Excess Molar Volumes for the Ternary Mixture *N*,*N*-Dimethylformamide + Methanol + Water at the Temperature 298.15 K

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Excess molar volumes for the ternary mixture *N*,*N*-dimethylformamide (DMF) + methanol + water and for the binary constituents, DMF + water, DMF + methanol and methanol + water at 298.15 K are reported. Several empirical expressions are used to predict and correlate the ternary excess molar volumes from experimental results on the constituent binaries. A pseudo binary mixture approach is used to analyze the system studied. The partial molar volumes of methanol at infinite dilution in DMF + water mixed solvent at several fixed compositions were evaluated and correlated with the composition.

Introduction

The thermodynamic properties of solution containing amides, amino acids, peptides, and their derivatives are of interest. The correlation between solute hydration and solute−solute interaction is complex (Lilley, 1994). In view of the fact that the interactions occurring between solutes in water and in amide solvent are different, it would be worthwhile to explore the effect of changing the solvent medium on molecular interactions.

Water + *N*,*N*-dimethylformamide (DMF) is a model mixed solvent which represents an environment of the protein's interiors (Lilley, 1988). Thermodynamic properties of this solution have been reported. Several studies concerning the volumetric properties of DMF + water (Chu et al., 1990; de Visser et al., 1977; Davis, 1987) have been published. Alcohols are model molecules for studying the hydrophobic interactions, because their alkyl shape and size change with the structure (Perron and Desnoyers, 1981). Because the environment of the solute affects the thermodynamic properties, it is of interesting to study the effect of the media changing from water to amide solvent on the thermodynamic properties of the alcohol. Zegers and Somsen (1984) reported the volumetric properties of DMF + alcohol mixtures. In order to give a better description of the solvation of DMF by water and by alcohol molecules in the ternary mixture DMF + alcohol + water, Zielkiewicz (1994, 1995a,b) published a series of papers on the excess molar volumes of the ternary mixtures at 313.15 K.

In this paper, the excess molar volumes for the ternary mixture DMF + methanol + water and for binary constituents DMF + water, DMF + methanol, and methanol + water at 298.15 K are reported. Several empirical expressions are used to correlate the ternary excess molar volumes from experimental results on the constituent binaries. In order to obtain some information about the correlation between alcohol + amide interactions with amide solvation, a pseudo binary mixture approach is proposed. Finally, the partial molar volumes of methanol at infinite dilution in DMF + water mixed solvent at several fixed compositions were evaluated and correlated with the composition of the DMF + water mixed solvent.

Experimental Section

DMF (analytical reagent grade, Shanghai Chemical Co.) was dried over freshly ignited Al_2O_3 for at least 48 h and fractionally distilled under reduced pressure. The product was stored over freshly ignited molecular sieves of 0.4 nm. Methanol (analytical regent grade, Shanghai Chemical) was refluxed with pieces of magnesium, fractionally distilled. The product was stored over freshly ignited molecular sieves of 0.3 nm. The purity was checked by gas chromatography, being more than 99.8%. The residual water was measured with a gas chromatograph equipped with a thermal conductivity detector. The water content was below 0.02 mass %. Water was deionized and distilled twice before use.

Densities of the pure liquids and mixtures were measured with an Anton Paar DMA 602 densimeter. Refractive indices were measured with an Abbe type refractometer (WZS-I model, made in Shanghai) with a precision of ±0.0001. The densimeter and refractometer were thermostated by a circulating-water bath with a precision of ±0.01 K.

Ternary mixtures were prepared by mixing a measured binary mixture (DMF + water at known composition) with a pure liquid (methanol, as the third component). All mixtures were prepared by mass. The compositions of the mixtures were determined by mass, their mole fraction being generally reliable to 1×10^{-4}. The sensitivity of the densimeter corresponds to a precision of symbol $\pm 1 \times 10^{-6}$ g·cm^{-3}. The reproducibility of the density estimates was found to be of the order $\pm 2 \times 10^{-5}$ g·cm^{-3}.

The measured physical properties of the pure materials together with literature values are included in Table 1. Literature values of density for pure methanol are different depending on their estimating method. Bensen's (Benson and Kiyohara, 1980) and Hales' (Hales and Ellender, 1976) values were estimated by extrapolating to the zero content of water. In spite of our precautions, the results indicate that our value is in agreement with the recommended value by Riddick et al. (1986). The literature values of density for pure DMF are different also. Our value is in better agreement with Chu's (Chu et al., 1990) value. The estimated accuracy in excess molar volume was found to be better than ±0.001 cm^3·mol^{-1}.

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Table 1. Densities, ρ, and Refractive Indices, n_D, of Pure Liquids at 298.15 K

	ρ /(g.cm^{-3})		n_D	
component	this work	literature	this work	literature
DMF	0.94403	0.944061[a]	1.4282	1.42817[e]
		0.94388[b]		1.4282[a]
methanol	0.78664	0.786350[c]	1.3265	1.32645[c]
		0.78636[d]		1.32652[e]
		0.78664[e]		

[a] Chu et al., 1990. [b] Davis, 1987. [c] Benson and Kiyohara, 1980. [d] Hales and Ellender, 1976. [e] Riddick et al., 1986.

Table 2. Densities, ρ, Excess Molar Volumes, V_m^E, at 298.15 K

x	ρ/ (g·cm^{-3})	V_m^E/ (cm^3·mol^{-1})	x	ρ/ (g·cm^{-3})	V_m^E/ (cm^3·mol^{-1})
		x DMF + (1 − x) Water			
0.0055	0.99667	−0.016	0.1783	0.99655	−0.720
0.0112	0.99649	−0.036	0.1941	0.99612	−0.772
0.0142	0.99640	−0.046	0.2042	0.99584	−0.805
0.0241	0.99620	−0.083	0.2078	0.99570	−0.816
0.0319	0.99616	−0.114	0.2361	0.99463	−0.897
0.0382	0.99614	−0.139	0.2623	0.99340	−0.961
0.0464	0.99620	−0.174	0.2907	0.99185	−1.018
0.0553	0.99630	−0.212	0.3610	0.98727	−1.110
0.0621	0.99641	−0.242	0.3651	0.98698	−1.113
0.0721	0.99657	−0.286	0.4429	0.98104	−1.130
0.0805	0.99670	−0.324	0.4623	0.97951	−1.123
0.0907	0.99685	−0.369	0.5202	0.97485	−1.076
0.0914	0.99686	−0.372	0.6582	0.96435	−0.865
0.1011	0.99698	−0.415	0.6893	0.96218	−0.803
0.1125	0.99708	−0.464	0.7392	0.95880	−0.694
0.1230	0.99713	−0.509	0.7943	0.95522	−0.558
0.1347	0.99712	−0.557	0.8240	0.95334	−0.477
0.1478	0.99704	−0.608	0.8885	0.94940	−0.288
0.1489	0.99703	−0.613	0.9235	0.94739	−0.181
0.1621	0.99682	−0.661	0.9606	0.94551	−0.078
		x Methanol + (1 − x) Water			
0.0072	0.99457	−0.017	0.2266	0.94150	−0.694
0.0165	0.99160	−0.042	0.3108	0.92282	−0.866
0.0256	0.98890	−0.068	0.4061	0.90178	−0.978
0.0344	0.98636	−0.095	0.5257	0.87610	−1.004
0.0440	0.98370	−0.125	0.6599	0.84897	−0.902
0.0502	0.98200	−0.144	0.7078	0.83960	−0.829
0.0581	0.98000	−0.171	0.7894	0.82392	−0.656
0.0661	0.97798	−0.198	0.8442	0.81380	−0.514
0.0738	0.97610	−0.224	0.8667	0.80968	−0.447
0.1003	0.96977	−0.315	0.9406	0.79688	−0.223
0.1600	0.95630	−0.509	0.9431	0.79646	−0.215
		x DMF + (1 − x) Methanol			
0.9187	0.93870	−0.133	0.4708	0.89297	−0.482
0.8784	0.93570	−0.183	0.4191	0.88534	−0.486
0.8348	0.93218	−0.229	0.3454	0.87315	−0.470
0.7875	0.92806	−0.269	0.2895	0.86280	−0.444
0.7560	0.92516	−0.294	0.2437	0.85357	−0.416
0.7172	0.92147	−0.326	0.1934	0.84254	−0.376
0.6872	0.91849	−0.350	0.1439	0.83060	−0.324
0.6544	0.91511	−0.375	0.1202	0.82443	−0.292
0.6152	0.91092	−0.407	0.0833	0.81411	−0.230
0.5465	0.90292	−0.452	0.0538	0.80510	−0.165

Results and Discussion

Excess Molar Volumes for Binary Mixtures

Excess molar volumes (V_m^E) were calculated from densities (ρ). Results of V_m^E and ρ for binary mixtures are given in Table 2. A function of the form

$$V_m^E/(\text{cm}^3\cdot\text{mol}^{-1}) = x(1-x)\sum_{i=1}^{n} B_i(2x-1)^{i-1} \qquad (1)$$

was fitted to the experimental results. Parameters of eq 1 were obtained by Powell's (1964) optimization method with eq 2 as the objective function,

$$F = \{\sum_{i=1}^{m}[V_m^E(expt)(x_i) - V_m^E(calc)(x_i)]^2/(m-n)\}^{1/2} \qquad (2)$$

where m is the number of experimental data and n the number of parameters to be used in eq 1. Parameters of eq 1 and the standard deviations (the root mean square deviation of the calculated values from experimental values) of the fitting are given in Table 3.

Figure 1 shows the comparison of the V_m^E for three binary mixtures, x DMF + (1 − x) water, x methanol + (1 − x) water and x DMF + (1 − x) methanol at 298.15 K with the literature values at 313.15 K (Zielkiewicz, 1995b). Both binary systems, DMF + water and methanol + water have nearly the same magnitude of V_m^E values, while those of DMF + methanol have a relatively smaller magnitude. These are indications that the molecular interactions between methanol + water, DMF + water are stronger than that of DMF + methanol.

A temperature effect on V_m^E is shown in Figure 1. The values of V_m^E for the binary mixture DMF + methanol at 298.15 K have greater absolute magnitudes than those at 313.15 K over the whole composition region. For the system of DMF + water, V_m^E have greater absolute values in the middle concentration area. But for the methanol + water system, the temperature effect is hardly observable.

Excess Molar Volumes for Ternary Mixtures

The experimental values of densities for the ternary system were obtained by adding the third component (methanol) to a constant ratio of the other two (DMF + water). Excess molar volumes were calculated by using the following equation.

$$V_{m,123}^E = x_1M_1(\rho^{-1} - \rho_1^{-1}) + x_2M_2(\rho^{-1} - \rho_2^{-1}) + x_3M_3(\rho^{-1} - \rho_3^{-1}) \qquad (3)$$

where M_1, M_2, and M_3 are the molar masses of components 1−3. ρ_1, ρ_2, and ρ_3 are densities of the pure components, and ρ is the density of the mixture. The values of ρ and $V_{m,123}^E$ for ternary mixtures are given in Table 4.

Several empirical methods have been suggested (Esteve et al., 1995; Bardvid et al., 1996) to estimate ternary excess properties from experimental results on the constituents. Some of the predictive methods were originally proposed to predict molar enthalpy, volume, or Gibbs free energy (Jasinski and Malanowski, 1970). Nevertheless, they should be applicable to any other excess property.

The first types of expressions are of the form of which there are no parameters of the ternary system. The ternary excess volume $V_{m,123}^E$ is the sum of the binary excess volumes of its constituents. The simplest expression is of the form

$$V_{m,123}^E/(\text{cm}^3\cdot\text{mol}^{-1}) = V_{m,12}^E(x_1,x_2) + V_{m,13}^E(x_1,x_3) + V_{m,23}^E(x_2,x_3) \qquad (4)$$

where $x_1 = 1 - x_2 - x_3$ and the values of $V_{m,ij}^E(x_i,x_j)$ being calculated according to

$$V_{m,ij}^E/(\text{cm}^3\cdot\text{mol}^{-1}) = x_ix_j\sum_k^n B_k(x_i - x_j)^{k-1} \qquad (5)$$

using values of B_k from Table 3 and at the composition (x_i, x_j).

Table 3. Fitting Parameters in Equation 1 (B_i) and the Standard Deviations (σ) of the Fitting for Three Binary Mixtures

	x DMF + $(1-x)$ methanol	x DMF + $(1-x)$ water	x methanol + $(1-x)$ water
B_1	−1.894 83	−4.383 92	−4.031 71
B_2	0.720 241	1.758 92	0.105 638
B_3	0.492 372	0.283 819	−0.214 851
B_4	−0.510 917	−1.800 05	−0.552 348
B_5	−2.677 86	0.560 583	1.783 81
B_6	0.783 466	1.760 02	1.181 20
B_7	1.352 35	0.447 975	−0.941 364
B_8		−0.894 894	−1.859 78
B_9		1.039 06	
$\sigma(V^E_m)$/ $cm^3 \cdot mol^{-1}$)	0.000 3	0.000 4	0.000 5

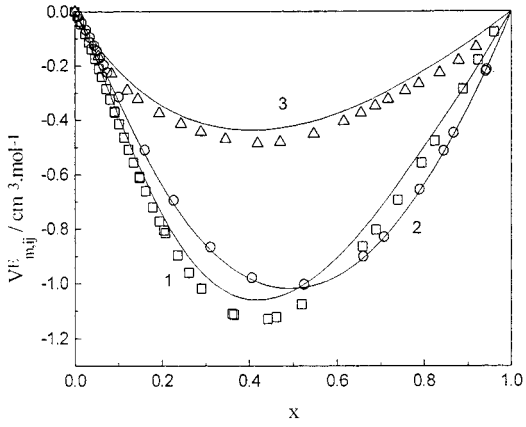

Figure 1. The excess molar volumes, $V^E_{m,ij}$, for three binary mixtures at 298.15 K and 313.15 K as a function of mole fraction x. For the system {x DMF + $(1-x)$ water}, □ represents the values at 298.15 K and curve 1 represents the values at 313.15 K; for the system {x methanol + $(1-x)$ water}, ○ is values at 298.15 K and curve 2 is values at 313.15 K; and for system {x DMF + $(1-x)$ methanol}, △ is values at 298.15 K and curve 3 is values at 313.15 K.

According to the Kohler expression (suggested by Esteve et al. (1995)), the excess molar volume for a ternary mixture is given by

$$V^E_{m,123}(cm^3 \cdot mol^{-1}) = (x_1 + x_2)^2 V^E_{m,12}(x_1^0, x_2^0) + (x_1 + x_3)^2 V^E_{m,13}(x_1^0, x_3^0) + (x_2 + x_3)^2 V^E_{m,23}(x_2^0, x_3^0) \quad (6)$$

in which, $V^E_{m,ij}$ denotes the excess molar volume for the binary mixture at composition (x_i^0, x_j^0), such that $x_i^0 = x_i/(x_i + x_j) = 1 - x_j^0 V^E_{m,ij}(x_i^0, x_j^0)$ being calculated by eq 5.

Equations 4 and 6 are symmetrical in the sense that all three binary mixtures are treated identically. Their numerical predictions do not depend on the arbitrary designation of component numbering. Contrarily, Tsao and Smith proposed an asymmetrical equation (suggested by Esteve et al. (1995))

$$V^E_{m,123}(cm^3 \cdot mol^{-1}) = x_2/(1-x_1) V^E_{m,12}(x_1, 1-x_1) + x_3/(1-x_1) V^E_{m,13}(x_1, 1-x_1) + (1-x_1) V^E_{m,23}(x_2^0, x_3^0) \quad (7)$$

in which, $x_2^0 = x_2/(1-x_1) = 1 - x_3^0$.

Hillert also suggested an asymmetrical equation (suggested by Esteve et al. (1995))

$$V^E_{m,123}(cm^3 \cdot mol^{-1}) = x_2/(1-x_1) V^E_{m,12}(x_1, 1-x_1) + x_3/(1-x_1) V^E_{m,13}(x_1, 1-x_1) + (x_2 x_3/\nu_{23}\nu_{32}) V^E_{m,23}(\nu_{23}, \nu_{32}) \quad (8)$$

where $\nu_{ij} = (1 + x_i - x_j)/2$. The standard deviations of the fits by these predictive equations are reported in Table 5.

Another type of equation is of the form that introduces ternary effect terms. Cibulka (1982) proposed the following expression

$$V^E_{m,123}(cm^3 \cdot mol^{-1}) = V^E_{m,12}(x_1,x_2) + V^E_{m,13}(x_1,x_3) + V^E_{m,23}(x_2,x_3) + x_1x_2(1 - x_1 - x_2)(C_1 + C_2x_1 + C_3x_2 + C_4{x_1}^2 + C_5{x_2}^2 + C_6x_1x_2 + ...) \quad (9)$$

in which $V^E_{m,ij}(x_i,x_j)$ were calculated by eq 5 at composition (x_i, x_j) and using values of B_i from Table 3. C_i is the fitting parameter of the ternary effect.

Singh et al. (1984) proposed an equation of the form

$$V^E_{m,123}(cm^3 \cdot mol^{-1}) = V^E_{m,12}(x_1,x_2) + V^E_{m,13}(x_1,x_3) + V^E_{m,23}(x_2,x_3) + x_1x_2(1 - x_1 - x_2)(C_1 + C_2x_1(x_2 - x_3) + C_3{x_1}^2(x_2 - x_3)^2 + C_4{x_1}^3(x_2 - x_3)^3 + ...) \quad (10)$$

Jasinski and Malanowski (1970) suggested an equation of the form

$$V^E_{m,123}(cm^3 \cdot mol^{-1}) = V^E_{m,12}(x_1,x_2) + V^E_{m,13}(x_1,x_3) + V^E_{m,23}(x_2,x_3) + x_1x_2(1 - x_1 - x_2)(C_1 + C_2(2x_1 - 1) + C_3(2x_1 - 1)^2 + ...) \quad (11)$$

In eqs 9−11, ternary effect parameters C_i are obtained by Powell's (1964) optimization method with eq 2 as the objective function, and the results are given in Table 6.

The standard deviations, $\sigma(V^E_{m,123})$, of the fits by predictive equations (eqs 4 and 6−8) and by correlative equations (eqs 9−11) are reported in Table 5. Correlative equations give lower values of $\sigma(V^E_{m,123})$ than those of predictive expressions (eqs 4 and 6−8). Among these equations, Cibulka's equation gives the lowest value of $\sigma(V^E_{m,123})$. For comparison with the experimental results, the values of $V^E_{m,123}$ calculated by Cibulka's equation (eq 9) are given in Table 4.

The asymmetrical equations give more weight to the binary constituents 1−2 and 1−3, and therefore component 1 plays the more important role. The rule for selecting the numbering of the component has been given by Pando et al. (1987). Instead of looking for the most dissimilar component in the ternary mixture, it is necessary to examine the three binary curves involved, look for the two binaries which exhibit the two largest absolute value of excess property in their maxima or minima, and designate as component 1 the common component of these two mixtures. For DMF + methanol + water ternary mixture, the two larger absolute values of V^E_m correspond to the minima of DMF + water and methanol + water. This means that following this rule water must be component 1, which coincides with the results in Table 5.

The temperature effect on $V^E_{m,123}$ for ternary mixtures can be observed by comparing our results at 298.15 K (Table 4) with the literature value at 313.15 K (Zielkiewicz, 1995b). The minima value of $V^E_{m,123}$ at 313.15 K is −1.084 $cm^3 \cdot mol^{-1}$, where the composition is $x_1 = 0.3237$ (for DMF) and $x_2 = 0.1275$ (for methanol). The minima value of $V^E_{m,123}$ at 298.15 K is −1.133 $cm^3 \cdot mol^{-1}$, where $x_1 = 0.2610$ and $x_2 = 0.1833$. These data indicate that, with increase

Table 4. Densities (ρ), Excess Molar Volumes for the Ternary Mixture ($V^E_{m,123}$), Excess Molar Volumes for Pseudo Binary Mixtures ($V^E_{m,2+13}$) at 298.15 K, and the Values Calculated by Equation 9 and by PBMA[a]

x_1	x_2	ρ/(g·cm^{-3})	$V^E_{m,123}$/(cm^3·mol^{-1}) (eq 9)		$V^E_{m,2+13}$/(cm^3·mol^{-1}) (PBMA)		x_1	x_2	ρ/(g·cm^{-3})	$V^E_{m,123}$/(cm^3·mol^{-1}) (eq 9)		$V^E_{m,2+13}$/(cm^3·mol^{-1}) (PBMA)	
						$f_m = 0.0117$							
0.0117	0.0000	0.996 48	−0.038	−0.037	0.000	0.000	0.0098	0.1640	0.956 20	−0.557	−0.554	−0.525	−0.525
0.0115	0.0177	0.991 20	−0.087	−0.085	−0.051	−0.050	0.0090	0.2265	0.942 23	−0.719	−0.719	−0.690	−0.690
0.0114	0.0268	0.988 62	−0.115	−0.112	−0.078	−0.078	0.0079	0.3212	0.920 93	−0.891	−0.897	−0.865	−0.866
0.0113	0.0355	0.986 28	−0.142	−0.139	−0.106	−0.106	0.0068	0.4174	0.899 70	−0.985	−0.991	−0.963	−0.963
0.0111	0.0442	0.984 00	−0.170	−0.166	−0.134	−0.134	0.0054	0.5405	0.873 51	−0.996	−0.999	−0.979	−0.979
0.0111	0.0527	0.981 82	−0.197	−0.194	−0.162	−0.162	0.0042	0.6417	0.852 89	−0.914	−0.921	−0.901	−0.901
0.0110	0.0611	0.979 78	−0.226	−0.222	−0.191	−0.191	0.0030	0.7452	0.832 60	−0.746	−0.754	−0.737	−0.737
0.0109	0.0698	0.977 62	−0.255	−0.251	−0.220	−0.220	0.0022	0.8074	0.820 92	−0.609	−0.609	−0.602	−0.602
0.0105	0.1031	0.969 84	−0.366	−0.363	−0.332	−0.333	0.0013	0.8852	0.806 90	−0.404	−0.393	−0.400	−0.400
						$f_m = 0.0246$							
0.0246	0.0000	0.996 20	−0.085	−0.084	0.000	0.000	0.0203	0.1779	0.953 79	−0.629	−0.628	−0.559	−0.559
0.0242	0.0200	0.990 70	−0.145	−0.140	−0.062	−0.062	0.0187	0.2429	0.939 20	−0.778	−0.781	−0.714	−0.714
0.0239	0.0302	0.988 03	−0.177	−0.171	−0.095	−0.095	0.0173	0.2984	0.926 80	−0.876	−0.880	−0.816	−0.816
0.0236	0.0430	0.984 80	−0.218	−0.212	−0.137	−0.137	0.0143	0.4202	0.899 85	−0.995	−0.998	−0.946	−0.946
0.0234	0.0506	0.982 90	−0.242	−0.236	−0.162	−0.162	0.0119	0.5181	0.878 71	−0.999	−1.006	−0.958	−0.958
0.0232	0.0594	0.980 81	−0.272	−0.265	−0.192	−0.192	0.0082	0.6676	0.847 73	−0.856	−0.885	−0.828	−0.828
0.0229	0.0714	0.977 92	−0.311	−0.304	−0.232	−0.232	0.0065	0.7379	0.834 13	−0.743	−0.766	−0.721	−0.721
0.0227	0.0785	0.976 29	−0.334	−0.327	−0.256	−0.255	0.0060	0.7580	0.830 39	−0.708	−0.724	−0.687	−0.687
0.0220	0.1081	0.969 47	−0.428	−0.423	−0.352	−0.352	0.0049	0.8021	0.822 39	−0.624	−0.620	−0.607	−0.607
						$f_m = 0.0529$							
0.0529	0.0000	0.996 27	−0.202	−0.202	0.000	0.000	0.0433	0.1825	0.954 12	−0.711	−0.713	−0.546	−0.546
0.0516	0.0262	0.989 80	−0.281	−0.276	−0.085	−0.085	0.0394	0.2566	0.937 41	−0.851	−0.859	−0.701	−0.700
0.0509	0.0388	0.986 80	−0.320	−0.313	−0.126	−0.126	0.0345	0.3488	0.916 80	−0.963	−0.971	−0.831	−0.831
0.0503	0.0504	0.984 02	−0.355	−0.348	−0.163	−0.164	0.0290	0.4519	0.894 33	−1.015	−1.016	−0.904	−0.904
0.0497	0.0622	0.981 30	−0.391	−0.384	−0.202	−0.202	0.0231	0.5644	0.870 56	−0.983	−0.983	−0.895	−0.894
0.0491	0.0726	0.978 95	−0.423	−0.416	−0.236	−0.235	0.0166	0.6874	0.845 40	−0.837	−0.849	−0.774	−0.774
0.0485	0.0849	0.976 10	−0.459	−0.453	−0.274	−0.274	0.0144	0.7285	0.837 24	−0.765	−0.777	−0.710	−0.710
0.0478	0.0976	0.973 26	−0.496	−0.490	−0.314	−0.314	0.0114	0.7838	0.826 49	−0.650	−0.659	−0.606	−0.606
0.0467	0.1182	0.968 60	−0.553	−0.549	−0.375	−0.375	0.0076	0.8556	0.813 00	−0.475	−0.474	−0.446	−0.446
						$f_m = 0.0875$							
0.0875	0.0000	0.996 82	−0.355	−0.355	0.000	0.000	0.0706	0.1926	0.953 22	−0.811	−0.818	−0.525	−0.525
0.0850	0.0279	0.990 30	−0.432	−0.427	−0.087	−0.087	0.0646	0.2614	0.937 83	−0.915	−0.923	−0.652	−0.652
0.0841	0.0390	0.987 76	−0.463	−0.457	−0.122	−0.121	0.0573	0.3446	0.919 40	−0.995	−1.000	−0.763	−0.762
0.0828	0.0528	0.984 63	−0.500	−0.494	−0.164	−0.163	0.0479	0.4528	0.895 90	−1.032	−1.026	−0.837	−0.837
0.0816	0.0670	0.981 39	−0.537	−0.532	−0.206	−0.206	0.0377	0.5687	0.871 40	−0.985	−0.976	−0.831	−0.831
0.0807	0.0769	0.979 20	−0.563	−0.558	−0.235	−0.234	0.0271	0.6902	0.846 32	−0.831	−0.836	−0.721	−0.721
0.0796	0.0901	0.976 20	−0.595	−0.592	−0.272	−0.273	0.0230	0.7370	0.836 90	−0.745	−0.752	−0.652	−0.651
0.0788	0.0995	0.974 10	−0.619	−0.616	−0.299	−0.298	0.0167	0.8088	0.822 70	−0.585	−0.592	−0.517	−0.517
0.0769	0.1212	0.969 21	−0.669	−0.668	−0.357	−0.357	0.0110	0.8739	0.810 19	−0.414	−0.420	−0.369	−0.369
						$f_m = 0.1321$							
0.1321	0.0000	0.997 12	−0.546	−0.546	0.000	0.000	0.1046	0.2079	0.951 11	−0.925	−0.933	−0.493	−0.492
0.1281	0.0303	0.990 30	−0.614	−0.611	−0.084	−0.084	0.0924	0.3008	0.930 68	−1.012	−1.017	−0.630	−0.630
0.1265	0.0423	0.987 60	−0.639	−0.638	−0.116	−0.117	0.0841	0.3633	0.917 02	−1.041	−1.041	−0.694	−0.693
0.1244	0.0586	0.984 00	−0.675	−0.673	−0.161	−0.160	0.0702	0.4687	0.894 30	−1.039	−1.031	−0.749	−0.750
0.1228	0.0703	0.981 41	−0.699	−0.698	−0.191	−0.190	0.0554	0.5804	0.870 80	−0.970	−0.961	−0.741	−0.740
0.1211	0.0835	0.978 48	−0.725	−0.726	−0.224	−0.224	0.0385	0.7086	0.844 37	−0.795	−0.794	−0.636	−0.636
0.1193	0.0970	0.975 50	−0.750	−0.753	−0.257	−0.257	0.0321	0.7573	0.834 50	−0.702	−0.701	−0.570	−0.569
0.1172	0.1126	0.972 07	−0.779	−0.783	−0.295	−0.295	0.0254	0.8081	0.824 30	−0.588	−0.587	−0.483	−0.483
0.1142	0.1355	0.967 02	−0.819	−0.825	−0.347	−0.347	0.0171	0.8705	0.811 90	−0.425	−0.425	−0.354	−0.353
						$f_m = 0.1930$							
0.1930	0.0000	0.996 18	−0.770	−0.769	0.000	0.000	0.1492	0.2271	0.947 99	−1.039	−1.044	−0.445	−0.444
0.1868	0.0325	0.989 30	−0.822	−0.821	−0.077	−0.078	0.1362	0.2946	0.933 60	−1.072	−1.072	−0.529	−0.530
0.1838	0.0477	0.986 09	−0.846	−0.844	−0.113	−0.112	0.1145	0.4068	0.909 80	−1.081	−1.067	−0.624	−0.624
0.1805	0.0647	0.982 50	−0.871	−0.870	−0.151	−0.151	0.0981	0.4916	0.891 90	−1.045	−1.026	−0.654	−0.654
0.1776	0.0797	0.979 30	−0.891	−0.892	−0.183	−0.183	0.0749	0.6121	0.866 60	−0.931	−0.919	−0.633	−0.632
0.1744	0.0964	0.975 77	−0.913	−0.915	−0.218	−0.218	0.0519	0.7309	0.841 88	−0.742	−0.740	−0.535	−0.535
0.1719	0.1096	0.973 00	−0.930	−0.933	−0.245	−0.244	0.0452	0.7657	0.834 70	−0.673	−0.671	−0.493	−0.493
0.1695	0.1221	0.970 34	−0.945	−0.948	−0.269	−0.269	0.0375	0.8058	0.826 48	−0.585	−0.582	−0.436	−0.435
0.1645	0.1476	0.964 92	−0.973	−0.977	−0.316	−0.316	0.0253	0.8689	0.813 60	−0.428	−0.424	−0.327	−0.327
						$f = 0.3195$							
0.3195	0.0000	0.990 12	−1.066	−1.065	0.000	0.000	0.2324	0.2728	0.938 42	−1.131	−1.138	−0.356	−0.356
0.3061	0.0421	0.982 49	−1.095	−1.087	−0.074	−0.074	0.2017	0.3687	0.919 62	−1.104	−1.105	−0.431	−0.431
0.3002	0.0605	0.979 07	−1.104	−1.097	−0.103	−0.103	0.1773	0.4452	0.904 33	−1.059	−1.059	−0.467	−0.468
0.2939	0.0802	0.975 38	−1.112	−1.106	−0.132	−0.132	0.1443	0.5484	0.883 40	−0.966	−0.968	−0.485	−0.484
0.2883	0.0976	0.972 07	−1.117	−1.114	−0.156	−0.156	0.1148	0.6407	0.864 40	−0.851	−0.855	−0.468	−0.468
0.2831	0.1140	0.968 96	−1.122	−1.120	−0.178	−0.178	0.0752	0.7648	0.838 40	−0.643	−0.645	−0.392	−0.392
0.2774	0.1320	0.965 52	−1.126	−1.126	−0.201	−0.201	0.0628	0.8036	0.830 10	−0.561	−0.564	−0.352	−0.352
0.2725	0.1473	0.962 60	−1.128	−1.131	−0.220	−0.220	0.0472	0.8522	0.819 56	−0.446	−0.453	−0.288	−0.287
0.2610	0.1833	0.955 70	−1.133	−1.138	−0.263	−0.262	0.0315	0.9014	0.808 70	−0.311	−0.327	−0.206	−0.206
σ (V^E_m)/(cm^3·mol^{-1})											0.0066		0.0003

[a] $\sigma(V^E_m)$: standard deviations for fitting the excess molar volumes by eq 9 and by the pseudo binary mixture approach (PBMA).

Table 5. Comparison of the Standard Deviations (σ) for Fitting the Excess Molar Volumes for Ternary Mixture DMF + Methanol + Water by Several Equations

eq	$\sigma(V_m^E)$/(cm^3·mol^{-1})	eq	$\sigma(V_m^E)$/(cm^3·mol^{-1})
eq 4	0.0322	eq 9	0.0066
eq 6	0.0390	eq 10, 1 (water), 2 (DMF), 3 (methanol)	0.0082
eq 7, 1 (water), 2 (DMF), 3 (methanol)	0.0814	eq 11, 1 (water)	0.0072
eq 8, 1 (water), 2 (DMF), 3 (methanol)	0.0241	PBMA[a]	0.0003

[a] The mean values of the standard deviations for fitting all the pseudo binary mixtures.

Table 6. Fitting Parameters C_i of Equations 9−11

param	eq 9	eq 10 1 (water), 2 (DMF), 3 (methanol)	eq 11 1 (water)
C_1	−0.456 325	2.394 27	3.612 05
C_2	3.527 41	−6.980 18	1.706 04
C_3	19.6411	10.2821	3.415 28
C_4	10.1880	−31.3470	1.721 74
C_5	−14.3075	180.197	−4.656 88
C_6	−40.3565	−595.365	0.005 923

in temperature, the absolute value of the minima for $V_{m,123}^E$ decreases.

Pseudo Binary Mixture Approach

In measuring densities of the ternary system, mixtures were made of several pseudo binary mixtures in which component 2 (pure methanol) was added to the binary mixture of components 1 (DMF) and 3 (water) having a fixed composition $f_m = x_1/(1 - x_2)$. There are three reasons to use a pseudo binary mixture approach (PBMA) to analyze the volume data. Firstly, in DMF + methanol + water, molecular interactions give rise to the asymmetric volume effect, which causes the standard deviation of ternary fits (Table 5) to be higher than those of binary fits (Table 3). Among the three binary mixtures, DMF + water and DMF + methanol show the largest and smallest negative values of V_m^E, respectively. So, we pay more attention to observation of the effect of the composition changing in DMF + water mixed solvents on the ternary excess volumes and to exploration of improved approaches. Secondly, the aqueous solution of amides is a model mixed solvent to represent an environment of protein's interiors (Lilley, 1988). Alcohols are model molecules for study of hydrophobic interactions. The interactions occurring between solutes in water and in amidic solvent are different. It is our goal to get some information about the effect of the media changing from water to amide solvent on the thermodynamic properties of alcohols. Thirdly, in the aqueous solution of some amides (DMF, *N*-methylformamide, and *N*,*N*-dimethylacetamide), a minimum value of partial molar volume of the amide exists in the water rich region (Davis and Hernandez, 1995). In this region, hydrogen bond interaction and hydrophobic interaction have an observable influence on the volume effect. For the ternary mixture, the minima of $V_{m,123}^E$ shift toward the water rich region. So, we measured more data in the water rich region to explore some information.

In a ternary mixture, the molar mass M_{13} of the mixed solvent [f_m(DMF) + (1 − f_m) water], which at a fixed composition f_m was the mean molar mass of its constituents.

$$M_{13} = f_m M_1 + (1 - f_m) M_3 \tag{12}$$

According to mass conservation,

$$x_1 M_1 + x_2 M_2 + (1 - x_1 - x_2) M_3 = (1 - x_2^0) M_{13} + x_2^0 M_2 \tag{13}$$

Note that the mole fraction (x_2^0) of alcohol in the pseudo binary mixture is equal to x_2, where M_1, M_2, and M_3 are the molar masses of the components. The excess molar volume $V_{m,2+13}^E$ were calculated from measured densities by eq 14, where ρ_{13} is the density of DMF + water mixed

$$V_{m,2+13}^E = (1 - x_2) M_{13} (\rho^{-1} - \rho_{13}^{-1}) + x_2 M_2 (\rho^{-1} - \rho_2^{-1}) \tag{14}$$

solvent at its fixed composition. The values of ρ and $V_{m,2+13}^E$ are given in Table 4. The values of $V_{m,123}^E$ can be obtained from $V_{m,2+13}^E$ by eq 15, where $V_{m,13}^E$ is the excess

$$V_{m,123}^E = V_{m,2+13}^E + (1 - x_2) V_{m,13}^E \tag{15}$$

molar volume of the binary mixture. For DMF + water mixed solvents at their several fixed compositions (f_m) used in this work, the values of $V_{m,13}^E$ are (−0.038, −0.085, −0.202, −0.355, −0.546, −0.770, and −1.066) cm^3·mol^{-1}, which can be found in Table 4. The values of $V_{m,2+13}^E$ were fitted by eq 1 just as the binary mixtures were. The fitting parameters are given in Table 7. The standard deviations of the fits by PBMA for every pseudo binary mixtures are included in Table 7. The mean values of the standard deviations for all the pseudo binary mixtures (marked by σ(PBMA)) is compared with other correlative equations in Table 5. It shows clearly that the pseudo binary mixture approach gives the minimum value of the standard deviation. The values of $V_{m,2+13}^E$ calculated by PBMA from the parameters in Table 7 are included in Table 4. They are in good agreement with the experimental data.

In Figure 2, one of the curves shows the dependence of B_1 (in Table 7) on f_m. The meaning of B_1 is the excess volume $V_{m,2+13}^E$ when $x_2 = 0.5$. The curve increases (its absolute value decreases) with the increase of f_m. This is an indication that the interaction between methanol and the mixed solvent (water + DMF) becomes weaker as f_m increase.

Table 7. Fitting Parameters (B_i) of Equation 1 for Pseudo Binary Mixtures [f_m DMF + (1 − f_m) Water] + Methanol, and the Standard Deviations (σ) of the Fitting at Their Several Fixed Compositions f_m

f_m	0.0117	0.0246	0.0529	0.0875	0.1321	0.1930	0.3195
B_1	−3.947 15	−3.846 86	−3.646 49	−3.385 42	−3.017 27	−2.619 39	−1.924 56
B_2	0.071 339	0.292 183	0.039 754	−0.039 781	−0.117 080	−0.195 67	−0.303 149
B_3	0.028 327	0.387 073	0.099 127	0.082 366	−0.149 395	−0.012 824	−0.193 483
B_4	0.333 117	−0.176 671	0.440 044	0.381 930	0.107 563	0.059 281	−0.453 923
B_5	0.380 701	−0.975 245	−0.096 480	−0.042 921	0.156 569	−0.215 002	0.015 107
B_6	−1.280 10	−1.583 70	−0.955 621	−0.548 846	−0.199 225	−0.266 457	0.610 452
$\sigma(V_m^E)$/(cm^3·mol^{-1})	0.0003	0.0003	0.0003	0.0003	0.0003	0.0002	0.0003

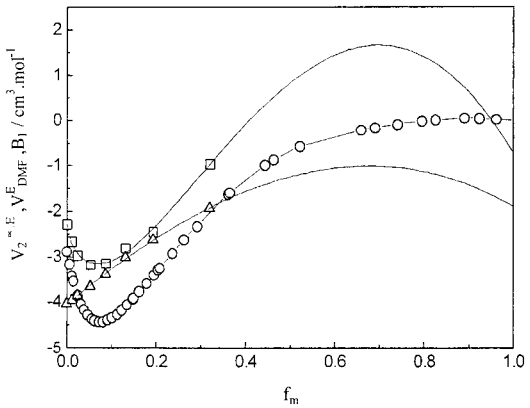

Figure 2. Excess partial molar volumes of methanol at infinite dilution ($V_2^{\infty,E}$), □; excess partial molar volumes of DMF in DMF + water binary mixture, (V_{DMF}^E), ○; and the fitting parameters B_1 for the pseudo binary mixture approach, △, as a function of f_m.

Table 8. Partial Molar Volumes at Infinite Dilution for Methanol (V_2^∞) in [f_m DMF + (1 − f_m) Water] Mixed Solvents at Their Several Fixed Composition f_m

f_m	V_2^∞/(cm^3·mol^{-1})	f_m	V_2^∞/(cm^3·mol^{-1})
0.0	38.454	0.1321	37.931
0.0117	38.070	0.1930	38.288
0.0246	37.766	0.3195	39.776
0.0529	37.565	1.0	39.998
0.0875	37.594		

Table 9. Fitting Parameters (A_i) of Equation 17, the Standard Deviations of the Fitting (σ), and the Correlative Coefficients (r)

A_1	38.4633	A_5	−64.5679
A_2	−2.82449	σ/(cm^3·mol^{-1})	0.049
A_3	−21.2940	r	0.9983
A_4	90.2212		

Partial Molar Volumes of Methanol in Pseudo Binary Mixture

In our mixture, the values $V_{m,2+13}^E$ are smooth functions of x_2. By using the parameters in Table 7, the partial molar volumes V_2 of methanol in pseudo binary mixtures can be calculated by eq 16. When x_2 approaches zero, the partial

$$V_2 = V_{m,2+13}^E + V_2^0 + (1 - x_2)(\partial V_{m,2+13}^E/\partial x_2)_{T,P} \quad (16)$$

molar volume of methanol at infinite dilution (V_2^∞) is obtained. The properties of solute at infinite dilution reflects, at least to a good approximation, how the solute interacts with the solvent. The values of V_2^∞ in DMF + water mixed solvents with fixed composition f_m were evaluated and listed in Table 8. Figure 2 presents the values of $V_2^{\infty,E}$, the excess partial molar volume of methanol at infinite dilution, as a function of f_m. The values of $V_2^{\infty,E}$ decease firstly with the f_m increase, and then reach to a minimum, where $f_m = 0.0529$. After that minimum, $V_2^{\infty,E}$ increases with an f_m increase. Another curve in Figure 2 shows the excess partial molar volumes of DMF, V_{DMF}^E, in water + DMF binary mixture as a function of f_m. It has a minima point at the region where f_m is about 0.072. The interesting thing is that this minimum correspond to the minimum of $V_2^{\infty,E}$ in its concentration neighborhood. In this region, the DMF + water mixed solvent is in a close packing state (Davis and Hernandez, 1995; Chu et al., 1990). The curve of V_{DMF}^E is a reflection of DMF hydration. The values of $V_2^{\infty,E}$ are reflections for the interactions of the solvated solute with the mixed solvent. The dependence of $V_2^{\infty,E}$ on V_{DMF}^E at different f_m is a reflection of the correlation between solute solvation and solute (methanol)−solute (DMF) interactions. The dependence of the B_1 curve on the V_{DMF}^E curve, as well as on f_m, is a reflection of the effect of media changing on methanol's property.

An empirical equation of the form

$$V_2^\infty/(\text{cm}^3\cdot\text{mol}^{-1}) = \sum_{i=1} A_i f_m^{(i-1)/2} \quad (17)$$

was used to fit the values of V_2^∞ with f_m. The fitting parameters A_i in eq 17, the standard deviations, and the correlative coefficients of the fits are given in Table 9. The correlation by eq 17 is in better agreement with the experimental results.

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