392 *J. Chem. Eng. Data* **2006,** *51,* 392−397

Excess Enthalpy, Density, and Speed of Sound for the Mixtures *β*-Pinene + 1-Butanol or 2-Butanol at (283.15, 298.15, and 313.15) K

Elisa Langa, Ana M. Mainar, Juan I. Pardo,* and José S. Urieta

Group of Applied Thermodynamics and Surfaces (GATHERS), Aragon Institute for Engineering Research (I3A),
Facultad de Ciencias, Universidad de Zaragoza, Zaragoza 50009, Spain

Excess enthalpies, densities, and speeds of sound at the temperatures (283.15, 298.15, and 313.15) K are reported for the binary mixtures *β*-pinene + ethanol and *β*-pinene + 1-propanol. Excess molar volumes, speed of sound deviations, isentropic compressibilities, and excess isentropic compressibilities have been calculated from the densities and speeds of sound. The excess isentropic compressibilities have been fitted to Redlich−Kister polynomials whereas the remaining excess properties and deviations of properties have been fitted to Padé approximants. Excess properties are positive for both mixtures while 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 *β*-pinene with ethanol and 1-propanol and of the mixtures of the butanols with cyclohexane.

Introduction

In an earlier paper,[1] the first results of a research program on the excess properties of mixtures containing compounds existing in essential oils of aromatic plants were reported. They referred specifically to mixtures of *β*-pinene (6,6-dimethyl-2-methylenebicyclo[3.1.1]heptane), one of the most usual compounds in a number of essential oils, with ethanol and 1-propanol. One of the reasons to select these systems was to obtain information of the interactions in mixtures of that hydrocarbon with compounds exhibiting specific interactions as hydrogen bonds. These interactions are relevant not only intrinsically but also in the supercritical extraction with carbon dioxide of essential oils of aromatic plants where ethanol and 1-propanol have been proposed as modifiers that can improve the extraction process. To achieve a better insight about those interactions, the study has been extended to mixtures of *β*-pinene with 1-butanol and 2-butanol. Then the effect of both the increase in the chain length for 1-alkanols and the shift from primary to secondary alcohol can be asessed.

So, excess enthalpy, density, and speed of sound have been measured over the whole composition range for the mixtures *β*-pinene + 1-butanol and *β*-pinene + 2-butanol at the temperatures (283.15, 298.15, and 313.15 K). From the experimental density and speed of sound values, excess volumes isentropic compressibilities, excess isentropic compressibilities, and speed of sound deviations have been calculated. As far as we know, there are no data for these mixtures. The results are discussed in terms of the mentioned intermolecular interactions. Moreover, the results for excess properties are compared with those reported for mixtures of *β*-pinene with ethanol or 1-propanol and cyclohexane (a simpler hydrocarbon similar to *β*-pinene) + 1-butanol or 2-butanol.

Experimental Section

Materials. The compounds used were 1-*S*-(−)-6,6-dimethyl-2-methylenebicyclo[3.1.1]heptane (purity 99 %), 1-butanol (purity +99.8 %), and 2-butanol (purity 99 %) from Aldrich. The purities of these liquids were corroborated by gas−liquid chromatography (HP 6890) using a flame ionization detector. No further purification was attempted. Both butanols were stored over Fluka molecular sieve 4 Å. Experimental values of density and speed of sound for the pure components are reported in Table 1 and compared with the available bibliographic values.[2−6] In general terms, a good agreement can be observed. Significant differences appear for *β*-pinene, but it must be taken into account that the bibliographic data have been determined from a correlation equation whose results shows uncertainties around 1 kg·m^{-3}. In fact, some of the densities[2] used in the correlation correspond to a product of 97 % purity, being all impurities less dense than *β*-pinene itself. This would explain why our values are higher. For a product similar to ours,[3] the results are much more similar. Also for *β*-pinene slight differences, that are significant at 313.15 K, have been observed between the values of density and speed of sound measured now and those of our preceding paper.[1] These differences could correspond to the fact that the liquid used in the measurements at that temperature came from a different production batch.

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

		ρ/kg·m^{-3}			u/m·s^{-1}		
T/K		*β*-pinene	1-butanol	2-butanol	*β*-pinene	1-butanol	2-butanol
283.15	expt	878.97	817.48	815.11	1355.9	1292.2	1266.6
	lit	877.95^{a}	817.0^{c}	815.2^{c}		1290.41^{d}	1263.90^{d}
			817.04^{d}	814.48^{d}			
298.15	expt	866.99	806.17	803.00	1295.0	1240.7	1212.4
	lit	865.95^{a}	806.0^{c}	802.6^{c}		1241^{e}	1212^{e}
		866.66^{b}	805.4^{e}	802.4^{e}			
313.15	expt	854.89	794.51	790.06	1237.4	1191.4	1158.0
	lit	853.95^{a}	794.6^{c}	789.7^{c}		1190^{e}	1157^{e}
			794.1^{e}	789.5^{e}			

[a] Ref 2. [b] Ref 3. [c] Ref 4. [d] Ref 5. [e] Ref 6.

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

---

* To whom correspondence should be addressed. E-mail: jupardo@unizar.es. Fax: +34 976 76 12 02.

10.1021/je050294+ CCC: $33.50

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

	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
			β-Pinene (1) + 1-Butanol (2)				
0.066	49	69	89	0.677	438	592	793
0.134	106	153	196	0.765	412	557	751
0.259	215	310	428	0.856	354	476	642
0.371	303	427	574	0.927	282	372	487
0.489	377	525	711	0.975	182	279	329
0.591	423	577	780				
			β-Pinene (1) + 2-Butanol (2)				
0.066	128	173	166	0.677	709	950	1158
0.134	263	364	405	0.765	650	870	1076
0.259	463	637	749	0.845	549	739	934
0.380	600	818	981	0.927	387	531	675
0.489	687	932	1122	0.963	280	378	469
0.581	720	972	1174				

conditions. Two Shimadzu LC-10ADVP HPLC pumps were used to drive the liquids. All the equipment was located in a room whose temperature is (302.15 ± 0.2) K. The pumps were calibrated for each liquid in order to relate the real flow to the programmed one. The calibration was made by determining through 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 were calibrated, the excess enthalpy was measured at several total flow rates of the mixture in order to determine the best total flow rate, which was that leading to the highest absolute value of excess enthalpy. For the systems reported in this paper, the total flow rate was 0.05 cm^3·mol^{-1} for the mixture β-pinene + 1-butanol and 0.1 cm^3·mol^{-1}for the mixture β-pinene + 2-butanol. As the flow rates were small, there was enough time to allow the mixture to reach the temperature of measurement.

Then the pumps were programmed in such a way that excess enthalpies were measured at selected mole fractions of the mixture. For each mole fraction, the calorimeter measures the power every 10 s during 30 min. The arithmetic average of these power data was used to calculate the excess enthalpy. The power readings showed ramdom variations (noise), but no periodic variations related with the pump were observed. The testing of the calorimeter was achieved with reference to recommended values[7] of the mixture hexane + cyclohexane, showing agreement between our data and the bibliographic ones within ± 1 % of the maximum excess enthalpy value for the reference mixture. To compare their values, the sensitivity, power measured against 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 an electric resistance. The sensitivities have been found to be very similar in all cases; their values differing by less than 1 %. The overall uncertainty in the excess enthalpy is estimated to be less than 2 J·mol^{-1}.

Densities and speeds of sounds were obtained by means of a vibrating tube densimeter and sound analyzer Anton Paar DSA48. Following the proposal of Troncoso et al.,[5] this apparatus is connected to a personal computer through a RS-232 connection. This arrangement leads to uncertainties for 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 speed of sound, speed of sound deviations, isentropic compressibilities, and excess isentropic compressibilities are gathered in Table 4. The excess enthalpy and excess volume values have been drawn in Figures 1 to 4. The speed of sound deviations (Δu) were calculated through the expression

$$\Delta u = u - x_1 u_1 - x_2 u_2 \tag{1}$$

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

283.15 K			298.15 K			313.15 K		
x_1	ρ / kg·m^{-3}	$10^6 \cdot V^E$ / m^3·mol^{-1}	x_1	ρ / kg·m^{-3}	$10^6 \cdot V^E$ / m^3·mol^{-1}	x_1	ρ / kg·m^{-3}	$10^6 \cdot V^E$ / m^3·mol^{-1}
				β-Pinene (1) + 1-Butanol (2)				
0.9179	875.44	0.080	0.9349	863.93	0.120	0.9540	852.44	0.146
0.9009	874.70	0.094	0.9003	862.46	0.145	0.8988	850.10	0.189
0.7975	870.17	0.139	0.7745	856.95	0.197	0.8017	845.70	0.269
0.6950	865.44	0.151	0.6946	853.25	0.209	0.7062	841.36	0.284
0.5929	857.70	0.144	0.6041	848.79	0.207	0.6003	836.12	0.292
0.5005	855.39	0.131	0.4987	843.18	0.190	0.5009	830.84	0.276
0.4007	849.50	0.106	0.4011	837.49	0.161	0.3998	825.01	0.237
0.3052	843.23	0.081	0.2992	830.92	0.122	0.3012	818.82	0.179
0.2040	835.80	0.051	0.1893	822.86	0.084	0.1988	811.57	0.120
0.1023	827.32	0.022	0.1027	815.79	0.040	0.1011	803.76	0.060
0.0494	822.40	0.011	0.0540	811.40	0.020	0.0493	799.21	0.026
				β-Pinene (1) + 2-Butanol (2)				
0.9401	875.92	0.134	0.9449	863.90	0.178	0.9453	851.52	0.226
0.8988	873.93	0.189	0.9067	862.02	0.236	0.8960	848.93	0.326
0.7995	869.14	0.273	0.8035	856.93	0.345	0.8035	844.16	0.446
0.7047	864.32	0.326	0.7011	851.61	0.419	0.6993	838.59	0.534
0.6023	858.87	0.345	0.6096	846.71	0.438	0.6027	833.19	0.572
0.5035	853.29	0.331	0.5017	840.58	0.424	0.5088	827.69	0.570
0.4019	847.14	0.287	0.3995	834.25	0.390	0.4043	821.27	0.514
0.3006	840.38	0.229	0.3006	827.65	0.324	0.2999	814.22	0.438
0.2058	833.37	0.164	0.2060	820.79	0.234	0.2028	807.25	0.315
0.1031	824.88	0.083	0.1050	812.54	0.137	0.0997	799.22	0.138
0.0526	820.26	0.043	0.0522	807.98	0.060	0.0526	794.95	0.085

Table 4. Speeds of Sound, Speed of Sound Deviations, Isentropic Compressibilities, and Excess Isentropic Compressibilities for the Mixtures of β-Pinene and Butanols 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}	κ_S/TPa^{-1}	κ_S^E/TPa^{-1}	x_1	u/m s^{-1}	Δu/m s^{-1}	κ_S/TPa^{-1}	κ_S^E/TPa^{-1}	x_1	u/m s^{-1}	Δu/m s^{-1}	κ_S/TPa^{-1}	κ_S^E/TPa^{-1}
β-Pinene (1) + 1-Butanol (2)														
0.0494	1295.8	0.5	724.2	0.8	0.0540	1243.7	0.1	796.8	1.4	0.0493	1193.1	−0.6	879.0	1.9
0.1023	1299.6	0.9	715.7	1.5	0.1027	1246.2	−0.1	789.3	2.3	0.1011	1194.6	−1.4	871.8	4.2
0.2040	1305.9	0.7	701.6	3.5	0.1893	1250.3	−0.7	777.4	5.1	0.1988	1197.8	−2.7	858.8	7.6
0.3052	1311.7	0.1	689.3	5.3	0.2992	1255.2	−1.8	763.9	7.6	0.3012	1201.0	−4.3	846.7	10.8
0.4007	1316.8	−0.8	678.9	6.8	0.4011	1259.4	−3.1	752.8	9.8	0.3998	1203.9	−5.9	836.3	13.6
0.5005	1321.9	−2.1	669.0	8.1	0.4987	1263.5	−4.3	743.0	11.2	0.5009	1207.3	−7.1	825.8	15.3
0.5929	1323.6	−3.1	665.5	13.9	0.6041	1268.1	−5.5	732.6	12.0	0.6003	1211.4	−7.6	815.0	15.5
0.6950	1332.0	−4.3	651.3	9.1	0.6946	1272.3	−6.2	724.0	11.9	0.7062	1216.2	−7.7	803.5	14.6
0.7975	1338.1	−4.7	641.8	8.2	0.7745	1276.6	−6.2	716.0	11.0	0.8017	1221.1	−7.2	793.0	12.9
0.9009	1345.2	−4.2	631.8	6.0	0.9003	1284.6	−5.1	702.6	7.6	0.8988	1227.1	−5.6	781.2	9.3
0.9179	1347.3	−3.2	629.3	4.8	0.9349	1287.4	−4.2	698.4	5.9	0.9540	1231.4	−3.9	773.6	6.1
β-Pinene (1) + 2-Butanol (2)														
0.0526	1271.9	0.6	753.6	1.4	0.0522	1216.6	−0.1	836.2	2.6	0.0526	1161.7	−0.5	932.1	3.3
0.1031	1276.6	0.8	743.9	2.8	0.1050	1220.2	−0.9	826.6	6.0	0.0997	1164.1	−1.8	923.3	7.2
0.2058	1285.1	0.1	726.6	6.2	0.2060	1227.3	−2.1	808.8	10.3	0.2028	1170.4	−3.7	904.3	13.5
0.3006	1292.5	−0.9	712.3	8.9	0.3006	1233.5	−3.7	794.1	14.0	0.2999	1175.7	−6.1	888.5	18.9
0.4019	1299.8	−2.7	698.7	11.5	0.3995	1240.0	−5.4	779.6	16.8	0.4043	1182.5	−7.6	870.8	21.7
0.5035	1307.2	−4.4	685.8	13.2	0.5017	1247.2	−6.6	764.8	18.0	0.5088	1189.9	−8.5	853.3	22.7
0.6023	1314.9	−5.5	673.4	13.6	0.6096	1255.5	−7.3	749.2	17.7	0.6027	1197.0	−8.9	837.7	22.0
0.7047	1323.5	−6.0	660.5	12.6	0.7011	1263.0	−7.3	736.1	16.3	0.6993	1205.0	−8.5	821.2	19.8
0.7995	1332.4	−5.6	684.1	10.4	0.8035	1272.5	−6.3	720.7	12.8	0.8035	1214.6	−7.2	803.0	15.6
0.8988	1342.4	−4.5	635.0	7.0	0.9067	1282.6	−4.7	705.2	8.3	0.8960	1223.2	−5.9	787.3	11.4
0.9401	1347.0	−3.6	629.2	5.1	0.9449	1287.0	−3.4	698.8	5.7	0.9453	1228.7	−4.4	777.9	7.8

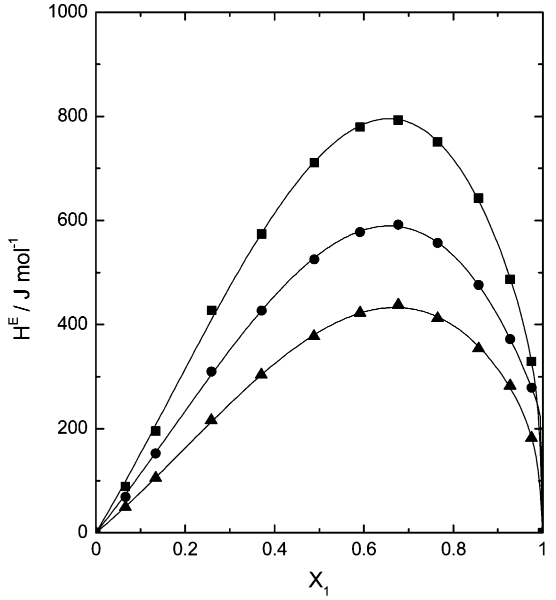

Figure 1. Excess Molar enthalpies for the mixture β-pinene (1) + 1-butanol (2): ▲, 283.15 K; ●, 298.15 K; ■, 313.15 K.

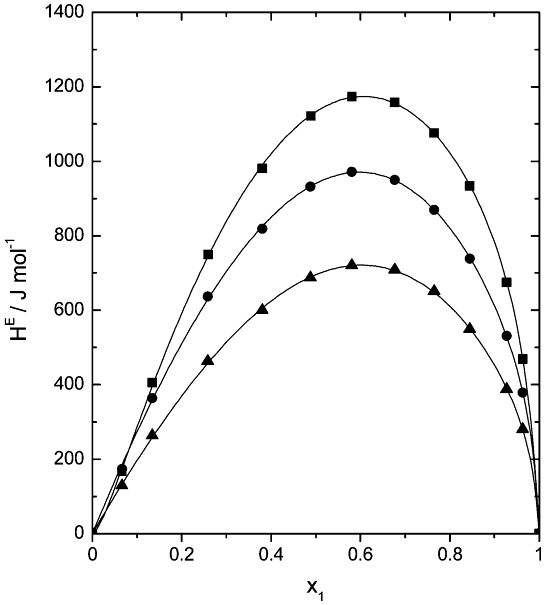

Figure 2. Excess molar enthalpies for the mixture β-pinene (1) + 2-butanol (2): ▲, 283.15 K; ●, 298.15 K; ■, 313.15 K.

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.

Isentropic compressibility (κ_S) is a property that can be calculated from density and speed of sound experimental values through the equation

$$\kappa_S = \frac{1}{\rho u^2} \tag{2}$$

where ρ is the density. The corresponding excess isentropic compressibility (κ_S^E) can also be calculated from the definition

$$\kappa_S^E = \kappa_S - \kappa_S^{id} \tag{3}$$

where κ_S^{id} stands for the isentropic compressibility for the ideal mixture, a property that can be rigorously obtained by means of the following expression deduced by Benson and Kiyohara:[8]

$$\kappa_S^{id} = \phi_1\left(\kappa_{S,1} + \frac{TV_1\alpha_1^2}{C_{p,1}}\right) + \phi_1\left(\kappa_{S,2} + \frac{TV_2\alpha_2^2}{C_{p,2}}\right) - \frac{T(x_1V_1 + x_2V_2)(\phi_1\alpha_1 + \phi_2\alpha_2)^2}{x_1C_{p,1} + x_2C_{p,2}} \tag{4}$$

with T being the temperature; ϕ_i and x_i being the volume fraction and the mole fraction of component i in the mixture; and $\kappa_{S,i}$, V_i, α_i, and $C_{p,i}$ being the isentropic compressibility, molar volume, isobaric thermal expansivity, and heat capacity at constant pressure of pure component i, respectively. Molar volumes and isobaric thermal expansivities were calculated from our measured densities. In the last case, the molar volumes were

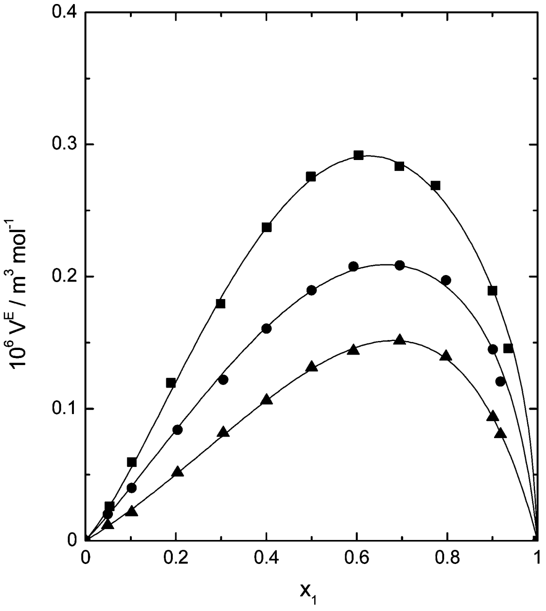

Figure 3. Excess molar volumes for the mixture β-pinene (1) + 1-butanol (2): ▲, 283.15 K; ●, 298.15 K; ■, 313.15 K.

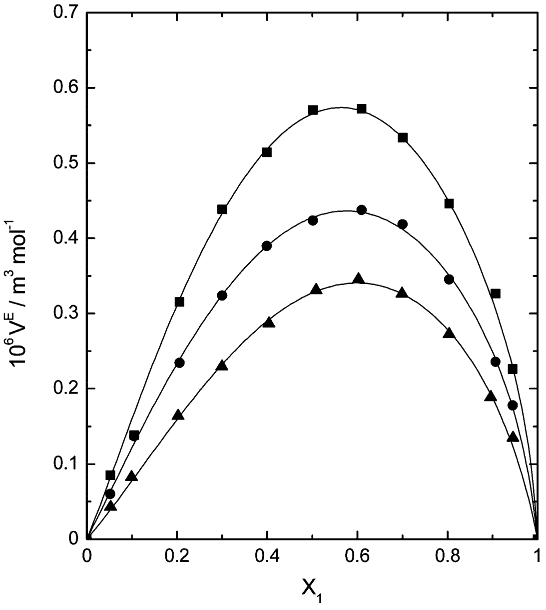

Figure 4. Excess molar volumes for the mixture β-pinene (1) + 2-butanol (2): ▲, 283.15 K; ●, 298.15 K; ■, 313.15 K.

considered as a linear function of the temperature. Referring to the heat capacities, they were obtained from the literature for both butanols[9] and β-pinene.[10] In the case of butanols, there were no data for the temperatures 283.15 and 313.15 K. Therefore, values from 280 to 320 K were fitted to a series of the temperature

$$C_{p,i} = a + bT + cT^2 + dT^3 \tag{5}$$

then the needed values interpolated. For β-pinene, the available C_p data correspond to temperatures higher than ours. Data from 318.15 to 353.15 K were fitted to the temperature and then extrapolated. There was a value at 313.15 K, but it deviated so markedly from the remaining data that it was not used either directly or in the fitting. Nevertheless, the influence on the excess isentropic compressibility of considering that point was negligible. The adjusting coefficients for molar volumes and heat capacities can be found in Table 5.

Table 5. Fitting Coefficients of Molar Volume V and Heat Capacity C_p for Pure Compounds Determined for Equation 5

	a	*b*	*c*	*d*
	β-Pinene			
$10^6 \cdot V$/m$^3 \cdot$mol^{-1}	113.4	0.15		
C_p/J$\cdot$mol^{-1}K^{-1}	10574.4	−89.9	0.26	−0.0002
	1-Butanol			
$10^6 \cdot V$/m$^3 \cdot$mol^{-1}	66.1	0.09		
C_p/J$\cdot$mol^{-1}K^{-1}	337.9	−1.7	0.004	
	2-Butanol			
$10^6 \cdot V$/m$^3 \cdot$mol^{-1}	63.5	0.10		
C_p/J$\cdot$mol^{-1}K^{-1}	−111.9	1.0		

The excess isentropic compressibilities have been fitted to Redlich−Kister equations, but the data of excess enthapies and excess volumes and also those of the speed of sound deviations cannot be fitted to that equation because the standard deviations obtained are too high. Consequently, the equation does not lead to a reliable reproduction of experimental data. Then they have been adjusted to the following equation:

$$Y = \frac{x_1 x_2 \sum_{i=0}^{p} A_i (2x_1 - 1)^{\mathrm{i}}}{1 + \sum_{j=1}^{q} B_j (2x_1 - 1)^i} \tag{6}$$

that is of the type Padé approximant. The symbol Y denotes the properties H^E/J$\cdot$mol^{-1}, V^E/10^6 m$^3\cdot$mol^{-1}, or speed of sound deviation, Δu/m$\cdot$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 6 along with the corresponding standard deviations defined by

$$\sigma = \left[\frac{\sum_m (Y^{\exp} - Y^{\mathrm{cal}})^2}{m - n}\right]^{1/2} \tag{7}$$

where $Y^{\exp}$ and Y^{cal} are the experimental and calculated 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 properties (namely, enthalpies, volumes, and isentropic compressibilities) are positive on the whole composition range for the mixtures of the hydrocarbon β-pinene with both alkanols at all temperatures. The values are clearly greater for the mixtures of β-pinene with 2-butanol than for the mixtures with 1-butanol as can be seen by comparing the values listed in the corresponding tables. As usually occurs near room temperature and atmospheric pressure in mixtures containing an alkanol, excess properties increase as temperature increases. The curves are asymmetrical with the maxima appearing in the zone rich in β-pinene (component 1), approximately at $x_1 = 0.7$ for the system containing 1-butanol and at $x_1 = 0.6$ for the system containing 2-butanol. The speed of sound deviations are negative over the composition range except for the mixtures β-pinene + 1-butanol and β-pinene + 2-butanol at 283.15 and for the mixture β-pinene + 1-butanol at 298.15 K. In these systems the speed of sound deviations are sigmoidal, being positive in a little composition range in the zone richest in alcohol. The values are lower for systems with the secondary alcohol.

The explanation of the observed behavior is that advanced[1] for the mixtures of β-pinene + ethanol or 1-propanol. The main

Table 6. Fitting Coefficients A_i and B_i and the Standard Deviations σ Determined for Equation 6

Y	T/K	A_0	A_1	A_2	A_3	B_1	B_2	σ
				β-Pinene (1) + 1-Butanol (2)				
H^E/J·mol^{-1}	283.15	1544	495	622		−0.981		3
	298.15	2141	839	847		−0.999		3
	313.15	2889	−1091	−1132		−0.988		8
10^6·V^E/m^3·mol^{-1}	283.15	0.518	0.404	0.198	0.146			0.001
	298.15	0.757	−0.230	−0.232		−0.919		0.002
	313.15	1.095	−0.494	−0.482	0.111	−0.981		0.002
Δu/m·s^{-1}	283.15	−8.4	−18.1	14.6		−0.9		0.05
	298.15	−17.4	−8.7	13.8		−0.9		0.03
	313.15	−27.9	8.0	12.7	−3.4	−0.9	−0.3	0.1
κ_S^E/TPa^{-1}	283.15	32.0	−20.4	13.0	−13.9			0.1
	298.15	44.3	−20.1	17.4	−25.4			0.2
	313.15	59.2	−16.7	20.4	−33.6			0.5
				β-Pinene (1) + 2-Butanol (2)				
H^E/J·mol^{-1}	283.15	2781	−1698	−428		−0.964		4
	298.15	3762	−2387	−448		−0.962		5
	313.15	4530	1549	−2910			−0.861	5
10^6·V^E/m^3·mol^{-1}	283.15	1.309		−0.593		−0.395	−0.371	0.003
	298.15	1.713	−1.168	−0.305		−0.981		0.004
	313.15	2.261		−1.460		−0.232	−0.683	0.004
Δu/m·s^{-1}	283.15	−17.1		41.3	−28.9	−1.7	0.8	0.1
	298.15	−26.3	−4.0	22.1		−0.6	−0.4	0.1
	313.15	−34.5	49.0		−26.5	−1.8	0.9	0.2
κ_S^E/TPa^{-1}	283.15	51.8	−19.0	2.1	−16.7			0.3
	298.15	71.3	−8.9	8.5	−21.5			0.3
	313.15	90.0	3.3	13.1	−51.3			0.5

cause of the observed behavior is the breaking of the hydrogen bonds of the alkanols that leads to an endothermic mixing process and a subsequent expansion of the mixture. There is also likely attractive interactions between the OH group of alcohol and the π cloud of double bond in β-pinene, but this interaction is far weaker than the original broken hydrogen bonds. The greater distances between molecules produced by the expansion would account for greater compressibilities and for speeds of sound that are lower than those predicted by the linear combination of speed of sound for the pure components. However, the positive values of speed of sound deviations observed when the concentration of alcohol is very high corroborate the well-known fact that this molecular property is not fully connected with the excess volume. For all of the properties, the asymmetry in the curves is due to the difference in both the type of interactions in the pure compounds and the geometry of the molecules involved.

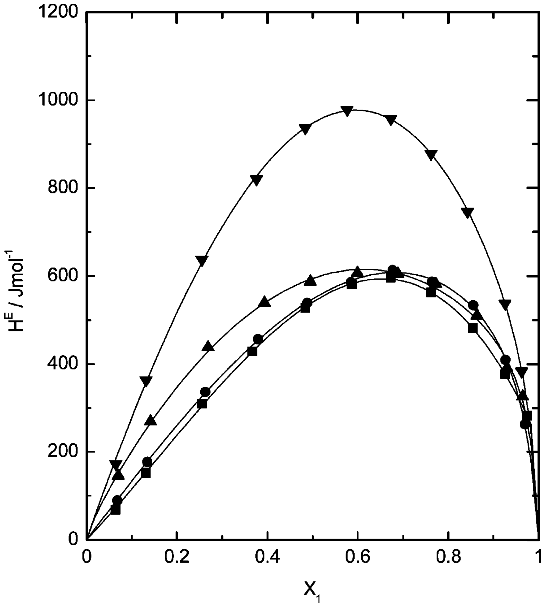

Figure 5. Excess molar enthalpies at 298.15 K for the mixtures: ▲, β-pinene + ethanol; ●, β-pinene + 1-propanol; ■, β-pinene + 1-butanol; ▼, β-pinene + 2-butanol. β-Pinene is component 1.

To determine the effect on excess enthalpies, excess volumes, and speed of sound deviations of both the chain length of 1-alcohols and the shift from primary to secondary alcohols, it is worth comparing the results obtained for the present mixtures with those reported for the mixtures of β-pinene with ethanol or 1-propanol.[1] In Figure 5, the experimental excess enthalpy data for all those mixtures at 298.15 K along with their corresponding fitting curves can be found. The excess volumes show the same disposition as the enthalpies whereas the region of negative values increases for the speed of sound deviations as the chain length increases and also for mixtures containing 2-butanol. Then, to the excess properties the effect of the chain length seems to be irrelevant, at least for these short alcohols, but speed of sound deviations are dependent on that chain length. Referring to excess enthalpies in Figure 5, all the mixtures with primary alcohols show very similar values whereas the mixture containing 2-butanol exhibits quite higher values. This would indicate that it is the place, terminal or not, of the OH group that mainly determines the value of the excess enthalpy. The presence of the OH group on a secondary carbon likely creates a structure where the molecules of β-pinene would be accommodated far worse than in the structures of 1-alcohols. The result would be a greater breaking of hydrogen bonds and a greater expansion of the mixture.

Another interesting comparison can be done with mixtures of cyclohexane + 1-butanol or 2-butanol because β-pinene is mainly constituted by a six carbon atom ring as occurs with cyclohexane. Excess enthalpies of the mixtures of cyclohexane + 1-butanol or 2-butanol at 298.15 and 313.15 K can be found in Vesely et al.[11] whereas excess volumes were measured for the same mixtures at 313.15 K by Artigas et al.[12] In relation to the excess enthalpies, for a given temperature and isomer of butanol, the excess enthalpies are very similar for the mixtures with either β-pinene or cyclohexane. In the case of 1-butanol, the excess enthalpy values are slightly lower for mixtures containing β-pinene (592 J·mol^{-1} at 298.15 K and 793 J·mol^{-1} at 313.15 K) than for mixtures with cyclohexane (634 J·mol^{-1}

at 298.15 K and 817 J·mol^{-1} at 313.15 K). On the contrary, in the case of 2-butanol, the excess enthalpy values are slightly higher for mixtures with β-pinene (972 J·mol^{-1} at 298.15 K and 1174 J·mol^{-1} at 313.15 K) than for mixtures containing cyclohexane (958 J·mol^{-1} at 298.15 K and 1158 J·mol^{-1} at 313.15 K). In any case, it is noticeable that the mixtures of both hydrocarbons with 1-butanol or 2-butanol show a similarity in the excess enthalpy maximum values that was already observed[1] when the alcohols were ethanol and 1-propanol. Then, as previously stated,[1] the excess enthalpies of mixtures of alcohols with this type of cyclic hydrocarbons seem to depend mainly on the hydrocarbon nature of these partners (at least for alcohols of short chain) with little influence from the shape or number of carbon atoms.

As for the excess volumes, they are always lower for the mixtures containing β-pinene (0.292×10^{-6} m^3·mol^{-1} for 1-butanol and 0.572×10^{-6} m^3·mol^{-1} for 2-butanol) than for those containing cyclohexane (0.448×10^{-6} m^3·mol^{-1} for 1-butanol and 0.750×10^{-6} m^3·mol^{-1} for 2-butanol), a feature that has been also observed for ethanol and 1-propanol[1]. β-Pinene allows a far better accommodation of alcohol molecules than cyclohexane does.

It can be concluded then that the behavior of mixtures of 1-butanol or 2-butanol with β-pinene as well as with other rather similar hydrocarbons is ruled by the place that the OH group occupies in the molecule, that is, by the primary or secondary character of the alcohol.

Literature Cited

(1) Langa, E.; Mainar, A. M.; Pardo, J. I.; Urieta, J. S. 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. *J. Chem. Eng. Data* **2005**, *50*, 1255−1261.

(2) Ribeiro, A.; Bernardo-Gil, G. Densities and refractive indices of components of pine resin. *J. Chem. Eng. Data* **1990**, *35*, 204−206.

(3) Comelli, F.; Francesconi., R.; Castellari, C. Excess molar enthalpies and excess molar volumes of binary mixtures containing dialkyl carbonates plus pine resins at (298.15 and 313.15) K. *J. Chem. Eng Data* **2001**, *46*, 63−68.

(4) *TRC Thermodynamic Tables. Non-Hydrocarbons*; Thermodynamic Research Center, Texas A&M University: College Station, TX, 1966; p d-5030.

(5) Troncoso, J.; Carballo, E.; Cerdeiriña, C. A.; González, D.; Romaní, L. Systematic determination of densities and speed of sound of nitroethane + isomers of butanol in the range (283−308.15) K. *J. Chem. Eng. Data* **2000**, *45*, 594−599.

(6) Rodríguez, A.; Canosa, J.; Tojo, J. Density, refractive index, and speed of sound of binary mixtures (diethyl carbonate + alcohols) at several temperatures. *J. Chem. Eng. Data* **2001**, *46*, 1506−1515.

(7) Marsh, K. N., Ed. *Recommended Reference Materials for the Realisation of Physicochemical Properties*; IUPAC, Blackwell Scientific Publications: Oxford, 1987.

(8) Benson, G. C.; Kiyohara, O. Evaluation of excess isentropic compressibilities and isochoric heat capacities. *J. Chem. Thermodyn.* **1979**, *11*, 1061−1064.

(9) *TRC Thermodynamic Tables. Non-Hydrocarbons*; Thermodynamic Research Center, Texas A&M University: College Station, TX, 1984; p vc-5033.

(10) Sampaio, M. O.; Nieto de Castro, C. A. Heat capacity of liquid terpenes. *Fluid Phase Equilib.* **1998**, *150−151*, 789−796.

(11) Vesely, F.; Dohnal, V.; Valetova, M.; Pick, J. Concentration and temperature dependence of heats of mixing of 1-butanol, 2-butanol, and 2-methyl-2-propanol with cyclohexane. *Collect. Czech. Chem. Commun.* **1983**, *48*, 3482−3494.

(12) Artigas, H.; Sanz, M. L.; Mainar, A. M.; Royo, F. M.; Urieta, J. S. Excess volumes and excess viscosities of binary mixtures of cyclohexane + an isomer of butanol at several temperatures. *Phys Chem. Liq.* **1995**, *30*, 17−28.

Received for review July 26, 2005. Accepted November 7, 2005. The authors are grateful for financial support from the Comisión de Investigación Científica y Técnica (IN96-0191), the Dirección General de Investigación (PPQ2002-04143-CO2-01), and the Diputación General de Aragón (GIA DGA 2002).

JE050294+