Densities and Viscosities for Binary Mixtures of Anisole with 2-Butanol, 2-Methyl-1-propanol, and 2-Methyl-2-propanol

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Densities and viscosities were measured for anisole with 2-butanol, 2-methyl-1-propanol, and 2-methyl-2-propanol binary liquid mixtures with a vibrating-tube densimeter and Cannon-Fenske routine viscometers over the temperature range between 303.15 and 323.15 K and at atmospheric pressure. Excess molar volumes and viscosity deviations were calculated at various temperatures. Both excess molar volumes and the viscosity deviations are negative for all investigated systems. The isothermal excess molar volumes and viscosity deviations were fitted to a Redlich−Kister type equation, and the kinematic viscosity data were correlated with the McAllister equation.

Introduction

A series of density and viscosity data were measured for highly polar organic mixtures in our laboratory. The results of three binary systems of anisole with 2-butanol, 2-methyl-1-propanol, and 2-methyl-2-propanol are reported in this paper. From a theoretical point of view those mixtures are useful for studying the interactions between molecules of ethers and alcohols. The aim of the present study is to investigate the effects of molecular structures of butanol isomers on the excess molar volumes and the viscosity deviations. No density and viscosity data are available for these mixtures in the literature, but some investigators reported the results of mixtures of butanol isomers with compounds other than anisole (Nikam et al., 1995, 1998; Aucejo et al., 1996a,b; Alonso and Corrales, 1990; Bhardwaj et al., 1996).

Experimental Section

Anisole (99.5 mol %), 2-butanol (99%), 2-methyl-1-propanol (99%), and 2-methyl-2-propanol (99%), were purchased from R.D.H. Products. All chemicals were used without further purification, since their purities were checked by gas chromatographic analysis, which showed the impurity in each substance was less than 1%. The mixture samples were prepared by mass using a Shimadzu electronic balance (Shimazu, Model AEX-200) with a precision of ±0.01 mg. The possible error of the mole fraction for each sample is below ±0.0001.

Density Measurement. A vibrating-tube densimeter (DMA-602H, Anton Paar) with a DMA-60 processing unit (Anton Paar) was applied in the present study to measure density data. Double-distilled water and dry air were used as calibration fluids. The temperature of the measuring cell was controlled by a circulation of thermostatic water to within ±0.03 K. The temperature was measured by a digital thermometer (Model 1560, Hart Scientific) incorporated with a thermistor probe with an accuracy of ±0.01 K.

The oscillation period (τ) of the sample in the vibrating U-tube was converted into density via

$$\rho = A(\tau^2 - B) \quad (1)$$

where A and B are apparatus constants, which were determined by using the literature density data of pure water (Harr et al., 1984) and of dry air (Vargaftik, 1975) at each

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

		ρ/g·cm^{-3}		η/mPa·s	
compound	T/K	this work	lit.	this work	lit.
anisole	303.15	0.9843	0.9846[a]	0.908	0.9315[a]
			0.9842[b]		0.9070[b]
	313.15	0.9749	0.9757[a]	0.786	0.7977[a]
			0.9750[b]		0.7814[b]
	323.15	0.9635		0.691	
2-butanol	303.15	0.7989	0.7984[d]	2.496	2.4989[d]
			0.79891[g]		2.492[g]
			0.79895[h]		2.495[h]
	313.15	0.7901	0.7897[d]	1.785	1.7833[d]
	323.15	0.7811	0.7809[d]	1.315	1.3149[d]
2-methyl-1-propanol	303.15	0.7944	0.7946[c]	2.845	2.881[c]
			0.7938[d]		2.8466[d]
			0.79435[i]		2.997[f]
			0.7941[f]		2.842[k]
			0.79431[k]		
	313.15	0.7862	0.7858[d]	2.116	2.112[d]
			0.78613[k]		2.080[k]
	323.15	0.7774	0.7776[d]	1.602	1.6004[d]
2-methyl-2-propanol	303.15	0.7753	0.7752[c]	3.381	3.378[c]
			0.7757[d]		3.390[d]
			0.7754[f]		3.372[f]
			0.77541[j]		3.3653[j]
			0.77551[k]		3.378[k]
	313.15	0.7648	0.7649[d]	2.106	2.1037[d]
			0.76481[j]		2.0807[j]
			0.76501[k]		2.047[k]
	323.15	0.7538	0.7540[d]	1.409	1.407[d]

[a] Joshi et al. (1990a). [b] Joshi et al. (1990b). [c] Nikam et al. (1996a). [d] TRC Thermodynamic Tables (1993). [e] Vijayalakshmi and Naidu (1992). [f] Nikam et al. (1996b). [g] Venkatesulu and Rao (1996). [h] Riddick et al. (1986). [i] Kumar et al. (1992). [j] Fuangfoo and Viswanath (1993). [k] Nikam et al. (1998).

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Table 2. Experimental Density and Viscosity for Anisole (1) + 2-Butanol (2)

T/K	x_1	ρ_m/g·cm^{-3}	V^E/cm^3·mol^{-1}	η/mPa·s	$\delta\eta$/mPa·s
303.15	0.0999	0.8216	−0.134	1.759	−0.578
	0.2001	0.8431	−0.209	1.366	−0.812
	0.3001	0.8633	−0.223	1.172	−0.848
	0.3998	0.8827	−0.231	1.068	−0.792
	0.5000	0.9013	−0.212	1.001	−0.701
	0.6001	0.9191	−0.175	0.969	−0.574
	0.7000	0.9363	−0.142	0.951	−0.433
	0.8002	0.9528	−0.088	0.934	−0.292
	0.9000	0.9688	−0.045	0.918	−0.149
313.15	0.0999	0.8125	−0.113	1.335	−0.350
	0.2001	0.8337	−0.165	1.068	−0.517
	0.3001	0.8539	−0.189	0.932	−0.553
	0.3998	0.8731	−0.182	0.862	−0.524
	0.5000	0.8917	−0.170	0.843	−0.442
	0.6001	0.9096	−0.150	0.831	−0.355
	0.7000	0.9268	−0.121	0.816	−0.270
	0.8002	0.9433	−0.071	0.803	−0.183
	0.9000	0.9593	−0.031	0.792	−0.094
323.15	0.0999	0.8030	−0.088	1.023	−0.230
	0.2001	0.8238	−0.126	0.852	−0.338
	0.3001	0.8437	−0.145	0.769	−0.359
	0.3998	0.8627	−0.144	0.745	−0.321
	0.5000	0.8812	−0.148	0.739	−0.263
	0.6001	0.8989	−0.131	0.731	−0.210
	0.7000	0.9158	−0.095	0.723	−0.155
	0.8002	0.9322	−0.058	0.709	−0.107
	0.9000	0.9480	−0.019	0.698	−0.055

Table 3. Experimental Density and Viscosity for Anisole (1) + 2-Methyl-1-propanol (2)

T/K	x_1	ρ_m/g·cm^{-3}	V^E/cm^3·mol^{-1}	η/mPa·s	$\delta\eta$/mPa·s
303.15	0.1001	0.8174	−0.117	1.789	−0.862
	0.2001	0.8398	−0.149	1.326	−1.132
	0.2999	0.8595	−0.166	1.157	−1.107
	0.4001	0.8796	−0.189	1.069	−1.002
	0.5000	0.8989	−0.205	1.011	−0.866
	0.6001	0.9174	−0.195	0.969	−0.714
	0.7000	0.9353	−0.188	0.951	−0.538
	0.8001	0.9524	−0.150	0.934	−0.361
	0.9002	0.9689	−0.108	0.921	−0.187
313.15	0.1001	0.8086	−0.067	1.355	−0.628
	0.2001	0.8301	−0.110	1.064	−0.786
	0.2999	0.8505	−0.131	0.933	−0.784
	0.4001	0.8704	−0.140	0.862	−0.722
	0.5000	0.8896	−0.161	0.845	−0.606
	0.6001	0.9080	−0.153	0.831	−0.487
	0.7000	0.9257	−0.135	0.816	−0.369
	0.8001	0.9429	−0.120	0.803	−0.249
	0.9002	0.9592	−0.063	0.792	−0.127
323.15	0.1001	0.7993	−0.043	1.063	−0.448
	0.2001	0.8203	−0.068	0.829	−0.591
	0.2999	0.8405	−0.088	0.768	−0.561
	0.4001	0.8601	−0.101	0.743	−0.495
	0.5000	0.8790	−0.115	0.736	−0.411
	0.6001	0.8971	−0.102	0.731	−0.324
	0.7000	0.9146	−0.090	0.718	−0.242
	0.8001	0.9315	−0.068	0.708	−0.165
	0.9002	0.9479	−0.049	0.697	−0.085

temperature of interest. The uncertainty of the density measurements is estimated to be less than $\pm 1 \times 10^{-4}$ g/cm^3.

Viscosity Measurement. Kinematic viscosities were measured by a Cannon-Fenske routine viscometer (size 75) at temperatures ranging from 303.15 to 323.15 K. The viscometer has been calibrated with double-distilled water over the entire experimental condition. The detail calibrated procedures have been described previously (Weng, 1999). The measurements were conducted in accordance with the standard method of ASTM D445. The viscometer was placed in a thermostatic water bath (TAMSON, TV-4000), in which the temperature was maintained to within ±0.01 K. The efflux time of liquid sample was determined by a digital stopwatch to ±0.01 s. At least triplicate measurements were made. The results were reproducible to within ±0.2%. The absolute viscosity of the sample (η) was obtained from multiplying kinematic viscosity by density. The accuracy of the measured kinematic viscosity is estimated to be better than ±1.0%.

Results and Discussion

Measurement results for pure compounds and the literature values are listed in Table 1. The agreement is within the experimental uncertainty. Tables 2−4 list the mixture densities (ρ_m), viscosities (η_m), excess molar volume (V^E), and viscosity deviations ($\delta\eta$) for the systems of anisole + 2-butanol, + 2-methyl-1-propanol, and + 2-methyl-2-propanol, respectively. In these tables, V^E and $\delta\eta$ were calculated respectively by the following equations:

$$V^E = V_m - \sum_i x_i V_i^\circ \qquad (2)$$

$$\delta\eta = \eta_m - \sum_i x_i \eta_i^\circ \qquad (3)$$

where V_m is the molar volume of liquid mixture, x_i is the mole fraction of component i, and V_i° and η_i° are the molar

Table 4. Experimental Density and Viscosity for Anisole (1) + 2-Methyl-2-propanol (2)

T/K	x_1	ρ_m/g·cm^{-3}	V^E/cm^3·mol^{-1}	η/mPa·s	$\delta\eta$/mPa·s
303.15	0.1000	0.8023	−0.403	2.101	−1.033
	0.1999	0.8265	−0.545	1.578	−1.308
	0.3002	0.8496	−0.622	1.484	−1.255
	0.4001	0.8716	−0.653	1.272	−1.165
	0.5000	0.8928	−0.635	1.143	−1.043
	0.6001	0.9133	−0.651	1.011	−0.886
	0.6998	0.9331	−0.635	0.954	−0.703
	0.8001	0.9519	−0.554	0.928	−0.475
	0.9001	0.9692	−0.370	0.919	−0.236
313.15	0.1000	0.7914	−0.360	1.585	−0.389
	0.1999	0.8157	−0.511	1.290	−0.552
	0.3002	0.8387	−0.568	1.099	−0.611
	0.4001	0.8609	−0.613	1.002	−0.576
	0.5000	0.8824	−0.644	0.915	−0.531
	0.6001	0.9029	−0.620	0.853	−0.461
	0.6998	0.9228	−0.599	0.825	−0.357
	0.8001	0.9416	−0.499	0.808	−0.242
	0.9001	0.9592	−0.328	0.798	−0.120
323.15	0.1000	0.7800	−0.332	1.222	−0.147
	0.1999	0.8039	−0.449	1.022	−0.243
	0.3002	0.8264	−0.455	0.887	−0.306
	0.4001	0.8486	−0.509	0.815	−0.307
	0.5000	0.8702	−0.559	0.773	−0.277
	0.6001	0.8908	−0.551	0.743	−0.235
	0.6998	0.9107	−0.532	0.722	−0.184
	0.8001	0.9297	−0.454	0.711	−0.124
	0.9001	0.9475	−0.302	0.701	−0.062

volume and the absolute viscosity of pure liquid i, respectively. The accuracy of excess molar volumes is estimated to be better than ±0.005 cm^3·mol, and viscosity deviations are accurate to ±0.03 mPa·s. The molar volume was calculated from

$$V_m = (\sum x_i M_i)/\rho_m \qquad (4)$$

where M_i is the molecular weight of pure fluid i. A Redlich−Kister type equation was applied to correlate the isotherms of both the excess molar volumes and the viscosity

Table 5. Correlated Results for Excess Molar Volume (V^E)

mixture (1) + (2)	T/K	A_0	A_1	A_2	A_3	$\sigma \times 10^3$/cm^3·mol^{-1}
anisole + 2-butanol	303.15	−0.8365	0.5307	−0.2455	0.1502	0.324
	313.15	−0.6890	0.3543	0.1715	0.3415	0.073
	323.15	−0.5752	0.1949	−0.0223	0.4496	0.079
anisole + 2-methyl-1-propanol	303.15	−0.7525	−0.1355	−0.7091	0.3075	0.240
	313.15	−0.6211	−0.0943	−0.1758	0.1830	0.122
	323.15	−0.4178	0.0117	−0.1096	-0.0775	0.120
anisole + 2-methyl-2-propanol	303.15	−2.5908	−0.2107	−2.5874	0.6571	0.294
	313.15	−2.4844	−0.2146	−2.0273	0.6851	0.255
	323.15	−2.0987	−0.5267	−2.1504	1.1716	0.406

Table 6. Correlated Results for Viscosity Deviations ($\delta\eta$)

mixture (1) + (2)	T/K	B_0	B_1	B_2	B_3	σ/mPa·s
anisole + 2-butanol	303.15	−2.7599	2.2980	−1.9754	1.0839	0.016
	313.15	−1.7852	1.6866	−1.0798	0.1473	0.007
	323.15	−1.0796	1.1948	−0.8105	0.0268	0.009
anisole + 2-methyl-1-propanol	303.15	−3.3898	2.9736	−3.6849	2.7595	0.032
	313.15	−2.3533	2.1175	−2.7594	2.0889	0.045
	323.15	−1.6142	1.7241	−2.0883	1.2538	0.014
anisole + 2-methyl-2-propanol	303.15	−3.8585	2.2038	−4.8739	5.2844	0.102
	313.15	−2.1172	1.3122	−1.0906	0.8688	0.014
	323.15	−1.1650	0.8604	0.2191	−0.7505	0.026

Table 7. Correlated Results of the McAllister Model

	three-body model (eq 8)			four-body model (eq 9)			
T/K	ν_{12}	ν_{21}	AAD%[a]	ν_{1112}	ν_{1122}	ν_{2221}	AAD%[a]
			Anisole + 2-Butanol				
303.15	1.1488	0.7912	1.25	0.9894	1.1189	1.0202	0.24
313.15	1.0085	0.6722	1.17	0.8513	0.9957	0.8274	0.65
323.15	0.9375	0.5782	1.70	0.7507	0.9635	0.6723	0.54
			Anisole + 2-Methyl-1-propanol				
303.15	1.2190	0.6796	3.81	0.9272	1.3903	0.7947	0.82
313.15	1.0766	0.5674	3.00	0.8123	1.1715	0.6565	0.45
323.15	0.9905	0.4817	3.90	0.7069	1.1504	0.5201	0.63
			Anisole + 2-Methyl-2-propanol				
303.15	0.9841	1.1505	4.26	0.7992	1.9409	0.8932	2.98
313.15	0.9123	0.8968	0.71	0.8494	0.9994	1.1194	0.56
323.15	0.8040	0.8361	0.90	0.7977	0.7750	1.0830	0.81

[a] AAD% = $(100/n)\sum_{k=1}^{n}|\upsilon_k^{\rm cal} - \upsilon_k^{\rm exp}|/\upsilon_k^{\rm exp}$.

deviations for each binary system.

$$V^E/(\text{cm}^3\cdot\text{mol}^{-1}) = x_1x_2\sum_{i=0}^{n} A_i(x_1 - x_2)^i \qquad (5)$$

$$\delta\eta/(\text{mPa}\cdot\text{s}) = x_1x_2\sum_{i=0}^{n} B_i(x_1 - x_2)^i \qquad (6)$$

where A_i and B_i are temperature-dependent parameters obtained by a least-squares method. The standard deviation was defined as

$$\sigma(Y^E) = [\sum(Y^E_{\rm expt} - Y^E_{\rm calc})^2/(n - p)]^{1/2} \qquad (7)$$

where n is the number of data points, p is the number of parameters, and Y^E refers to V^E or $\delta\eta$. The optimized values of A_i or B_i together with the standard deviation $\sigma(Y^E)$ for the correlation of V^E and $\delta\eta$ are presented in Tables 5 and 6, respectively.

The kinematic viscosities ($\nu = \eta/\rho$) of liquid mixtures are often correlated by the McAllister multibody interaction model (McAllister, 1960). The three-body model is defined as

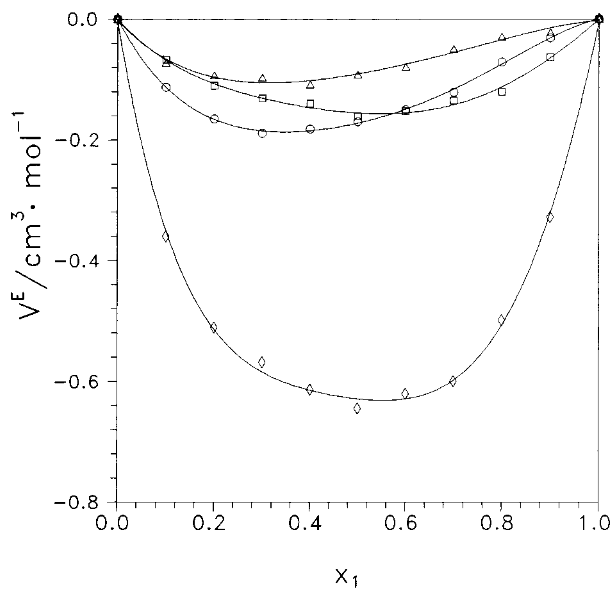

Figure 1. Excess molar volumes (V^E) for anisole (1) + butyl alcohols (2) at 313.15 K: (○) anisole + 2-butanol; (□) anisole + 2-methy-1-propanol; (◇) anisole + 2-methyl-2-propanol; (△) anisole + 1-butanol (Weng, 1999); (—) calculated from eq 5.

$$\ln \nu = x_1^3 \ln \nu_1 + 3x_1^2x_2 \ln \nu_{12} + 3x_1x_2^2 \ln \nu_{21} + x_2^3 \ln \nu_2 - \ln[x_1 + x_2(M_2/M_1)] + 3x_1^2x_2 \ln[(2 + (M_2/M_1))/3] + 3x_1x_2^2 \ln[(1 + 2(M_2/M_1))/3] + x_2^3 \ln(M_2/M_1) \qquad (8)$$

and the four-body model is given by

$$\ln \nu = x_1^4 \ln \nu_1 + 4x_1^3x_2 \ln \nu_{1112} + 6x_1^2x_2^2 \ln \nu_{1122} + 4x_1x_2^3 \ln \nu_{2221} + x_2^4 \ln \nu_2 - \ln[x_1 + x_2(M_2/M_1)] + 4x_1^3x_2 \ln[(3 + (M_2/M_1))/4] + 6x_1^2x_2^2 \ln[(1 + (M_2/M_1))/2] + 4x_1x_2^3 \ln[(1 + 3(M_2/M_1))/4] + x_2^4 \ln(M_2/M_1) \qquad (9)$$

where ν_{12}, ν_{21}, ν_{1112}, ν_{1122}, and ν_{2221} are model parameters. The calculated results are presented in Table 7. It is shown that the McAllister four-body model is obviously better than the three-body model for these three systems.

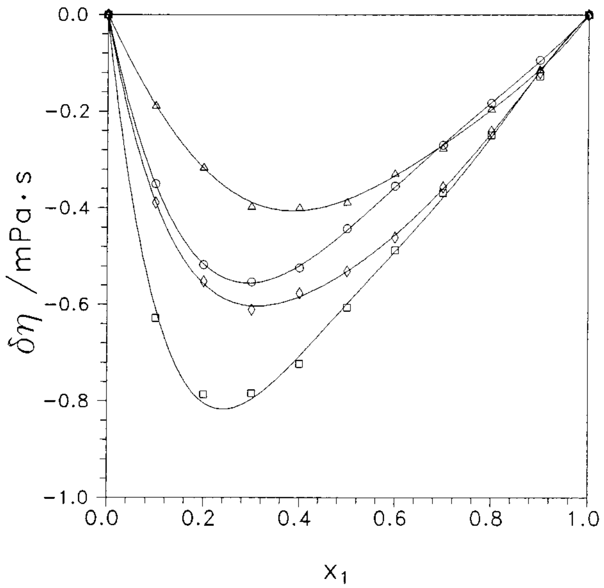

Figure 2. Viscosity deviations ($\delta\eta$) for anisole (1) + butyl alcohols (2) at 313.15 K: (○) anisole + 2-butanol; (□) anisole + 2-methyl-1-propanol; (◊) anisole + 2-methyl-2-propanol; (△) anisole + 1-butanol (Weng, 1999); (—) calculated from eq 6.

The variations of V^E and $\delta\eta$ with the mole fraction of anisole for the investigated systems at 313.15 K are presented in Figures 1 and 2, respectively. Figure 1 shows that the excess molar volumes are negative for these three systems. This means that volume contraction occurs upon mixing anisole with 1-butanol, 2-methyl-2-propanol, 2-butanol, or 2-methyl-1-propanol. More negatives exhibit on the system containing 2-methyl-2-propanol, which may result from the sterically hindered effect. Figure 2 illustrates that the viscosity deviations are also negative for all the investigated mixtures. The absolute value of the viscosity deviations was found to decrease with increasing temperature for each system.

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