Temperature Dependence of the Volumetric Properties of Binary and Ternary Mixtures of Water (1) + Methanol (2) + Ethanol (3) at Ambient Pressure (81.5 kPa)

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Densities, ρ, have been measured for three binary mixtures and a ternary mixture formed by water (1), methanol (2), and ethanol (3) over the entire range of compositions at temperatures from (283.15 to 313.15) K in 5 K intervals and at ambient pressure (81.5 kPa). 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 were correlated with the Redlich−Kister equation (for binary data) and the Cibulka equation (for ternary data). The excess molar volumes, V_m^E, were compared with values from the literature in the region of overlap.

Introduction

This ternary system is encountered in some antifreeze solutions and certain denatured alcohol formulas and pharmaceutical preparations.[1] The components of this mixture show the phenomena of association. Experimental data of excess thermodynamic properties of liquid mixtures provide useful information about molecular interactions and can be used to test thermodynamic models.[2,3]

We report 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 three binary mixtures and a ternary mixture formed by water (1), methanol (2), and ethanol (3) over the entire range of compositions at temperatures from (283.15 to 313.15) K in 5 K intervals and at ambient pressure (81.5 kPa). The excess molar volumes were correlated with the Redlich−Kister equation (for binary data) and the Cibulka equation (for ternary data). The excess molar volumes, V_m^E, were compared with values from the literature in the region of overlap.

Experimental

Materials. Methanol and ethanol 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,[4−9] 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 $\pm$ 1·10^{-4} g. Conversion to molar mass was based on the relative atomic mass table of 1996 issued by IUPAC.[10] The average uncertainty in the mole fraction is estimated to be $\pm$ 1.5·10^{-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 $\pm$ 1·10^{-5} g·cm^{-3}. The repeatability of the density measurements was $\pm$ 1·10^{-5} g·cm^{-3}. Refractive indices were measured at 298.15 K using a thermostated Abbé refractometer. The uncertainty of the refractive index is in the order of $\pm$ 0.0002 units.

Table 1. Sources, Purity Grades, Densities, ρ, Refractive Indices, n_D, and Thermal Expansion Coefficients, α, of the Pure Components at 298.15 K

	purity		ρ/(g·cm^{-3})		n_D		
component	purity/100 *w*	*T*/K	exptl	lit.	exptl	lit.	10$^4\alpha$/K^{-1}
methanol	99.8 %	283.15	0.80067	0.80067[4]			11.75
		288.15	0.79598	0.79599[4]			11.81
		293.15	0.79128	0.79129[4]			11.89
		298.15	0.78657	0.78658[4]	1.3270	1.32652[5]	12.99
		303.15	0.78185	0.78186[4]			12.11
		308.15	0.77710	0.77710[4]			12.26
		313.15	0.77232	0.77232[4]			12.43
ethanol	99.8 %	283.15	0.79799	0.79784[6]			10.68
		288.15	0.79373	0.79360[6]			10.73
		293.15	0.78947	0.78945[6]			10.82
		298.15	0.78518	0.7851[7]	1.3595	1.35941[5]	10.95
		303.15	0.78087	0.78096[6]			11.09
		308.15	0.77652	0.77642[6]			11.24
		313.15	0.77214	0.7721[8]			11.38
water		283.15	0.99973	0.99970[9]			0.87
		288.15	0.99913	0.99910[9]			1.52
		293.15	0.99823	0.99820[9]			2.08
		298.15	0.99707	0.99704[9]	1.3326	1.332503[5]	2.57
		303.15	0.99567	0.99565[9]			3.03
		308.15	0.99406	0.99403[9]			3.45
		313.15	0.99224	0.99221[9]			3.87

Results and Discussion

The experimental values of the densities, ρ, for pure compounds and for the binary and ternary mixtures were

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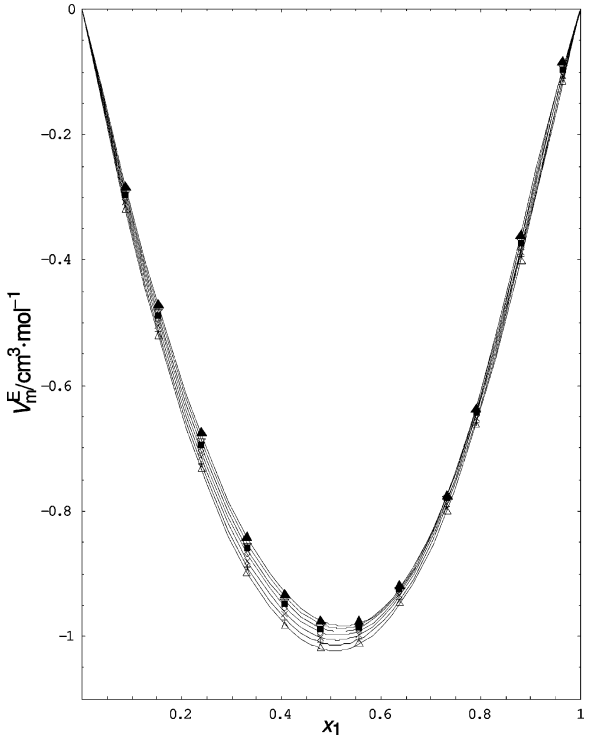

Figure 1. Experimental excess molar volumes for the water (1) + methanol (2) mixture at different temperatures: ▲, 283.15 K; ▽, 288.15 K; ■, 293.15 K; ◇, 298.15 K; ×, 303.15 K; +, 308.15; △, 313.15 K. Solid curves represent the values calculated from eq 2 with coefficients from Table 6.

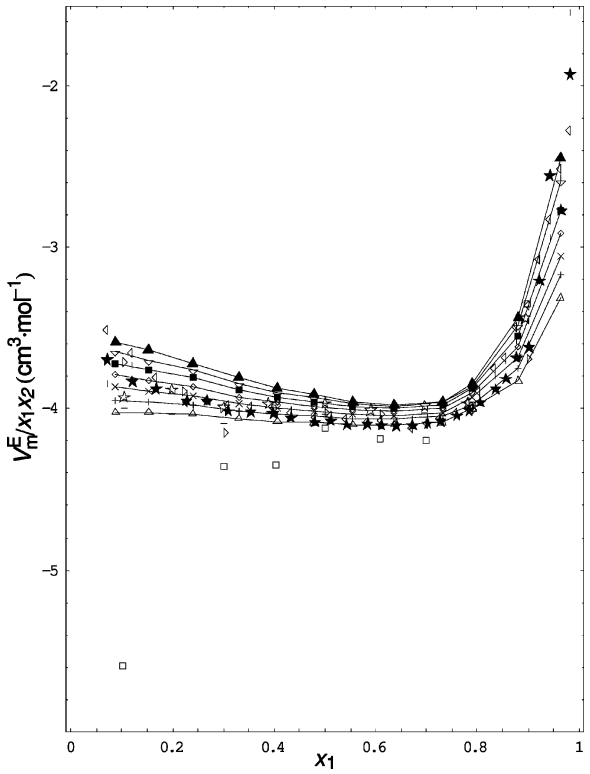

Figure 2. Experimental data of V_m^E/x_1x_2 for water (1) + methanol (2) at different temperatures. This work: ▲, 283.15 K; ▽, 288.15 K; ■, 293.15 K; ◇, 298.15 K; ×, 303.15 K; +, 308.15 K; △, 313.15 K; ☆, 298.15 K, ref 11; −, 308.15 K, ref 11; □, 283.15 K, ref 12; open arrow pointing right, 313.15 K, ref 12; open arrow pointing left, 283.15 K, ref 14; |, 293.15 K, ref 14; ★, 303.15 K, ref 14; ◆.

measured in the temperature range (283.15 to 313.15) K at intervals of 5 K and ambient pressure (81.5 kPa), and they are

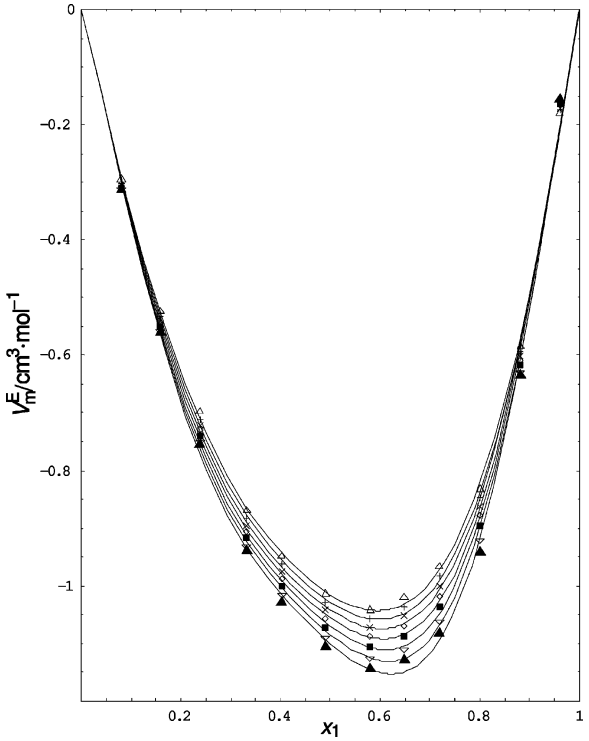

Figure 3. Experimental excess molar volumes for the water (1) + ethanol (3) mixture at different temperatures: ▲, 283.15 K; ▽, 288.15 K; ■, 293.15 K; ◇, 298.15 K; ×, 303.15 K; +, 308.15; △, 313.15 K. Solid curves represent the values calculated from eq 2 with coefficients from Table 6.

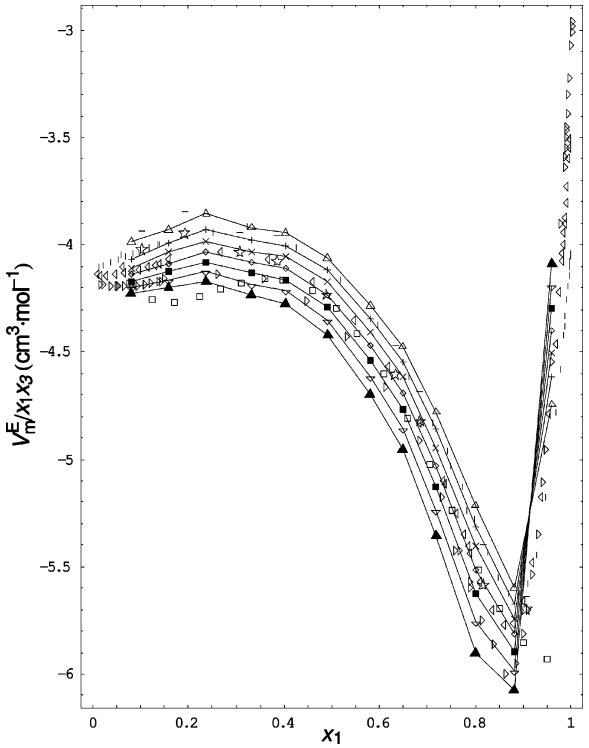

Figure 4. Experimental data of V_m^E/x_1x_3 for water (1) + ethanol (3) at different temperatures. This work: ▲, 283.15 K; ▽, 288.15 K; ■, 293.15 K; ◇, 298.15 K; ×, 303.15 K; +, 308.15 K; △, 313.15 K; ☆, 298.15 K, ref 11; −, 308.15 K, ref 11; □, 298.15 K, ref 17; open arrow pointing right, 288.15 K, ref 18; open arrow pointing left, 298.15 K, ref 18; |, 308.15 K, ref 18.

Table 2. Densities (ρ), Excess Molar Volumes (V_m^E), and Partial Excess Molar Volumes (V_i^E) for Binary Mixtures of Water (1) + Methanol (2) at Different Temperatures of (283.15 to 313.15) 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}	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}
			283.15 K						
0.0000			−3.21	0.00	0.5552	0.90406	−0.977	−0.86	−1.13
0.0871	0.81496	−0.285	−3.12	−0.01	0.6365	0.92103	−0.921	−0.54	−1.60
0.1529	0.82626	−0.471	−2.78	−0.06	0.7321	0.94106	−0.777	−0.21	−2.32
0.2395	0.84180	−0.677	−2.27	−0.18	0.7901	0.95273	−0.638	−0.07	−2.78
0.3306	0.85901	−0.843	−1.79	−0.37	0.8807	0.97064	−0.361	0.03	−3.25
0.4064	0.87383	−0.934	−1.46	−0.57	0.9640	0.98896	−0.085	0.01	−2.86
0.4788	0.88832	−0.976	−1.16	−0.80	1.0000			0.00	−2.21
			288.15 K						
0.0000			−3.32	0.00	0.5552	0.90044	−0.980	−0.85	−1.15
0.0871	0.81044	−0.29	−3.16	−0.01	0.6365	0.91769	−0.922	−0.54	−1.61
0.1529	0.82186	−0.479	−2.80	−0.06	0.7321	0.93820	−0.777	−0.22	−2.31
0.2395	0.83753	−0.685	−2.28	−0.19	0.7901	0.95029	−0.640	−0.08	−2.75
0.3306	0.85489	−0.851	−1.80	−0.38	0.8807	0.96911	−0.366	0.03	−3.24
0.4064	0.86985	−0.94	−1.45	−0.58	0.9640	0.98825	−0.090	0.01	−2.95
0.4788	0.88450	−0.981	−1.16	−0.82	1.0000			0.00	−2.39
			293.15 K						
0.0000			−3.44	0.00	0.5552	0.89675	−0.985	−0.84	−1.17
0.0871	0.80591	−0.296	−3.20	−0.02	0.6365	0.91428	−0.925	−0.53	−1.62
0.1529	0.81744	−0.487	−2.82	−0.07	0.7321	0.93524	−0.780	−0.22	−2.30
0.2395	0.83323	−0.694	−2.29	−0.20	0.7901	0.94770	−0.642	−0.09	−2.73
0.3306	0.85073	−0.860	−1.80	−0.39	0.8807	0.96739	−0.373	0.02	−3.23
0.4064	0.86581	−0.947	−1.45	−0.60	0.9640	0.98725	−0.096	0.01	−3.03
0.4788	0.88062	−0.987	−1.15	−0.84	1.0000			0.00	−2.57
			298.15 K						
0.0000			−3.55	0.00	0.5552	0.89300	−0.990	−0.84	−1.18
0.0871	0.80135	−0.301	−3.25	−0.02	0.6365	0.91078	−0.930	−0.53	−1.63
0.1529	0.81299	−0.496	−2.85	−0.07	0.7321	0.93218	−0.784	−0.23	−2.29
0.2395	0.82890	−0.704	−2.31	−0.20	0.7901	0.94500	−0.647	−0.10	−2.72
0.3306	0.84653	−0.869	−1.81	−0.40	0.8807	0.96547	−0.380	0.01	−3.22
0.4064	0.86173	−0.956	−1.45	−0.61	0.9640	0.98600	−0.101	0.01	−3.12
0.4788	0.87668	−0.994	−1.14	−0.86	1.0000			0.00	−2.74
			303.15 K						
0.0000			−3.67	0.00	0.5552	0.88917	−0.997	−0.83	−1.20
0.0871	0.79678	−0.307	−3.29	−0.02	0.6365	0.90720	−0.935	−0.53	−1.65
0.1529	0.80850	−0.504	−2.87	−0.08	0.7321	0.92902	−0.789	−0.24	−2.29
0.2395	0.82453	−0.714	−2.32	−0.21	0.7901	0.94219	−0.652	−0.11	−2.71
0.3306	0.84228	−0.879	−1.82	−0.41	0.8807	0.96337	−0.387	0.00	−3.22
0.4064	0.85759	−0.964	−1.45	−0.63	0.9640	0.98450	−0.106	0.01	−3.21
0.4788	0.87267	−1.002	−1.14	−0.87	1.0000			0.00	−2.91
			308.15 K						
0.0000			−3.78	0.00	0.5552	0.88526	−1.004	−0.83	−1.22
0.0871	0.79217	−0.314	−3.34	−0.02	0.6365	0.90352	−0.941	−0.54	−1.66
0.1529	0.80398	−0.513	−2.90	−0.08	0.7321	0.92574	−0.794	−0.24	−2.29
0.2395	0.82011	−0.724	−2.34	−0.22	0.7901	0.93927	−0.659	−0.12	−2.70
0.3306	0.83798	−0.889	−1.82	−0.43	0.8807	0.96109	−0.394	−0.01	−3.23
0.4064	0.85340	−0.974	−1.46	−0.64	0.9640	0.98279	−0.110	0.00	−3.30
0.4788	0.86859	−1.010	−1.14	−0.89	1.0000			0.00	−3.07
			313.15 K						
0.0000			−3.90	0.00	0.5552	0.88128	−1.012	−0.83	−1.24
0.0871	0.78752	−0.320	−3.38	−0.03	0.6365	0.89976	−0.948	−0.54	−1.67
0.1529	0.79941	−0.521	−2.93	−0.09	0.7321	0.92236	−0.801	−0.25	−2.30
0.2395	0.81564	−0.734	−2.36	−0.23	0.7901	0.93609	−0.663	−0.12	−2.70
0.3306	0.83361	−0.899	−1.83	−0.44	0.8807	0.95865	−0.402	−0.01	−3.24
0.4064	0.84913	−0.984	−1.46	−0.65	0.9640	0.98087	−0.115	0.00	−3.38
0.4788	0.86445	−1.019	−1.14	−0.91	1.0000			0.00	−3.23

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

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

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.

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 $\pm 2\cdot10^{-3}$ cm^3·mol^{-1}. The excess molar volumes for binary mixtures water (1) + methanol (2), water (1) + ethanol (3), and methanol (2) + ethanol (3) and

Table 3. Densities (ρ), Excess Molar Volumes (V_m^E), and Partial Excess Molar Volumes (V_i^E) for Binary Mixtures of Water (1) + Ethanol (3) at Different Temperatures of (283.15 to 313.15) 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}	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}
				283.15 K					
0.0000			−3.30	0.00	0.5806	0.88819	−1.144	−1.29	−0.94
0.0805	0.80805	−0.313	−3.75	0.01	0.6480	0.90357	−1.130	−1.05	−1.33
0.1584	0.81814	−0.560	−3.16	−0.08	0.7185	0.92165	−1.083	−0.72	−2.06
0.2376	0.82889	−0.756	−2.42	−0.26	0.8009	0.94460	−0.941	−0.32	−3.31
0.3322	0.84293	−0.939	−1.83	−0.49	0.8813	0.96596	−0.636	−0.06	−4.68
0.4026	0.85412	−1.028	−1.62	−0.61	0.9605	0.98404	−0.155	0.01	−5.35
0.4910	0.86986	−1.105	−1.48	−0.72	1.0000			0.00	−4.99
				288.15 K					
0.0000			−3.39	0.00	0.5806	0.88408	−1.124	−1.25	−0.96
0.0805	0.80379	−0.311	−3.70	0.00	0.6480	0.89955	−1.108	−1.01	−1.34
0.1584	0.81387	−0.555	−3.10	−0.08	0.7185	0.91778	−1.059	−0.70	−2.02
0.2376	0.82461	−0.747	−2.38	−0.26	0.8009	0.94107	−0.918	−0.32	−3.22
0.3322	0.83867	−0.928	−1.81	−0.48	0.8813	0.96349	−0.626	−0.07	−4.54
0.4026	0.84989	−1.014	−1.59	−0.61	0.9605	0.98311	−0.159	0.00	−5.30
0.4910	0.86567	−1.088	−1.44	−0.73	1.0000			0.00	−5.08
				293.15 K					
0.0000			−3.47	0.00	0.5806	0.87993	−1.106	−1.21	−0.97
0.0805	0.79951	−0.309	−3.64	−0.00	0.6480	0.89548	−1.088	−0.98	−1.33
0.1584	0.80957	−0.550	−3.04	−0.08	0.7185	0.91384	−1.037	−0.68	−1.99
0.2376	0.82029	−0.739	−2.35	−0.26	0.8009	0.93748	−0.897	−0.33	−3.12
0.3322	0.83437	−0.917	−1.79	−0.48	0.8813	0.96085	−0.617	−0.08	−4.41
0.4026	0.84561	−1.001	−1.57	−0.60	0.9605	0.98189	−0.163	0.00	−5.25
0.4910	0.86144	−1.072	−1.41	−0.74	1.0000			0.00	−5.17
				298.15 K					
0.0000			−3.53	0.00	0.5806	0.87571	−1.089	−1.17	−0.98
0.0805	0.79519	−0.306	−3.59	−0.01	0.6480	0.89135	−1.070	−0.95	−1.33
0.1584	0.80523	−0.545	−2.98	−0.09	0.7185	0.90985	−1.018	−0.67	−1.95
0.2376	0.81593	−0.730	−2.32	−0.25	0.8009	0.93381	−0.879	−0.33	−3.04
0.3322	0.83001	−0.905	−1.77	−0.47	0.8813	0.95806	−0.608	−0.09	−4.29
0.4026	0.84127	−0.988	−1.55	−0.60	0.9605	0.98042	−0.167	0.00	−5.21
0.4910	0.85716	−1.058	−1.37	−0.74	1.0000			0.00	−5.26
				303.15 K					
0.0000			−3.58	0.00	0.5806	0.87144	−1.073	−1.14	−0.98
0.0805	0.79085	−0.304	−3.53	−0.01	0.6480	0.88716	−1.053	−0.92	−1.33
0.1584	0.80084	−0.538	−2.93	−0.09	0.7185	0.90580	−1.000	−0.65	−1.92
0.2376	0.81153	−0.722	−2.29	−0.25	0.8009	0.93007	−0.862	−0.33	−2.95
0.3322	0.82561	−0.895	−1.76	−0.46	0.8813	0.95513	−0.601	−0.10	−4.18
0.4026	0.83689	−0.975	−1.53	−0.59	0.9605	0.97875	−0.171	−0.01	−5.17
0.4910	0.85281	−1.043	−1.35	−0.74	1.0000			0.00	−5.34
				308.15 K					
0.0000			−3.62	0.00	0.5806	0.86711	−1.058	−1.11	−0.99
0.0805	0.78645	−0.301	−3.46	−0.01	0.6480	0.88291	−1.037	−0.90	−1.32
0.1584	0.79641	−0.532	−2.87	−0.10	0.7185	0.90168	−0.983	−0.64	−1.89
0.2376	0.80707	−0.712	−2.26	−0.25	0.8009	0.92625	−0.847	−0.33	−2.88
0.3322	0.82115	−0.883	−1.75	−0.45	0.8813	0.95205	−0.594	−0.10	−4.08
0.4026	0.83245	−0.963	−1.52	−0.58	0.9605	0.97691	−0.175	−0.01	−5.15
0.4910	0.84840	−1.029	−1.32	−0.74	1.0000			0.00	−5.43
				313.15 K					
0.0000			−3.64	0.00	0.5806	0.86272	−1.043	−1.08	−0.99
0.0805	0.78201	−0.295	−3.40	−0.02	0.6480	0.87859	−1.021	−0.88	−1.32
0.1584	0.79193	−0.524	−2.81	−0.10	0.7185	0.89749	−0.967	−0.63	−1.86
0.2376	0.80250	−0.698	−2.23	−0.24	0.8009	0.92234	−0.832	−0.33	−2.81
0.3322	0.81663	−0.870	−1.74	−0.43	0.8813	0.94882	−0.586	−0.11	−3.98
0.4026	0.82794	−0.949	−1.51	−0.56	0.9605	0.97489	−0.180	−0.01	−5.12
0.4910	0.84395	−1.015	−1.30	−0.73	1.0000			0.00	−5.52

the ternary mixture water (1) + methanol (2) + ethanol (3) at different temperatures are recorded in Tables 2 to 5 and graphically represented in Figures 1 to 7.

The excess molar volumes for water (1) + methanol (2) are negative and become more negative with increasing temperature. The excess molar volumes are in agreement with reported data[7,11−14] in the region of overlap (Figure 2). The negative values of V_m^E over the entire range of mole fraction may be attributed to the dominance of molecular association over dissociation. This observation receives support from the negative heats of mixing and excess entropy.[15]

The excess molar volumes of water (1) + ethanol (3) are negative and become less negative with increasing temperature. The excess molar volumes are in agreement with reported

Table 4. Densities (ρ), Excess Molar Volumes (V_m^E), and Partial Excess Molar Volumes (V_i^E) for Binary Mixtures of Methanol (2) + Ethanol (3) at Different Temperatures of (283.15 to 313.15) K

	ρ	V_m^E	V_2^E	V_3^E		ρ	V_m^E	V_2^E	V_3^E
x_2	g·cm^{-3}	cm^3·mol^{-1}	cm^3·mol^{-1}	cm^3·mol^{-1}	x_2	g·cm^{-3}	cm^3·mol^{-1}	cm^3·mol^{-1}	cm^3·mol^{-1}
				283.15 K					
0.0000			0.00	0.00	0.7182	0.79960	0.006	0.01	0.01
0.0729	0.79811	0.001	0.02	0.00	0.8027	0.79988	0.005	0.00	0.01
0.1632	0.79827	0.003	0.02	0.00	0.8714	0.80012	0.004	0.00	0.02
0.3251	0.79858	0.005	0.01	0.00	0.9485	0.80043	0.002	0.00	0.03
0.5592	0.79914	0.006	0.01	0.01	1.0000			0.00	0.04
0.6349	0.79935	0.006	0.01	0.01					
				288.15 K					
0.0000			0.02	0.00	0.7182	0.79507	0.006	0.00	0.01
0.0729	0.79383	0.001	0.02	0.00	0.8027	0.79530	0.005	0.00	0.02
0.1632	0.79397	0.002	0.02	0.00	0.8714	0.79551	0.004	0.00	0.02
0.3251	0.79422	0.005	0.01	0.00	0.9485	0.79578	0.002	0.00	0.03
0.5592	0.79468	0.006	0.01	0.01	1.0000			0.00	0.05
0.6349	0.79485	0.006	0.01	0.01					
				293.15 K					
0.0000			0.03	0.00	0.7182	0.79052	0.006	0.00	0.02
0.0729	0.78954	0.002	0.02	0.00	0.8027	0.79071	0.005	0.00	0.02
0.1632	0.78964	0.003	0.02	0.00	0.8714	0.79089	0.004	0.00	0.02
0.3251	0.78984	0.006	0.02	0.00	0.9485	0.79110	0.003	0.00	0.03
0.5592	0.7902	0.007	0.01	0.01	1.0000			0.00	0.06
0.6349	0.79034	0.007	0.00	0.01					
				298.15 K					
0.0000			0.0 4	0.00	0.7182	0.78595	0.007	0.00	0.02
0.0729	0.78523	0.002	0.02	0.00	0.8027	0.78611	0.005	0.00	0.02
0.1632	0.78530	0.003	0.02	0.00	0.8714	0.78625	0.004	0.00	0.02
0.3251	0.78544	0.006	0.02	0.00	0.9485	0.78643	0.002	0.00	0.04
0.5592	0.78570	0.008	0.01	0.01	1.0000			0.00	0.06
0.6349	0.78581	0.008	0.00	0.01					
				303.15 K					
0.0000			0.04	0.00	0.7182	0.78136	0.008	0.00	0.02
0.0729	0.78089	0.002	0.02	0.00	0.8027	0.78149	0.006	0.00	0.02
0.1632	0.78094	0.003	0.02	0.00	0.8714	0.78159	0.005	0.00	0.02
0.3251	0.78102	0.007	0.02	0.00	0.9485	0.78173	0.003	0.00	0.04
0.5592	0.78119	0.009	0.01	0.01	1.0000			0.00	0.07
0.6349	0.78126	0.009	0.00	0.02					
				308.15 K					
0.0000			0.04	0.00	0.7182	0.77676	0.008	0.00	0.02
0.0729	0.77652	0.002	0.02	0.00	0.8027	0.77684	0.006	0.00	0.02
0.1632	0.77654	0.004	0.02	0.00	0.8714	0.77690	0.006	0.00	0.02
0.3251	0.77657	0.007	0.02	0.00	0.9485	0.77701	0.003	0.00	0.04
0.5592	0.77665	0.009	0.01	0.01	1.0000			0.00	0.07
0.6349	0.77669	0.009	0.01	0.02					
				313.15 K					
0.0000			0.04	0.00	0.7182	0.77212	0.008	0.01	0.02
0.0729	0.77212	0.002	0.02	0.00	0.8027	0.77216	0.007	0.00	0.02
0.1632	0.77211	0.004	0.02	0.00	0.8714	0.77219	0.006	0.00	0.03
0.3251	0.77209	0.007	0.02	0.00	0.9485	0.77226	0.003	0.00	0.05
0.5592	0.77208	0.009	0.01	0.01	1.0000			0.00	0.08
0.6349	0.77209	0.009	0.01	0.01					

data[11,16−18] in the region of overlap (Figure 4). The excess molar enthalpy of this system is negative[15] (exothermic). Considering these observations, it is due to dominance of molecular association over dissociation.

The excess molar volumes of methanol (2) + ethanol (3) are positive and become more positive with increasing temperature. The excess molar volumes are in agreement with reported data[19−21] in the region of overlap (Figure 6), but negative values for V_m^E were reported by Albuquerque et al.[22] The V_m^E values of this system at different temperatures which are reported in the literature[8,11] are scattered data. The excess molar enthalpy of this system is positive[23] (endothermic). Considering these observations, positive values of V_m^E are preferred.

The computed excess molar volumes of the binary mixtures were fitted using a temperature-dependent Redlich−Kister expression[24]

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

where x_i and x_j are the mole fraction; A_{pq} are the temperature-dependent parameters for the binary mixtures; and T is the absolute temperature. These parameters were obtained by the

Table 5. Densities (ρ), Excess Molar Volumes (V_m^E), and Partial Excess Molar Volumes (V_i^E) for Ternary Mixtures of Water (1) + Methanol (2) + Ethanol (3) at Different Temperatures (283.15 to 313.15) 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}
						283.15 K							
0.1017	0.1046	0.8114	−0.387	−3.54	−0.08	−0.03	0.2851	0.4041	0.84351	−0.838	−2.23	−0.25	−0.34
0.1009	0.1993	0.81178	−0.375	−3.46	−0.02	−0.05	0.2997	0.4995	0.84836	−0.848	−2.13	−0.26	−0.43
0.0978	0.2942	0.81218	−0.373	−3.42	0.00	−0.06	0.3020	0.6039	0.85126	−0.827	−2.04	−0.27	−0.58
0.0988	0.4034	0.81290	−0.361	−3.36	0.00	−0.07	0.3943	0.0984	0.85557	−1.026	−1.71	−0.62	−0.55
0.1011	0.4997	0.81391	−0.360	−3.30	0.00	−0.08	0.3787	0.2286	0.85644	−1.001	−1.83	−0.50	−0.49
0.0958	0.5537	0.81517	−0.430	−3.31	0.00	−0.08	0.3906	0.3010	0.86092	−1.009	−1.79	−0.48	−0.54
0.1037	0.6967	0.81602	−0.359	−3.20	−0.01	−0.11	0.3980	0.4012	0.86559	−0.998	−1.71	−0.46	−0.70
0.0970	0.8004	0.81587	−0.333	−3.18	−0.01	−0.14	0.3959	0.5113	0.86877	−0.965	−1.62	−0.48	−0.92
0.2031	0.1009	0.82536	−0.680	−2.63	−0.15	−0.20	0.4974	0.0976	0.87530	−1.124	−1.45	−0.86	−0.75
0.1987	0.1944	0.82586	−0.666	−2.64	−0.12	−0.21	0.5062	0.2068	0.88152	−1.106	−1.35	−0.83	−0.92
0.2071	0.2954	0.82849	−0.683	−2.59	−0.13	−0.22	0.5047	0.2974	0.88515	−1.084	−1.27	−0.80	−1.12
0.2003	0.3970	0.82884	−0.661	−2.65	−0.11	−0.20	0.4960	0.4083	0.88792	−1.040	−1.20	−0.79	−1.39
0.2022	0.4979	0.83057	−0.655	−2.64	−0.11	−0.21	0.6050	0.1015	0.89908	−1.129	−1.03	−1.14	−1.36
0.1988	0.6013	0.83132	−0.624	−2.63	−0.10	−0.24	0.6079	0.1941	0.90499	−1.100	−0.86	−1.25	−1.72
0.1997	0.6973	0.83300	−0.612	−2.58	−0.10	−0.30	0.6072	0.2977	0.91032	−1.037	−0.73	−1.33	−2.13
0.3004	0.1002	0.83993	−0.886	−2.02	−0.36	−0.40	0.7120	0.0923	0.92605	−1.041	−0.51	−1.64	−2.57
0.2650	0.2062	0.83626	−0.815	−2.25	−0.25	−0.32	0.7117	0.1949	0.93223	−0.949	−0.34	−2.00	−3.08
0.3019	0.2952	0.84418	−0.879	−2.14	−0.31	−0.35	0.8023	0.1009	0.95108	−0.798	−0.13	−2.45	−4.05
						288.15 K							
0.1017	0.1046	0.80712	−0.386	−3.50	−0.09	−0.03	0.2851	0.4041	0.83924	−0.837	−2.21	−0.26	−0.33
0.1009	0.1993	0.80747	−0.374	−3.44	−0.03	−0.05	0.2997	0.4995	0.84413	−0.850	−2.12	−0.27	−0.42
0.0978	0.2942	0.80785	−0.373	−3.42	−0.01	−0.06	0.3020	0.6039	0.84706	−0.832	−2.03	−0.28	−0.56
0.0988	0.4034	0.80856	−0.363	−3.36	0.00	−0.07	0.3943	0.0984	0.85134	−1.016	−1.68	−0.64	−0.55
0.1011	0.4997	0.80957	−0.364	−3.31	−0.01	−0.08	0.3787	0.2286	0.85221	−0.994	−1.80	−0.53	−0.49
0.0958	0.5537	0.81076	−0.432	−3.33	−0.01	−0.07	0.3906	0.3010	0.85673	−1.005	−1.76	−0.51	−0.54
0.1037	0.6967	0.81159	−0.362	−3.22	−0.01	−0.10	0.3980	0.4012	0.86145	−0.997	−1.69	−0.49	−0.69
0.0970	0.8004	0.81141	−0.338	−3.21	−0.01	−0.13	0.3959	0.5113	0.86470	−0.968	−1.60	−0.50	−0.90
0.2031	0.1009	0.82108	−0.676	−2.60	−0.16	−0.20	0.4974	0.0976	0.87120	−1.112	−1.41	−0.89	−0.76
0.1987	0.1944	0.82157	−0.663	−2.62	−0.13	−0.20	0.5062	0.2068	0.87743	−1.096	−1.32	−0.86	−0.92
0.2071	0.2954	0.82418	−0.681	−2.58	−0.14	−0.21	0.5047	0.2974	0.88113	−1.077	−1.25	−0.83	−1.10
0.2003	0.3970	0.82452	−0.661	−2.64	−0.12	−0.20	0.4960	0.4083	0.88400	−1.039	−1.18	−0.82	−1.36
0.2022	0.4979	0.82625	−0.657	−2.64	−0.12	−0.20	0.6050	0.1015	0.89509	−1.113	−1.00	−1.17	−1.34
0.1988	0.6013	0.82699	−0.628	−2.64	−0.11	−0.23	0.6079	0.1941	0.90111	−1.089	−0.84	−1.27	−1.69
0.1997	0.6973	0.82866	−0.618	−2.59	−0.11	−0.29	0.6072	0.2977	0.90666	−1.033	−0.72	−1.35	−2.07
0.3004	0.1002	0.83565	−0.877	−2.00	−0.38	−0.40	0.7120	0.0923	0.92234	−1.024	−0.51	−1.67	−2.50
0.2650	0.2062	0.83198	−0.811	−2.23	−0.27	−0.31	0.7117	0.1949	0.92885	−0.940	−0.34	−2.00	−2.99
0.3019	0.2952	0.83992	−0.876	−2.11	−0.33	−0.35	0.8023	0.1009	0.94813	−0.788	−0.14	−2.44	−3.92
						293.15 K							
0.1017	0.1046	0.80281	−0.384	−3.46	−0.09	−0.03	0.2851	0.4041	0.83494	−0.837	−2.19	−0.28	−0.33
0.1009	0.1993	0.80314	−0.372	−3.41	−0.04	−0.05	0.2997	0.4995	0.83985	−0.852	−2.11	−0.29	−0.41
0.0978	0.2942	0.80350	−0.373	−3.40	−0.01	−0.06	0.3020	0.6039	0.84282	−0.838	−2.03	−0.30	−0.54
0.0988	0.4034	0.80418	−0.363	−3.36	−0.01	−0.06	0.3943	0.0984	0.84706	−1.005	−1.66	−0.66	−0.54
0.1011	0.4997	0.80517	−0.366	−3.32	−0.02	−0.07	0.3787	0.2286	0.84794	−0.988	−1.77	−0.55	−0.49
0.0958	0.5537	0.80634	−0.435	−3.35	−0.01	−0.06	0.3906	0.3010	0.85249	−1.000	−1.73	−0.54	−0.54
0.1037	0.6967	0.80714	−0.366	−3.25	−0.02	−0.09	0.3980	0.4012	0.85726	−0.996	−1.66	−0.52	−0.68
0.0970	0.8004	0.80693	−0.343	−3.24	−0.01	−0.12	0.3959	0.5113	0.86057	−0.971	−1.59	−0.52	−0.87
0.2031	0.1009	0.81676	−0.670	−2.58	−0.19	−0.20	0.4974	0.0976	0.86700	−1.100	−1.38	−0.91	−0.77
0.1987	0.1944	0.81724	−0.659	−2.60	−0.15	−0.20	0.5062	0.2068	0.87328	−1.087	−1.29	−0.89	−0.91
0.2071	0.2954	0.81984	−0.679	−2.57	−0.16	−0.21	0.5047	0.2974	0.87705	−1.072	−1.22	−0.86	−1.08
0.2003	0.3970	0.82017	−0.661	−2.64	−0.14	−0.19	0.4960	0.4083	0.88001	−1.039	−1.17	−0.84	−1.32
0.2022	0.4979	0.82190	−0.659	−2.63	−0.13	−0.20	0.6050	0.1015	0.89103	−1.098	−0.98	−1.20	−1.33
0.1988	0.6013	0.82263	−0.632	−2.64	−0.12	−0.22	0.6079	0.1941	0.89717	−1.079	−0.83	−1.29	−1.65
0.1997	0.6973	0.82430	−0.624	−2.60	−0.12	−0.28	0.6072	0.2977	0.90290	−1.030	−0.71	−1.37	−2.01
0.3004	0.1002	0.83134	−0.869	−1.98	−0.40	−0.39	0.7120	0.0923	0.91857	−1.008	−0.51	−1.69	−2.43
0.2650	0.2062	0.82766	−0.806	−2.21	−0.29	−0.30	0.7117	0.1949	0.92539	−0.934	−0.35	−2.00	−2.90
0.3019	0.2952	0.83561	−0.872	−2.09	−0.35	−0.35	0.8023	0.1009	0.94508	−0.780	−0.15	−2.43	−3.80
						298.15 K							
0.1017	0.1046	0.79846	−0.381	−3.41	−0.10	−0.03	0.2851	0.4041	0.83059	−0.837	−2.18	−0.30	−0.32
0.1009	0.1993	0.79878	−0.371	−3.39	−0.05	−0.04	0.2997	0.4995	0.83553	−0.855	−2.10	−0.31	−0.40
0.0978	0.2942	0.79912	−0.373	−3.39	−0.02	−0.05	0.3020	0.6039	0.83853	−0.844	−2.03	−0.31	−0.53
0.0988	0.4034	0.79978	−0.364	−3.37	−0.02	−0.06	0.3943	0.0984	0.84273	−0.995	−1.63	−0.68	−0.54
0.1011	0.4997	0.80075	−0.368	−3.33	−0.02	−0.06	0.3787	0.2286	0.84363	−0.982	−1.74	−0.57	−0.49
0.0958	0.5537	0.80189	−0.438	−3.37	−0.02	−0.06	0.3906	0.3010	0.84820	−0.997	−1.71	−0.56	−0.54
0.1037	0.6967	0.80267	−0.371	−3.27	−0.02	−0.09	0.3980	0.4012	0.85302	−0.996	−1.64	−0.54	−0.66

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}
						298.15 K							
0.0970	0.8004	0.80242	−0.348	−3.27	−0.02	−0.11	0.3959	0.5113	0.85640	−0.976	−1.58	−0.54	−0.85
0.2031	0.1009	0.81240	−0.665	−2.55	−0.21	−0.19	0.4974	0.0976	0.86274	−1.088	−1.35	−0.94	−0.77
0.1987	0.1944	0.81287	−0.656	−2.58	−0.17	−0.19	0.5062	0.2068	0.86909	−1.079	−1.26	−0.92	−0.91
0.2071	0.2954	0.81547	−0.677	−2.56	−0.17	−0.20	0.5047	0.2974	0.87292	−1.068	−1.20	−0.89	−1.06
0.2003	0.3970	0.81579	−0.662	−2.63	−0.15	−0.18	0.4960	0.4083	0.87597	−1.040	−1.15	−0.87	−1.28
0.2022	0.4979	0.81751	−0.661	−2.63	−0.14	−0.19	0.6050	0.1015	0.88691	−1.085	−0.96	−1.23	−1.32
0.1988	0.6013	0.81824	−0.637	−2.64	−0.13	−0.21	0.6079	0.1941	0.89316	−1.071	−0.82	−1.31	−1.61
0.1997	0.6973	0.81991	−0.631	−2.61	−0.13	−0.27	0.6072	0.2977	0.89906	−1.028	−0.71	−1.38	−1.96
0.3004	0.1002	0.82698	−0.861	−1.97	−0.43	−0.38	0.7120	0.0923	0.91472	−0.995	−0.50	−1.71	−2.37
0.2650	0.2062	0.82330	−0.801	−2.20	−0.31	−0.30	0.7117	0.1949	0.92184	−0.928	−0.36	−1.99	−2.82
0.3019	0.2952	0.83126	−0.869	−2.07	−0.37	−0.34	0.8023	0.1009	0.94191	−0.774	−0.16	−2.43	−3.69
						303.15 K							
0.1017	0.1046	0.79409	−0.379	−3.37	−0.10	−0.03	0.2851	0.4041	0.82620	−0.837	−2.17	−0.32	−0.31
0.1009	0.1993	0.79439	−0.369	−3.36	−0.06	−0.04	0.2997	0.4995	0.83116	−0.858	−2.09	−0.32	−0.39
0.0978	0.2942	0.79471	−0.372	−3.38	−0.03	−0.05	0.3020	0.6039	0.83420	−0.850	−2.03	−0.32	−0.51
0.0988	0.4034	0.79534	−0.364	−3.37	−0.03	−0.05	0.3943	0.0984	0.83835	−0.985	−1.61	−0.71	−0.54
0.1011	0.4997	0.79629	−0.370	−3.35	−0.03	−0.05	0.3787	0.2286	0.83927	−0.976	−1.72	−0.60	−0.48
0.0958	0.5537	0.79741	−0.441	−3.38	−0.02	−0.05	0.3906	0.3010	0.84386	−0.993	−1.68	−0.58	−0.53
0.1037	0.6967	0.79817	−0.375	−3.30	−0.03	−0.08	0.3980	0.4012	0.84872	−0.996	−1.63	−0.57	−0.65
0.0970	0.8004	0.79789	−0.354	−3.31	−0.02	−0.10	0.3959	0.5113	0.85217	−0.981	−1.57	−0.56	−0.82
0.2031	0.1009	0.80800	−0.659	−2.52	−0.23	−0.19	0.4974	0.0976	0.85843	−1.077	−1.32	−0.96	−0.77
0.1987	0.1944	0.80846	−0.652	−2.57	−0.19	−0.18	0.5062	0.2068	0.86483	−1.071	−1.24	−0.94	−0.90
0.2071	0.2954	0.81105	−0.675	−2.55	−0.19	−0.19	0.5047	0.2974	0.86872	−1.065	−1.18	−0.91	−1.04
0.2003	0.3970	0.81137	−0.662	−2.62	−0.16	−0.17	0.4960	0.4083	0.87187	−1.043	−1.14	−0.89	−1.25
0.2022	0.4979	0.81309	−0.664	−2.63	−0.16	−0.18	0.6050	0.1015	0.88274	−1.073	−0.94	−1.26	−1.30
0.1988	0.6013	0.81380	−0.641	−2.65	−0.14	−0.20	0.6079	0.1941	0.88908	−1.063	−0.81	−1.34	−1.58
0.1997	0.6973	0.81548	−0.638	−2.62	−0.13	−0.26	0.6072	0.2977	0.89516	−1.027	−0.70	−1.40	−1.90
0.3004	0.1002	0.82257	−0.852	−1.95	−0.45	−0.37	0.712	0.0923	0.91081	−0.982	−0.50	−1.73	−2.30
0.2650	0.2062	0.81888	−0.795	−2.18	−0.33	−0.29	0.7117	0.1949	0.91821	−0.924	−0.36	−2.00	−2.73
0.3019	0.2952	0.82687	−0.866	−2.06	−0.39	−0.33	0.8023	0.1009	0.93864	−0.768	−0.17	−2.43	−3.58
						308.15 K							
0.1017	0.1046	0.78967	−0.376	−3.32	−0.11	−0.03	0.2851	0.4041	0.82176	−0.837	−2.15	−0.33	−0.30
0.1009	0.1993	0.78995	−0.367	−3.33	−0.07	−0.04	0.2997	0.4995	0.82675	−0.861	−2.08	−0.34	−0.38
0.0978	0.2942	0.79026	−0.372	−3.37	−0.04	−0.04	0.3020	0.6039	0.82982	−0.857	−2.03	−0.34	−0.49
0.0988	0.4034	0.79087	−0.365	−3.37	−0.03	−0.05	0.3943	0.0984	0.83392	−0.976	−1.59	−0.73	−0.53
0.1011	0.4997	0.7918	−0.372	−3.36	−0.03	−0.05	0.3787	0.2286	0.83485	−0.971	−1.70	−0.62	−0.48
0.0958	0.5537	0.7929	−0.444	−3.40	−0.03	−0.04	0.3906	0.3010	0.83946	−0.990	−1.66	−0.61	−0.53
0.1037	0.6967	0.79363	−0.379	−3.33	−0.03	−0.07	0.3980	0.4012	0.84437	−0.997	−1.61	−0.59	−0.64
0.0970	0.8004	0.79333	−0.360	−3.34	−0.02	−0.09	0.3959	0.5113	0.84788	−0.986	−1.57	−0.58	−0.79
0.2031	0.1009	0.80355	−0.653	−2.50	−0.25	−0.18	0.4974	0.0976	0.85407	−1.067	−1.29	−0.99	−0.77
0.1987	0.1944	0.80400	−0.648	−2.55	−0.21	−0.17	0.5062	0.2068	0.86052	−1.065	−1.22	−0.97	−0.89
0.2071	0.2954	0.80660	−0.674	−2.54	−0.21	−0.18	0.5047	0.2974	0.86446	−1.062	−1.17	−0.94	−1.02
0.2003	0.3970	0.80689	−0.662	−2.62	−0.18	−0.16	0.4960	0.4083	0.86770	−1.045	−1.13	−0.91	−1.21
0.2022	0.4979	0.80862	−0.666	−2.63	−0.17	−0.17	0.6050	0.1015	0.87849	−1.061	−0.92	−1.29	−1.29
0.1988	0.6013	0.80933	−0.646	−2.66	−0.15	−0.19	0.6079	0.1941	0.88494	−1.056	−0.80	−1.36	−1.54
0.1997	0.6973	0.81101	−0.645	−2.63	−0.14	−0.25	0.6072	0.2977	0.89117	−1.026	−0.70	−1.42	−1.85
0.3004	0.1002	0.81811	−0.844	−1.94	−0.48	−0.36	0.7120	0.0923	0.90682	−0.971	−0.50	−1.75	−2.24
0.2650	0.2062	0.81443	−0.791	−2.17	−0.35	−0.28	0.7117	0.1949	0.91449	−0.921	−0.37	−2.00	−2.66
0.3019	0.2952	0.82243	−0.864	−2.04	−0.41	−0.33	0.8023	0.1009	0.93525	−0.764	−0.18	−2.43	−3.48
						313.15 K							
0.1017	0.1046	0.78520	−0.372	−3.27	−0.12	−0.03	0.2851	0.4041	0.81727	−0.838	−2.14	−0.35	−0.29
0.1009	0.1993	0.78548	−0.365	−3.30	−0.08	−0.04	0.2997	0.4995	0.82229	−0.865	−2.07	−0.36	−0.37
0.0978	0.2942	0.78577	−0.371	−3.35	−0.05	−0.04	0.3020	0.6039	0.82537	−0.864	−2.03	−0.35	−0.47
0.0988	0.4034	0.78636	−0.366	−3.37	−0.04	−0.04	0.3943	0.0984	0.82942	−0.966	−1.58	−0.75	−0.52
0.1011	0.4997	0.78726	−0.373	−3.37	−0.04	−0.04	0.3787	0.2286	0.83036	−0.965	−1.68	−0.64	−0.47
0.0958	0.5537	0.78834	−0.447	−3.42	−0.03	−0.04	0.3906	0.3010	0.83501	−0.987	−1.65	−0.63	−0.52
0.1037	0.6967	0.78905	−0.383	−3.35	−0.03	−0.06	0.3980	0.4012	0.83996	−0.998	−1.60	−0.61	−0.62
0.0970	0.8004	0.78872	−0.365	−3.38	−0.03	−0.08	0.3959	0.5113	0.84352	−0.991	−1.56	−0.60	−0.76
0.2031	0.1009	0.79904	−0.646	−2.47	−0.27	−0.17	0.4974	0.0976	0.84963	−1.056	−1.27	−1.01	−0.76
0.1987	0.1944	0.79949	−0.643	−2.54	−0.23	−0.16	0.5062	0.2068	0.85614	−1.059	−1.20	−1.00	−0.88
0.2071	0.2954	0.80208	−0.671	−2.53	−0.22	−0.17	0.5047	0.2974	0.86014	−1.060	−1.16	−0.97	−1.00
0.2003	0.3970	0.80238	−0.662	−2.62	−0.19	−0.15	0.4960	0.4083	0.86346	−1.049	−1.13	−0.94	−1.17
0.2022	0.4979	0.80410	−0.669	−2.64	−0.18	−0.16	0.6050	0.1015	0.87419	−1.051	−0.90	−1.32	−1.27
0.1988	0.6013	0.80481	−0.650	−2.67	−0.16	−0.18	0.6079	0.1941	0.88073	−1.051	−0.79	−1.38	−1.51
0.1997	0.6973	0.80649	−0.652	−2.65	−0.15	−0.23	0.6072	0.2977	0.88711	−1.027	−0.70	−1.44	−1.79
0.3004	0.1002	0.81360	−0.836	−1.93	−0.50	−0.35	0.7120	0.0923	0.90276	−0.961	−0.50	−1.77	−2.19
0.2650	0.2062	0.80991	−0.786	−2.16	−0.37	−0.27	0.7117	0.1949	0.91069	−0.920	−0.38	−2.01	−2.58
0.3019	0.2952	0.81792	−0.860	−2.03	−0.43	−0.32	0.8023	0.1009	0.93176	−0.760	−0.19	−2.44	−3.39

Table 6. Coefficients A_{pq} of Equation 2 and Standard Deviation for the Fits of the Binary Excess Molar Volumes in the Temperature Range (283.15 to 313.15) K

	p					σ
q	0	1	2	3	4	$cm^3 \cdot mol^{-1}$
			Water (1) + Methanol (2)			
0	−8.3520	−12.9084	−5.3661	20.3374	23.4523	0.0033
1	0.0348	0.0759	0.0376	−0.1174	−0.1304	
2	$-6.78 \cdot 10^{-5}$	$1.12 \cdot 10^{-4}$	$-6.51 \cdot 10^{-5}$	$1.72 \cdot 10^{-4}$	$1.82 \cdot 10^{-4}$	
			Water (1) + Ethanol (3)			
0	−11.4546	−28.0525	−23.3114	16.9835	47.152	0.0184
1	0.0373	0.1668	0.1078	−0.09514	−0.2430	
2	$-4.4 \cdot 10^{-5}$	$-2.58 \cdot 10^{-4}$	$-1.25 \cdot 10^{-4}$	$1.32 \cdot 10^{-4}$	$3.08 \cdot 10^{-4}$	
			Methanol (2) + Ethanol (3)			
0	−1.6563	−0.4378	13.6442	2.9771	−16.3297	0.0004
1	0.0108	0.0028	−0.0908	−0.0199	0.1083	
2	$1.73 \cdot 10^{-5}$	$-4.53 \cdot 10^{-6}$	$1.51 \cdot 10^{-4}$	$3.33 \cdot 10^{-5}$	$-1.79 \cdot 10^{-4}$	

Table 7. Coefficients C_{iq} of Equation 6 and Standard Deviation for the Fits of the Ternary Excess Molar Volumes in the Temperature Range (283.15 to 313.15) K

	i			σ
q	0	1	2	$cm^3 \cdot mol^{-1}$
		Water (1) + Methanol (2) + Ethanol (3)		
0	4.6721	38.6271	16.5177	0.0112
1	−0.023	−0.2723	−0.1009	
2	$9.54 \cdot 10^{-6}$	$5.05 \cdot 10^{-4}$	$1.57 \cdot 10^{-4}$	

unweighted least-squares 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

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

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

The excess molar volumes for the ternary mixture were fitted to the temperature-dependent Cibulka equation[25]

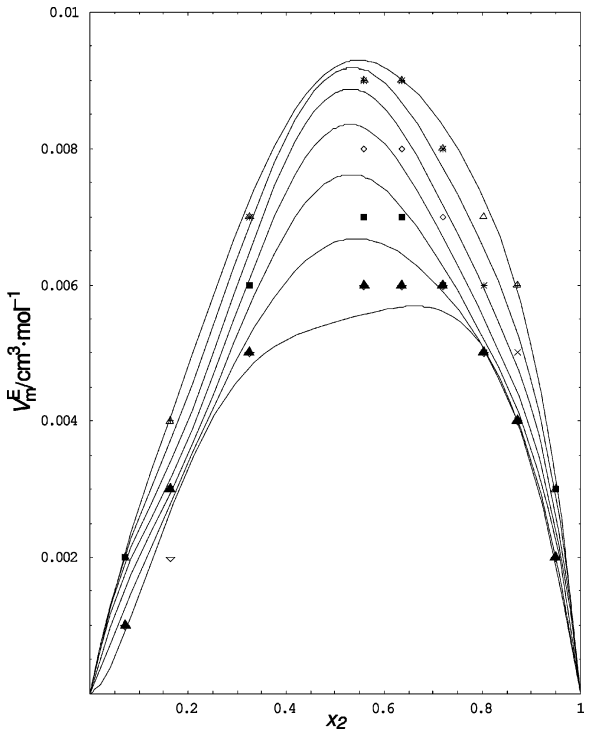

Figure 5. Experimental excess molar volumes for the methanol (2) + ethanol (3) mixture at different temperatures: ▲, 283.15 K; ▽, 288.15 K; ■, 293.15 K; ◇, 298.15 K; ×, 303.15 K; +, 308.15; △, 313.15 K. Solid curves represent the values calculated from eq 2 with coefficients from Table 6.

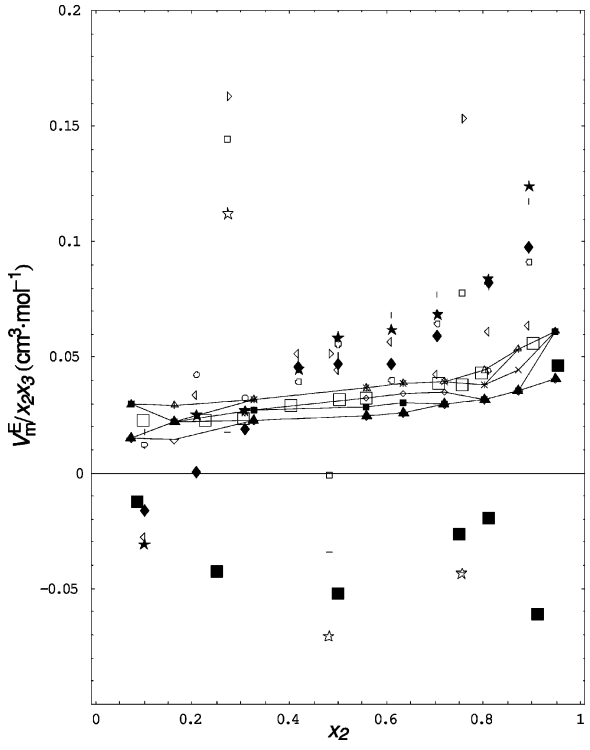

Figure 6. Experimental data of V_m^E/x_2x_3 for methanol (2) + ethanol (3) at different temperatures. This work: ▲, 283.15 K; ▽, 288.15 K; ■, 293.15 K; ◇, 298.15 K; ×, 303.15 K; +, 308.15 K; △, 313.15 K; ☆, 273.15 K, ref 8; −, 293.15 K, ref 8; □, 313.15 K, ref 8; open arrow pointing right, 333.15 K, ref 8; open arrow pointing left, 298.15 K, ref 11; |, 308.15 K, ref 11; ★, 318.15 K, ref 11; ◆, 328.15 K, ref 11; □, 338.15 K, ref 11; ■, 298.15 K, ref 19; ○, 298.15 K, ref 22.

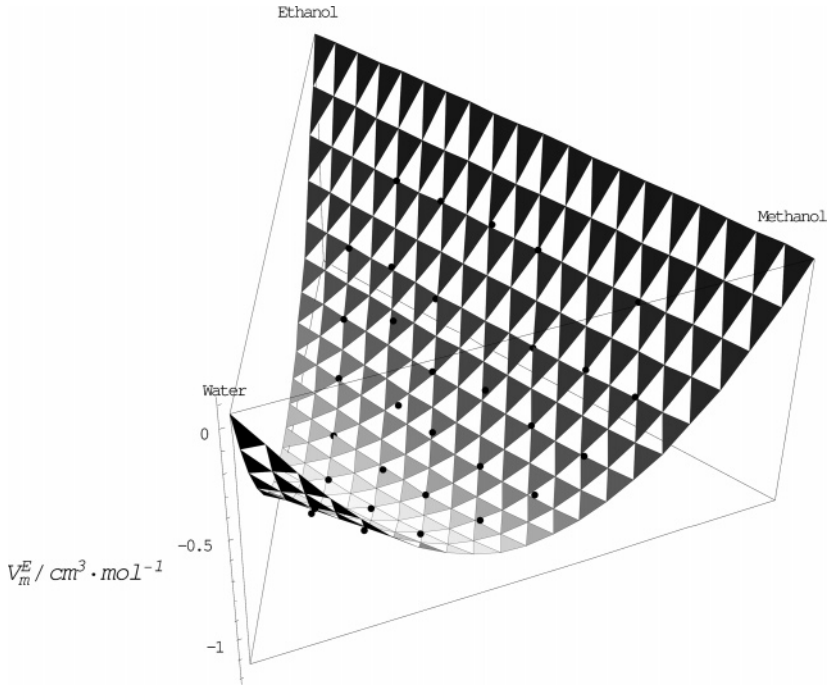

Figure 7. Representation of the experimental excess molar volume surface for the ternary mixture of water (1) + methanol (2) + ethanol (3) at 313.15 K. ●, represents experimental points. Curves represent the values calculated from eq 4 with coefficients from Table 7. The unit in the triangle plot is mole fraction.

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

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

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

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 the density of pure components was fitted to the equation

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

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 $\pm\ 5\cdot10^{-6}$ K^{-1}.

The partial excess molar volume, V^{E}_i, of a component in a two- and three-component mixture can be computed from excess molar volume data by using the following equation.[26]

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

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

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

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

The partial molar quantities are important in the study of the dependence of an extensive property on phase composition at constant pressure and temperature, showing its trend with composition. The partial excess molar volumes, V^{E}_i, and their values at infinite dilution, $V^{E,0}_i$, are recorded in Tables 2 to 5. The average uncertainty in the partial excess molar volume is estimated to be $\pm\ 2\cdot10^{-2}$ cm^3·mol^{-1}.

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