Densities and Volumetric Properties of Binary and Ternary Liquid Mixtures of Water (1) + Acetonitrile (2) + Dimethyl Sulfoxide (3) at Temperatures from (293.15 to 333.15) K and at Ambient Pressure (81.5 kPa)

Hossein A. Zarei,* M. Zare Lavasani, and H. Iloukhani

Faculty of Chemistry, Bu-Ali Sina University, Hamedan, Iran

Liquid densities, ρ, of the ternary mixtures of water (1) + acetonitrile (2) + dimethyl sulfoxide (DMSO) (3) and their constituent binaries were measured at temperatures (293.15, 303.15, 313.15, 323.15, and 333.15) K and at ambient pressure (81.5 kPa) as a function of mole fraction. The excess molar volumes, V_m^E, partial excess molar volumes, V_i^E, and their values at infinite dilution, $V_i^{E,0}$, for binary and ternary liquid mixtures and thermal expansion coefficients, α, of the pure component were calculated. The excess molar volumes are negative over the whole mole fraction range for binary mixtures of water (1) + acetonitrile (2) and water (1) + DMSO (3) and increase with increasing temperatures from (293.15 to 333.15) K. The excess molar volumes of acetonitrile (2) + DMSO (3) are negative and decrease with increasing temperatures from (293.15 to 333.15) K. The excess molar volumes are negative over the whole mole fraction range for the ternary mixture at all temperatures and decrease in the DMSO- and acetonitrile-rich region and increase in the water-rich region. The excess molar volumes were correlated with the Redlich–Kister equation and the Cibulka equation for the binary and ternary system, respectively. The excess molar volumes, V_m^E, were compared with values from the literature in the region of overlap.

Introduction

Excess quantities are useful measures of the effects of molecular interactions on thermodynamic properties of liquid mixtures. The binary mixtures of water + acetonitrile, water + DMSO, and acetonitrile + DMSO have been frequently used as a medium for the study of complexation, electrochemical oxidation, and ion salvation.[1–6] Review of the literature shows that volumetric studies of binary mixtures of water + acetonitrile, water + DMSO, and acetonitrile + DMSO have been done by several authores,[7–36] but the volumetric properties of the ternary mixtures of water + acetonitrile + DMSO have not been reported in the literature.

We report here densities, ρ, excess molar volumes, V_m^E, and partial excess molar volumes, V_i^E, and their values at infinite dilution, $V_i^{E,0}$, for ternary mixture of water (1) + acetonitrile (2) + DMSO (3) and their constituent binaries over the entire range of composition at temperatures (293.15, 303.15, 313.15, 323.15, and 333.15) K and at ambient pressure (81.5 kPa). The excess molar volumes were correlated with the Redlich–Kister equation and the Cibulka equation for the binary and ternary system, respectively. The excess molar volumes, V_m^E, were compared with values from the literature in the region of overlap.

Experimental

Materials. The acetonitrile gradient for liquid chromatography and DMSO dried (max. 0.05 % H_2O) were high purity grade reagents from Merck. Bidistilled water was used to prepare the sample mixtures. The densities and refractive indices of pure components were compared with those reported in the literature, and they are in good agreement. Prior to use the chemicals were degassed by heating and cooling. The purity grade, densities, refractive indices, and thermal expansion coefficients of pure components are given in Table 1.

Measurements. The mixtures were prepared just before use by mass using a Mettler AB 204-N balance with an uncertainty of $\pm 1 \cdot 10^{-4}$ g. Conversion to molar mass was based on the relative atomic mass table of 1996 issued by IUPAC.[41] The average uncertainty in the mole fraction is estimated to be $\pm 1.5 \cdot 10^{-5}$. The densities of the pure components and mixtures were measured using an Anton Paar DMA 4500 oscillating u-tube density meter, provided with automatic viscosity correction. The temperature in the cell was regulated to $\pm$ 0.01 K with a solid state thermostat. Uncertainty in the density was $\pm 1 \cdot 10^{-5}$ g·cm^{-3}. The repeatability of the density measurements was $\pm 1 \cdot 10^{-5}$ g·cm^{-3}. Refractive indices were measured at 298.15 K using a thermostatted Abbé refractometer. The uncertainty of the refractive index is in the order of $\pm$ 0.0002 units.

Results and Discussion

The experimental values of the densities, ρ, for pure compounds and for the binary and ternary mixtures were measured at temperatures (293.15, 303.15, 313.15, 323.15, and 333.15) K and at ambient pressure (81.5 kPa), and they are given in Tables 1 to 5. The excess molar volumes, V_m^E, of the binary and ternary mixtures were calculated from the densities using the following equation

$$V_m^E/\mathrm{cm}^3 \cdot \mathrm{mol}^{-1} = \sum_{i=1}^{n} x_i M_i (\rho^{-1} - \rho_i^{-1}) \qquad (1)$$

where M_i and ρ_i are the molecular mass and density of the pure component, respectively; ρ is the density of a mixture; and n is the number of components.

* Corresponding author. E-mail: zareih@basu.ac.ir.

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Table 1. Sources, Purity Grades, Densities, ρ, Refractive Indices, n_D, and Thermal Expansion Coefficients, α, of the Pure Components

component	purity	T/K	ρ/(g·cm^{-3})		n_D		$10^4\alpha$/K^{-1}
	purity/100 w		exptl	lit.	exptl	lit.	
aetonitrile	99.8 %	293.15	0.78197	0.781859[17]	1.3417[a]	1.3413[39]	13.74
		303.15	0.77115	0.771146[12]			14.12
		313.15	0.76020	0.7607[7]			14.49
		323.15	0.74912	0.7496[7]			14.89
		333.15	0.73787				15.39
DMSO	99.5 %	293.15	1.10041	1.10040[23]	1.4767[a]	1.4769[13]	9.14
		303.15	1.09037	1.09038[28]			9.20
		313.15	1.08034	1.0803[40]			9.23
		323.15	1.0703	1.0703[40]			9.38
		333.15	1.06027	1.06164[24]			9.44
water		293.15	0.99820	0.998203[37]	1.3326[a]	1.332503[38]	2.08
		303.15	0.99564	0.995645[37]			3.03
		313.15	0.99221	0.992212[37]			3.85
		323.15	0.98803	0.988030[37]			4.58
		333.15	0.98319	0.983191[37]			5.24

[a] At 298.15 K.

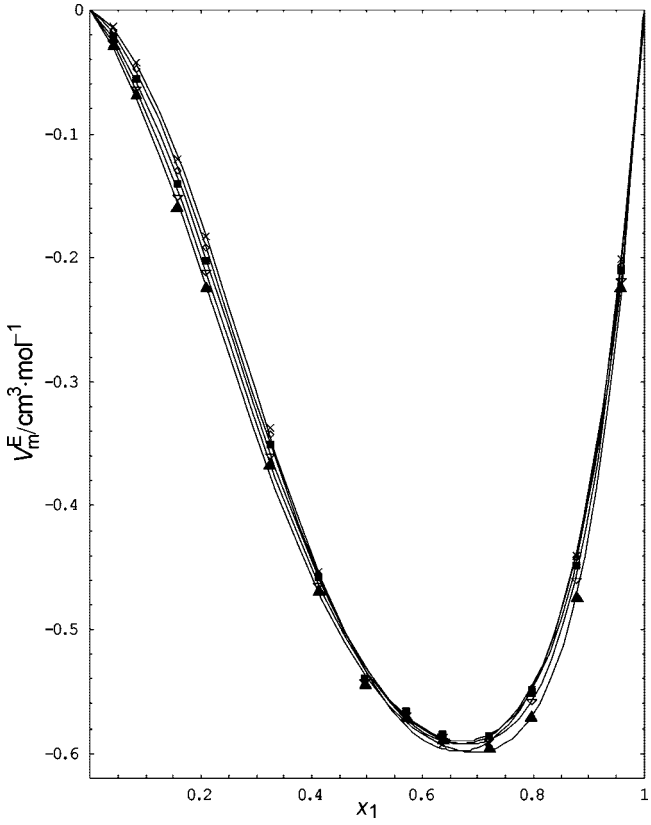

Figure 1. Experimental excess molar volumes for the water (1) + acetonitrile (2) mixture at different temperatures. ▲, 293.15 K; ∇, 303.15 K; ■, 313.15 K; ◇, 323.15 K; ×, 333.15 K. Solid curves represent the values calculated from eq 2 with coefficients from Table 6.

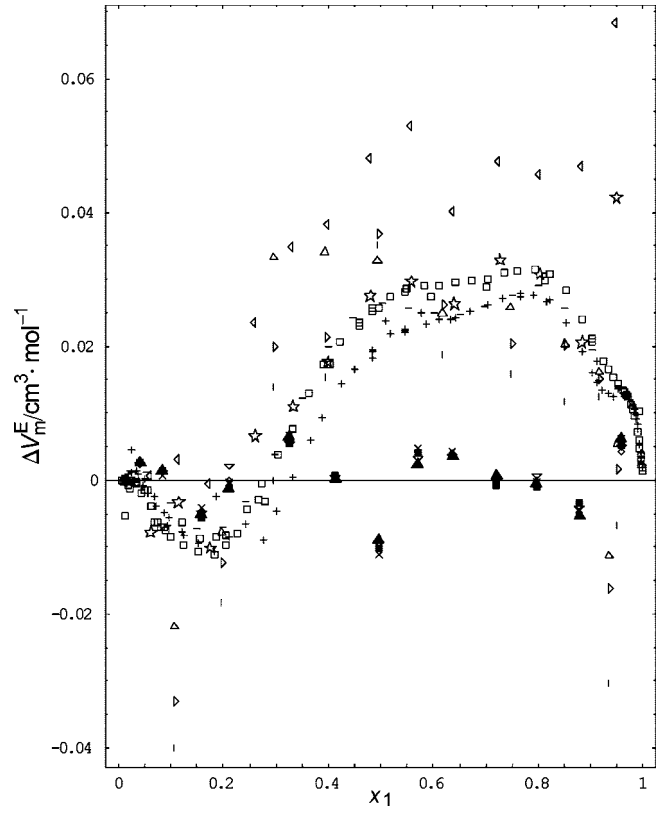

Figure 2. Differences ΔV_m^E between experimental and literature data and the fitted equation for the water (1) + acetonitrile (2) mixture at different temperatures. This work: ▲, 293.15 K; ∇, 303.15 K; ■, 313.15 K; ◇, 323.15 K; × , 333.15 K; +, 293.15 K, ref 17; Δ, 303.15 K, ref 7; ☆, 303.15 K, ref 8; –, 303.15 K, ref 12; □, 303.15 K, ref 17; open left triangle, 313.15 K, ref 7; open right triangle, 313.15 K, ref 8; |, 323.15 K, ref 7.

The uncertainty in the excess molar volume is determined by the uncertainties in the mole fraction, density, and molecular mass. The average uncertainty in V_m^E resulting from the propagation law of errors is $\pm 2 \cdot 10^{-3}$ cm^3·mol^{-1}. The excess molar volumes for binary mixtures water (1) + acetonitrile (2), water (1) + DMSO (3), and acetonitrile (2) + DMSO (3) and the ternary mixture water (1) + acetonitrile (2) + DMSO (3) at different temperatures are recorded in Tables 2 to 5 and graphically represented in Figures 1, 3, 5, and 6.

The excess molar volumes for water (1) + acetonitrile (2) are negative and increase with increasing temperatures from (293.15 to 333.15) K. The excess molar volumes are in agreement with reported data in the region of overlap. The differences between experimental and literature data and the fitted equation are graphically represented in Figure 2. The excess Gibbs energy and enthalpy of this system are both positive,[11,14,19] and they formed a minimum boiling point azeotrope,[9] whereas the excess molar volume is negative. Considering these observations, the negative values of V_m^E over the entire range of mole fraction may be attributed to the difference in size and shape of the component molecules.

The excess molar volumes of water (1) + DMSO (3) are negative and increase with increasing temperatures from (293.15 to 333.15) K. The excess molar volumes are in agreement with

Table 2. Densities (ρ), Excess Molar Volumes (V_m^E), and Partial Excess Molar Volumes (V_i^E) for Binary Mixtures of Water (1) + Acetonitrile (2) at Different Temperatures of (293.15 to 333.15) K

x_1	ρ / g·cm^{-3}	V_m^E / cm^3·mol^{-1}	V_1^E / cm^3·mol^{-1}	V_2^E / cm^3·mol^{-1}
		293.15 K		
0.0000	0.78197		−0.67	0.00
0.0417	0.7856	−0.029	−0.84	0.00
0.0833	0.78962	−0.069	−1.01	0.01
0.1568	0.79767	−0.16	−1.22	0.04
0.2095	0.80401	−0.225	−1.28	0.06
0.3247	0.81996	−0.368	−1.20	0.02
0.4127	0.83427	−0.47	−1.02	−0.08
0.4960	0.84971	−0.545	−0.86	−0.22
0.5704	0.86478	−0.572	−0.74	−0.35
0.6361	0.88012	−0.59	−0.66	−0.47
0.7201	0.90294	−0.597	−0.56	−0.68
0.7961	0.92699	−0.571	−0.44	−1.10
0.8788	0.95673	−0.475	−0.23	−2.17
0.9573	0.98472	−0.225	−0.04	−4.45
1.0000	0.99820		0.00	−6.54
		303.15 K		
0.0000	0.77115		−0.57	0.00
0.0417	0.77479	−0.025	−0.76	0.00
0.0833	0.77883	−0.062	−0.94	0.02
0.1568	0.78695	−0.149	−1.18	0.05
0.2095	0.79333	−0.21	−1.27	0.07
0.3247	0.80963	−0.359	−1.21	0.04
0.4127	0.82427	−0.463	−1.04	−0.06
0.4960	0.84011	−0.541	−0.86	−0.20
0.5704	0.85557	−0.567	−0.74	−0.35
0.6361	0.87132	−0.585	−0.65	−0.48
0.7201	0.89474	−0.589	−0.54	−0.71
0.7961	0.91947	−0.557	−0.41	−1.12
0.8788	0.95035	−0.459	−0.22	−2.15
0.9573	0.98043	−0.217	−0.04	−4.29
1.0000	0.99564		0.00	−6.26
		313.15 K		
0.0000	0.7602		−0.46	0.00
0.0417	0.76385	−0.021	−0.67	0.00
0.0833	0.76791	−0.055	−0.88	0.02
0.1568	0.77609	−0.14	−1.15	0.06
0.2095	0.7826	−0.203	−1.26	0.08
0.3247	0.79911	−0.351	−1.22	0.06
0.4127	0.81405	−0.458	−1.06	−0.04
0.4960	0.83025	−0.54	−0.88	−0.19
0.5704	0.84608	−0.566	−0.74	−0.35
0.6361	0.86222	−0.584	−0.64	−0.50
0.7201	0.88622	−0.586	−0.52	−0.74
0.7961	0.91161	−0.551	−0.39	−1.16
0.8788	0.94352	−0.448	−0.21	−2.14
0.9573	0.97545	−0.21	−0.04	−4.18
1.0000	0.99221		0.00	−6.04
		323.15 K		
0.0000	0.74912		−0.35	0.00
0.0417	0.75277	−0.017	−0.59	0.01
0.0833	0.75684	−0.048	−0.82	0.02
0.1568	0.76506	−0.13	−1.13	0.06
0.2095	0.77162	−0.192	−1.25	0.09
0.3247	0.78838	−0.343	−1.24	0.08
0.4127	0.8036	−0.455	−1.08	−0.02
0.4960	0.82014	−0.541	−0.89	−0.17
0.5704	0.83632	−0.568	−0.75	−0.34
0.6361	0.85282	−0.586	−0.64	−0.50
0.7201	0.87738	−0.586	−0.51	−0.77
0.7961	0.90339	−0.548	−0.38	−1.19
0.8788	0.93628	−0.442	−0.20	−2.16
0.9573	0.96987	−0.206	−0.04	−4.10
1.0000	0.98803		0.00	−5.88
		333.15 K		
0.0000	0.73787		−0.24	0.00
0.0417	0.74152	−0.013	−0.51	0.01
0.0833	0.7456	−0.042	−0.76	0.02
0.1568	0.75385	−0.12	−1.11	0.07
0.2095	0.76047	−0.183	−1.25	0.10
0.3247	0.77743	−0.337	−1.27	0.10
0.4127	0.79291	−0.454	−1.11	0.01
0.4960	0.80977	−0.544	−0.92	−0.15
0.5704	0.82629	−0.573	−0.76	−0.33
0.6361	0.84313	−0.592	−0.65	−0.51
0.7201	0.86822	−0.591	−0.51	−0.80
0.7961	0.89484	−0.549	−0.37	−1.23
0.8788	0.92867	−0.44	−0.19	−2.19
0.9573	0.96364	−0.201	−0.04	−4.07
1.0000	0.98319		0.00	−5.77

Table 3. Densities (ρ), Excess Molar Volumes (V_m^E), and Partial Excess Molar Volumes (V_i^E) for Binary Mixtures of Water (1) + DMSO (3) at Different Temperatures of (293.15 to 333.15) K

x_1	ρ / g·cm^{-3}	V_m^E / cm^3·mol^{-1}	V_1^E / cm^3·mol^{-1}	V_3^E / cm^3·mol^{-1}
		293.15 K		
0.0000	1.10041		−2.08	0.00
0.0568	1.10094	−0.128	−2.26	0.00
0.1605	1.10191	−0.354	−2.17	−0.01
0.2252	1.10254	−0.491	−2.06	−0.04
0.3187	1.10326	−0.673	−1.91	−0.09
0.3953	1.10354	−0.803	−1.76	−0.18
0.4582	1.10348	−0.896	−1.59	−0.30
0.5473	1.10205	−0.979	−1.25	−0.65
0.6473	1.09720	−0.981	−0.76	−1.39
0.7213	1.08955	−0.894	−0.39	−2.19
0.7997	1.07548	−0.707	−0.10	−3.13
0.8828	1.05112	−0.412	0.04	−3.81
0.9632	1.01698	−0.106	0.02	−3.36
1.0000	0.99820		0.00	−2.45
		303.15 K		
0.0000	1.09037		−2.09	0.00
0.0568	1.09097	−0.127	−2.24	0.00
0.1605	1.09210	−0.352	−2.16	−0.01
0.2252	1.09283	−0.487	−2.05	−0.03
0.3187	1.09373	−0.667	−1.89	−0.10
0.3953	1.09431	−0.801	−1.73	−0.19
0.4582	1.09425	−0.885	−1.55	−0.32
0.5473	1.09311	−0.964	−1.21	−0.67
0.6473	1.08867	−0.961	−0.73	−1.40
0.7213	1.08152	−0.873	−0.38	−2.16
0.7997	1.06831	−0.688	−0.09	−3.05
0.8828	1.04547	−0.401	0.03	−3.70
0.9632	1.01346	−0.106	0.01	−3.31
1.0000	0.99564		0.00	−2.50
		313.15 K		
0.0000	1.08034		−2.09	0.00
0.0568	1.08101	−0.127	−2.23	0.00
0.1605	1.08226	−0.35	−2.15	−0.01
0.2252	1.0831	−0.486	−2.05	−0.03
0.3187	1.08418	−0.665	−1.88	−0.10
0.3953	1.08489	−0.797	−1.71	−0.19
0.4582	1.08495	−0.878	−1.52	−0.33
0.5473	1.08403	−0.953	−1.17	−0.69
0.6473	1.07997	−0.946	−0.70	−1.40
0.7213	1.07328	−0.857	−0.36	−2.14
0.7997	1.06087	−0.674	−0.09	−2.99
0.8828	1.03940	−0.394	0.03	−3.61
0.9632	1.00919	−0.106	0.01	−3.25
1.0000	0.99221		0.00	−2.48
		323.15 K		
0.0000	1.07030		−2.09	0.00
0.0568	1.07103	−0.127	−2.22	0.00
0.1605	1.07241	−0.351	−2.15	−0.01
0.2252	1.07332	−0.485	−2.04	−0.04
0.3187	1.07452	−0.663	−1.86	−0.10
0.3953	1.07537	−0.794	−1.69	−0.20
0.4582	1.07554	−0.872	−1.50	−0.34
0.5473	1.07480	−0.944	−1.15	−0.70
0.6473	1.07108	−0.934	−0.68	−1.41
0.7213	1.06482	−0.844	−0.34	−2.13
0.7997	1.05313	−0.663	−0.08	−2.96
0.8828	1.03281	−0.387	0.03	−3.54
0.9632	1.00392	−0.1	0.01	−3.15
1.0000	0.98803		0.00	−2.38
		333.15 K		
0.0000	1.06027		−2.09	0.00
0.0568	1.06104	−0.127	−2.23	0.00
0.1605	1.0625	−0.349	−2.14	−0.01
0.2252	1.06349	−0.484	−2.03	−0.04
0.3187	1.06479	−0.661	−1.85	−0.11
0.3953	1.06574	−0.79	−1.67	−0.21
0.4582	1.06600	−0.867	−1.48	−0.35
0.5473	1.06541	−0.935	−1.13	−0.71
0.6473	1.06200	−0.922	−0.66	−1.41
0.7213	1.05612	−0.832	−0.33	−2.13
0.7997	1.04511	−0.654	−0.07	−2.95
0.8828	1.02492	−0.361	0.04	−3.50
0.9632	0.99873	−0.107	0.01	−3.04
1.0000	0.98319		0.00	−2.22

Table 4. Densities (ρ), Excess Molar Volumes (V_m^E), and Partial Excess Molar Volumes (V_i^E) for Binary Mixtures of Acetonitrile (2) + DMSO (3) at Different Temperatures of (293.15 to 333.15) K

x_2	ρ / g·cm^{-3}	V_m^E / cm^3·mol^{-1}	V_2^E / cm^3·mol^{-1}	V_3^E / cm^3·mol^{-1}
		293.15 K		
1.0000	0.78197		0.00	−1.33
0.9330	0.81130	−0.074	−0.02	−0.86
0.8337	0.85162	−0.129	−0.07	−0.45
0.7579	0.88041	−0.152	−0.11	−0.29
0.6896	0.90494	−0.159	−0.14	−0.21
0.5790	0.94239	−0.163	−0.17	−0.15
0.5273	0.95900	−0.162	−0.19	−0.13
0.4529	0.98191	−0.153	−0.21	−0.11
0.3723	1.00556	−0.142	−0.25	−0.08
0.2996	1.02583	−0.123	−0.31	−0.05
0.1751	1.05854	−0.085	−0.43	−0.01
0.1195	1.07232	−0.061	−0.48	0.00
0.0563	1.08732	−0.023	−0.51	0.00
0.0000	1.10041		−0.49	0.00
		303.15 K		
1.0000	0.77115		0.00	−1.56
0.9330	0.80060	−0.088	−0.02	−1.01
0.8337	0.84100	−0.151	−0.08	−0.54
0.7579	0.86988	−0.181	−0.12	−0.36
0.6896	0.89448	−0.190	−0.16	−0.27
0.5790	0.93208	−0.199	−0.20	−0.19
0.5273	0.94869	−0.195	−0.22	−0.16
0.4529	0.97168	−0.187	−0.26	−0.13
0.3723	0.99538	−0.172	−0.31	−0.09
0.2996	1.01569	−0.150	−0.38	−0.06
0.1751	1.04848	−0.104	−0.52	−0.02
0.1195	1.06227	−0.074	−0.58	−0.00
0.0563	1.07727	−0.029	−0.62	0.00
0.0000	1.09037		−0.62	0.00
		313.15 K		
1.0000	0.76020		0.00	−1.80
0.9330	0.78976	−0.102	−0.02	−1.18
0.8337	0.83029	−0.177	−0.09	−0.65
0.7579	0.85927	−0.213	−0.14	−0.44
0.6896	0.88396	−0.226	−0.18	−0.33
0.5790	0.92168	−0.237	−0.24	−0.23
0.5273	0.93836	−0.234	−0.26	−0.20
0.4529	0.96140	−0.223	−0.31	−0.15
0.3723	0.98518	−0.206	−0.38	−0.11
0.2996	1.00554	−0.179	−0.45	−0.07
0.1751	1.03838	−0.123	−0.61	−0.02
0.1195	1.05221	−0.089	−0.68	−0.01
0.0563	1.06722	−0.035	−0.74	0.00
0.0000	1.08034		−0.75	0.00
		323.15 K		
1.0000	0.74912		0.00	−2.05
0.9330	0.77879	−0.116	−0.02	−1.37
0.8337	0.81948	−0.206	−0.10	−0.77
0.7579	0.84857	−0.248	−0.16	−0.53
0.6896	0.87336	−0.266	−0.21	−0.40
0.5790	0.91122	−0.280	−0.28	−0.28
0.5273	0.92796	−0.277	−0.31	−0.23
0.4529	0.95109	−0.265	−0.37	−0.18
0.3723	0.97494	−0.244	−0.45	−0.12
0.2996	0.99535	−0.211	−0.54	−0.08
0.1751	1.02838	−0.151	−0.72	−0.02
0.1195	1.04211	−0.102	−0.80	−0.01
0.0563	1.05717	−0.043	−0.87	0.00
0.0000	1.07030		−0.89	0.00
		333.15 K		
1.0000	0.73787		0.00	−2.32
0.9330	0.76768	−0.132	−0.02	−1.57
0.8337	0.80855	−0.238	−0.11	−0.91
0.7579	0.83777	−0.289	−0.18	−0.63
0.6896	0.86266	−0.310	−0.24	−0.48
0.5790	0.90068	−0.327	−0.32	−0.33
0.5273	0.91750	−0.324	−0.37	−0.27
0.4529	0.94071	−0.309	−0.43	−0.21
0.3723	0.96464	−0.284	−0.53	−0.14
0.2996	0.98514	−0.248	−0.63	−0.09
0.1751	1.01815	−0.167	−0.84	−0.02
0.1195	1.03203	−0.120	−0.92	−0.01
0.0563	1.04711	−0.051	−1.00	0.00
0.0000	1.06027		−1.04	0.00

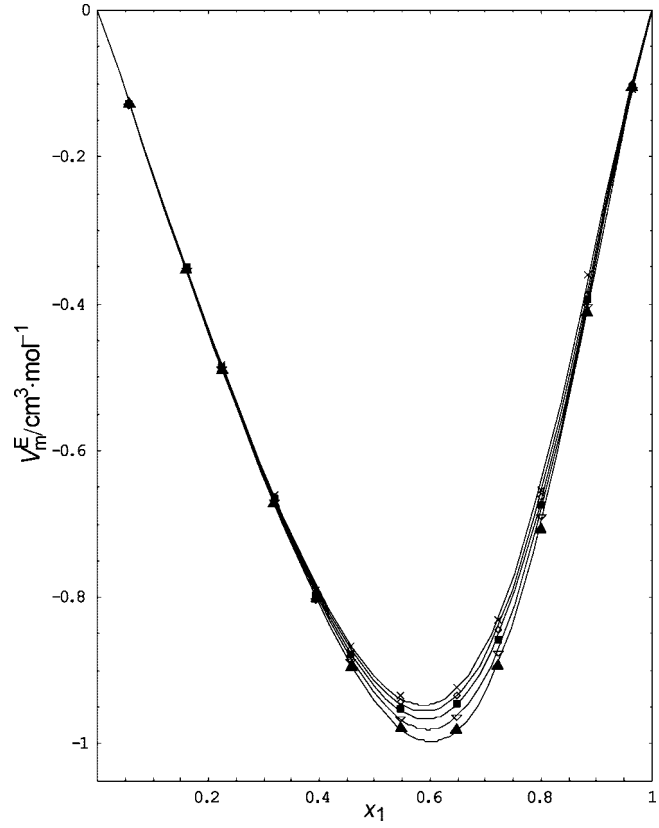

Figure 3. Experimental excess molar volumes for the water (1) + DMSO (3) mixture at different temperatures: ▲, 293.15 K; ▽, 303.15 K; ■, 313.15 K; ◇, 323.15 K; ×, 333.15 K. Solid curves represent the values calculated from eq 2 with coefficients from Table 6.

reported data in the region of overlap. The differences between experimental and literature data and the fitted equation are graphically represented in Figure 4. The excess molar enthalpy of this system is negative[34] (exothermic), and excess viscosity is positive.[22] Therefore the negative values of V_m^E may be attributed to the dominance of molecular association over dissociation.

The excess molar volumes of acetonitrile (2) + DMSO (3) are negative and become more negative with increasing temperature. The excess molar volumes are in agreement with reported data[35] at 298.15 K (Figure 5), but large positive values were reported by Bakshi et al.[36]

The computed excess molar volumes of the binary mixtures were fitted using a temperature-dependent Redlich–Kister expression:[42]

$$V_m^E/\mathrm{cm}^3\cdot\mathrm{mol}^{-1} = x_i x_j \sum_{p=0}^{4}\left(\sum_{q=0}^{2} A_{pq} T^q\right)(x_i - x_j)^p \qquad (2)$$

where x_i and x_j are the mole fraction; A_{pq} are the temperature-independent parameters for the binary mixtures; and T is the absolute temperature. These parameters were obtained by the unweighted least-squars method. The parameters A_{pq} for all the binary mixtures are listed in Table 6, along with standard deviations, σ, calculated by using the following relation

$$\sigma(V_m^E) = \left(\sum_{i=1}^{n} (V_{\mathrm{mexptl},i}^E - V_{\mathrm{mcalcd},i}^E)^2/(n-k)\right)^{1/2} \qquad (3)$$

where n is the number of experimental data points and k is the number of A_{pq} parameters.

Table 5. Densities (ρ), Excess Molar Volumes (V_m^E), and Partial Excess Molar Volumes (V_i^E) for Ternary Mixtures of Water (1) + Acetonitrile (2) + DMSO (3) at Different Temperatures of (293.15 to 333.15) K

x_1	x_2	ρ / g·cm^{-3}	V_m^E / cm^3·mol^{-1}	V_1^E / cm^3·mol^{-1}	V_2^E / cm^3·mol^{-1}	V_3^E / cm^3·mol^{-1}	x_1	x_2	ρ / g·cm^{-3}	V_m^E / cm^3·mol^{-1}	V_1^E / cm^3·mol^{-1}	V_2^E / cm^3·mol^{-1}	V_3^E / cm^3·mol^{-1}
						293.15 K							
0.8073	0.0936	1.00989	−0.648	−0.20	−2.20	−2.86	0.3003	0.3025	1.00263	−0.768	−1.75	−0.35	−0.33
0.7072	0.1014	1.03356	−0.853	−0.44	−1.39	−2.22	0.2357	0.2890	1.01327	−0.625	−1.97	−0.39	−0.17
0.6116	0.1041	1.05075	−0.996	−0.82	−0.90	−1.37	0.1026	0.3122	1.01673	−0.398	−2.39	−0.35	−0.06
0.5271	0.0868	1.06686	−0.966	−1.23	−0.74	−0.71	0.4955	0.4025	0.91406	−0.753	−0.87	−0.29	−1.97
0.4434	0.0926	1.07175	−0.983	−1.55	−0.67	−0.36	0.4224	0.3842	0.94535	−0.808	−1.15	−0.24	−1.25
0.3256	0.0928	1.07441	−0.743	−1.86	−0.66	−0.12	0.3153	0.3889	0.96510	−0.733	−1.58	−0.22	−0.62
0.2100	0.0961	1.07584	−0.526	−2.08	−0.63	−0.03	0.2030	0.3966	0.97877	−0.580	−2.02	−0.24	−0.26
0.1180	0.1128	1.07316	−0.369	−2.27	−0.58	0.00	0.1181	0.3987	0.98834	−0.458	−2.34	−0.25	−0.13
0.6955	0.2045	0.97198	−0.823	−0.50	−0.92	−2.42	0.4132	0.4885	0.89250	−0.667	−1.05	−0.13	−1.84
0.5986	0.2022	0.99993	−0.912	−0.76	−0.65	−1.68	0.3223	0.4823	0.92238	−0.698	−1.42	−0.09	−1.06
0.5130	0.1940	1.01978	−0.926	−1.11	−0.52	−0.99	0.2151	0.4859	0.94293	−0.582	−1.88	−0.11	−0.51
0.4239	0.1958	1.03114	−0.914	−1.46	−0.49	−0.51	0.1389	0.4808	0.95757	−0.495	−2.21	−0.15	−0.27
0.2993	0.2094	1.03639	−0.743	−1.84	−0.50	−0.18	0.3239	0.5743	0.87620	−0.579	−1.28	−0.01	−1.66
0.2054	0.2010	1.04452	−0.562	−2.08	−0.51	−0.06	0.2231	0.5756	0.90397	−0.553	−1.70	−0.01	−0.89
0.0874	0.2065	1.04798	−0.318	−2.38	−0.47	−0.01	0.1085	0.5910	0.92248	−0.450	−2.20	−0.07	−0.40
0.5988	0.2950	0.94576	−0.850	−0.69	−0.53	−2.17	0.1917	0.7055	0.85365	−0.415	−1.54	0.06	−1.41
0.5134	0.3114	0.96085	−0.877	−0.92	−0.38	−1.56	0.1138	0.6825	0.88513	−0.396	−1.94	−0.01	−0.69
0.4013	0.2953	0.99198	−0.883	−1.38	−0.34	−0.71	0.1166	0.7823	0.84136	−0.296	−1.56	0.04	−1.21
						303.15 K							
0.8073	0.0936	1.00254	−0.629	−0.19	−2.17	−2.80	0.3003	0.3025	0.99284	−0.784	−1.71	−0.40	−0.36
0.7072	0.1014	1.02530	−0.837	−0.42	−1.41	−2.19	0.2357	0.2890	1.00339	−0.642	−1.94	−0.44	−0.19
0.6116	0.1041	1.04194	−0.985	−0.78	−0.95	−1.38	0.1026	0.3122	1.00667	−0.422	−2.37	−0.41	−0.07
0.5271	0.0868	1.05780	−0.960	−1.18	−0.80	−0.74	0.4955	0.4025	0.90453	−0.754	−0.85	−0.31	−2.01
0.4434	0.0926	1.06112	−0.926	−1.50	−0.73	−0.39	0.4224	0.3842	0.93558	−0.812	−1.12	−0.27	−1.29
0.3256	0.0928	1.06485	−0.747	−1.83	−0.73	−0.13	0.3153	0.3889	0.95516	−0.745	−1.54	−0.25	−0.66
0.2100	0.0961	1.06602	−0.530	−2.07	−0.72	−0.04	0.2030	0.3966	0.96873	−0.601	−1.99	−0.28	−0.30
0.1180	0.1128	1.06323	−0.378	−2.25	−0.67	0.00	0.1181	0.3987	0.97828	−0.488	−2.32	−0.29	−0.16
0.6955	0.2045	0.96300	−0.795	−0.47	−0.96	−2.39	0.4132	0.4885	0.88261	−0.669	−1.04	−0.14	−1.90
0.5986	0.2022	0.99093	−0.904	−0.72	−0.70	−1.68	0.3223	0.4823	0.91231	−0.707	−1.39	−0.11	−1.12
0.5130	0.1940	1.01049	−0.923	−1.06	−0.59	−1.01	0.2151	0.4859	0.93278	−0.601	−1.85	−0.14	−0.56
0.4239	0.1958	1.02169	−0.919	−1.41	−0.55	−0.54	0.1389	0.4808	0.94739	−0.521	−2.19	−0.18	−0.31
0.2993	0.2094	1.02671	−0.756	−1.80	−0.56	−0.20	0.3239	0.5743	0.86604	−0.584	−1.27	−0.01	−1.75
0.2054	0.2010	1.03470	−0.578	−2.06	−0.59	−0.07	0.2231	0.5756	0.89368	−0.566	−1.67	−0.02	−0.97
0.0874	0.2065	1.03802	−0.338	−2.36	−0.55	−0.02	0.1085	0.5910	0.91212	−0.475	−2.17	−0.09	−0.46
0.5988	0.2950	0.93673	−0.846	−0.66	−0.57	−2.17	0.1917	0.7055	0.84315	−0.420	−1.52	0.07	−1.54
0.5134	0.3114	0.95146	−0.878	−0.88	−0.43	−1.58	0.1138	0.6825	0.87466	−0.415	−1.90	−0.01	−0.78
0.4013	0.2953	0.98231	−0.890	−1.34	−0.39	−0.75	0.1166	0.7823	0.83074	−0.303	−1.51	0.04	−1.35
						313.15 K							
0.8073	0.0936	0.99491	−0.618	−0.18	−2.17	−2.77	0.3003	0.3025	0.98293	−0.803	−1.68	−0.46	−0.38
0.7072	0.1014	1.01683	−0.828	−0.40	−1.45	−2.18	0.2357	0.2890	0.99345	−0.664	−1.91	−0.51	−0.21
0.6116	0.1041	1.03296	−0.979	−0.75	−1.02	−1.39	0.1026	0.3122	0.99662	−0.452	−2.34	−0.48	−0.08
0.5271	0.0868	1.04856	−0.956	−1.14	−0.87	−0.76	0.4955	0.4025	0.89477	−0.759	−0.84	−0.32	−2.05
0.4434	0.0926	1.05169	−0.928	−1.46	−0.81	−0.41	0.4224	0.3842	0.92567	−0.821	−1.09	−0.30	−1.34
0.3256	0.0928	1.05522	−0.753	−1.81	−0.82	−0.14	0.3153	0.3889	0.94511	−0.762	−1.51	−0.29	−0.70
0.2100	0.0961	1.05616	−0.536	−2.05	−0.82	−0.04	0.2030	0.3966	0.95861	−0.626	−1.96	−0.32	−0.33
0.1180	0.1128	1.05331	−0.392	−2.23	−0.78	0.00	0.1181	0.3987	0.96813	−0.519	−2.30	−0.35	−0.18
0.6955	0.2045	0.95433	−0.791	−0.45	−1.01	−2.38	0.4132	0.4885	0.87253	−0.674	−1.03	−0.14	−1.98
0.5986	0.2022	0.98174	−0.902	−0.69	−0.77	−1.69	0.3223	0.4823	0.90210	−0.720	−1.37	−0.13	−1.19
0.5130	0.1940	1.00104	−0.924	−1.02	−0.66	−1.03	0.2151	0.4859	0.92252	−0.623	−1.82	−0.16	−0.61
0.4239	0.1958	1.01208	−0.927	−1.37	−0.63	−0.56	0.1389	0.4808	0.93713	−0.551	−2.16	−0.22	−0.35
0.2993	0.2094	1.01693	−0.772	−1.77	−0.64	−0.22	0.3239	0.5743	0.85569	−0.590	−1.26	0.00	−1.86
0.2054	0.2010	1.02481	−0.596	−2.03	−0.67	−0.08	0.2231	0.5756	0.88327	−0.583	−1.65	−0.03	−1.05
0.0874	0.2065	1.02801	−0.360	−2.34	−0.63	−0.02	0.1085	0.5910	0.90174	−0.508	−2.14	−0.11	−0.53
0.5988	0.2950	0.92750	−0.849	−0.64	−0.61	−2.18	0.1917	0.7055	0.83252	−0.429	−1.49	0.07	−1.68
0.5134	0.3114	0.94186	−0.882	−0.86	−0.47	−1.61	0.1138	0.6825	0.86410	−0.438	−1.87	−0.03	−0.88
0.4013	0.2953	0.97251	−0.902	−1.30	−0.45	−0.78	0.1166	0.7823	0.82001	−0.314	−1.47	0.04	−1.50
						323.15 K							
0.8073	0.0936	0.98698	−0.611	−0.17	−2.21	−2.74	0.3003	0.3025	0.97291	−0.825	−1.65	−0.52	−0.41
0.7072	0.1014	1.00810	−0.822	−0.38	−1.52	−2.17	0.2357	0.2890	0.98341	−0.688	−1.89	−0.58	−0.23
0.6116	0.1041	1.02379	−0.977	−0.72	−1.10	−1.40	0.1026	0.3122	0.98649	−0.484	−2.32	−0.55	−0.10
0.5271	0.0868	1.03916	−0.955	−1.11	−0.96	−0.78	0.4955	0.4025	0.88480	−0.766	−0.83	−0.34	−2.11
0.4434	0.0926	1.04214	−0.932	−1.43	−0.90	−0.42	0.4224	0.3842	0.91559	−0.834	−1.07	−0.33	−1.39
0.3256	0.0928	1.04551	−0.761	−1.78	−0.91	−0.15	0.3153	0.3889	0.93493	−0.782	−1.49	−0.33	−0.75
0.2100	0.0961	1.04631	−0.547	−2.03	−0.92	−0.04	0.2030	0.3966	0.94840	−0.655	−1.94	−0.37	−0.36
0.1180	0.1128	1.04287	−0.377	−2.21	−0.89	−0.01	0.1181	0.3987	0.95790	−0.554	−2.27	−0.40	−0.21
0.6955	0.2045	0.94541	−0.791	−0.43	−1.07	−2.39	0.4132	0.4885	0.86225	−0.682	−1.03	−0.14	−2.07
0.5986	0.2022	0.97236	−0.904	−0.67	−0.83	−1.71	0.3223	0.4823	0.89175	−0.737	−1.35	−0.14	−1.26
0.5130	0.1940	0.99144	−0.929	−0.99	−0.73	−1.05	0.2151	0.4859	0.91216	−0.650	−1.80	−0.19	−0.67
0.4239	0.1958	1.00233	−0.938	−1.34	−0.71	−0.58	0.1389	0.4808	0.92679	−0.586	−2.14	−0.26	−0.40
0.2993	0.2094	1.00704	−0.789	−1.75	−0.72	−0.23	0.3239	0.5743	0.84517	−0.599	−1.26	0.00	−1.98
0.2054	0.2010	1.01486	−0.617	−2.01	−0.76	−0.09	0.2231	0.5756	0.87273	−0.604	−1.63	−0.04	−1.15
0.0874	0.2065	1.01797	−0.385	−2.32	−0.73	−0.03	0.1085	0.5910	0.89123	−0.543	−2.11	−0.14	−0.60
0.5988	0.2950	0.91801	−0.855	−0.62	−0.65	−2.21	0.1917	0.7055	0.82174	−0.440	−1.47	0.07	−1.83
0.5134	0.3114	0.93207	−0.891	−0.83	−0.51	−1.64	0.1138	0.6825	0.85343	−0.465	−1.83	−0.04	−0.98
0.4013	0.2953	0.96257	−0.917	−1.27	−0.50	−0.81	0.1166	0.7823	0.80914	−0.327	−1.43	0.04	−1.66
						333.15 K							
0.8073	0.0936	0.97873	−0.607	−0.16	−2.27	−2.73	0.3003	0.3025	0.96277	−0.850	−1.63	−0.59	−0.44
0.7072	0.1014	0.99916	−0.819	−0.36	−1.60	−2.19	0.2357	0.2890	0.97328	−0.715	−1.87	−0.65	−0.25
0.6116	0.1041	1.01442	−0.977	−0.70	−1.19	−1.41	0.1026	0.3122	0.97630	−0.519	−2.31	−0.63	−0.11
0.5271	0.0868	1.02961	−0.956	−1.09	−1.06	−0.79	0.4955	0.4025	0.87463	−0.778	−0.83	−0.35	−2.18
0.4434	0.0926	1.03244	−0.936	−1.41	−1.00	−0.43	0.4224	0.3842	0.90532	−0.849	−1.07	−0.36	−1.44
0.3256	0.0928	1.03547	−0.758	−1.77	−1.02	−0.16	0.3153	0.3889	0.92463	−0.806	−1.48	−0.37	−0.80

Table 5 Continued

x_1	x_2	ρ / g·cm^{-3}	V_m^E / cm^3·mol^{-1}	V_1^E / cm^3·mol^{-1}	V_2^E / cm^3·mol^{-1}	V_3^E / cm^3·mol^{-1}	x_1	x_2	ρ / g·cm^{-3}	V_m^E / cm^3·mol^{-1}	V_1^E / cm^3·mol^{-1}	V_2^E / cm^3·mol^{-1}	V_3^E / cm^3·mol^{-1}
0.2100	0.0961	1.03638	−0.558	−2.02	−1.04	−0.05	0.2030	0.3966	0.93808	−0.686	−1.92	−0.42	−0.40
0.1180	0.1128	1.03285	−0.391	−2.21	−1.00	−0.01	0.1181	0.3987	0.94761	−0.594	−2.25	−0.47	−0.24
0.6955	0.2045	0.93623	−0.796	−0.41	−1.13	−2.41	0.4132	0.4885	0.85178	−0.694	−1.04	−0.14	−2.17
0.5986	0.2022	0.96277	−0.909	−0.64	−0.91	−1.73	0.3223	0.4823	0.88125	−0.757	−1.35	−0.16	−1.35
0.5130	0.1940	0.98166	−0.937	−0.97	−0.81	−1.07	0.2151	0.4859	0.90167	−0.680	−1.78	−0.22	−0.74
0.4239	0.1958	0.99246	−0.952	−1.32	−0.79	−0.60	0.1389	0.4808	0.91636	−0.624	−2.11	−0.30	−0.45
0.2993	0.2094	0.99707	−0.810	−1.73	−0.81	−0.24	0.3239	0.5743	0.83447	−0.612	−1.27	0.00	−2.11
0.2054	0.2010	1.00484	−0.640	−2.00	−0.85	−0.10	0.2231	0.5756	0.86205	−0.628	−1.62	−0.05	−1.25
0.0874	0.2065	1.00787	−0.411	−2.31	−0.84	−0.03	0.1085	0.5910	0.88063	−0.582	−2.08	−0.17	−0.67
0.5988	0.2950	0.90830	−0.866	−0.61	−0.69	−2.25	0.1917	0.7055	0.81081	−0.454	−1.46	0.07	−2.00
0.5134	0.3114	0.92210	−0.904	−0.82	−0.56	−1.69	0.1138	0.6825	0.84263	−0.496	−1.80	−0.05	−1.10
0.4013	0.2953	0.95249	−0.936	−1.26	−0.56	−0.84	0.1166	0.7823	0.79813	−0.343	−1.39	0.04	−1.84

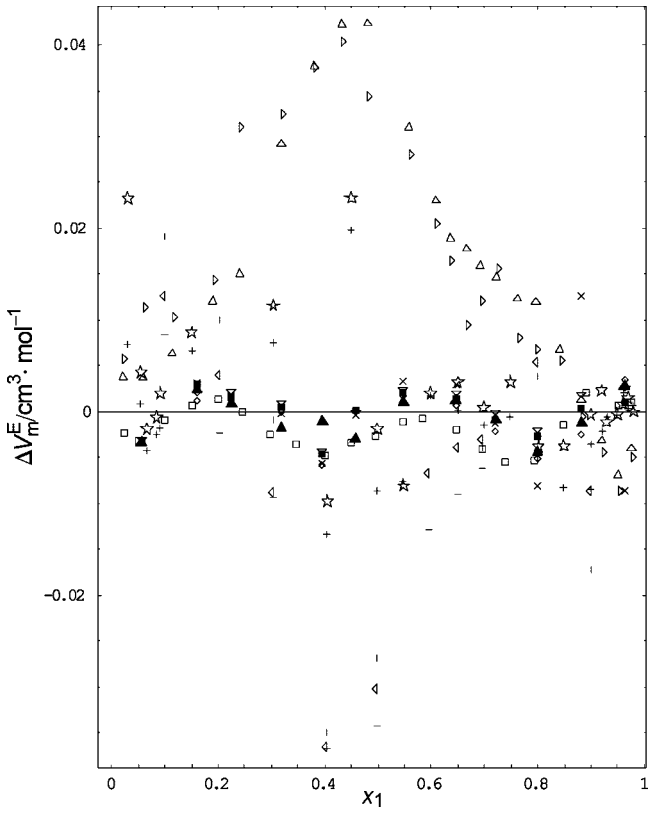

Figure 4. Differences ΔV_m^E between experimental and literature data and the fitted equation for the water (1) + DMSO (3) mixture at different temperatures. This work: ▲, 293.15 K; ▽, 303.15 K; ■, 313.15 K; ◇, 323.15 K; ×, 333.15 K; +, 293.15 K, ref 23; Δ, 303.15 K, ref 22; ☆, 303.15 K, ref 23; −, 303.15 K, ref 25; □, 303.15 K, ref 12; open left triangle, 313.15 K, ref 22; open right triangle, 313.15 K, ref 25; |, 323.15 K, ref 25.

The excess molar volumes for the ternary mixture were fitted to the temperature-dependent Cibulka equation[43]

$$V_{m,123}^E = V_{m,bin}^E + x_1x_2x_3(B_0 + B_1x_1 + B_2x_2) \quad (4)$$

where $V_{m,bin}^E$ are the contributions of binary mixture i,j.

$$V_{m,bin}^E = V_{m,12}^E + V_{m,13}^E + V_{m,23}^E \quad (5)$$

Every B_i ternary parameter is a function of temperature as expressed in eq 6

$$B_i = \sum_{q=0}^{2} C_{iq}T^q \quad (6)$$

The parameters C_{iq} for the ternary mixture are listed in Table 7, along with the standard deviation σ.

The temperature dependence of density of the pure components was fitted to the equation

Table 6. Coefficients A_{pq} of Equation 2 and Standard Deviation for the Fits of the Binary Excess Molar Volumes in the Temperature Range (293.15 to 333.15) K

	p					σ
q	0	1	2	3	4	cm^3·mol^{-1}
			Water (1) + Acetonitrile (2)			
0	−6.8762	7.7234	−14.8382	10.2321	0.6021	0.005
1	0.0300	−0.0469	0.0819	−0.0456	−0.0130	
2	−0.00004	0.00008	−0.0001	0.00005	0.00002	
			Water (1) + DMSO (3)			
0	−7.8450	16.8084	−14.5494	−33.2755	37.7386	0.004
1	0.0232	−0.0870	0.0873	0.1963	−0.2261	
2	−0.00003	0.0001	−0.0001	−0.0003	0.0003	
			Acetonitrile (2) + DMSO (3)			
0	−3.9658	−4.0855	−1.2676	2.8439	6.8101	0.004
1	0.0355	0.0280	0.0075	−0.0179	−0.0420	
2	−0.00008	−0.00005	−0.00001	0.00002		

Table 7. Coefficients C_{iq} of Equation 6 and Standard Deviation for the Fits of the Ternary Excess Molar Volumes in the Temperature Range (293.15 to 333.15) K

	i			σ
q	0	1	2	cm^3·mol^{-1}
		Water (1) + Acetonitrile (2) + DMSO (3)		
0	−2.3348	−34.1479	26.5432	0.011
1	0.0092	0.2265	−0.1677	
2	−0.00001	−0.0003	0.0002	

$$\rho(T)/\text{g}\cdot\text{cm}^{-3} = \sum_{i=0}^{4} a_iT^i \quad (7)$$

The thermal expansion coefficient, α, as in the case of pure components was obtained by analytical differentiation of the density fitting equation

$$\alpha = -\rho^{-1}(\partial\rho/\partial T)_P \quad (8)$$

The thermal expansion coefficients of pure components at different temperature are presented in Table 1. The average uncertainty in the thermal expansion coefficient is estimated to be ± 5·10^{-6} K^{-1}.

The partial excess molar volume, V_i^E, of a component in a two- and three-component mixture can be computed from excess molar volume data by using the following equation.[44]

$$V_i^E/\text{cm}^3\cdot\text{mol}^{-1} = V_m^E - \sum_{k\neq i}^{n} x_k(\partial V_m^E/\partial x_k)_{T,p,x_{j\neq i,k}} \quad (9)$$

where $(\partial V_m^E/\partial x_k)_{T,p,x_{j\neq i,k}}$ are calculated from eqs 2 and 4 using the parameters in Tables 6 and 7.

The excess partial molar volume at infinite dilution $V_i^{E,0}$ can be determined from the following equation

$$V_i^{E,0}/\text{cm}^3\cdot\text{mol}^{-1} = (\partial V_m^E/\partial x_i)_{T,p,x_i\to 0} \quad (10)$$

The partial molar quantities are important in the study of the dependence of an extensive property on phase composition at

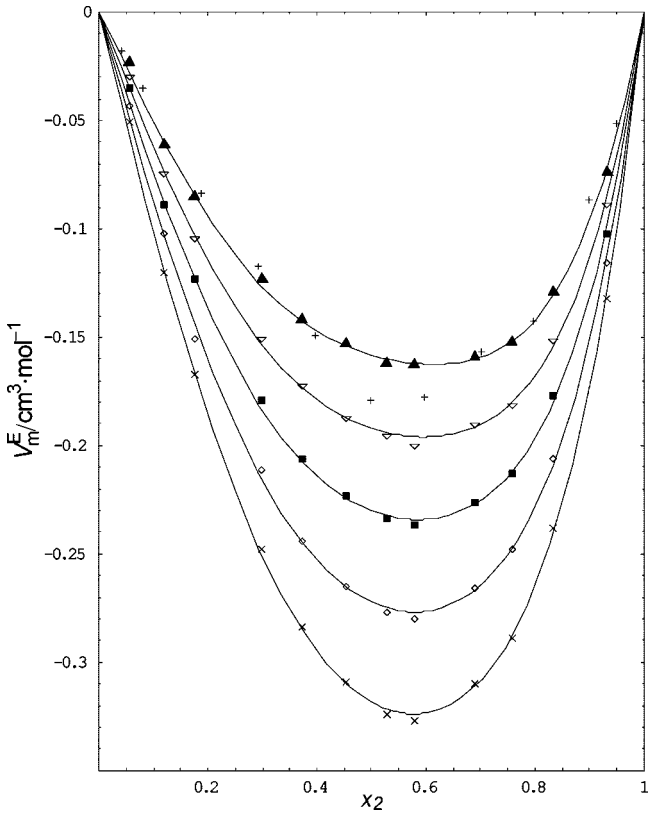

Figure 5. Experimental excess molar volumes for the acetonitrile (2) + DMSO (3) mixture at different temperatures. This work: ▲, 293.15 K; ∇, 303.15 K; ■, 313.15 K; ◇, 323.15 K; ×, 333.15 K; +, 298.15 K, ref 35. Solid curves represent the values calculated from eq 2 with coefficients from Table 6.

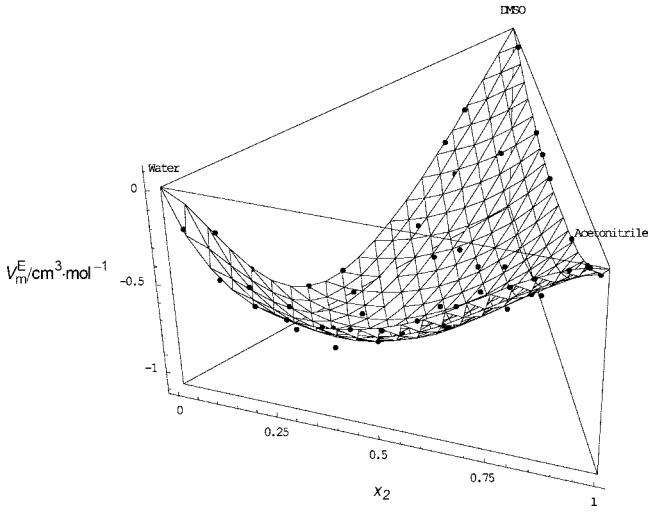

Figure 6. Representation of the experimental excess molar volume surface for the ternary mixture of water (1) + acetonitrile (2) + DMSO (3) at 333.15 K. ●, represents experimental points. Curves represent the values calculated from eq 4 with coefficients from Table 7. The unit in the triangle plot is mole fraction.

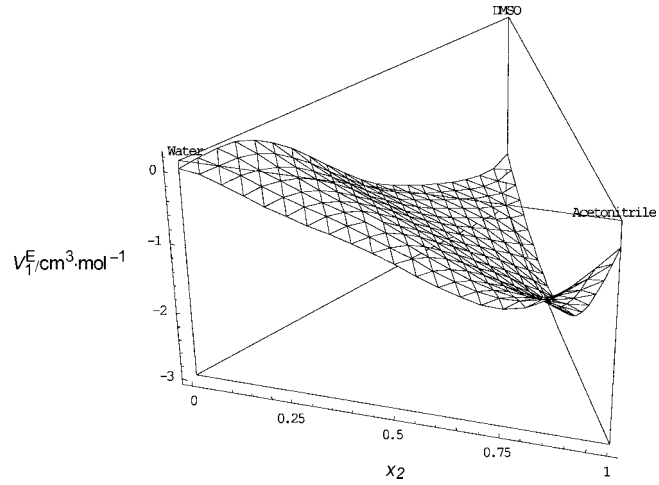

Figure 7. Representation of partial excess molar volume surface for water (1) at the ternary mixture of water (1) + acetonitrile (2) + DMSO (3) at 333.15 K. The unit in the triangle plot is mole fraction.

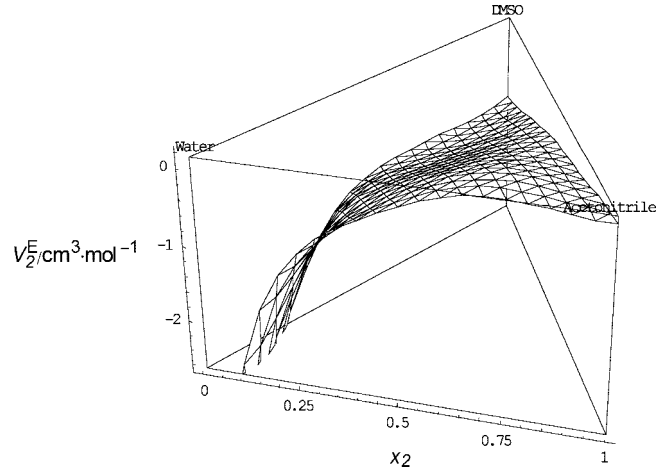

Figure 8. Representation of partial excess molar volume surface for acetonitrile (2) at the ternary mixture of water (1) + acetonitrile (2) + DMSO (3) at 333.15 K. The unit in the triangle plot is mole fraction.

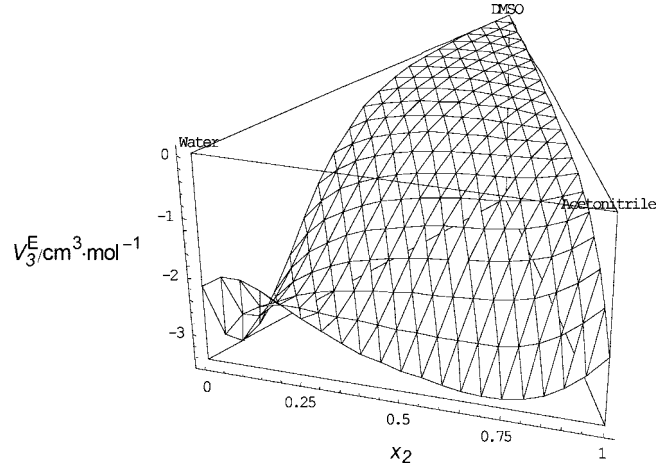

Figure 9. Representation of partial excess molar volume surface for DMSO (3) at the ternary mixture of water (1) + acetonitrile (2) + DMSO (3) at 333.15 K. The unit in the triangle plot is mole fraction.

constant pressure and temperature, showing its trend with composition. The partial excess molar volumes, V_i^E, and their values at infinite dilution, $V_i^{E,0}$, are recorded in Tables 2 to 5 and graphically represented in Figures 7 to 9. The average uncertainty in the partial excess molar volume is estimated to be $\pm\ 2 \cdot 10^{-2}$ cm^3·mol^{-1}.

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