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Excess Molar Volumes, Viscosities, and Refractive Indexes for Binary Mixtures of 1-Chlorobutane with Four Alcohols at T = (288.15, 298.15, and 308.15) K

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Densities, viscosities, and refractive indexes were measured for the binary mixtures formed by methanol, ethanol, propan-1-ol, and butan-1-ol with 1-chlorobutane at T = (288.15, 298.15, and 308.15) K and atmospheric pressure over the whole concentration range. Excess molar volumes (V^E) were determined from the densities of pure liquids and mixtures measured with a vibrating-tube densimeter. Excess molar volumes, which increase as the temperature increases, are positive except for mixtures in the high mole fraction region of propan-1-ol or butan-1-ol. Viscosities were measured with an automatic Ubbelohde capillary viscometer. Refractive indexes were measured using a digital refractometer. Deviations in viscosity ($\Delta\eta$) and deviations in refractive index (Δn_D) as a function of mole fraction for the mixtures were derived from the experimental data. The computed results of V^E, $\Delta\eta$, and Δn_D were fitted to the Redlich−Kister equation. Furthermore, McAllister's three-body interaction model is used to correlate the binary kinematic viscosities.

Introduction

The binary systems in this work have interesting characteristics with respect to the solubility of polymers. At 25 °C the pure liquids such as 1-chlorobutane, methanol, ethanol, propan-1-ol, and butan-1-ol are poor solvents of poly(methyl methacrylate), while the binary mixtures formed by 1-chlorobutane with these alcohols may act as very good solvents for the polymer.[1] To adequately interpret the thermodynamic behavior of the polymer in the mixed solvents, it is of interest to know the composition and temperature dependence of the thermodynamic properties of these binary mixtures.

In the present paper we report densities, viscosities, refractive indexes, and excess molar volumes for the binary systems methanol, ethanol, propan-1-ol, and butan-1-ol + 1-chlorobutane at the temperatures 288.15 K, 298.15 K, and 308.15 K and atmospheric pressure over the entire composition range. The experimental data are used to calculate excess molar volumes (V^E), deviations in viscosity ($\Delta\eta$), and deviations in refractive index (Δn_D) of the mixtures. These results might be useful for the interpretation of the nature of interactions that occur in the liquid mixtures containing −Cl and −OH groups. A survey of the literature shows previously reported excess molar volume data for isopropyl, isobutyl, and isopentyl alcohols[2,3] and isomeric butanols[4] + 1-chlorobutane, but no other alcohols with 1-chlorobutane are available.

Experimental Section

Materials. The chemicals used were of analytical grade and obtained from Aldrich, Tedia, and Merck. All organic chemicals used in this study were reagent grade. The purity of the chemicals was checked by gas chromatography (GC) analysis, and no impurity peak was detected. All chemicals were used without further purification. The purity of the final sample was also checked by comparing the densities, viscosities, and refractive indices with the literature values[5−8] at T = 298.15 K, as shown in Table 1. There was reasonable agreement between them.

Table 1. Comparison of Measured Densities, Viscosities, and Refractive Indexes of Pure Components with Literature Values at 298.15 K

	ρ/g·cm^{-3}		η/mPa·s		n_D	
compound	this work	lit.	this work	lit.	this work	lit.
methanol	0.786 64	0.786 37[a]	0.543	0.5513[a]	1.327 50	1.326 52[a]
ethanol	0.785 23	0.784 93[a] 0.785 2[b] 0.785 04[c]	1.085	1.0826[a]	1.359 06	1.359 41[a] 1.359 2[c]
propan-1-ol	0.799 60	0.799 6[a]	1.958	1.9430[a]	1.382 94	1.383 7[a]
butan-1-ol	0.805 87	0.805 75[a]	2.598	2.5710[a] 2.593[d]	1.397 20	1.397 41[a]
1-chlorobutane	0.880 98	0.880 95[a]	0.423	0.426[a]	1.399 30	1.399 96[a]

[a] Reference 5. [b] Reference 6. [c] Reference 7. [d] Reference 8.

Procedure. Liquids were dried over activated molecular sieves type 0.4 nm from Aldrich. Samples were prepared by mass in a 50 cm^3 Erlenmeyer flask provided with a joint stopper, using a Precisa 262SMA balance with an accuracy of ±3 × 10^{-5} g. The uncertainty of the mole fraction in composition was believed to be less than ±1 × 10^{-4}. Densities were measured with an Anton Paar DMA-5000 vibrating-tube densimeter with an accuracy of ±5 × 10^{-6} g·cm^{-3} and thermostatically controlled to ±0.001 K. Calibration was performed at atmospheric pressure periodically, in accordance with specifications, using deionized water and dry air. Precautions were taken in order to avoid evaporation losses and air dissolved during the experimental work. Refractive indices (n_D) were measured with a digital Abbe refractometer RX-5000 (ATAGO, Tokyo, Japan) thermostatically controlled to ±0.05 K, with a stated uncertainty of ±0.000 02 units.

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Table 2. Experimental Densities (ρ), Viscosities (η), Refractive Indexes (n_D), and Excess Molar Volumes (V^E) for Binary Mixtures at T = 288.15 K

x_1	ρ/g·cm^{-3}	η/mPa·s	n_D	V^E/cm^3·mol^{-1}	x_1	ρ/g·cm^{-3}	η/mPa·s	n_D	V^E/cm^3·mol^{-1}
Methanol (1) + 1-Chlorobutane (2)									
0.0000	0.8922	0.472	1.4045	0.000	0.6000	0.8546	0.536	1.3759	0.170
0.0500	0.8896	0.463	1.4032	0.091	0.7000	0.8442	0.559	1.3679	0.159
0.1000	0.8872	0.462	1.4015	0.108	0.8000	0.8317	0.581	1.3579	0.132
0.2000	0.8824	0.465	1.3978	0.135	0.9000	0.8159	0.601	1.3457	0.088
0.3000	0.8769	0.478	1.3936	0.156	0.9500	0.8066	0.613	1.3384	0.051
0.4000	0.8706	0.496	1.3885	0.168	1.0000	0.7961	0.627	1.3303	0.000
0.5000	0.8633	0.516	1.3827	0.172					
Ethanol (1) + 1-Chlorobutane (2)									
0.0000	0.8922	0.472	1.4045	0.000	0.6000	0.8464	0.708	1.3851	0.080
0.0500	0.8885	0.475	1.4030	0.098	0.7000	0.8358	0.807	1.3807	0.055
0.1000	0.8853	0.479	1.4016	0.125	0.8000	0.8239	0.932	1.3756	0.022
0.2000	0.8787	0.500	1.3988	0.147	0.9000	0.8100	1.099	1.3697	0.007
0.3000	0.8717	0.529	1.3958	0.145	0.9500	0.8022	1.209	1.3665	0.002
0.4000	0.8641	0.566	1.3925	0.135	1.0000	0.7938	1.317	1.3630	0.000
0.5000	0.8557	0.630	1.3890	0.108					
Propan-1-ol (1) +1-Chlorobutane (2)									
0.0000	0.8922	0.472	1.4045	0.000	0.6000	0.8481	0.965	1.3952	0.030
0.0500	0.8883	0.473	1.4036	0.094	0.7000	0.8392	1.202	1.3934	0.001
0.1000	0.8849	0.495	1.4028	0.117	0.8000	0.8296	1.503	1.3914	−0.017
0.2000	0.8782	0.525	1.4013	0.128	0.9000	0.8192	1.940	1.3892	−0.021
0.3000	0.8712	0.587	1.3998	0.117	0.9500	0.8135	2.200	1.3881	−0.015
0.4000	0.8640	0.672	1.3984	0.090	1.0000	0.8076	2.504	1.3869	0.000
0.5000	0.8563	0.795	1.3968	0.062					
Butan-1-ol (1) + 1-Chlorobutane (2)									
0.0000	0.8922	0.472	1.4045	0.000	0.600	0.8473	1.196	1.4024	0.019
0.0500	0.8880	0.490	1.4041	0.085	0.700	0.8394	1.528	1.4022	−0.011
0.1000	0.8843	0.506	1.4039	0.106	0.800	0.8312	1.979	1.4019	−0.029
0.2000	0.8770	0.569	1.4035	0.119	0.900	0.8226	2.601	1.4016	−0.030
0.3000	0.8697	0.655	1.4031	0.106	0.950	0.8181	2.966	1.4013	−0.017
0.4000	0.8624	0.781	1.4029	0.083	1.000	0.8135	3.394	1.4010	0.000
0.5000	0.8549	0.953	1.4027	0.054					

Table 3. Experimental Densities (ρ), Viscosities (η), Refractive Indexes (n_D), and Excess Molar Volumes (V^E) for Binary Mixtures at T = 298.15 K

x_1	ρ/g·cm^{-3}	η/mPa·s	n_D	V^E/cm^3·mol^{-1}	x_1	ρ/g·cm^{-3}	η/mPa·s	n_D	V^E/cm^3·mol^{-1}
Methanol (1) + 1-Chlorobutane (2)									
0.0000	0.8810	0.423	1.3993	0.000	0.6000	0.8439	0.469	1.3710	0.191
0.0500	0.8784	0.416	1.3980	0.098	0.7000	0.8337	0.489	1.3628	0.175
0.1000	0.8761	0.413	1.3964	0.115	0.8000	0.8214	0.506	1.3529	0.147
0.2000	0.8712	0.412	1.3927	0.150	0.9000	0.8060	0.521	1.3413	0.097
0.3000	0.8656	0.421	1.3885	0.174	0.9500	0.7969	0.532	1.3342	0.054
0.4000	0.8596	0.435	1.3835	0.187	1.0000	0.7866	0.543	1.3275	0.000
0.5000	0.8524	0.450	1.3778	0.192					
Ethanol (1) + 1-Chlorobutane (2)									
0.0000	0.8810	0.423	1.3993	0.000	0.6000	0.8361	0.601	1.3802	0.112
0.0500	0.8773	0.424	1.3978	0.107	0.7000	0.8259	0.680	1.3759	0.082
0.1000	0.8742	0.428	1.3964	0.142	0.8000	0.8144	0.781	1.3711	0.040
0.2000	0.8677	0.442	1.3937	0.175	0.9000	0.8009	0.903	1.3653	0.015
0.3000	0.8608	0.465	1.3907	0.177	0.9500	0.7934	0.994	1.3624	0.006
0.4000	0.8534	0.493	1.3875	0.167	1.0000	0.7852	1.085	1.3591	0.000
0.5000	0.8452	0.543	1.3840	0.143					
Propan-1-ol (1) + 1-Chlorobutane (2)									
0.0000	0.8810	0.423	1.3993	0.000	0.6000	0.8383	0.802	1.3904	0.062
0.0500	0.8772	0.426	1.3984	0.101	0.7000	0.8298	0.977	1.3888	0.025
0.1000	0.8738	0.440	1.3976	0.134	0.8000	0.8207	1.206	1.3870	0.000
0.2000	0.8673	0.461	1.3962	0.157	0.9000	0.8107	1.531	1.3850	−0.011
0.3000	0.8605	0.511	1.3948	0.151	0.9500	0.8053	1.729	1.3840	−0.009
0.4000	0.8535	0.576	1.3934	0.128	1.0000	0.7996	1.958	1.3829	0.000
0.5000	0.8461	0.670	1.3919	0.098					
Butan-1-ol (1) + 1-Chlorobutane (2)									
0.0000	0.8810	0.423	1.3993	0.000	0.6000	0.8380	0.977	1.3979	0.040
0.0500	0.8769	0.437	1.3989	0.088	0.7000	0.8305	1.221	1.3978	0.008
0.1000	0.8733	0.453	1.3987	0.117	0.8000	0.8227	1.563	1.3977	−0.017
0.2000	0.8663	0.499	1.3984	0.137	0.9000	0.8145	2.019	1.3975	−0.023
0.3000	0.8594	0.569	1.3982	0.130	0.9500	0.8103	2.328	1.3974	−0.015
0.4000	0.8524	0.665	1.3981	0.109	1.0000	0.8059	2.598	1.3972	0.000
0.5000	0.8453	0.798	1.3980	0.077					

The kinematic viscosities were determined with commercial Ubbelohde capillary viscometers (Cannon Instrument Co., State College, PA) of (0.36, 0.47, 0.53, and 0.63) mm diameter. The viscometer was kept in a Lauda D20 KP thermostat controlled to ±0.01 K with a proportional−integral−differential regulator. A computer-controlled measuring system (Lauda, Lauda-Königshofen, Germany) with an uncertainty of ±0.01 s was used for flow-time measurement. The range of the flow time for the liquids investigated is varied from 160 s to 750 s. The kinematic viscosity (ν) was then obtained 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

Table 4. Experimental Densities (ρ), Viscosities (η), Refractive Indexes (n_D), and Excess Molar Volumes (V^E) for Binary Mixtures at T = 308.15

x_1	ρ/g·cm^{-3}	η/mPa·s	n_D	V^E/cm^3·mol^{-1}	x_1	ρ/g·cm^{-3}	η/mPa·s	n_D	V^E/cm^3·mol^{-1}
				Methanol (1) + 1-Chlorobutane (2)					
0.0000	0.8697	0.382	1.3941	0.000	0.6000	0.8330	0.416	1.3660	0.220
0.0500	0.8671	0.375	1.3928	0.106	0.7000	0.8231	0.431	1.3579	0.199
0.1000	0.8647	0.374	1.3912	0.135	0.8000	0.8110	0.445	1.3478	0.165
0.2000	0.8599	0.376	1.3877	0.172	0.9000	0.7960	0.457	1.3365	0.108
0.3000	0.8545	0.382	1.3834	0.201	0.9500	0.7872	0.467	1.3298	0.062
0.4000	0.8484	0.393	1.3785	0.217	1.0000	0.7772	0.473	1.3254	0.000
0.5000	0.8413	0.407	1.3728	0.223					
				Ethanol (1) + 1-Chlorobutane (2)					
0.0000	0.8697	0.382	1.3941	0.000	0.6000	0.8257	0.515	1.3750	0.152
0.0500	0.8660	0.384	1.3925	0.120	0.7000	0.8158	0.581	1.3708	0.116
0.1000	0.8628	0.388	1.3912	0.169	0.8000	0.8047	0.670	1.3661	0.064
0.2000	0.8564	0.395	1.3885	0.211	0.9000	0.7917	0.765	1.3609	0.029
0.3000	0.8497	0.410	1.3855	0.221	0.9500	0.7845	0.839	1.3581	0.014
0.4000	0.8424	0.430	1.3823	0.211	1.0000	0.7766	0.902	1.3550	0.000
0.5000	0.8345	0.469	1.3788	0.189					
				Propan-1-ol (1) + 1-Chlorobutane (2)					
0.0000	0.8697	0.382	1.3941	0.000	0.6000	0.8283	0.673	1.3855	0.104
0.0500	0.8660	0.384	1.3931	0.102	0.7000	0.8203	0.804	1.3840	0.060
0.1000	0.8626	0.395	1.3923	0.157	0.8000	0.8115	0.989	1.3824	0.029
0.2000	0.8562	0.409	1.3909	0.192	0.9000	0.8020	1.229	1.3807	0.002
0.3000	0.8497	0.447	1.3895	0.193	0.9500	0.7969	1.375	1.3798	−0.001
0.4000	0.8429	0.498	1.3882	0.173	1.0000	0.7915	1.548	1.3789	0.000
0.5000	0.8358	0.572	1.3869	0.143					
				Butan-1-ol (1) + 1-Chlorobutane (2)					
0.0000	0.8697	0.382	1.3941	0.000	0.6000	0.8286	0.810	1.3932	0.069
0.0500	0.8657	0.388	1.3936	0.097	0.7000	0.8215	1.000	1.3933	0.032
0.1000	0.8623	0.410	1.3934	0.133	0.8000	0.8141	1.251	1.3933	0.004
0.2000	0.8555	0.442	1.3932	0.162	0.9000	0.8063	1.584	1.3933	−0.011
0.3000	0.8489	0.497	1.3931	0.161	0.9500	0.8023	1.784	1.3933	−0.009
0.4000	0.8422	0.570	1.3931	0.142	1.0000	0.7982	2.019	1.3932	0.000
0.5000	0.8354	0.676	1.3932	0.110					

Hagenbach correction. The viscometer constant (k) was provided by the manufacturer. The value θ, which is dependent on the flow time and the size of capillary, was taken from the tables supplied by the manufacturer. Triplicate measurements of flow times were reproducible within ±0.03%.

The densities, viscosities, and refractive indexes of the binary systems methanol, ethanol, propan-1-ol, and butan-1-ol + 1-chlorobutane were measured at the temperatures 288.15 K, 298.15 K, and 308.15 K and atmospheric pressure. A set with the compositions varying from 0.05 to 0.95 mole fraction of alcohol was prepared for each system. An average of at least three measurements was taken for each composition. The uncertainty of the density measurements for the systems investigated was estimated to be less than $\pm 1 \times 10^{-4}$ g·cm^{-3}. The excess molar volumes were calculated from density data with an uncertainty expected to be $\pm 5 \times 10^{-3}$ cm^3·mol^{-1}. The uncertainties of the viscosity and the refractive index measurements were estimated to be $\pm 6 \times 10^{-3}$ mPa·s and $\pm 2 \times 10^{-4}$, respectively.

Results and Discussion

Tables 2−4 list the experimental densities, viscosities, refractive indexes, and excess molar volumes of the four binary mixtures methanol, ethanol, propan-1-ol, and butan-1-ol + 1-chlorobutane at the temperatures 288.15 K, 298.15 K, and 308.15 K. The molar excess volumes (V^E) have been calculated from density data according to the equation

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

where V and ρ are respectively the molar volume and density of the mixture. The x_1, V_1, M_1, x_2, V_2, and M_2 are the mole fraction, molar volume, and molecular weight of pure components 1 and 2, respectively.

In the system studied, excess molar volumes are positive over the whole composition range except for mixtures in the high mole fraction region of propan-1-ol or butan-1-ol. The values of V^E increase systematically from 288.15 K to 308.15 K through the whole range of mole fractions and lead to maxima showing little variation with temperature. The excess molar volume $V^E(x{=}0.5)$ increases in the sequence butan-1-ol < propan-1-ol < ethanol < methanol, and the same sequence is valid for the maximum values of V^E. The values of V^E at 298.15 K vary from −0.008 cm^3·mol^{-1} to 0.192 cm^3·mol^{-1}. Figure 1 shows the excess molar volumes for the four systems at T = 298.15 K. In the literature, the system butan-1-ol + 1-chlorobutane has been measured at 298.15 K,[4] and our results are in good agreement with their measurements. On the other hand,

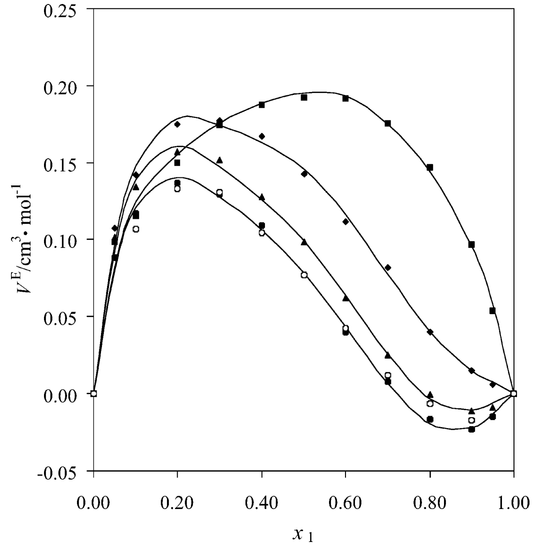

Figure 1. Variation of excess molar volume V^E with mole fraction x_1 of alcohol in 1-chlorobutane at T = 298.15 K: ■, methanol; ◆, ethanol; ▲, propan-1-ol; ●, butan-1-ol; ○, Artigas et al., 1993; —, Redlich−Kister equation.

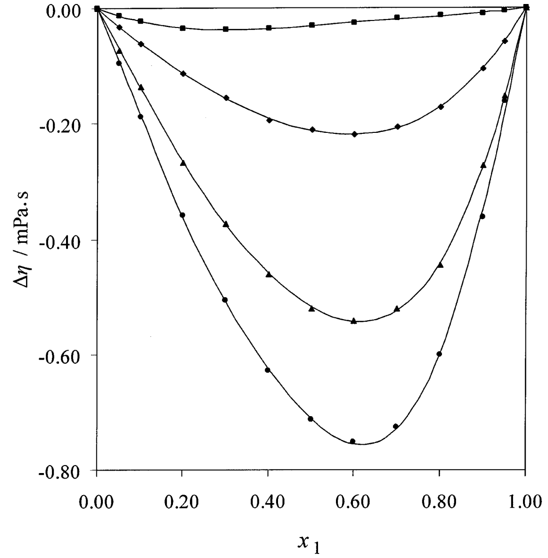

Figure 2. Change of viscosity deviation $\Delta\eta$ with mole fraction x_1 of alcohol in 1-chlorobutane at T = 298.15 K: ■, methanol; ◆, ethanol; ▲, propan-1-ol; ●, butan-1-ol; —, Redlich–Kister equation.

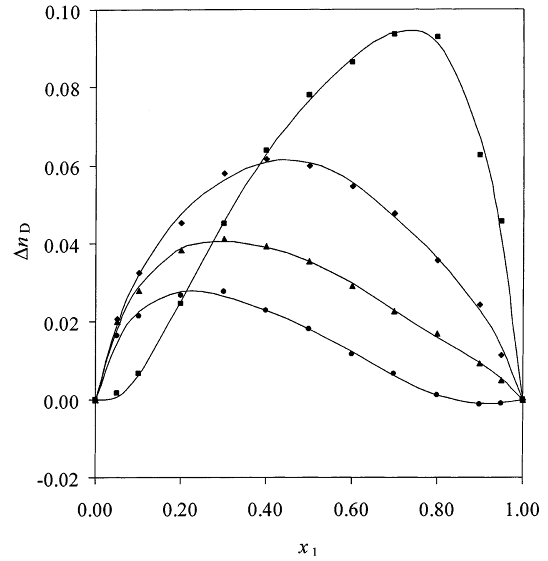

Figure 3. Change of refractive index deviation Δn_D with mole fraction x_1 of alcohol in 1-chlorobutane at T = 298.15 K: ■, methanol; ◆, ethanol; ▲, propan-1-ol; ●, butan-1-ol; —, Redlich–Kister equation.

the presence of the chlorine atom in the aliphatic chain-leads to a decrease in V^E, as can be seen by comparing these results with those for methanol, ethanol, and 1-propanol + alkanes[6,9] and also by a larger decrease of V^E for 1,2-dichloroethane + an isomeric butanol.[10]

The dependence of V^E on both composition and temperature for the mixtures may be explained as a balance between positive contributions (hydrogen bond rupture and dispersive interactions between unlike molecules) and negative contributions (dipole–dipole interactions and geometrical fitting between components). In the present investigation, alcohols containing a hydroxyl (–OH) group are strongly self-associated through hydrogen bonding. The interactions between the chlorine (–Cl) and hydroxyl (–OH) groups lead to the breaking of both the hydrogen bridges of alcohols and the dipole–dipole interaction of 1-chlorobutane, heightening the positive contribution to V^E values.

Table 5. Coefficients of the Redlich–Kister Equation and Standard Deviations (σ) for V^E, $\Delta\eta$, and Δn_D for Binary Mixtures from T = 288.15 K to T = 308.15 K

Y/unit	T/K	10^3a_0	10^3a_1	10^3a_2	10^3a_3	10^3a_4	$10^4\sigma$
		Methanol (1) + 1-Chlorobutane (2)					
V^E/cm^3·mol^{-1}	288.15	7.0092	1.1426	3.9169	−4.7860	9.9547	67
	298.15	7.8158	1.1702	6.3910	−4.9145	9.9241	75
	308.15	9.0574	1.0638	1.9447	−5.3362	1.1479	64
$\Delta\eta$/mPa·s	288.15	−1.3703	1.0909	−4.0928	1.0898	−9.2495	8
	298.15	−1.2401	1.1856	−7.4333	−3.2308		7
	308.15	−9.2859	6.8415	−5.8396	1.7544		7
Δn_D	288.15	2.4811	1.7921	−4.1057	1.1287		17
	298.15	3.0729	2.4235	1.5718	2.7809		24
	308.15	3.9552	3.1068	1.3528	6.3695	4.9783	49
		Ethanol (1) + 1-Chlorobutane (2)					
V^E/cm^3·mol^{-1}	288.15	4.4644	−4.4058	−4.8936	−6.5618	8.5471	57
	298.15	5.8171	−4.5863	−1.2941	−7.2675	8.1131	51
	308.15	7.6070	−5.0792	−6.6098	−7.7021	8.9371	46
$\Delta\eta$/mPa·s	288.15	−1.0621	−3.6501	−1.3051			33
	298.15	−8.5243	−2.8095	−7.3188	−4.7860	−6.2537	15
	308.15	−6.9996	−2.1369	1.1476			32
Δn_D	288.15	2.0476	−6.9744	7.5244			12
	298.15	2.4249	−5.3508	−6.8167	−1.9340	1.6782	16
	308.15	3.0296	1.3391	−5.0645	−1.3112	2.7295	18
		Propan-1-ol (1) + 1-Chlorobutane (2)					
V^E/cm^3·mol^{-1}	288.15	2.5144	−5.5728	−2.2620	−6.8484	8.0480	53
	298.15	3.9632	−6.2041	−2.9081	−6.5423	8.1541	44
	308.15	5.7172	−6.6902	1.0282	−6.1357	6.1222	25
$\Delta\eta$/mPa·s	288.15	−2.7685	−1.1879	−4.4862	−9.4238		43
	298.15	−2.0687	−8.8358	−5.3864	−1.2294	2.5498	48
	308.15	−1.5758	−6.1216	−2.3947	−8.8053		21
Δn_D	288.15	1.0689	−9.9477	2.9105	−9.9943	8.9241	6
	298.15	1.4164	−9.3526	4.2921	−6.8981	1.1246	9
	308.15	1.9712	−1.0205	3.4660	−1.0460	1.5932	15
		Butan-1-ol (1) + 1-Chlorobutane (2)					
V^E/cm^3·mol^{-1}	288.15	2.1798	−5.8729	−1.1024	−6.0007	7.7134	44
	298.15	3.1287	−6.2758	−6.2733	−5.7357	6.7671	40
	308.15	4.4191	−6.6529	−3.9127	−5.5485	7.0206	43
$\Delta\eta$/mPa·s	288.15	−2.7682	−1.2214	−4.5148		.	44
	298.15	−2.0736	−8.6416	−4.2453	−1.2476	1.1614	26
	308.15	−1.5758	−6.1216	−2.3947	−8.8053		21
Δn_D	288.15	4.8280	−9.7806	4.1715	−6.4250		8
	298.15	7.3080	−1.0656	1.3970	−9.2049	9.2274	10
	308.15	9.4493	−1.1868	2.1783	−1.4760	1.5721	14

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 viscosity of the mixture and the viscosities of pure components 1 and 2, respectively. There is a clear trend in $\Delta\eta$ values for all of the mixtures. The $\Delta\eta$ values, which increase as temperature increases, are negative. The values of $\Delta\eta$ show the order methanol > ethanol > propan-1-ol > butan-1-ol. Figure 2 plots the results of $\Delta\eta$ for the four mixtures at 298.15 K. The minima of the $\Delta\eta$ values at 298.15 K vary from −0.755 mPa·s to −0.038 mPa·s.

The deviations in refractive index from the mole fraction average (Δn_D) are given by

$$\Delta n_D = n_D - (x_1 n_{D1} + x_2 n_{D2}) \tag{4}$$

where n_D, n_{D1}, and n_{D2} are the refractive index of the mixture and the refractive indexes of pure components 1 and 2, respectively. The Δn_D values, which increase as the temperature increases, are positive for all of the systems over the entire range of composition except that small negative values were observed in the high mole fraction region of butan-1-ol. The values of $\Delta n_D(x{=}0.5)$ follow the order methanol > ethanol > propan-1-ol > butan-1-ol, and the same sequence is valid for the maximum values of Δn_D.

Table 6. Coefficients of McAllister's Three-Body Interaction Model and Standard Deviations (σ) for the Kinematic Viscosities (ν) of Binary Mixtures

T/K	$\nu_{12}/10^{-6}$ m^2·s^{-1}	$\nu_{21}/10^{-6}$ m^2·s^{-1}	$10^5\sigma/10^{-6}$ m^2·s^{-1}
	Methanol (1) + 1-Chlorobutane (2)		
288.15	0.7051	0.4864	8
298.15	0.8263	0.4849	10
308.15	0.9176	0.4944	13
	Ethanol (1) + 1-Chlorobutane (2)		
288.15	0.1467	0.4277	36
298.15	0.7361	0.5014	27
308.15	0.6404	0.4471	22
	Propan-1-ol (1) + 1-Chlorobutane (2)		
288.15	0.1107	0.5115	78
298.15	0.8920	0.4819	60
308.15	0.7807	0.4174	46
	Butanol (1) + 1-Chlorobutane (2)		
288.15	0.1612	0.6475	109
298.15	0.1300	0.5766	83
308.15	0.1061	0.5190	63

Figure 3 shows the results of Δn_D for the four mixtures at 298.15 K. The maxima of the Δn_D values at 298.15 K vary from 0.0278 to 0.0939.

The mixing functions V^E, $\Delta\eta$, and Δn_D were represented mathematically by the following type of Redlich–Kister equation[11] for correlating the experimental data:

$$Y = x_1(1 - x_1)\sum_{i=0}^{p} a_i(2x_1 - 1)^i \tag{5}$$

where Y refers to V^E/cm^3·mol^{-1}, $\Delta\eta$/mPa·s, or Δn_D, x_1 is the mole fraction of the alcohol, and a_i are the coefficients. The values of the 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 5. The standard deviation is defined by

$$\sigma = [\sum_{i=1}^{m}(Y_i^{\,\exp} - Y_i^{\,\text{calc}})^2/(m - p)]^{1/2} \tag{6}$$

where m is the number of experimental points and p is the number of adjustable parameters. The σ values lie between 0.0025 cm^3·mol^{-1} and 0.0075 cm^3·mol^{-1}, between 0.0007 mPa·s and 0.0040 mPa·s, and between 0.0006 and 0.0049 for V^E, $\Delta\eta$, and Δn_D, respectively. The largest σ value corresponds to the methanol system at 298.15 K, the ethanol system at 308.15 K, and the methanol system at 308.15 K for V^E, $\Delta\eta$, and Δn_D, respectively.

McAllister's multibody interaction model[12] is widely used for correlating the kinematic viscosity of liquid mixtures with mole fraction. The three-body model is defined as

$$\ln \nu = x_1^{\,3} \ln \nu_1 + 3x_1^{\,2}x_2 \ln \nu_{12} + 3x_1x_2^{\,2} \ln \nu_{21} + x_2^{\,3} \ln \nu_2 - \ln(x_1 + x_2M_2/M_1) + 3x_1^{\,2}x_2 \ln[(2 + M_2/M_1)/3] + 3x_1x_2^{\,2} \ln[(1 + 2M_2/M_1)/3] + x_2^{\,3} \ln(M_2/M_1) \tag{7}$$

where ν, ν_1, and ν_2 are the kinematic viscosity of the mixture and the viscosities of pure components 1 and 2, respectively. The ν_{12} and ν_{21} are the model parameters. Table 6 records the calculated results with the standard deviation defined as in eq 6. It is shown that the McAllister's three-body interaction model is adequate for those four systems. The $\sigma/10^{-6}$ m^2·s^{-1} values lie between 8×10^{-5} and 1.09×10^{-3}, and the largest σ value corresponds to the butan-1-ol system at 288.15 K.

Literature Cited

(1) Fernández-Piérola, I.; Horta, A. Cosolvents of PMMA. *Makromol. Chem.* **1981**, *182*, 1705–1714.

(2) Mouli, J. C.; Naidu, P. R.; Choudary, N. V. Excess Volumes, Ultrasonic Sound Velocities, and Isentropic Compressibilities of 1-Chlorobutane with Isopropyl, Isobutyl, and Isopentyl Alcohols. *J. Chem. Eng. Data* **1986**, *31*, 493–496.

(3) Ku, H. C.; Tu, C. H. Density and Viscosity of Binary Mixtures of 2-Propanol, 1-Chlorobutane and Acetonitrile. *J. Chem. Eng. Data* **1998**, *43*, 465–468.

(4) Artigas, H.; Santafé, J.; López, M. C.; Royo, F. M.; Urieta, J. S. Excess Volumes of (an Alkanol + a Haloalkane) at the Temperatures 298.15 K and 313.15 K. *J. Chem. Thermodyn.* **1993**, *25*, 1403–1407.

(5) Riddick, A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents, Physical Properties and Method of Purification*, 4th ed.; Wiley-Interscience: New York, 1986.

(6) Orge, B.; Iglesias, M.; Rodriguez, A.; Canosa, J. M.; Tojo, J. Mixing Properties of (Methanol, Ethanol, or 1-Propanol) with (*n*-Pentane, *n*-Hexane, *n*-Heptane and *n*-Octane) at 298.15 K. *Fluid Phase Equilib.* **1997**, *133*, 213–227.

(7) Gabaldón, C.; Martínez-Soria, V.; Marzal, P.; Montón, J. B. Isobaric Vapor-Liquid Equilibria for the Binary System 3-Methylpentane + Ethanol and for the Ternary System 2-Methyl-2-propanol + Ethanol + 3-Methylpentane at 101.3 kPa. *J. Chem. Eng. Data* **2000**, *45*, 882–886.

(8) Shan, Z.; Asfour, A.-F. A. Viscosities and Densities of Nine Binary 1-Alkanol Systems at 293.15 K and 298.15 K. *J. Chem. Eng. Data* **1999**, *44*, 118–123.

(9) Orge, B.; Rodríguez, A.; Canosa, J. M.; Marino, G.; Iglesias, M.; Tojo, J. Variation of Densities, Refractive Indices, and Speed of Sound with Temperature of Methanol or Ethanol with Hexane, Heptane, and Octane at 298.15 K. *Fluid Phase Equilib.* **1999**, *44*, 1041–1047.

(10) Rodríguez, V.; Artigas, H.; Lafuente, C.; Royo, F. M.; Urieta, J. S. Excess Volumes of (1,2-Dichloroethane or 1,2-Dibromoethane + Butan-1-ol or Butan-2-ol or 2-Methylpropan-1-ol or 2-Methylpropan-2-ol) at the Temperatures 298.15 K and 313.15 K. *J. Chem. Thermodyn.* **1994**, *26*, 1173–1178.

(11) Redlich, O.; Kister, A. T. Thermodynamics of Nonelectrolyte Solutions. Algebraic Representation of Thermodynamic Properties and the Classification of Solutions. *Ind. Eng. Chem.* **1948**, *40*, 345–348.

(12) McAllister, R. A. The Viscosity of Liquid Mixtures. *AIChE J.* **1960**, *6*, 427–431.

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