Densities, Viscosities, and Refractive Indices of Some Binary Liquid Systems of Methanol + Isomers of Hexanol at 298.15 K

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Viscosities, densities, and refractive indices of eight binary liquid systems containing methanol + some isomers of hexanol, have been determined at 298.15 K. The excess property values were fitted to a Redlich−Kister-type equation. The results with this model agree with experimental data with an average absolute deviation of less than 0.6%.

Introduction

In continuation of our programs on thermodynamic properties of binary nonelectrolyte systems (Aucejo et al., 1986, 1995**a**,**b**; Orts et al., 1988), we report in this paper experimental data on densities, viscosities, and refractive indices for eight mixtures of methanol, as the common component, with some isomers of hexanol, namely, 3,3-dimethyl-2-butanol, 2-ethyl-1-butanol, 2-methyl-1-pentanol, 3-methyl-3-pentanol, 4-methyl-2-pentanol, 2-hexanol, 3-hexanol, and 1-hexanol, over the entire range of composition at 298.15 K and atmospheric pressure. No data have been found for these systems in the literature.

The aim of this program is to characterize the molecular interactions in terms of excess volume (V^E) and viscosity deviations ($\Delta\eta$).

Experimental Section

All the chemicals used in the present study were supplied by Aldrich Chemical Co. and were used as received. No further purification treatment was carried out. The stated purity of all the chemicals exceeded 99 mass %. Before measurements the liquids were dried over molecular sieves (Union Carbide, type 4A, 1/16-in. pellets). The purities of the compounds were checked by determining their densities at 298.15 K and are reported in Table 1 in comparison with literature data (*TRC Thermodynamics Tables*, 1995).

All the solutions were prepared using a Mettler balance with an accuracy of ±0.0001 g, charging the heavier component first to minimize the error in composition. Densities of the pure components and their mixtures were measured with an Anton Paar (Model DMA 55) densimeter with a resolution of 2×10^{-5} g·cm^{-3}. The density determination is based on measuring the period of oscillation of the vibrating U-shaped sample tube filled with the sample. For each experimental set of measurements, the apparatus was calibrated with doubly distilled and degassed water and dry air at atmospheric pressure. The temperature of the thermostat was maintained constant to within ±0.01 K. Temperatures were detected with a digital precision thermometer (Anton Paar DT 100−20).

An Ubbelohde viscometer was used for determining the viscosities of pure liquids and the binary systems. The apparatus was submerged in a thermostatic bath at 25 °C with a resolution of ±0.1 K. The viscometer was calibrated with pure components whose viscosity and density were well-known, as has been described in a previous paper (Aucejo et al., 1986). Viscosity values were determined using the relation (Wright, 1961; Mulcahy, 1984)

Table 1. Comparison of Experimental Densities (ρ) of Pure Components with Literature Data at 298.15 K

component	ρ/g·cm^{-3} exptl	ρ/g·cm^{-3} lit.[a]
methanol	0.786 45	0.786 64
3,3-dimethyl-2-butanol	0.813 94	n.a.
2-ethyl-1-butanol	0.829 01	0.8295
2-methyl-1-pentanol	0.817 76	0.8206
3-methyl-3-pentanol	0.824 55	0.8238
4-methyl-2-pentanol	0.802 60	0.8033
2-hexanol	0.810 09	0.8105
3-hexanol	0.816 35	0.8144
1-hexanol	0.815 54	0.8162

[a] TRC Thermodynamic Tables, 1995.

$$\frac{\eta}{\rho} = At - \frac{B}{t} \tag{1}$$

where η is the viscosity, ρ is the liquid density, t is its flow time in the viscometer, and A and B are viscometer constants, determined for measurements with calibration fluids. Each experimental point is the average of 10 measurements with a maximum deviation of ±0.2% on flow time.

No changes in the composition were observed on comparing the value of the refractive index before and after the viscosity measurement. The refractive indices were measured with an Abbe refractometer (Type 3T) with an accuracy of ±0.0002.

Results and Discussion

The experimental densities, refractive indices, and viscosities of the eight binary mixtures are shown in Table 2, as well as the excess molar volumes (V^E) and the deviation in viscosities ($\Delta\eta$).

The excess molar volumes, V^E, were calculated with the following equation:

$$V^E = V - \sum x_i V_i \tag{2}$$

where V is the molar volume of the mixture and x_i and V_i are the mole fractions and molar volumes of the pure components, respectively. Figure 1 shows the excess molar volume−composition results for all systems studied together with the fitted curve.

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Table 2. Mole Fractions (x_1), Densities (ρ), Viscosities (η), Refractive Indices (n_D), Excess Volumes (V^E), and Viscosity Deviation ($\Delta\eta$) for Binary Mixtures

x_1	ρ/g·cm^{-3}	η/mPa·s	n_D	V^E/cm^3·mol^{-1}	$\Delta\eta$/mPa·s	x_1	ρ/g·cm^{-3}	η/mPa·s	n_D	V^E/cm^3·mol^{-1}	$\Delta\eta$/mPa·s
Methanol (1) + 3,3-Dimethyl-2-butanol (2)						Methanol (1) + 4-Methyl-2-pentanol (2)					
0.0000	0.813 94	4.4307	1.4147	0.0000	1.0000	0.0000	0.802 60	3.8229	1.4106	0.0000	1.0000
0.1018	0.815 23	4.1953	1.4121	−0.3243	1.1726	0.1191	0.802 41	3.5038	1.4058	−0.0705	1.1565
0.2939	0.815 30	3.6352	1.4067	−0.5722	1.5210	0.2078	0.801 90	3.2627	1.4032	−0.0757	1.2806
0.3306	0.814 99	3.4682	1.4050	−0.5800	1.5673	0.3157	0.800 96	2.8474	1.3989	−0.0547	1.3797
0.3710	0.814 53	3.2236	1.3986	−0.5778	1.5858	0.4359	0.799 52	2.2974	1.3928	−0.0134	1.4076
0.5073	0.812 02	2.5092	1.3956	−0.5049	1.6434	0.5125	0.798 38	1.9584	1.3888	0.0157	1.3935
0.6096	0.809 11	1.9593	1.3863	−0.4026	1.5908	0.6519	0.795 88	1.4586	1.3782	0.0591	1.3626
0.7100	0.805 21	1.5124	1.3788	−0.2793	1.5162	0.7023	0.794 84	1.2974	1.3736	0.0679	1.3373
0.8024	0.800 55	1.1368	1.3665	−0.1611	1.3837	0.8038	0.792 48	1.0024	1.3619	0.0695	1.2597
0.9102	0.793 60	0.7715	1.3486	−0.0455	1.1777	0.9042	0.789 72	0.7423	1.3488	0.0463	1.1348
1.0000	0.786 45	0.5425	1.3267	0.0000	1.0000	1.0000	0.786 45	0.5425	1.3267	0.0000	1.0000
Methanol (1) + 2-Ethyl-1-Butanol (2)						Methanol (1) + 2-Hexanol (2)					
0.0000	0.829 01	5.8191	1.4206	0.0000	1.0000	0.0000	0.810 09	4.0474	1.4129	0.0000	1.0000
0.1241	0.827 18	4.8058	1.4164	−0.0096	1.1086	0.1062	0.809 46	3.7467	1.4096	−0.0348	1.1459
0.2054	0.825 70	4.1425	1.4132	−0.0046	1.1589	0.2053	0.808 47	3.3370	1.4068	−0.0276	1.2455
0.3133	0.823 34	3.3804	1.4090	0.0111	1.2217	0.3128	0.807 21	2.8917	1.4023	−0.0180	1.3396
0.4534	0.819 46	2.4544	1.4004	0.0409	1.2368	0.4120	0.805 74	2.4302	1.3968	−0.0012	1.3742
0.5051	0.817 75	2.2143	1.3965	0.0528	1.2614	0.5053	0.803 96	2.0399	1.3928	0.0271	1.3914
0.6004	0.814 09	1.7435	1.3892	0.0726	1.2452	0.6071	0.801 52	1.6471	1.3856	0.0644	1.3785
0.7073	0.809 03	1.3297	1.3786	0.0867	1.2239	0.7030	0.798 77	1.3146	1.3769	0.0890	1.3341
0.8019	0.803 45	1.0406	1.3665	0.0857	1.1988	0.8146	0.795 04	0.9858	1.3628	0.0841	1.2519
0.9015	0.796 01	0.7598	1.3494	0.0620	1.1087	0.9006	0.791 62	0.7707	1.3492	0.0527	1.1633
1.0000	0.786 45	0.5425	1.3267	0.0000	1.0000	1.0000	0.786 45	0.5425	1.3267	0.0000	1.0000
Methanol (1) + 2-Methyl-1-pentanol (2)						Methanol (1) + 3-Hexanol (2)					
0.0000	0.817 76	5.3039	1.4160	0.0000	1.0000	0.0000	0.816 35	4.3405	1.4138	0.0000	1.0000
0.0849	0.816 84	4.6448	1.4149	0.0001	1.0628	0.1014	0.816 16	4.2984	1.4112	−0.1238	1.2228
0.2146	0.815 01	3.7573	1.4105	0.0251	1.1555	0.2029	0.815 56	3.9446	1.4086	−0.1987	1.3858
0.3193	0.813 20	3.0525	1.4062	0.0488	1.1919	0.3111	0.814 42	3.3630	1.4049	−0.2305	1.4796
0.4183	0.811 17	2.5256	1.3999	0.0715	1.2359	0.4188	0.812 53	2.7369	1.3986	−0.2061	1.5064
0.5192	0.808 67	2.0177	1.3941	0.0941	1.2427	0.5030	0.810 45	2.2777	1.3938	−0.1535	1.4936
0.6077	0.806 04	1.6763	1.3872	0.1110	1.2633	0.6078	0.806 88	1.7579	1.3845	−0.0510	1.4335
0.7069	0.802 50	1.2964	1.3761	0.1204	1.2249	0.7072	0.803 18	1.3832	1.3760	0.0006	1.3869
0.8045	0.798 25	1.0180	1.3670	0.1128	1.2016	0.7994	0.798 98	1.0540	1.3662	0.0351	1.2802
0.9002	0.793 14	0.7552	1.3501	0.0780	1.1088	0.9014	0.793 45	0.7655	1.3486	0.0321	1.1494
1.0000	0.786 45	0.5425	1.3267	0.0000	1.0000	1.0000	0.786 45	0.5425	1.3267	0.0000	1.0000
Methanol (1) + 3-Methyl-3-pentanol (2)						Methanol (1) + 1-Hexanol (2)					
0.0000	0.824 55	3.9176	1.4172	0.0000	1.0000	0.0000	0.815 54	4.4862	1.4161	0.0000	1.0000
0.1032	0.826 01	3.7987	1.4148	−0.3975	1.1891	0.1054	0.814 40	3.8807	1.4128	0.0090	1.0808
0.2156	0.825 89	3.5526	1.4122	−0.5768	1.3888	0.2016	0.813 16	3.3508	1.4094	0.0228	1.1435
0.3158	0.825 02	3.3171	1.4081	−0.6493	1.5808	0.3144	0.811 43	2.7779	1.4042	0.0403	1.2031
0.4019	0.823 64	3.0481	1.4052	−0.6575	1.7222	0.4093	0.809 68	2.3480	1.3993	0.0576	1.2426
0.5004	0.821 12	2.5996	1.3986	−0.6024	1.7845	0.5053	0.807 53	1.9676	1.3932	0.0774	1.2755
0.6084	0.817 00	2.0790	1.3900	−0.4784	1.7669	0.6027	0.804 89	1.6148	1.3858	0.0964	1.2859
0.7088	0.811 83	1.5677	1.3820	−0.3377	1.6249	0.7094	0.801 34	1.2781	1.3765	0.1080	1.2751
0.8021	0.805 82	1.1597	1.3680	−0.2155	1.4456	0.8038	0.797 51	1.0012	1.3643	0.1017	1.2193
0.9011	0.797 72	0.8027	1.3533	−0.1062	1.2168	0.9022	0.792 60	0.7601	1.3482	0.0694	1.1396
1.0000	0.786 45	0.5425	1.3267	0.0000	1.0000	1.0000	0.786 45	0.5425	1.3267	0.0000	1.0000

Table 3. Coefficients of the Redlich−Kister-Type Equation for Excess Molar Volume, V^E

system	B_0	B_1	B_2	B_3	AAD^a/%
methanol (1) + 3,3-dimethyl-2-butanol (2)	−2.0484	−1.6235	−0.0619	−0.3436	0.0009
methanol (1) + 2-ethyl-1-butanol (2)	0.2064	−0.4499	0.1274	−0.0669	0.0004
methanol (1) + 2-methyl-1-pentanol (2)	0.3636	−0.4381	0.1671	−0.1036	0.0009
methanol (1) + 3-methyl-3-pentanol (2)	−2.3670	−1.8641	−0.1362	0.3296	0.0102
methanol (1) + 4-methyl-2-pentanol (2)	0.0460	−0.7618	−0.1815	0.0074	0.0007
methanol (1) + 2-hexanol (2)	0.1162	−0.7205	0.1287	0.2562	0.0050
methanol (1) + 3-hexanol (2)	−0.6225	−1.5506	0.2230	0.7807	0.0061
methanol (1) + 1-hexanol (2)	0.3069	−0.4219	0.2325	0.0185	0.0005

[a] AAD = $[\sum_1^N(|V_{\mathrm{exptl}} - V_{\mathrm{calc}}|/V_{\mathrm{exptl}})100]/N$ (N = no. of data points).

The viscosity deviations, $\Delta\eta$, were calculated with the expression proposed by Ratcliff and Khan (1971):

$$\ln \Delta\eta = \ln \eta - \sum x_i \ln \eta_i \qquad (3)$$

where η is the viscosity of the mixture and x_i and η_i are the mole fractions and the viscosity of the pure components, respectively. Figure 2 shows the viscosity deviation−composition results for all systems studied.

The specific interactions due to the intermolecular hydrogen bonding between the different components of the binary systems studied in this paper are responsible for their behavior. The strength of these hydrogen bonds depends on the OH-group position (primary, secondary, and tertiary) and the molecular shape.

In Figure 1 it can be observed that the mixtures of methanol with primary alcohols give positive or slightly negative V^E values. The excess volume becomes more negative from secondary up to tertiary alcohols. Related to the molecular shape, the more negative V^E values of 3-methyl-3-pentanol and 3,3-dimethyl-2-butanol compared to those of all other hexanol isomers could be attributed to the more spherical form of the former. This spherical

Table 4. Coefficients of the Redlich−Kister-Type Equation for Viscosity Deviation, $\Delta\eta$

system	C_0	C_1	C_2	C_3	AAD[a]/%
methanol (1) + 3,3-dimethyl-2-butanol (2)	2.5762	0.1261	−0.6611	−0.7322	0.55
methanol (1) + 2-ethyl-1-butanol (2)	0.9862	−0.1496	0.2033	0.0257	0.47
methanol (1) + 2-methyl-1-pentanol (2)	1.0289	−0.3645	−0.0292	0.1776	0.59
methanol (1) + 3-methyl-3-pentanol (2)	3.1377	−0.6153	−1.5990	0.5388	0.53
methanol (1) + 4-methyl-2-pentanol (2)	1.6362	0.1764	0.0840	−0.3861	0.59
methanol (1) + 2-hexanol (2)	1.5652	−0.0609	0.1044	−0.0911	0.25
methanol (1) + 3-hexanol (2)	1.9782	0.6290	0.2491	−0.2625	0.36
methanol (1) + 1-hexanol (2)	1.0885	−0.4753	0.2012	0.0366	0.15

[a] AAD = $[\sum_1^N(|\eta_{\text{exptl}} - \eta_{\text{calc}}|/\eta_{\text{exptl}})100]/N$ (N = no. of data points).

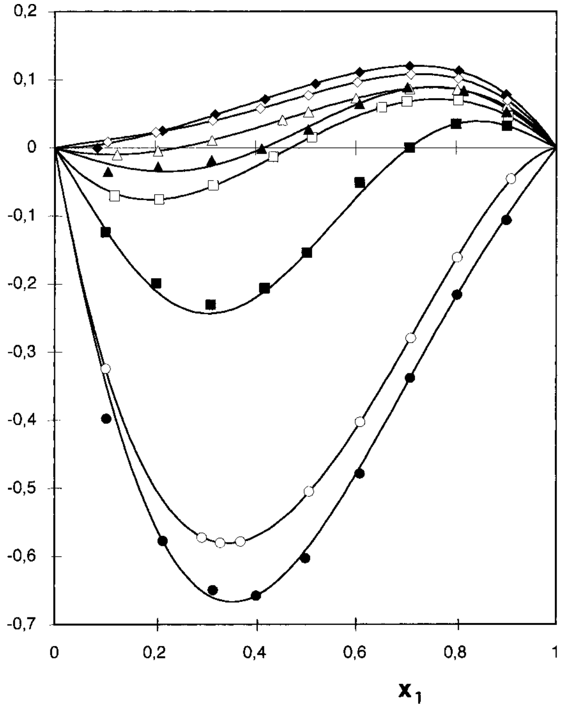

Figure 1. Excess volumes of methanol (1) with 3,3-dimethyl-2-butanol (2) (○), 2-ethyl-1-butanol (2) (△), 2-methyl-1-pentanol (2) (◆), 3-methyl-3-pentanol (2) (●), 4-methyl-2-pentanol (2) (□), 2-hexanol (2) (▲), 3-hexanol (2) (■), and 1-hexanol (2) (◇). The solid curves have been calculated from eq 4.

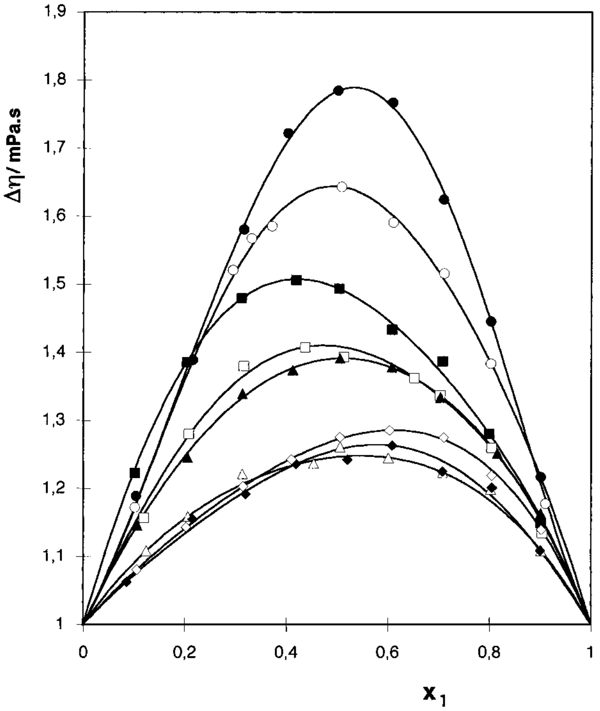

Figure 2. Viscosity deviations of methanol (1) with 3,3-dimethyl-2-butanol (2) (○), 2-ethyl-1-butanol (2) (△), 2-methyl-1-pentanol (2) (◆), 3-methyl-3-pentanol (2) (●), 4-methyl-2-pentanol (2) (□), 2-hexanol (2) (▲), 3-hexanol (2) (■), and 1-hexanol (2) (◇). The solid curves have been calculated from eq 5.

shape makes difficult the hydrogen bonding between themselves, so that the hydrogen bonding is mainly established with the smaller molecules such as methanol.

The trends in the viscosity deviation values are similar to those of the excess volume, as can be seen in Figure 2.

The composition dependences of excess molar volumes were correlated by a Redlich−Kister-type equation:

$$V^{E}/\text{cm}^3\cdot\text{mol}^{-1} = x_1x_2\sum_{i=0}^{3}B_i(x_2 - x_1)^i \qquad (4)$$

were x_1 is the mole fraction of methanol and x_2 is the mole fraction of hexanol isomers.

The values of the adjustable parameters B_i included in eq 4 were determined for the systems studied using a least-squares method. These values are reported in Table 3 together with the average absolute deviation (AAD).

In the same way, the composition dependences of viscosity deviation were correlated by a Redlich−Kister-type equation:

$$(\Delta\eta - 1)/\text{mPa}\cdot\text{s} = x_1x_2\sum_{i=0}^{3}C_i(x_2 - x_1)^i \qquad (5)$$

The values of the adjustable parameters C_i included in eq 5 were determined for the systems studied using a least-squares method. These values are reported in Table 4 together with the average absolute deviation (AAD).

The AAD of all fits indicate that the Redlich−Kister model fits the experimental data very well.

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