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CALORIMETRIC STUDY OF THE SOLVATION OF SOME IONS IN ACETONITRILE–DIMETHYLSULFOXIDE MIXTURES

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ABSTRACT

The heats of solution of $LiClO_4$, LiCl, $NaClO_4$, $NaBPh_4$, $Co(ClO_4)_2$, Ph_4AsCl and Ph_4AsClO_4 were measured in acetonitrile (AN)–dimethylsulfoxide (DMSO) mixtures over the whole range of solvent composition. The heats of transfer of single ions from DMSO to AN–DMSO mixtures were determined, based on the tetraphenylarsonium tetraphenylborate (TATB) assumption. The variation in the ionic heats of transfer with solvent composition is discussed.

INTRODUCTION

The solvation of ions in aprotic mixtures which do not show specific interactions between solvent molecules is determined mainly by ion–solvent interactions in the first solvation sphere of an ion. The changes in these interactions with mixture composition are reflected in the ionic heats of transfer which are also sensitive to changes in solvent structure.

The thermodynamic properties of electrolytes in aprotic binary mixtures have been investigated by several authors. De Visser and Somsen [1] measured heats of solution of tetraalkylammonium salts in binary mixtures of various amides. Cox et al. [2] reported the thermodynamic functions of transfer, ΔG_{tr}, ΔH_{tr} and ΔS_{tr}, of some cations from propylene carbonate to propylene carbonate–dimethylsulfoxide (DMSO) mixtures.

In the present paper, the detailed study of the ionic heats of transfer from DMSO to acetonitrile (AN)–DMSO mixtures is reported. The purpose of this work was to determine whether the contribution of anions to the overall heats of transfer of salts can be neglected in aprotic mixtures where the solvation of anions is expected to be rather weak [3]. The influence of the well-known DMSO structure resulting from dipole–dipole interactions [4] on the ionic heats of transfer was also checked.

In order to split the heats of transfer of salts into single-ion values, the widely accepted approach, i.e. the tetraphenylarsonium tetraphenylborate

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(TATB) assumption stating that Ph_4As^+ and BPh_4^- ions are equally solvated in all pairs of solvents, was applied.

EXPERIMENTAL

Dimethylsulfoxide (Reachim, U.S.S.R.) was dried over calcium hydride and purified by fractional distillation under reduced pressure. Acetonitrile (Apolda, G.D.R.) was kept over 3-Å molecular sieves and purified by successive distillation from phosphorous pentoxide and calcium hydride.

Sodium perchlorate (Merck, p.A.) was recrystallized from water and dried in vacuo over phosphorous pentoxide at 353 K. Lithium perchlorate and chloride obtained from lithium hydroxide (Chemapol, Czechoslovakia) and the respective acid were recrystallized twice from water and dried in vacuo at 428 K. Sodium tetraphenylborate (Serva, p.A.) was dried in vacuo at 333 K. Tetraphenylarsonium chloride (Schuchardt, p.A.) was recrystallized from acetone and kept in an oven at 453 K prior to use. Tetraphenylarsonium perchlorate was prepared from tetraphenylarsonium chloride by metathesis with aqueous $NaClO_4$ and recrystallized from acetonitrile. The product was dried in vacuo at 333 K.

All salts were kept in vacuo over phosphorous pentoxide.

Solid solvates $Co(ClO_4)_2 \cdot 6AN$ and $Co(ClO_4)_2 \cdot 6DMSO$ were obtained and kept as described previously [5,6].

All manipulations with salts and solvents were carried out in a dry-box. The heats of solution were determined using a calorimeter of constant temperature–environment type which has been described previously [5,6]. The salts were dissolved within 1–2 min, except Ph_4AsClO_4 and LiCl for which the dissolution process was practically complete within 5–8 min. Final salt concentrations were in the range 10^{-3}–10^{-2} mol dm^{-3}. The ΔH_s^0 values were reproducible to 0.3 kJ mol^{-1}, except for LiCl and $LiClO_4$ in AN-rich mixtures for which the reproducibility was 1 kJ mol^{-1}. The heats of solution were independent of the salt concentration within experimental error and, therefore, they were taken as the standard values.

RESULTS

The heats of solution, ΔH_s^0, of $NaClO_4$, $LiClO_4$, LiCl, $NaBPh_4$, Ph_4AsCl and Ph_4AsClO_4 in AN–DMSO mixtures are listed in Table 1. For comparison, the ΔH_s^0 values in pure solvents, available in the literature, are also reported. The heats of transfer of the above salts from DMSO to AN–DMSO mixtures, calculated directly from the heats of solution, are shown in Figs. 1 and 2. In the case of $Co(ClO_4)_2$ occurring in the solid state in the form of solvates, the heats of solution of the two solvates of well-defined stoichiome-

TABLE 1

Heats of solution (kJ mol^{-1}) of the salts studied in AN–DMSO mixtures for varying mole fractions of DMSO (298.15 K)

x_{DMSO}	ΔH_s^0 [a]	x_{DMSO}	ΔH_s^0 [a]
$NaClO_4$		LiCl	
1	−34.76 [c]	1	−47.58 [j]
0.774	−34.62	0.817	−48.13
0.601	−34.74	0.587	−48.30
0.494	−34.64	0.422	−48.07
0.327	−33.48	0.262	−47.70
0.307	−33.04	0.170	−46.83
0.213	−31.98	0.103	−45.08
0.103	−28.71	0.049	−40.88
0.056	−25.94	0.008	−17.26
0.0224	−22.51	0.003	−13.08
0.0214	−22.22	0	−8.91
0	−16.59 [d]		
		$LiClO_4$	
$NaBPh_4$		1	−76.05 [k]
1	−59.43 [e]	0.797	−75.62
0.810	−59.98	0.602	−75.60
0.604	−59.97	0.399	−75.13
0.470	−59.98	0.199	−74.83
0.402	−59.76	0.141	−74.20
0.274	−59.24	0.108	−72.96
0.142	−56.37	0.051	−69.63
0.129	−55.46	0.026	−67.17
0.050	−51.57	0.025	−66.09
0.0234	−47.58	0.0132	−58.65
0	−42.05 [f]	0.0033	−54.20
		0	−37.53
Ph_4AsClO_4			
1	23.14 [g]	$Co(ClO_4)_2 \cdot 6AN$	
0.797	23.73	1	−58.10 [b]
0.603	24.53	0.410	−58.19
0.390	25.08	0.299	−55.44
0.216	25.65	0.210	−54.47
0	26.34	0.100	−45.63
		0.049	−38.81
Ph_4AsCl		0.027	−31.67
1	−3.61 [h]	0.010	−21.60
0.810	−3.73	0	12.00 [b]
0.808	−3.75		
0.617	−3.76	$Co(ClO_4)_2 \cdot 6DMSO$	
0.455	−3.42	1	40.27
0.345	−3.06	0.774	40.11
0.231	−2.48	0.588	39.89
0.105	−1.92	0.406	40.82
0	−1.42 [i]	0.204	44.61
		0.107	52.07

[a] The data for $x_{\mathrm{DMSO}} = 1$ are the average value of at least three measurements. [b] Data from ref. 5. For comparison: [c] −33.1 [7]; [d] −17.4 [8]; [e] −59.54 [9], −59.4 [7], −59.8 [10]; [f] −43.5 [11]; [g] 26.02 [12], 23.34 [2]; [h] −5.9 [7], −3.9 [12]; [i] −0.2 [13], −2.93 [14]; [j] −45.6 [7]; [k] −76.6 [2].

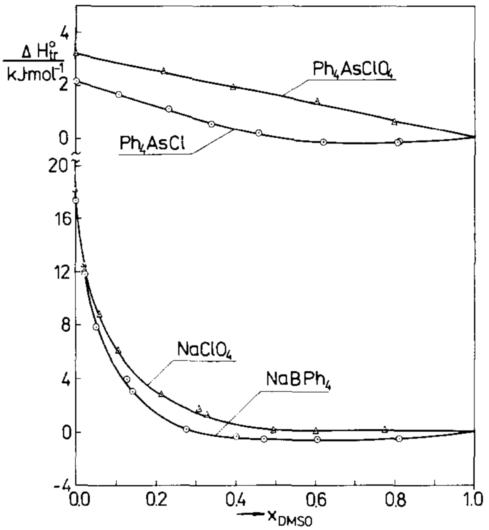

Fig. 1. Heats of transfer of Ph_4AsCl, Ph_4AsClO_4, $NaBPh_4$ and $NaClO_4$ from DMSO to AN–DMSO mixtures at 298.15 K.

try, $Co(ClO_4)_2 \cdot 6AN$ and $Co(ClO_4)_2 \cdot 6DMSO$, were measured (Table 1). According to the method proposed by Libuš et al. [5] described earlier [6], the heats of transfer of $Co(ClO_4)_2$ could be obtained from the above data and from the differential heats of solution of the solvent forming the crystalline solvate, ΔH_s^L, as follows

$$\Delta H^0_{tr}\left[Co(ClO_4)_2 \cdot 6L\right]_{x_{DMSO} \leftarrow DMSO}$$

$$= \Delta H_s^0\left[Co(ClO_4)_2 \cdot 6L\right]_{x_{DMSO}} - 6\Delta H^L_{s,x_{DMSO}} - \Delta H_s^0\left[Co(ClO_4)_2 \cdot 6L\right]_{DMSO}$$

$$6\Delta H^L_{s,DMSO} \qquad (1)$$

The ΔH_s^L values were practically zero for AN in the solvent-composition range where $Co(ClO_4)_2 \cdot 6AN$ was used ($0 < x_{DMSO} < 0.4$); they could be also neglected for DMSO in the concentration range $0.4 < x_{DMSO} \leqslant 1$. As can be seen from Fig. 2 the results obtained from both solvates agree well.

TABLE 2

Comparison of the ionic heats of transfer (kJ mol^{-1}) from DMSO to AN obtained by various authors (298.15 K)

	This work	Johnsson and Persson [15]	Ahrland et al. [13]	Hedwig and Parker [16]
Na^+	16.2	15.8	14.5	14.6
Ph_4As^+	1.2	1.0	1.7	1.2
Cl^-	1.0	2.4	1.7	–
ClO_4^-	2.0	2.8	3.0	0.8

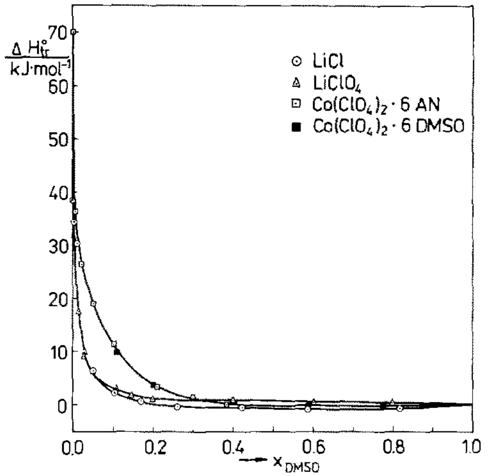

Fig. 2. Heats of transfer of LiCl, $LiClO_4$ and $Co(ClO_4)_2$ from DMSO to AN–DMSO mixtures at 298.15 K.

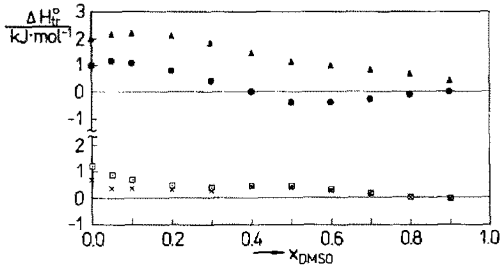

Fig. 3. Heats of transfer of Ph_4As^+ (⊡, from eqn. (2); ×, from eqn. (3)], ClO_4^- (▲), and Cl^- (●) ions from DMSO to AN–DMSO mixtures at 298.15 K.

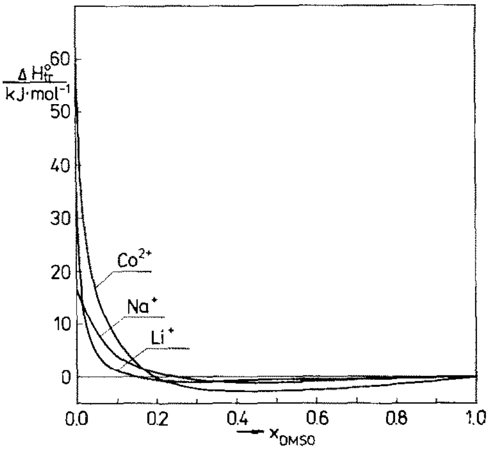

Fig. 4. Heats of transfer of Li^+, Na^+ and Co^{2+} ions from DMSO to AN–DMSO mixtures at 298.15 K.

In the AN-rich region, the DMSO solvate could not be used because of the considerably stronger donor properties of DMSO as compared to AN.

In order to check the consistency of the data obtained, the differences of $\Delta H^0_{tr}(\mathrm{Ph_4AsClO_4}) - \Delta H^0_{tr}(\mathrm{Ph_4AsCl})$ and $\Delta H^0_{tr}(\mathrm{LiClO_4}) - \Delta H^0_{tr}(\mathrm{LiCl})$ were calculated over the whole solvent-composition range. The ΔH^0_{tr} values for each salt were taken from the interpolation curves. The differences did not exceed the value of 0.3 kJ mol^{-1} in the range of $1 \geqslant x_{\mathrm{DMSO}} > 0.2$ and increased up to 1.3 kJ mol^{-1} in pure AN. The discrepancies in the AN-rich region may be explained by the presumable association of LiCl.

The heats of transfer of single ions were determined by the application of the TATB assumption, i.e. $\Delta H^0_{tr}(\mathrm{Ph_4As^+}) = \Delta H^0_{tr}(\mathrm{BPh_4^-})$. The latter heats could be calculated from the heats of transfer of salts by two different routes

$$\Delta H^0_{tr}(\mathrm{Ph_4As^+}) = \tfrac{1}{2}[\Delta H^0_{tr}(\mathrm{Ph_4AsClO_4}) + \Delta H^0_{tr}(\mathrm{NaBPh_4}) - \Delta H^0_{tr}(\mathrm{NaClO_4})] \qquad (2)$$

$$\Delta H^0_{tr}(\mathrm{Ph_4As^+}) = \tfrac{1}{2}[\Delta H^0_{tr}(\mathrm{Ph_4AsCl}) + \Delta H^0_{tr}(\mathrm{NaBPh_4}) - \Delta H^0_{tr}(\mathrm{NaClO_4}) + \Delta H^0_{tr}(\mathrm{LiClO_4}) - \Delta H^0_{tr}(\mathrm{LiCl})] \qquad (3)$$

In the second way, the heats of transfer of $\mathrm{NaClO_4}$, $\mathrm{LiClO_4}$ and LiCl were used instead of NaCl, the solubility of which was too low in the investigated mixtures.

The graphically interpolated ΔH^0_{tr} values for the salts were used in calculating the single-ion heats of transfer. The results are shown in Figs. 3 and 4. As can be seen from Fig. 3 the differences in the ΔH^0_{tr} values of the $\mathrm{Ph_4As^+}$ ion found by different routes are small. ΔH^0_{tr} values for other ions were calculated using ΔH^0_{tr} values of $\mathrm{Ph_4As^+}$ ion obtained from eqn. (2).

For comparison, the heats of transfer of single ions from DMSO to pure AN determined in this study and those derived from the data of various authors are listed in Table 2. The results seem to be in good agreement, especially if it is taken into account that they were obtained in different ways.

DISCUSSION

As can be seen from Fig. 3, the heats of transfer of tetraphenylarsonium and tetraphenylborate ions from DMSO to the AN–DMSO mixtures are close to zero for a wide range of solvent composition, except for in the AN-rich region where they become slightly positive. Taking into account that the energy consumed in the reorganization of the bulk solvent structure by an ion is expected to be the greatest in pure DMSO, the positive heats of transfer suggest stronger interactions of the above ions with DMSO than with AN molecules. The heats of transfer of perchlorate ion (all positive) and of chloride ion (positive in the AN-rich region) clearly indicate that these ions are more strongly solvated in DMSO than in AN. This is reasonable because anions are solvated in aprotic solvents through weak electrostatic interactions between an ion and the dipoles of the solvent molecules; the dipole moment of DMSO is higher than that of AN.

The variation in the heats of transfer with mixed aprotic solvent composition for metal cations is mainly determined by the donor properties of the solvents. As can be seen from Fig. 4, the common feature of these dependencies is a large decrease in the ΔH_{tr}^0 values on addition of small amounts of DMSO to AN. As the replacement of AN molecule in the solvation sphere of a cation by a DMSO molecule is exothermic (Gutman's donor numbers of AN and DMSO are 14.1 and 29.8, respectively), the variation in ΔH_{tr}^0 with solvent composition indicates the strong preferential solvation of cations by DMSO.

This effect is most pronounced for the Co(II) ion which is able to form covalent bonds with solvent molecules. Comparing two alkali-metal ions which are solvated through electrostatic interactions only, it can be noted that the preferential solvation by DMSO is stronger for the lithium ion, because of its higher charge density, than for the sodium one.

The second characteristic feature of ΔH_{tr}^0 versus x_{DMSO} dependences for strongly solvated ions, i.e. for metal cations and perhaps for chloride ion, is a slight decrease in ΔH_{tr}^0 values on passing from DMSO to the DMSO-rich mixtures. The exothermic transfer of cations over a fairly wide solvent-composition range seems to reveal the bulk structure of DMSO due to its high dipole moment [4]. Ionic heats of solvation in DMSO contain an unfavourable term which is associated with removing DMSO molecules from the bulk solvent structure. This term should be smaller in the mixtures where the ordering of bulk DMSO is partly destroyed. As a result the heats of transfer from DMSO to the mixtures are negative. At higher AN contents this effect is masked by a strongly endothermic replacement of DMSO by AN molecules in the solvation sphere of the ion.

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