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Densities, Refractive Indices, Absolute Viscosities, and Static Dielectric Constants of 2-Methylpropan-2-ol + Hexane, + Benzene, + Propan-2-ol, + Methanol, + Ethanol, and + Water at 303.2 K

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Densities (ϱ), refractive indices (n), absolute viscosities (η), and static dielectric constants (ϵ) have been measured over the entire range of composition for binary mixtures of 2-methylpropan-2-ol with hexane, benzene, propan-2-ol, methanol, ethanol, and water at 303.2 K. Excess molar volumes were fitted to Redlich–Kister equations.

Introduction

The knowledge of densities, refractive indices, absolute viscosities, and static dielectric constants is essential to understand the molecular interactions between the different molecules in binary liquid mixtures. The variation of these properties with composition gives us important information about the intermolecular interactions and the solvent structure.

In previous works (Rosés *et al.*, 1993; Bosch *et al.*, 1994), we measured some microscopic properties (dissociation p*K* values of electrolytes, Dimroth–Reichardt $E_T(30)$ polarity, and Kamlet–Taft π^*, α, and β solvatochromic parameters) of five binary mixtures containing 2-methylpropan-2-ol, hexane, benzene, propan-2-ol, ethanol, and methanol. In this work we have measured the density, refractive index, absolute viscosity, and static dielectric constant over the entire range of composition of the same binary solvents at 303.2 K. In addition, we have measured the same properties for 2-methylpropan-2-ol + water.

Experimental Section

Materials. The solvents used (with the specifications given by the manufacturers) were 2-methylpropan-2-ol (Merck, GR >99.5%, water content ≤0.1%), propan-2-ol (Merck, GR >99.7%, water content ≤0.1%), absolute ethanol (Merck, GR >99.8%, water content ≤0.2%), methanol (Merck, GR >99.5%, water content ≤0.01%), benzene (Merck, GR >99.7%, water content ≤0.01%), hexane (Merck, GR >99.0%, water content ≤0.01%), and bidistilled water. However, the water contents determined by the Karl-Fischer method are for 2-methylpropan-2-ol 0.073%, propan-2-ol 0.035%, absolute ethanol 0.075%, methanol 0.069%, benzene 0.039%, and hexane <0.02%.

Apparatus and Procedure. Mixtures were prepared by mass, on a Sartorius 2004 MP (±0.1 mg), in a dry bottle and just before use to avoid atmospheric moisture. Densities were measured with an Anton Paar DMA-38 vibrating-tube densitometer. The densitometer was calibrated, using air and bidistilled water, at 303.2 K before to any series of measurements. The precision of the results as given by the manufacturer is $\pm 2 \times 10^{-4}$ g cm^{-3}.

Refractive indices (sodium D line) were determined using an Abbé refractometer, model 2AW, thermostated with a water bath to (303.2 ± 0.1) K with a precision of $\pm 2 \times 10^{-4}$.

For the determination of viscosities, a Cannon-Fenske viscometer was employed. The constant of the viscometer was determined at 303.2 K using bidistilled water. All the measurements were made with the viscometer kept in a water bath controlled to (303.2 ± 0.1) K. The time was measured using a stopwatch capable of measuring ±0.2 s. The total time was approximately 350 s, and the precision of the results was between 0.07% and 0.15%.

The dielectric constants were determined using a WTW cell (model MFL-3) connected to a capacitance meter Boonton (model 7200). The cell was thermostated with a water bath to (303.2 ± 0.1) K. The precision of the measurements was about 0.2%.

Results and Discussion

The experimental results of densities ϱ, refractive indices n, absolute viscosities η, and dielectric constants ϵ are reported in Tables 1–4, and the plots of these properties vs the solvent composition are shown in Figures 1–4.

The plots for the density are presented in Figure 1. The density of the mixtures decreases with the content of hexane, which has a density lower than that of 2-methylpropan-2-ol and increases with the content of benzene or water, of higher density. The alcohols have densities similar to that of 2-methylpropan-2-ol, and the variation of density in these mixtures is very small. Our results for 2-methylpropan-2-ol + water mixtures at 303.2 K are in very good agreement with those of Broadwater and Kay (1970) at 298.2 K.

The plots for refractive index are presented in Figure 2. n increases markedly with the content of benzene, much more polarizable than 2-methylpropan-2-ol, and decreases with the content of the other solvents, less polarizable than 2-methylpropan-2-ol.

Figure 3 presents the experimental results obtained for viscosities together with some literature values. The data of Matsuo and Makita (1991) at 303.2 K for 2-methylpropan-2-ol + methanol are in very good agreement with our results. However, this is not the case for the data of Westmeier (1977) for 2-methylpropan-2-ol + water. Except for the most water rich mixtures, the results of Westmeier (1977) are markedly higher than ours (about +0.30 mPa s). The value of Westmeier (1977) for pure 2-methylpropan-2-ol (3.48 mPa s) is also higher than our experimental value (3.33 mPa s). The latter agrees better with other literature values; e.g., Matsuo and Makita (1991) give 3.38 mPa s, and Pikkareinen (1988) gives 3.376 mPa s. For this reason we think that our results are more accurate than those of Westmeier (1977). The viscosity results for the water mixtures are markedly different from those for the other mixtures. Whereas the viscosity of the other mix-

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Table 1. Experimental Densities for 2-Methylpropan-2-ol (1) + Solvent (2) at 303.2 K

	ρ/(g cm^{-3})					
x_2	hexane	benzene	propan-2-ol	ethanol	methanol	water
0.000	0.7752	0.7752	0.7752	0.7752	0.7752	0.7752
0.050	0.7664	0.7794	0.7762	0.7766	0.7768	0.7786
0.100	0.7570	0.7827	0.7767	0.7773	0.7774	0.7817
0.150	0.7478	0.7861	0.7770	0.7777	0.7778	0.7853
0.200	0.7396	0.7899	0.7773	0.7782	0.7782	0.7892
0.300	0.7243	0.7978	0.7776	0.7787	0.7786	0.7983
0.400	0.7105	0.8062	0.7777	0.7789	0.7788	0.8094
0.500	0.6980	0.8154	0.7777	0.7794	0.7790	0.8232
0.600	0.6869	0.8248	0.7777	0.7797	0.7792	0.8400
0.700	0.6766	0.8349	0.7776	0.7800	0.7795	0.8632
0.800	0.6671	0.8452	0.7774	0.7803	0.7802	0.8934
0.850	0.6628	0.8507	0.7773	0.7805	0.7806	0.9137
0.900	0.6583	0.8563	0.7772	0.7807	0.7811	0.9388
0.950	0.6543	0.8624	0.7770	0.7809	0.7816	0.9682
1.000	0.6506	0.8685	0.7768	0.7810	0.7821	0.9956

Table 2. Experimental Values of Refractive Indices *n* for 2-Methylpropan-2-ol (1) + Solvent (2) at 303.2 K

	n					
x_2	hexane	benzene	propan-2-ol	ethanol	methanol	water
0.000	1.3836	1.3836	1.3836	1.3836	1.3836	1.3836
0.050	1.3824	1.3876	1.3836	1.3835	1.3834	1.3833
0.100	1.3809	1.3918	1.3835	1.3830	1.3822	1.3833
0.150	1.3794	1.3968	1.3833	1.3822	1.3809	1.3831
0.200	1.3781	1.4017	1.3830	1.3814	1.3796	1.3830
0.300	1.3761	1.4118	1.3821	1.3797	1.3763	1.3827
0.400	1.3747	1.4226	1.3814	1.3777	1.3722	1.3821
0.500	1.3730	1.4332	1.3804	1.3753	1.3680	1.3810
0.600	1.3719	1.4445	1.3796	1.3726	1.3624	1.3794
0.700	1.3710	1.4564	1.3783	1.3696	1.3566	1.3761
0.800	1.3705	1.4689	1.3771	1.3666	1.3487	1.3710
0.850	1.3702	1.4757	1.3764	1.3650	1.3436	1.3666
0.900	1.3700	1.4815	1.3758	1.3629	1.3385	1.3601
0.950	1.3700	1.4890	1.3752	1.3610	1.3329	1.3505
1.000	1.3705	1.4962	1.3746	1.3590	1.3264	1.3332

Table 3. Experimental Values of Absolute Viscosity η for 2-Methanolpropan-2-ol (1) + Solvent (2) at 303.2 K

	η/(mPa s)					
x_2	hexane	benzene	propan-2-ol	ethanol	methanol	water
0.000	3.333	3.333	3.333	3.333	3.333	3.333
0.050	2.298	2.528	3.297	3.256	3.285	3.236
0.100	1.677	1.968	3.237	3.156	3.166	3.214
0.150	1.306	1.598	3.172	3.039	3.000	3.247
0.200	1.052	1.356	3.101	2.914	2.806	3.309
0.300	0.749	1.060	2.931	2.645	2.400	3.455
0.400	0.568	0.870	2.750	2.360	2.016	3.599
0.500	0.465	0.753	2.572	2.070	1.649	3.743
0.600	0.410	0.671	2.396	1.793	1.360	3.877
0.700	0.361	0.609	2.224	1.548	1.069	3.836
0.800	0.319	0.570	2.059	1.336	0.842	3.541
0.850	0.302	0.559	1.979	1.239	0.746	3.182
0.900	0.289	0.553	1.903	1.147	0.658	2.604
0.950	0.281	0.552	1.831	1.059	0.574	1.738
1.000	0.277	0.554	1.765	0.974	0.497	0.797

tures decreases smoothly with the content of the other solvent, the viscosity of water mixtures presents a maximum for a mole fraction of water of about 0.65. Similar behavior has been observed for propan-2-ol + water mixtures.

The results for the dielectric constant are presented in Figure 4. Winkelmann (1974) and Taniewska-Osińska and Witkowsky (1978) measured the static dielectric constant of mixtures of 2-methylpropan-2-ol with water at 303.2 K in the whole range of composition. Their results are in good agreement with ours.

Mateos *et al.* (1986) measured the static dielectric constant in mixtures of 2-methylpropan-2-ol with hexane at 298.2 and 308.2 K. Our results, at 303.2 K, are intermediate between theirs (see Figure 5).

Table 4. Experimental Values of Static Dielectric Constants ϵ for 2-Methylpropan-2-ol (1) + Solvent (2) at 303.2 K

	ϵ					
x_2	hexane	benzene	propan-2-ol	ethanol	methanol	water
0.000	10.90	10.90	10.90	10.90	10.90	10.90
0.050	9.68	9.84	11.46	11.90	12.06	10.55
0.100	8.50	8.86	11.99	12.78	13.08	10.51
0.150	7.28	8.00	12.47	13.58	13.96	10.70
0.200	6.30	7.26	12.90	14.31	14.67	11.07
0.300	4.76	6.03	13.75	15.55	16.23	12.26
0.400	3.69	5.08	14.43	16.66	17.68	14.05
0.500	3.06	4.40	15.03	17.73	19.16	16.64
0.600	2.63	3.82	15.60	18.80	20.78	20.38
0.700	2.36	3.37	16.16	19.86	22.68	26.32
0.800	2.16	2.97	16.68	20.99	24.92	36.02
0.850	2.10	2.80	16.96	21.60	26.25	42.92
0.900	2.03	2.62	17.21	22.22	27.66	52.35
0.950	1.96	2.45	17.45	22.89	29.87	64.48
1.000	1.87	2.26	17.70	23.60	31.70	76.60

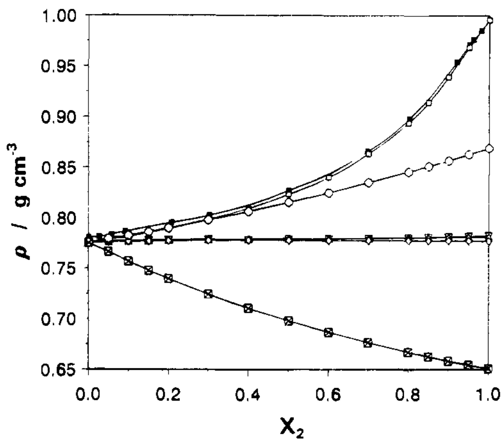

Figure 1. Density (g cm^{-3}) of mixtures of 2-methylpropan-2-ol + propan-2-ol (◇), + ethanol (△), + methanol (▽), + water (□), + hexane (× in □), and + benzene (O) at 303.2 K. The solid symbols are from Broadwater and Kay (1970) at 298.2 K.

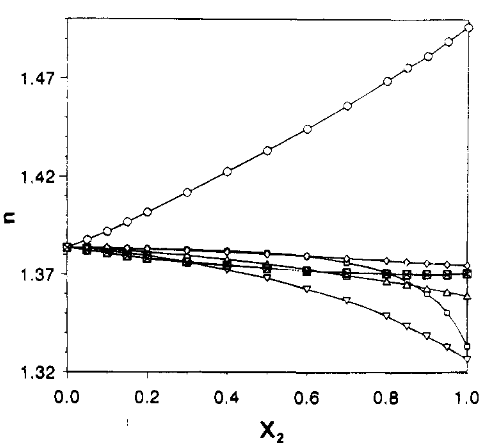

Figure 2. Refractive index of mixtures of 2-methylpropan-2-ol + propan-2-ol, + ethanol, + methanol, + water, + hexane, and + benzene at 303.2 K. Symbols are as in Figure 1.

From the density results the molar volumes of the mixtures have been calculated. They are tabulated in Table 5 and plotted in Figure 6.

The excess molar volume, V_m^E has been calculated by the usual equation

$$V_m^E = V_m - (V_{m1}x_1 + V_{m2}x_2) \quad (1)$$

where V_m denotes the property in the binary mixture and the subscripts 1 and 2 denote the property in pure 2-methyl-propan-2-ol and the other solvent, respectively. The results are plotted in Figure 7.

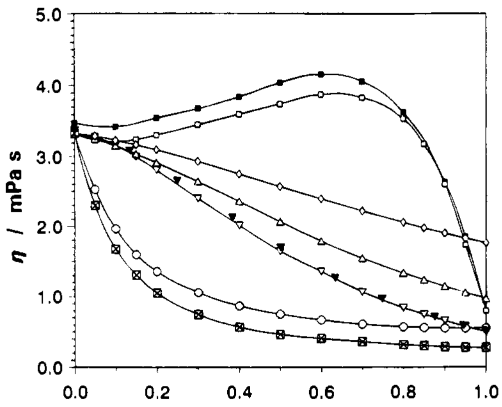

Figure 3. Absolute viscosity (mPa s) of mixtures of 2-methylpropan-2-ol + propan-2-ol, + ethanol, + methanol, + water, + hexane and + benzene at 303.2 K. Symbols are as in Figure 1. The solid symbols are from Westmeier (1977) for mixtures with water and Matsuo and Makita (1991) for mixtures with methanol.

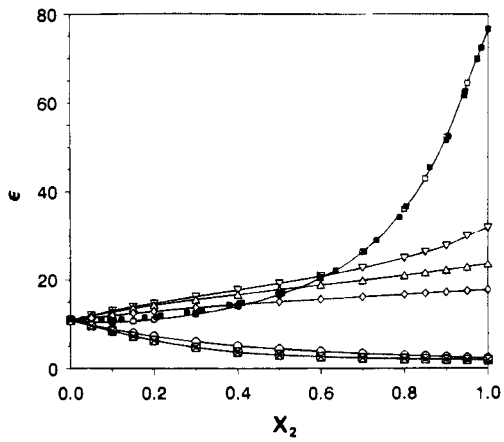

Figure 4. Dielectric constant of mixtures of 2-methylpropan-2-ol + propan-2-ol, + ethanol, + methanol, + water, + hexane, and + benzene at 303.2 K. Symbols are as in Figure 1. The solid symbols are from Winkelmann (1974) and Taniewska-Osińska and Witkowsky (1978).

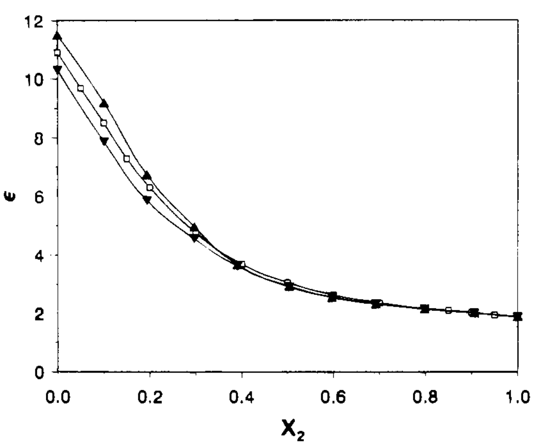

Figure 5. Dielectric constant of mixtures of 2-methylpropan-2-ol + hexane (× in □) at 303.2 K. The solid symbols are from Mateos *et al.* (1986) at 298.2 and 308.2 K.

This excess property has been fitted to a Redlich–Kister equation (Redlich and Kister, 1948) of the type

$$G = x_1 x_2 \sum_{i=0}^{i=4} A_i (x_2 - x_1)^i \quad (2)$$

Table 5. Calculated Values of Molar Volume V_m for 2-Methylpropan-2-ol (1) + Solvent (2) at 303.2 K

	V_m/(cm^3 mol^{-1})					
x_2	hexane	benzene	propan-2-ol	ethanol	methanol	water
0.000	95.61	95.61	95.61	95.61	95.61	95.61
0.050	97.49	95.36	94.59	93.64	92.71	91.59
0.100	99.50	95.21	93.62	91.75	89.93	87.64
0.150	101.52	95.05	92.69	89.90	87.18	83.67
0.200	103.46	94.85	91.75	88.04	84.43	79.70
0.300	107.30	94.41	89.91	84.38	78.98	71.77
0.400	111.08	93.92	88.10	80.75	73.56	63.85
0.500	114.79	93.35	86.29	77.10	68.14	55.96
0.600	118.39	92.77	84.49	73.48	62.72	48.17
0.700	121.96	92.13	82.70	69.85	57.30	40.37
0.800	125.50	91.48	80.92	66.23	51.85	32.73
0.850	127.22	91.12	80.02	64.42	49.13	28.93
0.900	129.00	90.76	79.13	62.60	46.41	25.17
0.950	130.70	90.35	78.25	60.79	43.68	21.51
1.000	132.37	89.95	77.37	58.99	40.97	18.10

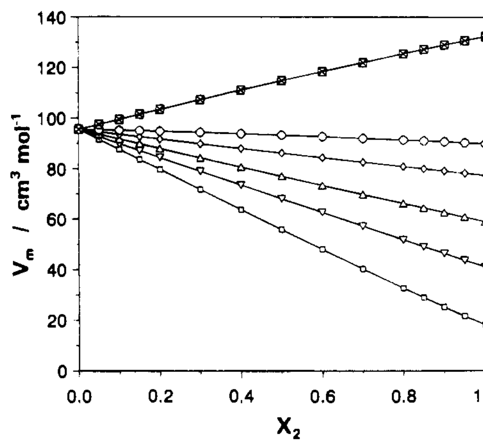

Figure 6. Molar volume (cm^3 mol^{-1}) of mixtures of 2-methylpropan-2-ol + propan-2-ol, + ethanol, + methanol, + water, + hexane, and + benzene at 303.2 K. Symbols are as in Figure 1.

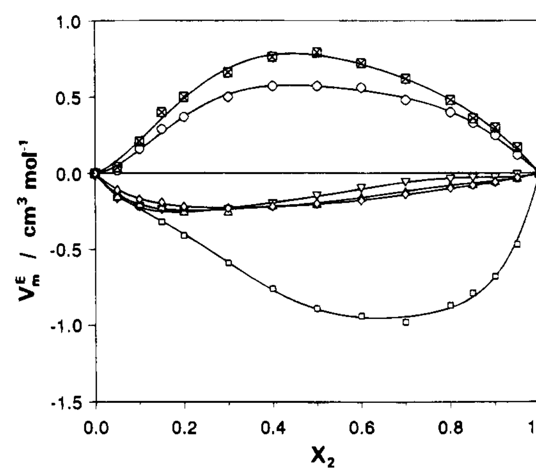

Figure 7. Excess molar volume (cm^3 mol^{-1}) of mixtures of 2-methylpropan-2-ol + propan-2-ol, + ethanol, + methanol, + water, + hexane, and + benzene at 303.2 K. Symbols are as in Figure 1.

where G is the excess property (V_m^E), x_1 and x_2 are, respectively, the mole fractions of 2-methylpropan-2-ol and the other solvent, and A_i are the adjustable parameters evaluated by the method of least squares.

The adjustable parameters, A_i, obtained for the excess property in study are summarized in Table 6. In this table the overall standard deviations obtained are given as σ.

Table 6. A_i Coefficients of Eq 2 and the Standard Deviation Obtained for the Excess Molar Volume ($cm^3\ mol^{-1}$) for 2-Methylpropan-2-ol (1) + Solvent (2) at 303.2 K

solvent (2)	A_0	A_1	A_2	A_3	A_4	$\sigma(V_m^E)$
hexane	3.09	−0.70	0.30	1.83	−1.26	0.03
benzene	2.28	−0.37	1.11	1.50	−2.00	0.02
propan-2-ol	−0.82	0.42	−0.25	0.52	−0.66	0.01
ethanol	−0.78	0.58	−0.22	0.75	−1.21	0.01
methanol	−0.61	0.89	−0.27	0.73	−1.49	0.01
water	−3.58	−1.79	0.22	−2.06	−4.02	0.02

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