

## ENTHALPIC PAIR INTERACTION COEFFICIENTS OF NaI–NON-ELECTROLYTE MIXTURES IN DMF SOLUTION AT 25 °C PART 2. APPLICATION OF THE GROUP ADDITIVITY CONCEPT TO INTERACTIONS IN DMF SOLUTIONS \*

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### ABSTRACT

Dissolution enthalpies of NaI in mixtures of 2-methoxyethanol, ethylene glycol and 1,4-dioxane with *N,N*-dimethylformamide have been measured. From these data the enthalpic pair interaction coefficients,  $h_{xy}$  ( $\text{Na}^+\text{I}^-$ -non-electrolyte) in DMF have been determined and analysed together with the appropriate data concerning other  $\text{Na}^+\text{I}^-$ -non-electrolyte pairs in DMF. The Wood–Savage group additivity model appeared to be applicable to correlation of  $h_{xy}$  coefficients in DMF solution.

### INTRODUCTION

Studies on McMillan–Mayer pair interaction coefficients have been carried out in our laboratory for several years [1–7]. We have found that in aqueous systems the enthalpic pair interaction coefficients  $h_{xy}$  of an electrolyte (NaI or NaCl) with different non-electrolytes are correlated with the molecular polarizability ( $\alpha$ ) of the non-electrolyte, with its acidity parameter (e.g. Kosover  $Z$  parameter), as well as with the heat capacity of hydration of the non-electrolytes [1–3]. The above findings allow us to conclude that in aqueous solutions the effect of changes in water structure in the solute solvation shells is the main cause of variation in the  $h_{xy}$  coefficients under discussion, and only within a group of solutes which exhibit a similar hydration mechanism the ion–dipole (or dipole–dipole) type interactions make the main contribution to the variation in  $h_{xy}$  values [1,3,6]. Moreover, the  $h_{xy}$  coefficients in these systems could be presented as a sum of group contributions [1,3,4]. Recently, our studies have been extended to non-aqueous systems [5–7]. The analysis of  $h_{xy}$  coefficients for  $\text{Na}^+\text{I}^-$ -non-electrolyte pairs in *N,N*-dimethylformamide solutions has shown that the changes in solvent structure in the vicinity of dissolved particles exert a smaller influence on the  $h_{xy}$  values in DMF than in water.

\* For part 1 see H. Piekarski, *J. Chem. Soc., Faraday Trans. 1*, 84 (1988) 591.

Moreover, a direct interaction between the ion and the non-electrolyte, leading to the replacement of DMF molecules by the non-electrolyte in the ionic solvation shell, has an effect on the  $h_{xy}$  values in DMF that is comparable with structural effects and sometimes even predominant [5,6]. It then seemed advisable to check whether the Savage and Wood group interaction concept [8] also could be applied for correlation of  $\text{Na}^+\text{I}^-$ -non-electrolyte enthalpic interaction coefficients in DMF solution. In order to increase the number of data for this analysis, some additional  $h_{xy}$  values for  $\text{Na}^+\text{I}^-$ -non-electrolyte interactions have been determined by measuring the enthalpies of solution of NaI in mixtures of DMF with 2-methoxyethanol (2-MeEtOH), ethylene glycol and 1,4-dioxane.

## EXPERIMENTAL

Sodium iodide (Merck, p.a.), 2-methoxyethanol (Merck, p.a.) and *N,N*-dimethylformamide (Fluka) were purified and dried using the procedure described in previous papers [1,6]. Ethylene glycol (Fluka) and 1,4-dioxane (BDH) were purified by means of methods described in the literature [9].

The mixtures were prepared by weight in a dry-box, using freshly distilled DMF.

Measurements of dissolution enthalpies were performed in the calorimetric system described in a previous paper [4]. The electrolyte concentration was within  $2 \times 10^{-3}$  to  $2 \times 10^{-2}$  mol kg<sup>-1</sup> in each mixture investigated. The error involved in the measurements was estimated to be  $\pm 0.5\%$ .

## RESULTS AND DISCUSSION

The measured enthalpies of solution  $\Delta H_s$  of NaI in mixtures of DMF with 2-methoxyethanol, ethylene glycol and 1,4-dioxane, listed in Table 1, were extrapolated to infinite dilution by means of the method presented in detail by Criss and Cobble [10] in order to obtain the standard dissolution enthalpies  $\Delta H_s^\ominus$  of NaI in the mixtures examined. From these data, the molar enthalpies of transfer of NaI from pure DMF to DMF-non-electrolyte mixtures  $\Delta H_{tr}^\ominus$  were calculated:

$$H_{tr}^\ominus (\text{DMF} \rightarrow \text{DMF} + \text{Y}) = \Delta H_s^\ominus (\text{in DMF} + \text{Y}) - \Delta H_s^\ominus (\text{in DMF}) \quad (1)$$

The standard dissolution enthalpy  $\Delta H_s^\ominus$  of NaI in pure DMF determined in this work is equal to  $-55.31$  kJ mol<sup>-1</sup> and is in reasonable agreement with the appropriate literature data ( $-55.0 \pm 0.3$  kJ mol<sup>-1</sup> [11],  $-56.82$  kJ mol<sup>-1</sup> [12]). The molar enthalpies of transfer of NaI from DMF to mixtures of DMF with 2-methoxyethanol, 1,4-dioxane and ethylene glycol obtained are presented in Table 2.

In order to calculate the  $h_{xy}$  coefficients, the method described in detail in previous papers was employed [3,6]. The values of  $h_{xy}$  obtained in this

TABLE 1

Molar enthalpies of solution of NaI in DMF–non-electrolyte mixtures at 25°C

2-Methoxyethanol		Ethylene glycol		1,4-Dioxane	
<i>m</i> (mol kg <sup>-1</sup> )	$\Delta H_s$ (J mol <sup>-1</sup> )	<i>m</i> (mol kg <sup>-1</sup> )	$\Delta H_s$ (J mol <sup>-1</sup> )	<i>m</i> (mol kg <sup>-1</sup> )	$\Delta H_s$ (J mol <sup>-1</sup> )
$\omega_y^a = 0.05$					
0.002347	-54285	0.002365	-54180	0.002040	-54720
0.003498	-54225	0.002717	-54170	0.002244	-54610
0.006637	-54050	0.004808	-53850	0.003568	-54620
0.008065	-53950	0.005574	-53860	0.004791	-54590
$\omega_y^a = 0.10$					
0.002465	-53685	0.002231	-52850	0.002122	-54395
0.003177	-53640	0.002772	-52840	0.002537	-54335
0.005140	-53595	0.004152	-52605	0.004212	-54355
0.007322	-53310	0.004403	-52675	0.004554	-54250
$\omega_y^a = 0.15$					
0.002155	-53350	0.002329	-52020	0.001828	-53970
0.002747	-53305	0.002704	-51840	0.002771	-53850
0.005165	-53140	0.003270	-51730	0.004148	-53700
0.005366	-52780	0.006976	-51565	0.005500	-53595
$\omega_y^a = 0.20$					
0.002888	-53055	0.002622	-50590	0.001960	-53400
0.004721	-52890	0.003103	-50625	0.002234	-53385
0.005630	-52805	0.004726	-50575	0.003394	-53200
0.007051	-52720	0.006230	-50480	0.004687	-53010

<sup>a</sup>  $\omega_y$ , Mass fraction of the non-electrolyte.

way are presented in Table 3. This table also gives the  $h_{xy}$  data for other non-electrolytes not investigated in this work. The uncertainties in the  $h_{xy}$  values are estimated to be ca. 10%. In a similar way as in our previous papers [1–4,6] the  $h_{xy}$  coefficients constitute, in each case, the “mean ionic” pair interaction coefficients; more precisely, in the case of 1:1 electrolytes they correspond to half of the enthalpic effect of the interaction between the

TABLE 2

Molar enthalpy of transfer of NaI from pure DMF to mixtures of DMF with non-electrolytes at 25°C

Wt.% of cosolvent	$\Delta H_s^\ominus$ (J mol <sup>-1</sup> )		
	2-Methoxyethanol	Ethylene glycol	1,4-Dioxane
5	585	960	225
10	1090	2175	520
15	1465	3095	795
20	1675	4330	1130

TABLE 3

Enthalpic pair interaction coefficients  $h_{xy}$  ( $\text{J kg mol}^{-2}$ ) for  $\text{Na}^+ \text{I}^-$ -non-electrolyte pairs in DMF

Non-electrolyte	$h_{xy}$	Non-electrolyte	$h_{xy}$
Water	780	Ethylene glycol	310
Methanol	230	<i>N</i> -Methylformamide	380
Propanol	430	Tetrahydrofuran	250
Isopropanol	480	1,4-Dioxane	95
Isobutanol	500	Acetonitrile	120
2-Methoxyethanol	255	Dimethylsulphoxide	135
Acetone	210		

molecule of a given non-electrolyte Y and the cation  $\text{C}^+$  and anion  $\text{A}^-$ :

$$h_{xy} = \frac{1}{2} [h_{xy}(\text{C}^+ \text{A}^-) - Y] = \frac{1}{2} (h_{y\text{C}^+} + h_{y\text{A}^-}) \quad (2)$$

As may be seen from Table 3, the calculated  $h_{xy}$  values are positive—just as are the  $h_{xy}$  coefficients for all NaI–non-electrolyte pairs in DMF investigated thus far. The positive values of  $h_{xy}$  for  $\text{Na}^+ \text{I}^-$ -ethylene glycol probably reflect the replacement of a DMF molecule by an ethylene glycol molecule in the solvation region of the electrolyte in this system, similarly as found for other NaI–non-electrolyte pairs in DMF presented in a previous paper [6]. The endothermic enthalpy of transfer of NaI from pure DMF to ethylene glycol,  $\Delta H_{\text{tr}}^{\ominus} = 24.27 \text{ kJ mol}^{-1}$ , seems to confirm this opinion. A different behaviour is observed for the NaI–2-methoxyethanol pair. In this case, the  $h_{xy}$  value is positive despite a slightly negative enthalpy of transfer of NaI from pure DMF to 2-MeEtOH, ( $\Delta H_{\text{tr}}^{\ominus} = -0.20 \text{ kJ mol}^{-1}$ ) [4]. A lack of dissolution enthalpy data for NaI in pure 1,4-dioxane makes the analysis of the  $h_{xy}$  value for the NaI–dioxane pair in a similar way impossible. To find out which of the possible interactions is responsible for such behaviour of the latter systems, it is necessary to analyse the pairwise interaction parameters in greater detail. The use of the Savage and Wood group interaction concept [8] enables this to be done.

Based on the model presented in previous papers [1,3,4], three types of interaction in the system analysed can be distinguished here: ( $\text{Na}^+ \text{I}^- - \text{CH}_2$ ), ( $\text{Na}^+ \text{I}^- - \text{OH}$ ) and ( $\text{Na}^+ \text{I}^- - \text{O}$ ). In this case,  $h_{xy}$  may be presented as a sum:

$$h_{xy} = \sum_i n_{yi} h_{yi} \quad (3)$$

where  $n_{yi}$  is the number of groups  $i$  in a molecule Y (a non-electrolyte molecule) and  $h_{yi}$  is a characteristic contribution to  $h_{xy}$  of an average ionic interaction with a selected  $i$ -type group in a molecule Y. According to Savage and Wood [8], a CH group is counted as 0.5 and a  $\text{CH}_3$  group as 1.5  $\text{CH}_2$  groups. Applying the method of multiple linear regression to solve eqn. (3) for  $h_{xy}$  values for non-electrolytes which contain in their molecule the specified groups (methanol, propanol, isopropanol, isobutanol, 2-methoxy-

TABLE 4

Functional group interaction parameters  $h_{yi}$  with their standard deviations in DMF

Functional group combinations $i$	$h_{yi}$ (J kg mol <sup>-2</sup> )
$\frac{1}{2}\text{Na}^+\text{I}^- - \text{CH}_2$	$101 \pm 4$
$\frac{1}{2}\text{Na}^+\text{I}^- - \text{OH}$	$58 \pm 9$
$\frac{1}{2}\text{Na}^+\text{I}^- - \text{O}$	$-156 \pm 11$
Standard error of fit	15.61
Regression coefficient $r^2$	0.9955

ethanol, tetrahydrofuran, ethylene glycol and 1,4-dioxane), the group contributions at 298.15 K presented in Table 4 were calculated. A comparison of the experimental  $h_{xy}$  values with those calculated from group contributions (Fig. 1) shows that despite the simplicity of the model its application to the system discussed yields fully satisfactory results.

As may be seen from the data in Table 4, the interactions with the  $\text{CH}_2$  group in DMF are positive while with ether oxygen they are negative, similarly as was found for aqueous systems [1,3,4]. The negative value of  $(\text{Na}^+\text{I}^- - \text{O})$  contributions is probably a result of the electrostatic interactions of the ion-dipole type, which are weaker in DMF than was found for aqueous solutions [3,4]. In contrast to this, the origin of the positive values for the  $(\text{Na}^+\text{I}^- - \text{CH}_2)$  contribution in both solvents mentioned does not seem to be the same. In aqueous solutions, the positive enthalpic effect of the interactions between the ions and the  $\text{CH}_2$  group is a result of the breaking of the structured water around the methylene group [3]. The analogous phenomenon does not seem to be present in the DMF solution. In this case, the positive  $h_{yi}$  value can illustrate the repulsion forces between the ions and the non-polar group. There is also another possible explanation of the observed positive  $h_{yi}$  value. If we assume that the interactions

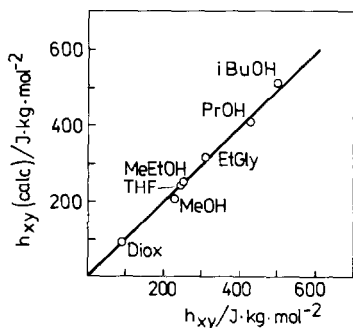


Fig. 1. Comparison of the enthalpic pair interaction coefficients of  $\text{Na}^+\text{I}^-$ -non-electrolyte pairs determined experimentally ( $h_{xy}$ ), and calculated from group contributions ( $h_{xy}^{\text{calc}}$ ). Diox, 1,4-dioxane; MeEtOH, 2-methoxyethanol.

between DMF molecules in the vicinity of the ions are mostly of the dipole-dipole type, the replacement of a highly polar DMF molecule by a less polar alkanol one in the ionic solvation shell should give a positive enthalpic effect, reflected by  $h_{yi} > 0$ . The same phenomenon could also influence the effect of interaction between the ions and the OH group, leading to a positive value of the (Na<sup>+</sup>I<sup>-</sup>-OH) contribution in DMF solution. However, there are still some other possible explanations for the observed positive value of  $h_{yi}$  for the (Na<sup>+</sup>I<sup>-</sup>-OH) interactions. The inclusion of the hydroxylic molecule into the ionic solvation shell in the DMF solution requires the breaking of the hydrogen bond between the hydroxyl group and the surrounding DMF molecules, which can give the observed positive contribution. The positive values of  $h_{xy}$  for (Na<sup>+</sup>I<sup>-</sup>-water) interactions in DMF (Table 3) could confirm this opinion. It is also possible that an increase in the chain length of alkanol molecules results in a decrease in the strength of Na<sup>+</sup>I<sup>-</sup>-alkanol interactions through the OH group. In such a case, the separation of (Na<sup>+</sup>I<sup>-</sup>-CH<sub>2</sub>)- and (Na<sup>+</sup>I<sup>-</sup>-OH)-type interactions as independent interactions would be doubtful.

It can be concluded, therefore, that the group additivity model is applicable to the correlation of Na<sup>+</sup>I<sup>-</sup>-non-electrolyte  $h_{xy}$  values both in water and in DMF solution. Nevertheless, in contrast to aqueous systems [3,4], the interpretation of the calculated group contributions in DMF solution seems not to be as clear as that in aqueous solutions.

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