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Enthalpy of interaction of tetra-*n*-alkylammonium bromides and CsI with dimethyl sulfoxide in water at 298.15 K

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Abstract

Excess enthalpies in water of dimethyl sulfoxide (DMSO) with various electrolytes (CsI, Me_4NBr, Et_4NBr, Pr_4NBr, Bu_4NBr and Pen_4NBr) have been determined by flow microcalorimetry at 298.15 K. Enthalpic pair interaction coefficients, h_{NE}, of the virial expansion of the mixing enthalpy were calculated. The interaction of DMSO with CsI, Me_4NBr, Et_4NBr gives negative and that with the remaining electrolytes gives positive coefficients. In the tetraalkylammonium series, h_{NE} becomes increasingly positive when the number of carbon atoms in the hydrocarbon chain is increased. © 1997 Elsevier Science B.V.

Keywords: Tetra-*n*-Alkylammonium bromides; Dimethyl sulfoxide; Electrolytes; Flow microcalorimetry; Pair interaction coefficients

1. Introduction

Information on the thermodynamic behavior of aqueous systems involving two solutes can be obtained by pair interaction coefficients. These are calculated from the virial expansion of the excess thermodynamic properties [1]. Pairwise interaction coefficients represent the corresponding energy, enthalpy or entropy results when two solvated solutes interact in solution.

Numerous studies with non-electrolytic solutes in terms of homotactic and heterotactic enthalpic pairwise coefficients in water have been completed [2,3]. A classification of non-electrolytes in water into three classes, based on the sign and value of the homotaxial coefficients, have been carried out [4]. Nevertheless, studies in which electrolytes participate as one of the solutes are noticeably fewer.

In the present paper, enthalpies of the mixing of CsI and tetra-*n*-alkylammonium bromides with dimethyl sulfoxide (DMSO) at 298.15 K in water are reported and discussed in terms of enthalpic pair interactions coefficients, h_{NE}.

2. Experimental

2.1. Reagents

CsI (Merck) was oven-dried for two days at 393.15 K. Tetra-*n*-alkylammonium bromides, R_4NBr ($R = Me, Et, Pr, Bu, Pen$), from Fluka or Merck of the best quality available were purified and checked as described by Conway et al. [5]. Their purities were

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greater than 99.7%. All salts were kept in a vacuum desiccator with P_2O_5. DMSO (Merck, stated purity from GC > 99.5 mol%, $H_2O < 0.03\%$) was kept over a thermally activated 4A molecular sieve prior to use. Water obtained from a Milli-Q water system (Millipore, $\kappa \approx 10^{-6}$ S cm^{-1}) and DMSO were degassed prior to making up solutions by weight.

Table 1
Enthalpies of dilution of CsI and Pen_4NBr in water at 298.15 K

m_i/ (mol kg^{-1})	m_f/ (mol kg^{-1})	$\Delta_{dil}H_{m,N}$/ (J mol^{-1})
CsI		
0.0542	0.0263	38.6
0.0789	0.0387	64.5
0.0979	0.0474	89.4
0.1632	0.0799	178.9
0.2056	0.0997	226.3
0.2523	0.1231	283.7
0.2523	0.1234	287.1
0.2972	0.1433	342.5
0.4185	0.2033	482.7
0.4842	0.2371	530.6
0.5877	0.2808	657.7
0.7403	0.3599	783.8
Pen_4NBr		
0.0194	0.0074	−172.3
0.0206	0.0102	−163.5
0.0435	0.0216	−377.6
0.0445	0.0214	−394.9
0.0456	0.0223	−387.5
0.6090	0.0291	−576.5
0.0746	0.0367	−1080.4
0.0815	0.0388	−850.9
0.1016	0.0493	−1071.6
0.1319	0.0623	−1565.5
0.1342	0.0632	−1565.5
0.1552	0.0756	−1653.8
0.1702	0.0797	−2093.6

2.2. *Calorimetric procedure*

Enthalpies of dilution and mixing were determined with a ThermoMetric (TAM 2277) flow microcalorimeter at 298.15 ± 0.01 K. Details of this apparatus, associated equipment and experimental procedure adopted, have been reported in previous papers [6,7].

3. Results and discussion

The excess enthalpy $H^{ex}(m_N, m_E)$ of a solution containing 1 kg of water, m_N mol of a non-electrolyte 'N' and m_E mol of an electrolyte 'E' can be expressed in terms of a virial expansion of the molalities [8]

$$\begin{aligned} H^{ex}(m_N, m_E) &\equiv H(m_N, m_E) - H_w^0 - H_N^\infty m_N \\ &- H_E^\infty m_E = h_{NN} m_N^2 \\ &+ 2h_{NE} m_N m_E + h_{EE} m_E^2 + h_{EE} m_E^2 \\ &+ h_{NNN} m_N^3 + 3h_{NNE} m_N^2 m_E \\ &+ 3h_{NEE} m_N m_E^2 + h_{EEE} m_E^3 \cdots \end{aligned} \tag{1}$$

where $H(m_N, m_E)$ is the absolute enthalpy of the solution, H_w^0 is the standard enthalpy of 1 kg of water and H_N^∞ and H_E^∞ are the limiting partial molar enthalpies of N and E, respectively. h_{ij} and h_{ijk} terms are enthalpic virial coefficients representing interactions between the subscripted species. To evaluate these coefficients, the excess enthalpies of the binary solutions must be known. Introducing an auxiliary function ΔH^*, defined as

$$\begin{aligned} \Delta H^* &\equiv \Delta_{mix} H_{N,E} - \Delta_{dil} H_N - \Delta_{dil} H_E \\ &= H^{ex}(m_N, m_E) - H^{ex}(m_N) - H^{ex}(m_E) \end{aligned} \tag{2}$$

and combining Eqs. (1) and (2)

$$\begin{aligned} \Delta H^* &= 2h_{NE} m_N m_E + 3h_{NNE} m_N^2 m_E \\ &+ 3h_{NEE} m_N m_E^2 + \cdots \end{aligned} \tag{3}$$

which can be expressed in a general form as

$$\Delta H^* = A_0 m_N m_E + A_1 m_N^2 m_E + A_2 m_N m_E^2 + \cdots \tag{4}$$

Molar enthalpies of dilution of DMSO, Me_4NBr, Et_4NBr, Pr_4NBr and Bu_4NBr were taken from previous papers [6,9], and those corresponding to CsI and Pen_4NBr were determined in this work and are given in Table 1.

The enthalpy of dilution for an electrolyte from an initial to a final molality, $\Delta_{dil}H_m(m_i \rightarrow m_f)$, can be expressed as [10]

Table 2
Values of coefficients for Eq. (5) and standard deviations of the fit[a]

Electrolyte	B_L/ (J kg mol^{-2})	C_L/ (J kg$^{3/2}$ mol$^{-5/2}$)	D_L/ (J kg^2 mol^{-3})	s/ (J mol^{-1})
CsI	−7512 (460)	5824 (1105)	−2140 (718)	2.45
Pen_4NBr	2890 (1365)	33756 (3066)	—	19.6

[a] Numbers in parentheses are the 95% confidence limits.

$$\Delta_{\rm dil}H - A_L(m_f^{1/2} - m_i^{1/2}) = B_L(m_f - m_i) + C_L(m_f^{3/2} - m_i^{3/2}) + D_L(m_f^2 - m_i^2) + \dots \qquad (5)$$

where $A_L = 1972\,\mathrm{J\,kg^{1/2}\,mol^{3/2}}$ is the limiting Debye-Hückel slope at 298.15 K, and B_L, C_L, etc., are curve fitting parameters which are related to the solute–solute interactions. B_L, C_L , D_L, etc. were obtained using a least squares analysis. In Table 2, the coefficients of Eq. (5) are reported. The experimental enthalpies of mixing,$\Delta_{\rm mix}H_{\rm N,E}$, and the coefficients A_0, A_1 and A_2 obtained from Eq. (4) by an analysis of non-linear least squares regression are shown in Table 3 and Table 4 respectively. Since $A_1 = 3h_{\rm NNE}$ and $A_2 = 3h_{\rm NEE}$ are complicated quantities encapsulating triplet contributions from both the anion and cation with the non-electrolyte, attention was directed toward the enthalpy pairwise coefficients $h_{\rm NE}$. These are reported in Table 5. Other systems including *N,N*-dimethylformamide (DMF) [11], urea [12], tert-butanol (TBA) [13] and 2-metyl-2-butanol (TPA) [7] as non-electrolytes are also given in the same table for the purpose of comparison. Enthalpic pairwise coefficients relative to the interaction of urea with Pr_4NBr and Pen_4NBr are lacking and have been estimated by numerical interpolation and extrapolation, respectively, from those corresponding to Et_4NBr and Bu_4NBr, which were calculated, along with that for Me_4NBr, from limiting enthalpies of transfer. On the other hand, values of $h_{\rm NE}$ for CsI with DMF [14], urea [15], TBA [13] and TPA [7] have been obtained by means of the additivity rule.

$h_{\rm NE}$ is exothermic for the interaction of DMSO with CsI, Me_4NBr and Et_4NBr, and endothermic for the three remaining R_4NBr studied. In the tetraalkylammonium series, $h_{\rm NE}$ becomes increasingly positive when the number of carbon atoms, n_C, in the hydrocarbon chain is increased. This tendency is also fulfilled by other non-electrolytes in their interaction with tetraalkylammonium bromides in water, as shown in Fig. 1. A good linear dependence between $h_{\rm NE}$ and n_C is obtained, excluding the Me_4NBr salt from the plot.

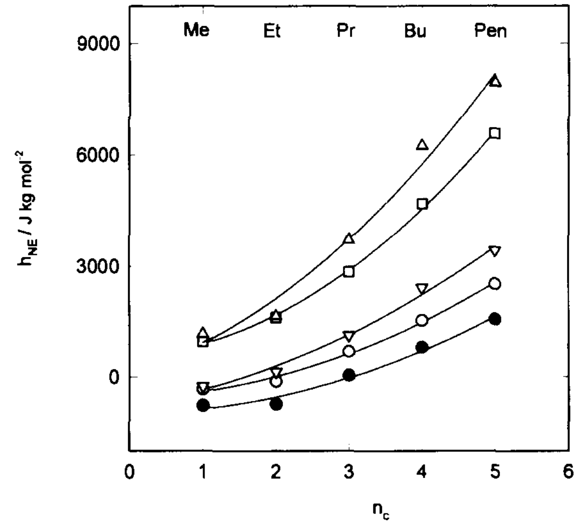

Fig. 1. Dependence of enthalpic pair interaction coefficient, $h_{\rm NE}$, with the number of carbon atoms, n_C, in the hydrocarbon chain. (○) – DMSO; (△) – DMF; (□) – TBA; (▽) –TPA; and (•) – urea.

As shown in Table 5, the sign and value of $h_{\rm NE}$ depend largely on the type of non-electrolyte and salt used. The coefficient $h_{\rm NE}$ represents the thermochemical result when two hydrated solutes approach each other from an infinite distance to an adequate critical distance. Based on an overlap co-sphere model, the value of $h_{\rm NE}$ can be considered as a result of two contributions [16]: one endothermic (positive) due to the partial dehydration of solutes and the other exothermic (negative) arising from solute–solute interactions. The interaction of Me_4NBr and CsI with the co-solvents shown in Table 5 fell into two different groups – one comprising that with DMSO, DMF and urea in which electrolyte–co-solvent interactions govern the value of $h_{\rm NE}$, and the other corresponding to

Table 3
Enthalpies of mixing of aqueous dimethyl sulfoxide with several electrolyte solutions

$m_{i,\mathrm{N}}/(\mathrm{mol\,kg^{-1}})$	$m_{i,\mathrm{E}}/(\mathrm{mol\,kg^{-1}})$	$m_{f,\mathrm{N}}/(\mathrm{mol\,kg^{-1}})$	$m_{f,\mathrm{E}}/(\mathrm{mol\,kg^{-1}})$	$\Delta_{\mathrm{mix}}H/(\mathrm{J\,kg^{-1}})$	$\Delta H^{*}/(\mathrm{J\,kg^{-1}})$
Me_4NBr					
0.1045	0.2202	0.0537	0.1071	35.4	−2.7
0.1045	0.3824	0.0542	0.1842	98.8	−4.1
0.2024	0.2202	0.1037	0.1074	28.2	−6.0
0.2024	0.3824	0.1046	0.1848	89.6	−9.4
0.2170	0.2169	0.1111	0.1058	24.0	−8.3
0.2196	0.1127	0.1128	0.0548	0.6	−3.8
0.2196	0.1372	0.1129	0.0667	5.1	−4.6
0.2196	0.2476	0.1136	0.1195	35.2	−7.4
0.2196	0.2565	0.1137	0.1238	38.3	−7.5
0.4596	0.2202	0.2334	0.1084	−1.3	−13.4
0.4596	0.3824	0.2355	0.1865	55.9	−21.0
0.6064	0.1127	0.3075	0.0556	−46.7	−10.0
0.6064	0.1372	0.2963	0.0702	−42.1	−10.6
0.6064	0.2476	0.3098	0.1211	−18.5	−19.9
0.6064	0.2565	0.2983	0.1303	−15.2	−19.7
0.8260	0.1127	0.4000	0.0581	−87.8	−11.5
0.8260	0.1372	0.4006	0.0707	−85.6	−14.6
0.8260	0.2169	0.4025	0.1112	−71.1	−22.4
0.8260	0.2474	0.4188	0.122	−65.8	−27.6
0.8260	0.2565	0.4034	0.1312	−62.5−	−27.4
Et_4NBr					
0.1045	0.0987	0.0535	0.0482	9.1	−0.6
0.1045	0.1891	0.0539	0.0916	33.9	−1.3
0.2024	0.0987	0.1033	0.0483	4.9	−0.9
0.2024	0.1891	0.1040	0.0919	29.5	−1.6
0.2196	0.1556	0.1306	0.0631	17.8	−1.6
0.4596	0.0987	0.2325	0.0488	−17.8	−1.5
0.4596	0.1891	0.2342	0.0927	6.6	−2.4
0.6064	0.1556	0.3568	0.0640	−23.2	−3
0.826	0.1556	0.4832	0.0646	−61.7	−3
Pr_4NBr					
0.1290	0.0489	0.0647	0.0244	1.2	2.2
0.1290	0.0923	0.0651	0.0457	6.6	4.1
0.1290	0.1892	0.0658	0.0927	17.3	8.4
0.3283	0.0489	0.1637	0.0245	−7.9	4.9
0.3283	0.0923	0.1645	0.0461	0.0	9.5
0.3283	0.1892	0.1663	0.0934	17.5	20.5
0.3283	0.1892	0.1663	0.0934	16.4	19.4
0.5804	0.0489	0.2869	0.0247	−33.5	8.8
0.5804	0.0923	0.2889	0.0464	−21.9	16.9
0.5804	0.1892	0.2916	0.0941	3.1	35.6
Bu_4NBr					
0.1110	0.0608	0.0570	0.0295	−0.3	5.4
0.1110	0.0867	0.0572	0.0420	−3.7	7.5
0.1110	0.0999	0.0574	0.0483	−6.4	8.7
0.1110	0.1394	0.0577	0.067	−19.4	12.3
0.1110	0.1811	0.0580	0.0865	−43.1	14.3
0.3007	0.0608	0.1536	0.0297	−3.3	12.6
0.3007	0.0867	0.1541	0.0423	−1.9	19.5

Table 3
(Continued)

$m_{i,\mathrm{N}}/(\mathrm{mol\,kg^{-1}})$	$m_{i,\mathrm{E}}/(\mathrm{mol\,kg^{-1}})$	$m_{f,\mathrm{N}}/(\mathrm{mol\,kg^{-1}})$	$m_{f,\mathrm{E}}/(\mathrm{mol\,kg^{-1}})$	$\Delta_{\mathrm{mix}}H/(\mathrm{J\,kg^{-1}})$	$\Delta H^{*}/(\mathrm{J\,kg^{-1}})$
0.3007	0.0999	0.1544	0.0486	−3.7	21.6
0.3007	0.1394	0.1553	0.0674	−11.4	30.5
0.3007	0.1811	0.1562	0.0871	−29.7	40.0
0.6348	0.0608	0.3207	0.0301	−29.7	26.4
0.6348	0.0867	0.3219	0.0427	−20.3	41.2
0.6348	0.0999	0.3225	0.0491	−17.8	47.6
0.6348	0.1394	0.3243	0.0682	−15.4	66.7
0.6348	0.1811	0.3261	0.0881	−22.9	85.1
$\mathrm{Pen_4NBr}$					
0.1110	0.0206	0.0561	0.0102	−0.6	2.9
0.1110	0.0456	0.0564	0.0224	−4.6	6.1
0.1110	0.1016	0.0569	0.0495	−41.4	12.8
0.1812	0.0445	0.0940	0.0214	−3.6	9.5
0.1812	0.0609	0.0919	0.0300	−8.7	12.6
0.1812	0.0815	0.0946	0.0390	−20.3	16.1
0.1812	0.1319	0.0953	0.0625	−75.3	23.6
0.1812	0.1342	0.0931	0.0653	−77.1	26.1
0.1812	0.1702	0.0936	0.0823	−139.4	35.7
0.3007	0.0206	0.1008	0.0137	−3.5	8.7
0.3007	0.0456	0.1517	0.0226	−6.6	14.4
0.3007	0.1016	0.1532	0.0498	−31.4	33.1
0.3516	0.0445	0.1813	0.0216	−6.9	18.4
0.3516	0.0609	0.1773	0.0302	−8.6	24.6
0.3516	0.0815	0.1825	0.0392	−16.4	31.8
0.3516	0.1319	0.1840	0.0629	−61.7	49.1
0.3516	0.1342	0.1796	0.0657	−63.3	51.8
0.3516	0.1702	0.1806	0.0828	−123.9	63.2
0.6223	0.0445	0.3181	0.0218	−27.4	31.3
0.6223	0.0609	0.3111	0.0305	−23.8	43.2
0.6223	0.0815	0.3202	0.0396	−24.8	57.3
0.6223	0.1319	0.3229	0.0635	−52.3	92.4
0.6223	0.1342	0.3150	0.0663	−53.5	95.5
0.6223	0.1702	0.3169	0.0835	−112.4	108.7
0.6348	0.0206	0.3154	0.0104	−39.5	14.3
0.6348	0.0456	0.3168	0.0228	−28.5	32.6
0.6348	0.1016	0.3199	0.0504	−31.9	72.7
CsI					
0.0878	0.0542	0.0458	0.0259	−1.8	−1.4
0.0878	0.0789	0.0456	0.0379	−0.6	−1.9
0.0878	0.0978	0.0459	0.0467	0.5	−2.7
0.0878	0.1632	0.0457	0.0782	9.2	−3.8
0.0878	0.2523	0.0459	0.1205	26.3	−8.2
0.0878	0.2972	0.0461	0.1412	41.6	−6.7
0.0878	0.4185	0.0460	0.1991	90.9	−4.2
0.0878	0.5877	0.0465	0.2767	175.0	−6.8
0.1183	0.0542	0.0619	0.0259	−3.2	−2.0
0.1183	0.0789	0.0614	0.0389	−2.3	−2.7
0.1183	0.0978	0.0619	0.0466	−1.1	−3.3
0.1183	0.1632	0.0615	0.0783	6.8	−5.4
0.1183	0.2523	0.0617	0.1207	24.4	−9.2
0.1183	0.2972	0.0623	0.1407	38.5	−8.9

Table 3
(Continued)

$m_{i,\mathrm{N}}/(\mathrm{mol\,kg^{-1}})$	$m_{i,\mathrm{E}}/(\mathrm{mol\,kg^{-1}})$	$m_{f,\mathrm{N}}/(\mathrm{mol\,kg^{-1}})$	$m_{f,\mathrm{E}}/(\mathrm{mol\,kg^{-1}})$	$\Delta_{\mathrm{mix}}H/(\mathrm{J\,kg^{-1}})$	$\Delta H^{*}/(\mathrm{J\,kg^{-1}})$
0.1183	0.4185	0.0620	0.1993	86.5	−7.7
0.1183	0.5877	0.0628	0.2758	170.8	−10.0
0.1812	0.2056	0.0912	0.1022	8.7	−10.1
0.1812	0.4842	0.0919	0.2386	101.5	−21.0
0.1812	0.7403	0.0926	0.3622	249.8	−28.9
0.3516	0.2056	0.1759	0.1027	−13.1	−19.4
0.3516	0.4842	0.1773	0.2400	70.2	−39.8
0.3516	0.7403	0.1786	0.3643	210.9	−55.3
0.6223	0.2056	0.3085	0.1037	−62.3	−33.3
0.6223	0.4842	0.3110	0.2422	5.4	−69.2
0.6223	0.7403	0.3133	0.3676	133.6	−97.2
0.8072	0.0542	0.4130	0.0265	−99.7	−13.3
0.8072	0.0789	0.4096	0.0389	−107.3	−22.5
0.8072	0.0978	0.4135	0.0477	−106.6	−23.7
0.8072	0.1632	0.4106	0.0802	−114.1	−41.1
0.8072	0.2523	0.4119	0.1236	−110.0	−58.4
0.8072	0.2972	0.4158	0.1441	−100.0	−62.3
0.8072	0.4185	0.4135	0.2041	−73.0	−82.1
0.8072	0.5877	0.4192	0.2825	−6.3	−102.3

Table 4
Values of coefficients for Eq. (4) and standard deviations s of the fit *

Electrolyte	$A_0/(\mathrm{J\,kg\,mol^{-2}})$	$A_1/(\mathrm{J\,kg^2\,mol^{-3}})$	$A_2/(\mathrm{J\,kg^2\,mol^{-3}})$	$s/(\mathrm{J\,kg^{-1}})$
$\mathrm{Me_4NBr}$	−657 (88)	123 (197)	884 (64)	0.95
$\mathrm{Et_4NBr}$	−234 (41)	334 (170)		0.57
$\mathrm{Pr_4NBr}$	1373 (74)	−439 (382)		0.55
$\mathrm{Bu_4NBr}$	3068 (136)	−490 (650)		1.18
$\mathrm{Pen_4NBr}$	5037 (432)	−775 (1518)	−8287 (6669)	2.16
CsI	−1202 (119)	−335 (372)	1588 (543)	4.01

* Numbers in parentheses are 95% confidence limits.

Table 5
Enthalpic pair interaction coefficients $h_{\mathrm{NE}}/$ $(\mathrm{J\,kg\,mol^{-2}})$ at 298.15 K [a]

	CsI	$\mathrm{Me_4NBr}$	$\mathrm{Et_4NBr}$	$\mathrm{Pr_4NBr}$	$\mathrm{Bu_4NBr}$	$\mathrm{Pen_4NBr}$	Ref.
DMSO	−601 (60)	−329 (44)	−117 (21)	687 (37)	1534 (68)	2518 (216)	this work
DMF	−455	−254	141	1129	2414	3424	[11,14]
Urea	−898	−765	−725	40	804	1569	[12,15]
TBA	688	960	1610	2840	4680	6560	[13]
TPA	1189	1174	1654	3712	6242	7928	[7]

[a] Numbers in parentheses are 95% confidence limits.

TBA and TPA for which the partial desolvation of solutes seems to be the leading factor in the coefficient value. The interaction of the tetramethylammonium bromide with the nonelectrolytes shown in Table 5 resembles more an alkali-metal chloride [9] than that corresponding to a hydrophobic electrolyte.

It is interesting to note that the enthalpic pair interaction coefficients for all non-electrolytes shown in Table 5 are positive with the highest terms of the tetraalkylammonium series and they increase with the increasing alkyl chain length of the electrolyte. The overlap of hydrophobic co-spheres reduces the strong

Table 6
Single-ion enthalpic pair interaction coefficients $h_{N,\mathrm{ion}}$/ (J kg mol^{-2}) at 298.15 K

	Cs^+	Br^-	I^-	Me_4N^+	Et_4N^+	Pr_4N^+	Bu_4N^+	Pen_4N^+
DMSO	365	−913	−966	584	796	1600	2447	3431
TPA	−1310	2349	2499	−1153	−672	1385	3916	5602

water–water interactions around hydrophobic solutes (hydrophobic hydration) giving rise to an endothermic contribution toward h_{NE}. Similar results are observed with urea, a hydrophilic structure-breaker solute [17], which also exerts a disruptive action on the hydrophobic hydration of tetraalkylammonium ions and contributes positively to h_{NE}.

In previous papers, single-ion enthalpic pair interaction coefficients, $h_{N,\mathrm{ion}}$, have been obtained for the interaction of TPA [7] and DMSO [9] with the bromide and caesium ion in water. An extra-thermodynamic assumption, namely tetraphenylphosphonium-tetraphenylborate (TPTB) reference electrolyte method was used. Table 6 shows single-ion values of pairwise coefficients, $h_{N,\mathrm{ion}}$, using those previously determined. DMSO exhibits different behavior from that observed for TPA in its interaction with Cs^+, Br^-, I^-, Me_4N^+ and Et_4N^+. Nevertheless, in both cases the contribution due to non-electrolyte–anion interaction is the factor which governs the sign of h_{NE} for the whole electrolyte. On the other hand, the interaction of both non-electrolytes with the highest terms of the tetraalkylammonium series yields positive single-ion enthalpic pair interaction coefficients. The sign of h_{NE} is mainly determined by non-electrolyte–R_4N^+ interaction.

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