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Volumetric and Viscometric Properties of Binary Mixtures of Aliphatic Alcohols (C_1−C_4) with Nitroethane from 293.15 K to 313.15 K

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Densities and viscosities were measured for the binary mixtures of methanol, ethanol, propan-1-ol, propan-2-ol, butan-2-ol, and 2-methylpropan-2-ol with nitroethane at temperatures from 293.15 K to 313.15 K and atmospheric pressure. Densities were determined using a vibrating-tube densimeter. Viscosities were measured with an automatic Ubbelohde capillary viscometer. The estimated uncertainties are less than ±0.05% for density and ±0.7% for viscosity. Excess volumes and viscosity deviations as a function of mole fraction average were derived, and the computed results were fitted to the Redlich−Kister equation. Furthermore, McAllister's three-body-interaction model is used to correlate the binary kinematic viscosities and the binary densities.

Introduction

Nitroethane is an aprotic solvent with high polarity which is used in a variety of engineering applications. Strong interaction may exist between the $-NO_2$ group of nitroethane and the −OH group of an alcohol. Upon mixing with alcohols of varying chain lengths, these mixtures might generate interesting properties due to specific interactions, hydrogen bond effects, etc. On the other hand, alcohols are the most well-known solvents with protic and self-associated properties, which are used to study the hydrophobic effects. Thus, accurate knowledge of their thermodynamic mixing properties, such as excess volume, excess enthalpy, and excess Gibbs energy, has great relevance in theoretical and applied areas of research.

To gain some understanding about the nature of molecular interaction between alcohol and nitroethane, we measure the experimental density and viscosity for the binary mixtures of methanol, ethanol, propan-1-ol, propan-2-ol, butan-2-ol, and 2-methylpropan-2-ol with nitroethane in the temperature interval of 293.15 K to 313.15 K over the entire composition range. The experimental results are used to calculate excess molar volumes and viscosity deviations from the mole fraction average. These results are used to qualitatively discuss the nature of interactions from mixing the components. The calculated quantities have been fitted to the Redlich−Kister equation (Redlich and Kister, 1948) to estimate the coefficients. Attempts have also been made to correlate the binary densities and viscosities with the McAllister equation (McAllister, 1960). The present paper is, therefore, concerned about the study of the influence of the hydrocarbon chain of the alcohols and chemical structure of the nitroethane upon the excess volumes and viscosity deviations. To the best of our knowledge, none of these mixtures have been measured previously.

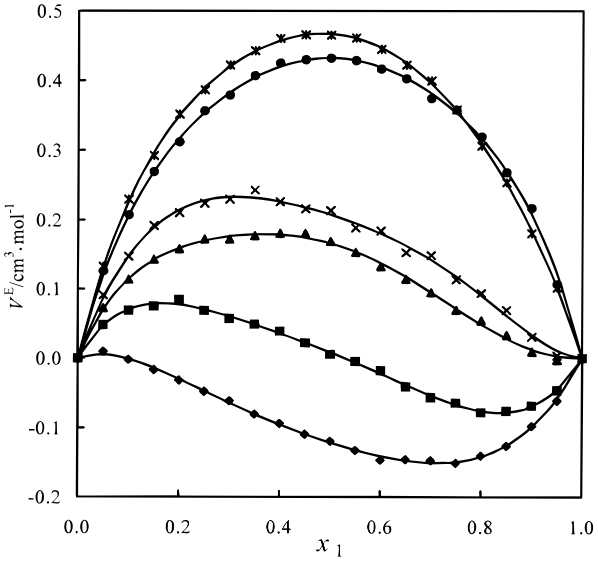

Figure 1. Excess volume variation with mole fraction at 303.15 K: (◆) methanol (1) + nitroethane (2), (■) ethanol (1) + nitroethane (2), (▲) propan-1-ol (1) + nitroethane (2), (×) propan-2-ol (1) + nitroethane (2), (*) butan-2-ol (1) + nitroethane (2), (●) 2-methylpropan-2-ol (1) + nitroethane (2), (−) the Redlich−Kister equation.

Table 1. Comparison of Measured Densities, Viscosities, and Refractive Indices of Pure Components with Literature Values (Riddick et al., 1986) at 298.15 K

	ρ/g·cm^{-3}		η/mPa·s		n_D	
compound	this work	lit.	this work	lit.	this work	lit.
nitroethane	1.044 37	1.044 64	0.638	0.638	1.389 60	1.392 4
methanol	0.786 68	0.786 37	0.553	0.5513	1.326 85	1.326 52
ethanol	0.785 30	0.784 93	1.083	1.0826	1.359 48	1.359 41
propan-1-ol	0.799 64	0.799 60	1.943	1.9430	1.383 17	1.383 70
propan-2-ol	0.781 20	0.781 26	2.049	2.0436	1.375 17	1.375 2
butan-2-ol	0.802 50	0.802 41	3.084	2.998	1.395 12	1.395 30
2-methylpropan-2-ol	0.780 80	0.781 2	4.518	4.438	1.384 86	1.385 2

Experimental Section

The chemicals used were of analytical grade and obtained from Fisher, Tedia, and Merck. All components were dried over molecular sieves (Aldrich, 0.3 nm). Nitroethane was distilled through a glass column (23-mm i.d. and 470-mm length, Teflon mesh packing) under nitrogen. The

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Table 2. Experimental Densities (ρ), Dynamic Viscosities (η), and Excess Molar Volumes (V^E) for Methanol (1) + Nitroethane (2)

x_1	ρ/g·cm^{-3}	η/mPa·s	V^E/cm^3·mol^{-1}	x_1	ρ/g·cm^{-3}	η/mPa·s	V^E/cm^3·mol^{-1}
		293.15 K				293.15 K	
0.0000	1.0505	0.679	0.000	0.5500	0.9471	0.556	−0.1479
0.0501	1.0430	0.657	0.0011	0.6000	0.9343	0.553	−0.1603
0.0999	1.0354	0.634	−0.0146	0.6500	0.9205	0.552	−0.1582
0.1503	1.0275	0.617	−0.0397	0.6999	0.9060	0.552	−0.1611
0.2000	1.0192	0.603	−0.0555	0.7500	0.8904	0.555	−0.1630
0.2500	1.0105	0.593	−0.0725	0.8000	0.8736	0.558	−0.1524
0.3000	1.0011	0.584	−0.0818	0.8500	0.8556	0.562	−0.1354
0.3501	0.9916	0.576	−0.1014	0.9000	0.8359	0.567	−0.1015
0.4000	0.9814	0.570	−0.1150	0.9500	0.8147	0.576	−0.0645
0.4500	0.9707	0.564	−0.1350	1.0000	0.7915	0.591	0.0000
0.5000	0.9593	0.559	−0.1432				
		303.15 K				303.15 K	
0.0000	1.0383	0.605	0.0000	0.5500	0.9357	0.489	−0.1325
0.0501	1.0308	0.586	0.0097	0.6000	0.9231	0.487	−0.1465
0.0999	1.0232	0.565	−0.0019	0.6500	0.9094	0.485	−0.1456
0.1503	1.0152	0.549	−0.0162	0.6999	0.8950	0.486	−0.1470
0.2000	1.0070	0.536	−0.0314	0.7500	0.8797	0.486	−0.1507
0.2500	0.9983	0.526	−0.0476	0.8000	0.8630	0.487	−0.1404
0.3000	0.9892	0.517	−0.0610	0.8500	0.8452	0.490	−0.1261
0.3501	0.9797	0.510	−0.0802	0.9000	0.8258	0.495	−0.0973
0.4000	0.9696	0.504	−0.0935	0.9500	0.8049	0.501	−0.0606
0.4500	0.9589	0.498	−0.1093	1.0000	0.7820	0.514	0.0000
0.5000	0.9476	0.493	−0.1195				
		313.15 K				313.15 K	
0.0000	1.0262	0.544	0.0000	0.5500	0.9241	0.433	−0.1053
0.0501	1.0185	0.527	0.0216	0.6000	0.9118	0.430	−0.1180
0.0999	1.0110	0.508	0.0115	0.6500	0.8982	0.428	−0.1243
0.1503	1.0030	0.493	0.0031	0.6999	0.8840	0.428	−0.1288
0.2000	0.9948	0.480	−0.0083	0.7500	0.8688	0.427	−0.1355
0.2500	0.9862	0.471	−0.0225	0.8000	0.8525	0.428	−0.1293
0.3000	0.9770	0.462	−0.0329	0.8500	0.8349	0.430	−0.1159
0.3501	0.9677	0.455	−0.0574	0.9000	0.8157	0.434	−0.0869
0.4000	0.9577	0.448	−0.0678	0.9500	0.7915	0.437	−0.0555
0.4500	0.9472	0.442	−0.0891	1.0000	0.7726	0.448	0.0000
0.5000	0.9360	0.438	−0.0968				

Table 3. Experimental Densities (ρ), Dynamic Viscosities (η), and ExcessVolumes (V^E) for Ethanol (1) + Nitroethane (2)

x_1	ρ/g·cm^{-3}	η/mPa·s	V^E/cm^3·mol^{-1}	x_1	ρ/g·cm^{-3}	η/mPa·s	V^E/cm^3·mol^{-1}
		293.15 K				293.15 K	
0.0000	1.0505	0.679	0.0000	0.5500	0.9209	0.716	−0.0471
0.0500	1.0392	0.669	0.0358	0.6000	0.9077	0.738	−0.0577
0.1001	1.0281	0.655	0.0477	0.6500	0.8944	0.769	−0.0752
0.1500	1.0169	0.648	0.0485	0.7000	0.8807	0.804	−0.0891
0.2000	1.0055	0.645	0.0530	0.7499	0.8667	0.839	−0.0951
0.2500	0.9942	0.650	0.0330	0.8000	0.8522	0.886	−0.0979
0.3000	0.9826	0.651	0.0167	0.8499	0.8374	0.944	−0.0925
0.3500	0.9707	0.658	0.0099	0.9000	0.8221	1.015	−0.0832
0.4000	0.9586	0.668	−0.0017	0.9499	0.8062	1.103	−0.0500
0.4500	0.9463	0.681	−0.0152	1.0000	0.7897	1.192	0.0000
0.5000	0.9337	0.697	−0.0332				
		303.15 K				303.15 K	
0.0000	1.0383	0.605	0.0000	0.5500	0.9099	0.618	−0.0048
0.0500	1.0271	0.598	0.0477	0.6000	0.8970	0.636	−0.0178
0.1001	1.0159	0.584	0.0689	0.6500	0.8839	0.656	−0.0407
0.1500	1.0049	0.576	0.0748	0.7000	0.8704	0.682	−0.0561
0.2000	0.9935	0.573	0.0841	0.7499	0.8565	0.712	−0.0640
0.2500	0.9823	0.570	0.0684	0.8000	0.8424	0.748	−0.0777
0.3000	0.9709	0.571	0.0566	0.8499	0.8278	0.793	−0.0757
0.3500	0.9591	0.575	0.0485	0.9000	0.8127	0.847	−0.0679
0.4000	0.9471	0.583	0.0384	0.9499	0.7972	0.914	−0.0460
0.4500	0.9350	0.593	0.0217	1.0000	0.7810	0.986	0.0000
0.5000	0.9226	0.603	0.0049				
		313.15 K				313.15 K	
0.0000	1.0262	0.544	0.0000	0.5500	0.8989	0.538	0.0493
0.0500	1.0149	0.538	0.0619	0.6000	0.8861	0.550	0.0405
0.1001	1.0038	0.526	0.0926	0.6500	0.8733	0.567	0.0139
0.1500	0.9928	0.519	0.1056	0.7000	0.8599	0.586	0.0032
0.2000	0.9816	0.512	0.1188	0.7499	0.8463	0.608	−0.0114
0.2500	0.9705	0.507	0.1100	0.8000	0.8324	0.637	−0.0228
0.3000	0.9591	0.506	0.1042	0.8499	0.8181	0.672	−0.0261
0.3500	0.9474	0.509	0.0993	0.9000	0.8033	0.715	−0.0264
0.4000	0.9356	0.513	0.0920	0.9499	0.7881	0.770	−0.0128
0.4500	0.9236	0.519	0.0781	1.0000	0.7726	0.823	0.0000
0.5000	0.9114	0.528	0.0621				

other components were used without further purification. The purity of all chemicals was checked by gas chromatography. In all cases chemicals with a purity greater than 99.5 mass % were used for the experimental investigations. The purity of solvents was further ascertained by comparing their densities, viscosities, and refractive indices at

Table 4. Experimental Densities (ρ), Dynamic Viscosities (η), and Excess Molar Volumes (V^E) for Propan-1-ol (1) + Nitroethane (2)

x_1	ρ/g·cm^{-3}	η/mPa·s	V^E/cm^3·mol^{-1}	x_1	ρ/g·cm^{-3}	η/mPa·s	V^E/cm^3·mol^{-1}
		293.15 K				293.15 K	
0.0000	1.0505	0.679	0.0000	0.5500	0.9107	0.951	0.1034
0.0500	1.0368	0.686	0.0570	0.6000	0.8987	1.016	0.0796
0.1000	1.0235	0.683	0.0912	0.6500	0.8867	1.085	0.0645
0.1499	1.0105	0.690	0.1096	0.7000	0.8748	1.170	0.0444
0.2001	0.9976	0.702	0.1215	0.7500	0.8630	1.282	0.0282
0.2500	0.9849	0.720	0.1252	0.8000	0.8510	1.391	0.0188
0.3000	0.9724	0.748	0.1271	0.8500	0.8392	1.539	0.0051
0.3500	0.9598	0.776	0.1280	0.9000	0.8275	1.717	−0.0106
0.4000	0.9474	0.808	0.1295	0.9500	0.8157	1.945	−0.0165
0.4500	0.9350	0.848	0.1300	1.0000	0.8037	2.197	0.0000
0.5000	0.9228	0.898	0.1151				
		303.15 K				303.15 K	
0.0000	1.0383	0.605	0.0000	0.5500	0.9003	0.800	0.1525
0.0500	1.0247	0.609	0.0726	0.6000	0.8886	0.852	0.1322
0.1000	1.0115	0.605	0.1135	0.6500	0.8768	0.902	0.1139
0.1499	0.9986	0.607	0.1425	0.7000	0.8651	0.967	0.0944
0.2001	0.9860	0.617	0.1577	0.7500	0.8535	1.043	0.0692
0.2500	0.9733	0.629	0.1717	0.8000	0.8419	1.133	0.0540
0.3000	0.9610	0.647	0.1717	0.8500	0.8303	1.243	0.0329
0.3500	0.9487	0.667	0.1767	0.9000	0.8188	1.377	0.0094
0.4000	0.9364	0.694	0.1806	0.9500	0.8073	1.559	−0.0027
0.4500	0.9242	0.724	0.1800	1.0000	0.7956	1.725	0.0000
0.5000	0.9122	0.758	0.1684				
		313.15 K				313.15 K	
0.0000	1.0262	0.544	0.0000	0.5500	0.8898	0.681	0.2138
0.0500	1.0125	0.544	0.0870	0.6000	0.8783	0.718	0.1857
0.1000	0.9995	0.539	0.1365	0.6500	0.8668	0.756	0.1672
0.1499	0.9868	0.539	0.1724	0.7000	0.8553	0.808	0.1471
0.2001	0.9742	0.547	0.1963	0.7500	0.8439	0.881	0.1173
0.2500	0.9618	0.554	0.2161	0.8000	0.8325	0.947	0.0929
0.3000	0.9495	0.567	0.2245	0.8500	0.8212	1.035	0.0685
0.3500	0.9374	0.581	0.2286	0.9000	0.8100	1.125	0.0375
0.4000	0.9253	0.609	0.2352	0.9500	0.7987	1.239	0.0168
0.4500	0.9133	0.623	0.2406	1.0000	0.7874	1.369	0.0000
0.5000	0.9016	0.655	0.2237				

Table 5. Experimental Densities (ρ), Dynamic Viscosities (η), and Excess Molar Volumes (V^E) for Propan-2-ol (1) + Nitroethane (2)

x_1	ρ/g·cm^{-3}	η/mPa·s	V^E/cm^3·mol^{-1}	x_1	ρ/g·cm^{-3}	η/mPa·s	V^E/cm^3·mol^{-1}
		293.15 K				293.15 K	
0.0000	1.0505	0.679	0.0000	0.5499	0.8987	0.881	0.1190
0.0501	1.0352	0.680	0.0763	0.6001	0.8857	0.932	0.1076
0.1000	1.0206	0.672	0.1213	0.6500	0.8731	1.000	0.0758
0.1500	1.0062	0.671	0.1535	0.7000	0.8602	1.080	0.0770
0.2000	0.9922	0.678	0.1661	0.7499	0.8477	1.180	0.0501
0.2500	0.9784	0.698	0.1692	0.8000	0.8351	1.276	0.0334
0.3000	0.9648	0.707	0.1721	0.8499	0.8227	1.467	0.0149
0.3500	0.9512	0.729	0.1761	0.9000	0.8103	1.681	−0.0096
0.4000	0.9380	0.766	0.1562	0.9500	0.7980	1.983	−0.0246
0.4501	0.9248	0.800	0.1456	1.0000	0.7853	2.396	0.0000
0.5000	0.9116	0.827	0.1399				
		303.15 K				303.15 K	
0.0000	1.0383	0.605	0.0000	0.5499	0.8879	0.731	0.1880
0.0501	1.0231	0.605	0.0908	0.6001	0.8751	0.777	0.1837
0.1000	1.0085	0.595	0.1467	0.6500	0.8626	0.819	0.1522
0.1500	0.9942	0.592	0.1913	0.7000	0.8500	0.877	0.1483
0.2000	0.9803	0.594	0.2100	0.7499	0.8377	0.949	0.1132
0.2500	0.9666	0.601	0.2236	0.8000	0.8253	1.052	0.0938
0.3000	0.9532	0.613	0.2293	0.8499	0.8131	1.154	0.0692
0.3500	0.9397	0.628	0.2424	0.9000	0.8011	1.305	0.0306
0.4000	0.9266	0.647	0.2255	0.9500	0.7891	1.507	0.0038
0.4501	0.9136	0.670	0.2156	1.0000	0.7768	1.765	0.0000
0.5000	0.9006	0.697	0.2130				
		313.15 K				313.15 K	
0.0000	1.0262	0.544	0.0000	0.5499	0.8769	0.620	0.2647
0.0501	1.0110	0.536	0.1005	0.6001	0.8643	0.648	0.2523
0.1000	0.9964	0.530	0.1713	0.6500	0.8520	0.683	0.2224
0.1500	0.9821	0.526	0.2301	0.7000	0.8395	0.725	0.2169
0.2000	0.9683	0.526	0.2583	0.7499	0.8275	0.774	0.1756
0.2500	0.9548	0.530	0.2726	0.8000	0.8153	0.849	0.1500
0.3000	0.9414	0.538	0.2908	0.8499	0.8034	0.915	0.1169
0.3500	0.9281	0.546	0.3022	0.9000	0.7916	1.021	0.0709
0.4000	0.9152	0.559	0.2925	0.9500	0.7799	1.160	0.0223
0.4501	0.9022	0.576	0.2902	1.0000	0.7680	1.326	0.0000
0.5000	0.8894	0.597	0.2842				

298.15 K, which agreed reasonably with the corresponding literature values (Table 1). Refractive indices, n_D, of pure chemicals were measured with an Abbe refractometer, Atago RX-5000, with an accuracy of ±0.000 01 unit.

All dried liquids were boiled to remove dissolved air. Solutions of different composition were prepared by mass in a 50-cm^3 Erlenmeyer flask provided with a joint stopper, using a Mettler AB204 balance accurate to within ±0.1 mg.

Table 6. Experimental Densities (ρ), Dynamic Viscosities (η), and Excess Molar Volumes (V^E) for Butan-2-ol (1) + Nitroethane (2)

x_1	ρ/g·cm^{-3}	η/mPa·s	V^E/cm^3·mol^{-1}	x_1	ρ/g·cm^{-3}	η/mPa·s	V^E/cm^3·mol^{-1}
		293.15 K				293.15 K	
0.0000	1.0505	0.679	0.0000	0.5500	0.8971	1.034	0.3928
0.0500	1.0332	0.679	0.1259	0.5999	0.8858	1.123	0.3775
0.1000	1.0171	0.680	0.2081	0.6499	0.8749	1.236	0.3529
0.1500	1.0018	0.684	0.2638	0.7000	0.8641	1.378	0.3555
0.2001	0.9870	0.704	0.3139	0.7497	0.8539	1.516	0.2990
0.2500	0.9730	0.727	0.3385	0.8000	0.8438	1.723	0.2536
0.3002	0.9592	0.759	0.3709	0.8499	0.8340	1.983	0.2107
0.3500	0.9460	0.793	0.3852	0.8998	0.8246	2.353	0.1495
0.4000	0.9332	0.845	0.3951	0.9499	0.8154	2.873	0.0860
0.4500	0.9209	0.904	0.3984	1.0000	0.8065	3.737	0.0000
0.5000	0.9088	0.971	0.3981				
		303.15 K				303.15 K	
0.0000	1.0383	0.605	0.0000	0.5500	0.8867	0.847	0.4610
0.0500	1.0213	0.605	0.1324	0.5999	0.8757	0.909	0.4446
0.1000	1.0052	0.601	0.2291	0.6499	0.8649	0.980	0.4220
0.1500	0.9901	0.604	0.2920	0.7000	0.8543	1.070	0.3991
0.2001	0.9755	0.616	0.3511	0.7497	0.8443	1.169	0.3580
0.2500	0.9615	0.632	0.3863	0.8000	0.8344	1.319	0.3060
0.3002	0.9479	0.652	0.4220	0.8499	0.8249	1.484	0.2535
0.3500	0.9349	0.676	0.4426	0.8998	0.8157	1.724	0.1803
0.4000	0.9223	0.716	0.4603	0.9499	0.8068	2.050	0.1016
0.4500	0.9101	0.750	0.4656	1.0000	0.7982	2.567	0.0000
0.5000	0.8983	0.800	0.4648				
		313.15 K				313.15 K	
0.0000	1.0262	0.544	0.0000	0.5500	0.8762	0.707	0.5318
0.0500	1.0093	0.543	0.1433	0.5999	0.8653	0.750	0.5138
0.1000	0.9934	0.538	0.2454	0.6499	0.8547	0.801	0.4890
0.1500	0.9784	0.536	0.3218	0.7000	0.8443	0.862	0.4623
0.2001	0.9638	0.542	0.3904	0.7497	0.8344	0.935	0.4203
0.2500	0.9500	0.555	0.4367	0.8000	0.8248	1.026	0.3637
0.3002	0.9366	0.569	0.4751	0.8499	0.8155	1.144	0.3024
0.3500	0.9237	0.586	0.5037	0.8998	0.8065	1.304	0.2225
0.4000	0.9112	0.610	0.5272	0.9499	0.7978	1.511	0.1247
0.4500	0.8992	0.640	0.5332	1.0000	0.7895	1.822	0.0000
0.5000	0.8875	0.675	0.5380				

Table 7. Experimental Densities (ρ), Dynamic Viscosities (η), and Excess Molar Volumes (V^E) for 2-Methylpropan-2-ol (1) + Nitroethane (2)

x_1	ρ/g·cm^{-3}	η/mPa·s	V^E/cm^3·mol^{-1}	x_1	ρ/g·cm^{-3}	η/mPa·s	V^E/cm^3·mol^{-1}
		298.15 K[a]				298.15 K[a]	
0.0000	1.0444	0.638	0.0000	0.5500	0.8773	0.988	0.4140
0.0502	1.0256	0.646	0.1135	0.6000	0.8650	1.075	0.4169
0.1001	1.0080	0.647	0.1944	0.6499	0.8532	1.185	0.4045
0.1499	0.9911	0.655	0.2627	0.6998	0.8417	1.323	0.3851
0.2002	0.9750	0.670	0.3034	0.7498	0.8306	1.499	0.3654
0.2501	0.9595	0.691	0.3478	0.7998	0.8198	1.730	0.3290
0.3001	0.9446	0.718	0.3771	0.8498	0.8094	2.063	0.2792
0.3500	0.9302	0.753	0.3992	0.8997	0.7994	2.505	0.2175
0.4000	0.9163	0.794	0.4111	0.9500	0.7899	3.231	0.1165
0.4501	0.9028	0.845	0.4207	1.0000	0.7808	4.518	0.0000
0.5001	0.8898	0.909	0.4247				
		303.15 K				303.15 K	
0.0000	1.0383	0.605	0.0000	0.5500	0.8716	0.886	0.4286
0.0502	1.0194	0.610	0.1256	0.6000	0.8594	0.958	0.4164
0.1001	1.0019	0.609	0.2072	0.6499	0.8477	1.047	0.4023
0.1499	0.9851	0.615	0.2691	0.6998	0.8363	1.158	0.3737
0.2002	0.9691	0.626	0.3115	0.7498	0.8252	1.300	0.3575
0.2501	0.9536	0.643	0.3561	0.7998	0.8145	1.475	0.3189
0.3001	0.9388	0.667	0.3786	0.8498	0.8041	1.728	0.2678
0.3500	0.9244	0.694	0.4066	0.8997	0.7941	2.068	0.2163
0.4000	0.9105	0.730	0.4248	0.9500	0.7847	2.574	0.1064
0.4501	0.8971	0.778	0.4298	1.0000	0.7755	3.427	0.0000
0.5001	0.8841	0.824	0.4317				
		313.15 K				313.15 K	
0.0000	1.0262	0.544	0.0000	0.5500	0.8604	0.728	0.4417
0.0502	1.0073	0.546	0.1304	0.6000	0.8484	0.777	0.4285
0.1001	0.9899	0.544	0.2104	0.6499	0.8367	0.836	0.4132
0.1499	0.9733	0.546	0.2741	0.6998	0.8255	0.907	0.3829
0.2002	0.9572	0.547	0.3278	0.7498	0.8144	0.997	0.3695
0.2501	0.9418	0.563	0.3717	0.7998	0.8038	1.104	0.3242
0.3001	0.9271	0.580	0.3972	0.8498	0.7936	1.258	0.2738
0.3500	0.9128	0.597	0.4239	0.8997	0.7836	1.449	0.2218
0.4000	0.8990	0.622	0.4394	0.9500	0.7742	1.718	0.1148
0.4501	0.8857	0.652	0.4423	1.0000	0.7651	2.123	0.0000
0.5001	0.8728	0.687	0.4485				

[a] The normal freezing point of 2-methylpropan-2-ol is 298.15 K (Riddick et al., 1986).

The accuracy in the mole fraction is 5 × 10^{-5}. Densities were measured by using a DMA-58 vibrating-tube densimeter (Anton-Paar, Graz, Austria) with a stated precision of 0.02 kg/m^3. The temperature in the measuring cell was regulated to ±0.01 K. The uncertainty of the density measurements was less than ±0.05%.

Table 8. Coefficients of the Redlich–Kister Equation and Standard Deviations for V^E and $\Delta\eta$

Y^E/unit	T/K	$a_0 \times 10^2$	$a_1 \times 10^2$	$a_2 \times 10^2$	$a_3 \times 10^2$	σ
Methanol (1) + Nitroethane (2)						
V^E/cm^3·mol^{-1}	293.15	−56.553	39.507	−19.018	34.101	0.004
	303.15	−48.772	45.966	−12.133	33.981	0.003
	313.15	−38.920	48.540	−7.498	39.175	0.004
$\Delta\eta$/mPa·s	293.15	−30.103	−2.423	−11.489	−0.882	0.001
	303.15	−26.230	−2.943	−9.526	1.763	0.001
	313.15	−23.380	2.793	−7.126	1.286	0.001
Ethanol (1) + Nitroethane (2)						
V^E/cm^3·mol^{-1}	293.15	−13.216	56.409	−8.650	52.404	0.003
	303.15	2.877	57.866	−5.303	59.997	0.003
	313.15	24.777	55.684	14.920	40.893	0.004
$\Delta\eta$/mPa·s	293.15	−95.587	32.862	−25.060	3.124	0.003
	303.15	−77.148	24.105	−18.912	8.702	0.002
	313.15	−62.950	18.545	−11.793	7.952	0.002
Propan-1-ol (1) + Nitroethane (2)						
V^E/cm^3·mol^{-1}	293.15	44.298	42.296	−3.954	40.379	0.005
	303.15	65.213	41.155	2.618	46.195	0.005
	313.15	88.257	41.784	−9.662	39.509	0.005
$\Delta\eta$/mPa·s	293.15	−216.599	101.496	−72.207	34.867	0.004
	303.15	−162.734	74.225	−45.588	13.206	0.006
	313.15	−122.644	51.398	−23.152	−4.134	0.004
Propan-2-ol (1) + Nitroethane (2)						
V^E/cm^3·mol^{-1}	293.15	54.629	50.759	17.022	61.476	0.006
	303.15	83.603	45.760	29.896	52.192	0.006
	313.15	112.462	41.953	38.423	45.458	0.006
$\Delta\eta$/mPa·s	293.15	−279.614	169.718	−182.510	131.395	0.007
	303.15	−193.950	105.791	−98.883	68.976	0.004
	313.15	−135.320	68.438	−61.889	35.497	0.003
Butan-2-ol (1) + Nitroethane (2)						
V^E/cm^3·mol^{-1}	293.15	158.148	15.830	58.455	35.581	0.005
	303.15	185.570	9.887	59.605	31.785	0.004
	313.15	213.502	7.471	66.027	12.532	0.004
$\Delta\eta$/mPa·s	293.15	−489.488	306.256	−401.468	358.677	0.025
	303.15	−312.157	186.940	−229.742	192.411	0.012
	313.15	−203.245	112.123	−132.651	104.589	0.005
2-Methylpropan-2-ol (1) + Nitroethane (2)						
V^E/cm^3·mol^{-1}	298.15	168.325	−4.593	88.226	−12.921	0.004
	303.15	170.757	1.259	81.868	−1.781	0.007
	313.15	176.646	7.250	83.291	−12.488	0.007
$\Delta\eta$/mPa·s	298.15	−653.211	456.270	−638.400	621.396	0.046
	303.15	−468.377	316.691	−404.165	367.196	0.025
	313.15	−256.285	155.353	−172.700	143.018	0.008

The kinematic viscosities were determined with a commercial capillary viscometer of the Ubbelohde type. The kinematic viscosity (ν) was then calculated from the following relationship

$$\nu \equiv \eta/\rho = k(t - \theta) \tag{1}$$

where t is the flow time, η is the absolute viscosity, and k and θ are respectively the viscometer constant and the Hagenbach correction (Hardy, 1962). The constants k for several viscometers were provided by the manufacturer (SCHOTT-GERÄTE, Hofheim, Germany) and checked at room temperature by measurement of the viscosity of pure water. The viscometer was kept in a D20 KP (LAUDA, Lauda-Königshofen, Germany) thermostat controlled to ±0.01 K with a proportional–integral–differential regulator. The accuracy of the flow-time measurement is ±0.01 s. Triplicate measurements of flow times were reproducible within ±0.02%. The uncertainty of the viscosity measurement was less than ±0.7%.

The densities and viscosities of binary mixtures were measured at temperatures from 293.15 K to 313.15 K and atmospheric pressure. A set of 19 compositions were prepared with an increment of 0.05 mole fraction for each system. An average of at least two measurements was taken for each composition.

Results and Discussion

The experimental densities, viscosities, and excess volumes for all of the binary mixtures are given in Tables 2–7. The molar excess volumes, V^E, have been calculated from density data according to the equation

$$V^E = (x_1M_1 + x_2M_2)/\rho - (x_1M_1/\rho_1 + x_2M_2/\rho_2) \tag{2}$$

where ρ is the density of the mixture and x_1, ρ_1, M_1, x_2, ρ_2, and M_2 are the mole fraction, density, and molecular weight of pure components 1 and 2, respectively. The deviation of the viscosity from the mole fraction average is given by

$$\Delta\eta = \eta - (x_1\eta_1 + x_2\eta_2) \tag{3}$$

where η, η_1, and η_2 are the absolute viscosities of the mixture and the viscosities of pure components 1 and 2, respectively. The excess molar volumes and deviations in viscosity were represented mathematically by the Redlich–Kister equation

$$Y^E = x_1(1 - x_1)\sum_{i=0}^{3} a_i(2x_i - 1)^i \tag{4}$$

where Y^E is V^E or $\Delta\eta$, x_1 is the mole fraction of alcohol, and a_i are the coefficients. The values of coefficients a_i were determined by a multiple regression analysis based on the least-squares method and are summarized along with the standard deviations between the experimental and fitted values of the respective functions in Table 8.

Table 9. Parameters of McAllister's Three-Body-Interaction Model and Standard Deviations for Kinematic Viscosities and Densities

	kinematic viscosity			density		
T/K	ν_{12}	ν_{21}	$\sigma/10^{-6}$ m^2·s^{-1}	ν_{12}	ν_{21}	σ/g·cm^{-3}
			Methanol (1) + Nitroethane (2)			
293.15	0.581 81	0.553 64	0.003	1.022 74	1.010 68	0.0018
303.15	0.517 04	0.498 03	0.003	1.010 36	0.998 25	0.0018
313.15	0.461 99	0.450 48	0.002	0.997 02	0.986 27	0.0017
			Ethanol (1) + Nitroethane (2)			
293.15	0.757 59	0.617 56	0.004	0.923 55	0.986 01	0.0003
303.15	0.652 72	0.554 16	0.003	0.912 39	0.973 98	0.0003
313.15	0.568 65	0.503 47	0.003	0.900 48	0.962 18	0.0002
			Propan-1-ol (1) + Nitroethane (2)			
293.15	1.065 20	0.709 72	0.008	0.889 51	0.965 59	0.0001
303.15	0.901 06	0.623 03	0.008	0.879 37	0.954 03	0.0001
313.15	0.789 27	0.547 48	0.005	0.869 01	0.942 35	0.0001
			Propan-2-ol (1) + Nitroethane (2)			
293.15	0.824 75	0.724 99	0.026	0.875 70	0.956 44	0.0002
303.15	0.727 44	0.617 93	0.012	0.864 62	0.944 75	0.0002
313.15	0.625 34	0.509 65	0.008	0.853 48	0.932 79	0.0002
			Butan-2-ol (1) + Nitroethane (2)			
293.15	0.962 78	0.780 14	0.064	0.868 26	0.942 58	0.0003
303.15	0.810 52	0.678 53	0.037	0.857 89	0.931 46	0.0003
313.15	0.707 69	0.592 01	0.022	0.847 41	0.920 12	0.0003
			2-Methylpropan-2-ol (1) + Nitroethane (2)			
298.15	0.785 04	0.809 87	0.090	0.844 80	0.927 25	0.0003
303.15	0.765 79	0.735 11	0.056	0.839 53	0.921 23	0.0003
313.15	0.710 05	0.620 40	0.025	0.828 81	0.909 36	0.0003

In the system studied, excess molar volume increases with a rise in temperature for all of the mixtures. The experimental V^E values are also graphically represented as a function of alcohol mole fractions for 303.15 K in Figure 1. It is observed that the values of V^E for the binary mixtures of propan-1-ol, propan-2-ol, butan-2-ol, and 2-methylpropan-2-ol with nitroethane are positive over the entire mole fraction range. For mixtures of methanol or ethanol with nitroethane, positive values of V^E are observed in the alcohol-poor region (i.e., x_1 up to 0.1 for methanol or 0.5 for ethanol) while negative values of V^E are observed at higher concentrations of alcohol in the mixture. Thus, sigmoidal shapes are observed for these mixtures. The V^E values at equimolar concentrations follow the order: methanol < ethanol < propan-1-ol < propan-2-ol < 2-methylpropan-2-ol ≈ butan-2-ol.

The observed V^E may be discussed in terms of several effects which may be arbitrarily divided into physical, chemical, and geometrical contributions (Aminabhavi et al., 1993). The physical interactions involve mainly dispersion force giving a positive contribution. The chemical or specific interaction results in a volume decrease, and these interactions include formation of hydrogen bonds and other complex-forming interactions. Structure contributions arising from geometrical fitting of one component into the other, because of differences in the molar volume and free volume between components, lead to negative contributions to volume V^E.

In the present investigation, alcohols are strongly self-associated through hydrogen bonding, but nitroethane does not exhibit this property because it has no hydrogen atom having that ability. With higher alcohols, structure contribution is negligible, and association decreases with an increase in the chain length of alcohols. Therefore, mixtures of nitroethane with higher alcohols give larger V^E as compared to lower alcohols. The observed V^E data for the present mixtures may be further explained if it is assumed that (i) the addition of a $C_2H_5NO_2$ molecule causes a rupture of some of the hydrogen bonds of alcohols, (ii) the alcohol molecule interacts with the $C_2H_5NO_2$ molecule because of specific interactions, and (iii) steric repulsion exists between the alkyl chain of the alcohol and that of nitroethane. Factors i and iii produce an expansion in volume, whereas factor ii results in a contraction. The observed V^E would then be the cumulative sum of the contributions of these factors, so that V^E is either positive or negative values. Such results can also be seen in the work of Aminabhavi et al. (1993) for methyl acetoacetate + alcohol mixtures.

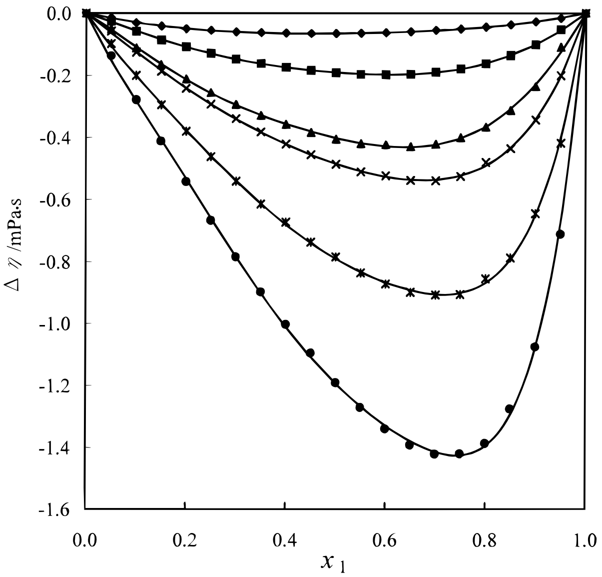

Figure 2. Viscosity deviation variation with mole fraction at 303.15 K: (◆) methanol (1) + nitroethane (2), (■) ethanol (1) + nitroethane (2), (▲) propan-1-ol (1) + nitroethane (2), (×) propan-2-ol (1) + nitroethane (2), (*) butan-2-ol (1) + nitroethane (2), (●) 2-methyl propan-2-ol (1) + nitroethane (2), (—) the Redlich−Kister equation.

The values of the deviations in viscosity calculated from eq 3 are presented in Figure 2. There is a clear trend in $\Delta\eta$ values for all of the mixtures. The $\Delta\eta$ values, which generally decrease with increasing size of the alcohol molecules, are negative. Mixtures of alcohols with nitroethane studied show the trend as methanol > ethanol >

propan-1-ol > propan-2-ol > butan-2-ol > 2-methylpropan-2-ol. The minima of the $\Delta\eta$ values versus x_1 curves occur in the high mole fraction region of the alcohol.

McAllister's multibody interaction model (McAllister, 1960) is widely used for correlating the kinematic viscosity of liquid mixtures with mole fraction. The three-body-interaction model is defined as

$$\ln \nu = x_1^3 \ln \nu_1 + 3x_1^2x_2 \ln \nu_{12} + 3x_1x_2^2 \ln \nu_{21} + x_2^3 \ln \nu_2 - \ln(x_1 + x_2M_2/M_1) + 3x_1^2x_2 \ln[(2 + M_2/M_1)/3] + 3x_1x_2^2 \ln[(1 + 2M_2/M_1)/3] + x_2^3 \ln(M_2/M_1) \quad (5)$$

where ν_{12} and ν_{21} are the model parameters. Kinematic viscosities and densities of the present study were fitted to the McAllister equation. A reasonable fit was found for all mixtures. Table 9 records the calculated results, which include McAllister's parameters and standard deviations. It is observed that McAllister's model correlates both the mixture viscosity and the mixture density to a significantly high degree of accuracy for all of the systems as evidenced by small standard deviations.

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