Densities, Excess Molar Volumes, Viscosity, and Refractive Indices of Binary and Ternary Liquid Mixtures of Methanol (1) + Ethanol (2) + 1,2-Propanediol (3) at $P = 81.5$ kPa

Hossein A. Zarei,* Narjes Mirhidari, and Zinab Zangeneh
Faculty of Chemistry, Bu-Ali Sina University, Hamedan, Iran

Excess molar volume, V_m^E, and excess partial molar volume, V_i^E, of the ternary mixtures of methanol (1) + ethanol (2) + 1,2-propanediol (3) and of two binaries of methanol (1) + 1,2-propanediol (3) and ethanol (2) + 1,2-propanediol (3) have been investigated from the density, ρ, measurements over the entire range of compositions at temperatures (298.15, 303.15, and 308.15) K and at $P = 81.5$ kPa. The limiting values of the excess partial molar volumes at infinite dilution, $V_i^{E,\infty}$, and thermal expansion coefficients, α, of the pure components are also evaluated. The dynamic viscosity, η, of the ternary and the relevant binary mixtures and the refractive indices, n_D, of the binary mixtures at temperature 303.15 K were measured. The measured systems exhibited negative values of V_m^E and become more negative with increasing temperatures. The excess molar volumes, dynamic viscosity, and refractive index deviations were correlated with the Redlich−Kister and the Cibulka equations for the binary and ternary system, 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

The influence of hydrogen bonding on solution properties is of great interest to researchers. The 1,2-propanediol molecules are self-associated through inter- and intrahydrogen bonding, and monohydroxylic alcohol molecules are self-associated through interhydrogen bonding. Upon mixing 1,2-propanediol with methanol and ethanol, a disruption of the associated like molecule occurs, and significant interaction through interhydrogen bonding between unlike molecules occurs. Thermophysical properties of binary and ternary liquid mixtures of 1,2-propanediol with methanol and ethanol should provide insight into hydrogen bonding interactions between like and unlike molecules.

Review of the literature shows that some thermophysical properties of binary mixtures of methanol + 1,2-propanediol and ethanol + 1,2-propanediol have been reported,[1−6] but with regard to the ternary mixtures of methanol + ethanol + 1,2-propanediol, there are no experimental values of excess molar volume and viscosity deviation.

We report densities, ρ, excess molar volumes, V_m^E, and partial excess molar volumes, V_i^E, over the composition range and their values at infinite dilution, $V_i^{E,\infty}$, for the ternary mixture of methanol (1) + ethanol (2) + 1,2-propanediol (3) and two binaries of methanol (1) + 1,2-propanediol (3) and ethanol (2) + 1,2-propanediol (3) at temperatures (298.15, 303.15, and 308.15) K and $P = 81.5$ kPa. Also, the dynamic viscosity, η, of the ternary and the relevant binary mixtures and the refractive indices, n_D, of the binary mixtures at temperature 303.15 K were reported. The thermophysical properties of binary mixtures were compared with values from the literature in the region of overlap. The thermophysical properties were correlated with the Redlich−Kister and the Cibulka equations for the binary and ternary system, respectively.

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

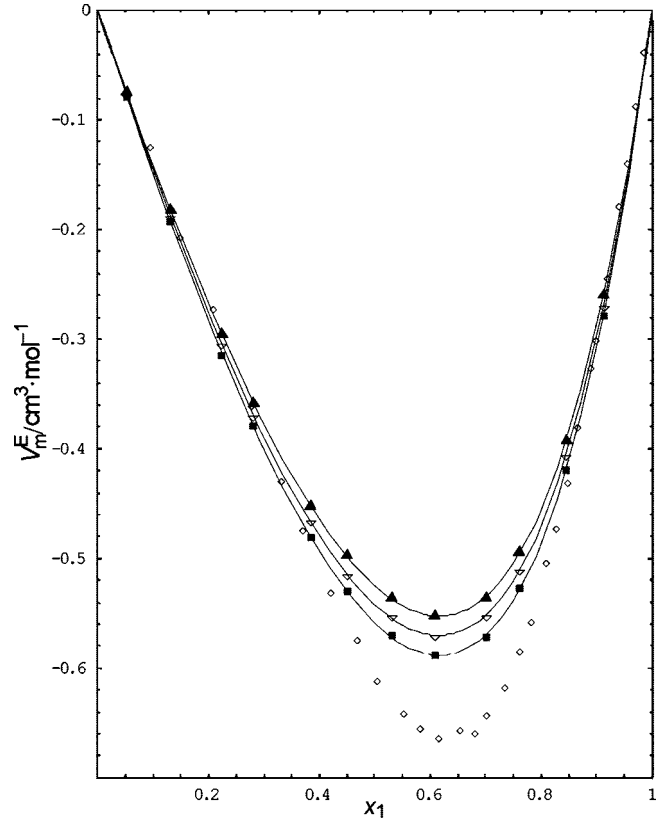

Figure 1. Experimental excess molar volumes for the methanol (1) + 1,2-propanediol (3) mixture at different temperatures. ▲, 298.15 K; ▽, 303.15 K; ■, 308.15 K; ◇, 303.15 K, ref 5. Solid curves represent the values calculated from eq 5 with coefficients from Table 7.

Experimental

Materials. The methanol, ethanol, and 1,2-propanediol were high-purity grade reagents from Merck. All chemicals were used without further purification. Prior to use, the chemicals were

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

	purity		ρ/(g·cm^{-3})		n_D		η/mPa·s		$10^4\alpha$/K^{-1}	
component	100 w	T/K	exptl	lit.	exptl	lit.	exptl	lit.	exptl	lit.
methanol	99.8	298.15	0.78657	0.78658[7]	1.3270	1.32652[8]			11.99	12[8]
		303.15	0.78185	0.78186[7]			0.525	0.526[13]	12.11	
		308.15	0.77710	0.77710[7]					12.26	
ethanol	99.8	298.15	0.78518	0.78510[9]	1.3595	1.35941[8]			10.95	11.2,[2] 11[8]
		303.15	0.78087	0.78096[10]			0.994	0.994[13]	11.09	
		308.15	0.77652	0.77644[9]					11.24	
1,2-propanediol	99.5	298.15	1.03261	1.0327[11]	1.4323	1.4314[8]			7.16	7.32[2]
		303.15	1.02890	1.028939[12]			33.878	33.902[12]	7.24	
		308.15	1.02516						7.32	

Table 2. Densities (ρ), Excess Molar Volumes (V_m^E), and Partial Excess Molar Volumes (V_i^E) for Binary Mixtures of Methanol (1) + 1,2-Propanediol (3) at Different Temperatures of (298.15 to 308.15) K

	ρ	V_m^E	V_1^E	V_3^E
x_1	(g·cm^{-3})	(cm^3·mol^{-1})	(cm^3·mol^{-1})	(cm^3·mol^{-1})
		T = 298.15 K		
1.0000			0.00	−3.67
0.9133	0.82735	−0.260	−0.05	−2.43
0.8454	0.85503	−0.393	−0.15	−1.74
0.7601	0.88496	−0.494	−0.29	−1.14
0.7006	0.90339	−0.536	−0.40	−0.85
0.6083	0.92851	−0.553	−0.57	−0.53
0.5300	0.94716	−0.536	−0.70	−0.35
0.4496	0.96421	−0.498	−0.83	−0.22
0.3841	0.97676	−0.452	−0.94	−0.15
0.2820	0.99424	−0.358	−1.10	−0.07
0.2246	1.00313	−0.296	−1.19	−0.04
0.1319	1.01621	−0.182	−1.31	−0.01
0.0533	1.02626	−0.075	−1.40	0.00
0.0000			−1.43	0.00
		T = 303.15 K		
1.0000			0.00	−3.83
0.9133	0.82302	−0.270	−0.06	−2.50
0.8454	0.85061	−0.406	−0.15	−1.79
0.7601	0.88067	−0.510	−0.30	−1.18
0.7006	0.89917	−0.553	−0.41	−0.88
0.6083	0.92441	−0.571	−0.58	−0.55
0.5300	0.94312	−0.553	−0.72	−0.37
0.4496	0.96026	−0.515	−0.86	−0.23
0.3841	0.97284	−0.466	−0.97	−0.15
0.2820	0.99039	−0.370	−1.14	−0.07
0.2246	0.99931	−0.305	−1.23	−0.04
0.1319	1.01245	−0.188	−1.35	−0.01
0.0533	1.02252	−0.077	−1.44	0.00
0.0000			−1.48	0.00
		T = 308.15 K		
1.0000			0.00	−3.95
0.9133	0.81845	−0.279	−0.06	−2.59
0.8454	0.84616	−0.419	−0.16	−1.85
0.7601	0.87635	−0.527	−0.31	−1.21
0.7006	0.89496	−0.572	−0.43	−0.90
0.6083	0.92025	−0.588	−0.60	−0.56
0.5300	0.93907	−0.571	−0.75	−0.37
0.4496	0.95625	−0.530	−0.89	−0.24
0.3841	0.96891	−0.481	−1.00	−0.15
0.2820	0.98648	−0.379	−1.17	−0.07
0.2246	0.99547	−0.315	−1.26	−0.04
0.1319	1.00864	−0.193	−1.39	−0.01
0.0533	1.01875	−0.079	−1.48	0.00
0.0000			−1.52	0.00

Table 3. Densities (ρ), Excess Molar Volumes (V_m^E), and Partial Excess Molar Volumes (V_i^E) for Binary Mixtures of Ethanol (2) + 1,2-Propanediol (3) at Different Temperatures (298.15 to 308.15) K

	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})
		T = 298.15 K		
1.0000			0.00	−2.24
0.9232	0.81057	−0.145	−0.02	−1.60
0.8332	0.83849	−0.261	−0.09	−1.11
0.7613	0.85954	−0.322	−0.16	−0.84
0.677	0.88299	−0.366	−0.25	−0.61
0.6103	0.90063	−0.380	−0.33	−0.46
0.5261	0.92185	−0.379	−0.44	−0.31
0.4478	0.94070	−0.367	−0.55	−0.21
0.3633	0.95986	−0.322	−0.67	−0.13
0.2706	0.97989	−0.263	−0.80	−0.07
0.2072	0.99305	−0.217	−0.88	−0.04
0.1220	1.00990	−0.138	−1.01	−0.02
0.0492	1.02364	−0.058	−1.15	0.00
0.0000			−1.28	0.00
		T = 303.15 K		
1.0000			0.00	−2.25
0.9232	0.80630	−0.147	−0.02	−1.63
0.8332	0.83425	−0.265	−0.09	−1.14
0.7613	0.85537	−0.330	−0.16	−0.87
0.6770	0.87884	−0.373	−0.26	−0.62
0.6103	0.89655	−0.389	−0.34	−0.47
0.5261	0.91781	−0.387	−0.45	−0.32
0.4478	0.93673	−0.376	−0.56	−0.21
0.3633	0.95592	−0.329	−0.68	−0.13
0.2706	0.97603	−0.270	−0.81	−0.07
0.2072	0.98922	−0.223	−0.90	−0.04
0.1220	1.00614	−0.143	−1.03	−0.02
0.0492	1.01991	−0.060	−1.19	0.00
0.0000			−1.34	0.00
		T = 308.15 K		
1.0000			0.00	−2.31
0.9232	0.80198	−0.150	−0.02	−1.66
0.8332	0.82999	−0.271	−0.09	−1.17
0.7613	0.85113	−0.336	−0.16	−0.89
0.6770	0.87469	−0.383	−0.26	−0.64
0.6103	0.89241	−0.397	−0.34	−0.49
0.5261	0.91376	−0.398	−0.46	−0.33
0.4478	0.93270	−0.384	−0.58	−0.22
0.3633	0.95197	−0.338	−0.70	−0.13
0.2706	0.97212	−0.276	−0.83	−0.07
0.2072	0.98536	−0.228	−0.92	−0.05
0.1220	1.00231	−0.145	−1.05	−0.02
0.0492	1.01616	−0.063	−1.22	−0.01
0.0000			−1.38	0.00

degassed by heating and cooling. The purity grade, densities, refractive indices, and thermal expansion coefficients of pure components are given in Table 1 and compared with the literature values.[7−13]

Measurements. A digital density meter (Anton Paar DMA 4500) provided with automatic viscosity correction was employed for the determination of the densities. All the mixtures were prepared by mass on a Mettler AB 204-N balance with an uncertainty of ± 1·10^{-4} g. Conversion to molar mass was based on the relative atomic mass table of 1996 issued by IUPAC.[14] The average uncertainty in the mole fraction from the propagation law of errors is estimated to be ± 2·10^{-5}. Uncertainty in the density was ± 1·10^{-5} g·cm^{-3}. Details of the apparatus and procedure have been described elsewhere.[15,16]

The viscosity was measured with an Ubbleohde viscometer. The viscosities were determined according to eq 1.

$$\eta = \rho\nu = \rho(kt - c/t) \quad (1)$$

where k and c are the viscometer constant, determined by calibration, and t, ρ, η, and ν are the efflux time, density, and dynamic and kinematic viscosities, respectively. The calibration of the viscosity meter was carried out with spectroscopic grade 1-butanol and 1-propanol at the working temperature. An electronic digital stop watch with readability of ± 0.01 s was used for the flow time measurements. At least three repetitions of each data were obtained, and the results were averaged. The uncertainty in dynamic viscosities is of the order of ± 0.003 mPa·s.

Refractive indices were measured using a thermostatted Abbe refractometer with uncertainty less than 0.0001 units. Water was circulated into the prism of the refractometer by a circulation pump connected to an external thermostatted water bath. The temperature of the sample was controlled to within ± 0.1 K.

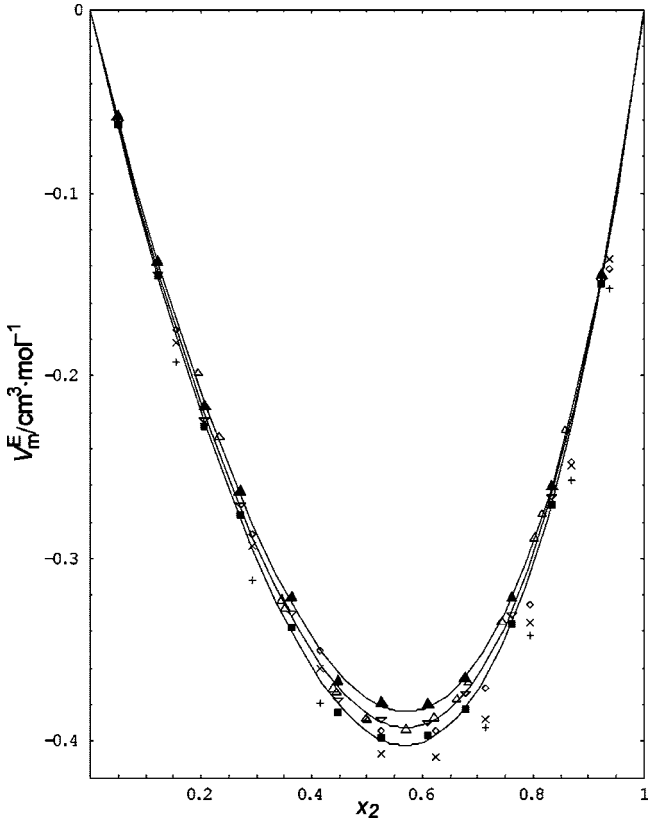

Figure 2. Experimental excess molar volumes for the ethanol (2) + 1,2-propanediol (3) mixture at different temperatures. ▲, 298.15 K; ▽, 303.15 K; ■, 308.15 K; ◇, 298.15 K, ref ; ×, 303.15 K, ref 2; +, 308.15 K, ref 2; △, 298.15 K, ref 6. Solid curves represent the values calculated from eq 5 with coefficients from Table 7.

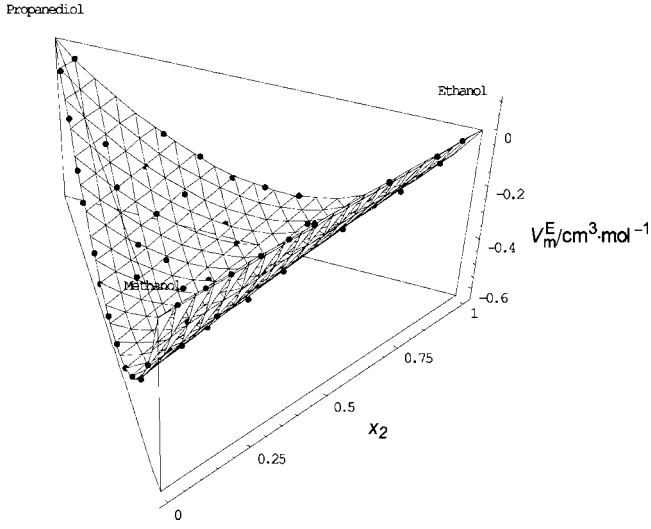

Figure 3. Representation of the experimental excess molar volume surface for the ternary mixture of methanol (1) + ethanol (2) + 1,2-propanediol (3) at 303.15 K. ●, represents experimental points. Curves represent the values calculated from eq 8 with coefficients from Table 9. The unit in the triangle plot is mole fraction.

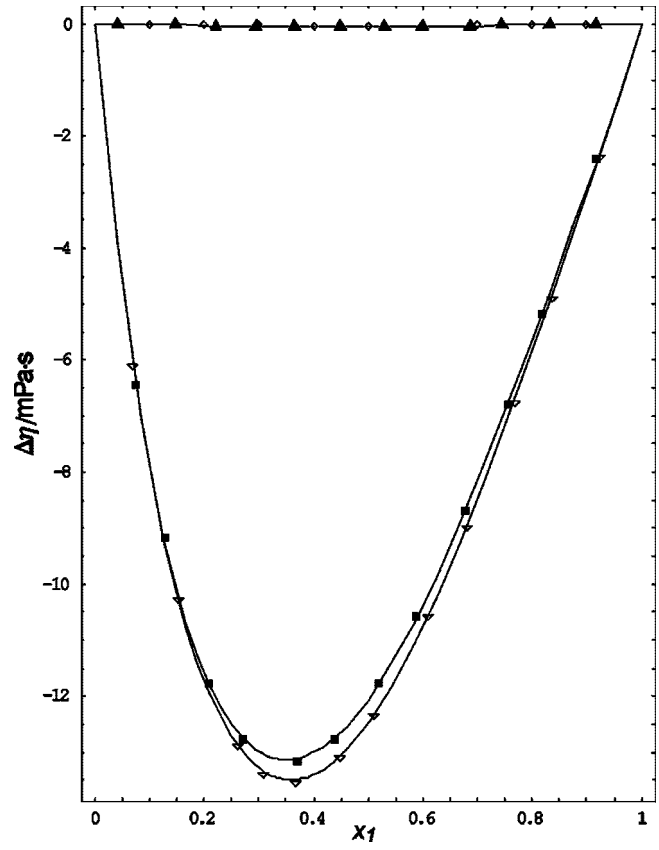

Figure 4. Experimental deviation in viscosities for the binary mixtures of ▲, methanol (1) + ethanol (2); ▽, methanol (1) + 1,2-propanediol (2); □, ethanol (1) + 1,2-propanediol (2); ◇, methanol (1) + ethanol (2), ref 2; at 303.15 K. Solid curves represent the values calculated from eq 5 with coefficients from Table 8.

Results and Discussion

The excess molar volumes, V_m^E, viscosity, and refractive index deviations of the binary and ternary mixtures were evaluated by the following equations

$$V_m^E = \sum_{i=1}^{n} x_i M_i (\rho^{-1} - \rho_i^{-1}) \quad (2)$$

$$\Delta\eta = \eta - \sum_{i=1}^{n} x_i \eta_i \quad (3)$$

$$\Delta n_D = n_D - \sum_{i=1}^{n} x_i n_{D_i} \quad (4)$$

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. η and η_i are the dynamic viscosity for the mixture and the pure component i, respectively. n_D and n_{D_i} are the refractive index for the mixture and the pure component i, respectively.

Table 4. Densities (ρ), Excess Molar Volumes (V_m^E), and Partial Excess Molar Volumes (V_i^E) for Ternary Mixtures of Methanol (1) + Ethanol (2) + 1,2-Propanediol (3) at Different Temperatures (298.15 to 308.15) 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})
					$T = 298.15$ K								
0.1224	0.0956	0.99804	−0.256	−1.19	−0.90	−0.04	0.2986	0.4021	0.88678	−0.452	−0.43	−0.18	−0.78
0.0998	0.1981	0.97983	−0.323	−1.09	−0.77	−0.08	0.3269	0.4802	0.85396	−0.348	−0.25	−0.06	−1.24
0.1165	0.2946	0.95496	−0.381	−0.94	−0.61	−0.17	0.3010	0.5985	0.82204	−0.207	−0.11	0.00	−1.75
0.1194	0.3955	0.93045	−0.451	−0.78	−0.45	−0.30	0.4026	0.0993	0.94742	−0.482	−0.75	−0.49	−0.30
0.1015	0.5020	0.90640	−0.419	−0.64	−0.33	−0.47	0.3966	0.2144	0.91685	−0.483	−0.57	−0.31	−0.53
0.1137	0.5922	0.87857	−0.379	−0.46	−0.20	−0.73	0.4005	0.2993	0.89044	−0.448	−0.42	−0.17	−0.81
0.0985	0.7025	0.84996	−0.292	−0.29	−0.10	−1.06	0.4031	0.3970	0.85796	−0.345	−0.25	−0.05	−1.25
0.0998	0.7983	0.81981	−0.198	−0.12	−0.03	−1.55	0.3950	0.5033	0.82364	−0.204	−0.10	0.01	−1.83
0.2002	0.1020	0.98462	−0.345	−1.08	−0.78	−0.08	0.5029	0.1140	0.92055	−0.529	−0.55	−0.30	−0.55
0.2018	0.2013	0.96154	−0.411	−0.94	−0.63	−0.16	0.5109	0.1904	0.89482	−0.497	−0.41	−0.16	−0.84
0.1974	0.3126	0.93508	−0.452	−0.77	−0.46	−0.30	0.4979	0.3006	0.86186	−0.401	−0.24	−0.04	−1.29
0.2003	0.3980	0.91183	−0.445	−0.63	−0.33	−0.47	0.4985	0.4055	0.82355	−0.227	−0.09	0.03	−1.97
0.1987	0.5014	0.88318	−0.413	−0.45	−0.19	−0.75	0.5999	0.1055	0.89744	−0.523	−0.39	−0.15	−0.87
0.2012	0.5964	0.85374	−0.334	−0.28	−0.08	−1.12	0.5902	0.2136	0.86288	−0.412	−0.23	−0.02	−1.35
0.1950	0.7041	0.82055	−0.191	−0.11	−0.01	−1.65	0.6000	0.2986	0.82763	−0.262	−0.09	0.05	−2.02
0.3080	0.1272	0.95942	−0.441	−0.87	−0.59	−0.20	0.6950	0.1018	0.86861	−0.422	−0.23	−0.01	−1.35
0.3170	0.1955	0.94019	−0.470	−0.75	−0.46	−0.31	0.7024	0.2020	0.82701	−0.250	−0.08	0.06	−2.15
0.3276	0.2919	0.91176	−0.494	−0.57	−0.29	−0.54	0.7944	0.1021	0.83242	−0.289	−0.08	0.08	−2.16
					$T = 303.15$ K								
0.1224	0.0956	0.99422	−0.263	−1.23	−0.92	−0.04	0.2986	0.4021	0.88261	−0.464	−0.45	−0.18	−0.80
0.0998	0.1981	0.97594	−0.330	−1.12	−0.79	−0.08	0.3269	0.4802	0.84969	−0.357	−0.26	−0.05	−1.27
0.1165	0.2946	0.95099	−0.389	−0.96	−0.62	−0.17	0.3010	0.5985	0.81770	−0.212	−0.11	0.00	−1.80
0.1194	0.3955	0.92643	−0.462	−0.80	−0.46	−0.31	0.4026	0.0993	0.94340	−0.496	−0.78	−0.50	−0.31
0.1015	0.5020	0.90230	−0.428	−0.66	−0.33	−0.48	0.3966	0.2144	0.91274	−0.497	−0.59	−0.31	−0.55
0.1137	0.5922	0.87440	−0.388	−0.48	−0.20	−0.75	0.4005	0.2993	0.88625	−0.461	−0.43	−0.17	−0.83
0.0985	0.7025	0.84572	−0.298	−0.30	−0.10	−1.09	0.4031	0.3970	0.85366	−0.353	−0.26	−0.05	−1.28
0.0998	0.7983	0.81551	−0.201	−0.13	−0.03	−1.58	0.3950	0.5033	0.81927	−0.209	−0.11	0.01	−1.88
0.2002	0.1020	0.98075	−0.354	−1.11	−0.80	−0.08	0.5029	0.1140	0.91644	−0.545	−0.57	−0.30	−0.57
0.2018	0.2013	0.95759	−0.421	−0.97	−0.64	−0.16	0.5109	0.1904	0.89062	−0.511	−0.42	−0.16	−0.86
0.1974	0.3126	0.93105	−0.463	−0.80	−0.47	−0.31	0.4979	0.3006	0.85756	−0.411	−0.25	−0.03	−1.32
0.2003	0.3980	0.90774	−0.456	−0.65	−0.33	−0.48	0.4985	0.4055	0.81915	−0.233	−0.09	0.03	−2.03
0.1987	0.5014	0.87901	−0.423	−0.47	−0.19	−0.77	0.5999	0.1055	0.89323	−0.539	−0.41	−0.15	−0.89
0.2012	0.5964	0.84950	−0.342	−0.29	−0.08	−1.15	0.5902	0.2136	0.85857	−0.425	−0.24	−0.02	−1.39
0.1950	0.7041	0.81624	−0.195	−0.12	−0.01	−1.69	0.6000	0.2986	0.82322	−0.270	−0.10	0.05	−2.07
0.3080	0.1272	0.95556	−0.460	−0.90	−0.60	−0.21	0.6950	0.1018	0.86428	−0.435	−0.24	−0.01	−1.39
0.3170	0.1955	0.93616	−0.482	−0.77	−0.47	−0.32	0.7024	0.2020	0.82255	−0.257	−0.08	0.07	−2.22
0.3276	0.2919	0.90764	−0.507	−0.59	−0.29	−0.56	0.7944	0.1021	0.82794	−0.298	−0.09	0.09	−2.22
					$T = 308.15$ K								
0.1224	0.0956	0.99035	−0.270	−1.26	−0.93	−0.04	0.2986	0.4021	0.87840	−0.476	−0.47	−0.18	−0.83
0.0998	0.1981	0.97202	−0.338	−1.15	−0.80	−0.08	0.3269	0.4802	0.84538	−0.365	−0.27	−0.05	−1.31
0.1165	0.2946	0.94699	−0.398	−0.99	−0.64	−0.18	0.3010	0.5985	0.81333	−0.217	−0.12	0.00	−1.84
0.1194	0.3955	0.92237	−0.473	−0.82	−0.47	−0.32	0.4026	0.0993	0.93935	−0.511	−0.81	−0.51	−0.31
0.1015	0.5020	0.89817	−0.437	−0.67	−0.34	−0.49	0.3966	0.2144	0.90860	−0.511	−0.61	−0.31	−0.56
0.1137	0.5922	0.87021	−0.397	−0.49	−0.20	−0.77	0.4005	0.2993	0.88203	−0.474	−0.45	−0.17	−0.85
0.0985	0.7025	0.84145	−0.303	−0.31	−0.10	−1.11	0.4031	0.3970	0.84935	−0.363	−0.27	−0.04	−1.32
0.0998	0.7983	0.81118	−0.204	−0.13	−0.03	−1.61	0.3950	0.5033	0.81489	−0.216	−0.11	0.02	−1.93
0.2002	0.1020	0.97683	−0.364	−1.15	−0.81	−0.08	0.5029	0.1140	0.91229	−0.561	−0.59	−0.31	−0.59
0.2018	0.2013	0.95360	−0.432	−1.00	−0.65	−0.17	0.5109	0.1904	0.88639	−0.526	−0.44	−0.16	−0.89
0.1974	0.3126	0.92699	−0.475	−0.82	−0.48	−0.31	0.4979	0.3006	0.85324	−0.423	−0.27	−0.03	−1.36
0.2003	0.3980	0.90362	−0.467	−0.67	−0.34	−0.50	0.4985	0.4055	0.81472	−0.239	−0.10	0.04	−2.08
0.1987	0.5014	0.87481	−0.433	−0.48	−0.19	−0.79	0.5999	0.1055	0.88900	−0.556	−0.42	−0.15	−0.92
0.2012	0.5964	0.84522	−0.349	−0.30	−0.08	−1.17	0.5902	0.2136	0.85423	−0.439	−0.25	−0.01	−1.44
0.1950	0.7041	0.81190	−0.200	−0.12	−0.01	−1.72	0.6000	0.2986	0.81877	−0.277	−0.10	0.05	−2.14
0.3080	0.1272	0.95155	−0.473	−0.93	−0.61	−0.21	0.6950	0.1018	0.85993	−0.449	−0.25	0.00	−1.43
0.3170	0.1955	0.93209	−0.495	−0.80	−0.48	−0.33	0.7024	0.2020	0.81806	−0.265	−0.09	0.07	−2.29
0.3276	0.2919	0.90349	−0.520	−0.61	−0.30	−0.57	0.7944	0.1021	0.82344	−0.308	−0.09	0.09	−2.30

The average uncertainties in the excess molar volumes and viscosity deviations are estimated to be $\pm 2 \cdot 10^{-3}$ cm^3·mol^{-1} and $\pm 4 \cdot 10^{-3}$ mPa·s, respectively.

The experimental values of the densities, ρ, for pure compounds and for the binary and ternary mixtures were measured at temperatures (298.15, 303.15, and 308.15) K and at $P = 81.5$ kPa, and they are given in Tables 1 to 4.

The excess molar volumes for binary mixtures methanol (1) + 1,2-propanediol (3) and ethanol (2) + 1,2-propanediol (3) and the ternary mixture methanol (1) + ethanol (2) + 1,2-propanediol (3) at different temperatures are recorded in Tables 2 to 4 and graphically represented in Figures 1, 2, and 3.

The excess molar volumes for methanol (1) + 1,2-propanediol (3) are negative and become more negative with increasing temperatures from (298.15 to 303.15) K. The excess molar volumes at temperature 303.15 K were compared with the reported data[5] (Figure 1). The discrepancy between experimental data and the literature value may be due to the viscosity correction on the density measurements in the vibrating tube density meter. Our instrument has an automatic viscosity correction. The viscosity and refractive index deviations of this system are negative and positive, respectively, and they are given in Table 5 and graphically represented in Figures 4 and 5. The excess molar enthalpy of this system is negative.[1]

Table 5. Viscosity (η), Viscosity Deviations ($\Delta\eta$), Refractive Index (n_D), and Refractive Index Deviations (Δn_D) for Binary Systems at 303.15 K

x_1	η (mPa·s)	$\Delta\eta$ (mPa·s)	n_D	Δn_D
methanol (1) + ethanol (2)				
0.0417	0.968	−0.007	1.3567	0.0009
0.1476	0.906	−0.019	1.3541	0.0017
0.2214	0.865	−0.025	1.3522	0.0022
0.2952	0.828	−0.028	1.3502	0.0026
0.3644	0.793	−0.031	1.3485	0.0031
0.4488	0.753	−0.030	1.3462	0.0036
0.5290	0.717	−0.029	1.3437	0.0037
0.5995	0.685	−0.028	1.3415	0.0038
0.6859	0.648	−0.025	1.3385	0.0036
0.7442	0.624	−0.021	1.3363	0.0033
0.8320	0.588	−0.016	1.3328	0.0026
0.9166	0.556	−0.008	1.3286	0.0012
methanol (1) + 1,2-propanediol (2)				
0.0688	25.51	−6.08	1.4262	0.0040
0.1545	18.49	−10.24	1.4220	0.0088
0.2606	12.31	−12.88	1.4155	0.0134
0.3086	10.21	−13.37	1.4129	0.0158
0.3666	8.11	−13.54	1.4096	0.0186
0.4494	5.81	−13.08	1.4029	0.0206
0.5100	4.54	−12.33	1.3983	0.0223
0.6098	2.99	−10.55	1.3883	0.0228
0.6811	2.21	−8.96	1.3783	0.0202
0.7687	1.51	−6.73	1.3665	0.0176
0.8363	1.11	−4.87	1.3571	0.0153
0.9225	0.75	−2.36	1.3404	0.0076
ethanol (1) + 1,2-propanediol (2)				
0.0738	25.01	−6.44	1.4260	0.0019
0.1285	20.47	−9.18	1.4233	0.0032
0.2099	15.20	−11.78	1.4187	0.0045
0.2725	12.14	−12.78	1.4153	0.0056
0.3701	8.55	−13.16	1.4093	0.0066
0.4389	6.68	−12.77	1.4052	0.0075
0.5193	5.03	−11.77	1.3998	0.0079
0.5871	3.98	−10.59	1.3946	0.0076
0.6780	2.90	−8.68	1.3876	0.0071
0.7554	2.23	−6.80	1.3817	0.0068
0.8185	1.80	−5.16	1.3765	0.0062
0.9171	1.29	−2.42	1.3672	0.0040

The excess molar volumes of ethanol (2) + 1,2-propanediol (3) are negative and become more negative with increasing temperature. The excess molar volumes are in agreement with some reported data[2,6] in the region of overlap. The observed discrepancy may be due to the viscosity correction as mentioned above. The viscosity and refractive index deviations of this system are negative and positive, respectively, and they are given in Table 5 and graphically represented in Figures 4 and 5. The refractive deviations of this system were compared with literature data.[3] The excess molar enthalpy of this system is positive.[1]

The viscosities, viscosity deviations, refractive indices, and refractive index deviations of methanol (1) + ethanol (2) are recorded in Table 5 and represented in Figures 4 and 5. The viscosity deviation of this system is negative, and refractive index deviation is positive at temperature 303.15 K. The experimental data of viscosity and refractive deviations are in agreement with available literature data.[17−19] The excess molar volume and enthalpy of this system are positive.[20,21]

The binary mixture values were fitted to a Redlich−Kister equation

$$\Delta Q = x_i x_j \sum_{p=0}^{n} B_p (x_i - x_j)^p \tag{5}$$

where ΔQ is the excess molar volume, viscosity, and refractive index deviations; x_i and x_j are the mole fraction; B is the fitting parameter; and n is the degree of the polynomial expansion. For excess molar volume, B is the temperature-dependent parameters as expressed in eq 6

$$B_p = \sum_{q=0}^{2} A_{pq} T^q \tag{6}$$

These parameters were obtained by the unweighted least-squars method. The parameters $A_{pq}$for all the binary mixtures are listed in Tables 7 and 8, along with standard deviations, σ, calculated by using eq 7

$$\sigma(V_m^E) = \left(\sum_{i=1}^{N} (V_{m,i}^E - V_{mcalcd,i}^E)^2 / (n-k) \right)^{1/2} \tag{7}$$

where N is the number of experimental data points and k is the number of parameters.

The excess molar volumes of the ternary liquid mixture of methanol (1) + ethanol (2) + 1,2-propanediol (3) are negative and become more negative with increasing temperature. The ternary contribution to excess molar volumes is negative. The minimum value (−0.069 $cm^3 \cdot mol^{-1}$) at temperature 303.15 K was observed at $x_1 = 0.3803$ and $x_2 = 0.3500$ mole fraction.

Table 6. Viscosity (η) and Viscosity Deviations ($\Delta\eta$) for Ternary Mixtures of Methanol (1) + Ethanol (2) + 1,2-Propanediol (3) at 303.15 K

x_1	x_2	η (mPa·s)	$\Delta\eta$ (mPa·s)
0.1224	0.0956	14.508	−12.14
0.0998	0.1981	10.979	−13.06
0.1165	0.2946	7.225	−13.08
0.1194	0.3955	4.976	−11.91
0.1015	0.5020	3.649	−10.34
0.1137	0.5922	2.539	−8.08
0.0985	0.7025	1.838	−5.65
0.0998	0.7983	1.319	−2.98
0.2002	0.1020	10.673	−13.18
0.2018	0.2013	7.348	−13.18
0.1974	0.3126	4.949	−12.06
0.2003	0.3980	3.577	−10.53
0.1987	0.5014	2.503	−8.26
0.2012	0.5964	1.777	−5.78
0.1950	0.7041	1.247	−2.98
0.3080	0.1272	6.358	−13.06
0.3170	0.1955	4.752	−12.13
0.3276	0.2919	3.215	−10.14
0.2986	0.4021	2.400	−8.30
0.3269	0.4802	1.623	−5.56
0.3010	0.5985	1.182	−2.98
0.4026	0.0993	4.838	−12.35
0.3966	0.2144	3.218	−10.38
0.4005	0.2993	2.328	−8.35
0.4031	0.3970	1.585	−5.80
0.3950	0.5033	1.120	−3.03
0.5029	0.1140	3.025	−10.33
0.5109	0.1904	2.199	−8.38
0.4979	0.3006	1.539	−5.85
0.4985	0.4055	1.039	−2.88
0.5999	0.1055	2.086	−8.32
0.5902	0.2136	1.442	−5.73
0.6000	0.2986	1.005	−3.04
0.6950	0.1018	1.397	−5.95
0.7024	0.2020	0.924	−2.88
0.7944	0.1021	0.903	−3.12

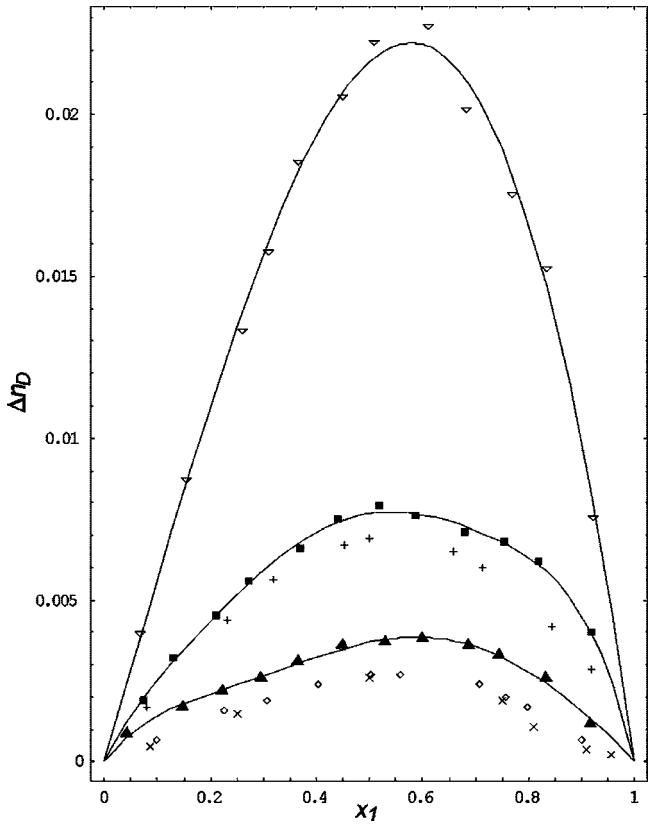

Figure 5. Experimental deviation in refractive indices for the binary mixtures of ▲, methanol (1) + ethanol (2); ▽, methanol (1) + 1,2-propanediol (2); ■, ethanol (1) + 1,2-propanediol (2), at 303.15 K; ◇, methanol (1) + ethanol (2), 298.15 K, ref 19; ×, methanol (1) + ethanol (2), 298.15 K, ref 18; +, ethanol (1) + 1,2- propanediol (2), 303.15 K, ref 3. Solid curves represent the values calculated from eq 5 with coefficients from Table 8.

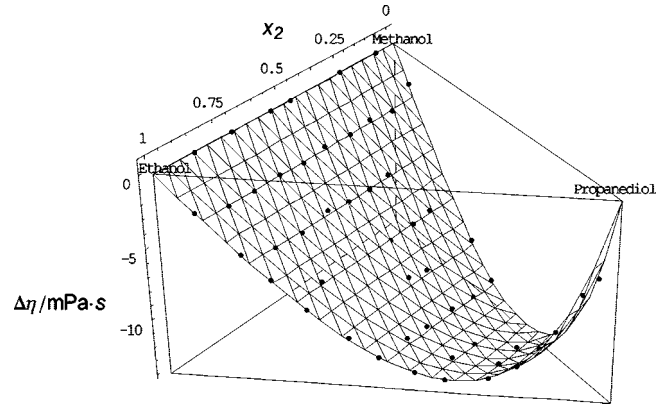

Figure 6. Representation of the experimental viscosity deviation surface for the ternary mixture of methanol (1) + ethanol (2) + 1,2-propanediol (3) at 303.15 K. ●, represents experimental points. Curves represent the values calculated from eq 8 with coefficients from Table 10. The unit in the triangle plot is mole fraction.

The viscosities and viscosity deviations of the ternary mixture are recorded in Table 6 and represented in Figure 6. The viscosity deviation of the ternary mixture is negative at temperature 303.15 K. The ternary contribution to viscosity deviation is positive. The maximum value (2.073 mPa·s) at temperature 303.15 K was observed at $x_1 = 0.2745$ and $x_2 = 0.2743$ mole fraction.

The excess molar volumes and viscosity deviations of the ternary mixture were correlated by applying the Cibulka equation[22]

$$\Delta Q = \Delta Q_{12} + \Delta Q_{13} + \Delta Q_{23} + x_1x_2x_3(B_0 + B_1x_1 + B_2x_2) \quad (8)$$

where ΔQ_{ij} are the contributions of binary mixture i,j.

The excess molar volume data of the binary mixture methanol (1) + ethanol (2) were taken from ref 20.

For excess molar volume, every B_p ternary parameter is a function of temperature as expressed in eq 6.

The parameters B_p for the ternary mixture are listed in Tables 9 and 10, along with the standard deviation σ.

Table 7. Coefficients A_{pq} of Equations 5 and 6 and Standard Deviation for the Fits of Excess Molar Volumes (V_m^E/(cm^3·mol^{-1})) for Binary Mixtures in the Temperatures Range (298.15 to 308.15) K

	p					
q	0	1	2	3	4	σ(cm^3·mol^{-1})
			methanol (1) + 1,2-propanediol (2)			
0	5.0159	28.801	−41.2668	−53.3768	86.2775	
1	−0.0339	−0.1903	0.2717	0.3507	−0.5674	0.0014
2	$3.356\cdot10^{-5}$	$3.2545\cdot10^{-4}$	$-4.520\cdot10^{-4}$	$-5.7328\cdot10^{-4}$	$9.3224\cdot10^{-4}$	
			ethanol (2) + 1,2-propanediol (3)			
0	−9.8138	−0.0710	86.9079	51.3774	−113.362	
1	0.0619	0.0014	−0.5760	−0.3355	0.7502	0.0026
2	$-11.404\cdot10^{-5}$	$5.5629\cdot10^{-7}$	$9.5289\cdot10^{-4}$	$5.4801\cdot10^{-4}$	$-1.2424\cdot10^{-3}$	

Table 8. Coefficients B_P of Equation 5 and Standard Deviation for the Fits of Viscosity and Refractive Index Deviations for the Binary Mixtures at 303.15K

property	B_0	B_1	B_2	B_3	B_4	σ/(mPa·s)
			methanol (1) + ethanol (2)			
$\Delta\eta$/(mPa·s)	−0.1203	−0.0289	−0.0245			0.0006
Δn_D	0.0148	−0.0068	−0.0008	0.0090	0.0059	0.0001
			methanol (1) + 1,2-propanediol (3)			
$\Delta\eta$/(mPa·s)	−49.9917	−26.882	−9.8029	−10.4284	−11.0212	0.07
Δn_D	0.0865	−0.0293				0.0006
			ethanol (2) + 1,2-propanediol (3)			
$\Delta\eta$/(mPa·s)	−48.2708	−26.8732	−11.0901	−11.756	−11.7199	0.06
Δn_D	0.03071	−0.0049	−0.0009	−0.0144	0.0230	0.0002

Table 9. Coefficients A_{pq} of Equations 8 and 6 and Standard Deviation for the Fits of the Ternary Excess Molar Volumes (V_m^E/(cm^3·mol^{-1})) in the Temperatures Range (298.15 to 308.15) K

	p			
q	0	1	2	σ/(cm^3·mol^{-1})
0	−69.9053	385.2074	175.942	0.009
1	0.4530	−0.2379	−1.1693	
2	−0.0007	0.0003	0.0019	

Table 10. Coefficients B_P of Equation 8 and Standard Deviation for the Fits of the Ternary Viscosity Deviations ($\Delta\eta$/(mPa·s)) at 303.15 K

B_0	B_1	B_2	σ/(mPa·s)
108.634	−86.539	−86.9886	0.0787

Table 11. Coefficients a_i of Equation 9 for the Fits of the Pure Components Densities in the Temperature Range (298.15 to 308.15) K

component	a_0	a_1	a_2	a_3	a_4
methanol	0.862452	0.000571279	$-1.95384\cdot10^{-6}$	$-7.03903\cdot10^{-9}$	$1.44271\cdot10^{-11}$
ethanol	0.830419	0.00060586	$-1.66687\cdot10^{-6}$	$-6.47608\cdot10^{-9}$	$1.18902\cdot10^{-11}$
1,2-propanediol	1.03775	0.000812422	$-1.84312\cdot10^{-6}$	$-7.5229\cdot10^{-9}$	$1.46617\cdot10^{-11}$

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

$$\rho(T)/\mathrm{g\cdot cm^{-3}} = \sum_{i=0}^{4} a_i T^i \qquad (9)$$

The parameters a_i for the pure components are listed in Table 11. The thermal expansion coefficient, α, as in the case of pure components was obtained by analytical differentiation of the density fitting equation

$$\alpha = -\rho^{-1}(\partial\rho/\partial T)_P \qquad (10)$$

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_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.[23]

$$V_i^E/\mathrm{cm^3\cdot mol^{-1}} = V_m^E - \sum_{k\neq i}^{n} x_k\left(\partial V_m^E/\partial x_k\right)_{T,p,x_{j\neq i,k}} \qquad (11)$$

where $(\partial V_m^E/\partial x_k)_{T,p,x_{j\neq i,k}}$ are calculated from eqs 5 and 8 using the parameters in Tables 7 and 9.

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

$$V_i^{E,\infty}/\mathrm{cm^3\cdot mol^{-1}} = \left(\partial V_m^E/\partial x_i\right)_{T,p,x_i\to 0} \qquad (12)$$

The partial excess molar volumes, V_i^E, and their values at infinite dilution, $V_i^{E,\infty}$, are recorded in Tables 2 to 4. The average uncertainty in the partial excess molar volume is estimated to be $\pm\ 2\cdot10^{-2}$ cm^3·mol^{-1}.

Conclusion

Excess molar volumes, viscosity, and refractive index deviations were calculated for the binary mixtures of methanol + 1,2-propanediol and ethanol + 1,2-propanediol and also for the ternary mixture methanol + ethanol + 1,2-propanediol from measured density and viscosity. The excess molar volume of the binary and ternary mixtures decreases with increasing temperature. The hydrogen bond is a relatively strong, highly directional interaction. Orientation order of molecules changes with increasing temperature. The average number of hydrogen bonds per molecules decreases as the temperature is increased. The decreases of excess molar volume with increasing temperature point out the decrease in average interaction between unlike molecules with increasing temperature. The decreases of V_m^E in methanol (1) + 1,2-propanediol (3) are larger than ethanol (2) + 1,2-propanediol (3) with increasing temperature. These observation indicate that hydrogen bonding between methanol (1) + 1,2-propanediol (3) is stronger than ethanol (1) + 1,2-propanediol (3). This explanation receives support from the excess molar enthalpy of these systems.

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