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THERMOCHEMICAL PROPERTIES OF NaI SOLUTIONS IN WATER–2-METHOXYETHANOL AND WATER–2-ETHOXYETHANOL MIXTURES. THE TEMPERATURE DEPENDENCE OF ENTHALPIC PAIR INTERACTION COEFFICIENTS IN WATER SOLUTION

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ABSTRACT

Enthalpies of solution of NaI in mixtures of water with 2-methoxyethanol and 2-ethoxyethanol (known as cellosolves) at 298.15, 308.15 and 318.15 K were measured. The enthalpies of solution in all investigated systems pass through a maximum in the water-rich region. This extremum is lower and flatter than that observed in water–unsubstituted alkanol mixtures. The enthalpic pair interaction coefficients $h_{xy}\{(Na^+ + I^-)\text{-cellosolve}\}$ were calculated and compared with appropriate data for $(Na^+ + I^-)$–alkanol pairs. The group additivity concept was used for the analysis of h_{xy} coefficients calculated at 308.15 K, and the influence of the temperature change on the group contributions was discussed.

INTRODUCTION

Enthalpic pair interaction coefficients are frequently used for analysis of interactions that occur in two- or three-component systems. These coefficients are regarded as a measure of the heat effect (i.e., enthalpy of interaction) when two solute particles approach each other. Owing to the difficulties in theoretical calculations [1–3], attention is focused on the interpretation of the enthalpic interaction coefficients determined experimentally on the basis of dilution enthalpies (interaction between similar solutes) and enthalpies of mixing or of dissolution, leading to three-component systems (interaction between dissimilar solutes) [1,4,5]. As is known, the group additivity concept developed by Savage and Wood [6] appeared to be very useful in analysis of the interaction coefficients as well as for predicting unknown values in aqueous non-electrolyte solutions. It has recently also been found that the enthalpic pair interaction coefficients h_{xy} for (Na^+I^-)–non-electrolyte and (Na^+Cl^-)–non-electrolyte pairs at 298.15 K could be presented as a sum of group contributions [7,8]. It is thus of

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interest to examine the influence of the temperature change on the group contributions to h_{xy} for electrolyte–non-electrolyte pairs.

In a previous paper of one of the present authors (H.P.), the enthalpic interaction coefficients in aqueous systems containing (Na^+I^-) as a solute and an alkanol, formamide or DMF as a cosolute at several temperatures were determined [9]. However, for calculation of the group contributions to h_{xy}, using the same model of interactions as in the papers mentioned earlier [7,8] it was necessary to perform additional experiments with the cosolutes containing an ether oxygen atom in their molecule. 2-Methoxyethanol and 2-ethoxyethanol, known as "cellosolves" were selected for this purpose, and the dissolution enthalpies of NaI in the mixtures of both mentioned alkoxyalkanols with water were measured at 298.15, 308.15 and 318.15 K.

EXPERIMENTAL

Sodium iodide (Merck suprapur) was dried under vacuum for several days at 335 K. 2-Methoxyethanol (Merck p.a.) and 2-ethoxyethanol (Loba Chemie) were dried using molecular sieves of the 4A type, and fractionally distilled. The water was deionized and twice distilled. The water–organic mixtures were prepared by weight. Measurements of the enthalpies of solution were performed with the use of an "isoperibol" type calorimeter. The glass calorimetric vessel, capacity of ca. 100 cm^3 equipped with a calibration heater, the thermistor and stirrer-ampoule holder was tightly closed with a "Teflon" lock. A thin-walled glass ampoule with the sample of the salt to be dissolved was attached to the ampoule holder and crushed against the bottom of the calorimetric vessel during the experiment. The thermistor (10 kohm) was connected to a Wheatstone bridge. The voltage of the unbalanced bridge was measured using a Keithley K-148 nanovoltmeter connected to a digital voltmeter "Mera-Tronik" V 540 type. The overall temperature sensitivity of the calorimeter was found to be ca. 5×10^{-5} K. The ampoule breaking-heat effect in the reaction vessel was negligible. The calorimeter was in an hermetically closed brass jacket with a capacity of about 1 dm^3, within a water thermostat. The temperature stability of the thermostat was better than 1×10^{-3} K. The error involved in the measurements was estimated to be $\pm 0.5\%$.

RESULTS AND DISCUSSION

Enthalpy of solution

The measurements of the heat of solution of NaI in aqueous mixtures of 2-methoxyethanol were performed within the whole composition range of the mixture. The investigations using mixtures of 2-ethoxyethanol with water were limited to the composition range covering 0–20 mol% of the cellosolve, due to experimental difficulties (the NaI solutions in the mixtures containing more than 20 mol% of the cellosolve were unstable). The measurements were made at 298.15, 308.15 and 318.15 K *. The results of the measurements are represented in Tables 1 and 2. The measured enthalpies of the NaI solution were next extrapolated to infinite dilution by means of the method presented in detail in the Criss and Cobble paper [10]. The molal solution enthalpies of NaI at infinite dilution $\Delta H_s^{\ominus}$ in the investigated mixtures are listed in Table 3 and represented as a function of the mixed solvent composition in Figs. 1 and 2. In both systems investigated in this study, i.e. NaI–water–2-methoxyethanol and NaI–water–2-ethoxyethanol the enthalpy of solution of NaI ($\Delta H_s^{\ominus}$) passes through a maximum at low cellosolve content and next decreases rapidly along with the increasing of the organic component concentration. A similar extremum of $\Delta H_s^{\ominus}$ has been observed for different electrolytes, polar and neutral non-electrolytes in all alkanol–water mixtures investigated so far.

These maxima have been attributed to the stabilizing effect of hydrocarbon moieties of alkanol on the three-dimensional structure of liquid water. The position of the maxima, their height and sharpness depend on the structure-forming propensity of the examined alkanol. Generally, the maximum position shifts towards a lower alkanol content when the size of the hydrocarbon group increases. However, it seems to be not quite true for the systems investigated here. The maximum $\Delta H_s^{\ominus}$ of NaI in the mixtures of water with 2-methoxyethanol appears at ca. 2 mol% of cellosolve, while in the systems containing bigger molecules of 2-ethoxyethanol it corresponds to ca. 4 mol%. The position of the maximum of NaI in 2-methoxyethanol–water mixtures agrees very well with that for NaCl solutions investigated earlier [8]. On the other hand, the enthalpy and entropy of transfer of *p*-nitroaniline (*p*-NA) from water to water–methylcellosolve mixtures calculated from solubility data pass through a maximum at a composition of about 11 mol% of cosolvent [11]. However when this organic base is replaced by the ionic *p*-nitroaniline hydrochloride, its free enthalpy of transfer shows a maximum at 2.58 mol%, that is close to the $\Delta H_s^{\ominus}$ position for NaI and NaCl. Unfortunately, the authors of the mentioned paper did not determine the transfer enthalpy of *p*-NA · HCl. The difference in behaviour of both investigated substances is explained by a different mechanism of solvation. According to the authors of the cited paper "... hydrophobism of the base is presumably the largest single factor causing an increased affinity of *p*-nitroaniline towards the organic cosolvent", and "... it may be that halide

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* Preliminary results concerning the mixtures of 2-methoxyethanol with water at 298.15 K are presented in ref. 7.

ions (in p-NA · HCl) are more strongly stabilized by one solvent component than by the other". To confirm these opinions additional data are necessary.

The maxima of $\Delta H_s^{\ominus}$ of NaI in both systems investigated in this work are

TABLE 1

Enthalpies of solution ΔH_s of NaI in water–2-methoxyethanol mixtures

$m \times 10^3$ (mol kg^{-1})	$-\Delta H_s$ (kJ mol^{-1})	$m \times 10^3$ (mol kg^{-1})	$-\Delta H_s$ (kJ mol^{-1})	$m \times 10^3$ (mol kg^{-1})	$-\Delta H_s$ (kJ mol^{-1})
$T = 298.15$ K					
x [a] $= 0.02$		$x = 0.05$		$x = 0.10$	
5.46	7.120	11.14	7.518	8.23	10.410
9.51	7.210	13.52	7.465	10.69	10.320
13.09	7.070	16.49	7.515	11.89	10.340
21.69	7.067	21.08	7.470	17.10	10.270
$x = 0.15$		$x = 0.30$		$x = 0.60$	
7.41	14.07	3.81	24.45	2.62	40.31
10.54	13.95	4.86	24.40	3.54	40.30
12.67	13.89	5.62	24.32	3.96	40.24
17.56	13.77	10.61	24.17	4.86	39.95
$x = 0.90$		$x = 1.00$			
1.75	52.21	2.40	53.84		
2.10	51.96	2.90	53.31		
3.52	51.22	3.16	53.24		
4.61	50.83	3.08	53.22		
$T = 308.15$ K					
$x = 0.02$		$x = 0.05$		$x = 0.10$	
6.37	8.305	6.20	8.895	7.71	11.475
7.02	8.280	6.99	8.845	8.19	11.465
8.67	8.182	7.65	8.880	10.61	11.280
12.25	7.840	10.44	8.825		
$x = 0.15$		$x = 0.30$		$x = 0.60$	
3.21	14.81	4.15	25.27	2.19	40.91
4.80	14.71	4.40	25.17	3.24	40.43
5.21	14.76	5.31	25.13	3.81	39.99
9.57	14.74	10.10	25.07	4.18	39.92
$x = 0.90$		$x = 1.00$			
2.13	52.52	1.39	54.99		
2.22	52.40	1.78	54.66		
3.10	52.12	2.25	53.82		
3.68	51.66	2.28	53.49		
		3.99	53.28		
$T = 318.15$ K					
$x = 0.02$		$x = 0.05$		$x = 0.10$	
6.45	9.48	6.00	10.14	6.11	12.56
14.35	9.38	6.81	10.04	7.53	12.57
19.81	9.35	15.04	10.01	13.48	12.45
23.40	9.30	20.40	9.97	15.81	12.50
37.60	9.24	33.61	9.90	24.60	12.45

TABLE 1 (continued)

$m \times 10^3$ (mol kg^{-1})	$-\Delta H_s$ (kJ mol^{-1})	$m \times 10^3$ (mol kg^{-1})	$-\Delta H_s$ (kJ mol^{-1})	$m \times 10^3$ (mol kg^{-1})	$-\Delta H_s$ (kJ mol^{-1})
$x = 0.20$		$x = 0.50$		$x = 0.70$	
3.30	19.28	4.82	36.14	5.50	44.74
7.41	19.12	5.01	36.10	11.96	43.98
9.12	19.11	10.73	35.44	19.42	43.38
15.01	18.90	11.64	35.36	27.81	42.86
24.04	18.66	18.02	35.06		
$x = 0.90$		$x = 1.00$			
4.12	52.68	1.82	55.17		
5.24	52.24	2.63	54.83		
9.30	51.64	5.50	54.66		
11.22	51.20	11.62	53.58		
15.04	51.02	19.08	51.98		

[a] Mole fraction of organic cosolvent.

flat and shorter than those in water–propanol and water–tert-butanol mixtures [7,12] in which the organic components have the same number of carbon atoms as the respective cellosolves. As is known, alkoxyalkanols can be assumed to be ethylene glycol derivatives in which one of the hydroxyl protons is replaced by an alkyl group. Many experimental data indicate that ethylene glycol in the mixtures with water behaves as the water-structure breaker [13]. Therefore, it can be supposed that the $-OCH_2CH_2OH$ group in the cellosolve molecule disorders the structure of water and only the terminal alkyl group exhibits structure-promoting properties. As a result of this competition, only a small stabilizing effect is observed, particularly in 2-methoxyethanol. This effect decreases significantly as the temperature increases.

The enthalpy of solution of NaI in pure 2-methoxyethanol is highly exothermic (-56.60 kJ mol^{-1} at 298.15 K) and close to the value of $\Delta H_s^{\ominus}$ for NaI in such low structured solvents as DMF (-55.0 kJ mol^{-1} [14]) or DMSO (-48.24 kJ mol^{-1} [15]), but quite different from the dissolution enthalpy of NaI in unsubstituted alkanols [7]. This is probably due to the possibility of the formation of an internal hydrogen bond, and to the steric configuration of the cellosolve molecule, which hinders formation of a more complex structure in the pure liquid [16].

The thermal effect of NaI dissolution in all investigated mixtures becomes more exothermic as the temperature increases, with the shape of $\Delta H_s^{\ominus} = f(x)$ isotherms remaining essentially unchanged. The only effect that is observed is lowering and flattening of the $\Delta H_s^{\ominus}$ maximum. This is a kind of behaviour that was also observed in NaI–water–alkanol systems [9].

TABLE 2

Enthalpies of solution ΔH_s of NaI in water–2-ethoxyethanol mixtures

$m \times 10^3$ (mol kg^{-1})	$-\Delta H_s$ (kJ mol^{-1})	$m \times 10^3$ (mol kg^{-1})	$-\Delta H_s$ (kJ mol^{-1})	$m \times 10^3$ (mol kg^{-1})	$-\Delta H_s$ (kJ mol^{-1})
$T = 298.15$ K					
x[a] $= 0.02$		$x = 0.04$		$x = 0.06$	
7.56	6.690	4.62	6.590	4.81	7.110
8.83	6.665	7.34	6.525	5.94	7.090
17.41	6.610	11.81	6.515	12.56	6.990
19.65	6.590	15.15	6.475	15.32	6.920
28.39	6.545	20.18	6.460	18.26	6.855
$x = 0.08$		$x = 0.10$		$x = 0.12$	
7.42	8.185	5.90	9.335	7.50	10.60
7.54	8.180	7.41	9.305	8.20	10.55
13.81	8.075	7.70	9.295	15.61	10.45
15.30	8.052	14.90	9.170	21.30	10.39
24.58	7.951	15.91	9.135	25.10	10.24
$x = 0.15$		$x = 0.20$			
5.70	12.55	4.07	15.55		
6.33	12.52	6.23	15.44		
6.81	12.50	8.41	15.35		
12.65	12.40	19.70	14.98		
13.54	12.35	29.05	14.75		
$T = 308.15$ K					
$x = 0.02$		$x = 0.04$		$x = 0.06$	
6.23	8.060	6.83	7.915	4.91	8.390
7.41	8.040	9.25	7.875	6.35	8.355
14.90	7.945	13.76	7.805	9.28	8.300
23.62	7.855	19.54	7.740	14.53	8.235
$x = 0.10$		$x = 0.15$		$x = 0.20$	
5.74	10.44	4.88	13.50	4.35	16.36
7.83	10.39	7.80	13.41	6.71	16.26
10.77	10.33	9.12	13.37	8.38	16.21
14.23	10.25	16.01	13.22	9.66	16.16
16.37	10.18	24.00	13.05	16.25	15.92
$T = 318.15$ K					
$x = 0.02$		$x = 0.04$		$x = 0.06$	
7.39	9.370	6.81	9.245	8.55	9.570
10.10	9.310	7.61	9.220	17.44	9.425
15.61	9.250	13.70	9.115	26.88	9.310
16.32	9.245	15.02	9.085	35.60	9.215
21.12	9.160	21.80	8.765		
$x = 0.08$		$x = 0.10$		$x = 0.12$	
7.51	10.35	8.20	11.46	7.62	12.55
7.91	10.35	8.61	11.46	15.60	12.35
16.43	10.19	16.50	11.28	17.80	12.31
26.10	10.03	18.01	11.26	25.31	12.18
28.14	10.03	26.03	10.87		

TABLE 2 (continued)

$m \times 10^3$ (mol kg^{-1})	$-\Delta H_s$ (kJ mol^{-1})	$m \times 10^3$ (mol kg^{-1})	$-\Delta H_s$ (kJ mol^{-1})	$m \times 10^3$ (mol kg^{-1})	$-\Delta H_s$ (kJ mol^{-1})
$x = 0.15$		$x = 0.20$			
5.35	14.23	6.07	16.75		
7.90	14.14	8.01	16.64		
10.31	14.06	9.73	16.55		
16.72	13.92	14.50	16.34		

[a] Mole fraction of organic cosolvent.

Enthalpic pair interaction coefficients

Enthalpic pair interaction coefficients $h_{xy}\{(Na^+ + I^-)$–alkoxyethanol$\}$ in water were determined from the dissolution enthalpies of NaI in water–cellosolve mixtures, measured in this work. In order to calculate the h_{xy} coefficients, the method described in the previous paper was used [8]. The molal enthalpy of solution of NaI at an infinite dilution in the examined mixtures in the water-rich region was presented as a function

$$\Delta H_s^\ominus\ (\text{NaI in W + Y}) = \Delta H_s^\ominus\ (\text{NaI in W}) + bX_y + cX_y^2 \qquad (1)$$

TABLE 3

Molal enthalpy of solution $\Delta H_s^\ominus$ of NaI at infinite dilution in aqueous mixtures of 2-methoxyethanol and 2-ethoxyethanol

x [a]	$-\Delta H_s^\ominus$ (kJ mol^{-1})					
	Water–2-methoxyethanol			Water–2-ethoxyethanol		
	298.15 K	308.15 K	318.15 K	298.15	308.15 K	318.15 K
0	7.575	8.595	9.805	7.575	8.595	9.805
0.02	7.345	8.515	9.760	6.915	8.275	9.640
0.04	–	–	–	6.775	8.170	9.540
0.05	7.845	9.145	10.44	–	–	–
0.06	–	–	–	7.320	8.630	9.945
0.08	–	–	–	8.470	–	10.72
0.10	10.73	11.78	12.95	9.600	10.75	11.88
0.12	–	–	–	10.94	–	12.98
0.15	14.35	15.17	–	12.87	13.85	14.64
0.20	–	–	19.72	16.02	16.75	17.50
0.30	24.90	25.79	–			
0.50	–	–	37.55			
0.60	41.34	42.26	–			
0.70	–	–	47.69			
0.90	54.15	55.06	56.16			
1.00	56.60	57.40	58.20			

[a] Mole fraction of organic cosolvent.

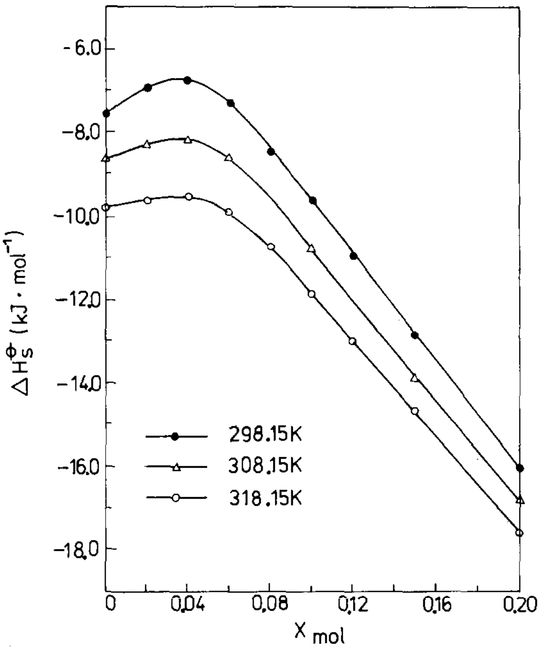

Fig. 1. Enthalpies of solution of NaI in mixtures of water with 2-methoxyethanol vs. mole fraction of the non-aqueous component.

where $\Delta H_s^\ominus$ (NaI in W) is the molal enthalpy of solution of NaI in pure water, X_y is the molar fraction of cosolvent y, b and c are coefficients that can be determined by the least-squares method. Parameter b in equation (2) representing the limiting slope of function $\Delta H_s^\ominus$ (NaI in W + Y) is related to the McMillan–Mayer interaction coefficient h_{xy} as follows

$$b = 2\nu h_{xy}\left(\partial m_y/\partial X_y\right)_{X_y\to 0} \qquad (2)$$

where ν is the number of ions. Denoting the molecular weight of water by M_w we obtain for dilute solutions

$$\left(\partial m_y/\partial X_y\right)_{X_y\to 0} = 1/M_w \qquad (3)$$

where the molality of the cosolvent in water m_y is in mol kg^{-1}, M_w in kg mol^{-1}. Hence

$$h_{xy} = b \cdot M_w/2\nu \qquad (4)$$

For the sake of simplicity, the electrolyte is not separated into its ionic components: furthermore until now there has been no method good enough for partition of the electrolyte transfer enthalpy in a mixed solvent into ionic contributions. As a result, the pair interaction enthalpies, defined as above, constitute for the systems containing an electrolyte of the 1–1 type a half of

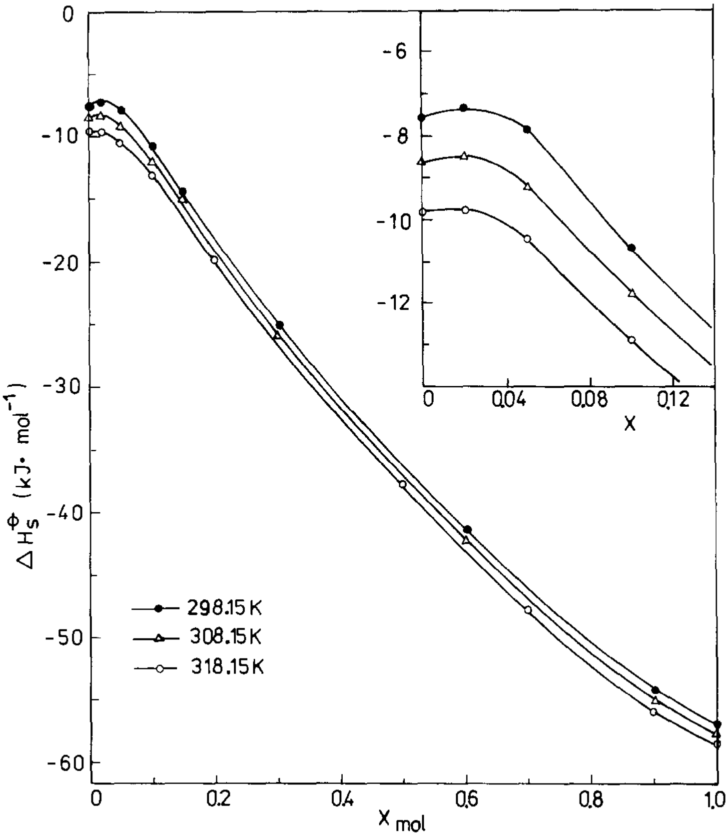

Fig. 2. Enthalpies of solution of NaI in mixtures of water with 2-ethoxyethanol vs. mole fraction of the non-aqueous component.

the sum of the enthalpic effect of the interaction between a molecule of a given non-electrolyte (Y) and cation (C^+) and anion (A^-).

$$h_{xy} = (h/2)\{(C^+ + A^-)-Y\} = (1/2)\{h(C^+-Y) + h(A^--Y)\} \tag{5}$$

The pairwise enthalpic interaction coefficients for ($Na^+ + I^-$)-2-methoxyethanol and ($Na^+ + I^-$)-2-ethoxyethanol in water are reported in Table 4. The calculated h_{xy} values are positive just as the h_{xy} coefficients for all electrolyte–alkanol pairs in water investigated thus far, but they are significantly lower than those for the pairs containing an appropriate unsubstituted alkanol. The positive h_{xy} values can be considered a result of the destruction by the ions of the hydrophobic cosphere around the hydrocarbon moieties in the alkanol molecule. The introduction of the ether oxygen atom into the alkanol molecule brings large, negative contributions in h_{xy}. This indicates the possibility of a strong electrostatic interaction between the ion and the ether group. The effect of temperature on the h_{xy}

TABLE 4

Enthalpic and heat capacity pair interaction coefficients for $(Na^+ + I^-)$–2-methoxyethanol and $(Na^+ + I^-)$–2-ethoxyethanol pairs at several temperatures

Cosolute	h_{xy} (J kg mol^{-2})			C_{xy} (J kg K^{-1} mol^{-2})
	298.15 K	308.15 K	318.15 K	
2-Methoxyethanol	97	46	10	−4.4
2-Ethoxyethanol	223	130	30	−10.0

values can be presented in quantitative terms by means of the heat capacity of pair interaction C_{xy} defined by the equation

$$h_{xy}(T_2) = h_{xy}(T_1) + C_{xy}(T_2 - T_1) \qquad (6)$$

The calculated mean values of C_{xy} for $(Na^+ + I^-)$–cellosolves in the temperature range 298.15–318.15 K are also given in Table 4. The values of C_{xy} presented are negative, as are values of C_{xy} for $(Na^+ + I^-)$–alkanol pairs examined earlier. The interaction coefficients determined in this work, together with appropriate data from the literature [9], allow us to calculate the group contributions to h_{xy} at 308.15 K, just as was done at 298.15 K in the previous paper [8]. It makes possible an analysis of the influence of the temperature on the group contributions. Using the model described in the works already mentioned [7,8], three interaction types in the system analyzed can be distinguished here: $\{(Na^+ + I^-)–CH_2\}$, $\{(Na^+ + I^-)–OH\}$, and $\{(Na^+ + I^-)–O\}$. In this case h_{xy} may be presented as a sum

$$h_{xy} = \sum^{i} n_{yi} h_{yi} \qquad (7)$$

where n_{yi} is the number of group "i" in molecule Y, and h_{yi} is a characteristic contribution to h_{xy} of an average ionic interaction with a selected "i" type group in molecule Y. Following other authors it is accepted that the CH_3 group corresponds to 1.5 CH_2 while CH and C correspond to 0.5 CH_2[6,17]. Applying the method of multiple linear regression to solve eqn. (7) for h_{xy} values for non-electrolytes that have in their molecule the specified groups (methanol, ethanol, propanol, isopropanol, s-butanol, t-butanol, 2-methoxyethanol and 2-ethoxyethanol), the group contributions at 308.15, collected in Table 5, were calculated. Despite the simplicity of the model its application to the discussed systems yields fully satisfactory results. The slope and the regression coefficient for the function

$$h_{xy}\ (\text{experimental}) = \alpha h_{xy}\ (\text{calculated}) + \beta \qquad (8)$$

are equal 1.000 ± 0.051 and 0.9929, respectively. Table 5 also shows analogous group contributions to $(Na^+ + I^-)$–nonelectrolyte pairs at 298.15 K as presented in the previous paper [8]. As can be seen from these data, the

TABLE 5

Functional group interaction parameters h_{yi} and C_{yi} with their standard deviations in water

Functional group combinations "i"	h_{yi} (J kg mol^{-2})		C_{yi} (J kg K^{-1} mol^{-2})
	298.15 K [a]	308.15 K	
$\{(Na^+ + I^-)–CH_2\}$	$+145 \pm 11$	$+127 \pm 10$	-1.8
$\{(Na^+ + I^-)–OH\}$	-48 ± 36	-71 ± 35	-2.4
$\{(Na^+ + I^-)–O\}$	-394 ± 34	-350 ± 24	$+4.4$
Standard error of fit	40.7	28.5	
Regression coefficient r^2	0.9928	0.9922	

[a] Ref. 9.

interaction of the electrolyte with the CH_2 group is positive, giving a leading contribution to positive h_{xy} values in all the analyzed systems. The interaction between the ions and the –OH as well as the –O group are negative, with the $(Na^+ + I^-)$–O contribution more exothermic than that of $(Na^+ + I^-)$–OH. It is worthwhile to mention that the presented group contributions have the same signs and similar relative magnitude as appropriate group contributions in non-electrolyte–non-electrolyte pairs in which instead of an electrolyte there is a polar group, like –OH, –CONH or –COOH [18]. It confirms the earlier observation that from the point of view of the enthalpic pair interaction coefficients, inorganic electrolytes behave like highly polar non-electrolytes [19].

A comparison of h_{yi} group contributions related to two different temperatures indicates that the interaction between the ions and the CH_2 group becomes less endothermic when the temperature grows. It means that the destruction of the hydrophobic cage is less energy consuming at a higher temperature. This conclusion is in agreement with the observation of many authors. Among others, De Visser and Somsen have found that the enthalpic effect of hydrophobic hydration Hb(W) is reduced with the rise of temperature, and that this decrease may be attributed to the loosening of the water hydrogen bonds [20].

The interaction contribution of $(Na^+ + I^-)$–O is less exothermic at higher temperatures, probably as a result of the weakening of electrostatic interactions because of larger thermal motions of the interacting species.

The influence of the temperature on the $(Na^+ + I^-)$–OH interaction seems to be more complex. The increase of the exothermic contribution might be a result of the summation of several opposite effects: the loosening of water hydrogen bonds and the weakening of the ion–OH electrostatic interactions, and for these reasons, a greater possibility of cellosolve–water mixed associates formation.

The h_{yi} values at 298.15 and 308.15 K allow the determination of the C_{yi} function that illustrates the effect of the temperature on enthalpic group contributions in the quantitative form as discussed above. The calculated mean values of C_{yi} for interaction of a selected group with $(Na^+ + I^-)$ are also represented in Table 5. Having collected some observations concerning the pair interaction coefficients for electrolyte–non-electrolyte systems in water, it seems interesting to check how the same systems behave in non-aqueous media. Appropriate studies are already under way.

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