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Excess Enthalpy, Excess Volume, and Speed of Sound Deviation for the Mixtures β-Pinene + Ethanol and β-Pinene + 1-Propanol at (283.15, 298.15, and 313.15) K

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Excess enthalpies, densities, and speeds of sound at temperatures of (283.15, 298.15, and 313.15) K are reported for binary mixtures of β-pinene + ethanol and β-pinene + 1-propanol. Excess molar volumes have been calculated from the densities. The deviations in the speeds of sound have also been estimated. All of the properties have been fitted to Padé approximants. Excess molar enthalpies and excess molar volumes are positive for both mixtures, whereas the speed of sound deviations show negative values. The values of these properties are discussed in terms of the molecular interactions. The enthalpic and volumetric behaviors of the mixtures are compared with those of the mixtures of ethanol or 1-propanol with cyclohexane or methylcyclohexane, which are two simple hydrocarbons whose basic ring is similar to that of β-pinene.

Introduction

Essential oils are natural products responsible for the vital activity of aromatic plants from which they are extracted and are useful in the cosmetic, pharmaceutical, and food industries. From a chemical point of view, essential oils are mixtures formed by a large number of different compounds. Given their economical importance, a better knowledge of these mixtures is clearly relevant, and this also applies to the knowledge of their thermodynamic behavior. However, there have been few studies dedicated to this subject. For this reason, research on this topic seems advisable.

We have started a research program on the excess properties of mixtures containing compounds existing in essential oils of aromatic plants. In the first stage, the study does not focus on mixtures formed only by compounds in essential oils. Because these compounds are quite complex, it has been considered more fruitful to study mixtures of them with several common solvents with the aim of obtaining information about the interactions and structural effects involved in both pure compounds and their mixtures.

Mixtures of β-pinene (1-*S*-(−)-6,6-dimethylenebicyclo-[3.1.1]heptane), one of the most commonly found compounds in a number of essential oils, with two alkanols were chosen. There are two reasons for this selection. The mixture of a hydrocarbon such as β-pinene with compounds having a specific interaction such as a hydrogen bond can provide interesting results regarding the interactions in these systems and also in other related systems composed of natural or manufactured mixtures.

Besides, our group is also studying the extraction of essential oil from aromatic plants using supercritical carbon dioxide. In this type of extraction, alkanols, specially ethanol and 1-propanol,[1] are commonly employed as modifiers. These modifiers are added to carbon dioxide to increase the polarity of the solvent, thus improving its performance in separating the most polar components. β-Pinene is not a very polar compound, but the presence of the modifier could affect its extraction. In this sense, information about the thermodynamic behavior of mixtures of β-pinene + an alkanol could be of interest for these extraction processes even if the temperature and pressure conditions are rather different.

The excess enthalpy, density, and speed of sound have been measured over the composition range for mixtures of β-pinene + ethanol and β-pinene + 1-propanol at (283.15, 298.15, and 313.15 K). From the experimental density and speed of sound values, excess volumes and speed of sound deviations have been calculated, respectively. The results are discussed in terms of the intermolecular interactions. Moreover, the results for excess properties are compared with those reported for mixtures of cyclohexane or methylcyclohexane with ethanol or 1-propanol because of the similarity of these hydrocarbons to β-pinene. As far as we know, there are no data for these mixtures. In fact, only six papers can be found in the literature concerning the thermodynamic properties of mixtures containing β-pinene.[2−7]

Experimental Section

Materials. The compounds used were 1*S*-(−)-6,6-dimethyl-2-methylenebicyclo[3.1.1]heptane (purity 99%) and ethanol (purity +99.9%) from Aldrich and 1-propanol (purity 99%) from Scharlau. The purities of these liquids were corroborated by gas−liquid chromatography (HP 6890) using a flame ionization detector. No further purification was attempted. Experimental values of the density and speed of sound for the pure components are reported in Table 1 and compared with the available bibliographic values.[3−11] In general terms, good agreement can be observed. Significant differences appear for β-pinene, but it must be taken into account that the bibliographic data

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

		ρ/kg·m^{-3}			u/m·s^{-1}		
T/K		β-pinene	ethanol	1-propanol	β-pinene	ethanol	1-propanol
283.15	expt	879.07	797.94	811.48	1356.8	1195.2	1257.9
	lit	877.95^{a}	797.9^{c}	811.6^{c}			
298.15	expt	866.97	785.12	799.66	1298.7	1143.3	1206.0
	lit	865.95^{a} 866.66^{b}	785.09^{c}	799.75^{c}		1143^{e}	1206^{e}
313.15	expt	855.50	772.53	787.76	1232.8	1093.8	1155.1
	lit	853.95^{a}	772.1^{c} 772.97^{d}	787.5^{c}		1093^{e}	1155^{e}

[a] Reference 8. [b] Reference 3. [c] Reference 9. [d] Reference 10. [e] Reference 11.

Table 2. Excess Molar Enthalpies for the Mixtures of β-Pinene at (283.15, 298.15, and 313.15) K

	H^{E}/J·mol^{-1}				H^{E}/J·mol^{-1}				H^{E}/J·mol^{-1}		
x_1	283.15 K	298.15 K	313.15 K	x_1	283.15 K	298.15 K	313.15 K	x_1	283.15 K	298.15 K	313.15 K
					β-Pinene (1) + Ethanol (2)						
0.071	109	146	181	0.496	457	587	793	0.864	440	510	700
0.142	206	270	340	0.599	489	607	835	0.930	353	390	575
0.269	334	437	564	0.689	490	605	831	0.964	278	325	395
0.394	417	539	715	0.773	482	582	800				
					β-Pinene (1) + 1-Propanol (2)						
0.067	61	89	116	0.488	373	539	742	0.855	360	533	682
0.135	127	177	243	0.585	403	586	802	0.926	282	409	519
0.263	236	336	462	0.677	416	613	822	0.970	198	262	331
0.380	316	456	626	0.764	406	587	788				

have been calculated with a correlation equation whose results shows uncertainties around 1 kg·m^{-3}. In fact, some of the densities[12] used in the correlation correspond to a product of 97% purity, and all of the impurities are compounds that are less dense than β-pinene. This would explain why our values are higher. For a product similar to ours,[3] the results are much more similar.

Apparatus and Procedure. The excess enthalpies were determined with a Thermometrics 2277 thermal activity monitor maintained at ±0.0002 K and operating under constant flow conditions. Two Shimadzu LC-10ADVP HPLC pumps were used to drive the liquids. All of the equipment is located in a room whose temperature is (302.15 ± 0.2) K. The pumps were calibrated for each liquid to relate the real flow to the programmed one. The calibration was made by determining, with a Sartorius analytical balance with a precision of $\pm 10^{-5}$ g, the mass of liquid pumped during a controlled time interval for a suitable range of flow rates (usually from 0 to 0.5 cm^{3}·min^{-1}). A determination was made every 0.025 cm^{3}·min^{-1}. Given the uncertainty in the flow rate, the uncertainty in the mole fractions of the mixtures was estimated to be ±0.001. Once the pumps are calibrated, the excess enthalpy is measured at several total mixture flow rates to determine the best total flow rate, which is that leading to the highest absolute value of the excess enthalpy. For the systems reported in this article, the total flow rate was 0.1 cm^{3}·mol^{-1} for all of the mixtures. Because the flow rates are small, there is time enough to allow the mixture to reach the temperature of measurement.

Then the pumps are programmed in such a way that excess enthalpies are measured at selected mole fractions of the mixture. For each mole fraction, the calorimeter measures the power every 10 s for 30 min. The arithmetic average of these power data is used to calculate the excess enthalpy. The power readings show random variations (noise), but no periodic variations related to the pump pulses have been observed. The testing of the calorimeter was achieved with reference to recommended values[13] of the mixture hexane + cyclohexane, the agreement between our data and the bibliographic data being within ±1% of the maximum excess enthalpy value for the reference mixture. To compare their sensitivity values, the power measured against the total power released has been estimated for each pure liquid at the working temperatures through electric calibrations in which a known amount of power is dissipated in electric resistance. The sensitivities have been found to be very similar in all cases, differing in value by less than 1%.

Densities and speeds of sounds were obtained by means of an Anton Paar DSA48 vibrating tube densimeter and sound analyzer. Following the proposal of Troncoso et al.,[14] we connected this apparatus to a personal computer through an RS-232 connection. This arrangement leads to uncertainties in the measured properties of ±0.01 kg·m^{-3} and ±0.1 m·s^{-1}. In these measurements, the composition of the binary mixtures was determined by mass using a Sartorius analytical balance with a precision of $\pm 10^{-5}$ g. Hence, the uncertainty in the mole fraction was estimated to be less than ±0.0001.

Results and Discussion

Excess enthalpies are listed in Table 2, densities and excess volumes can be found in Table 3, and speeds of sound and speed of sound deviations are gathered in Table 4. The excess enthalpies, excess volumes, and speed of sound deviation values have been plotted in Figures 1 to 6. The speed of sound deviations, Δu, were calculated through the expression

$$\Delta u = u - x_1 u_1 - x_2 u_2 \qquad (1)$$

where u is the speed of sound in the mixture, u_i is the speed of sound in pure component i, and x_i is the mole fraction of component i.

The data of the excess properties and also those of the speed of sound deviations cannot be fitted to the usual Redlich−Kister equation. Therefore, they have been ad-

Table 3. Densities and Excess Molar Volumes for Mixtures of β-Pinene at (283.15, 298.15, and 313.15) K

283.15 K						298.15 K						313.15 K					
x_1	ρ / kg·m^{-3}	10^6V^E / m^3·mol^{-1}	x_1	ρ / kg·m^{-3}	10^6V^E / m^3·mol^{-1}	x_1	ρ / kg·m^{-3}	10^6V^E / m^3·mol^{-1}	x_1	ρ / kg·m^{-3}	10^6V^E / m^3·mol^{-1}	x_1	ρ / kg·m^{-3}	10^6V^E / m^3·mol^{-1}	x_1	ρ / kg·m^{-3}	10^6V^E / m^3·mol^{-1}
β-Pinene (1) + Ethanol (2)																	
0.0507	807.27	0.066	0.6019	861.60	0.193	0.0502	794.53	0.058	0.6017	849.06	0.234	0.0520	782.17	0.080	0.6014	836.54	0.352
0.1012	815.62	0.095	0.6981	866.52	0.187	0.1022	803.02	0.105	0.6999	854.18	0.223	0.1041	790.76	0.126	0.6979	841.70	0.342
0.2046	829.52	0.145	0.7932	870.77	0.173	0.1999	816.23	0.163	0.7626	857.17	0.199	0.2043	804.04	0.222	0.8090	846.76	0.332
0.3015	839.85	0.170	0.8762	874.13	0.144	0.3045	827.43	0.200	0.8900	862.45	0.154	0.3029	814.57	0.278	0.8844	850.12	0.262
0.4042	848.66	0.189	0.9355	876.41	0.107	0.4019	835.85	0.221	0.9415	864.49	0.109	0.4046	823.44	0.313	0.9356	852.26	0.207
0.5145	856.44	0.192	0.9799	878.19	0.046	0.5000	842.91	0.231	0.9800	866.07	0.050	0.4981	830.17	0.342	0.9850	854.60	0.069
β-Pinene (1) + 1-Propanol (2)																	
0.0505	818.13	0.011	0.5990	861.68	0.143	0.0530	806.47	0.024	0.6005	849.44	0.188	0.0514	794.24	0.041	0.6004	837.06	0.311
0.1024	824.20	0.031	0.7026	866.65	0.158	0.1036	812.35	0.043	0.6990	854.20	0.197	0.1021	800.04	0.076	0.7051	842.20	0.319
0.2046	834.58	0.060	0.8026	871.06	0.144	0.2039	822.40	0.082	0.7931	858.43	0.175	0.2032	810.14	0.132	0.7928	846.14	0.306
0.3046	843.01	0.093	0.8834	874.33	0.122	0.3038	830.81	0.116	0.8937	862.59	0.130	0.3070	818.69	0.201	0.8931	850.44	0.245
0.4050	850.35	0.106	0.9489	876.85	0.090	0.3966	837.49	0.146	0.9426	864.54	0.093	0.4050	825.65	0.249	0.9407	852.42	0.198
0.5035	856.46	0.129	0.9812	878.27	0.032	0.5122	844.67	0.171	0.9834	866.31	0.022	0.5007	831.57	0.287	0.9786	854.11	0.127

Table 4. Speeds of Sound and Speed of Sound Deviation for Mixtures of β-Pinene 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}	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}
β-Pinene (1) + Ethanol (2)																	
0.0507	1209.5	6.1	0.6019	1309.4	16.9	0.0502	1156.2	5.1	0.6017	1249.8	13.0	0.0520	1104.8	3.8	0.6014	1189.8	12.4
0.1012	1222.5	10.9	0.6981	1320.5	12.5	0.1022	1168.9	9.7	0.6999	1260.6	8.5	0.1041	1116.6	8.3	0.6979	1198.7	7.9
0.2046	1246.3	18.0	0.7932	1330.4	7.0	0.1999	1189.9	15.5	0.7626	1264.9	3.1	0.2043	1135.7	13.5	0.8090	1207.0	0.8
0.3015	1265.4	21.5	0.8762	1339.3	2.5	0.3045	1209.0	18.4	0.8900	1280.4	−1.2	0.3029	1151.7	15.8	0.8844	1213.6	−3.1
0.4042	1282.4	21.9	0.9355	1345.8	−0.6	0.4019	1224.1	18.3	0.9415	1286.3	−3.3	0.4046	1167.0	17.0	0.9356	1221.9	−2.0
0.5145	1298.8	20.4	0.9799	1353.4	−0.2	0.5000	1237.4	16.4	0.9800	1294.5	−1.1	0.4981	1178.5	15.5	0.9850	1228.9	−1.8
β-Pinene (1) + 1-Propanol (2)																	
0.0505	1265.6	2.7	0.5990	1321.2	4.1	0.0530	1212.9	2.0	0.6005	1261.8	0.1	0.0514	1160.5	1.4	0.6004	1202.0	0.2
0.1024	1272.7	4.7	0.7026	1328.8	1.4	0.1036	1219.0	3.4	0.6990	1268.6	−2.2	0.1021	1165.7	2.7	0.7051	1206.4	−2.7
0.2046	1285.3	7.2	0.8026	1336.3	−1.0	0.2039	1229.7	4.8	0.7930	1275.4	−4.1	0.2032	1175.0	4.1	0.7928	1213.3	−3.9
0.3046	1296.0	8.0	0.8834	1342.6	−2.7	0.3038	1239.1	4.9	0.8937	1283.3	−5.5	0.3070	1183.4	4.5	0.8931	1222.1	−3.1
0.4050	1305.5	7.5	0.9488	1348.5	−3.2	0.3966	1246.9	4.1	0.9426	1287.9	−5.5	0.4050	1190.4	3.8	0.9407	1225.6	−2.5
0.5035	1313.7	6.0	0.9812	1352.9	−2.0	0.5122	1255.7	2.2	0.9834	1293.6	−3.6	0.5007	1196.5	2.5	0.9786	1228.9	−0.9

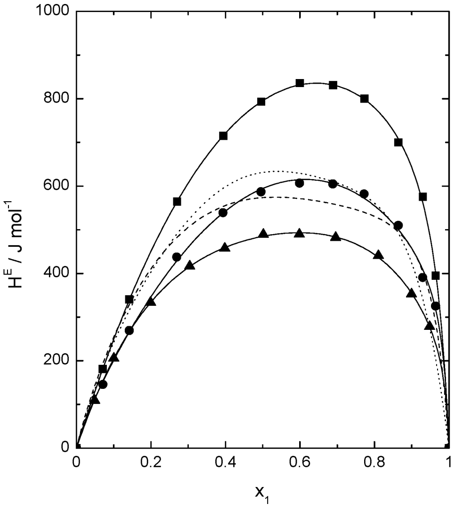

Figure 1. Excess molar enthalpies for the mixture β-pinene (1) + ethanol (2): ▲, 283.15 K; ●, 298.15 K; ■, 313.15 K. They are also represented by the excess molar enthalpies at 298.15 K of the mixtures cyclohexane (···) (ref 15) or methylcyclohexane (- - -) (ref 23) + ethanol. The hydrocarbon is component 1.

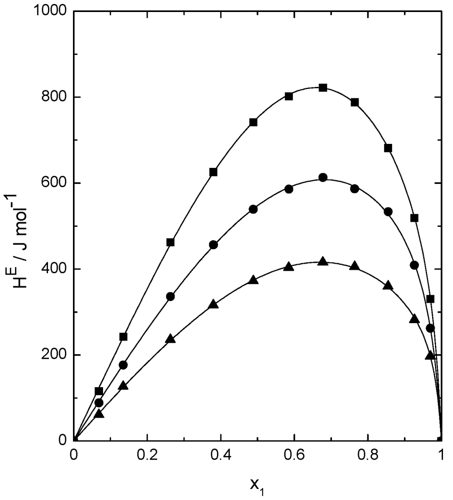

Figure 2. Excess molar enthalpies for the mixture β-pinene (1) + 1-propanol (2): ▲, 283.15 K; ●, 298.15 K; ■, 313.15 K.

justed to the following equation

$$Y = \frac{x_1x_2\sum_{i=0}^{p}A_i(2x_1 - 1)^i}{1 + \sum_{j=1}^{q}B_j(2x_1 - 1)^i} \qquad (2)$$

that is of the Padé approximant type. The symbol Y denotes the property H^E/J·mol^{-1}, V^E/10^{6}m^3·mol^{-1}, or speed of sound deviation Δu/m·s^{-1}, x_i is the mole fraction of component i, and A_i and B_j are adjustable coefficients. The fitting was carried out by using a Levenberg−Marquardt algorithm. The adjusting coefficients are listed in Table 5 along with the corresponding standard deviations defined by

$$\sigma = \left[\frac{\sum_m (Y^{\text{exptl}} - Y^{\text{calcd}})^2}{m - n}\right]^{1/2} \qquad (3)$$

where Y^{exptl} and Y^{calcd} are the experimental and calculated

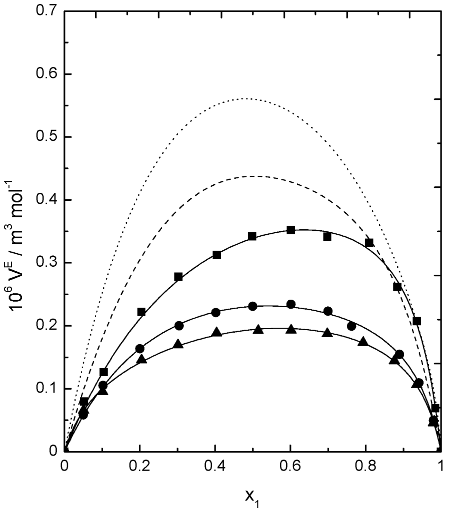

Figure 3. Excess molar volumes for the mixture β-pinene (1) + ethanol (2): ▲, 283.15 K; ●, 298.15 K; ■, 313.15 K. They are also represented by the excess molar volumes at 298.15 K of the mixtures cyclohexane (···) (ref 21) or methylcyclohexane (- - -) (ref 26) + ethanol. The hydrocarbon is component 1.

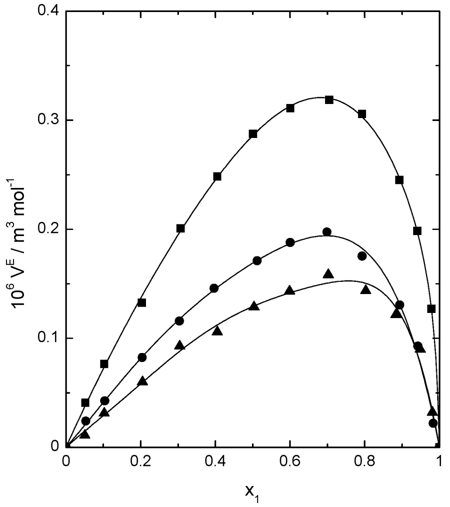

Figure 4. Excess molar volumes for the mixture β-pinene (1) + 1-propanol (2): ▲, 283.15 K; ●, 298.15 K; ■, 313.15 K.

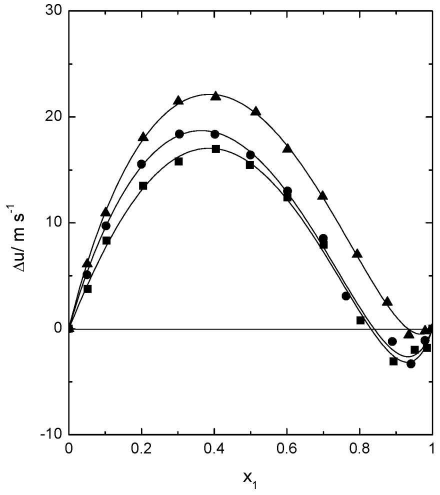

Figure 5. Speed of sound deviation for the mixture β-pinene (1) + ethanol (2): ▲, 283.15 K; ●, 298.15 K; ■, 313.15 K.

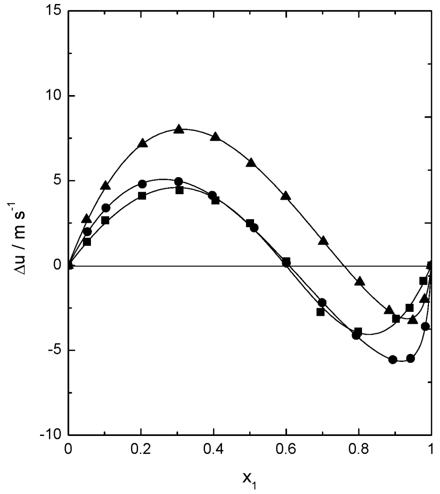

Figure 6. Speed of sound deviation for the mixture β-pinene (1) +1-propanol (2): ▲, 283.15 K; ●, 298.15 K; ■ 313.15 K.

values of property Y, m is the number of experimental points, and n is the number of coefficients used in the fitting equation. The curves obtained are also represented in the corresponding figures.

The excess enthalpies are positive over the whole composition range for mixtures of hydrocarbon β-pinene with both alkanols at all temperatures. They increase as the temperature increases, a usual characteristic near room temperature and atmospheric pressure in mixtures containing alkanols. However, the variation with temperature is different for 1-propanol than for ethanol. For 1-propanol, a regular variation is observed, whereas for ethanol there is a much greater gap between 313.15 K and 298.15 K than between 298.15 K and 283.15 K. As a result, the values of the maxima are very similar for mixtures of β-pinene with both alkanols at the higher temperatures, whereas they are clearly greater (about 75 $J \cdot mol^{-1}$) for the mixture with ethanol than for the mixture with 1-propanol at 283.15 K.

The positive values of the excess enthalpies point out that the prevailing energetic factor in the mixing process is the breaking of interactions. In this case, the most important contribution would come from the breaking of the hydrogen bonds of the alkanols. The interactions existing between the molecules of β-pinene will also be broken, but their strength is obviously smaller than those of hydrogen bonds. Moreover, a negative contribution can be expected from the possibility of interaction between the hydrogen atom of the OH group of alkanol and the electronic charge in the double bond of β-pinene, but this interaction would be not strong enough to match the breaking of the hydrogen bonds, which will then rule the energetic behavior of the mixtures.

It can be seen in Figures 1 and 2 that the excess enthalpy curves are skewed with the maxima lying in the zone rich in hydrocarbon. The asymmetry is more pronounced in the mixtures with 1-propanol, which show the maxima at about $x_1 = 0.7$, whereas those of mixtures with ethanol are placed at about $x_1 = 0.6$. This skewedness arises from the fact that the molecules involved in the mixtures are asymmetrical and very different each other in nature and geometry. This asymmetry is the main cause of the impossibility of fitting the data to the Redlich−Kister equation.

Another noticeable feature of the curves corresponding to the β-pinene + ethanol mixture is a certain "flatness" that is more marked at lower temperatures. In fact, this is the consequence of the rapid increase of the excess enthalpy to values near the maximum. An explanation can be found by taking into account the very different natures of the alkanol and the hydrocarbon. As we have verified, methanol is not completely miscible with β-pinene. Ethanol

Table 5. Fitting Coefficients, A_i and B_i, for Equation 2, and Standard Deviations, σ, Determined from Equation 2

Y	T/K	A_0	A_1	A_2	A_3	A_4	B_1	B_2	σ
				β-Pinene (1) + Ethanol (2)					
H^E/J·mol^{-1}	283.15	1939	−1564	809	−671		−0.976		3
	298.15	2378	723	−1390				−0.927	9
	313.15	3182	−1813	269			−0.917		6
10^6·V^E/m^3·mol^{-1}	283.15	0.776	0.112	−0.194				−0.766	0.003
	298.15	0.924	−0.220				−0.321	−0.446	0.003
	313.15	1.356	−0.136				−0.386	−0.391	0.008
Δu/m·s^{-1}	283.15	82.8	−49.2	−53.7				−0.437	0.3
	298.15	66.7	−58.0	−59.1				−0.452	0.6
	313.15	62.5	−48.9	−68.9				−0.498	0.6
				β-Pinene (1) + 1-Propanol (2)					
H^E/J·mol $^{-1}$	283.15	1517	−634	−282			−0.958		3
	298.15	2190	−793	−370			−0.931		4
	313.15	3009	−1193	−703			−0.945		3
10^6V^E/m^3·mol^{-1}	283.15	0.516	0.297	0.249	0.513	0.359			0.006
	298.15	0.675	0.420	0.397	0.266		−1.738	0.696	0.004
	313.15	1.144	−0.422	−0.211	−0.157		−0.974		0.003
Δu/m·s^{-1}	283.15	24.5	−60.1	24.2			−0.941		0.1
	298.15	9.5	−49.1	24.2			−0.962		0.1
	313.15	9.5	−47.8				−0.612	0.389	0.2

is miscible, but the dissimilarity with β-pinene will still be great and the mixing will then lead to a rapid and pronounced disruption of the structure of ethanol. This is confirmed by the fact that mixtures with 1-propanol whose hydrocarbon chain is longer do not show that flatness. Instead, they exhibit a steady increase of the values of excess enthalpy with mole fraction until the maximum is reached.

The excess volumes follow the pattern described for excess enthalpies. They are also positive throughout, as would expected from the positive values of the excess enthalpies. Also, the higher the temperature, the greater the value, as usual. Again, a flatness can be seen in the data corresponding to the mixture of β-pinene with ethanol that disappears in the case of 1-propanol. Therefore, the volumetric behavior of the mixtures depends mainly on the same causes as the enthalpic behavior. Nevertheless, there are two differences to be noted. On one hand, the excess volumes are clearly smaller for the mixture of β-pinene with 1-propanol than for the mixture of β-pinene with ethanol at all temperatures, whereas the excess enthalpies, as mentioned above, are similar in most cases. Then, steric factors play a significant role in the results in such a way that the molecules of β-pinene and 1-propanol can be more closely packed. On the other hand, the mixtures with both alkanols show an irregular variation of the excess volume with temperature, a variation that reproduces that of the excess enthalpy for the system β-pinene + ethanol. However, for β-pinene + 1-propanol the trend marked by excess enthalpies is not followed by excess volumes, and this also should probably be attributed to packing effects.

The speed of sound deviations are sigmoidal for all of the systems considered. The deviations are positive over most of the composition range, becoming negative in the zone rich in hydrocarbon: mole fractions of β-pinene are approximately equal to 0.92 at 283.15 K, 0.85 at 298.15 K, and 0.80 at 313.15 K. In the mixtures involving 1-propanol, the values are lower, and the composition range of negative values increases; it begins approximately at mole fractions equal to 0.62 at 298.15 K and 0.77 at 283.15 K. The variation of the speed of sound deviations with temperature in the intervals where they are positive is opposite to that observed for the excess properties (i.e., the values decrease as the temperature rises). It is remarkable that the curve corresponding to 313.15 K cuts across those of the remaining temperatures in the zone of negative values.

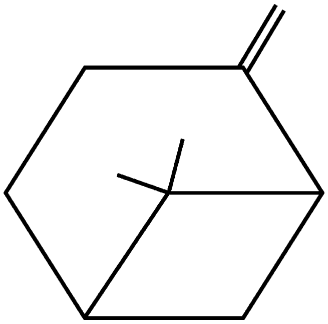

Figure 7. Schematic representation of β-pinene.

The interpretation of the speed of sound deviations is not as straightforward as those of the excess properties. The negative values can be justified on the grounds of the volume changes in the mixtures. The systems undergo an expansion, and then the molecules are at greater distances and the speed of sound travels more slowly. But it is evident from the positive values that the intermolecular distance cannot be the sole cause and that other contributions are included in the deviations.

Besides all of the former considerations, it is interesting to pay attention to the molecule of β-pinene. As shown in Figure 7, it is basically a six-carbon ring with a one-carbon bridge and a branch constituted by the methylene group. From this description, it seems worth comparing the properties measured with those of ethanol or 1-propanol with the similar but less complex hydrocarbons cyclohexane or methylcyclohexane because no data are available in the literature for the most similar methylenecyclohexane.

Excess enthalpies for cyclohexane + ethanol can be found, for example, in Stokes and Adamson,[15] Nagata and Kazuma,[16] or Lu and Benson.[17] Nagata and Kazuma[16] also provide values of excess enthalpies for the cyclohexane + 1-propanol mixture, values that have also been measured by Vesely et al.,[18] Singh et al.,[19] and Lu and Benson[20]. Excess volumes for mixtures with cyclohexane can be found in Marsh and Burfitt[21] for ethanol and in Singh et al.[19] for 1-propanol. For the mixtures involving methylcyclohexane, excess enthalpies have been reported by Brown et al.[22] and Nagata and Yamada[23] for ethanol and by Vesely et al.[24] and Letcher and Nevines[25] for ethanol and 1-propanol. Excess volumes of methylcyclohexane + ethanol or + 1-propanol have been measured by Letcher and Nevines.[26]

Table 6. Maximum Values of the Excess Properties for Mixtures of Cyclohexane and Methylcyclohexane with Ethanol and 1-Propanol at Several Temperatures

property	283.15 K	298.15 K	308.15 K	313.15 K	318.15 K
		Cyclohexane + Ethanol			
H^E/J·mol^{-1}	575^{a}	638^{a}	738^{a}		870^{a}
10^6V^E/ m^3·mol^{-1}	0.499^{b}	0.558^{b}			0.662^{b}
		Methylcyclohexane + Ethanol			
H^E/J·mol^{-1}		569^{c}	707^{c}		834^{c}
10^6V^E/ m^3·mol^{-1}			0.439^{d}		
		Cyclohexane + 1-Propanol			
H^E/J·mol^{-1}		622^{e} 605^{f}	738^{e} 834^{f}	810^{e}	884^{e}
10^6V^E/ m^3·mol^{-1}		0.426^{f}	0.660^{f}		
		Methylcyclohexane + 1-Propanol			
H^E/J·mol^{-1}			547^{g}		
10^6V^E/ m^3·mol^{-1}			0.249^{d}		

[a] Reference 15. [b] Reference 21. [c] Reference 23. [d] Reference 26. [e] Reference 18. [f] Reference 19. [g] Reference 25.

There is fair agreement between the different papers, so a representative one has been selected for each system and property, with preference given to the papers covering a wider range of temperature. There is an exception for the enthalpy data of Singh et al.[19] at 308.15 K—their values have also been selected. The maximum values for each mixture at several temperatures (when available) have been indicated in Table 6 along with the literature source.

In Figure 1, the excess enthalpy curves for mixtures of cyclohexane and methylcyclohexane with ethanol at 298.15 K have been plotted. The maximum values follow the order cyclohexane > β-pinene > methylcyclohexane.

Identical behavior is observed in mixtures with 1-propanol. Referring to this order, Letcher and Nevines[25] attribute the smaller excess enthalpy in mixtures with methylcyclohexane with respect to those with cyclohexane to the enhanced London dispersive interactions resulting from the increased number of carbons in the substituted hydrocarbon. β-Pinene should have, in principle, the greatest breaking effect because it is the largest, but the greatest endothermic effect that would be expected is partially compensated for by more enhanced London dispersive interactions and also by the aforementioned OH−double bond interaction.

It can be observed from the values in Table 6 that the maximum excess enthalpies when each hydrocarbon is mixed with ethanol or 1-propanol are very similar for the three hydrocarbons. This is in agreement with the close similarity between ethanol and 1-propanol. On this side, the values in the maxima for the mixtures of each alkanol with every hydrocarbon are not very different. (For example, the maxima range from 569 to 638 J·mol^{-1} in the case of ethanol.) Although β-pinene is rather different from cyclohexane and methylcyclohexane, the fact that all of the compounds are hydrocarbons is the main feature that determines the ability to break hydrogen bonds. This is corroborated by the excess enthalpies of the mixtures of ethanol with linear hydrocarbons such as hexane[27] (573 J·mol^{-1} in the maximum), heptane[28] (595 J·mol^{-1}), and octane[29] (644 J·mol^{-1}).

A feature to be mentioned in all of these systems is that the shape of the curves for cyclohexane and methylcyclohexane with ethanol exhibits a certain flatness, as seen for β-pinene. Once again, this feature confirms both the relevance of the hydrocarbon nature of the compounds and the origin of this flatness because cyclohexane and methylcyclohexane are not completely miscible with methanol.

In relation to the effect of the temperature on the excess enthalpy, it is the usual (i.e., the property values increase as the temperature increases). An enhancement of the breaking ability of β-pinene at higher temperatures is observed when mixed with ethanol, given that the maximum excess enthalpy for the mixture containing β-pinene at 313.15 K is very similar to that of methylcyclohexane[23] and only slightly lower than that of cyclohexane,[15] both at the higher temperature of 318.15 K. This enhancement is not as clear in the mixtures with 1-propanol where cyclohexane[18] and β-pinene at 313.15 K present very similar maximum values. (In fact, the excess enthalpy curves are almost identical.) However, Singh et al.[19] obtained a greater maximum value (834 J·mol^{-1}) at the lower temperature of 308.15 K. Although more data are necessary to assess which values are more correct, the results of Singh et al.[19] seem to deviate far from the trends depicted by the present comparison.

The excess volumes for the mixtures of cyclohexane and methylcyclohexane with ethanol at 298.15 K have been represented in Figure 3. It can be seen that the order of the maximum values is cyclohexane > methylcyclohexane > β-pinene.

The excess volume does not show the same order as the excess enthalpy, corroborating the relevance of the packing effects. The reciprocal hydrocarbon−alkanol accommodation is better for β-pinene when each alkanol is considered and for 1-propanol when each hydrocarbon is considered. The variation of the excess volume with the temperature, available for cyclohexane with both alkanols,[19,21] shows that the excess volume increases as the temperature increases. In any case, the difference between the corresponding properties is so great that the highest excess volumes for β-pinene (at 313.15 K) are lower than the lowest for cyclohexane (at 283.15 K).

Conclusions

Excess enthalpies, densities, and speeds of sound for mixtures of β-pinene + ethanol and β-pinene + 1-propanol have been measured at three temperatures, and the corresponding excess volumes and speed of sound deviations have been calculated. The values of the excess properties have been discussed, and we conclude that the main property responsible for the enthalpic and volumetric behavior is the breaking of the hydrogen bonds of the alkanols. Nevertheless, steric factors are acting in the mixtures, as indicated by the lower excess volume values for the mixtures with 1-propanol. The comparison with the six-carbon-ring hydrocarbons cyclohexane and methylcyclohexane has been carried out. This comparison shows that the enthalpic behavior of all of the mixtures is mainly determined by the breaking of hydrogen bonds of alkanols. The extent of the breaking effect is similar in all of the cyclic (and even linear) hydrocarbons. The relevance of steric factors to the volumetric behavior is strengthened by this comparison.

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