

# Enthalpic interaction coefficients of NaI–alkanediol pairs in methanol and in water

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**Abstract** The dissolution enthalpies of NaI in the mixtures of methanol with 1,2-alkanediols (1,2-propanediol, 1,2-butanediol, 1,2-pentanediol) and with  $\alpha,\omega$ -alkanediols (1,3-propanediol, 1,4-butanediol, 1,5-pentanediol), as well as NaI in the mixtures of water with 1,3-propanediol and 1,2-pentanediol, were determined at 298.15 K. The energetic effect of interactions between the investigated alkanediols and NaI in methanol and in water was calculated using the enthalpic pair interaction coefficients ( $h_{xy}$ ) model. These results along with the other data concerning the NaI–non-electrolyte pairs taken from our earlier reports and from the literature were analyzed with respect to the effect of the non-electrolyte properties on the variations of the  $h_{xy}$  values. The group contributions illustrating the interactions of NaI with selected functional groups in non-electrolyte (alkanediol and alkanol) molecules, namely:  $\text{CH}_2$  and OH groups were calculated and discussed.

**Keywords** Enthalpic pair interaction coefficients · Electrolytes · Alkanediols · Methanol and aqueous solutions

## Introduction

Systems containing an electrolyte and non-electrolyte in aqueous and *N,N*-dimethylformamide (DMF) solutions have been of interest to our laboratory for a long time [1–8]. In order to analyze intermolecular interactions in the systems under investigation the so-called enthalpic interaction

coefficients model, derived from McMillan–Mayer’s theory, was used [9]. The systematic studies on these systems have shown that the enthalpic interaction coefficients of electrolyte–non-electrolyte pair (NaI/NaCl–Y) in water and in DMF can be presented in the form of the sum of group contributions [4, 5]. Moreover, in aqueous solutions, some correlations between these coefficients and the functions describing the solvation of non-electrolyte have been found [5]. Such correlations have not been observed in analogous systems containing DMF as solvent [4]. The comparison of findings concerning appropriate aqueous and DMF solutions show that a decisive role in the differentiation of interactions seems to be played in the first system by hydrophobic hydration and in the second one by selective solvation.

The further studies carried out in our laboratory have been devoted to interactions in methanol solutions [10–14]. Methanol solutions in some respects show similar properties to those of aqueous solutions and in others they resemble DMF solutions. Recently, we have turned our attention to systems containing a diol as a non-electrolyte. The wide applications of diols to different chemical products of everyday use as well as their significance in biological systems justify our interest in this group of compounds. Moreover, thanks to the molecular structure their interactions with other molecules are more diversified than those in which simpler molecules take part. The results of heat capacity measurements of alkanediol in methanol made it possible to determine the molar heat capacity of the interaction between alkanediol molecule and methanol,  $\Delta C_{p(\text{int})}$  [15]. The comparison of the values of  $\Delta C_{p(\text{int})}$  of diols in methanol with analogous data concerning aqueous systems has shown that the intermolecular solute–solvent interactions in water are stronger than those in methanol. The observations of the alkanediol–methanol mixtures investigated were interesting enough to impel us

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to compare the interactions between an electrolyte such as NaI and alkanediol in methanol with analogous interactions in water on the basis of enthalpic pair interaction coefficients,  $h_{xy}$ . In order to get more data for such comparison the data concerning aqueous solutions [7, 16] were completed with those for the systems: NaI–1,3-propanediol–water and NaI–1,2-pentanediol–water.

## Experimental section

### Materials

Methanol (Chempur, pro analysis) was dried by means of iodine-activated magnesium using Lund–Bjerrum's method. It was then distilled to collect the fraction with a boiling point of 64.7 °C. 1,2-propanediol (1,2PD), 1,3-propanediol (1,3PD), 1,2-butanediol (1,2BD), 1,4-butanediol (1,4BD) (Aldrich, pro analysis), 1,2-pentanediol (1,2PeD), and 1,5-pentanediol (1,5PeD) (Fluka, pro analysis) were dried over 4A molecular sieves for several days followed by distillation under vacuum. Water used for the investigations was deionised and distilled three times. Sodium iodide (99.5% Merck) was dried for several days at a temperature of about 333 K and stored in a desiccator.

### Method

The dissolution enthalpies of sodium iodide in the mixture investigated,  $\Delta_{\text{sol}}H$ , were measured with the use of an "isoperibol" calorimeter [7]. The relative error of measurement was  $\Delta_{\text{sol}}H \pm 1.42\%$ . Salts containing ampoules were weighed with an accuracy of  $\pm 0.00001$  g; the mixtures of methanol and the alkanediols mentioned as well as the aqueous mixtures were prepared by weight with an accuracy of  $\pm 0.01$  g. The concentration of NaI in solutions ranged from 0.004 to 0.03 mol kg<sup>-1</sup>. All the solution heat measurements were performed within the range of diol content from 0 to 30 mol% at a temperature of 298.15 K.

## Results and discussion

### Solution enthalpies

The standard dissolution enthalpies  $\Delta_{\text{sol}}H^\infty$  of NaI in each examined mixture were calculated by the extrapolation of the measured enthalpies of solution  $\Delta_{\text{sol}}H$  as a function of square root of molality  $m$  to  $m = 0$ :

$$\Delta_{\text{sol}}H = \Delta_{\text{sol}}H^\infty + A \cdot m^{1/2} \quad (1)$$

where  $A$  is an experimental slope.

The determined values of the standard dissolution enthalpies of NaI in the mixtures investigated are listed in Tables 1 and 2. The values of  $\Delta_{\text{sol}}H^\infty$  for NaI in pure solvents are in good agreement with the appropriate literature data: in methanol  $\Delta_{\text{sol}}H^\infty(\text{NaI}) = -32.35$  kJ mol<sup>-1</sup> ( $-31.88$  [10],  $-32.05$  kJ mol<sup>-1</sup> [17]), in water  $\Delta_{\text{sol}}H^\infty(\text{NaI}) = -7.61$  kJ mol<sup>-1</sup> ( $-7.58$  [5],  $-7.62$  kJ mol<sup>-1</sup> [17]).

The dependence of the standard solution enthalpy,  $\Delta_{\text{sol}}H^\infty$  of NaI on the alkanediol content in methanol mixture is shown in Fig. 1a. As is seen from the figure, within the range 0–30 mol% of diol, a small increase in  $\Delta_{\text{sol}}H^\infty$  of sodium iodide (a decrease in the exothermic dissolution effect) takes place with the increase of diol concentration in the system. This increase is the higher, the greater the diol molecules dimensions. The comparison of the course of NaI solution enthalpy in the mixtures of methanol with 1,2-diols and with  $\alpha,\omega$ -diols shows that in

**Table 1** Standard enthalpies of solution,  $\Delta_{\text{sol}}H^\infty$  (kJ mol<sup>-1</sup>) of NaI in methanol–alkanediol mixtures at temp. 298.15 K;  $x_2$ —mole fraction of alkanediol

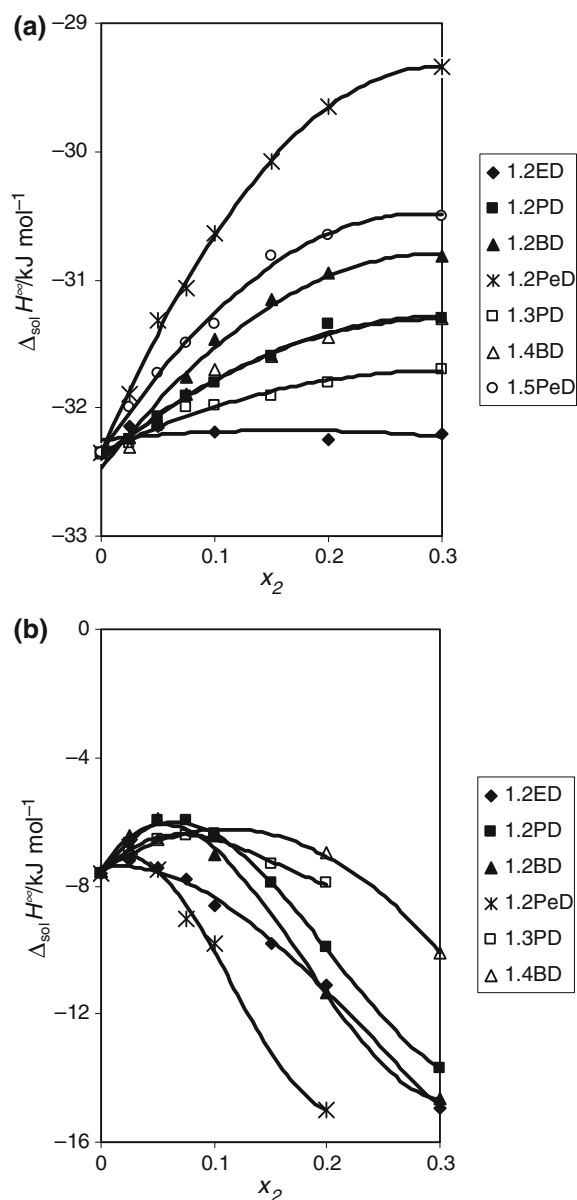
$\Delta_{\text{sol}}H^\infty$						
$x_2$	1,2PD	1,2BD	1,2PeD	1,3PD	1,4BD	1,5PeD
0	-32.35	-32.35	-32.35	-32.35	-32.35	-32.35
0.025	-32.24	-32.23	-31.90	-32.28	-32.30	-32.00
0.050	-32.07	-32.12	-31.22	-32.15	-32.11	-31.73
0.075	-31.91	-31.76	-31.57	-32.00	-31.90	-31.50
0.100	-32.01	-31.47	-31.34	-31.98	-31.72	-31.35
0.150	-31.67	-30.75	-31.43	-31.91	-31.61	-30.81
0.200	-31.35	-30.95	-30.00	-31.80	-31.45	-30.65
0.300	-31.62	-30.99	-30.00	-31.70	-31.30	-30.52

1,2- and  $\alpha,\omega$ -alkanediols: propanediol (PD), butanediol (BD), pentanediol (PeD)

**Table 2** Standard enthalpies of solution,  $\Delta_{\text{sol}}H^\infty$  (kJ mol<sup>-1</sup>) of NaI in water–alkanediol mixtures at temp. 298.15 K;  $x_2$ —mole fraction of alkanediol

$\Delta_{\text{sol}}H^\infty$		
$x_2$	1,3PD	1,2PeD
0	-7.61	-7.61
0.025	-6.91	-6.81
0.05	-6.54	-7.21
0.075	-6.47	-9.02
0.1	-6.56	-10.1
0.125	-6.83	-
0.15	-7.33	-
0.2	-9.62	-14.35

1,3PD 1,3-propanediol, 1,2PeD 1,2-pentanediol



**Fig. 1** Standard molar enthalpies of solution of NaI in diol + methanol mixtures (a) and diol + water mixtures (b) against diol content

the case of the latter the increase in  $\Delta_{\text{sol}}H^\infty$  within the methanol-rich range is smaller.

In the thermochemical respect the NaI–diol systems in methanol behave differently than in water (Fig. 1b). In the mixtures of methanol with the examined alkanediols, the curves of  $\Delta_{\text{sol}}H^\infty(\text{NaI}) = f(x_2)$  run monotonically, with no extremum, within the methanol-rich range, and the slope of curves for the series of 1,2-alkanediols regularly increases with the increase in carbon chain length in the diol molecule. In contrast, in water, the maximum of standard solution enthalpy is observed which is ascribed to the hydrophobic hydration of diol molecules. The lack of the  $\Delta_{\text{sol}}H^\infty$  maximum in methanolic solutions of diols

indicates the lack of one of the main symptoms of the solvophobic solvation in this solvent postulated in some papers. It should be, however, kept in mind that this does not constitute any proof of the lack of this phenomenon.

### Enthalpic pair interaction coefficients

The model of enthalpic interaction coefficients of electrolyte–non-electrolyte pairs,  $h_{xy}$  [2] was used to quantitatively characterize the interactions in methanol and in water. These coefficients derived from McMillan–Mayer’s theory [9] can be regarded as a measure of the heat effect when two solute particles approach each other in dilute solutions. In our earlier articles [2] it was demonstrated that in three-component systems  $h_{xy}$  illustrate the heat effect of replacing the solvent molecule by the cosolvent one in the ionic solvation shell.

In order to calculate the  $h_{xy}$  coefficients the standard molar solution enthalpies of electrolyte X (NaI) in the mixtures of the solvent  $S$  investigated (water or methanol) and non-electrolyte  $Y$  (alkanediol),  $\Delta_{\text{sol}}H^\infty(M)$  are presented as the following function:

$$\Delta_{\text{sol}}H^\infty(M) = \Delta_{\text{sol}}H^\infty(S) + bm_y + cm_y^2 + \dots \quad (2)$$

where  $\Delta_{\text{sol}}H^\infty(S)$  is the standard solution enthalpy of NaI in pure solvent  $S$ ,  $m_y$  the molality of non-electrolyte,  $b$  and  $c$  the polynomial coefficients.

Parameter  $b$ , limiting slope of the function under discussion, is connected with the enthalpic pair interaction coefficient,  $h_{xy}$ , by the relationship:

$$b = 2h_{xy} \quad (3)$$

Parameter  $c$  is connected with the enthalpic triplet interaction coefficient,  $h_{xyy}$  which in our case regards to the interactions of NaI with two cosolute particles. These coefficients will not be discussed here as they contain also some energy contributions from different type pair interactions and their meaning is obscured.

The values of  $h_{xy}$  obtained contain the contributions connected with both cation and anion, thus they illustrate the sum of enthalpic effects of the interactions between non-electrolyte molecule and electrolyte. The estimated uncertainty of the calculated  $h_{xy}$  coefficients is  $\pm 20 \text{ J kg mol}^{-2}$ . The values of  $h_{xy}$  determined for NaI–alkanediol pairs and the data concerning other, previously examined systems in methanol are given in Table 3. For the sake of comparison the values of  $h_{xy}$  for the same pairs in water are also listed in the Table 3.

The enthalpic interaction coefficients of the NaI–non-electrolyte pair in methanol, similarly as in water, assume both positive and negative values. In the case of the NaI–alkanediol pairs, coefficients  $h_{xy}$  are positive in both solvents. In methanol, the  $h_{xy}$  values for 1,2- as well as for

**Table 3** Enthalpic pair interaction coefficients  $h_{xy}$  of NaI–nonelectrolyte Y in methanol and in water at temp. 298.15 K;  $h_{xy}$  (J kg mol<sup>-2</sup>)

Y <sup>a</sup>	$h_{xy}$ (NaI–Y) in methanol	$h_{xy}$ (NaI–Y) in water
MeOH	–	314 [5]
EtOH	31 [10]	596 [5]
1-PrOH	23 [10]	780 [5]
2-PrOH	26 [10]	1018 [5]
1,2ED	0 <sup>b</sup>	178 [7]
1,2PD	82	381 [7]
1,3PD	50	280
1,2BD	153	518 [7]
1,4BD	133	268 <sup>c</sup>
1,2PeD	220	524
1,5PeD	193	–
AN	–335 [11]	–494 [5]
DMF	–950 [11]	–350 [5]
PC	–20 [11]	–
NM	40 [11]	–

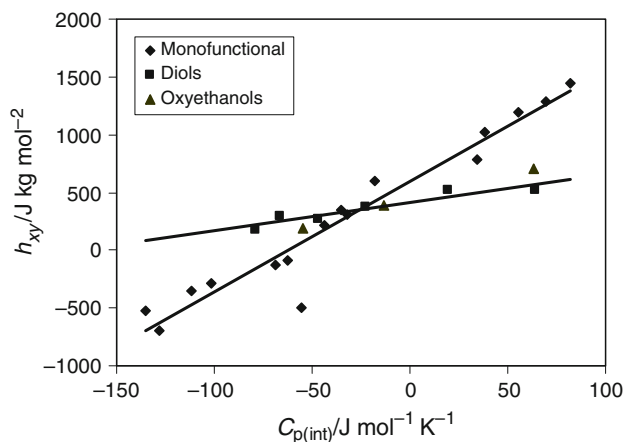
<sup>a</sup> Nonelectrolytes: methanol (MeOH), 1-propanol (1-PrOH), 2-propanol (2-PrOH), acetonitrile (AN), *N,N*-dimethylformamide (DMF), propylene carbonate (PC), nitromethane (NM)

<sup>b</sup> Calculated from the solution enthalpies taken from ref. [18]

<sup>c</sup> Calculated from the solution enthalpies taken from ref. [16]

$\alpha,\omega$ -alkanediols increase with the increase of the carbon chain length and the  $h_{xy}$  values for NaI–1,2-diol pairs are more positive than those for NaI– $\alpha,\omega$ -diol ones. Comparing the pair interaction coefficients,  $h_{xy}$ , (NaI–Y) in methanol with those in water, one can notice that they are much lower in the methanol solution, except the system containing acetonitrile.

As is generally accepted, positive values of  $h_{xy}$  are observed when the endothermic effects connected with desolvation (dehydration in the case of water) exceed the exothermic effects of ion–dipole attraction. Thus, one can assume that the interaction between electrolyte and non-electrolyte molecule is energetically more favorable in methanol than that in water. The solvation effects as well as the ion–dipole and dipole–dipole interactions occurring in the system under study are closely connected with the properties of the system components. As it is known, one of the functions which are sensitive to structural changes in solution is the heat capacity of solvation,  $\Delta C_{p(\text{solv})}$ . It can be presented in the form of the sum of contributions associated with the formation of cavity in the solvent structure to encapsulate the solute,  $\Delta C_{p(\text{cav})}$ , and with the interactions between the solute molecule and surroundings solvent molecules,  $\Delta C_{p(\text{int})}$ . The method of determining these quantities on the base of the scaled particle theory (SPT) has been described in details in articles [19, 20]. The values of  $\Delta C_{p(\text{cav})}$  and  $\Delta C_{p(\text{int})}$  calculated by us for the



**Fig. 2** Enthalpic pair interaction coefficients  $h_{xy}$  for NaI–non-electrolyte pairs in water as a function of  $C_{p(\text{int})}$  of the non-electrolyte. Dependence for monofunctional compounds from ref. [5]

methanol–alkanediol and water–alkanediol mixtures have been presented and discussed in our recent article [15].

As could be expected on the basis of previous results concerning the studies on aqueous solutions [5], the best correlation is observed for the values of  $h_{xy}$  presented as a function of  $\Delta C_{p(\text{int})}$ . This dependence, considering the enthalpic interaction coefficients of NaI–alkanediol pair obtained in this study, is shown in Fig. 2.

The linear  $h_{xy}$  dependence of the given electrolyte on the function, which characterizes the interactions with the solvent of non-electrolytes with various molecular structures and various properties, testifies to the decisive role played by the dehydration of non-electrolyte (Y) in water. While observing Fig. 2 it is worth paying attention to the fact that the dependence discussed presents two straight lines—one of them for mono-functional compounds and the other for bi-functional compounds. One can assume that the incorporation of an additional polar group into the molecule of alcohol (OH group in diols or ether oxygen in cellosolve) increases the exothermic contribution of the electrostatic ion–dipole interaction. However, to provide more complete analysis, it seems proper to verify the relationship investigated for a greater group of non-electrolytes possessing two functional groups in the structure of their molecules.

On the other hand, no correlation was found between the values of  $h_{xy}$  and the molar heat capacity of the interactions,  $\Delta C_{p(\text{int})}$  in methanol. Therefore, one can assume that the differentiation of  $h_{xy}$  is more affected in methanol than in water by the effects of direct ion–non-electrolyte molecule interactions, especially the effects of selective ion solvation [12–14]. The addition of an organic non-electrolyte to methanol modifies the properties of methanol as the solvent of the electrolyte. Depending on its type, one can observe the preferential solvation of ions by methanol or cosolvent (non-electrolyte).

Finally, the lack of correlation of the enthalpic pair interaction coefficients confirms the variety of interactions in methanol; on the other hand it confirms the suggestion of the dominating influence of hydration effects in dilute aqueous solutions.

#### Model of group interactions SWAG

To verify the above opinions, the enthalpic pair interaction coefficients can be correlated by means of the well known Savage and Wood group additivity model (SWAG) [21]. The SWAG method has been successfully applied to the electrolyte–non-electrolyte pairs in water. In that case, the analysed  $h_{xy}$  coefficients consist of anionic and cationic contributions, therefore, the electrolyte is treated as an individual species corresponding to a single functional group (MA) [3, 5, 22–24]. The  $h_{xy}$  coefficient is then presented as a sum:

$$h_{xy} = \sum_j n_{y,j} h_{MA-j} \quad (4)$$

where  $n_{y,j}$  is the number of  $j$  groups in the molecule of non-electrolyte  $Y$ , while  $h_{MA-j}$  is the group coefficient illustrating the interactions between group  $j$  and the ions of electrolyte  $X \equiv MA$ . The presented model of group interaction additivity has been developed to correlate the values of enthalpic pair interaction coefficients concerning various systems as well as to make it possible to predict the values of such coefficients for unexamined systems [25]. As shown by the authors of this study, even if the coefficients of group interactions are not very accurately determined, the foreseen values of  $h_{xy}$  are close to those experimentally found due to the compensation of errors. An important advantage of SWAG model is the possibility of discovering abnormal behaviors of some systems, which appears as a considerable divergence between the calculated and real values of interaction coefficients.

Applying the multiple linear regression method to solve Eq. 4 for 16 non-electrolytes from ref. [5] and our data for alkanediols in water the group contributions were calculated and presented in Table 4. The values of group contributions determined on the basis of the data concerning alkanediols in methanol are given in Table 4, too.

As follows from the presented data, the higher values of  $h_{NaI-CH_2}$  in water in comparison with those in methanol emphasize the role of organic cosolvent hydrophobicity in water. It is interesting that the coefficient  $h_{NaI-OH}$  obtained in water has the same value and sign as that obtained in methanol. The negative coefficient results from the dominating ion–dipole attraction forces that occur in the system under investigation.

The enthalpic interaction coefficients of the NaI–diol pair calculated on the basis of group contributions in

**Table 4** Enthalpic pair interaction coefficients of NaI–alkanediol in water at temp. 298.15 K: values calculated from experimental data ( $h_{xy}$ ), from SWAG model ( $h_{xy}^*$ ) and calculated according to a model presented in ref. [27] assuming cyclic H-bonded structure of diol molecule;  $h_{xy}$  (J kg mol<sup>-2</sup>)

	$h_{xy}$	$h_{xy}^*$	$h_{xy}^{**}$
NaI-1,2ED	178	294	-127
NaI-1,2PD	381	573	168
NaI-1,3PD	280	573	168
NaI-1,2BD	518	843	459
NaI-1,4BD	268	843	459
NaI-1,2PeD	524	1,134	750

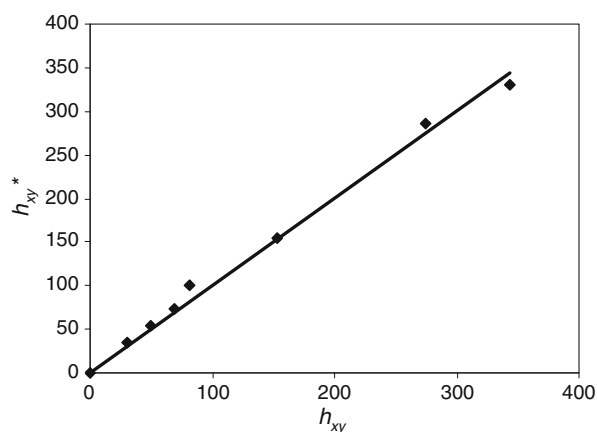
**Table 5** Group-additivity coefficients (in J kg mol<sup>-2</sup>) for NaI–non-electrolyte pairs in methanol and in water

Solvent	Methanol	Water <sup>a</sup>
$h_{MA-CH_2}$	100 ± 23	271 ± 21
$h_{MA-OH}$	-123 ± 42	-123 ± 53
$r$	0.993	0.992

<sup>a</sup> Literature values calculated without the data for alkanediols [5]:  $h_{MA-CH_2} = 291 \pm 22$ ;  $h_{MA-OH} = -134 \pm 62$

aqueous solution,  $h_{xy}^*$ , differ from the values determined experimentally (Table 5). The cause of this state can be sought in the structure of the diols under discussion that impedes the formation of hydration sheaths around non-polar molecule fragments in the vicinity of OH groups.

The discrepancy observed confirms the conclusion resulting from the theoretical considerations of the mutual influence of neighboring polar and non-polar groups in the molecule on the structure of hydration sheath [26]. Another explanation of the above discrepancy can be presented using the suggestions contained in paper [27]. If diols are intramolecularly associated in dilute aqueous solution, one



**Fig. 3** Enthalpic interaction coefficients  $h_{xy}^*$  obtained using SWAG model vs. values  $h_{xy}$  determined experimentally for investigated alkanediols in methanol;  $r = 0.993$

of the oxygen atoms in hydroxyl group can be treated as ether oxygen. On the other hand, the hydrogen atom combined by hydrogen bond can be accepted, according to SWAG model, as the equivalent of 0.5 CH<sub>2</sub>. The enthalpic interaction coefficients,  $h_{xy}^{**}$ , calculated with the use of the above assumptions (Table 5) are more similar to the values determined experimentally, except 1,2-ethanediol.

In the methanol solution, the values calculated on the basis of group contributions,  $h_{xy}^*$  are in good agreement with the experimental data  $h_{xy}$  (Fig. 3).

## Conclusions

The analysis of tri-component systems carried out in the present study has shown that in the solutions of water that is a solvent of three-dimensional structure, a dominating role is played by hydration interactions. In the case of solutions in methanol, the differentiation of interaction effects is smaller than that in aqueous solutions. From the point of view of enthalpic pair interaction coefficients,  $h_{xy}$ , methanol is a solvent that differentiates to a smaller extent than water.

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