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Density and Viscosity of Binary Mixtures of Propan-2-ol, 1-Chlorobutane, and Acetonitrile

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Densities and viscosities were measured for the three binary mixtures formed by propan-2-ol, 1-chlorobutane, and acetonitrile at (293.15, 303.15, 313.15, and 323.15) K. Excess volumes and viscosity deviations from the mole fraction average were derived. The kinematic viscosities were compared with McAllister's model.

Introduction

The binary systems in this work have interesting characteristics with respect to the solubility of polymers. At 25 °C the pure liquids propan-2-ol, 1-chlorobutane, and acetonitrile are poor solvents of poly(methyl methacrylate), while the binary mixtures of these liquids act as very good solvents for the polymer (Fernández-Piérola and Horta, 1981). To adequately interpret the thermodynamic behavior of polymers in mixed solvents, it is of interest to know the composition and temperature dependence of volumetric and transport properties of the binary mixtures.

In the present paper we report density and viscosity for the binary systems propan-2-ol + 1-chlorobutane, propan-2-ol + acetonitrile, and 1-chlorobutane + acetonitrile at atmospheric pressure (nominal value 0.1 MPa) over the entire composition range at (293.15, 303.15, 313.15, and 323.15) K. These results are used to calculate excess volumes and deviations in viscosity.

Experimental Section

All organic chemicals used in this study were reagent grade. Propan-2-ol (99.9 mass %), 1-chlorobutane (99.5 mass %), and acetonitrile (99.9 mass %) were supplied by Fisher Scientific (United States). The purity of the chemicals was checked by gas chromatography (GC) analysis, and no impurity peak was detected. All chemicals were dried with 3-Å molecular sieves. In all cases, water contents in the liquids used were not greater than 0.05 vol % on the GC analyses.

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. Densities, ρ, of pure components and mixtures were measured by using a DMA-58 vibrating-tube densimeter (Anton-Paar/Austria), calibrated with deionized doubly distilled water and dry air. The temperature in the measuring cell was regulated to ±0.01 K. The uncertainty of the density measurements was $\pm 1 \times 10^{-5}$ g/cm^3.

Table 1. Comparison of Measured Densities and Viscosities of Pure Components with Literature Values

		ρ/(g·cm^{-3})		η/(mPa·s)	
components	T/K	this work	lit.	this work	lit.
propan-2-ol	293.15	0.7853	0.7851^a	2.4143	2.29^a
	303.15	0.7768	0.7767^a	1.7913	1.778^a
			0.7768^b		1.78^b
			0.7770^c		1.767^c
					1.791^d
					1.783^e
	313.15	0.7680	0.7678^a	1.3581	1.331^a
			0.7680^b		1.35^b
			0.7683^c		1.340^c
					1.358^f
	323.15	0.7589	0.7591^a	1.0462	1.032^a
			0.7593^b		1.04^b
			0.7593^e		1.033^e
					1.045^f
1-chlorobutane	293.15	0.8865	0.8858^g	0.4552	0.461^g
	303.15	0.8755	0.8747^g	0.4107	0.416^g
			0.87543^h		
			0.87549^i		
	313.15	0.8640	0.8634^g	0.3714	0.378^g
	323.15	0.8525	0.8518^g	0.3368	0.345^g
acetonitrile	293.15	0.7820	0.7821^a	0.3645	0.3579^a
			0.7816^j		0.408^j
			0.7822^k		
	303.15	0.7712	0.7710^a	0.3307	0.3254^a
			0.7715^j		0.371^j
			0.77125^k		0.325^k
	313.15	0.7603	0.7602^a	0.3005	0.2974^a
			0.7601^j		0.339^j
	323.15	0.7492	0.7491^a	0.2746	0.2729^a
			0.7495^j		0.309^j

[a] Paez and Contreras, 1989. [b] Lee and Lin, 1995. [c] TRC, 1994. [d] Sollman and Marschall, 1990. [e] Pikkarainen, 1988. [f] Vargaftik, 1975. [g] Ma, 1982. [h] Mouli et al., 1986. [i] Timmermans, 1950. [j] Garcia and Ortega, 1988. [k] Riddick and Bunger, 1970.

The kinematic viscosities of pure components and liquid mixtures are determined with a calibrated Ubbelohde capillary viscometers supplied by SCHOTT-GERÄTE/Germany. The kinematic viscosity (ν) is 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 viscometer was kept in a D20 KP (LAUDA/Germany) thermostat controlled to ±0.01 K with a PID regulator. The accuracy of the flow-time measurement is ±0.01 s. The evaporation losses are negligible and can be controlled by the steps of flow times, which in less favorable cases do not exceed 0.04 s. The densities and viscosities of binary mixtures were measured at four temperatures: (293.15, 303.15, 313.15, and 323.15)

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Table 2. Experimental Densities (ρ), Kinematic Viscosities (ν), and Excess Volumes (V^E) for Propan-2-ol (1) + 1-Chlorobutane (2)

x_1	ρ/(g·cm^{-3})	ν/(10^{-6} m^2·s^{-1})	V^E/(cm^3·mol^{-1})	ρ/(g·cm^{-3})	ν/(10^{-6} m^2·s^{-1})	V^E/(cm^3·mol^{-1})
	293.15 K			303.15 K		
0.0000	0.8865	0.5135	0.0000	0.8755	0.4691	0.0000
0.0499	0.8815	0.5180	0.1430	0.8706	0.4720	0.1558
0.1000	0.8771	0.5280	0.2084	0.8659	0.4814	0.2631
0.1500	0.8727	0.5443	0.2577	0.8615	0.4913	0.3189
0.2000	0.8683	0.5623	0.2853	0.8572	0.5057	0.3537
0.2500	0.8640	0.5860	0.3038	0.8529	0.5250	0.3784
0.3000	0.8595	0.6133	0.3149	0.8486	0.5456	0.3971
0.3500	0.8550	0.6477	0.3183	0.8441	0.5726	0.4116
0.4000	0.8505	0.6993	0.3081	0.8396	0.6033	0.4076
0.4499	0.8459	0.7548	0.2949	0.8351	0.6377	0.4007
0.5000	0.8412	0.8074	0.2792	0.8305	0.6804	0.3838
0.5500	0.8364	0.8779	0.2539	0.8257	0.7340	0.3639
0.6000	0.8314	0.9750	0.2269	0.8207	0.8120	0.3433
0.6500	0.8263	1.0564	0.2019	0.8159	0.8963	0.3085
0.6999	0.8211	1.1869	0.1706	0.8110	0.9748	0.2664
0.7500	0.8156	1.3336	0.1464	0.8057	1.0871	0.2290
0.8000	0.8100	1.5246	0.1174	0.8004	1.2229	0.1863
0.8500	0.8042	1.7695	0.0825	0.7948	1.3973	0.1434
0.9000	0.7981	2.0859	0.0588	0.7891	1.6183	0.0962
0.9500	0.7918	2.5054	0.0359	0.7831	1.9147	0.0539
1.0000	0.7853	3.0745	0.0000	0.7768	2.3061	0.0000
	313.15 K			323.15 K		
0.0000	0.8640	0.4299	0.0000	0.8525	0.3950	0.0000
0.0499	0.8590	0.4303	0.1746	0.8476	0.3965	0.1778
0.1000	0.8544	0.4368	0.2885	0.8429	0.3995	0.3239
0.1500	0.8500	0.4464	0.3688	0.8384	0.4056	0.4224
0.2000	0.8457	0.4586	0.4553	0.8341	0.4160	0.4847
0.2500	0.8414	0.4735	0.4781	0.8299	0.4277	0.5302
0.3000	0.8371	0.4909	0.4981	0.8255	0.4398	0.5658
0.3501	0.8327	0.5259	0.4944	0.8212	0.4560	0.5899
0.4000	0.8283	0.5376	0.4966	0.8168	0.4789	0.6046
0.4499	0.8238	0.5620	0.4903	0.8123	0.5016	0.6093
0.5000	0.8193	0.5957	0.4718	0.8079	0.5267	0.6016
0.5500	0.8147	0.6354	0.4505	0.8035	0.5562	0.5843
0.6000	0.8098	0.6961	0.4249	0.7986	0.5954	0.5552
0.6500	0.8051	0.7611	0.3894	0.7940	0.6329	0.5104
0.6999	0.8003	0.8180	0.3466	0.7895	0.7026	0.4510
0.7500	0.7952	0.9039	0.2998	0.7847	0.7679	0.3883
0.8000	0.7902	1.0026	0.2383	0.7798	0.8330	0.3267
0.8500	0.7850	1.1364	0.1811	0.7747	0.9273	0.2586
0.9000	0.7794	1.2898	0.1287	0.7696	1.0379	0.1798
0.9500	0.7738	1.4904	0.0631	0.7643	1.1835	0.0929
1.0000	0.7680	1.7684	0.0000	0.7589	1.3785	0.0000

K. An average of at least two measurements was taken into account, and these were reproducible within ±0.1 kg/m^3 and ±0.03% for density and kinematic viscosity, respectively.

Results and Discussion

The observed densities and viscosities for the pure components at (293.15, 303.15, 313.15, and 323.15) K are compared with published values in Table 1. Tables 2−4 list the experimental densities, viscosities, and excess volumes of three binary mixtures propan-2-ol + 1-chlorobutane, propan-2-ol + acetonitrile, and 1-chlorobutane + acetonitrile at various mole fractions and at the four temperatures. The molar excess volumes, V^E, have been calculated from density data according to the equations

$$V^E = V - (x_1V_1 + x_2V_2) \tag{2}$$

$$\text{with} \quad V = (x_1M_1 + x_2M_2)/\rho \tag{3}$$

where V and ρ are the molar volume and density of the mixture. 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.

Table 3. Experimental Densities (ρ), Kinematic Viscosities (ν), and Excess Volumes (V^E) for Propan-2-ol (1) + Acetonitrile (2)

x_1	ρ/(g·cm^{-3})	ν/(10^{-6} m^2·s^{-1})	V^E/(cm^3·mol^{-1})	ρ/(g·cm^{-3})	ν/(10^{-6} m^2·s^{-1})	V^E/(cm^3·mol^{-1})
	293.15 K			303.15 K		
0.0000	0.7820	0.4661	0.0000	0.7712	0.4288	0.0000
0.0500	0.7814	0.4747	0.0601	0.7707	0.4342	0.0648
0.1000	0.7811	0.4888	0.0956	0.7705	0.4453	0.1075
0.1500	0.7809	0.5070	0.1261	0.7704	0.4598	0.1441
0.2000	0.7809	0.5342	0.1491	0.7704	0.4790	0.1712
0.2500	0.7809	0.5620	0.1663	0.7705	0.5047	0.1936
0.3000	0.7810	0.5972	0.1750	0.7707	0.5319	0.2094
0.3501	0.7812	0.6389	0.1795	0.7709	0.5621	0.2240
0.4000	0.7814	0.6905	0.1794	0.7711	0.6053	0.2304
0.4500	0.7816	0.7404	0.1778	0.7715	0.6438	0.2319
0.5000	0.7819	0.8063	0.1722	0.7718	0.6940	0.2265
0.5500	0.7822	0.8828	0.1641	0.7723	0.7528	0.2181
0.5999	0.7825	0.9723	0.1534	0.7727	0.8207	0.2075
0.6499	0.7828	1.0795	0.1383	0.7732	0.9019	0.1904
0.7000	0.7832	1.2044	0.1195	0.7737	0.9962	0.1699
0.7499	0.7836	1.3629	0.0955	0.7742	1.1154	0.1432
0.7999	0.7840	1.5529	0.0793	0.7747	1.2568	0.1196
0.8499	0.7843	1.7901	0.0598	0.7752	1.4289	0.0907
0.8999	0.7847	2.0918	0.0355	0.7758	1.6434	0.0581
0.9500	0.7851	2.5086	0.0082	0.7764	1.9410	0.0171
1.0000	0.7853	3.0745	0.0000	0.7768	2.3061	0.0000
	313.15 K			323.15 K		
0.0000	0.7603	0.3952	0.0000	0.7492	0.3666	0.0000
0.0500	0.7599	0.4002	0.0665	0.7489	0.3698	0.0707
0.1000	0.7598	0.4091	0.1149	0.7489	0.3762	0.1263
0.1500	0.7598	0.4232	0.1569	0.7490	0.3867	0.1743
0.2000	0.7599	0.4364	0.1872	0.7492	0.4018	0.2090
0.2500	0.7601	0.4552	0.2140	0.7494	0.4144	0.2375
0.3000	0.7603	0.4771	0.2361	0.7497	0.4324	0.2643
0.3501	0.7606	0.5037	0.2543	0.7501	0.4531	0.2859
0.4000	0.7609	0.5341	0.2665	0.7505	0.4803	0.3019
0.4500	0.7613	0.5685	0.2709	0.7509	0.5062	0.3123
0.5000	0.7617	0.6060	0.2714	0.7514	0.5376	0.3168
0.5500	0.7622	0.6514	0.2652	0.7520	0.5748	0.3105
0.5999	0.7628	0.7035	0.2537	0.7526	0.6224	0.2995
0.6499	0.7633	0.7645	0.2370	0.7533	0.6705	0.2801
0.7000	0.7639	0.8361	0.2139	0.7540	0.7208	0.2537
0.7499	0.7646	0.9246	0.1850	0.7548	0.7858	0.2170
0.7999	0.7652	1.0259	0.1570	0.7556	0.8556	0.1857
0.8499	0.7659	1.1497	0.1221	0.7564	0.9460	0.1462
0.8999	0.7667	1.3017	0.0763	0.7572	1.0562	0.0980
0.9500	0.7675	1.5096	0.0231	0.7583	1.2080	0.0287
1.0000	0.7680	1.7684	0.0000	0.7589	1.3785	0.0000

In the system studied, excess volumes are positive, which increase systematically from 293.15 K to 323.15 K through the whole range of mole fractions and lead to maxima showing little variation with temperature. Figure 1 shows the results for the three mixtures at 313.15 K with a maximum located near $x_1 \approx 0.5$. The order in the values of V^E for the three binary mixtures is propan-2-ol + 1-chlorobutane > propan-2-ol + acetonitrile > 1-chlorobutane + acetonitrile. The positive V^E values have been explained in terms of complex formation (Sandhu et al., 1986) or dispersion type interactions between mixing components (Hirschfelder et al., 1954). Palmer and Smith (1984), on the basis of their investigation for 1-propanol + dichloromethane mixtures at 25 °C, attributed positive V^E to a breaking of hydrogen bridges, caused by dichloromethane. In the literature, Paez and Contreras (1989) presented the values of density for the mixture of propan-2-ol with acetonitrile at four temperatures: (20, 30, 40, and 50) °C. Mouli et al. (1986) investigated the mixture of 1-chlorobutane with propan-2-ol and gave the values of V^E at two temperatures: 303.15 and 313.15 K. Comparison of our V^E values with theirs at 313.15 K as shown in Figure 1 suggests reasonably good agreement for the two systems. The shapes of the curves also remain identical to our data.

Table 4. Experimental Densities (ρ), Kinematic Viscosities (ν), and Excess Volumes (V^E) for 1-Chlorobutane (1) + Acetonitrile (2)

x_1	ρ/(g·cm^{-3})	ν/(10^{-6} m^2·s^{-1})	V^E/(cm^3·mol^{-1})	ρ/(g·cm^{-3})	ν/(10^{-6} m^2·s^{-1})	V^E/(cm^3·mol^{-1})
	293.15 K			303.15 K		
0.0000	0.7820	0.4661	0.0000	0.7713	0.4288	0.0000
0.0501	0.7915	0.4649	0.0282	0.7806	0.4268	0.0369
0.1000	0.8002	0.4651	0.0542	0.7892	0.4261	0.0635
0.1500	0.8081	0.4668	0.0753	0.7971	0.4262	0.0894
0.2000	0.8155	0.4692	0.0939	0.8045	0.4275	0.1092
0.2500	0.8223	0.4716	0.1096	0.8112	0.4294	0.1280
0.3000	0.8286	0.4743	0.1204	0.8174	0.4316	0.1421
0.3500	0.8345	0.4768	0.1297	0.8234	0.4339	0.1533
0.4000	0.8400	0.4794	0.1365	0.8289	0.4362	0.1604
0.4499	0.8452	0.4818	0.1401	0.8340	0.4386	0.1624
0.5000	0.8501	0.4846	0.1379	0.8389	0.4412	0.1596
0.5500	0.8546	0.4872	0.1347	0.8435	0.4440	0.1547
0.6000	0.8590	0.4901	0.1282	0.8478	0.4470	0.1465
0.6499	0.8631	0.4926	0.1209	0.8519	0.4494	0.1386
0.6999	0.8669	0.4954	0.1107	0.8558	0.4517	0.1255
0.7498	0.8706	0.4980	0.0978	0.8595	0.4543	0.1096
0.8000	0.8741	0.5007	0.0814	0.8630	0.4567	0.0913
0.8499	0.8774	0.5037	0.0655	0.8663	0.4583	0.0721
0.8999	0.8806	0.5069	0.0437	0.8695	0.4620	0.0511
0.9499	0.8836	0.5102	0.0253	0.8725	0.4655	0.0288
1.0000	0.8865	0.5135	0.0000	0.8755	0.4691	0.0000
	313.15 K			323.15 K		
0.0000	0.7603	0.3952	0.0000	0.7492	0.3666	0.0000
0.0501	0.7695	0.3926	0.0452	0.7582	0.3629	0.0555
0.1000	0.7779	0.3913	0.0824	0.7665	0.3615	0.1017
0.1500	0.7857	0.3913	0.1121	0.7743	0.3613	0.1318
0.2000	0.7931	0.3920	0.1337	0.7816	0.3615	0.1506
0.2500	0.7998	0.3934	0.1522	0.7883	0.3620	0.1706
0.3000	0.8060	0.3950	0.1669	0.7945	0.3628	0.1843
0.3500	0.8119	0.3969	0.1753	0.8004	0.3640	0.1944
0.4000	0.8174	0.3991	0.1786	0.8059	0.3658	0.1996
0.4499	0.8225	0.4013	0.1796	0.8110	0.3677	0.2026
0.5000	0.8274	0.4036	0.1757	0.8159	0.3695	0.1998
0.5500	0.8320	0.4057	0.1688	0.8205	0.3716	0.1910
0.6000	0.8363	0.4080	0.1595	0.8248	0.3736	0.1798
0.6499	0.8404	0.4104	0.1496	0.8289	0.3758	0.1680
0.6999	0.8443	0.4131	0.1345	0.8328	0.3781	0.1497
0.7498	0.8480	0.4157	0.1176	0.8365	0.3803	0.1273
0.8000	0.8516	0.4188	0.0949	0.8401	0.3826	0.1034
0.8499	0.8549	0.4215	0.0748	0.8435	0.3851	0.0810
0.8999	0.8581	0.4242	0.0493	0.8467	0.3881	0.0567
0.9499	0.8611	0.4269	0.0225	0.8497	0.3919	0.0311
1.0000	0.8640	0.4299	0.0000	0.8525	0.3950	0.0000

The deviation of the viscosity from the mole fraction average is given by

$$\Delta\eta = \eta - (x_1\eta_1 + x_2\eta_2) \tag{4}$$

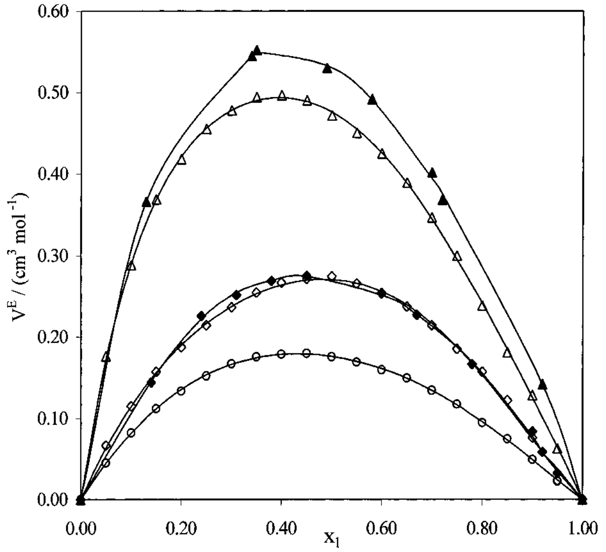

Figure 1. Excess volume variation with mole fraction at 313.15 K: propan-2-ol (1) + 1-chlorobutane (2), (△) present work, (▲) Mouli et al., 1986; propan-2-ol (1) + acetonitrile (2), (◇) present work, (◆) Paez and Contreras, 1989; 1-chlorobutane (1) + acetonitrile (2), (○) present work.

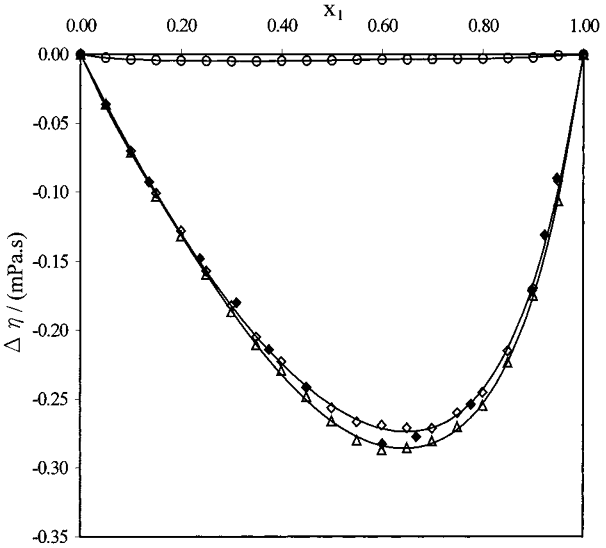

Figure 2. Viscosity deviation variation with mole fraction at 323.15 K: propan-2-ol (1) + 1-chlorobutane (2), (△) present work; propan-2-ol (1) + acetonitrile (2), (◇) present work, (◆) Paez and Contreras, 1989; 1-chlorobutane (1) + acetonitrile (2), (○) present work.

Table 5. Coefficients of McAllister's Models and Standard Deviations for Kinematic Viscosities

	three-body model			four-body model			
T/K	ν_{12}	ν_{21}	σ/(10^{-6}m^2·s^{-1})	ν_{1112}	ν_{1111}	ν_{2221}	σ/(10^{-6}m^2·s^{-1})
			Propan-2-ol + 1-Chlorobutane				
293.15	0.824 29	0.580 78	0.016 98	1.049 57	0.802 70	0.516 53	0.004 41
303.15	0.695 46	0.514 16	0.011 34	0.891 79	0.650 22	0.477 98	0.006 23
313.15	0.605 06	0.468 55	0.009 13	0.749 74	0.581 74	0.435 03	0.005 86
323.15	0.532 86	0.418 13	0.006 93	0.646 60	0.507 02	0.394 82	0.004 75
			Propan-2-ol + Acetonitrile				
293.15	0.857 15	0.572 20	0.019 78	1.074 83	0.822 88	0.494 97	0.004 39
303.15	0.743 67	0.504 08	0.010 85	0.917 91	0.693 54	0.449 88	0.002 81
313.15	0.639 79	0.458 78	0.009 00	0.771 28	0.608 08	0.411 72	0.002 13
323.15	0.581 24	0.412 24	0.008 42	0.673 68	0.550 44	0.373 63	0.003 47
			1-Chlorobutane + Acetonitrile				
293.15	0.502 85	0.496 56	0.000 69	0.499 25	0.502 96	0.479 51	0.000 39
303.15	0.459 39	0.447 90	0.000 92	0.453 62	0.460 99	0.432 31	0.000 29
313.15	0.421 12	0.407 29	0.000 57	0.418 06	0.416 87	0.396 59	0.000 32
323.15	0.382 92	0.373 34	0.000 70	0.379 76	0.383 04	0.363 28	0.000 16

where η, η_1, and η_2 are the absolute viscosities of the mixture and the viscosities of pure components 1 and 2, respectively. Figure 2 shows the results of $\Delta\eta$ for the three mixtures at 323.15 K with a maximum located near $x_1 \approx 0.6$. Viscosities of propan-2-ol + acetonitrile have been measured at four temperatures: (20, 30, 40, and 50) °C (Paez and Contreras, 1989). The calculated $\Delta\eta$ values at 50 °C of their study are also plotted for comparison and agree with the present values. McAllister's multibody interaction model (McAllister, 1960) is widely used for correlating the kinematic viscosity of liquid mixtures with mole fraction. The three-body model is defined as

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

and the four-body model is given by

$$\ln \nu = x_1^4 \ln \nu_1 + 4x_1^3x_2 \ln \nu_{1112} + 6x_1^2x_2^2 \ln \nu_{1122} + 4x_1x_2^3 \ln \nu_{2221} + x_2^4 \ln \nu_2 - \ln(x_1 + x_2M_2/M_1) + 4x_1^3x_2 \ln[(3 + M_2/M_1)/4] + 6x_1^2x_2^2 \ln[(1 + M_2/M_1)/2] + 4x_1x_2^3 \ln[(1 + 3M_2/M_1)/4] + x_2^4 \ln(M_2/M_1) \quad (6)$$

where ν_{12}, ν_{21}, ν_{1112}, ν_{1122}, and ν_{2221} are the model parameters. Table 5 records the calculated results. It is shown that McAllister's model is adequate for those three systems.

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