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Enthalpies of Interaction of *N*,*N*-Dimethylformamide with Polyalcohols in Aqueous Solutions at 298.15 K

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Enthalpies of mixing of aqueous DMF solutions with aqueous polyalcohols (glycol, 1,2-propanediol, 1,3-propanediol, and glycerol) solutions and their respective enthalpies of dilution have been determined at 298.15 K using flow microcalorimetry. The experimental results obtained have been analyzed to give the heterotactic enthalpic interaction (or virial) coefficients of the solutes in terms of the McMillan−Mayer model. The enthalpic pairwise interaction coefficients h_{xy} have been discussed from the points of view of solute−solute interactions. In addition, using the additivity groups approach by Savage and Wood (SWAG), contributions of each of the functional group of DMF and the polyalcohol studied have been estimated.

Introduction

The study of hydrophobic hydration and hydrophobic "non-bonding" solute−solute interactions is an important step for understanding several phenomena in biological systems. Mixtures of aliphatic amides and water have been the subject of many studies.[1,2] Since these amides cover a very wide range of dielectric constants and are usually miscible with water, their aqueous mixtures have attracted considerable attention for many years.[3,4] In addition, the amides can serve as model compounds for the investigations of the properties of peptides in aqueous solutions.[5,6] Among these amides, *N*,*N*-dimethylformamide (DMF), a very good aprotic protophilic medium for organic and inorganic substances, is of particular interest in view of the lack of hydrogen bonding in the pure solvent and of the structure alteration of its aqueous mixtures.[7]

Many investigations have shown that polyalcohol can increase the thermal stability of globular proteins or reduce the extent of denaturation by other reagents.[8−10] Although the diols under investigation are not found in cellular or extracellular fluids of living organisms, they find wide application in pharmacoloty and the cosmetics industry. When introduced into a living organism as vehicles for pharmaceuticals or cosmetics, they affect the components of cellular fluids. This has been confirmed by numerous biochemical studies devoted to the interactions between diols and components of biological cells.[11] On the other hand, glycerol occurs as a primary biomolecule in the intestine as a product of hydrolysis of lipids and also in the liver where it participates in the metabolism of glucose.

To understand the nature of interactions between polyalcohols and proteins in aqueous solutions, it is necessary to study simple compounds that model molecules. So it is worthwhile to explore the interaction between DMF and polyalcohols in aqueous solutions.

Virial coefficients of the power series of the excess enthalpies as a function of the molalities permit access to information about the interactions between hydrated molecules.[12] They can be easily derived from enthalpies of dilution and mixing of solutions containing n solutions. As an extension to our previous studies,[13−18] in the present paper we report the heterotactic enthalpic interaction (or virial) coefficients of interactions between DMF and the polyalcohol molecules in aqueous solutions according to the McMillan−Mayer theory.[19] These coefficients reflect the sum of the enthalpic effects of interactions between the components in aqueous solutions. The heterotactic enthalpic pairwise interaction coefficients between DMF and polyalcohols in the aqueous solutions have also been studied by a group contribution additivity approach.

Materials and Methods

DMF, glycol, 1,2-propanediol, 1,3-propanediol, and glycerol (AR grade, from Shanghai Chem. Co.) were used without further purification. The water used for the preparation of solution was deionized and distilled using a quartz sub-boiling purifier. All the aqueous solutions used in the experiment were prepared by weight with a Mettler AE 200 balance with a precision of ± 0.0001 g.

The enthalpies of dilution and mixing were measured with LKB-2277 Bio Activity Monitor. With an external water circulator, its stability over 24 h is better than $\pm\ 10^{-4}$ K. Experimental temperatures were maintained at (298.15 ± 0.01) K using a Haake model DC 30. The experimental details are reported in the literature. Errors in the determinations of the molar enthalpies of dilution and mixing were estimated to be < 1 %. The flow rates were determined by weighing the masses of the liquids passing through pumps within 8 min. The liquids passing through pumps A and B were changed in the following sequence:

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$A_{water} + B_{water}$ baseline determined
$A_x + B_{water}$ $\Delta_{dil}H(x)$
$A_x + B_y$ $\Delta_{mix}H$
$A_{water} + B_y$ $\Delta_{dil}H(y)$
$A_{water} + B_{water}$ reestablish baseline

The excess enthalpy of a solution containing two solute species *x* and *y* can be analyzed using the McMillan−Mayer theory,[19] which allows the separation of effects arising from molecular pairwise, triplet, and higher interactions between the two solutes:

$$\{H^E(n_x, n_y)\}/\{m_1\} = \{H(n_x, n_y)\}/\{m_1\} - h_w^* - n_x H^\infty_{x,m} - n_y H^\infty_{y,m} = h_{xx} n_x^2 + 2h_{xy} n_x n_y + h_{yy} n_y^2 + h_{xxx} n_x^3 + 3h_{xxy} n_x^2 n_y + 3h_{xyy} n_x n_y^2 + h_{yyy} n_y^3 + ... \tag{1}$$

where $H^E(n_x, n_y)$ and $H(n_x, n_y)$ refer to the excess enthalpy and the total enthalpy of a solution containing n_x (mol of *x* species) and n_y (mol of *y* species) in m_1 (kg of water), respectively; h_w^* is the standard enthalpy of 1 kg of pure water; $H^\infty_{x,m}$ and $H^\infty_{y,m}$ are the limiting partial molar enthalpies of solutes *x* and *y*; and the various h_{ij} and h_{iij} are the pairwise and triplet virial coefficients representing interactions between subscripted species.

The enthalpy of dilution is obtained by measuring thermal power *P* and flow rates of solution and solvent (f_A and f_B):

$$\Delta_{dil}H = P/(f_A + f_B - b_{x,i} M_x f_A) \tag{2}$$

where M_x is the molar mass of solute and $b_{x,i}$ is initial molality. The final molality b_x may be calculated by using the equation

$$b_x = b_{x,i} f_A/[f_B(b_{x,i} M_x + 1) + f_A] \tag{3}$$

The enthalpy of mixing of aqueous *x* solution and aqueous *y* solution is calculated from the equation

$$\Delta_{mix}H = P^*/(f_x + f_y - b_{x,i} M_x f_x - b_{y,i} M_y f_y) \tag{4}$$

where P^* is the mixing thermal power; f_x and f_y are the flow rates of solutions *x* and *y*, respectively; and $b_{x,i}$ and $b_{y,i}$ are the initial molalities of solutions *x* and *y* before mixing.

To make the calculations easier, an auxiliary function ΔH^* is introduced:

$$\Delta H^* = \Delta_{mix}H - \Delta_{dil}H(x) - \Delta_{dil}H(y) = H^E(b_x, b_y) - H^E(b_x) - H^E(b_y) \tag{5}$$

where the first term on the right side of eq 5 denotes the mixing enthalpy of the ternary solution. The second and the third terms are the dilution enthalpies of the corresponding binary solutions. Therefore, the equation for the heterotactic interaction coefficients can be evaluated for the combination of eqs 1 and 5:

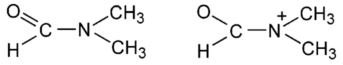
$$\Delta H^*/m_1 = 2h_{xy} b_x b_y + 3h_{xxy} b_x^2 b_y + 3h_{xyy} b_x b_y^2 + ... \tag{6}$$

If the mixing experiments are carried out at different values of b_x and b_y, then the pairwise and triplet heterotactic enthalpic interaction coefficients can be evaluated.

Results and Discussion

Values of ΔH^* calculated from experimental data using eq 6 by the least-squares procedure, together with the experimental $\Delta_{mix}H$, $\Delta_{dil}H(x)$, and $\Delta_{dil}H(y)$, are given in Table 1. The data were fitted to eq 6 to obtain the heterotactic enthalpic interaction coefficients (Table 2). The enthalpic pairwise interaction coefficients are regarded as a measure of the enthalpy effect (i.e., the enthalpy of interaction) when two solute particles approach each other. The physical meaning of the pair interaction coefficients of an excess property is linked to the variation of the thermodynamic property when two hydrated molecules are brought from an infinite distance, where solute−solvent interactions prevail, to a finite distance where solute−solute, water-mediated interactions are operating.[20] Since it is difficult to interpret the higher *h* coefficients, only the pairwise coefficients h_{xy} are considered here.

Heterotactic Enthalpic Interaction between DMF and Polyalcohols in Aqueous Solutions. Unsubstituted and N-monosubstituted carboxamides, which have a proton donor group, the NH group, are capable of self-association through formation of NH···OC hydrogen bonds. Such association is not possible in N,N-disubstituted amides (DMF), where both NH protons are replaced by alkyl group. According to the study on the thermodynamic properties, Chu et al. [21] assumed DMF to have the resonance structure:



The negative pole in DMF is on an oxygen atom that juts out from the rest of the molecule. Through unshared pairs of electrons on these negatively charged, well-exposed atoms are solvated very strongly. The positive pole on the other hand is buried within the molecule. In DMF the presence of two electron-repelling -CH_3 groups make the lone pair at nitrogen still more perceptible toward donation.[22]

The enthalpic interaction coefficients represent the enthalpic properties of the solution, and a measure of interactions between two hydrated solutes depends on the interactions between the solute molecules and the solvent water. Thus, the overall effect reflects the following three superimposed processes:

(i) partial dehydration of the hydration shell of DMF molecule (an endothermic process leading to a positive contribution to h_{xy})

(ii) partial dehydration of hydration shells of polyalcohols hydroxyl groups (an endothermic process leading to a positive contribution to h_{xy})

(iii) direct interaction between DMF and polyalcohols

The DMF molecule is considered to be highly polarized, and the positive pole is surrounded by two methyl groups. The DMF molecule is associated with cation or the center of the positive charge.[23] Interaction (iii) between DMF and the polyalcohol molecule comprises three kinds of group−group interactions:

(a) hydrogen bonds between the carbonyl oxygen of DMF and the hydroxyl group of polyalcohols. This effect is strengthened by the nitrogen atom due to the resonance structure of DMF[24] (an exothermic process leading to a negative contribution to h_{xy})

(b) hydrophobic−hydrophilic interaction between the apolar group and the hydroxyl group (an endothermic process leading to a positive contribution to h_{xy})

(c) hydrophobic−hydrophobic interaction between the apolar group of DMF molecules and that of the polyalcohol molecules (an endothermic process leading to a positive contribution to h_{xy})

The resulting sign and magnitude of h_{xy} would be a consequence of the competitive equilibrium between the above effects. Among these effects, the direct interaction between DMF

Table 1. Enthalpies of Dilution and Mixing of Aqueous DMF Solutions and Aqueous Polyalcohol Solutions at 298.15 K[a]

$b_{x,i}$ / mol·kg^{-1}	$b_{y,i}$ / mol·kg^{-1}	$b_{x,f}$ / mol·kg^{-1}	$b_{y,f}$ / mol·kg^{-1}	$\Delta_{dil}H_{(x)}/m_1$ / J·kg^{-1}	$\Delta_{dil}H_{(y)}/m_1$ / J·kg^{-1}	$\Delta_{mix}H/m_1$ / J·kg^{-1}	$\Delta H^*/m_1$ / J·kg^{-1}
DMF + Glycol							
0.1000	0.1000	0.0544	0.0452	−1.77	−1.07	0.41	3.25
0.1500	0.1500	0.0815	0.0677	−4.04	−2.24	0.45	6.73
0.1800	0.1800	0.0977	0.0812	−5.59	−3.06	0.92	9.56
0.2000	0.2000	0.1085	0.0902	−6.58	−3.76	1.02	11.36
0.2200	0.2200	0.1193	0.0991	−8.78	−5.17	0.45	14.41
0.2500	0.2500	0.1354	0.1125	−11.38	−6.47	0.83	18.69
0.2800	0.2800	0.1515	0.1259	−14.29	−7.68	1.44	23.41
0.3000	0.3000	0.1622	0.1348	−15.06	−8.38	2.16	25.60
0.3200	0.3200	0.1729	0.1437	−18.19	−9.41	2.38	29.98
0.3500	0.3500	0.1889	0.1570	−21.32	−12.16	2.22	35.70
0.3800	0.3800	0.2049	0.1703	−24.61	−14.07	3.66	42.34
0.4000	0.4000	0.2156	0.1792	−26.65	−15.42	4.01	46.08
0.4200	0.4200	0.2262	0.1880	−29.04	−16.57	4.44	50.05
0.4500	0.4500	0.2421	0.2012	−33.26	−18.44	4.91	56.61
0.5000	0.5000	0.2686	0.2232	−41.08	−23.23	6.04	70.34
DMF + 1,2-Propanediol							
0.1000	0.1000	0.0544	0.0452	−1.77	−1.57	0.78	4.12
0.1500	0.1500	0.0815	0.0677	−4.04	−3.31	1.59	8.95
0.1800	0.1800	0.0977	0.0811	−5.59	−4.80	2.22	12.61
0.2000	0.2000	0.1085	0.0900	−6.58	−5.83	2.51	14.91
0.2200	0.2200	0.1193	0.0990	−8.78	−7.55	2.56	18.89
0.2500	0.2500	0.1354	0.1123	−11.38	−10.78	3.17	25.34
0.2800	0.2800	0.1515	0.1256	−14.29	−11.83	4.41	30.53
0.3200	0.3200	0.1622	0.1345	−15.06	−12.94	5.78	33.78
0.3500	0.3500	0.1729	0.1434	−18.19	−15.57	6.64	40.40
0.3800	0.3800	0.1889	0.1566	−21.32	−18.92	7.70	47.94
0.4000	0.4000	0.2049	0.1698	−24.61	−21.53	8.90	55.05
0.4200	0.4200	0.2156	0.1786	−26.65	−23.01	10.02	59.69
0.4500	0.4500	0.2262	0.1874	−29.04	−25.13	11.23	65.40
0.5000	0.5000	0.2421	0.2005	−33.26	−28.94	12.66	74.85
DMF + 1,3-Propanediol							
0.1000	0.1000	0.0544	0.0452	−1.77	−1.44	0.45	3.66
0.1500	0.1500	0.0815	0.0677	−4.04	−3.00	0.84	7.87
0.1800	0.1800	0.0977	0.0811	−5.59	−4.36	1.01	10.96
0.2000	0.2000	0.1085	0.0900	−6.58	−5.33	1.24	13.15
0.2200	0.2200	0.1193	0.0990	−8.78	−7.03	0.89	16.70
0.2500	0.2500	0.1354	0.1123	−11.38	−9.80	0.68	21.87
0.2800	0.2800	0.1515	0.1256	−14.29	−10.66	1.53	26.48
0.3000	0.3000	0.1622	0.1345	−15.06	−11.84	2.41	29.31
0.3200	0.3200	0.1729	0.1434	−18.19	−13.80	2.75	34.74
0.3500	0.3500	0.1889	0.1566	−21.32	−17.23	2.57	41.12
0.3800	0.3800	0.2049	0.1698	−24.61	−19.43	3.85	47.89
0.4000	0.4000	0.2156	0.1786	−26.65	−20.42	4.19	51.27
0.4200	0.4200	0.2262	0.1874	−29.04	−22.68	4.87	56.59
0.4500	0.4500	0.2421	0.2005	−33.26	−26.35	5.59	65.20
0.5000	0.5000	0.2686	0.2224	−41.08	−32.78	6.76	80.62
DMF + Glycerol							
0.1000	0.1000	0.0544	0.0452	−1.77	−1.03	0.50	3.30
0.1500	0.1500	0.0815	0.0676	−4.04	−2.21	0.93	7.18
0.1800	0.1800	0.0977	0.0810	−5.59	−2.95	1.11	9.64
0.2000	0.2000	0.1085	0.0899	−6.58	−3.79	1.29	11.66
0.2200	0.2200	0.1193	0.0988	−8.78	−5.19	0.98	14.95
0.2500	0.2500	0.1354	0.1121	−11.38	−6.11	1.41	18.90
0.2800	0.2800	0.1515	0.1253	−14.29	−7.80	2.04	24.14
0.3000	0.3000	0.1622	0.1342	−15.06	−8.04	2.98	26.08
0.3200	0.3200	0.1729	0.1430	−18.19	−9.45	3.07	30.71
0.3500	0.3500	0.1889	0.1561	−21.32	−12.09	3.12	36.53
0.3800	0.3800	0.2049	0.1693	−24.61	−13.58	4.72	42.92
0.4000	0.4000	0.2156	0.1780	−26.65	−15.21	5.07	46.93
0.4200	0.4200	0.2262	0.1867	−29.04	−16.15	5.79	50.98
0.4500	0.4500	0.2421	0.1998	−33.26	−17.58	6.33	57.17
0.5000	0.5000	0.2686	0.2214	−41.08	−22.40	8.13	71.62

[a] $b_{x,i}$ and $b_{y,i}$ are the initial molalities of solutes x and y; $b_{x,f}$ and $b_{y,f}$ are the final molalities of solutes x and y.

and polyalcohol molecules is considered as the most important interaction and plays the dominant role during the overall interaction processes.

As can be seen from Table 2, the h_{xy} values between DMF and polyalcohols are positive. This indicates that the processes of mixing of DMF and polyalcohol aqueous solutions are exothermic. The discrepancy of h_{xy} between DMF and polyalcohols in the aqueous solutions mainly depends on the differences in the structure of the polyalcohols studied.

The value of h_{xy} for propanediol, which has a longer apolar alkyl group chain, is larger than that of glycol. This experimental result can be interpreted from the following two sides: On one

Table 2. Heterotactic Enthalpic Interaction Coefficients between DMF and Polyalcohol in Aqueous Solutions at 298.15 K[a]

solutes $x + y$	h_{xy} J·kg·mol^{-2}	$h_{xxy} \times 10^{-3}$ J·kg^2·mol^{-3}	$h_{xyy} \times 10^{-3}$ J· kg^2·mol^{-3}	SD	R^2
DMF + glycol	612.7 (107.2)	−212.3 (902.6)	255.4 (1086.4)	0.49	0.9995
DMF + 1,2-propanediol	980.8 (175.9)	105.2 (131.2)	−126.8 (157.8)	0.80	0.9993
DMF + 1,3-propanediol	866.5 (138.2)	121.8 (103.1)	−146.6 (124.0)	0.62	0.9994
DMF + glycerol	672.2 (131.3)	6.8 (47.2)	−8.5 (57.1)	0.59	0.9993

[a] SD = standard derivation, which is given by the least-squares procedure. R = correlation coefficient. The data in the parentheses are the estimated deviations, which are given by the computer during the multiple linear regression analysis.

side, this can be accounted for by reinforcement of hydrogen bonds of water molecules in the hydrating layers hydroxyl group (directly combined with alkyl groups) as well as the DMF molecule interacting with them. This brings about an increase in the endothermic dehydrating effects of interacting molecules which increase with increasing alkyl group size. On the other side, in comparison with glycol, propanediol has the longer apolar alkyl chain, which results in the interaction (c) for propanediol being stronger than for glycol. In other words, the positive contribution to the h_{xy} value for propanediol is larger. Because of the above two reasons, the h_{xy} values of propanediol with DMF are more positive than that of glycol with DMF. The length of the alkyl chain for propanediol is the same as that of glycerol. The former only has two hydroxyl groups, but the later has three. So interactions (a) and (b) concerning the hydroxyl groups have certain discrepancies between the direct interactions of propanediol and glycerol with DMF. The discrepancies of h_{xy} values for DMF + propanediol and DMF + glycerol mainly depend on the competitive equilibrium between the above effects. The experimental result is that h_{xy}(propanediol) > h_{xy}(glycerol). This indicates that interaction (a) plays a dominant role in the two interactions. Compared to glycol, glycerol has a longer apolar alkyl chain and more hydroxyl groups, so interactions (a), (b), and (c) have some differences for DMF + glycol and DMF + glycerol in the aqueous solutions. The result is that h_{xy}(glycerol) > h_{xy}(glycol). This shows that interactions (b) and (c), which can make positive contributions to the h_{xy} values, dominate during the interaction process. Thus the relative magnitude of the h_{xy} values between DMF and the polyalcohols decrease in the order: h_{xy}(propanediol) > h_{xy}(glycerol) > h_{xy}(glycol).

The obtained h_{xy} value of 1,2-propanediol + DMF is slightly higher than that of 1,3-propanediol + DMF. This difference seems to be due to a stronger effect of the hydrophobic hydration of methyl group (CH_3), methylene (CH_2), and methylidyne (CH), which screen the hydroxyl group in 1,2-propanediol, than that of the three methyl groups.

SWAG Analysis on the Enthalpic Pairwise Interaction Coefficients between DMF and Polyalcohol. The advantages and limitations of the SWAG approach[25] have been discussed extensively. Its most useful application is for a series of compounds related in structure. This approach assumes that, in nonbonding interactions, each group of molecule x interacts with every group of molecule y and that the value of the contribution of every interaction to the overall pairwise coefficient is independent of the position of the interacting groups in the molecule.[26] The enthalpic pairwsie coefficients is then given by:

$$h_{xy} = \sum_{i,j} n_i^x n_j^y H_{ij} \tag{7}$$

where n_i^x and n_j^y are the number of i and j groups, respectively, on molecules x and y, and H_{ij} is the enthalpic contribution of an $i-j$ interaction.

Table 3. Experimental and Calculated Values of h_{xy} for DMF with Polyalcohol (Glycol, 1,2-Propanediol, and Glycerol) Molecules at 298.15 K

solutes $x + y$	h_{xy}(expt) J·kg·mol^{-2}	h_{xy}(calc) J·kg·mol^{-2}	100 δ[a]
DMF + glycol	612.7	586	−4.29
DMF + 1,2-propanediol	980.8	984	0.30
DMF + glycerol	672.2	681	−1.31

[a] Relative deviation, $\delta = \{[h_{xy}(\text{calc}) - h_{xy}(\text{expt})]/h_{xy}(\text{expt})\}$.

To apply this additivity approach, it is necessary to divide each molecule in the set into a number of functional groups. The way this is carried out, of course, is somewhat arbitrary. DMF cannot be separated into domains because of the strong inductive effects between the next-neighbor functional groups (also the salvation spheres are strictly interconnected). So the overall DMF molecule is considered as one group, which have been symbolized as A. Following the literature,[27] the groups chosen for describing the polyalcohols are -CH_2- and -OH. The hydrocarbon function is based on the methylene unit. A CH_3 group is equivalent to 1.5 CH_2 groups, a CH group is equivalent to 0.5 CH_2 groups, and H is also counted as 0.5 CH_2 group. For the group contributions of DMF (x) and polyalcohols (y), eq 7 can be expressed as

$$h_{xy} = n_{\text{OH}}(y)H_{\text{A-OH}} + n_{\text{CH}_2}(y)H_{\text{A-CH}_2} \tag{8}$$

The experimental results of DMF + glycol and DMF + glycerol along with the data of DMF + 1,2-propanediol and DMF + 1,3- propanediol were treated using the SWAG approach, respectively. Using this scheme, the multiple linear regression analysis applied to eq 8 for the h_{xy} data obtained in the DMF + polyalcohols system studied yields the following H_{ij} values:

$$H_{\text{A-OH}} = -(104 \pm 18)\ \text{J·kg·mol}^{-2}\ H_{\text{A-CH}_2} = (397 \pm 18)\ \text{J·kg·mol}^{-2} \tag{9}$$

$$H_{\text{A-OH}} = -(28 \pm 35)\ \text{J·kg·mol}^{-2}\ H_{\text{A-CH}_2} = (310 \pm 33)\ \text{J·kg·mol}^{-2} \tag{10}$$

The correlation coefficients are 0.9990 and 0.9959, respectively, and the values after the ± symbol are the estimated deviations, which are given by the computer during the multiple linear regression analysis.

Tables 3 and 4 give a comparison of the experimental enthalpic pairwise interaction coefficients and the calculated values on the basis the contributions mentioned by eq 9 and eq 10, respectively. As can be seen, despite the simplicity of the model of interactions, the two sets of data are in good agreement in most cases. The results obtained from the SWAG approach mainly reflect the rules of the interactions between the groups of an interacting molecule pair.

Table 4. Experimental and Calculated Values of h_{xy} for DMF with Polyalcohol (Glycol, 1,3-Propanediol, and Glycerol) Molecules at 298.15 K

solutes $x + y$	h_{xy}(expt) J·kg·mol^{-2}	h_{xy}(calc) J·kg·mol^{-2}	100 δ^{a}
DMF + glycol	612.7	563	8.2
DMF + 1,3-propanediol	866.5	872	−0.65
DMF + glycerol	672.2	689	−2.5

[a] Relative deviation, $\delta = \{[h_{xy}(\text{calc}) - h_{xy}(\text{expt})]/h_{xy}(\text{expt})\}$.

The results show that the hydrophilic−hydrophilic interaction between DMF and the hydroxyl group of polyalcohol can make a smaller negative contribution to the value of h_{xy}. And this kind of interaction can be considered as a consequence of the balance of the hydrogen bond interaction between the carbonyl oxygen of DMF and the hydroxyl group of polyalcohols (namely, interaction (a) above) and the hydrophobic−hydrophilic interaction between the apolar group and the hydroxyl group between the apolar group of DMF and the hydroxyl group of polyalcohols (namely, interaction (b) in part 1). Equations 9 and 10 also display that the hydrophobic-hydrophobic interaction between the apolar group of DMF molecules and that of the polyalcohol molecules can make a larger positive contributions to the value of h_{xy}. This indicates that although DMF molecule has hydrophilic carbonyl oxygen and hydrophobic apolar groups, it behaves mainly as a hydrophilic solute in the aqueous solutions. This conclusion is consistent with that of the literature: [28] DMF is a kind of nonelectrolyte whose molecule is aprotic in character, and it exhibits electron-donor properties.

It can be seen from eqs 9 and 10, the group contributions of $H_{\text{A}-\text{OH}}$ and $H_{\text{A}-\text{CH}_2}$ to the values of h_{xy} are different, especially for $H_{\text{A}-\text{OH}}$. The cause of this can be ascribed to the too simple basic assumption of SWAG, which ignores the position of each group and neglects the steric and cooperative effects.[29] This is also the main reason that there exists a certain derivation between the experimental results and the results obtained by the SWAG approach. In a word, although the basic assumption of the SWAG approach is very simple and it exists some limitations, this approach still is of some value to the analysis on the solute−solute pairwise interactions of the systems studied.

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