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Enthalpic interaction coefficients of *N*,*N*-dimethylformamide in aqueous ethylene glycol and glycerol solutions at 298.15 K

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ABSTRACT

The dilution enthalpies of *N*,*N*-dimethylformamide (DMF) in aqueous ethylene glycol and glycerol solutions have been determined using a CSC-4400 isothermal calorimeter at 298.15 K. The experimental data have been analyzed in terms of McMillan–Mayer formalism to obtain the enthalpic virial coefficients for heterotactic interaction. The results have been interpreted from the point of view of solute–solute interactions and solute–solvent interactions.

1. Introduction

Proteins play a vital role in nearly all chemical and biological processes. However, it is quite difficult to study the interactions between proteins directly because the conformational and configurational factors that affect the structures of proteins in different solvents are very complicated. Therefore, one useful approach is to study their model compounds, such as amino acids, small peptides, and acylamides [1–4]. The importance of acylamides for structural chemistry and biochemistry is obvious: this is the molecule containing the CONH unit that is characteristic of the peptide bond.

The majority of the proteins exist in aqueous mixed solutions containing many organic substances. Many investigations have shown that polyalcohol can increase the thermal stability of globular proteins or reduce the extent of denaturation by other reagents [5,6]. Although the diols under investigation are not found in cellular or extracellular fluids of living organisms, they find wide application in pharmacy and cosmetics industry. 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.

In spite of large number of studies the mechanism through which polyalcohol affect the stability and solubility of protein remains unresolved. As a continuation of our work [7–10], the present study reports the dilution enthalpies of *N*,*N*-dimethylformamide in aqueous ethylene glycol and glycerol solutions of different compositions at 298.15 K.

2. Experimental

2.1. Materials and sample preparation

Analytical grade DMF (purity >99.5%, purchased from shanghai Chem. Co.) was dried by storage over molecular sieves of 0.4 nm for 2 days and then was used without further purification. Ethylene glycol (analytical grade, purity >99%, purchased from shanghai Chem. Co.) and glycerol (analytical grade, purity >99%, purchased from shanghai Chem. Co.) were distilled, under atmospheric pressure with middle fraction was collected. All of the products were stored over P_2O_5 in a vacuum desiccator for 72 h at room temperature prior to use.

Twice distilled water was deionized by passing through a quartz sub-boiling purifier before use in the preparation of solutions. Both the aqueous solutions, which were used as mixed solvents (water + polyalcohol), and the DMF solutions (DMF + polyalcohol + water) were prepared by mass using a Mettler AE 200 balance precise to ±0.1 mg. All the solutions were degassed and used within 12 h after preparation.

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2.2. Calorimetric procedure

The enthalpies of dilution of DMF in aqueous polyalcohol solutions were measured with an isothermal calorimeter (model 4400 IMC, Calorimeter Science Corporation, USA) at 298.15 K. Details of this apparatus, associated equipment, and the experimental procedure have been reported elsewhere [11–13]. The details of the thermodynamic procedures have been described elsewhere [7–10].

The enthalpies of dilution $\Delta_{\text{dil}}H_{\text{m}}$ were calculated from the equation [14].

$$\Delta_{\text{dil}}H_{\text{m}} = \frac{P(1+m_{\text{i}}M)}{m_{\text{i}}f_2} \tag{1}$$

in which P is the dilution thermal power (μW), m_{i} is the initial molality of the DMF solution (mol kg^{-1}), M is the molar mass of DMF (kg mol^{-1}), f_2 is the flow rate of DMF solution (mg s^{-1}). The uncertainty of $\Delta_{\text{dil}}H_{\text{m}}$ calculated according to Eq. (1) was estimated to be within ± 0.01 J mol^{-1} based on the uncertainties of the measured variables (uncertainties of P, m_{i}, and f_2 are ± 0.2 μW, ± 0.0001 mol kg^{-1}, and ± 0.002 mg s^{-1}, respectively).

The final molality m_{f}, which is a necessary parameter in data processing, can be calculated from the equation.

$$m_{\text{f}} = \frac{m_{\text{i}}f_2}{f_1(m_{\text{i}}M_2+1)+f_2} \tag{2}$$

where f_1 is the flow rate of diluents (water or aqueous polyalcohol solutions).

3. Results and discussion

Information about the interaction mechanism can be inferred from the pairwise interaction coefficients of the virial expansion of an excess thermodynamic property. According to the McMillan–Mayer theory [15,16], thermodynamic properties of multicomponent solutions can be expressed using a viral expansion of in molality that relates the nonideal contributions of any total thermodynamic function to a series of interaction parameters. If aqueous polyalcohol solution is regarded as solvent, the excess enthalpy per kg of solvent (H^{E}) of a solution containing DMF at molality m is given by:

$$H^{\text{E}} = h_2m^2 + h_3m^3 + h_4m^4 + \cdots \tag{3}$$

where h_2, h_3, h_4, etc. are enthalpic coefficients representing pairwise, triplet, quart, etc., higher-order interactions between solvated solute species. The molar enthalpy change ($\Delta_{\text{dil}}H_{\text{m}}$) on diluting a solution of nonelectrolytic solute from an initial molality m_{i} to a final molality m_{f} can be written as:

$$\begin{aligned}\Delta_{\text{dil}}H_{\text{m}} &= H_{\text{m}}^{\text{E}}(m_{\text{f}}) - H_{\text{m}}^{\text{E}}(m_{\text{i}}) = h_2(m_{\text{f}}-m_{\text{i}}) + h_3(m_{\text{f}}^2-m_{\text{i}}^2)\\ &\quad + h_4(m_{\text{f}}^3-m_{\text{i}}^3)+\cdots \end{aligned} \tag{4}$$

in which H_{m}^{E} (m_{i}) and H_{m}^{E} (m_{f}) are the molar excess enthalpies of the solute in the solutions before and after dilution.

The experimental values of $\Delta_{\text{dil}}H_{\text{m}}$ of DMF in aqueous ethylene glycol and glycerol solutions together with the initial and final molalities are listed in Tables 1 and 2. The enthalpic interaction coefficients calculated from Eq. (4) using the least-squares procedure is given in Tables 3 and 4. The highest-order coefficients contain contributions from multiple interactions in a complex way and at the present time it is a hopeless task to attempt any interpretation of them [17], only the pairwise coefficient h_2 is considered.

The enthalpic pairwise interaction coefficients are regarded as a measure of the heat effects when two solute species approach each other. This process is accompanied by overlapping of the solvation cospheres of the solute molecules, resulting in a partial reorganization of the salvation cospheres and a change of the solute–solvent interactions. Therefore, the enthalpic pairwise interaction coefficients h_2 are the results of solvation effects and direct solute–solute interaction effects [18].

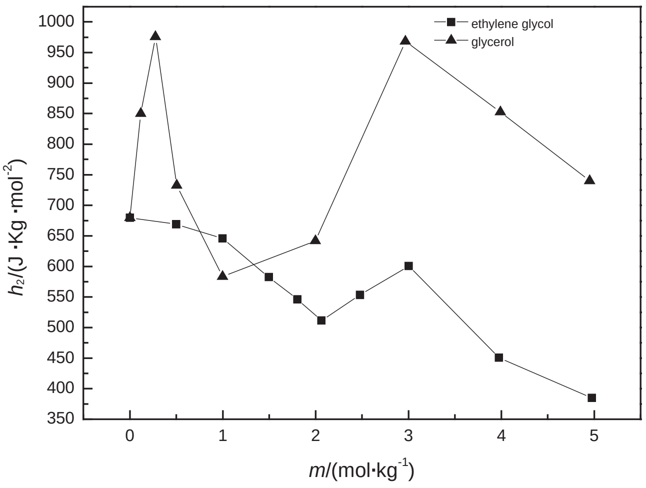

Fig. 1. Variations in enthalpic pair interaction coefficients (h_2) of DMF with the molality (m) of solute in aqueous solutions at 298.15 K.

The h_2 values of DMF in pure water is 679.60 J kg mol^{-2} and the difference comparing to that of the literature [19] result from using a different experimental approach and concentration range. This could be attributed to the cooperative effects of partial dehydration of the hydration shell (positive contribution to h_2), solvent reorganization in the neighborhood of the hydrophobic groups (negative contribution to h_2 [20]), and direct interaction between the DMF molecules.

From Fig. 1, it can be clearly seen that the trend of the h_2 coefficients of DMF in aqueous polyalcohol solutions. The enthalpic pair interaction coefficients h_2 of DMF are all positive in aqueous polyalcohol solutions. In H_2O-rich region in aqueous ethylene glycol solutions, the h_2 coefficients of DMF become less positive with increasing ethylene glycol concentrations; in H_2O-rich region in aqueous glycerol solutions, the h_2 coefficients of DMF are all positive in aqueous glycerol solutions and pass through a maximum. In polyalcohol-rich region in polyalcohol solutions(ethylene glycol $\geq$2 mol kg^{-1} and glycerol $\geq$1 mol kg^{-1}), the trend of the h_2 coefficients of DMF in aqueous ethylene glycol solutions is similar to that of the h_2 coefficients of DMF in aqueous glycerol solutions. The enthalpic pair interaction coefficients h_2 of DMF are all positive in aqueous polyalcohol solutions and pass through a maximum, respectively. In the meantime the h_2 coefficients of DMF in aqueous glycerol solutions are more positive than that in aqueous ethylene glycol solutions.

In H_2O-rich region in aqueous polyalcohol solutions, the essential feature of liquid H_2O is retained. The two non-polar side chain of DMF can form large hydrophobic hydration shell in aqueous solution and the hydrophobic–hydrophobic interactions between two DMF molecules dominate. The effect of ethylene glycol in the H_2O-rich region is partly similar to that of glycerol. Namely, –OH groups in ethylene glycol or glycerol participate in hydrogen bonding to the network of H_2O and enhance the structure of water [21]. So the hydrophobic–hydrophobic interactions are stronger in aqueous polyalcohol solutions. At the same time, ethylene glycol or glycerol molecules will be included in the hydrophobic hydration shell of DMF in H_2O-rich region in aqueous polyalcohol solutions [22]. It can form hydrogen bond between the –OH groups in ethylene glycol or glycerol molecule and water around hydration shell of DMF, so hydrophobic hydration layer is damaged, leading to reduce hydrophobic interaction. The effect h_2 of DMF in H_2O-rich region

Table 1
Enthalpies of dilution of DMF in aqueous ethylene glycol solutions at 298.15 K.

m (ethylene glycol) (mol kg^{-1})	m_i (mol kg^{-1})	m_f (mol kg^{-1})	$\Delta_{dil}H_m$ (J mol^{-1})	m_i (mol kg^{-1})	m_f (mol kg^{-1})	$\Delta_{dil}H_m$ (J mol^{-1})
0.0000	2.0169	1.5655	−250.72	2.0169	0.7388	−738.91
	2.0169	1.5164	−281.81	2.0169	0.6084	−829.30
	2.0169	1.4569	−311.34	2.0169	0.5181	−884.34
	2.0169	1.3817	−354.67	2.0169	0.4523	−936.43
	2.0169	1.2810	−410.64	2.0169	0.4010	−965.39
	2.0169	1.1403	−496.20	2.0169	0.3593	−985.22
0.5000	1.9945	1.5487	−233.69	1.9945	0.9271	−585.77
	1.9945	1.5002	−260.78	1.9945	0.7314	−701.17
	1.9945	1.4413	−290.95	1.9945	0.6023	−782.66
	1.9945	1.3671	−334.94	1.9945	0.5129	−841.81
	1.9945	1.2676	−388.31	1.9945	0.4478	−877.35
	1.9945	1.1284	−464.84	1.9945	0.3971	−912.42
0.9979	1.9768	1.5353	−221.71	1.9768	0.7253	−667.08
	1.9768	1.4872	−247.77	1.9768	0.5973	−746.59
	1.9768	1.4289	−276.99	1.9768	0.5087	−800.89
	1.9768	1.3553	−316.43	1.9768	0.4441	−840.39
	1.9768	1.2567	−370.07	1.9768	0.3938	−869.72
	1.9768	1.1188	−444.58	1.9768	0.3529	−892.50
	1.9768	0.9193	−555.14			
1.4968	1.9772	1.5367	−209.60	1.9772	0.7269	−630.42
	1.9772	1.4887	−233.87	1.9772	0.5988	−702.77
	1.9772	1.4305	−262.47	1.9772	0.5100	−755.00
	1.9772	1.3570	−298.52	1.9772	0.4453	−791.23
	1.9772	1.2584	−348.90	1.9772	0.3949	−813.71
	1.9772	1.1206	−419.84	1.9772	0.3539	−841.86
	1.9772	0.9211	−522.57			
1.8034	1.9785	1.5382	−204.06	1.9785	0.7281	−610.45
	1.9785	1.4903	−226.91	1.9785	0.5999	−684.08
	1.9785	1.4320	−253.71	1.9785	0.5110	−729.08
	1.9785	1.3585	−290.37	1.9785	0.4462	−767.72
	1.9785	1.2600	−338.81	1.9785	0.3957	−783.94
	1.9785	1.1221	−406.25	1.9785	0.3546	−818.41
	1.9785	0.9224	−510.37			
2.0628	1.9644	1.5259	−196.04	1.9644	0.7210	−588.11
	1.9644	1.4781	−218.50	1.9644	0.5939	−659.86
	1.9644	1.4202	−243.92	1.9644	0.5058	−705.40
	1.9644	1.3471	−279.96	1.9644	0.4416	−740.45
	1.9644	1.2491	−325.83	1.9644	0.3915	−761.56
	1.9644	1.1121	−390.48	1.9644	0.3509	−785.01
	1.9644	0.9138	−490.68			
2.4784	1.9847	1.5408	−188.79	1.9847	0.7274	−566.48
	1.9847	1.4925	−209.66	1.9847	0.5990	−638.21
	1.9847	1.4339	−236.19	1.9847	0.5101	−678.68
	1.9847	1.3600	−268.23	1.9847	0.4453	−713.04
	1.9847	1.2609	−313.52	1.9847	0.3948	−736.50
	1.9847	1.1224	−378.23	1.9847	0.3538	−762.92
	1.9847	0.9221	−471.80			
3.0034	1.9779	1.5352	−174.52	1.9779	0.7245	−536.80
	1.9779	1.4871	−194.30	1.9779	0.5966	−601.22
	1.9779	1.4286	−219.92	1.9779	0.5080	−647.33
	1.9779	1.3550	−252.36	1.9779	0.4434	−677.32
	1.9779	1.2562	−295.61	1.9779	0.3932	−703.35
	1.9779	1.1181	−357.58	1.9779	0.3523	−726.50
	1.9779	0.9185	−446.15			
3.9755	1.9784	1.5359	−158.18	1.9784	0.7250	−484.03
	1.9784	1.4877	−177.17	1.9784	0.5970	−543.92
	1.9784	1.4293	−198.50	1.9784	0.5084	−581.95
	1.9784	1.3556	−226.90	1.9784	0.4438	−613.76
	1.9784	1.2568	−266.68	1.9784	0.3935	−634.61
	1.9784	1.1188	−320.82	1.9784	0.3526	−646.95
	1.9784	0.9191	−401.36			
4.9755	1.9986	1.5513	−140.87	1.9986	0.7321	−436.81
	1.9986	1.5027	−157.92	1.9986	0.6029	−490.31
	1.9986	1.4437	−177.15	1.9986	0.5134	−523.27
	1.9986	1.3692	−202.89	1.9986	0.4482	−554.50
	1.9986	1.2694	−238.78	1.9986	0.3974	−570.48
	1.9986	1.1299	−286.97	1.9986	0.3561	−583.40
	1.9986	0.9282	−361.48			

reflects the equilibrium among above two effects. As the ethylene glycol molecules are smaller, increasing the content of ethylene glycol solution, there will be more ethylene glycol molecules into the hydrophobic shell and the h_2 coefficients of DMF become less positive in H_2O-rich region in aqueous ethylene glycol solutions.

Study of Oakenfull and Fenwick [23] found that the hydrophobic interaction depends on the solvent structure in water-organic solvent mixture, the strongest concentration of the hydrophobic effect is often the most water hydrogen-bond developed. Glycerol is a hydrophilic material, which can be easily built into the three-

Table 2
Enthalpies of dilution of DMF in aqueous glycerol solutions at 298.15 K.

m (glycerol) (mol kg^{-1})	m_i (mol kg^{-1})	m_f (mol kg^{-1})	$\Delta_{dil}H_m$ (J mol^{-1})	m_i (mol kg^{-1})	m_f (mol kg^{-1})	$\Delta_{dil}H_m$ (J mol^{-1})
0.0000	2.0169	1.5655	−250.72	2.0169	0.7388	−738.91
	2.0169	1.5164	−281.81	2.0169	0.6084	−829.30
	2.0169	1.4569	−311.34	2.0169	0.5181	−884.34
	2.0169	1.3817	−354.67	2.0169	0.4523	−936.43
	2.0169	1.2810	−410.64	2.0169	0.4010	−965.39
	2.0169	1.1403	−496.20	2.0169	0.3593	−985.22
	2.0169	0.9367	−614.92			
0.1179	1.9847	1.5420	−239.41	1.9847	0.7290	−721.82
	1.9847	1.4938	−266.28	1.9847	0.6004	−797.11
	1.9847	1.4353	−299.03	1.9847	0.5114	−864.25
	1.9847	1.3615	−339.62	1.9847	0.4465	−900.94
	1.9847	1.2625	−396.67	1.9847	0.3959	−942.61
	1.9847	1.1241	−480.34	1.9847	0.3548	−976.36
	1.9847	0.9238	−601.15			
0.2756	1.9953	1.5507	−227.16	1.9953	0.7335	−701.90
	1.9953	1.5023	−253.96	1.9953	0.6042	−780.72
	1.9953	1.4435	−283.78	1.9953	0.5146	−846.56
	1.9953	1.3693	−326.56	1.9953	0.4493	−891.10
	1.9953	1.2699	−382.68	1.9953	0.3985	−941.82
	1.9953	1.1308	−463.32	1.9953	0.3571	−962.65
	1.9953	0.9294	−582.78			
0.5056	1.9904	1.5462	−236.62	1.9904	0.7308	−712.04
	1.9904	1.4978	−263.15	1.9904	0.6019	−796.79
	1.9904	1.4391	−295.27	1.9904	0.5126	−851.04
	1.9904	1.3651	−334.63	1.9904	0.4475	−898.96
	1.9904	1.2658	−391.47	1.9904	0.3968	−933.15
	1.9904	1.1270	−473.54	1.9904	0.3556	−956.87
	1.9904	0.9261	−589.34			
0.9988	1.9891	1.5440	−225.03	1.9891	0.7286	−683.69
	1.9891	1.4955	−249.54	1.9891	0.6000	−755.64
	1.9891	1.4368	−281.91	1.9891	0.5109	−824.07
	1.9891	1.3627	−319.59	1.9891	0.4460	−848.48
	1.9891	1.2634	−374.22	1.9891	0.3955	−893.57
	1.9891	1.1245	−451.50	1.9891	0.3544	−903.57
	1.9891	0.9238	−566.00			
1.9992	1.9891	1.5440	−201.18	1.9891	0.7287	−616.67
	1.9891	1.4956	−223.02	1.9891	0.6000	−693.96
	1.9891	1.4368	−251.75	1.9891	0.5109	−745.42
	1.9891	1.3627	−288.36	1.9891	0.4460	−783.71
	1.9891	1.2634	−338.95	1.9891	0.3955	−810.90
	1.9891	1.1246	−406.03	1.9891	0.3544	−836.06
	1.9891	0.9238	−515.02			
2.9663	2.0014	1.5524	−194.26	2.0014	0.7316	−585.58
	2.0014	1.5036	−216.12	2.0014	0.6023	−672.49
	2.0014	1.4443	−241.21	2.0014	0.5128	−732.11
	2.0014	1.3697	−274.86	2.0014	0.4476	−770.81
	2.0014	1.2696	−320.30	2.0014	0.3969	−809.34
	2.0014	1.1299	−387.76	2.0014	0.3556	−838.09
	2.0014	0.9278	−489.40			
3.9921	1.9887	1.5390	−180.91	1.9887	0.7223	−563.70
	1.9887	1.4902	−201.95	1.9887	0.5942	−634.20
	1.9887	1.4311	−227.72	1.9887	0.5057	−683.71
	1.9887	1.3566	−258.60	1.9887	0.4413	−725.98
	1.9887	1.2569	−302.86	1.9887	0.3911	−766.47
	1.9887	1.1177	−367.50	1.9887	0.3504	−784.65
	1.9887	0.9169	−461.25			
4.9531	2.0016	1.5527	−169.70	2.0016	0.7319	−528.55
	2.0016	1.5039	−189.50	2.0016	0.6026	−599.32
	2.0016	1.4447	−212.86	2.0016	0.5130	−647.42
	2.0016	1.3700	−242.90	2.0016	0.4478	−686.20
	2.0016	1.2700	−284.12	2.0016	0.3970	−720.44
	2.0016	1.1302	−343.81	2.0016	0.3558	−736.26
	2.0016	0.9282	−432.95			

dimensional network of hydrogen bonds in water and become one of the nodes, and enhance the structure of water [24]. In H_2O-rich region in aqueous glycerol solutions, the h_2 coefficients of DMF are all positive in aqueous glycerol solutions and pass through a maximum. The maximum is the place where is the most water hydrogen-bond developed [25].

In polyalcohol-rich region, a solute molecule can also interact with a solvent polyalcohol molecule. This hinders the solute–solute interaction. The direct interaction between two solute molecules provokes partial dehydration of dissolved molecules or polyalcohol near them, which is an endothermic process. Another endothermic effect results from the removal of a number of water molecules from the DMF hydration shells. Therefore, the partial dehydration of solutes gives positive contribution to h_2. The effect is the most prevailing at different concentrations of the cosolutes, leading to a maximum of h_2 coefficients. The phenomenon is related to the fact that polyalcohols may stabilize, or rigidify, the structure of aqueous solutions [26] up to some critical polyalcohol concentration. Fur-

Table 3
Enthalpic interaction coefficients of DMF in aqueous ethylene glycol solutions at 298.15 K.

m (ethylene glycol) (mol kg^{-1})	h_2 (J kg mol^{-2})	h_3 (J kg^2 mol^{-3})	h_4 (J kg^3 mol^{-4})	r
0.0000	679.60(71.35)	−7.72	−16.81	0.9998
0.5000	672.58(45.34)	−33.74	−4.65	0.9999
0.9979	645.51(29.94)	−33.01	−4.82	0.9998
1.4968	582.67(38.23)	−8.53	−10.99	0.9999
1.8034	546.18(64.20)	6.46	−14.14	0.9998
2.0628	511.59(37.72)	34.22	−25.06	0.9999
2.4784	553.39(39.55)	−33.58	−2.52	0.9999
3.0034	600.85(21.41)	−108.67	23.49	0.9999
3.9755	450.82(42.98)	3.74	−13.91	0.9998
4.9755	384.90(38.93)	24.54	−19.35	0.9998

Table 4
Enthalpic interaction coefficients of DMF in aqueous glycerol solutions at 298.15 K.

m (glycerol) (mol kg^{-1})	h_2 (J kg mol^{-2})	h_3 (J kg^2 mol^{-3})	h_4 (J kg^3 mol^{-4})	r
0.0000	679.60(71.35)	−7.72	−16.81	0.9998
0.1179	850.13(66.72)	−220.15	48.73	0.9998
0.2756	975.68(75.62)	−317.60	81.06	0.9998
0.5056	732.51(35.12)	−72.17	3.72	0.9999
0.9988	583.29(100.34)	46.33	−31.45	0.9996
1.9992	641.78(32.99)	−60.02	2.18	0.9999
2.9663	968.21(59.26)	−358.27	82.45	0.9998
3.9921	852.41(50.63)	−283.77	64.09	0.9998
4.9531	740.03(43.21)	−195.81	35.70	0.9999

thermore, the influence of polyalcohol on water depends mainly on the size and shape of the alkyl group in a polyalcohol molecule [27].

When two solute species approach each other, this process is accompanied by overlapping of the solvation cospheres of the solute molecules, resulting in a partial dehydration of the salvation cospheres. Dehydration of the polyalcohol molecule is accompanied by the effect brought about by the influence of polyalcohol's alkyl groups that results in a reinforcement of the hydrogen bonds among water molecules surrounding these non-polar groups [28,29]. The cooperative behavior of hydrogen bonds reinforces the interaction between water molecules in the hydration layers and the hydroxyl groups that are accompanied by non-polar groups in the polyalcohol molecule. This enhances the endothermic partial dehydration of the hydroxyl groups. Compared to ethylene glycol, glycerol has a longer apolar alkyl chain. This causes an increase in the endothermic effect resulting from the partial dehydration of the glycerol molecule, which gives a more positive contribution to h_2 in glycerol solutions than in ethylene glycol solutions.

4. Conclusion

Enthalpies of dilution of DMF in aqueous ethylene glycol and glycerol solutions have been determined using an isothermal calorimeter (4400 IMC) at 298.15 K. Experiential enthalpies of dilution varying with the concentration of polyalcohol were correlated with the virial expansion equation. Enthalpic interaction coefficients h_2, h_3, and h_4 in the equations are obtained, and the values of the pairwise enthalpic interaction coefficient h_2 have been discussed. In H_2O-rich region in aqueous ethylene glycol solutions, the h_2 coefficients of DMF become less positive with increasing ethylene glycol concentrations; in H_2O-rich region in aqueous glycerol solutions, the h_2 coefficients of DMF are all positive in aqueous glycerol solutions and pass through a maximum. In polyalcohol-rich region in polyalcohol solutions(ethylene glycol $\geq$2 mol Kg^{-1} and glycerol $\geq$1 mol Kg^{-1}), the trend of the h_2 coefficients of DMF in aqueous ethylene glycol solutions is similar to that of the h_2 coefficients of DMF in aqueous glycerol solutions. The enthalpic pair interaction coefficients h_2 of DMF are all positive in aqueous polyalcohol solutions and pass through a maximum, respectively. In the meantime the h_2 coefficients of DMF in aqueous glycerol solutions are more positive than that in aqueous ethylene glycol solutions. The different structures of ethylene glycol and glycerol make a contribution to their different values of h_2.

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