at 26.9°. Slopes of the linear plots of heat of solution ( $\Delta H_s$ ) versus square-root of concentration ( $\sqrt{C}$ ) are comparable to that of Debye-Hückel limiting slope (except those of LiCl and LiClO<sub>4</sub> which are respectively six and eight times higher) indicating complete dissociation of these electrolytes. Standard heats of solutions ( $\Delta H_s^\circ$ ) of the electrolytes in HMPT are higher than those in formamide and N-methylformamide showing thereby lack of hydrogen bonding in this solvent. A modified Buckingham's model has been used to compute the solvation enthalpies of various ions in HMPT. The results indicate that ion solvation enthalpies decrease with the increase in the size of the ions which is consistent with the findings in the case of other solvents.

CONDUCTANCE studies<sup>1,2</sup> have revealed that electrolytes are completely dissociated in hexamethylphosphotriamide (HMPT) at relatively low concentrations. However, there is no report regarding the thermochemical studies of electrolytes in this solvent. Alkali metal, silver, ammonium and substituted ammonium perchlorates, lithium chloride and potassium thiocyanate are appreciably soluble in HMPT and their dissolution is accompanied with heat change. We report in this paper the heats of solution of these electrolytes in HMPT in order to have some additional information regarding their behaviour at relatively high concentrations and to evaluate ion solvation enthalpies.

## Materials and Methods

Hexamethylphosphotriamide (Fluka AG) was purified as reported earlier<sup>2</sup>. The electrolytes used here were prepared and/or purified as reported earlier<sup>2</sup>.

Heats of solution of the electrolytes were measured in an isothermal phase-change calorimeter designed after Dainton *et al.*<sup>3</sup>. Diphenyl ether (m.p. 26.9°) was used as a dilatometric fluid. The details of experimental procedure are the same as reported earlier<sup>4</sup> (accuracy  $\pm 0.2$  kJ mole<sup>-1</sup>).

## Results and Discussion

Heats of solution of various electrolytes have been measured in the concentration range  $1.26-61.2 \times 10^{-3}$  mole litre<sup>-1</sup>. Plots of heats of solution ( $\Delta H_s$ ) versus square-root of the concentration ( $\sqrt{C}$ ) of the electrolytes (except KClO<sub>4</sub>) are linear (Figs. 1 and 2) and have been extrapolated to infinite dilution to give standard heats of solution ( $\Delta H_s^\circ$ ). The experimental slopes of these plots agree well with the theoretical Debye-Hückel slope except those of LiCl and LiClO<sub>4</sub> which are respectively six and eight times higher than the theoretical ones. Generally the higher values are attributed to the ion-pair formation in the solution. However, conductance measurements<sup>2</sup> have already shown these electrolytes to be fully dissociated in hexamethylphosphotriamide (HMPT) in the relatively low con-

centration range. In view of the high dielectric constant and dipole moment values of HMPT, the deviations are too small to show significant ion-pair formation of the electrolytes. However, at the most, these electrolytes may be considered as only slightly associated in this concentrations range ( $1.26-61.2 \times 10^{-3}$  mole litre<sup>-1</sup>).

Examination of Table 1 reveals that with the exception of ammonium perchlorate, heats of solution of the electrolytes having common anion decrease with increase in the size of the cation which is consistent with the reported findings in most of the solvents<sup>5-8</sup>. However, no such generalization can be given for electrolytes having common cations due to the lack of sufficient data.

A comparison of the thermochemical data in various amide solvents reveals that heats of solution decrease as: Hexamethylphosphotriamide (HMPT) > Dimethylformamide (DMF) > N-Methylformamide (NMF) > Formamide (F). The higher values of heats of solution in HMPT than those given in DMF\* indicate that HMPT is the least hydrogen-bonded solvent. Spectroscopic<sup>9</sup> and cryoscopic<sup>10</sup> data also support this fact.

TABLE 1—HEATS OF SOLUTION ( $\Delta H_s^\circ$ ), LATTICE ENERGIES ( $U$ ) AND HEATS OF SOLVATION ( $\Delta H_{solv}^\circ$ ) OF SOME ELECTROLYTES IN HEXAMETHYLPHOSPHOTRIAMIDE AT 26.9°

Salt	$-\Delta H^\circ$ (kJ mole <sup>-1</sup> )	$-U$ (kJ mole <sup>-1</sup> )	$-\Delta H_{solv}^\circ$ (kJ mole <sup>-1</sup> )
LiCl	67.02	842.22	909.24
LiClO <sub>4</sub>	97.45	707.43	804.88
NaClO <sub>4</sub>	56.34	643.81	700.15
KSCN	33.99	622.46	656.45
KClO <sub>4</sub>	28.09	584.78	612.87
RbClO <sub>4</sub>	18.04	564.69	582.73
CsClO <sub>4</sub>	13.90	538.32	552.22
AgClO <sub>4</sub>	35.46	593.57	629.03
NH <sub>4</sub> ClO <sub>4</sub>	48.68	569.71	618.39
Me <sub>4</sub> NClO <sub>4</sub>	10.38	385.53	395.91
Et <sub>4</sub> NClO <sub>4</sub>	-5.44	363.76	358.32

\*The hydrogen bonding in DMF may be expected through formyl hydrogen.

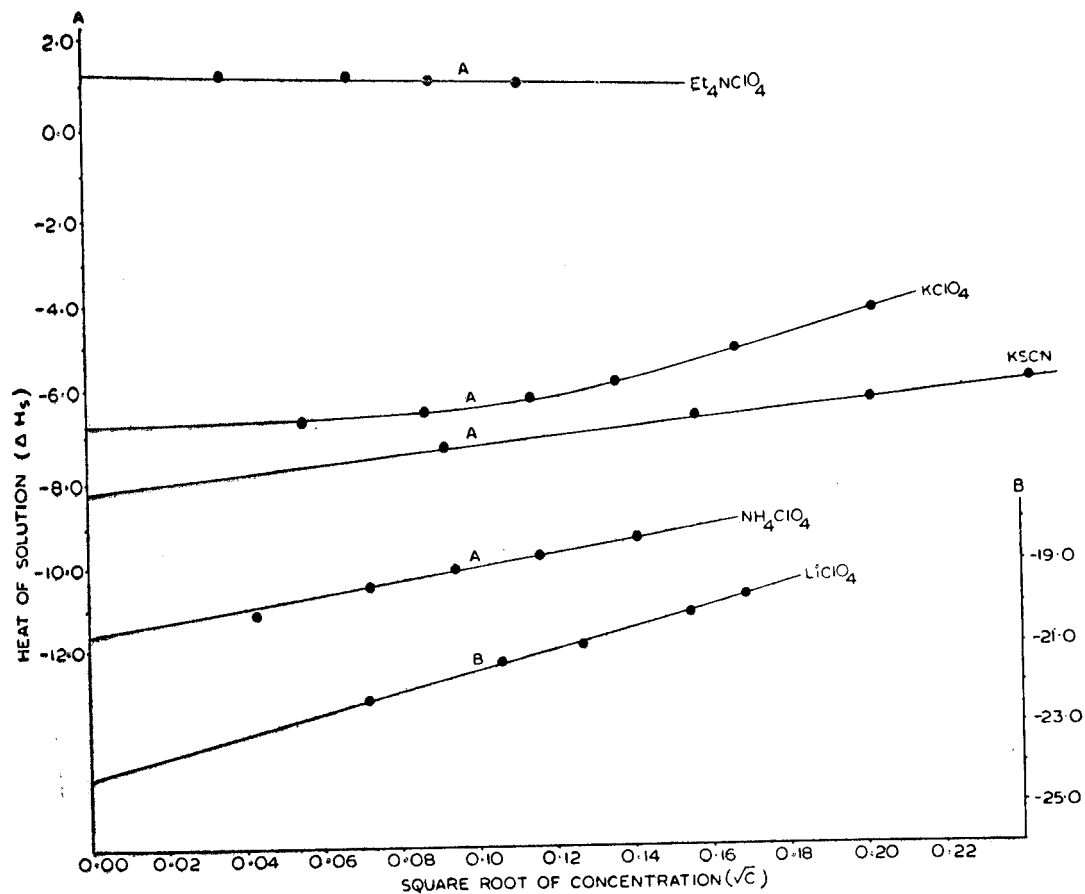


Fig. 1 — Plots of  $\Delta H_s$  versus  $\sqrt{C}$  for various electrolytes in HMPT

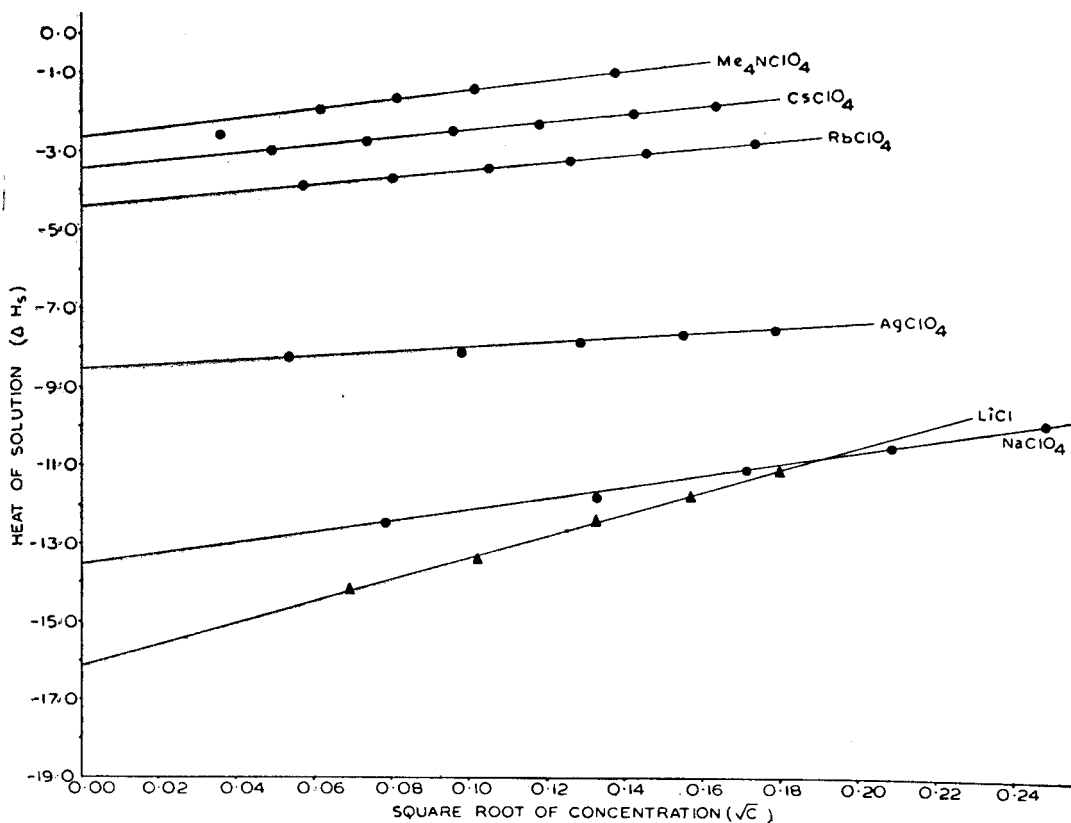


Fig. 2 — Plots of  $\Delta H_s$  versus  $\sqrt{C}$  for various electrolytes in HMPT

The combined ion-solvation enthalpies ( $\Delta H_{\text{solv}}^{\circ}$ ) for all the electrolytes have been calculated from the standard heats of solution and lattice energies (U) using Eq. (1)

$$\Delta H_{\text{solv}}^{\circ} = \Delta H_s^{\circ} + U \quad \dots(1)$$

The lattice energies for alkali metal salts, ammonium and substituted ammonium perchlorates have been taken from the literature<sup>4,8</sup> and that of silver perchlorate has been calculated using Kapustinskii's equation<sup>11</sup>.

*Ion-Solvation enthalpies*—Ion solvation enthalpies ( $\Delta H_{\text{solv}(\pm)}^{\circ}$ ) of various ions in HMPT have been evaluated using Buckingham's model<sup>12,13</sup>. This model shows that ions of equal radii and opposite charges have different solvation enthalpies and the difference, when four-fold coordination around the ion is considered, is given by Eq. 2 (ref. 14).

$$\frac{1}{2}[\Delta H_{\text{solv}(\text{M}^+)}^{\circ} - \Delta H_{\text{solv}(\text{X}^-)}^{\circ}] = -A(r_i + r_{\text{solv}})^{-3} + B(r_i + r_{\text{solv}})^{-4} \quad \dots(2)$$

where  $A = 4Nz_i e_0^2 \mu_{\text{solv}}^{\circ}$  and  $B = (135\sqrt{2}/32\sqrt{3})\mu_{\text{solv}}^{\circ}$

All the symbols have their usual meanings. Relative solvation enthalpies ( $\Delta H_{\text{rel}(\text{solv}(\pm))}^{\circ}$ ) of various ions in HMPT have been calculated by assuming  $\Delta H_{\text{rel}(\text{solv}(\text{Na}^+))}^{\circ} = 0.0$  kJ mole<sup>-1</sup>. Substituting  $\Delta H_{\text{solv}(\text{M}^+)}^{\circ}$  and  $\Delta H_{\text{solv}(\text{X}^-)}^{\circ}$  in terms of relative ion-solvation enthalpies, Eq. (2) reduces to Eq. 3.

$$\frac{1}{2}[\Delta H_{\text{rel}(\text{solv}(\text{M}^+))}^{\circ} - \Delta H_{\text{rel}(\text{solv}(\text{X}^-))}^{\circ}] = -\Delta H_{\text{solv}(\text{Na}^+)}^{\circ} - A(r_i + r_{\text{HMPT}})^{-3} + B(r_i + r_{\text{HMPT}})^{-4} \quad \dots(3)$$

Difference in relative enthalpies of hypothetical ion-pairs of equal radii and opposite charges have been evaluated<sup>14</sup> from the plots of cation and anion solvation enthalpies against  $(r_i + r_{\text{HMPT}})^{-3}$ . The radius of the HMPT molecule has been found to be 3.6 Å on constructing a Fischer model of its molecule. The solvation enthalpy of sodium ion has been evaluated from Eq. (3) by the method of least-squares.

Recently, Conway and Salomon<sup>15,16</sup> have pointed out that ion-dipole term is not equal for ions of equal radii and opposite charges if the orientations of the solvent at the cation and anion are not mirror images<sup>17</sup>. Salomon<sup>18</sup> has evaluated ion-solvation enthalpies in water and propylene carbonate by modifying the Halliwell and Nyburg equation as shown below:

$$\frac{1}{2}[\Delta H_{\text{rel}(\text{solv}(\text{M}^+))}^{\circ} - \Delta H_{\text{rel}(\text{solv}(\text{X}^-))}^{\circ}] = -\Delta H_{\text{sal}(\text{Na}^+)}^{\circ} + C(r_i + r_{\text{solv}})^{-2} - D(r_i + r_{\text{solv}})^{-3} \quad \dots(4)$$

The results so obtained are significantly different and the difference has been attributed to the variation of ion-dipole interaction energies between solvent and the ions, due to the different orientation of solvent molecules. The data obtained in the case of HMPT as the solvent have also been analysed using Salomon's equation. However, the solvation enthalpies of sodium ion obtained by the two methods differ only by 3.76 kJ mole<sup>-1</sup> which is not significant. This may suggest that ion-dipole interactions are almost the same in HMPT.

Knowing the solvation enthalpy of Na<sup>+</sup>, solvation enthalpies of various ions ( $\Delta H_{\text{solv}(\pm)}^{\circ}$ ) can be calcu-

TABLE 2—RELATIVE ION-SOLVATION ( $\Delta H_{\text{rel}(\text{solv}(\pm))}^{\circ}$ ) AND ION-SOLVATION ( $\Delta H_{\text{solv}(\pm)}^{\circ}$ ) ENTHALPIES TO VARIOUS IONS IN HEXAMETHYLPHOSPHOTRIAMIDE

Ion	$\Delta H_{\text{rel}(\text{solv}(\pm))}^{\circ}$	$\Delta H_{\text{solv}(\pm)}^{\circ}$ (kJ mole <sup>-1</sup> )	
		Halliwell and Nyburg method	Salomon method
Li <sup>+</sup>	-106.41	519.52	523.28
Na <sup>+</sup>	-0.00	413.12	416.88
K <sup>+</sup>	+87.28	325.83	329.60
Rb <sup>+</sup>	+117.42	295.70	299.46
Cs <sup>+</sup>	+147.93	266.86	270.62
Ag <sup>+</sup>	+71.12	342.00	345.76
NH <sub>4</sub> <sup>+</sup>	+81.75	331.36	335.12
Me <sub>4</sub> N <sup>+</sup>	+304.24	108.96	112.72
Et <sub>4</sub> N <sup>+</sup>	+341.82	71.29	75.05
Cl <sup>-</sup>	-802.83	389.72	292.48
SCN <sup>-</sup>	-743.72	330.61	334.37
ClO <sub>4</sub> <sup>-</sup>	-700.15	287.03	390.79

lated using Eq. (5).

$$\Delta H_{\text{solv}(\pm)}^{\circ} = \Delta H_{\text{rel}(\text{solv}(\pm))}^{\circ} (\pm \Delta H_{\text{solv}(\text{Na}^+)}^{\circ}) \quad \dots(5)$$

where plus and minus signs are for cations and anions respectively. It is clear from the Table 2 that solvation enthalpies of ions decrease with increase in the size of the ion and follow the order: Li<sup>+</sup> > Na<sup>+</sup> > Ag<sup>+</sup> > NH<sub>4</sub><sup>+</sup> > K<sup>+</sup> > Rb<sup>+</sup> > Cs<sup>+</sup> > Me<sub>4</sub>N<sup>+</sup> > Et<sub>4</sub>N<sup>+</sup> and Cl<sup>-</sup> > SCN<sup>-</sup> > ClO<sub>4</sub><sup>-</sup>.

This order is in accord with the one reported in the case of other solvents including water<sup>6,8,15,17</sup> and also with the solvation numbers of the ions obtained in HMPT<sup>2</sup>.

It may thus be concluded that HMPT is an excellent dissociating solvent for alkali metal, silver, ammonium and substituted ammonium perchlorates.

## References

- BRUNO, P., DELLA-MONICA, M. & RIGHETTI, E., *J. phys. Chem.*, **77** (1973), 1258.
- PAUL, R. C., BANAIT, J. S. & NARULA, S. P., *Z. phys. Chem. (N.F.)*, **94** (1975), 199.
- DAINTON, F. S., DIAPER, J., IVIN, K. J. & SHEARD, D. R., *Trans. Faraday Soc.*, **53** (1957), 1269.
- PAUL, R. C., GILL, D. S. & NARULA, S. P., *Indian J. Chem.*, **8** (1970), 936.
- PAUL, R. C., JAUHAR, S. P., BANAIT, J. S. & NARULA, S. P., *J. chem. Soc. (Faraday I)*, **73** (1977), 833.
- SOMSEN, G., *Recl. Trav. chim. Pays-Bas. Belg.*, **85** (1966), 517; 526.
- SOMSEN, G. & COOPS, J., *Recl. Trav. chim. Pays-Bas. Belg.*, **84** (1965), 985.
- GILL, D. S., SINLGA, J. P., PAUL, R. C. & NARULA, S. P., *J. chem. Soc. (Dalton's Trans.)*, (1972), 522.
- HERAIL, F., *C.r. hebd. Séanc Acad. Sci. Paris, Ser. C.*, **262** (1966), 22.
- BANAIT, J. S., (unpublished results).
- KAPUSTINSKII, *Q. Rev. chem. Soc.*, **10** (1956), 283.
- BUCKINGHAM, A. D., *Discuss. Faraday Soc.*, **24** (1957), 151.
- BOCKRIS, J. O'M. & REDDY, A. K. N., *Modern electrochemistry*, Vol. I (Plenum Press, New York), 1970.
- HALLIWELL, H. F. & NYBURG, S. C., *Trans. Faraday Soc.*, **58** (1963), 1126.
- CONWAY, B. E. & SALOMON, M., *Chemical physics of ionic solutions*, edited by B. E. Conway & R. G. Barradas (Wiley, New York), 1966.
- CONWAY, B. E., *Modern aspects of electrochemistry*, edited by B. E. Conway and J. O'M. Bockris (Butterworths, London), 1964.
- VERWAY, E. J. W., *Recl. Trav. chim. Pays-Bas. Belg.*, **61** (1942), 127.
- SALOMON, M., *J. phys. Chem.*, **74** (1970), 2519.