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Enthalpy of interaction of several electrolytes with 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidone in water at 298.15 K

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Abstract

Enthalpies of mixing in water of 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidone (DMPU) with several alkali-metal halides (LiCl, NaCl, KCl, CsCl, KF, KBr, KI) and tetra-*n*-alkylammonium bromides, R_4NBr (R=Me, Et, Pr, Bu) have been determined by flow microcalorimetry at 298.15 K. The results were used to calculate enthalpic pair interaction coefficients, h_{NE}, of virial expansion of excess enthalpy. A decrease of the h_{NE} coefficient with anionic size in the potassium halides series is observed. In the tetra-*n*-alkylammonium bromides series, the coefficients are positive and they become more positive when the number of carbon atoms in the hydrocarbon chain is increased. A comparison to other systems obtained from the literature is reported. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Electrolytes; DMPU; Flow microcalorimetry; Mixing enthalpy; Enthalpic pairwise coefficients

1. Introduction

Enthalpic pair interaction coefficients, h_{NE}, might supply information about the energy arising when two solvated solutes interact in solution [1]. Most studies based on these coefficients are representative of uncharged solutes and numerous papers have been published about them. Qualitative and quantitative predictions of these coefficients have been made with variable success by means of the Savage-Wood group additivity method (SWAG) [2]. A similar procedure has also been tested for non-electrolyte–electrolyte systems [3–5]. The results indicate that the group contribution to h_{NE} is positive for the interaction between two apolar CH_2 groups and between an apolar CH_2 group and NaCl, KCl or NaI, and negative for these salts with OH or CO groups.

In recent papers, Castronuovo et al. [6–9] have correlated the influence of the number and position of hydrophilic groups on the strength of hydrophobic interactions in water by means of enthalpic pair interaction coefficients, using several series of non-electrolytes and amino acids. It is possible that similar correlations are also operative in the interactions of certain non-electrolytes with determined electrolytes. However, at present, the available number of h_{NE} coefficients relative to the non-electrolyte-salt interaction is scarce, and therefore, the possible correlations are limited to a few systems.

The aim of our studies is to obtain an extensive set of pairwise interaction coefficients concerning non-electrolyte-salt interactions in water, which would enable us to correlate the influence among various functional groups, bearing on both an

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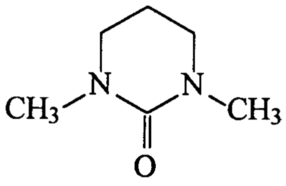
uncharged solute and an electrolyte. Recently, we reported the enthalpy of interaction of 2-methyl-2-butanol [10] and dimethyl sulphoxide [11,12] with several electrolytes in water by means of enthalpic pair interaction coefficients h_{NE}. As part of this systematic study we have chosen as the non-electrolyte 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (DMPU), a *N,N′*-dialkylated cyclic urea, which is a dipolar aprotic solvent, with a large dipole moment (4.23 D) and a high dielectric constant (36.12) [13]. DMPU is used as solvent in conductivity measurements of electrolytes [14] and as cosolvent in electrochemical studies in water [15]. Several physical properties [16] at 298.15 K for their aqueous mixtures as well as excess molar volumes and molar refractions over the entire mole fraction range at 10 K intervals from 278.15 to 318.15 K were determined [17].



(DMPU)

In the present paper, enthalpies of mixing of 1:1 electrolytes and DMPU in water are reported and discussed in terms of enthalpic pair interactions coefficients, h_{NE}. A brief comparison to other systems is also presented.

2. Experimental

2.1. Reagents

Alkali-metal halides (LICl, NaCl, KCl, CsCl, KF, KBr, KI) from Merck (GR) were oven-dried for two days at 393.15 K. Tetra-*n*-alkylammonium bromides, R_4NBr (R=Me, Et, Pr, Bu), from Fluka or Merck of the best quality available were purified and checked as before [18]. All salts were kept in a vacuum desiccator with P_2O_5. 1,3-Dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidone (DMPU) (Fluka, puriss.; stated purity from GC>99 mol%, H_2O<0.03%) was kept over a thermally activated 0.3 nm molecular sieve and under N_2 atmosphere. Since DMPU is hygroscopic and readily picks up moisture during operations of solutions preparation, pure DMPU aliquots were taken out with a dry syringe from the stock and they were quickly injected into closed vials with silicone septa in order to mix and weigh them with weighed aliquots of degassed water (Millipore, $k \approx 10^{-6}$ S cm^{-1}).

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 [10,18].

3. Results

The excess enthalpy $H^{\mathrm{ex}}(m_{\mathrm{N}},m_{\mathrm{E}})$ 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 [19]:

$$\begin{aligned} H^{\mathrm{ex}}(m_{\mathrm{N}},m_{\mathrm{E}}) &= H(m_{\mathrm{N}},m_{\mathrm{E}}) - H_{\mathrm{w}}^{0} - H_{\mathrm{N}}^{\infty} m_{\mathrm{N}} \\ &\quad - H_{\mathrm{E}}^{\infty} m_{\mathrm{E}} + h_{\mathrm{NN}} m_{\mathrm{N}}^{2} + 2h_{\mathrm{NE}} m_{\mathrm{N}} m_{\mathrm{E}} + h_{\mathrm{EE}} m_{\mathrm{E}}^{2} \\ &\quad + h_{\mathrm{NNN}} m_{\mathrm{N}}^{3} + 3h_{\mathrm{NNE}} m_{\mathrm{N}}^{2} m_{\mathrm{E}} + 3h_{\mathrm{NEE}} m_{\mathrm{N}} m_{\mathrm{E}}^{2} \\ &\quad + h_{\mathrm{EEE}} m_{\mathrm{E}}^{3} \ldots \end{aligned} \tag{1}$$

where $H(m_{\mathrm{N}},m_{\mathrm{E}})$ 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

$$\begin{aligned} \Delta H^{*} &= \Delta_{\mathrm{mix}} H_{\mathrm{N,E}} - \Delta_{\mathrm{dil}} H_{\mathrm{N}} - \Delta_{\mathrm{dil}} H_{\mathrm{E}} \\ &= H^{\mathrm{ex}}(m_{\mathrm{N}},m_{\mathrm{E}}) - H^{\mathrm{ex}}(m_{\mathrm{N}}) - H^{\mathrm{ex}}(m_{\mathrm{E}}) \end{aligned} \tag{2}$$

and combining Eqs. (1) and (2)

$$\begin{aligned} \Delta H^{*} &= 2h_{\mathrm{NE}} m_{\mathrm{N}} m_{\mathrm{E}} + 3h_{\mathrm{NNE}} m_{\mathrm{N}}^{2} m_{\mathrm{E}} \\ &\quad + 3h_{\mathrm{NEE}} m_{\mathrm{N}} m_{\mathrm{E}}^{2} + \ldots \end{aligned} \tag{3}$$

Table 1
Enthalpies of dilution of DMPU in water at 298.15 K

m_i (mol kg^{-1})	m_f (mol kg^{-1})	$\Delta_{dil} H_{m,N}$ (J mol^{-1})	m_i (mol kg^{-1})	m_f (mol kg^{-1})	$\Delta_{dil} H_{m,N}$ (J mol^{-1})
0.1020	0.0509	−93.9	0.4822	0.2410	−405.6
0.1140	0.0582	−103.6	0.6002	0.2912	−485.0
0.2019	0.0960	−189.3	0.6117	0.2981	−493.2
0.2019	0.0986	−183.8	0.6202	0.2878	−544.1
0.2019	0.0995	−179.3	0.6202	0.2957	−530.7
0.2030	0.1007	−175.2	0.8001	0.3674	−676.6
0.2180	0.1080	−188.0	0.8001	0.3776	−662.4
0.2180	0.1086	−186.9	0.8001	0.3811	−645.5
0.3169	0.1598	−276.8	0.8389	0.4016	−649.0
0.3481	0.1641	−318.3	0.9472	0.4532	−717.5
0.3481	0.1685	−311.0	1.0024	0.4546	−826.8
0.3481	0.1701	−302.0	1.0024	0.4594	−804.6
0.4080	0.2001	−342.0	1.0024	0.4678	−816.5
0.4551	0.2130	−410.8	1.1995	0.5386	−949.2
0.4551	0.2132	−409.1	1.1995	0.5538	−939.3
0.4551	0.2210	−390.0			

which can be expressed in a general form as

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

The experimental results obtained for molar enthalpies of dilution of the non-electrolyte DMPU from an initial molality m_i to a final molality m_f, $\Delta_{dil} H_m(m_i \rightarrow m_f)$, are given in Table 1. $\Delta_{dil}H_m$ is related to enthalpic pair interaction coefficients, h_{NN} (homotactic interactions), by the following equation:

$$\Delta_{dil}H_m(m_i \rightarrow m_f) = h_{NN}(m_f - m_i) + h_{NNN}(m_f^2 - m_i^2) + \ldots \tag{5}$$

The coefficients $h_{NN}=1805\pm38$ (J kg mol^{-2}) and $h_{NNN}=-212\pm28$ (J kg^2 mol^{-3}), along with the standard deviation of the fit ($s=5.3$ J mol^{-1}), were calculated using a least-squares analysis. The molar enthalpy of dilution for the electrolytes was taken from the literature data [18,20]. A compilation of the experimental enthalpies of mixing are shown in Table 2. Coefficients A_0, A_1 and A_2 from Eq. (4) obtained by an analysis of non-linear least squares regression are reported in Table 3. The coefficients $A_1=3h_{NNE}$ and $A_2=3h_{NEE}$ are complicated quantities [21] corresponding to the triple interaction of the anion, the cation and the non-electrolyte, therefore we will focus our attention on the h_{NE}.

4. Discussion

The h_{NE} coefficients for the electrolyte-DMPU interaction in water are shown in Table 4. They are all positive with the exception of the KBr and KI-DMPU systems. In the alkali-metal halide series, enthalpic pair interaction coefficients decrease when the ion size increases, both in potassium halide series and alkali-metal chloride series, excepting LiCl-DMPU interaction. On the other hand, the R_4NBr-DMPU interaction is characterized by enthalpic pairwise coefficients that become progressively more positive when the length of the alkyl chain is increased.

In the water-rich region strong solute–water and solute–solute interactions occur and the value and sign of h_{NE} is the result of the balance between the tendencies solutes have to interact in solution as well as their solvation characteristics [21,22]. Although we are only considering enthalpic pairwise coefficients due to the complexity of triplet and higher order terms, in the case of one of the solutes being an electrolyte, an added difficulty arises as a consequence of anion and cation simultaneous participation. Since enthalpic pairwise coefficients are rigorously additive ($h_{NE} = h_{N,M^+} + h_{N,A^-}$), in order to examine the ionic contributions to h_{NE} it is necessary to split them by means of an extra-thermodynamic method. Thus, the reference

Table 2
Enthalpies of mixing of aqueous DMPU with several electrolyte solutions at 298.15 K

$m_{\mathrm{i,N}}$ (mol kg^{-1})	$m_{\mathrm{i,E}}$ (mol kg^{-1})	$m_{\mathrm{f,N}}$ (mol kg^{-1})	$m_{\mathrm{f,E}}$ (mol kg^{-1})	$\Delta_{\mathrm{mix}}H$ (J kg^{-1})	ΔH^{*} (J kg^{-1})
LiCl					
0.1020	0.5175	0.0509	0.2595	−63.5	2.2
0.1020	0.7275	0.0510	0.3640	−102.6	4.5
0.1020	1.0268	0.0511	0.5111	−175.4	7.5
0.2030	0.5175	0.1013	0.2594	−75.8	3.1
0.2030	0.7275	0.1015	0.3639	−114.2	6.2
0.2030	0.8969	0.1008	0.4515	−148.4	12.1
0.2030	1.0268	0.1017	0.5121	−185.3	10.8
0.2148	0.6174	0.1067	0.3108	−86.3	13.2
0.3973	0.6174	0.1953	0.3140	−130.8	14.6
0.4080	0.5175	0.2012	0.2623	−125.4	5.0
0.4080	0.7275	0.2016	0.3680	−163.4	8.3
0.4080	0.8969	0.2003	0.4567	−196.9	14.7
0.4080	1.0268	0.2022	0.5180	−233.8	13.7
0.6002	0.2523	0.2896	0.1306	−159.2	7.2
0.6002	0.5175	0.2928	0.2651	−197.2	8.2
0.6002	0.7275	0.2934	0.3719	−234.3	12.5
0.6002	0.8969	0.2914	0.4614	−267.0	19.6
0.6002	1.0268	0.2942	0.5234	−303.81	18.5
0.6142	0.6174	0.2982	0.3176	−211.4	18.8
0.8389	0.5175	0.4012	0.2700	−311.2	18.5
0.8389	0.7275	0.4021	0.3788	−345.7	25.2
NaCl					
0.1029	0.5300	0.0511	0.2666	36.3	6.0
0.2019	0.3007	0.0996	0.1524	−7.8	6.0
0.2019	0.5300	0.0998	0.2681	28.5	11.2
0.2050	0.1991	0.1010	0.1010	−16.8	3.1
0.2050	0.5999	0.1013	0.3033	45.2	14.0
0.2180	0.5941	0.0985	0.3257	42.9	14.4
0.3481	0.3007	0.1706	0.1533	−38.2	9.0
0.3481	0.5300	0.1710	0.2697	2.0	18.0
0.5199	0.1989	0.2515	0.1027	−105.3	6.7
0.5199	0.6009	0.2525	0.3091	−29.6	30.9
0.5199	0.6009	0.2525	0.3091	−30.4	30.0
0.6117	0.5941	0.2698	0.3321	−68.7	30.9
0.6202	0.3007	0.2993	0.1556	−134.2	15.7
0.6202	0.5300	0.3000	0.2737	−87.8	30.8
0.9472	0.5941	0.4095	0.3373	−244.1	39.1
0.9472	1.0326	0.4511	0.5408	−47.8	106.8
0.9472	1.0326	0.4511	0.5408	−47.4	107.2
KCl					
0.2030	0.2034	0.1013	0.1019	−17.0	2.4
0.2030	0.3996	0.1016	0.1997	0.9	6.1
0.2030	0.5846	0.1018	0.2913	32.8	9.4
0.2030	1.0689	0.1026	0.5289	176.4	22.4
0.2148	0.2080	0.1068	0.1046	−19.0	2.4
0.2148	0.5896	0.1074	0.2948	31.1	8.7
0.2148	0.9693	0.1080	0.4821	140.7	19.4
0.3973	0.2080	0.1955	0.1056	−63.2	4.1
0.3973	0.5896	0.1966	0.2979	−8.2	15.3
0.3973	0.9693	0.1976	0.4871	106.5	31.0
0.3973	0.9693	0.1976	0.4871	107.7	32.2

Table 2 (*Continued*)

$m_{\mathrm{i,N}}$ (mol kg^{-1})	$m_{\mathrm{i,E}}$ (mol kg^{-1})	$m_{\mathrm{f,N}}$ (mol kg^{-1})	$m_{\mathrm{f,E}}$ (mol kg^{-1})	$\Delta_{\mathrm{mix}}H$ (J kg^{-1})	ΔH^* (J kg^{-1})
0.4080	0.2034	0.2012	0.1031	−67.2	3.7
0.4080	0.3996	0.2018	0.2019	−46.4	10.3
0.4080	0.5846	0.2024	0.2947	−11.7	16.3
0.4080	1.0689	0.2038	0.5350	140.8	38.2
0.6002	0.2034	0.2929	0.1041	−141.4	4.7
0.6002	0.3996	0.2937	0.2041	−117.4	14.5
0.6002	0.5846	0.2945	0.2977	−80.0	23.2
0.6002	1.0689	0.2966	0.5407	80.6	53.2
0.6142	0.2080	0.2986	0.1069	−146.2	6.3
0.6142	0.5896	0.3002	0.3014	−84.1	24.4
0.6142	0.5896	0.3002	0.3014	−83.8	24.7
0.6142	0.9693	0.3019	0.4929	38.88	48.3
CsCl					
0.4080	0.1143	0.2005	0.0581	−65.4	3.4
0.4080	0.2945	0.2012	0.1492	−46.0	5.0
0.4080	0.5266	0.2022	0.2656	5.2	5.0
0.4080	0.8187	0.2034	0.4106	100.7	−3.0
0.6002	0.1143	0.2918	0.0587	−136.9	7.2
0.6002	0.2945	0.2929	0.1508	−114.8	11.4
0.6002	0.5266	0.2943	0.2684	−58.4	16.7
0.6002	0.8187	0.2960	0.4149	41.4	13.0
0.8389	0.1143	0.4028	0.0594	−256.2	12.6
0.8389	0.2945	0.4043	0.1526	−227.7	23.1
0.8389	0.5266	0.4063	0.2716	−161.3	38.4
0.8389	0.8187	0.4107	0.4179	−65.1	31.2
KF					
0.1140	0.0968	0.0565	0.0489	−7.2	3.4
0.1140	0.1664	0.0568	0.0835	−9.5	5.0
0.1140	0.2884	0.0569	0.1446	−10.5	9.5
0.1140	0.3179	0.0565	0.1603	−9.9	11.2
0.1140	0.5200	0.0569	0.2604	−8.9	17.7
0.1140	0.5358	0.0566	0.2699	−7.7	19.1
0.1140	0.6754	0.0574	0.3351	−4.6	25.1
0.1140	0.6933	0.0580	0.3404	−2.9	27.3
0.3169	0.1664	0.1561	0.0844	−34.3	17.1
0.3169	0.2884	0.1562	0.1462	−27.3	29.5
0.3169	0.2884	0.1556	0.1468	−26.2	30.6
0.3169	0.5200	0.1564	0.2634	−8.8	54.4
0.3169	0.5200	0.1558	0.2644	−7.8	55.4
0.3169	0.5358	0.1555	0.2730	−5.9	57.5
0.3169	0.6754	0.1578	0.3391	6.5	72.9
0.3169	0.6933	0.1556	0.3529	10.2	76.7
0.4822	0.1664	0.2353	0.0852	−76.2	28.1
0.4822	0.2884	0.2355	0.1476	−62.0	47.8
0.4822	0.2884	0.2345	0.1481	−60.6	49.1
0.4822	0.5200	0.2358	0.2658	−30.4	85.7
0.4822	0.5200	0.2348	0.2668	−27.9	88.1
0.4822	0.6754	0.2350	0.3462	−1.9	117.1
0.7079	0.2884	0.3399	0.1499	−137.0	74.1
0.7079	0.5200	0.3404	0.2700	−83.9	133.3
0.7079	0.6754	0.3407	0.3504	−44.1	176.1

Table 2 (*Continued*)

$m_{\mathrm{i,N}}$ (mol kg^{-1})	$m_{\mathrm{i,E}}$ (mol kg^{-1})	$m_{\mathrm{f,N}}$ (mol kg^{-1})	$m_{\mathrm{f,E}}$ (mol kg^{-1})	$\Delta_{\mathrm{mix}}H$ (J kg^{-1})	ΔH^{*} (J kg^{-1})
KBr					
0.1140	0.0982	0.0562	0.0498	−8.6	−1.6
0.1140	0.2882	0.0564	0.1456	1.6	−2.1
0.1140	0.5252	0.0567	0.2641	39.2	−6.0
0.1140	0.7524	0.0569	0.3772	110.8	−4.7
0.3169	0.0982	0.1544	0.0504	−48.1	−4.1
0.3169	0.2882	0.1549	0.1473	−41.5	−8.2
0.3169	0.5252	0.1557	0.2672	−6.4	−14.6
0.3169	0.7524	0.1572	0.3815	64.2	−14.4
0.4822	0.0982	0.2327	0.0508	−104.7	−7.5
0.4822	0.2882	0.2335	0.1486	−99.7	−13.2
0.4822	0.5252	0.2347	0.2696	−67.3	−22.3
0.4822	0.7524	0.2355	0.3850	2.2	−23.4
0.4822	0.0982	0.2340	0.0505	−104.3	−7.1
0.4822	0.2882	0.2348	0.1479	−99.9	−13.4
0.4822	0.5252	0.2359	0.2682	−66.7	−21.7
0.4822	0.7524	0.2367	0.3830	2.4	−23.1
0.7079	0.0982	0.3392	0.0512	−210.7	−11.5
0.7079	0.2882	0.3403	0.1496	−208.8	−20.3
0.7079	0.5252	0.3421	0.2714	−178.7	−31.8
0.7079	0.7524	0.3432	0.3876	−107.9	−31.5
KI					
0.1107	0.1025	0.0540	0.0525	−9.0	−3.7
0.1107	0.3107	0.0542	0.1585	8.1	−10.1
0.1107	0.4915	0.0557	0.2443	48.3	−15.5
0.1107	0.6719	0.0559	0.3325	110.3	−20.6
0.3080	0.1025	0.1484	0.0531	−49.8	−9.5
0.3080	0.3107	0.1491	0.1603	−41.9	−25.2
0.3080	0.4915	0.1532	0.2470	−8.0	−36.9
0.3080	0.6719	0.1538	0.3363	48.6	−47.4
0.4961	0.1025	0.2364	0.0537	−115.5	−14.7
0.4961	0.3107	0.2376	0.1619	−116.7	−39.5
0.4961	0.4915	0.2442	0.2496	−89.6	−58.1
0.4961	0.6719	0.2452	0.3398	−37.7	−73.2
0.7160	0.1025	0.3370	0.0543	−222.2	−21.3
0.7160	0.3107	0.3387	0.1637	−235.8	−58.4
0.7160	0.4915	0.3401	0.2580	−214.8	−83.2
0.7160	0.6719	0.3416	0.3513	−168.8	−104.1
Me_4NBr					
0.2148	0.0300	0.1072	0.0150	−18.6	1.1
0.21458	0.0495	0.1082	0.0246	−17.8	0.7
0.2148	0.0614	0.1068	0.0309	−15.9	1.3
0.2148	0.1207	0.1072	0.0605	−6.0	1.7
0.2148	0.2435	0.1079	0.1212	24.6	−2.7
0.2319	0.1334	0.1170	0.0661	−6.3	1.9
0.2319	0.1818	0.1173	0.0898	4.9	0.6
0.2319	0.2896	0.1180	0.1422	36.4	−4.9
0.3973	0.0300	0.1963	0.0152	−62.3	3.7
0.3973	0.0495	0.1982	0.0248	−61.8	2.9
0.3973	0.0614	0.1955	0.0312	−59.5	4.1
0.3973	0.1207	0.1962	0.0611	−50.5	3.5
0.4516	0.1334	0.2251	0.0669	−63.9	5.8

Table 2 (*Continued*)

$m_{i,N}$ (mol kg^{-1})	$m_{i,E}$ (mol kg^{-1})	$m_{f,N}$ (mol kg^{-1})	$m_{f,E}$ (mol kg^{-1})	$\Delta_{mix}H$ (J kg^{-1})	ΔH^* (J kg^{-1})
0.4516	0.1818	0.2257	0.0909	−53.0	4.2
0.4516	0.2896	0.2271	0.1440	−24.4	−4.1
0.6142	0.0495	0.3027	0.0251	−142.9	7.4
0.6142	0.0614	0.2986	0.0315	−139.0	10.1
0.6142	0.1207	0.2997	0.0618	−130.0	9.6
0.6142	0.2435	0.3018	0.1239	−96.5	8.1
0.9174	0.1334	0.4458	0.0686	−277.0	25.6
0.9174	0.1818	0.4471	0.0932	−262.6	27.6
0.9174	0.2896	0.4498	0.1476	−236.9	16.4
Et$_4$NBr					
0.2385	0.0583	0.1274	0.0272	−15.1	5.6
0.2385	0.1272	0.1205	0.0630	3.4	9.7
0.2385	0.2065	0.1289	0.0949	32.4	14.5
0.3500	0.0666	0.1731	0.0337	−36.8	9.9
0.3500	0.1140	0.1738	0.0574	−23.0	13.9
0.3500	0.1852	0.1749	0.0927	4.7	21.1
0.4957	0.0666	0.2432	0.0339	−79.4	16.3
0.4957	0.1140	0.2442	0.0578	−63.7	22.3
0.4957	0.1852	0.2457	0.0934	−33.3	32.2
0.4978	0.0583	0.2624	0.0276	−83.8	13.5
0.4978	0.1272	0.2638	0.0598	−60.2	22.6
0.4978	0.2065	0.2655	0.0964	−24.4	34.2
0.9222	0.0583	0.4757	0.0282	−285.3	29.6
0.9222	0.1272	0.4783	0.0612	−249.0	51.2
0.9222	0.2065	0.4814	0.0987	−207.4	68.4
0.9343	0.0666	0.4475	0.0347	−281.6	40.9
0.9343	0.1140	0.4494	0.0592	−260.7	52.0
0.9343	0.1852	0.4521	0.0956	−222.5	69.9
Pr$_4$NBr					
0.2319	0.1198	0.1151	0.0603	16.6	32.7
0.2319	0.1820	0.1160	0.0910	38.0	50.3
0.2319	0.2668	0.1171	0.1321	60.9	77.9
0.2385	0.1212	0.1191	0.0607	16.6	33.8
0.4516	0.1198	0.2215	0.0611	−14.7	62.6
0.4516	0.1820	0.2231	0.0921	22.0	95.5
0.4516	0.2668	0.2252	0.1337	66.5	144.8
0.9174	0.1820	0.4417	0.0944	−117.4	188.8
0.9174	0.2668	0.4460	0.1371	−34.1	277.2
0.9222	0.1911	0.4470	0.0985	−109.3	199.7
Bu$_4$NBr					
0.3500	0.0604	0.1710	0.0309	−5.3	50.4
0.3500	0.1232	0.1726	0.0624	26.9	101.1
0.3500	0.1743	0.1739	0.0877	38.0	141.1
0.4957	0.0604	0.2402	0.0311	−33.9	70.9
0.4957	0.1232	0.2424	0.0629	18.3	141.6
0.4957	0.1743	0.2443	0.0884	45.2	197.5
0.9343	0.0604	0.4418	0.0318	−200.0	131.4
0.9343	0.1232	0.4460	0.0644	−90.9	259.1
0.9343	0.1743	0.4494	0.0905	−20.2	358.9

Table 3
Values of coefficients for Eq. (4) and standard deviations s of the fit[a]

Electrolyte	A_0 (J kg mol^{-1})	A_1 (J kg^2 mol^{-3})	A_2 (J kg^2 mol^{-3})	s (J kg^{-1})
LiCl	240 (66)	−292 (287)		3.90
NaCl	325 (54)	−398 (145)	517 (147)	2.71
KCl	216 (29)	−245 (110)	369 (55)	1.16
CsCl	103 (88)	1128 (257)	−881 (161)	2.36
KF	1121 (64)	813 (224)	346 (217)	1.65
KBr	−550 (99)	−203 (357)	950 (270)	1.87
KI	−1345 (72)	542 (239)	905 (237)	1.88
Me_4NBr	517 (189)	2085 (612)	−8062 (1603)	1.34
Et_4NBr	1755 (287)	1639 (647)	−9381 (3222)	3.61
Pr_4NBr	4634 (187)	−1030 (349)	3209 (1666)	2.28
Bu_4NBr	9983 (139)	−1153 (322)	−6538 (1583)	0.96

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

electrolyte assumption, namely Ph_4PBPh_4 (TPTB), was tried. This assumption assumes that the enthalpic pairwise coefficients for DMPU-Ph_4P^+ ion and DMPU-BPh_4^- ion are equal. Unfortunately, we observed that the aqueous solutions formed after the mixing process, Ph_4PCl+DMPU and $NaPh_4B$+DMPU, were both cloudy at the outlet of the microcalorimeter. Possibly a salting-out effect exerted by the above electrolytes on the DMPU is the cause, and consequently, that convention had to be rejected. Nevertheless, Booji and Somsen [23] noticed the validity of the CsI assumption to describe transfer enthalpies of single-ions in DMF+water mixtures. That assumption is based on the convention: $h_{\mathrm{DMPU,Cs^+}} = h_{\mathrm{DMPU,I^-}}$, obtained in our case via: $h_{\mathrm{DMPU,CsI}} = h_{\mathrm{DMPU,CsCl}} + h_{\mathrm{DMPU,KI}} - h_{\mathrm{DMPU,KCl}}$. The application of this method to the data reported in Table 4 yields the results shown in Table 5. Exothermic coefficients for the interaction between alkali-metal ions and DMPU are observed. Possibly as result of interactions of electrostatic origin (ion-dipole interactions), because interactions with apolar residues of the DMPU are endothermic. In the case of halide ions, enthalpic coefficients become increasingly less positive with the increase of halide size, even a negative value for DMPU-I^- interaction is observed.

Table 4
Enthalpic pair interaction coefficients, h_{NE} (J kg mol^{-2}), for DMPU and various electrolytes in water at 298.15 K[a]

LiCl	120 (33)
NaCl	163 (27)
KCl	108 (15)
CsCl	52 (44)
KF	561 (32)
KCl	108 (15)
KBr	−275 (50)
KI	−673 (36)
Me_4NBr	259 (95)
Et_4NBr	878 (144)
Pr_4NBr	2317 (94)
Bu_4NBr	4992 (70)

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

In the case of tetraalkylammonium ions, enthalpic single-ion pairwise coefficients are positive and follow a reverse order to that observed for both alkali-metal ions and halide ions, that is, they become increasingly endothermic as the size of the alkyl groups on the R_4N^+ ion increases. For these hydrophobic ions, the apolar groups govern their interaction with water (hydrophobic hydration) and the overlap of their cospheres with those of a molecule such as DMPU, which exhibits various apolar groups, gives rise to structural changes in both solutes (loss of hydrophobic hydration), leading to positive values of $h_{\mathrm{DMPU,R_4N^+}}$, and consequently, more endothermic with the size of the cation R_4N^+.

It is interesting to compare the results of the interaction of several non-electrolytes with electrolytes in water in terms of enthalpic pairwise coefficients. A set of h_{NE} coefficients collected from the literature are listed in Table 6. We have only chosen those uncharged solute-electrolyte systems where the number of electrolytes participating was considerable although the acetone-salt system is also included with

Table 5
Enthalpic single-ion pair coefficients, $h_{\mathrm{N,ion}}$ (J kg mol^{-2}), for the interaction between DMPU and several ions in water at 298.15 K

Li^+	Na^+	K^+	$Cs^+(=I^-)$	F^-	Cl^-	Br^-	Me_4N^+	Et_4N^+	Pr_4N^+	Bu_4N^+
−296	−253	−308	−365	869	416	33	226	845	2284	4959

the aim of comparison. Some comments can be made about the value and sign of the coefficients. We can clearly distinguished two well differentiated groups, one corresponding to the interaction with alkali-metal halides and the other with R_4NBr electrolytes.

In the first one, a strong dependence of enthalpic pairwise coefficients on the position, nature and number of functional groups or apolar residues in the non-electrolyte is observed. So, the influence of an apolar residue position is clearly reflected for the systems containing NMA and DMF, two isomeric solutes, which show endothermic and exothermic coefficients, respectively, in their interaction with alkali-metal chlorides, with the exception of that for the NMA-CsCl system. On the other hand, the value of h_{NE} resulting in the interaction of NaCl with acetone and DMSO, reveals the importance of the functional group nature. In contrast, the interaction of alkali-metal halides with DMSO and DMF, two solutes similar in some aspects, such as dipole moment and polarizability, takes place with exothermic coefficients, though more negative in the case of DMSO. The number of hydrophobic and hydrophilic groups on the same non-electrolyte and the balance between them seems to be a determinant factor in the value of enthalpic pairwise coefficients. This fact is made clear when comparing the interaction of urea, DMSO and DMPU with alkali-metal chlorides. The negative enthalpic pairwise coefficients observed for the urea, increase in the case of DMSO, even though negative, and they acquire fully endothermic values with DMPU.

The interaction of potassium halides with the non-electrolytes presented in Table 6 is noteworthy. For alkanols, the enthalpic pairwise coefficients become more positive in the following order: F<Cl<Br<I. Nevertheless, this sequence is the reverse in the case of the remaining non-electrolytes, where a progressive

Table 6
Enthalpic pair interaction coefficients, $h_{\mathrm{N,E}}$ (J kg mol^{-2}), for various non-electrolyte–electrolyte systems in water at 298.15 K

Non-electrolyte	F[a]	NMA[a]	DMF[a]	DMSO[b]	Acetone[c]	Urea[d]	DMPU[e]	TBA[f]	TPA[g]
LiCl	−293	46	−202	−260		−462	120	557	557
NaCl	−452	266	−79	−152	48	−531	163	972	972
KCl	−451	189	−168	−205	−132	−545	108	960	960
CsCl	−580	−231	−299	−351		−718	52	826	826
KF	−213	424	323	276		−727	561	855	855
KBr	−474	175	−329	−365	−212	−675	−275	1110	1173
KI	−604	115	−364	−578		−727	−673	1366	1323
Me_4NBr	−234		−254	−329		−765	259	960	10174
Et_4NBr			141	−117		−725	878	1610	1654
Pr_4NBr			1129	687		40	2317	2840	3712
Bu_4NBr	1176		2414	1534		804	4992	4680	6242
Pen_4NBr			3424	2518		1569		6560	7928

Abbreviations: F, formamide; NMA, *N*−methylacetamide; DMF, *N*,*N*−dimethylformamide; DMSO, dimethyl sulphoxide; TBA, tert−butyl alcohol; TPA, 2-methyl-2-butanol.

[a] From Ref. [24,25].

[b] From Ref. [11,12].

[c] From Ref. [26].

[d] From Ref. [12,27].

[e] This work.

[f] From Ref. [28].

[g] From Ref. [10].

decrease in the value of coefficients with the increasing halide size is shown.

In the second group, the h_{NE} coefficients for the interaction between R_4NBr and all non-electrolytes increase upon increasing the alkyl chain length of the cation R_4N^+, showing a clear dependence on the non-electrolyte nature. Therefore, the coefficients are initially negative for hydrophylic non-electrolytes, such as urea, formamide, DMSO and DMF, and even the exothermicity of the h_{NE} values extends to the interaction of Et_4NBr with urea and DMSO. In a certain sense, the interaction of Me_4NBr with the more hydrophylic solutes resembles more that of KBr or KI than that corresponding to a net hydrophobic cation. On the other hand, in the case of the fully hydrophobic non-electrolytes, such as DMPU, TBA and TPA, the enthalpic pairwise coefficients are largely positive with all tetraalkylammonium bromides. It is a consequence of the cosphere overlap of two hydrophobic solutes that leads to an attractive interaction with endothermic enthalpic pairwise coefficients.

According to the above, the h_{NE} coefficients, resulting from the non-electrolyte-R_4NBr interaction in water, can be used to establish a tentative hydrophobicity order for the non-electrolytes displayed in Table 6: urea<formamide<DMSO<DMF<DMPU<TBA<TPA. As we pointed out above, the enthalpic pairwise coefficient gives a measure of the interaction between two solvated solutes.

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