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Densities and Viscosities of Binary Mixtures of 1,4-Dioxane with 1-Propanol and 2-Propanol at (25, 30, 35, and 40) °C

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Densities and viscosities for 1,4-dioxane with 1-propanol and 2-propanol mixtures have been measured as a function of mole fraction at atmospheric pressure at (25, 30, 35, and 40) °C. The calculated excess volumes (V^E) are positive over the whole range of composition in both systems. The V^E data were fitted by means of a Redlich−Kister type equation. Furthermore, McAllister's three-body-interaction model was used to correlate the kinematic viscosities of these systems.

Introduction

Many engineering problems require quantitative data on the viscosity and density of liquid mixtures. Binary systems of 1,4-dioxane with alcohols are interesting from the viewpoint of the low polarity of 1,4-dioxane and for the type of interaction between the components of the mixture. The literature shows that there are very few reports of viscosity or density data of 1,4-dioxane + alkanol systems.[1−4]

The present paper reports excess volumes and viscosities of binary mixtures of 1,4-dioxane with 1-propanol and 2-propanol at four temperatures at atmospheric pressure. Related to these systems we have not found published work on viscosities. For V^E data there is only one study at 30 °C.[1]

Experimental Procedures

Materials. All of the chemicals used were of analytical grade and purchased from commercial sources. The propanols (Merck, >99.5%) were used with no further purification other than being dried with molecular sieves. 1,4-Dioxane (Aldrich, 99+%) was further purified with sodium metal and redistilled. In all cases the water contents, determined according to the Karl Fischer method, were <0.03 vol %. Mixtures of 1,4-dioxane with propanols were prepared by mass in a 50 cm^3 Erlenmeyer flask provided with a joint stopper, using a Precisa 125A balance with a precision of ±0.1 mg. The possible uncertainty in mole fraction was estimated to be <±0.0002.

Apparatus and Procedure. The densities of the pure liquids and the mixtures were measured with an Anton Paar (DMA 602 + DMA 60) vibrating tube densimeter. It was calibrated with double-distilled water and air.[5,6] The temperatures were regulated using a circulating bath Heto DBT with a precision of ±0.01 K. The estimated uncertainty in density was $\pm 5 \times 10^{-6}$ g/cm^3.

The kinematic viscosities were measured with Ubbelhode viscometers with a Schott-Gerätte automatic measuring unit model AVS 350 provided with a transparent thermostat CT 1450/2, which makes possible temperature stabilization with a tolerance of 0.01 K. Four sets of viscometers were used with capillary diameters of 0.46 and 0.56 mm for kinematic ranges of 0.5−3 and 0.8−5 cSt, respectively. Each time 15 cm^3 of solution was measured. The calibration was carried out with double-distilled water. Quadruplicate measurements of flow times were reproducible within ±0.06%. The uncertainty of the viscosity measurement was <±0.5%.

Table 1. Densities and Viscosities for the Pure Liquids at Different Temperatures

		ρ /(g·cm^{-3})		η /(mPa·s)	
liquid	t/°C	exptl	lit.	exptl	lit.
dioxane	25	1.027882	1.02812[a]	1.196	1.1944[a]
	30	1.022219	1.02223[a] 1.02225[b]	1.101	1.0937[a]
	35	1.016595	1.01689[a]	1.014	1.0112[a]
	40	1.011033	1.01157[b]	0.9425	−
1-propanol	25	0.799765	0.799649[c] 0.79958[d]	1.967	1.967[d]
	30	0.795833	0.795648[c]	1.745	1.705[d,e]
	35	0.791619	0.791598[c] 0.79158[d]	1.542	1.500[d]
	40	0.787776	0.787495[c]	1.391	1.380[e] 1.336[d]
2-propanol	25	0.780942	0.780921[c] 0.78123[d]	2.081	2.052[d]
	30	0.776601	0.776719[c]	1.792	1.778[e] 1.779[d]
	35	0.772559	0.772417[c]	1.550	1.542[d]
	40	0.768128	0.768010[c] 0.76798[d]	1.352	1.331[e] 1.336[d]

[a] Reference 3. [b] Reference 5. [c] Reference 6 (interpolated values). [d] Reference 7. [e] Reference 8.

The kinematic viscosities (ν) were determined according to the equation

$$\nu = \eta/\rho = K(t - \theta) \tag{1}$$

where η is the absolute viscosity, ρ is the density, t is the flow time, θ is the Hagenbach correction, and K is the viscosimeter constant, determined by calibration.

Results and Discusion

The measured physical properties of the pure liquids together with literature values are included in Table 1. The experimental densities, excess volumes, and dynamic viscosities at (25, 30, 35, and 40) °C are listed in Tables 2 and 3.

Excess Volumes. The excess volumes V^E can be computed from experimental density data using the relationship

$$V^E = x_1M_1(1/\rho_m - 1/\rho_1) + x_2M_2(1/\rho_m - 1/\rho_2) \tag{2}$$

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Table 2. Experimental Densities, ρ, Excess Volumes, V^E, and Dynamic Viscosities, η, for 1,4-Dioxane (1) + 1-Propanol (2) Mixtures

x_1	ρ/(g·cm^{-3})	V^E/(cm^3·mol^{-1})	η/(mPa·s)
25 °C			
0.0000	0.799765	0.0000	1.967
0.0923	0.823185	0.0268	1.609
0.1220	0.830606	0.0340	1.499
0.2236	0.855475	0.0666	1.284
0.2793	0.868884	0.0707	1.223
0.3323	0.881414	0.0838	1.158
0.3964	0.896308	0.1051	1.106
0.4347	0.905137	0.1079	1.057
0.5294	0.926644	0.1158	1.040
0.5833	0.938756	0.1109	1.028
0.6365	0.950512	0.1091	1.028
0.6538	0.954351	0.1041	1.033
0.7379	0.972634	0.0924	1.051
0.8132	0.988852	0.0672	1.085
0.8989	1.006910	0.0419	1.117
1.0000	1.027882	0.0000	1.196
30 °C			
0.0000	0.795833	0.0000	1.745
0.0923	0.818982	0.0368	1.420
0.1220	0.826204	0.0486	1.332
0.2236	0.851071	0.0704	1.150
0.2793	0.864292	0.0881	1.084
0.3323	0.876685	0.1046	1.065
0.3964	0.891584	0.1110	1.014
0.4347	0.900269	0.1233	0.9719
0.5294	0.921553	0.1364	0.9553
0.5833	0.933540	0.1342	0.9490
0.6365	0.945281	0.1255	0.9503
0.6538	0.949065	0.1257	0.9567
0.7379	0.967225	0.1090	0.9745
0.8132	0.983298	0.0851	0.9921
0.8989	1.001299	0.0529	1.028
1.0000	1.022219	0.0000	1.101
35 °C			
0.0000	0.791619	0.0000	1.542
0.0923	0.814473	0.0516	1.289
0.1220	0.821684	0.0693	1.209
0.2236	0.846269	0.0941	1.057
0.2793	0.859366	0.1156	0.9926
0.3323	0.871772	0.1239	0.9698
0.3964	0.886483	0.1389	0.9229
0.4347	0.895173	0.1458	0.8966
0.5294	0.916414	0.1507	0.8788
0.5833	0.928350	0.1462	0.8777
0.6365	0.939949	0.1435	0.8792
0.6538	0.943713	0.1404	0.8791
0.7379	0.961719	0.1299	0.9054
0.8132	0.977600	0.1135	0.9184
0.8989	0.995623	0.0684	0.9533
1.0000	1.016595	0.0000	1.014
40 °C			
0.0000	0.787776	0.0000	1.391
0.0923	0.810214	0.0760	1.179
0.1220	0.817438	0.0875	1.100
0.2236	0.841754	0.1206	0.9732
0.2793	0.854820	0.1359	0.9135
0.3323	0.867107	0.1465	0.8894
0.3964	0.881695	0.1625	0.8503
0.4347	0.890339	0.1675	0.8243
0.5294	0.911470	0.1675	0.8135
0.5833	0.923253	0.1684	0.8149
0.6365	0.934789	0.1631	0.8185
0.6538	0.938523	0.1599	0.8196
0.7379	0.956378	0.1500	0.8374
0.8132	0.972219	0.1258	0.8578
0.8989	0.990126	0.0779	0.8870
1.0000	1.011033	0.0000	0.9425

Table 3. Experimental Densities, ρ, Excess Volumes, V^E, and Dynamic Viscosities, η, for 1,4-Dioxane (1) + 2-Propanol (2) Mixtures

x_1	ρ/(g·cm^{-3})	V^E/(cm^3·mol^{-1})	η/(mPa·s)
25 °C			
0.0000	0.780942	0.0000	2.081
0.0380	0.790991	0.0350	1.821
0.1103	0.809840	0.1025	1.479
0.2130	0.836283	0.1753	1.224
0.3316	0.866391	0.2251	1.075
0.3634	0.874352	0.2360	1.055
0.4318	0.891485	0.2411	1.014
0.5184	0.912867	0.2427	0.9926
0.6312	0.940384	0.2223	0.9873
0.6592	0.947146	0.2145	0.9898
0.7870	0.977668	0.1665	1.048
0.8910	1.002320	0.0951	1.101
0.9350	1.012800	0.0484	1.131
1.0000	1.027882	0.0000	1.196
30 °C			
0.0000	0.776601	0.0000	1.792
0.0380	0.786588	0.0360	1.578
0.1103	0.805224	0.1146	1.312
0.2130	0.831467	0.1931	1.099
0.3316	0.861437	0.2407	0.9775
0.3634	0.869292	0.2575	0.9613
0.4318	0.886292	0.2661	0.9242
0.5184	0.907529	0.2701	0.9100
0.6312	0.934973	0.2425	0.9117
0.6592	0.941716	0.2331	0.9161
0.7870	0.972202	0.1736	0.9473
0.8910	0.996609	0.1114	1.010
0.9350	1.007048	0.0630	1.048
1.0000	1.022219	0.0000	1.101
35 °C			
0.0000	0.772559	0.0000	1.550
0.0380	0.782287	0.0559	1.380
0.1103	0.800743	0.1410	1.170
0.2130	0.826842	0.2174	0.9913
0.3316	0.856502	0.2761	0.8870
0.3634	0.864397	0.2842	0.8738
0.4318	0.881247	0.2964	0.8492
0.5184	0.902384	0.2967	0.8350
0.6312	0.929684	0.2655	0.8370
0.6592	0.936370	0.2571	0.8392
0.7870	0.966757	0.1879	0.8747
0.8910	0.991151	0.1124	0.9326
0.9350	1.001442	0.0705	0.9724
1.0000	1.016595	0.0000	1.014
40 °C			
0.0000	0.768128	0.0000	1.352
0.0380	0.777713	0.0659	1.218
0.1103	0.796013	0.1580	1.039
0.2130	0.821920	0.2411	0.8984
0.3316	0.851458	0.2979	0.8129
0.3634	0.859258	0.3115	0.8044
0.4318	0.876105	0.3164	0.7791
0.5184	0.897205	0.3108	0.7724
0.6312	0.924407	0.2766	0.7769
0.6592	0.931106	0.2642	0.7780
0.7870	0.961338	0.1961	0.8157
0.8910	0.985692	0.1139	0.8715
0.9350	0.995918	0.0735	0.8943
1.0000	1.011033	0.0000	0.9425

where x_i, M_i, and ρ_i designate the mole fraction, the molar mass, and the density of component i. ρ_m is the density of the mixture. The calculated V^E values are shown in Figures 1 and 2. For each mixture the excess volumes were fitted with a Redlich–Kister equation of the form

$$V^E/(\mathrm{cm^3{\cdot}mol^{-1}}) = x_1 x_2 \sum_{i=1}^{m} a_{i-1}(x_1 - x_2)^{i-1} \qquad (3)$$

The coefficients a_{i-1} and the standard deviation $\sigma(V^E)$, listed in Table 4, were estimated by the least-squares method. The standard deviation was calculated as

$$\sigma(V^E) = [\sum(V^E_{\mathrm{exptl}} - V^E_{\mathrm{calcd}})^2/(N-m)]^{1/2} \qquad (4)$$

where N is the number of experimental points and m is the number of coefficients in eq 3.

Figures 1 and 2 show that excess volumes exhibit positive values, increasing slightly with temperature. The V^E-x curves are almost symmetrical about $x = 0.5$. Only 1,4-dioxane + 1-propanol mixtures exhibit a maximum slightly shifted toward the dioxane-rich zone. Similar effects have been observed in other 1,4-dioxane + n-alkanol mixtures.[4]

Our values are similar to those previously reported at 30 °C.[1] For the mixture of 1,4-dioxane + 1-propanol our results are 0.006 cm^3·mol^{-1} higher and for the mixture of

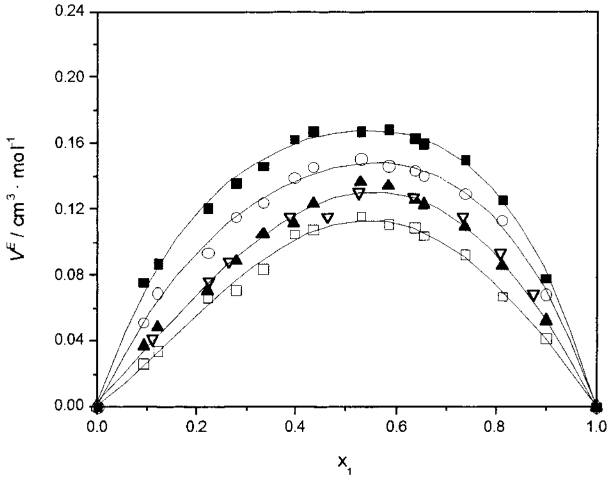

Figure 1. Excess molar volumes of 1,4-dioxane + 1-propanol: □, 25 °C; ▲, 30 °C; ○, 35 °C; ■, 40 °C; ▽, values from ref 1 at 30 °C.

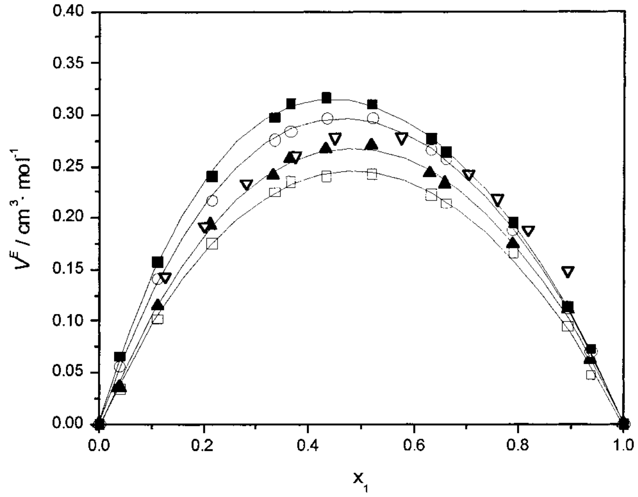

Figure 2. Excess molar volumes of 1,4-dioxane + 2-propanol: □, 25 °C; ▲, 30 °C; ○, 35 °C; ■, 40 °C; ▽, values from ref 1 at 30 °C.

Table 4. Coefficients of Equation 3 and Standard Deviations

t/°C	a_0	a_1	a_2	$\sigma(V^E)$/(cm^3·mol^{-1})
		1,4-Dioxane + 1-Propanol		
25	0.4449	0.09198	−0.09736	0.0027
30	0.5188	0.09167	−0.02069	0.0029
35	0.5854	0.09791	0.1740	0.0037
40	0.6633	0.03450	0.3223	0.0049
		1,4-Dioxane + 2-Propanol		
25	1.0006	−0.06855	−0.07829	0.0062
30	1.0861	−0.01784	−0.01771	0.0073
35	1.1706	−0.1794	0.2009	0.0035
40	1.2323	−0.2863	0.2981	0.0045

1,4-dioxane + 2-propanol our results are 0.01 cm^3·mol^{-1} smaller at the maximum.

The observed V^E may be analyzed in terms of several effects, which may be divided into physical, chemical, and geometrical contributions.[11] The physical interactions comprise mainly dispersion forces and nonspecific physical interactions giving a positive contribution. The chemical interactions involve the breaking up of H-bond structure, which tends to make V^E larger, and specific interactions such as H-bond formation and charge-transfer complexes, resulting in contraction of volume. Geometrical or structural contributions arising from geometrical fitting of one component into the other, due to differences in molar volume and free volumes between the components, lead to negative contributions to V^E. In our case the structural effect can be discarded, due to similar molar volumes between 1,4-dioxane and propanols, because 1,4-dioxane induces H-bond cleavage between alcohol molecules. By comparing 1,4-dioxane + propanols with acetonitrile + propanols systems,[10] it is possible to observe similar magnitudes of V^E, althought 1,4-dioxane has a negligible dipole moment compared with acetonitrile.

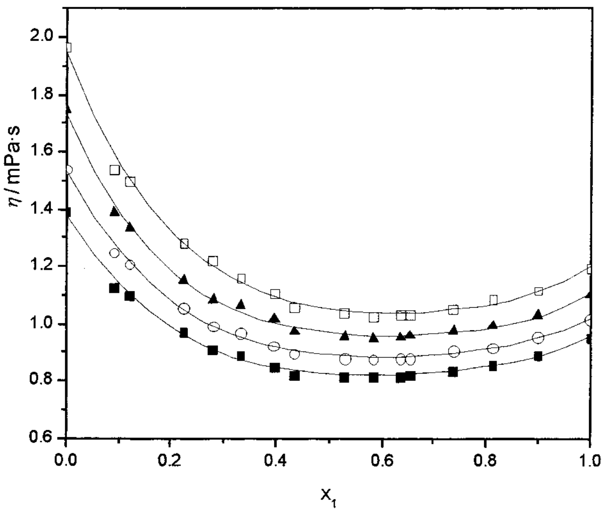

Figure 3. Viscosities of 1,4-dioxane + 1-propanol: □, 25 °C; ▲, 30 °C; ○, 35 °C; ■, 40 °C.

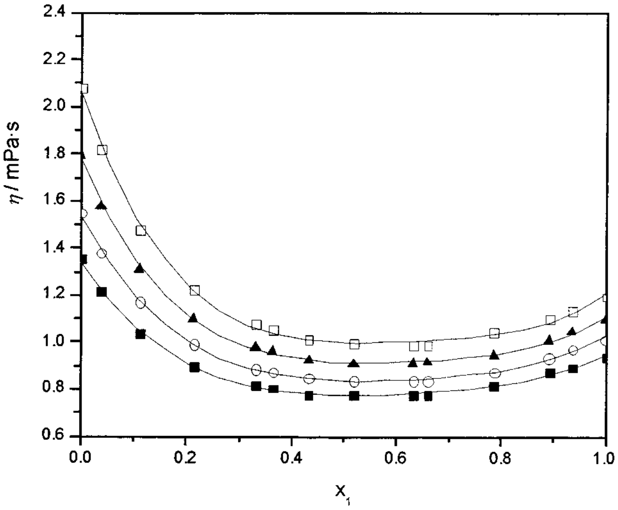

Figure 4. Viscosities of 1,4-dioxane + 2-propanol: □, 25 °C; ▲, 30 °C; ○, 35 °C; ■, 40 °C.

Viscosity. The analysis of V^E behavior is in agreement with the negative deviation of viscosities with respect to the absolute viscosity of pure liquids. Furthermore, the graphs of viscosity against mole fraction present a broad minimum around the composition $x_1 \approx 0.43-0.65$, as is observed in Figures 3 and 4.

The kinematic viscosities were correlated by means of the McAllister equation[12] considering a three-body interaction model, which for two-component mixtures gives

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

In eq 5, ν refers to the kinematic viscosity of the mixture of components 1 and 2, having mole fractions x_1 and x_2, respectively. ν_1 and ν_2 refer to the kinematic viscosities of

Table 5. Interactions Parameters of McAllister Equation and Percent Standard Deviations

t/°C	ν_{12}	ν_{21}	$(\Delta\%)_{av}$	$(\Delta\%)_{max}$
		1,4-Dioxane + 1-Propanol		
25	1.0147	0.9890	0.75	1.37
30	0.9605	0.8951	1.09	2.13
35	0.8911	0.8455	0.64	1.35
40	0.8340	0.7896	0.65	1.14
		1,4-Dioxane + 2-Propanol		
25	1.0447	0.8150	1.59	3.38
33	0.9548	0.7737	1.58	2.93
35	0.8791	0.7303	1.31	2.22
40	0.8195	0.6902	1.24	2.55

pure liquids 1 and 2, respectively, and ν_{12} and ν_{21} represent the interaction parameters obtained by nonlinear regression analysis. M_1 and M_2 have the same meaning as in eq 2. The percent average deviation, $(\Delta\%)_{av}$, was defined as

$$(\Delta\%)_{av} = \left[\frac{1}{N}\sum_{i}^{N}\delta_{i}^{2}\right]^{1/2} \qquad (6)$$

where $\delta_i = 100(\nu_i - \nu_{icalcd})/\nu_i$. ν_i and ν_{icalcd} are the experimental and calculated viscosities of a particular mole fraction of 1,4-dioxane. For each temperature, the percent maximal deviation $(\Delta\%)_{max}$ was determined as

$$(\Delta\%)_{av} = |\delta_i|_{max}$$

The values of the parameters ν_{12} and ν_{21}, along with those of percent average deviation and percent maximal deviation for both systems, are given in Table 5.

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