Volumetric Properties of Binary and Ternary Liquid Mixtures of 1-Propanol (1) + 2-Propanol (2) + Water (3) at Different Temperatures and Ambient Pressure (81.5 kPa)

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Excess molar volume, V_m^E, and excess partial molar volume, V_i^E, of the ternary mixtures of 1-propanol (1) + 2-propanol (2) + water (3) and of two binaries of 1-propanol (1) + water (3) and 2-propanol (2) + water (3) have been investigated from the density, ρ, measurements over the entire range of composition at temperatures (293.15, 303.15, 313.15, and 323.15) K and at ambient pressure (81.5 kPa). The limiting values of the excess partial molar volumes at infinite dilution, $V_i^{E,0}$, and thermal expansion coefficients, α, of the pure component are also evaluated. The systems exhibited negative values of V_m^E that increase with increasing temperatures. The excess molar volumes were correlated with the Redlich−Kister equation and the Cibulka equation for binary and ternary systems, respectively. The excess molar volumes, V_m^E, of the binary mixtures were compared with values from the literature in the region of overlap.

Introduction

Thermodynamic properties of binary and ternary liquid mixtures of water with alkanol are interesting because of industrial applications and the theoretical interest in studying the structure of such solutions. Aqueous solutions of alcohols have served as useful industrial solvent media for a variety of separation processes and pharmaceutical applications. It also has become more popular to use in solar thermal systems.[1] Review of the literature show that volumetric properties of binary mixtures of 1-propanol + water and 2-propanol + water have been reported,[2–19] but with regard to the ternary mixtures of 1-propanol + 2-propanol + water there are practically no experimental values.

As a part of our continuing in exploring the effect of the position of the hydroxyl group−upon the thermodynamic properties 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 ternary mixture of 1-propanol (1) + 2-propanol (2) + water (3) and two binaries of 1-propanol + water, and 2-propanol + water over the entire range of composition at temperatures (293.15, 303.15, 313.15, and 323.15) K and at ambient pressure (81.5 kPa). The excess molar volumes, V_m^E, were compared with values from the literature in the region of overlap. The excess molar volumes were correlated with the Redlich−Kister equation and the Cibulka equation for binary and ternary system, respectively.

Experimental

Materials. The 1-propanol (GC, min 99.8 %) and 2-propanol (extra pure > 99.5 %) were obtained from Merck chemicals. Both were used without further purification. Water was double distilled. Prior to use the chemicals were degassed by heating and cooling. The densities and thermal expansion coefficients of pure components are given in Table 1 and compared with the literature values.[20–23]

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Table 1. Densities, ρ, and Thermal Expansion Coefficients, α,of the Pure Components

		$\rho/(g\cdot cm^{-3})$		
component	T/K	exptl	lit	$10^4\alpha/K^{-1}$
1-propanol	293.15	0.80359	0.80366[20]	9.96
	303.15	0.79553	0.79560[21]	10.15
	313.15	0.78738	0.7875[21]	10.42
	323.15	0.77892	0.7790[21]	10.31
2-propanol	293.15	0.78510	0.78534[20]	10.78
	303.15	0.77663	0.77662[22]	11.04
	313.15	0.76784		11.74
	323.15	0.75868		12.15
water	293.15	0.99820	0.998203[23]	2.09
	303.15	0.99564	0.995645[23]	3.03
	313.15	0.99221	0.992212[23]	3.86
	323.15	0.98803	0.988030[23]	4.57

Measurements. The sample densities were measured with a vibrating u-tube density meter (Anton Paar DMA 4500) provided with automatic viscosity correction. All the mixtures were prepared by mass on a Mettler AB 204-N balance with an uncertainty of $\pm 1\cdot10^{-4}$ g. Conversion to molar mass was based on the relative atomic mass table of 1996 issued by IUPAC.[24] The average uncertainty in the mole fraction from the propagation law of errors is estimated to be $\pm 2\cdot10^{-5}$. Uncertainty in the density was $\pm 1\cdot10^{-5}$ g·cm^{-3}. Details of the apparatus and procedure have been described elsewhere.[25]

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, and 323.15) K and at ambient pressure (81.5 kPa), and they are given in Tables 1 to 4. The excess molar volumes, V_m^E, of the binary and ternary mixtures were calculated from the densities using eq 1

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Table 2. Densities ρ, Excess Molar Volumes V_m^E, and Partial Excess Molar Volumes V_i^E for Binary Mixtures of 1-Propanol (1) + Water (3) at Different Temperatures of (293.15 to 323.15) 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}
		$T = 293.15$ K		
1.0000	0.80359		0.00	−3.25
0.9052	0.81117	−0.238	−0.05	−2.06
0.8383	0.81674	−0.361	−0.10	−1.70
0.7485	0.82484	−0.488	−0.17	−1.41
0.6792	0.83169	−0.557	−0.25	−1.22
0.5986	0.84082	−0.626	−0.37	−1.01
0.5197	0.85112	−0.672	−0.51	−0.84
0.4399	0.86300	−0.681	−0.64	−0.72
0.3599	0.87753	−0.679	−0.74	−0.65
0.2798	0.89560	−0.661	−0.87	−0.59
0.2000	0.91886	−0.629	−1.26	−0.47
0.1202	0.94794	−0.527	−2.36	−0.27
0.0401	0.98098	−0.238	−5.08	−0.05
0.0000	0.99820		−7.47	0.00
		$T = 303.15$ K		
1.0000	0.79553		0.00	−3.03
0.9052	0.80294	−0.219	−0.05	−1.87
0.8383	0.80845	−0.335	−0.09	−1.56
0.7485	0.81647	−0.452	−0.15	−1.33
0.6792	0.82334	−0.518	−0.22	−1.16
0.5986	0.83248	−0.584	−0.33	−0.96
0.5197	0.84287	−0.630	−0.47	−0.79
0.4399	0.85486	−0.638	−0.60	−0.67
0.3599	0.86957	−0.636	−0.70	−0.60
0.2798	0.88791	−0.618	−0.83	−0.54
0.2000	0.91137	−0.581	−1.16	−0.44
0.1202	0.94135	−0.488	−2.18	−0.25
0.0401	0.97693	−0.229	−4.75	−0.04
0.0000	0.99564		−7.04	0.00
		$T = 313.15$ K		
1.0000	0.78738		0.00	−2.82
0.9052	0.79455	−0.195	−0.05	−1.68
0.8383	0.79996	−0.301	−0.08	−1.42
0.7485	0.80791	−0.410	−0.13	−1.24
0.6792	0.81476	−0.473	−0.18	−1.11
0.5986	0.82392	−0.538	−0.29	−0.92
0.5197	0.83437	−0.584	−0.42	−0.75
0.4399	0.84649	−0.594	−0.56	−0.63
0.3599	0.86138	−0.594	−0.66	−0.56
0.2798	0.87998	−0.580	−0.77	−0.51
0.2000	0.90385	−0.547	−1.07	−0.42
0.1202	0.93448	−0.457	−2.02	−0.24
0.0401	0.97223	−0.223	−4.49	−0.04
0.0000	0.99221		−6.72	0.00
		$T = 323.15$ K		
1.0000	0.77892		0.00	−2.60
0.9052	0.78594	−0.152	−0.04	−1.51
0.8383	0.79125	−0.250	−0.07	−1.29
0.7485	0.79913	−0.354	−0.11	−1.16
0.6792	0.80595	−0.416	−0.15	−1.05
0.5986	0.81516	−0.483	−0.25	−0.89
0.5197	0.82564	−0.531	−0.37	−0.72
0.4399	0.83786	−0.544	−0.50	−0.60
0.3599	0.85293	−0.550	−0.60	−0.53
0.2798	0.87178	−0.541	−0.70	−0.49
0.2000	0.89605	−0.513	−0.98	−0.40
0.1202	0.92731	−0.430	−1.89	−0.24
0.0401	0.96691	−0.218	−4.31	−0.04
0.0000	0.98803		−6.51	0.00

Table 3. Densities ρ, Excess Molar Volumes V_m^E, and Partial Excess Molar Volumes V_i^E for Binary Mixtures of 2-Propanol (2) + Water (3) at Different Temperatures of (293.15 to 323.15) 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}
$T = 293.15$ K				
1.0000	0.78510		0.00	−3.57
0.9225	0.79203	−0.254	−0.02	−3.02
0.8403	0.79995	−0.480	−0.10	−2.44
0.7552	0.80856	−0.641	−0.22	−1.97
0.6801	0.81714	−0.762	−0.33	−1.69
0.5995	0.82756	−0.864	−0.44	−1.50
0.5204	0.83936	−0.937	−0.53	−1.38
0.4384	0.85411	−1.001	−0.66	−1.26
0.3590	0.87115	−1.027	−0.89	−1.11
0.2800	0.89187	−1.016	−1.37	−0.89
0.2017	0.91663	−0.933	−2.29	−0.60
0.1197	0.94888	−0.755	−4.03	−0.27
0.0399	0.97961	−0.278	−6.85	−0.04
0.0000	0.99820		−8.81	0.00
$T = 303.15$ K				
1.0000	0.77663		0.00	−3.32
0.9225	0.78334	−0.231	−0.02	−2.76
0.8403	0.79110	−0.442	−0.09	−2.28
0.7552	0.79967	−0.598	−0.18	−1.90
0.6801	0.80826	−0.718	−0.28	−1.66
0.5995	0.81872	−0.819	−0.38	−1.47
0.5204	0.83058	−0.891	−0.49	−1.33
0.4384	0.84546	−0.957	−0.64	−1.20
0.3590	0.86265	−0.982	−0.87	−1.04
0.2800	0.88356	−0.969	−1.32	−0.83
0.2017	0.90864	−0.884	−2.17	−0.57
0.1197	0.94164	−0.709	−3.79	−0.27
0.0399	0.97600	−0.281	−6.54	−0.04
0.0000	0.99564		−8.53	0.00
$T = 313.15$ K				
1.0000	0.76784		0.00	−3.05
0.9225	0.77433	−0.209	−0.02	−2.53
0.8403	0.78197	−0.409	−0.07	−2.14
0.7552	0.79048	−0.558	−0.15	−1.84
0.6801	0.79908	−0.677	−0.23	−1.64
0.5995	0.80960	−0.780	−0.33	−1.45
0.5204	0.82154	−0.854	−0.45	−1.30
0.4384	0.83652	−0.919	−0.61	−1.15
0.3590	0.85389	−0.946	−0.85	−0.99
0.2800	0.87501	−0.933	−1.28	−0.80
0.2017	0.90042	−0.846	−2.07	−0.55
0.1197	0.93418	−0.675	−3.61	−0.26
0.0399	0.97152	−0.283	−6.30	−0.04
0.0000	0.99221		−8.30	0.00
$T = 323.15$ K				
1.0000	0.75868		0.00	−2.75
0.9225	0.76497	−0.189	−0.02	−2.32
0.8403	0.77247	−0.376	−0.05	−2.03
0.7552	0.78098	−0.525	−0.11	−1.80
0.6801	0.78960	−0.644	−0.18	−1.62
0.5995	0.80016	−0.747	−0.28	−1.44
0.5204	0.81220	−0.824	−0.41	−1.28
0.4384	0.82731	−0.891	−0.58	−1.13
0.3590	0.84485	−0.919	−0.83	−0.97
0.2800	0.86623	−0.908	−1.25	−0.77
0.2017	0.89198	−0.820	−2.00	−0.54
0.1197	0.92648	−0.651	−3.49	−0.26
0.0399	0.96620	−0.283	−6.13	−0.04
0.0000	0.98803		−8.12	0.00

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

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 average uncertainty in the excess molar volumes was estimated to be $\pm\ 2\cdot10^{-3}$ cm^3·mol^{-1}. The excess molar volumes for binary mixtures 1-propanol (1) + water (3), and 2-propanol (2) + water (3) and the ternary mixture1-propanol (1) + 2-propanol (2) + water (3) at different temperatures are recorded in Tables 2 to 4 and graphically represented in Figures 1, 3, and 5.

The excess molar volumes for 1-propanol (1) + water (3) are negative and increase with increasing temperatures from (293.15 to 323.15) K. The excess molar volumes are in

Table 4. Densities ρ, Excess Molar Volumes V_m^E, and Partial Excess Molar Volumes V_i^E for Ternary Mixtures of 1-Propanol (1) + 2-Propanol (2) + Water (3) at Different Temperatures of (293.15 to 323.15) 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}
					$T = 293.15$ K								
0.8021	0.1001	0.80952	−0.259	−0.05	−0.23	−2.14	0.2997	0.4004	0.82123	−0.663	−0.21	−0.43	−1.39
0.7788	0.1485	0.80766	−0.301	−0.03	−0.16	−2.41	0.2002	0.4996	0.81916	−0.69	−0.15	−0.40	−1.48
0.6001	0.3000	0.80593	−0.294	−0.04	−0.18	−2.34	0.1047	0.5965	0.81705	−0.719	−0.05	−0.36	−1.60
0.4995	0.4000	0.80407	−0.307	−0.04	−0.15	−2.40	0.4975	0.1048	0.83815	−0.671	−0.35	−0.68	−1.06
0.3992	0.4996	0.80217	−0.314	−0.07	−0.11	−2.47	0.3990	0.2016	0.83627	−0.714	−0.32	−0.62	−1.11
0.3023	0.5980	0.80013	−0.317	−0.08	−0.09	−2.56	0.2998	0.2997	0.83445	−0.768	−0.26	−0.58	−1.19
0.1990	0.7013	0.79808	−0.319	−0.07	−0.07	−2.64	0.1996	0.4003	0.83216	−0.805	−0.15	−0.54	−1.29
0.0997	0.8001	0.79614	−0.320	−0.09	−0.06	−2.72	0.0996	0.5004	0.82995	−0.843	−0.01	−0.50	−1.39
0.7005	0.0999	0.81810	−0.444	−0.13	−0.41	−1.62	0.4000	0.0999	0.85173	−0.736	−0.43	−0.92	−0.92
0.6002	0.2001	0.81612	−0.467	−0.13	−0.35	−1.66	0.2999	0.2000	0.84950	−0.792	−0.29	−0.79	−1.05
0.5000	0.3004	0.81392	−0.473	−0.13	−0.32	−1.69	0.2002	0.3001	0.84684	−0.827	−0.14	−0.69	−1.18
0.4000	0.3999	0.81214	−0.507	−0.14	−0.28	−1.73	0.0995	0.3999	0.84518	−0.906	0.03	−0.62	−1.28
0.2998	0.5000	0.80948	−0.473	−0.14	−0.25	−1.79	0.3002	0.1002	0.86698	−0.728	−0.41	−1.26	−0.87
0.2001	0.5998	0.80792	−0.527	−0.11	−0.23	−1.89	0.2000	0.2000	0.86592	−0.851	−0.17	−1.00	−1.03
0.0996	0.7002	0.80588	−0.541	−0.07	−0.20	−2.02	0.1002	0.3001	0.86341	−0.913	0.00	−0.82	−1.15
0.6004	0.0996	0.82755	−0.575	−0.23	−0.54	−1.29	0.2008	0.1003	0.88865	−0.777	−0.43	−1.75	−0.79
0.5003	0.1994	0.82563	−0.616	−0.24	−0.48	−1.30	0.0997	0.1998	0.88693	−0.871	−0.27	−1.37	−0.90
0.3998	0.3001	0.82345	−0.641	−0.24	−0.45	−1.33	0.1001	0.0998	0.91747	−0.761	−1.06	−2.66	−0.56
					$T = 303.15$ K								
0.8021	0.1001	0.80125	−0.241	−0.05	−0.22	−1.95	0.2997	0.4004	0.81258	−0.623	−0.18	−0.39	−1.34
0.7788	0.1485	0.79934	−0.284	−0.03	−0.15	−2.19	0.2002	0.4996	0.81044	−0.649	−0.12	−0.36	−1.43
0.6001	0.3000	0.79757	−0.277	−0.03	−0.18	−2.15	0.1047	0.5965	0.80825	−0.677	−0.03	−0.32	−1.56
0.4995	0.4000	0.79565	−0.288	−0.04	−0.14	−2.21	0.4975	0.1048	0.82975	−0.630	−0.31	−0.65	−1.01
0.3992	0.4996	0.79369	−0.295	−0.07	−0.10	−2.27	0.3990	0.2016	0.82777	−0.672	−0.28	−0.59	−1.06
0.3023	0.5980	0.79159	−0.296	−0.08	−0.08	−2.35	0.2998	0.2997	0.82588	−0.726	−0.22	−0.55	−1.14
0.1990	0.7013	0.78949	−0.298	−0.08	−0.07	−2.43	0.1996	0.4003	0.82350	−0.762	−0.12	−0.51	−1.24
0.0997	0.8001	0.78746	−0.295	−0.09	−0.06	−2.49	0.0996	0.5004	0.82121	−0.800	0.02	−0.45	−1.35
0.7005	0.0999	0.80970	−0.412	−0.11	−0.40	−1.51	0.4000	0.0999	0.84341	−0.694	−0.40	−0.89	−0.87
0.6002	0.2001	0.80767	−0.435	−0.11	−0.34	−1.56	0.2999	0.2000	0.84107	−0.749	−0.26	−0.77	−0.99
0.5000	0.3004	0.80542	−0.442	−0.11	−0.30	−1.60	0.2002	0.3001	0.83834	−0.785	−0.11	−0.67	−1.12
0.4000	0.3999	0.80357	−0.475	−0.12	−0.26	−1.64	0.0995	0.3999	0.83654	−0.862	0.06	−0.59	−1.22
0.2998	0.5000	0.80086	−0.440	−0.13	−0.23	−1.71	0.3002	0.1002	0.85879	−0.684	−0.39	−1.22	−0.81
0.2001	0.5998	0.79921	−0.491	−0.11	−0.20	−1.80	0.2000	0.2000	0.85759	−0.806	−0.15	−0.98	−0.97
0.0996	0.7002	0.79710	−0.504	−0.07	−0.17	−1.92	0.1002	0.3001	0.85497	−0.869	0.02	−0.81	−1.08
0.6004	0.0996	0.81911	−0.536	−0.20	−0.52	−1.22	0.2008	0.1003	0.88069	−0.733	−0.39	−1.69	−0.74
0.5003	0.1994	0.81714	−0.578	−0.21	−0.46	−1.24	0.0997	0.1998	0.87882	−0.827	−0.23	−1.32	−0.85
0.3998	0.3001	0.81488	−0.603	−0.20	−0.42	−1.27	0.1001	0.0998	0.90986	−0.716	−0.95	−2.52	−0.53
					$T = 313.15$ K								
0.8021	0.1001	0.79280	−0.218	−0.04	−0.23	−1.77	0.2997	0.4004	0.80369	−0.585	−0.15	−0.36	−1.29
0.7788	0.1485	0.79083	−0.261	−0.03	−0.16	−1.98	0.2002	0.4996	0.80146	−0.611	−0.10	−0.32	−1.39
0.6001	0.3000	0.78899	−0.256	−0.03	−0.18	−1.97	0.1047	0.5965	0.79918	−0.639	−0.01	−0.27	−1.52
0.4995	0.4000	0.78700	−0.268	−0.04	−0.14	−2.03	0.4975	0.1048	0.82110	−0.586	−0.27	−0.63	−0.96
0.3992	0.4996	0.78497	−0.274	−0.07	−0.10	−2.09	0.3990	0.2016	0.81904	−0.630	−0.24	−0.57	−1.02
0.3023	0.5980	0.78279	−0.274	−0.09	−0.07	−2.17	0.2998	0.2997	0.81707	−0.686	−0.19	−0.53	−1.09
0.1990	0.7013	0.78061	−0.276	−0.09	−0.06	−2.23	0.1996	0.4003	0.81458	−0.722	−0.08	−0.47	−1.20
0.0997	0.8001	0.77850	−0.271	−0.10	−0.05	−2.29	0.0996	0.5004	0.81219	−0.761	0.06	−0.41	−1.32
0.7005	0.0999	0.80110	−0.375	−0.09	−0.39	−1.41	0.4000	0.0999	0.83485	−0.651	−0.35	−0.86	−0.83
0.6002	0.2001	0.79901	−0.401	−0.09	−0.33	−1.46	0.2999	0.2000	0.83240	−0.708	−0.23	−0.74	−0.95
0.5000	0.3004	0.79670	−0.409	−0.09	−0.29	−1.50	0.2002	0.3001	0.82958	−0.746	−0.07	−0.65	−1.07
0.4000	0.3999	0.79476	−0.442	−0.11	−0.24	−1.55	0.0995	0.3999	0.82765	−0.824	0.09	−0.56	−1.18
0.2998	0.5000	0.79198	−0.406	−0.12	−0.20	−1.62	0.3002	0.1002	0.85036	−0.642	−0.35	−1.18	−0.77
0.2001	0.5998	0.79024	−0.457	−0.10	−0.17	−1.72	0.2000	0.2000	0.84903	−0.767	−0.11	−0.95	−0.92
0.0996	0.7002	0.78802	−0.468	−0.07	−0.15	−1.83	0.1002	0.3001	0.84627	−0.831	0.05	−0.79	−1.03
0.6004	0.0996	0.81046	−0.494	−0.17	−0.50	−1.16	0.2008	0.1003	0.87249	−0.695	−0.34	−1.63	−0.71
0.5003	0.1994	0.80842	−0.538	−0.17	−0.44	−1.19	0.0997	0.1998	0.87044	−0.791	−0.18	−1.27	−0.82
0.3998	0.3001	0.80607	−0.563	−0.17	−0.40	−1.22	0.1001	0.0998	0.90201	−0.680	−0.86	−2.42	−0.51
					$T = 323.15$ K								
0.8021	0.1001	0.78413	−0.205	−0.04	−0.24	−1.59	0.2997	0.4004	0.79453	−0.553	−0.12	−0.34	−1.25
0.7788	0.1485	0.78210	−0.247	−0.03	−0.17	−1.78	0.2002	0.4996	0.79219	−0.579	−0.07	−0.29	−1.36
0.6001	0.3000	0.78017	−0.243	−0.03	−0.18	−1.79	0.1047	0.5965	0.78981	−0.607	0.01	−0.24	−1.49
0.4995	0.4000	0.77809	−0.255	−0.04	−0.14	−1.86	0.4975	0.1048	0.81221	−0.550	−0.23	−0.61	−0.93
0.3992	0.4996	0.77597	−0.260	−0.07	−0.10	−1.92	0.3990	0.2016	0.81005	−0.595	−0.20	−0.55	−0.98
0.3023	0.5980	0.77373	−0.261	−0.10	−0.07	−1.99	0.2998	0.2997	0.80797	−0.653	−0.14	−0.50	−1.06
0.1990	0.7013	0.77143	−0.259	−0.11	−0.06	−2.06	0.1996	0.4003	0.80538	−0.690	−0.04	−0.44	−1.17
0.0997	0.8001	0.76923	−0.252	−0.12	−0.04	−2.12	0.0996	0.5004	0.80288	−0.730	0.10	−0.37	−1.30
0.7005	0.0999	0.79229	−0.348	−0.08	−0.39	−1.30	0.4000	0.0999	0.82601	−0.615	−0.31	−0.83	−0.80
0.6002	0.2001	0.79012	−0.375	−0.07	−0.33	−1.36	0.2999	0.2000	0.82347	−0.675	−0.18	−0.72	−0.92
0.5000	0.3004	0.78772	−0.383	−0.08	−0.28	−1.41	0.2002	0.3001	0.82055	−0.716	−0.03	−0.62	−1.04
0.4000	0.3999	0.78566	−0.413	−0.09	−0.23	−1.46	0.0995	0.3999	0.81845	−0.793	0.14	−0.53	−1.15
0.2998	0.5000	0.78282	−0.379	−0.11	−0.19	−1.54	0.3002	0.1002	0.84167	−0.609	−0.30	−1.15	−0.74
0.2001	0.5998	0.78097	−0.429	−0.10	−0.15	−1.64	0.2000	0.2000	0.84019	−0.736	−0.07	−0.92	−0.90
0.0996	0.7002	0.77865	−0.438	−0.07	−0.12	−1.76	0.1002	0.3001	0.83730	−0.803	0.10	−0.76	−1.00
0.6004	0.0996	0.80159	−0.461	−0.14	−0.50	−1.11	0.2008	0.1003	0.86402	−0.665	−0.28	−1.58	−0.68
0.5003	0.1994	0.79944	−0.505	−0.14	−0.43	−1.13	0.0997	0.1998	0.86178	−0.762	−0.12	−1.23	−0.79
0.3998	0.3001	0.79703	−0.533	−0.14	−0.38	−1.17	0.1001	0.0998	0.89393	−0.654	−0.77	−2.34	−0.50

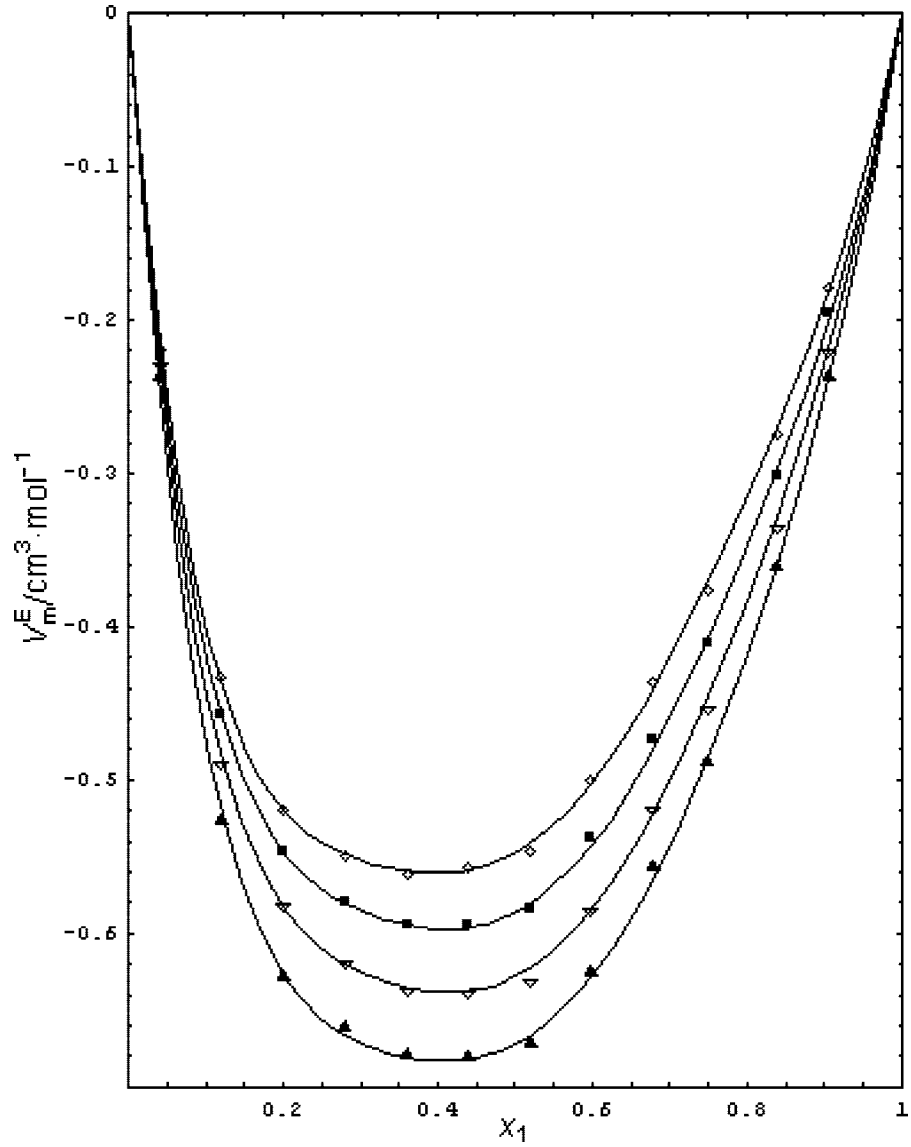

Figure 1. Experimental excess molar volumes for the 1-propanol (1) + water (3) mixture at different temperatures. ▲, 293.15 K; ∇, 303.15 K; ■, 313.15 K; ◇, 323.15 K. Solid curves represent the values calculated from eq 2 with coefficients from Table 5.

agreement with some reported data in the region of overlap. The differences between experimental and literature data and the fitted equation are graphically represented in Figure 2. In this figure, all of the data nearly distributed about the fitted equation except the data of refs 2 and 3 which 1-propanol have different densities with respect to the other literature. These large deviations may be due to purity grade of 1-propanol or to density measurements because the deviations observed at 1-propanol-rich region. The excess Gibbs energy[13] and viscosity deviation[26] of this system are both positive and the excess molar enthalpy is negative and positive value[13] and they formed a minimum boiling point azeotrope,[17] whereas the excess molar volumes and excess entropies[13] are negative.

The excess molar volumes of 2-propanol (2) + water (3) are negative and become less negative with increasing temperatures. The excess molar volumes are in agreement with some reported data in the region of overlap. The differences between experimental and literature data and the fitted equation are graphically

Table 5. Coefficients A_{pq} of Equation *2* and Standard Deviation for the Fits of the Binary Excess Molar Volumes in the Temperatures Range (293.15 to 323.15) K

	p					*σ*
q	0	1	2	3	4	cm^3·mol^{-1}
			1-Propanol (1) + Water (3)			
0	−11.8588	13.4530	−36.2015	15.6268	10.0128	0.005
1	0.0447	−0.0855	0.2132	−0.0852	−0.0694	
2	$-4.57\cdot10^{-5}$	$1.412\cdot10^{-4}$	$-3.178\cdot10^{-4}$	$1.274\cdot10^{-4}$	$1.008\cdot10^{-4}$	
			2-Propanol (2) + Water (3)			
0	−21.0200	16.8706	−59.9386	5.1836	61.0732	0.011
1	0.0991	−0.0999	0.3431	−0.0284	−0.3760	
2	$-1.377\cdot10^{-4}$	$1.623\cdot10^{-4}$	$-5.017\cdot10^{-4}$	$4.855\cdot10^{-5}$	$5.730\cdot10^{-4}$	

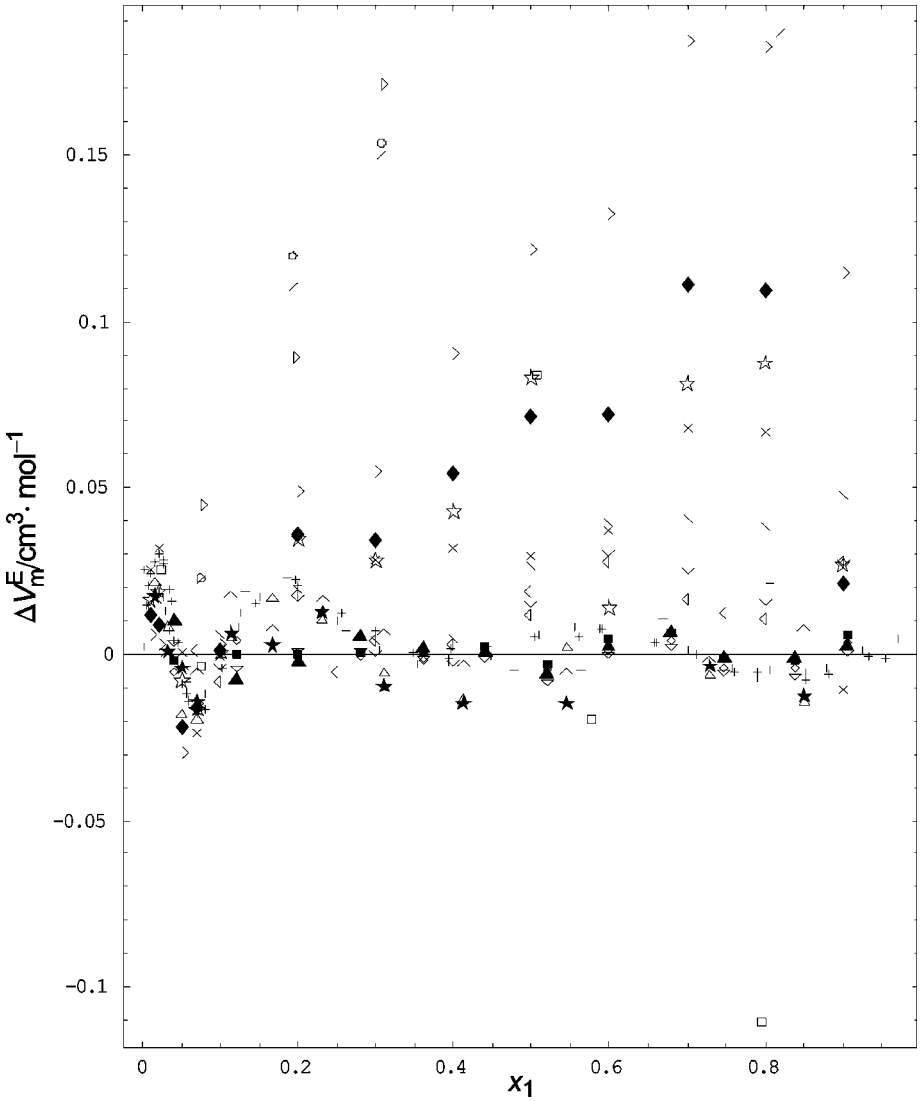

Figure 2. Differences ΔV_m^E between experimental and literature data and the fitted equation for the 1-propanol (1) + water (3) mixture at different temperatures. This work: ▲, 293.15 K; ▽, 303.15 K; ■, 313.15 K; ◇, 323.15 K; ×, 293.15 K, ref 2; +, 293.15 K, ref 12; Δ, 303.15 K, ref 15; ☆, 303.15 K, ref 2; −, 303.15 K, ref 11; □, 303.15 K, ref 18; triangle pointing right, 303.15 K, ref 3; triangle pointing left, 303.15 K, ref 6; |, 303.15 K, ref 12; ★, 313.15 K, ref 15; ◆, 313.15 K, ref 2; ○, 313.15 K, ref 3; arrow pointing down, 313.15 K, ref 6; arrow pointing up, 323.15 K, ref 15; >, 323.15 K, ref 2; <, 323.15 K, ref 10; /, 323.15 K, ref 3; \, 323.15 K, ref 6.

represented in Figure 4. In this figure, the large deviations of the data of ref 2 at different temperatures that had similar deviations for the 1-propanol + water system may be due to density measurements at different temperatures. The excess molar enthalpy of this system is negative and positive[9] and the excess Gibbs energy[9] and viscosity deviation is positive[26] and they formed a minimum boiling point azeotrope.[27] Considering these observations, the negative values of V_m^E over the entire range of mole fraction may be attributed to accommodation of water molecules in the propanol network.

The computed excess molar volumes of the binary mixtures were fitted using a temperature-dependent Redlich−Kister expression[25]

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

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-squares method. The parameters A_{pq} for all the binary mixtures are listed in Table 5, along with standard deviations, σ, calculated by using the equation 3

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

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

The excess molar volumes of ternary liquid mixture of 1-propanol (1) + 2-propanol (2) + water (3) are negative and increase with increasing temperatures from (293.15 to 323.15) K. The ternary contribution to excess molar volumes is positive. The maximum value (0.116 cm^3·mol^{-1}) at temperature 323.15 K was observed at $x_1 = 0.2320$ mol fraction and $x_2 = 0.2395$ mol fraction.

Table 6. Coefficients C_{iq} of Equation *6* and Standard Deviation for the Fits of the Ternary Excess Molar Volumes in the Temperatures Range (293.15 to 323.15) K

	i			σ
q	0	1	2	cm^3·mol^{-1}
	1-Propanol (1) + 2-Propanol (2) + Water (3)			
0	146.5160	−198.1919	−177.5906	0.016
1	−0.8283	1.1013	0.9630	
2	$1.2400\cdot10^{-3}$	$-1.6018\cdot10^{-3}$	$-1.3658\cdot10^{-3}$	

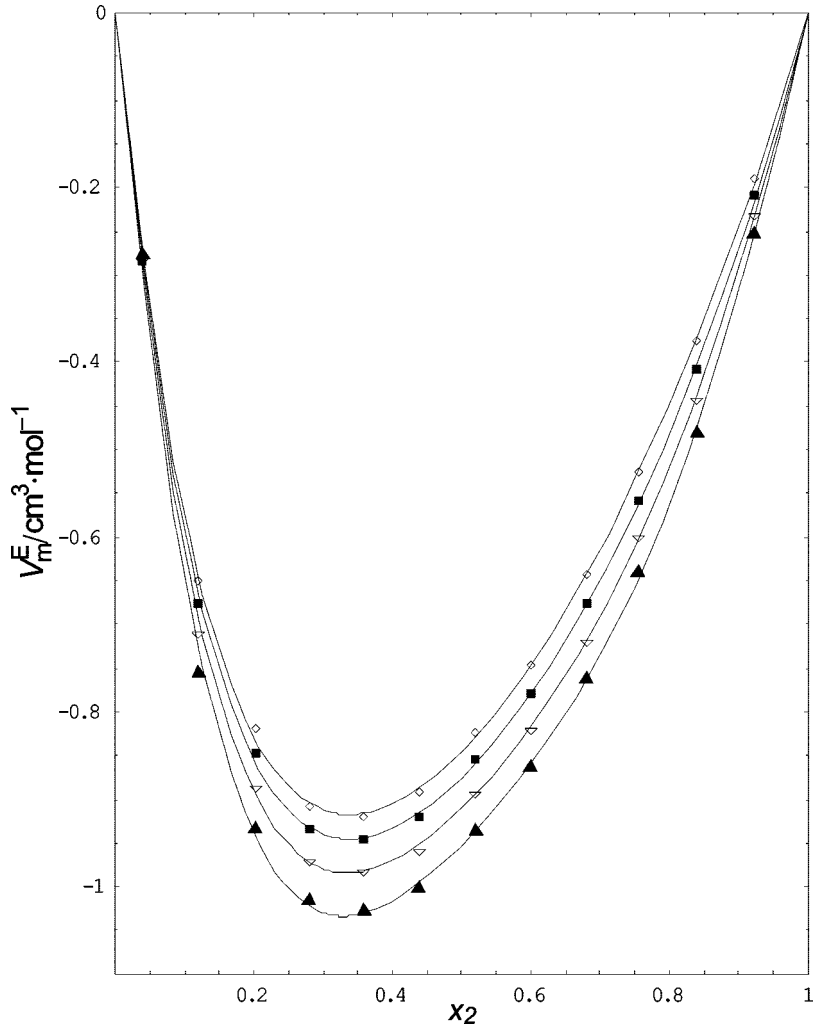

Figure 3. Experimental excess molar volumes for the 2-propanol (2) + water (3) mixture at different temperatures. ▲, 293.15 K; ∇, 303.15 K; ■, 313.15 K; ◊, 323.15 K; Solid curves represent the values calculated from eq 2 with coefficients from Table 5.

The excess molar volumes for the ternary mixture were fitted to the temperature-dependent Cibulka equation[28]

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

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

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

The data of binary mixture 1-propanol (1) + 2-propanol (2) were taken from ref 29.

Every B_i ternary parameter is a function of temperature as expressed in equation 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 6, along with the standard deviation σ.

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

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

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:[30]

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

where $(\partial V^{E}_m/\partial x_k)_{T,p,xj\neq i,k}$ are calculated from eqs 2 and 4 using the parameters in Tables 5 and 6.

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

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

The partial molar quantities are important in the study of the dependence of an extensive property on phase composition at 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 4 and graphically represented in Figures 6 to 8. The average

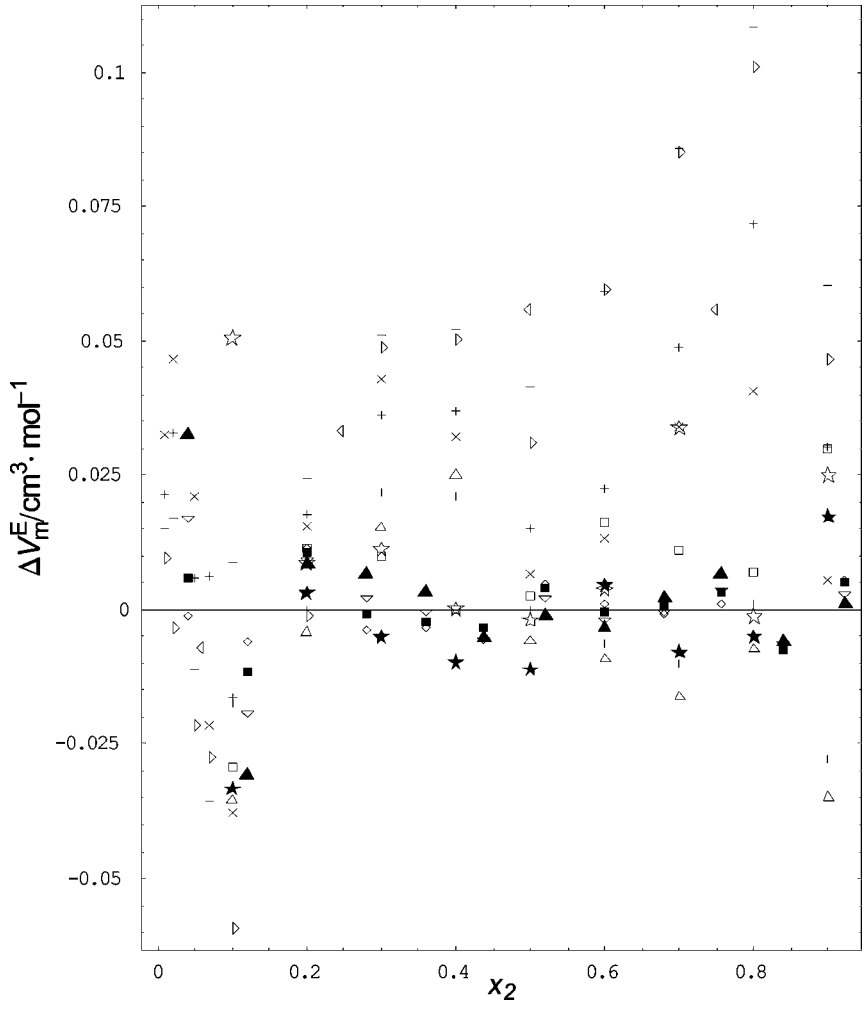

Figure 4. Differences ΔV_m^E between experimental and literature data and the fitted equation for the 2- propanol (2) + water (3) mixture at different temperatures. This work: ▲, 293.15 K; ▽, 303.15 K; ■, 313.15 K; ◇, 323.15 K; ×, 293.15 K, ref 2; +, 303.15 K, ref 2; Δ, 303.15 K, ref 5; ☆, 303.15 K, ref 6; −, 313.15 K, ref 2; □, 313.15 K, ref 6; triangle pointing right, 323.15 K, ref 2; triangle pointing left, 323.15 K, ref 10; |, 323.15 K, ref 5; ★, 323.15 K, ref 6.

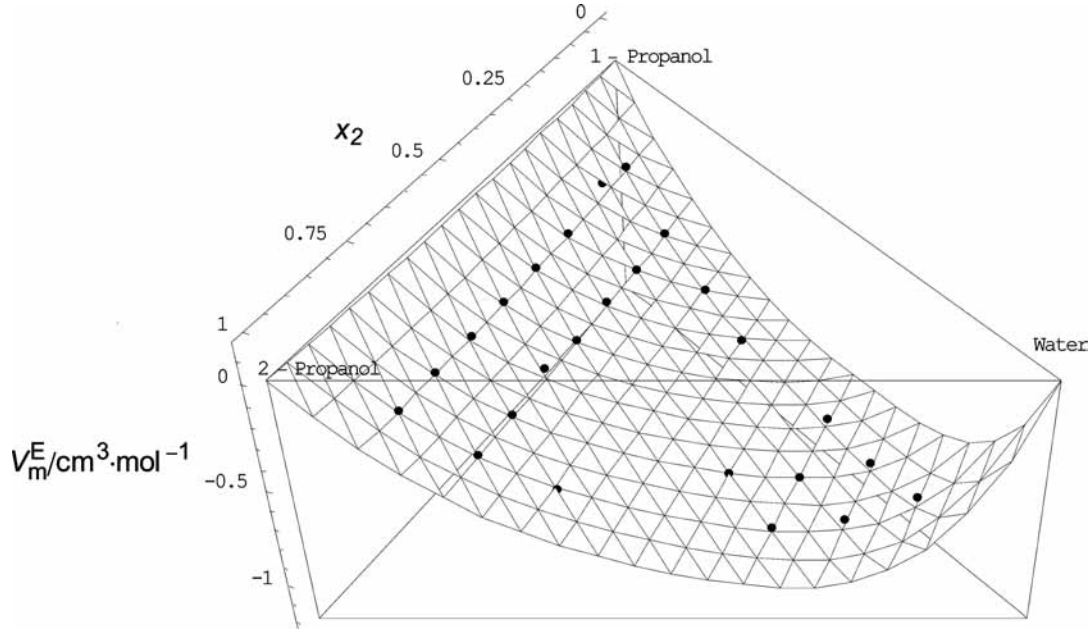

Figure 5. Representation of the experimental excess molar volume surface for ternary mixture of 1-propanol (1) + 2-propanol (2) + water (3) at 293.15 K. •, represent experimental points. Curves represent the values calculated from eq 4 with coefficients from Table 6. The unit in the triangle plot is mole fraction.

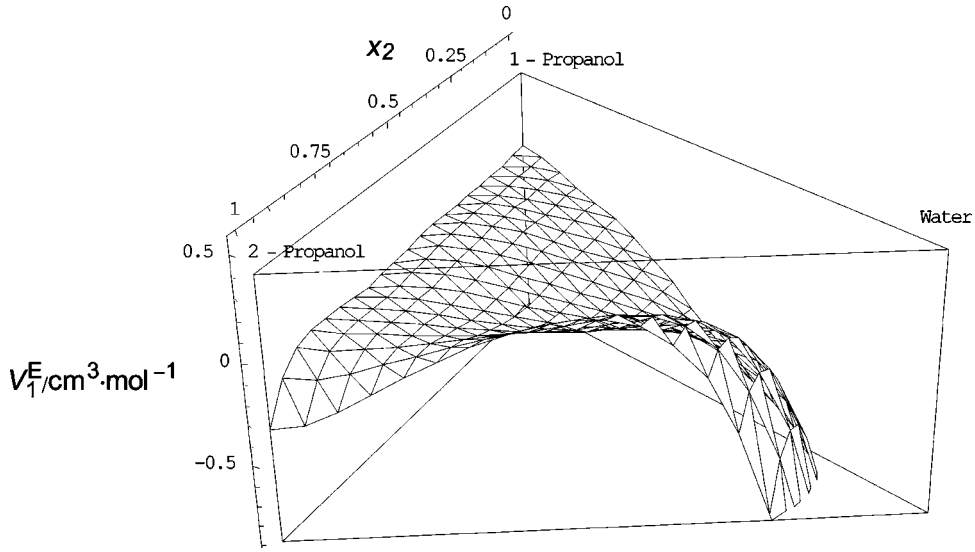

Figure 6. Representation of partial excess molar volume surface for 1-propanol (1) at the ternary mixture of 1-propanol (1) + 2-propanol (2) + water (3) at 293.15 K. The unit in the triangle plot is mole fraction.

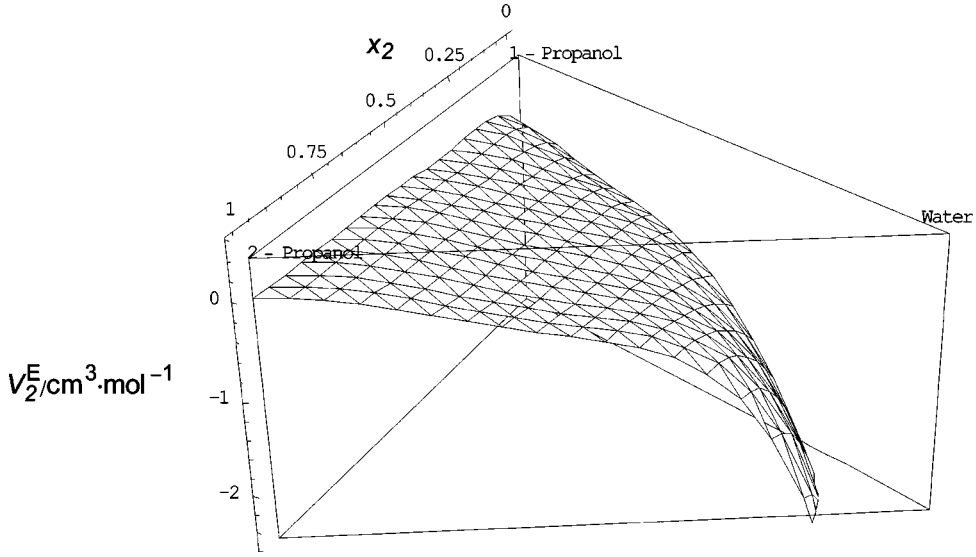

Figure 7. Representation of partial excess molar volume surface for 2-propanol (2) at the ternary mixture of 1-propanol (1) + 2-propanol (2) + water (3) at 293.15 K. The unit in the triangle plot is mole fraction.

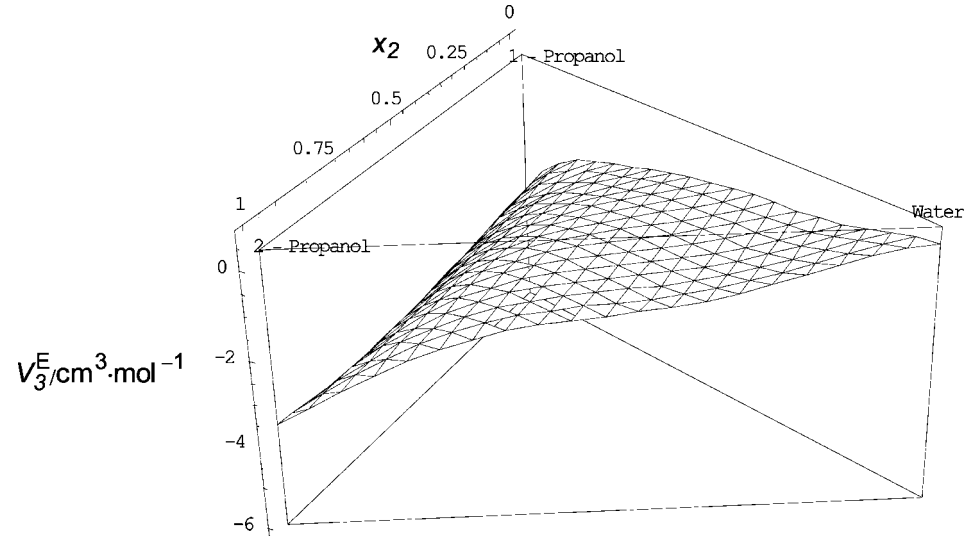

Figure 8. Representation of partial excess molar volume surface for water (2) at the ternary mixture of 1-propanol (1) + 2-propanol (2) + water (3) at 293.15 K. The unit in the triangle plot is mole fraction.

uncertainty in the partial excess molar volume is estimated to be $\pm 2 \cdot 10^{-2}$ $cm^3 \cdot mol^{-1}$.

Conclusions

The water binary mixtures with 1-propanol and 2-propanol help to understand the effect of the position of the hydroxyl group in hydrogen bond systems on the excess thermodynamic properties. As for the experimental results, the formation of hydrogen bonding in position two of propanol is better than the first.

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