Excess Enthalpy, Density, Viscosity, and Speed of Sound for the Mixture Tetrahydropyran + 1-Butanol at (283.15, 298.15, and 313.15) K

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Excess enthalpies, densities, speeds of sound, and viscosities at (283.15, 298.15, and 313.15) K are reported for the binary mixture tetrahydropyran + 1-butanol. Excess molar volumes have been calculated from the densities. The deviations in both the speeds of sound and the absolute viscosities have also been estimated. All of the properties have been fit to Redlich−Kister equations.

Introduction

Excess properties and deviations of properties for liquids can reveal the existence of specific molecular interactions. Therefore, the systematic study of these properties has great importance in gaining a better knowledge of these interactions. Moreover, knowledge of the thermodynamic and transport properties is essential for the proper design of industrial processes. We report in this work measurements of excess enthalpies, densities, speeds of sound, and absolute viscosities for the binary mixture tetrahydropyran + 1-butanol at (283.15, 298.15, and 313.15) K. We have also calculated excess volumes, deviations of the speed of sound, and deviations of the absolute viscosity.

1-Butanol[1,2] is a substance that is heavily used in the pharmaceutical industry as a solvent, and an extraction agent, and in processes that produce medicins, flavors,[1] and other compounds. It is also used in clothing and plastics manufacturing and in wastewater treatment.[2] Finally, because of the fact that it is a highly associated liquid, 1-butanol is a very common substance in theoretical studies of hydrogen bonds and structural effects in excess thermodynamic properties.[3,4] Tetrahydropyran is used in polymerization processes[5] and also in the pharmaceutical industry as a reaction intermediate. As far as we know, there are no literature data for this binary system.

Materials

The compounds used were tetrahydropyran (purity better than 99%) and 1-butanol (purity better than 99%) from Aldrich. The claimed purities of these liquids were verified by gas−liquid chromatography (HP 6890) using a flame ionization detector. Experimental values of density, viscosity, and speed of sound for the pure components are reported in Table 1 along with the available bibliographic values.

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Apparatus and Procedure

The excess enthalpies were determined with a Thermometrics 2277 thermal activity monitor maintained at ±0.0002 K operating under constant flow conditions. Two Shimadzu LC-10ADVP HPLC pumps were used to drive the liquids. The pumps were calibrated for each liquid to relate the real flow to the programmed one. The uncertainty in the mole fractions of the mixtures was ±0.001. The calibration of the calorimeter was achieved with reference to the recommended values[6] of the mixture hexane + cyclohexane, the agreement between our data and the bibliographic data being within ±1%. Densities and speeds of sound were determined by means of a vibrating tube densimeter and an Anton Paar DSA48 sound analyzer, the uncertainties being ±0.00001 g·cm^{-3} and ±0.1 m·s^{-1}, respectively.

Kinematic viscosities were determined with a capillary Ubbelohde viscosimeter connected to an automatic Schott-Geräte AVS-440, for which the uncertainty in the flow time measurement is ±0.01 s, and the temperature was kept constant within ±0.01 K by means of a Schott-Geräte thermostat. At least four flow time measurements that did not differ by more than 0.05% from one another were performed for each composition and temperature, and the results were averaged. The uncertainty in the kinematic viscosity is estimated to be ±10^{-4} mm^2·s^{-1}.

The binary mixtures used to measure densities, speeds of sound, and viscosities were prepared by mass using a Sartorius analytical balance with a precision of ±10^{-5} g. Hence, the uncertainty in the mole fraction was estimated to be less than ±0.0001.

Results and Discussion

The excess molar volume, V^E, has been calculated from the density as

$$V^E = x_1 M_1(\rho^{-1} - {\rho_1}^{-1}) + x_2 M_2(\rho^{-1} - {\rho_2}^{-1}) \qquad (1)$$

where x_i, ρ_i, and M_i are the mole fraction, density, and

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Table 1. Densities, ρ, and Viscosities, η, of Pure Compounds at (283.15, 298.15, and 313.15) K and Comparison with Literature Data

		ρ/kg·m^{-3}		η/mPa·s		u/m·s^{-1}	
T/K		tetrahydropyran	1-butanol	tetrahydropyran	1-butanol	tetrahydropyran	1-butanol
283.15	exptl	894.72	816.92	1.0240	3.8690	1339.7	1292.0
	lit	894.08[a]	817.0[e]	1.0047[a]	3.87[e]	1335.8[a]	
298.15	exptl	880.83	805.73	0.8090	2.5609	1273.1	1243.1
	lit	877.2[b]	806.0[e]	0.764[b]	2.58[e]	1270.0[d]	1239.39[g]
		879.18[a]	805.75[b]	0.8008[f]	2.5710[b]	1255.0[a]	1239.3[h]
		879.16[c]		0.8005[a]			1241[i]
313.15	exptl	864.60	794.38	0.6278	1.7567	1197.6	1186.2
	lit	863.8[d]	794.6[e]	0.6494[a]	1.78[e]	1202.1[d]	1189.5[h]
						1199.8[a]	1190[i]

[a] Reference 9. [b] Reference 16. [c] Reference 17. [d] Reference 18. [e] Reference 19. [f] Reference 20. [g] Reference 21. [h] Reference 22. [i] Reference 23.

Table 2. Excess Enthalpies for the Mixture Tetrahydropyran (1) + 1-Butanol (2) at (283.15, 298.15, and 313.15) K

x_1	283.15 K	298.15 K	313.15 K
	H^E/kJ·mol^{-1}		
0.040	0.118	0.125	0.119
0.090	0.24	0.257	0.258
0.188	0.452	0.492	0.517
0.288	0.627	0.691	0.736
0.390	0.761	0.841	0.899
0.490	0.833	0.920	0.981
0.593	0.852	0.931	0.989
0.694	0.802	0.865	0.912
0.796	0.664	0.698	0.716
0.901	0.403	0.412	0.408
0.952	0.221	0.222	0.216

molar mass of the pure components, respectively, and ρ is the density of the mixture. From speeds of sound, u, and absolute viscosity ($\eta = \nu\rho$), the deviations in the speeds of sound, Δu, and absolute viscosity, respectively, were calculated as

$$\Delta u = u - u_1x_1 - u_2x_2 \quad (2)$$

$$\Delta\eta = \eta - \eta_1x_1 - \eta_2x_2 \quad (3)$$

where η_i and u_i are, respectively, the speeds of sound and absolute viscosities of pure components in the mixtures. u and η are the corresponding properties of the mixture. The experimental values of the excess properties and the deviations at (283.15, 298.15, and 313.15) K are reported in Tables 2−5.

All of the excess properties and deviations have been fit to the Redlich−Kister equation[7]

$$Y^E(\text{or } \Delta Y) = x_1(1 - x_1)\sum_{i=1}^{p} A_i(2x_1 - 1)^{i-1} \quad (4)$$

where Y^E denotes the excess property and ΔY denotes the

Table 3. Excess Volumes for the Mixture Tetrahydropyran (1) + 1-Butanol (2) at (283.15, 298.15, and 313.15) K

283.15 K			298.15 K			313.15 K		
	ρ	10^6V^E		ρ	10^6V^E		ρ	10^6V^E
x_1	kg·m^{-3}	m^3·mol^{-1}	x_1	kg·m^{-3}	m^3·mol^{-1}	x_1	kg·m^{-3}	m^3·mol^{-1}
0.1036	825.58	−0.018	0.0508	809.82	−0.005	0.1039	802.15	−0.004
0.2049	833.85	−0.025	0.1039	814.08	−0.013	0.2027	809.43	0.007
0.3039	841.76	−0.023	0.2056	822.12	−0.021	0.3254	818.28	−0.004
0.4059	849.75	−0.014	0.3050	829.77	−0.017	0.4063	824.00	0.003
0.4905	856.26	−0.003	0.4060	837.37	−0.004	0.4883	829.70	0.014
0.6081	865.20	0.014	0.4909	843.65	0.010	0.6215	838.80	0.034
0.7057	872.53	0.026	0.6079	852.23	0.027	0.7037	844.36	0.044
0.8027	879.78	0.033	0.7054	859.31	0.038	0.8037	851.10	0.049
0.8990	887.01	0.028	0.8047	866.47	0.045	0.8978	857.50	0.039
			0.9043	873.67	0.040			
			0.9580	877.60	0.028			

Table 4. Speeds of Sound and Deviation of the Speed of Sound for the Mixture Tetrahydropyran (1) + 1-Butanol (2) at (283.15, 298.15, and 313.15) K

283.15 K			298.15 K			313.15 K		
x_1	u/m·s^{-1}	Δu/m·s^{-1}	x_1	u/m·s^{-1}	Δu/m·s^{-1}	x_1	u/m·s^{-1}	Δu/m·s^{-1}
0.0448	1294.9	0.8	0.0471	1245.5	1.0	0.1081	1189.1	1.7
0.1051	1298.7	1.7	0.0972	1247.7	1.7	0.1937	1190.6	2.2
0.2010	1304.0	2.4	0.2026	1251.7	2.5	0.2954	1192.1	2.5
0.3026	1309.0	2.6	0.2903	1254.4	2.6	0.4021	1193.4	2.6
0.4115	1313.8	2.2	0.3266	1255.4	2.5	0.5032	1194.4	2.5
0.5038	1317.5	1.5	0.3987	1257.3	2.2	0.6035	1195.1	2.0
0.6065	1321.9	1.0	0.5146	1260.2	1.7	0.6615	1195.5	1.8
0.7044	1326.1	0.5	0.6077	1262.6	1.3	0.7114	1195.9	1.6
0.7888	1330.0	0.4	0.7128	1265.5	1.0	0.8138	1197.0	1.5
0.8925	1334.9	0.3	0.7996	1267.9	0.8	0.8906	1197.8	1.4
0.9533	1337.6	0.1	0.8595	1269.5	0.6	0.9373	1198.0	1.1
			0.8915	1270.4	0.6			
			0.9350	1271.5	0.3			

Table 5. Absolute Viscosities and Deviations of the Absolute Viscosity for the Mixture Tetrahydropyran (1) + 1-Butanol (2) at (283.15, 298.15, and 313.15) K

	η/mPa·s			$\Delta\eta$/mPa·s		
x_1	283.15 K	298.15 K	313.15 K	283.15 K	298.15 K	313.15 K
0.0478	3.3403	2.2945	1.6327	-0.3928	−0.1827	−0.0701
0.0969	2.9182	2.0561	1.4827	-0.6752	−0.3351	−0.1647
0.1984	2.2990	1.6619	1.2552	−1.0056	−0.5515	−0.2776
0.2880	1.9304	1.4256	1.0859	−1.1191	−0.6307	−0.3457
0.3973	1.6180	1.2224	0.9459	−1.1207	−0.6424	−0.3624
0.5005	1.4136	1.0866	0.8494	−1.0316	−0.5975	−0.3424
0.6788	1.1818	0.9310	0.7345	−0.7560	−0.4407	−0.2559
0.7023	1.1607	0.9162	0.7252	−0.7103	−0.4144	−0.2387
0.8041	1.0855	0.8645	0.6832	−0.4959	−0.2877	−0.1658
0.9024	1.0528	0.8316	0.6584	−0.2489	−0.1483	−0.0796

Table 6. Fitting Coefficients of the Redlich−Kister Equation for the Properties at (283.15, 298.15, and 313.15) K and Standard Deviations

	T/K	A_1	A_2	A_3	A_4	A_5	s
	283.15	−0.008	0.284	0.07	0.05	0.05	2×10^{-4}
$V^E \times 10^6$/m^3·mol^{-1}	298.15	0.046	0.316	−0.05	0.080	0.35	2×10^{-4}
	313.15	0.0623	0.299	0.168	−0.015	0.053	5×10^{-5}
	283.15	6.2	−13.1	7	6	−2	0.05
Δu/m·s^{-1}	298.15	6.9	−9.4	10	1.2	−3	0.02
	313.15	9.8	−6.6	−2	8.2	20	0.02
	283.15	3.35	0.87	0.58	0.2		3×10^{-3}
H^E/kJ·mol^{-1}	298.15	3.69	0.84	0.29	0.1		3×10^{-3}
	313.15	3.96	0.82	−0.10	0.1		3×10^{-3}
	283.15	−4.12	2.24	−1.7	1.2		4×10^{-3}
$\Delta\eta$/mPa·s	298.15	−2.40	1.30	−0.6	0.1		4×10^{-3}
	313.15	−1.39	0.67	0.0	−0.2		7×10^{-3}

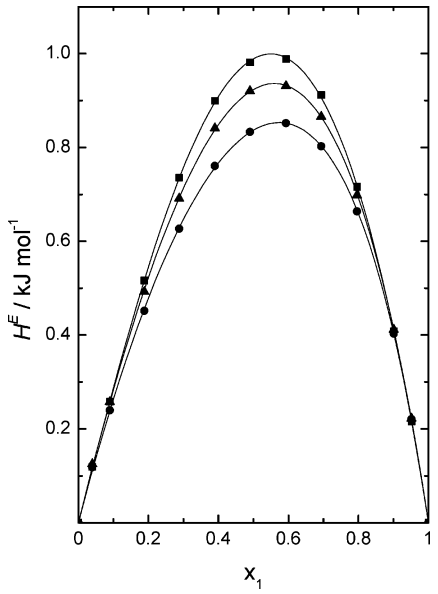

Figure 1. Excess enthalpies for the mixture tetrahydropyran (1) + 1-butanol (2): ●, 283.15; ▲, 298.15; ■, 313.15 K.

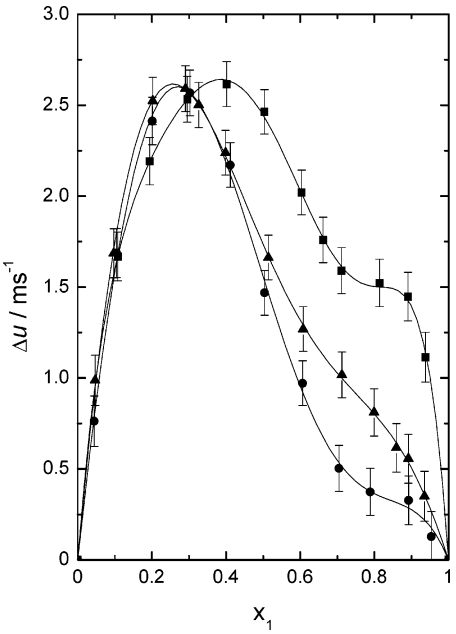

Figure 2. Deviations in the speed of sound and experimental uncertainty for the mixture tetrahydropyran (1) + 1-butanol (2): ●, 283.15; ▲, 298.15; ■, 313.15 K.

deviation in the property, x_1 is the mole fraction of component 1 in the mixture, and A_i are the fitting coefficients determined by the least-squares method. The parameters that best fit the experimental results are summarized in Table 6, together with the standard deviation, defined as

$$\sigma = \left[\frac{\sum (Y^E_{exp} - Y^E_{cal})^2}{N - p}\right]^{1/2} \quad (5)$$

where N and p are the number of experimental points and parameters, respectively.

Figures 1−4 show the excess molar property or deviation in the property for tetrahydropyran (1) + 1-butanol (2) plotted against the mole fraction of the cyclic ether at (283.15, 298.15, and 313.15) K. In these Figures, lines from fitting eq 4 are also included.

It can be observed that the excess enthalpies are positive over the whole composition range (Figure 1) and increase when the temperature increases.

The deviations in the speed of sound (Figure 2) are always positive and show an M-shaped curve with the absolute maxima between $x_1 = 0.3$ and 0.5. The values of the other maxima located in the region rich in tetrahydropyran significantly increase as the temperature increases. Related to the alcohol-rich region, it must be noted that

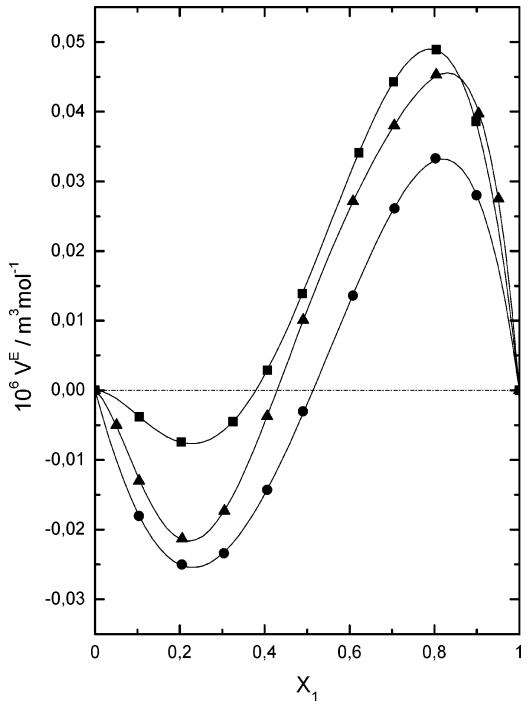

Figure 3. Excess volumes for the mixture tetrahydropyran (1) + 1-butanol (2): ●, 283.15; ▲, 298.15; ■, 313.15 K.

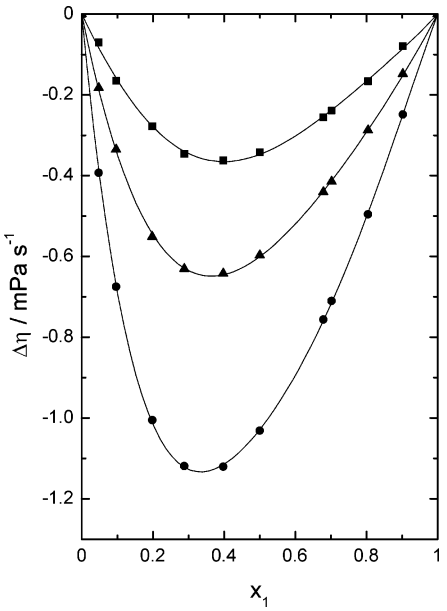

Figure 4. Deviations in the absolute viscosity for the mixture tetrahydropyran (1) + 1-butanol (2): ●, 283.15; ▲, 298.15; ■, 313.15 K.

the values of the deviations are very similar. Therefore, no conclusions can be drawn about the dependence of the speed-of-sound deviation on the temperature in this region given the experimental uncertainty. The excess volumes show sigmoidal behavior, being negative at low x_1 and positive at high x_1 (Figure 3).

Finally, the deviation in the absolute viscosities (Figure 4) is negative over the whole composition range, and the higher the temperature, the less negative the values, as is usual in mixtures with alcohols.[8−11]

Some authors have shown that the formation of solute−solvent structures leads to positive deviations in the viscosity,[12] but they have also pointed out that when one of the compounds is strongly associated the deviations are usually negative,[13,14] which seems to fit this case indeed. Attending to the reported values of viscosity deviation along with those of excess enthalpy, the prevailing effect for the mixture seems to be the breaking of hydrogen bonds existing between the butanol molecules. This can be corroborated by the fact that our excess enthalpy and absolute viscosity deviations follow the same pattern observed for the mixture 1-butanol + cyclohexane[10,15] in which no significant solute−solvent interactions are expected but only the breading of hydrogen bonds. However, the small values of excess volume and deviation of the speed of sound and the shape of their graphics show that more effects should be taken into account in the mixture process, such as structural ones. In fact, sigmoidal curves for the excess volume have been observed for mixtures containing 1-butanol and another compound showing dipole−dipole interactions.[11] Different effects may prevail either in the tetrahydropyran- or 1-butanol-rich region, although the tendency seems to be the disappearance of both the sigmoid and the M shape when the temperature rises. This behavior is probably due to a different dependence of the structure of the pure liquids on the temperature.

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