J. Chem. Eng. Data **1996,** *41,* 1131−1134

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

Antonio Aucejo,* M. Cruz Burguet, and Rosa Muñoz

Departamento de Ingeniería Química, Facultad de Química, Universitat de Valencia, 46100 Burjassot, Valencia, Spain

Viscosities, densities, and refractive indices of eight binary liquid systems containing ethanol + some isomers of hexanol have been determined at 298.15 K. The excess property values were fitted to the Redlich−Kister equation to estimate the binary coefficients and the standard deviations.

Introduction

This work is part of a systematic study on thermodynamic properties of binary nonelectrolyte systems (Aucejo et al., 1986, 1995a,b, 1996; Orts et al., 1988). In a previous paper (Aucejo et al., 1996) we reported densities and viscosities for binary systems of methanol, as the common component, with eight isomers of hexanol at 298.15 K and atmospheric pressure. As an extension of that work we have measured the densities and viscosities for the same isomers of hexanol (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) with ethanol as the common component, over the entire range of composition at 298.15 K and atmospheric pressure. No data have been found for these systems in the literature at the same conditions.

The results were used to calculate the excess molar volumes (V^E) and viscosity deviations ($\Delta\eta$). Some systems show strong negative deviations, whereas others exhibit slight positive deviations. The trends in V^E and $\Delta\eta$ for the eight systems studied are similar to those which contain methanol, but the values are smaller.

While different approaches have been suggested to the problem of fitting experimental data of densities and viscosities of mixtures, in the present work we have selected the Redlich−Kister equation. The fit to the data is very satisfactory, as was the case with methanol.

Experimental Section

All the chemicals used 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 by mass using a Mettler balance with an accuracy of ±0.0001 g, charging the heavier component first to minimize the error in composition. The possible error in the mole fraction is less than ±0.0002. Densities of the pure components and their mixtures were measured with an Anton Paar (Model DMA 55) vibrating tube densimeter. The density determination, with an accuracy of 2×10^{-5} g·cm^{-3}, 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 then dry air at atmospheric pressure. The temperature of the thermostat was maintained constant to within ±0.01 K. Temperatures were determined with a digital precision thermometer (Anton Paar DT 100-20).

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]
ethanol	0.785 04	0.78509
3,3-dimethyl-2-butanol	0.813 94	n.a.[b]
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). [b] Not available.

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 298.15 K 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)

$$\frac{\eta}{\rho} = At - \frac{B}{t} \qquad (1)$$

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 from measurements with calibration fluids. Each experimental point was the average of 10 measurements with a maximum deviation of ±0.2% in the flow time. The estimated accuracy of experimental viscosities is ±0.0005.

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 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,

S0021-9568(96)00126-4 CCC: $12.00

Table 2. Mole Fractions of Ethanol (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
Ethanol (1) + 3,3-Dimethyl-2-butanol (2)											
0.0000	0.813 94	4.4307	1.4147	0.000	1.000	0.5921	0.806 74	2.5520	1.3935	−0.478	1.336
0.1189	0.813 92	4.0297	1.4108	−0.245	1.077	0.6931	0.803 03	2.1184	1.3872	−0.388	1.281
0.2073	0.813 76	3.8312	1.4088	−0.407	1.161	0.8064	0.797 53	1.6778	1.3788	−0.241	1.191
0.3070	0.813 04	3.5675	1.4060	−0.524	1.246	0.9041	0.791 96	1.3499	1.3699	−0.129	1.101
0.4071	0.811 59	3.2384	1.4028	−0.566	1.304	1.0000	0.785 04	1.0694	1.3591	0.000	1.000
0.5091	0.809 35	2.8477	1.3985	−0.548	1.325						
Ethanol (1) + 2-Ethyl-1-butanol (2)											
0.0000	0.829 01	5.8191	1.4206	0.000	1.000	0.6076	0.810 77	2.3501	1.3942	−0.043	1.130
0.1055	0.826 83	5.1436	1.4169	−0.022	1.057	0.6966	0.806 30	1.9722	1.3887	−0.025	1.103
0.2003	0.824 67	4.5018	1.4138	−0.046	1.086	0.8051	0.800 08	1.6167	1.3797	−0.020	1.087
0.3067	0.821 85	3.8439	1.4096	−0.062	1.111	0.9036	0.793 20	1.3448	1.3702	−0.009	1.068
0.4044	0.818 81	3.2906	1.4027	−0.064	1.122	1.0000	0.785 04	1.0694	1.3591	0.000	1.000
0.5030	0.815 22	2.7771	1.3985	−0.057	1.119						
Ethanol (1) + 2-Methyl-1-pentanol (2)											
0.0000	0.817 76	5.3039	1.4160	0.000	1.000	0.6144	0.803 67	2.2535	1.3914	0.009	1.136
0.1048	0.816 14	4.6149	1.4129	−0.012	1.029	0.7136	0.799 84	1.8841	1.3854	0.027	1.114
0.2134	0.814 29	3.9956	1.4061	−0.031	1.060	0.7984	0.796 18	1.6231	1.3788	0.027	1.099
0.3147	0.812 30	3.4814	1.4030	−0.044	1.086	0.9049	0.790 83	1.3027	1.3696	0.016	1.046
0.4122	0.809 98	3.0135	1.4012	−0.039	1.099	1.0000	0.785 04	1.0694	1.3591	0.000	1.000
0.5011	0.807 50	2.6636	1.3976	−0.026	1.120						
Ethanol (1) + 3-Methyl-3-pentanol (2)											
0.0000	0.824 55	3.9176	1.4172	0.000	1.000	0.6138	0.812 81	2.6317	1.3945	−0.539	1.491
0.1124	0.823 95	3.6185	1.4139	−0.231	1.069	0.7104	0.807 73	2.2026	1.3880	−0.424	1.414
0.2131	0.823 19	3.4054	1.4114	−0.418	1.146	0.7975	0.802 62	1.8373	1.3808	−0.339	1.321
0.2990	0.821 97	3.3450	1.4090	−0.516	1.259	0.9010	0.794 37	1.4049	1.3709	−0.155	1.155
0.4102	0.819 94	3.2321	1.4054	−0.614	1.405	1.0000	0.785 04	1.0694	1.3591	0.000	1.000
0.5116	0.816 94	3.0073	1.4006	−0.609	1.492						
Ethanol (1) + 4-Methyl-2-pentanol (2)											
0.0000	0.802 60	3.8229	1.4106	0.000	1.000	0.6098	0.795 85	2.1596	1.3882	−0.065	1.228
0.1103	0.802 04	3.6824	1.4054	−0.058	1.109	0.7078	0.793 75	1.8828	1.3826	−0.041	1.213
0.2012	0.801 37	3.4953	1.4038	−0.085	1.181	0.8008	0.791 34	1.6005	1.3764	−0.013	1.161
0.3207	0.800 20	3.1306	1.4000	−0.097	1.232	0.8981	0.788 40	1.3424	1.3690	0.009	1.103
0.4152	0.799 06	2.8169	1.3966	−0.098	1.251	1.0000	0.785 04	1.0694	1.3591	0.000	1.000
0.5152	0.797 58	2.4871	1.3928	−0.087	1.254						
Ethanol (1) + 2-Hexanol (2)											
0.0000	0.810 09	4.0474	1.4129	0.000	1.000	0.6033	0.799 78	2.1598	1.3903	−0.007	1.191
0.1065	0.808 90	3.7829	1.4100	−0.019	1.077	0.7079	0.796 72	1.8358	1.3842	0.009	1.164
0.2102	0.807 55	3.4845	1.4066	−0.031	1.139	0.8023	0.793 55	1.5716	1.3776	0.015	1.130
0.3167	0.805 91	3.1151	1.4031	−0.034	1.173	0.9063	0.789 50	1.3012	1.3693	0.008	1.074
0.4096	0.804 19	2.8265	1.3996	−0.026	1.205	1.0000	0.785 04	1.0694	1.3591	0.000	1.000
0.5036	0.802 23	2.5117	1.3954	−0.020	1.213						
Ethanol (1) + 3-Hexanol (2)											
0.0000	0.816 35	4.3405	1.4138	0.000	1.000	0.6027	0.804 28	2.4594	1.3916	−0.121	1.318
0.1028	0.815 73	4.2359	1.4114	−0.145	1.127	0.6987	0.800 63	2.0535	1.3853	−0.083	1.259
0.2116	0.814 17	3.9746	1.4082	−0.188	1.232	0.7994	0.796 06	1.6727	1.3782	−0.039	1.181
0.3124	0.812 37	3.6585	1.4048	−0.206	1.306	0.9044	0.790 53	1.3627	1.3694	−0.011	1.115
0.4135	0.809 99	3.2178	1.4010	−0.186	1.323	1.0000	0.785 04	1.0694	1.3591	0.000	1.000
0.5018	0.807 59	2.8803	1.3970	−0.164	1.340						
Ethanol (1) + 1-Hexanol (2)											
0.0000	0.815 54	4.4862	1.4161	0.000	1.000	0.5903	0.803 38	2.2143	1.3930	−0.014	1.151
0.1094	0.814 16	4.0014	1.4126	−0.040	1.043	0.6925	0.799 77	1.8939	1.3864	0.011	1.140
0.2099	0.812 59	3.5373	1.4096	−0.058	1.065	0.8012	0.795 41	1.5741	1.3786	0.017	1.107
0.2971	0.810 99	3.1944	1.4064	−0.064	1.090	0.8990	0.790 82	1.3047	1.3700	0.010	1.056
0.3973	0.808 73	2.8285	1.4026	−0.047	1.115	1.0000	0.785 04	1.0694	1.3591	0.000	1.000
0.5015	0.806 05	2.4836	1.3976	−0.032	1.136						

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:

$$V^E = V - \sum x_i V_i \qquad (2)$$

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. Also shown for each set of data is the Redlich−Kister fitted curve.

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

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

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.

Interactions due to the intermolecular hydrogen bonding between the 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.

Table 3. Coefficients for the Redlich–Kister type Equation for Excess Molar Volume, V^E

system	B_0	B_1	B_2	B_3	B_4	σ^a
ethanol (1) + 3,3-dimethyl-2-butanol (2)	−2.20	−0.97	0.48	0.69		0.006
ethanol (1) + 2-ethyl-1-butanol (2)	−0.23	−0.24	0.08	0.27		0.002
ethanol (1) + 2-methyl-1-pentanol (2)	−0.09	−0.47	0.35	0.46	−0.26	0.003
ethanol (1) + 3-methyl-3-pentanol (2)	−2.43	−0.53	0.60	0.38		0.013
ethanol (1) + 4-methyl-2-pentanol (2)	−0.35	−0.29	0.15	0.23		0.001
ethanol (1) + 2-hexanol (2)	−0.07	−0.26	0.06	0.09		0.002
ethanol (1) + 3-hexanol (2)	−0.64	−0.67	−0.25	−0.34		0.006
ethanol (1) + 1-hexanol (2)	−0.12	−0.45	−0.02	0.17		0.003

[a] $\sigma = [\sum_1^N (V^E_{\text{exptl}} - V^E_{\text{calc}})^2/(N - \rho)]^{1/2}$ (N = no. of data points; p = no. of parameters).

Table 4. Coefficients for the Redlich–Kister type Equation for Viscosity Deviation, $\Delta\eta$

system	C_0	C_1	C_2	C_3	C_4	σ^a
ethanol (1) + 3,3-dimethyl-2-butanol (2)	1.33	−0.23	−0.63	−0.08		0.006
ethanol (1) + 2-ethyl-1-butanol (2)	0.49	0.03	0.22	−0.17		0.008
ethanol (1) + 2-methyl-1-pentanol (2)	0.49	−0.30	−0.05	0.25		0.006
ethanol (1) + 3-methyl-3-pentanol (2)	1.93	−1.12	−2.04	0.64	1.47	0.007
ethanol (1) + 4-methyl-2-pentanol (2)	1.01	0.14	0.18	−0.20		0.005
ethanol (1) + 2-hexanol (2)	0.82	0.06	−0.02	−0.16		0.006
ethanol (1) + 3-hexanol (2)	1.34	0.24	−0.11	−0.22		0.011
ethanol (1) + 1-hexanol (2)	0.55	−0.36	−0.04	0.40		0.002

[a] $\sigma = [\sum_1^N (\Delta\eta_{\text{exptl}} - \Delta\eta_{\text{calc}})^2/(N - p)]^{1/2}$ (N = no. of points; p = no. of parameters).

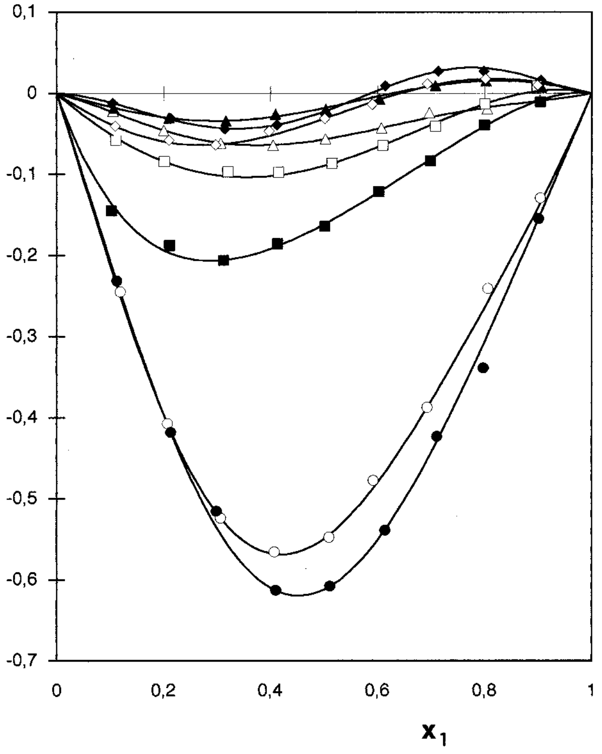

Figure 1. Excess volumes of ethanol (1) with 3,3-dimethyl-2-butanol (2) (○),2-ethyl-1-butanol (2) (△), 2-methyl-1-pentanol (2) (◆), 3-methyl-3-pentanol (2) (●), 4-methyl-2-pentanol (2) (□), 2-hexanol (2) (▲), 3-hexanol (2) (■), 1-hexanol (2) (◇). The solid curves have been calculated from eq 4.

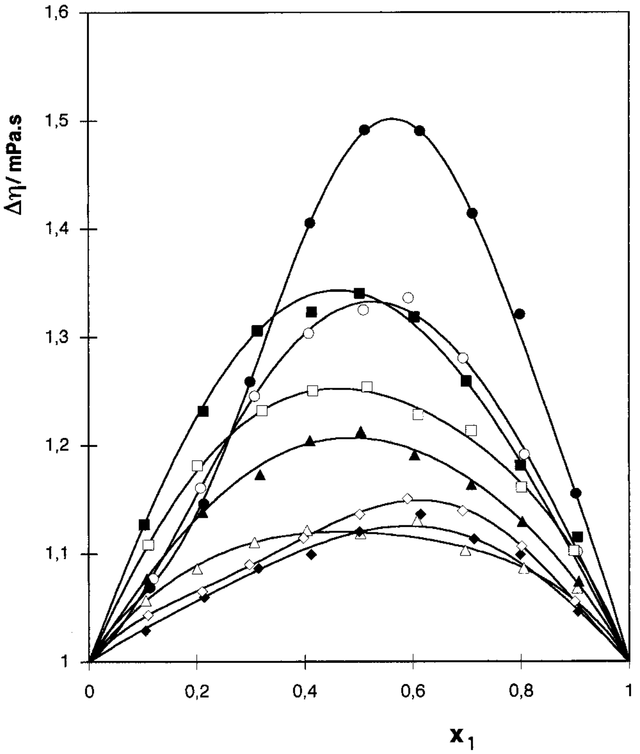

Figure 2. Viscosity deviations of ethanol (1) with 3,3-dimethyl-2-butanol (2) (○), 2-ethyl-1-butanol (2) (△), 2-methyl-1-pentanol (2) (◆), 3-methyl-3-pentanol (2) (●), 4-methyl-2-pentanol (2) (□), 2-hexanol (2) (▲), 3-hexanol (2) (■), 1-hexanol (2) (◇). The solid curves have been calculated from eq 5.

Figure 1 shows that the mixtures of ethanol with primary alcohols have negative V^E values in the low concentration range of ethanol, where the effect of molecular compacting between small and big molecules prevails, and slightly positive V^E values in the high concentration range of ethanol, where the breaking of hydrogen bonds leads to an increase of the mixture molar volume. The excess volumes become negative over the whole mole fraction range from secondary up to tertiary alcohols. The more negative values found for 3-methyl-3-pentanol and 3,3-dimethyl-2-butanol compared to those of all the other hexanol isomers may be attributed to their more spherical shape. This spherical shape makes it difficult to hydrogen bond between themselves, so that hydrogen bonding is mainly established with smaller molecules such as ethanol.

Comparing the V^E data obtained in this paper with the corresponding values obtained in a previous work (Aucejo et al., 1996) for methanol + the same hexanol isomers, the same trends can be observed. The effects were greater for methanol than ethanol. The viscosity deviation values (Figure 2) have trends with the hexanol isomers similar to those of the excess volume.

The composition dependences of excess molar volumes were correlated by a Redlich–Kister equation:

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

where x_1 is the mole fraction of ethanol and x_2 is the mole fraction of the hexanol isomer. For the ethanol + 2-methyl-1-pentanol system an extra fourth-order term was required for a good fit.

The values of the adjustable parameters B_i included in eq 4 were determined using a least-squares method. These values are reported in Table 3 together with the standard deviation (σ).

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

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

For the ethanol + 3-methyl-3-pentanol system an extra fourth-order term was required for a good fit. 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 standard deviation (σ).

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

Literature Cited

Aucejo, A.; Part, E.; Medina, P.; Sanchotello, M. Viscosity of Some n-Alkane/1-Chloroalkane Binary Mixtures. *J. Chem. Eng. Data* **1986**, *31*, 143−145.

Aucejo, A.; Burguet, M. C.; Muñoz, R.; Marqués, J. Densities, Viscosities, and Refractive Indices of Some n-Alkane Binary Liquid Systems at 298.15 K. *J. Chem. Eng. Data* **1995a**, *40*, 141−147.

Aucejo, A.; Burguet, M. C.; Muñoz, R.; Marqués, J. Densities, Viscosities, and Refractive Indices of the Binary Liquid Systems n-Alkane + Isomers of Hexane at 298.15 K. *J. Chem. Eng. Data* **1995b**, *40*, 871−874.

Aucejo, A.; Burguet, M. C.; Muñoz, R.; Sanchotello, M. Densities, Viscosities, and Refractive Indices of Some Binary Liquid Systems of Methanol + Isomers of Hexanol at 298.15 K. *J. Chem. Eng. Data* **1996**, *41*, 508−510.

Mulcahy, D. E. Flow equation for a Hared-capillary Viscosimeter. *J. Phys. D: Appl. Phys.* **1984**, *17*, 219−223.

Orts, M. J.; Medina, P.; Aucejo, A.; Burguet, M. C. Viscosity of n-Alcohol Binary Mixtures. *Can. J. Chem. Eng.* **1988**, *66*, 651−655.

Ratcliff, G. A.; Khan, M. A. Prediction of the Viscosities of Liquid Mixtures by a Group Solution Model. *Can. J. Chem. Eng.* **1971**, *49*, 125−129.

TRC-Tables-Non-Hydrocarbons; Thermodynamics Research Center, The Texas A&M University System: College Station, TX, 1995.

Wright, F. J. Influence of Temperature on Viscosity of Nonassociated Liquids. *J. Chem. Eng. Data* **1961**, *6*, 454−456.

Received for review April 2, 1996. Accepted June 26, 1996.⊗ This work was supported by the CAICYT, Project PA85-0076.

JE9601265

⊗ Abstract published in *Advance ACS Abstracts,* August 1, 1996.