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

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Excess molar enthalpies, densities, and speeds of sound at the temperatures (283.15, 298.15, 313.15) K are reported for the binary mixtures 6,6-dimethyl-2-methylenebicyclo[3.1.1]heptane (β-pinene) + 1-pentanol and β-pinene + 2-pentanol. 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 properties and property deviations have been fitted to either Redlich−Kister polynomials or Padé approximants to reproduce the experimental data as accurately as possible. 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.

Introduction

This paper is the continuation of two earlier contributions,[1,2] all of them corresponding to a research program on the excess properties of mixtures containing compounds existing in essential oils from aromatic plants. The component chosen in these papers is 6,6-dimethyl-2-methylenebicyclo[3.1.1]heptane commonly known as β-pinene, one of the most usual compounds in a number of essential oils. β-Pinene is usually obtained by distillation of pine wood turpentine whose main constituent is along with its isomer α-pinene. Turpentine is used as a solvent for resins, varnishes, and oil-based paints as well as in the manufacture of polymers and perfumes for soaps and cosmetics. β-pinene is used as raw material for the industrial production of compounds such as camphor, menthol, myrcene, and also of some insecticides.

Recently, the thermodynamic properties of mixtures with ethanol,[1] 1-propanol,[1] 1-butanol,[2] or 2-butanol[2] have been determined. Now, excess molar enthalpy, density, and speed of sound have been measured over the whole composition range for the mixtures β-pinene + 1-pentanol and β-pinene + 2-pentanol at the temperatures (283.15, 298.15, and 313.15) K. From the experimental density and speed of sound values, excess molar volumes, speed of sound deviations, isentropic compressibilities, and excess isentropic compressibilities have been calculated. As far as we know, there are no data for these mixtures. The results are discussed in terms of intermolecular interactions. Moreover, the results for excess properties are compared with those reported for mixtures of β-pinene + ethanol,[1] 1-propanol,[1] 1-butanol,[2] or 2-butanol[2] and also those reported for mixtures of cyclohexane (a simpler hydrocarbon similar to β-pinene) + 1-pentanol.[3]

The data secured for the new systems would allow us to verify the conclusions advanced before[2] referring to the effect of both the increase in the chain length for 1-alkanols and the shift from primary to secondary alcohol on the behavior of these mixtures that are characterized by the breaking of the hydrogen bond in the alkanols.

Experimental Section

Materials. The compounds used were β-pinene (purity 99 %) and 1-pentanol (purity better than 99 %) from Aldrich and 2-pentanol (purity better than 98 %) from Fluka. The purities of these liquids were corroborated by gas−liquid chromatography (HP 6890) using a flame ionization detector. No further purification was attempted. Both alkanols 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.[4−9] In general terms, a good agreement can be observed except for β-pinene. In this case, it must be taken into account that the bibliographic data have been determined from a correlation equation whose results show uncertainties around 1 $kg \cdot m^{-3}$. In fact, some of the densities used in the correlation correspond to a product of 97 % purity with all the impurities compounds being less dense than β-pinene. This would explain why our values are higher. For a product similar to ours,[5] the results are much better. Also, for β-pinene, slight differences have been observed between the values of density and speed of sound measured now and those of our preceding papers.[1,2] These differences could be attributed to properties changing with the production batches.

Apparatus and Procedure. The excess molar 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. The whole equipment was 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 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 $cm^3 \cdot min^{-1}$). A determination was made every 0.025 $cm^3 \cdot min^{-1}$. 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 molar enthalpy was measured at several total flow rates of the mixture to determine

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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

		$\rho/\text{kg}\cdot\text{m}^{-3}$			$u/\text{m}\cdot\text{s}^{-1}$		
T/K		β-pinene	1-pentanol	2-pentanol	β-pinene	1-pentanol	2-pentanol
283.15	expt	879.07	821.79	816.77	1354.3	1325.9	1286.7
	lit	877.95[a]	822.05[c,g]	817.19[e,g]		1326[f]	1286[e,g]
298.15	expt	867.11	810.83	804.97	1295.6	1274.1	1232.6
	lit	865.95[a] 866.66[b]	810.96[c] 810.80[d]	805.01[e]		1276[f]	1232[e]
313.15	expt	854.87	799.80	792.42	1236.3	1225.5	1168.1
	lit	853.95[a]	799.78[c]	792.77[e,g]		1225[f]	1178[e,g]

[a] Reference 4. [b] Reference 5. [c] Reference 6. [d] Reference 7. [e] Reference 8. [f] Reference 9. [g] Extrapolated value.

the best total flow rate, which was that leading to the highest absolute value of excess molar enthalpy. For the systems reported in this paper, the total flow rate was 0.15 $\text{cm}^3\cdot\text{mol}^{-1}$ for the mixture β-pinene + 1-pentanol and 0.1 $\text{cm}^3\cdot\text{mol}^{-1}$ for the mixture β-pinene + 2-pentanol. Because 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 molar enthalpies were measured at selected mole fractions of 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 molar enthalpy. The power readings showed random variations (noise), but no periodic variations related with the pump were observed. The testing of the calorimeter was achieved with reference to recommended values[10] of the mixture hexane + cyclohexane, with the agreement between our data and the bibliographic ones being within ±1 % of the maximum excess molar enthalpy value for the reference mixture. As usual, the sensitivities, power measured against total power released, have 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. Those sensitivities have been found to be very similar in all cases, differing their values by less than 1 %. The overall uncertainty in the excess molar enthalpy is estimated to be less than 2 $\text{J}\cdot\text{mol}^{-1}$.

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.,[11] this apparatus is connected to a personal computer through a RS-232 connection. This arrangement leads to uncertainties for the measured properties of $\pm 0.01\ \text{kg}\cdot\text{m}^{-3}$ and $\pm 0.1\ \text{m}\cdot\text{s}^{-1}$. 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 molar enthalpies are listed in Table 2, densities and excess molar volumes can be found in Table 3, and finally the speed of sound, speed of sound deviations, isentropic compressibilities, and excess isentropic compressibilities are gathered in Table 4. The excess molar enthalpies and excess molar volumes values have been drawn in Figures 1 to 4. The speed of sound deviations, Δu, were calculated through the expression

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

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.

Table 2. Excess Molar Enthalpies H_m^E for the Mixtures of β-Pinene + Isomers of Pentanol at (283.15, 298.15, and 313.15) K

	$H_\text{m}^\text{E}/\text{J}\cdot\text{mol}^{-1}$		
x_1	283.15 K	298.15 K	313.15 K
	β-Pinene (1) + 1-Pentanol (2)		
0.049	28	74	107
0.096	65	155	224
0.192	136	314	443
0.286	209	459	647
0.388	270	585	812
0.488	315	671	926
0.588	339	720	989
0.690	345	726	994
0.791	322	673	929
0.892	253	528	762
0.950	200	385	536
0.970	150	306	399
0.990	95	246	137
	β-Pinene (1) + 2-Pentanol (2)		
0.049	125	160	209
0.100	264	336	413
0.193	490	622	749
0.294	683	862	1026
0.395	811	1018	1211
0.495	878	1100	1319
0.591	878	1102	1345
0.695	810	1060	1310
0.794	704	938	1196
0.900	514	719	880
0.942	385	520	642
0.971	276	366	405
0.985	149	189	185

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

$$\kappa_\text{S} = \frac{1}{\rho u^2} \tag{2}$$

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

$$\kappa_\text{S}^\text{E} = \kappa_\text{S} - \kappa_\text{S}^\text{id} \tag{3}$$

where $\kappa_\text{S}^\text{id}$ 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[12]

$$\kappa_\text{S}^\text{id} = \phi_1\left(\kappa_{\text{S},1} + \frac{TV_{\text{m}1}\alpha_1^{\,2}}{C_{P,1}}\right) + \phi_1\left(\kappa_{\text{S},2} + \frac{TV_{\text{m}2}\alpha_2^{\,2}}{C_{P,2}}\right) - \frac{T\,(x_1 V_{\text{m}1} + x_2 V_{\text{m}2})\,(\phi_1\alpha_1 + \phi_2\alpha_2)^2}{x_1 C_{P,1} + x_2 C_{P,2}} \tag{4}$$

with T being the temperature, ϕ_i and x_i the volume fraction and mole fraction of component i in the mixture, and $\kappa_{\text{S},i}$, $V_{\text{m}i}$,

Table 3. Densities, ρ, and Excess Molar Volumes, V_m^E, for the Mixtures of β-Pinene + Isomers of Pentanol at (283.15, 298.15, and 313.15) K

283.15 K			298.15 K			313.15 K		
x_1	ρ / kg·m^{-3}	$10^6 \cdot V_m^E$ / m^3·mol^{-1}	x_1	ρ / kg·m^{-3}	$10^6 \cdot V_m^E$ / m^3·mol^{-1}	x_1	ρ / kg·m^{-3}	$10^6 \cdot V_m^E$ / m^3·mol^{-1}
			β-Pinene (1) + 1-Pentanol (2)					
0.1075	830.13	0.021	0.1057	819.15	0.020	0.1007	807.27	0.036
0.2016	836.79	0.044	0.2012	825.47	0.055	0.2048	814.01	0.108
0.3016	843.32	0.069	0.3032	831.91	0.096	0.3027	819.95	0.166
0.4028	849.41	0.097	0.4023	837.67	0.139	0.4019	825.60	0.211
0.5026	854.98	0.124	0.4984	842.91	0.173	0.5024	830.92	0.254
0.6034	860.24	0.144	0.6021	848.24	0.197	0.5976	835.75	0.271
0.7014	865.12	0.148	0.6945	852.74	0.206	0.6977	840.54	0.281
0.8036	869.97	0.136	0.7994	857.65	0.195	0.7991	845.26	0.257
0.9009	874.43	0.101	0.8997	862.25	0.147	0.9066	850.18	0.187
0.9481	876.59	0.067	0.9465	864.37	0.111	0.9468	852.10	0.131
			β-Pinene (1) + 2-Pentanol (2)					
0.1040	824.99	0.093	0.1056	812.89	0.152	0.1069	800.02	0.223
0.2047	832.20	0.195	0.2051	819.88	0.273	0.1981	806.39	0.353
0.3071	839.03	0.288	0.3052	826.49	0.376	0.3039	813.43	0.468
0.3997	844.95	0.341	0.4038	832.72	0.444	0.4034	819.78	0.537
0.4964	850.86	0.373	0.5068	838.99	0.479	0.5067	826.14	0.568
0.6058	857.28	0.376	0.6010	844.56	0.473	0.6023	831.84	0.561
0.6929	862.26	0.345	0.6950	849.94	0.439	0.7005	837.55	0.514
0.8016	868.23	0.282	0.8014	855.84	0.365	0.7975	843.07	0.425
0.9040	873.67	0.192	0.9001	861.15	0.265	0.8957	848.53	0.298
0.9454	875.83	0.145	0.9499	863.90	0.180	0.9497	851.60	0.192

Table 4. Speeds of Sound u, Speed of Sound Deviations Δu, Isentropic Compressibilities κ_S, and Excess Isentropic Compressibilities κ_S^E for the Mixtures of β-Pinene + Isomers of Pentanol 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-Pentanol (2)								
0.1075	1327.7	−1.3	683.4	1.8	0.1004	1275.0	−1.3	751.3	1.5	0.1023	1223.7	−2.9	827.0	3.4
0.2016	1328.9	−2.7	676.7	3.7	0.2024	1275.5	−3.0	744.7	4.1	0.2007	1221.7	−6.0	823.4	7.8
0.3016	1330.6	−4.2	670.1	5.5	0.3081	1275.8	−4.9	738.5	6.8	0.3049	1220.9	−7.9	818.2	10.6
0.4028	1331.6	−5.7	663.9	7.2	0.3975	1275.9	−6.7	733.7	9.1	0.4019	1220.4	−9.4	813.3	12.6
0.5026	1333.2	−7.0	658.0	8.5	0.4982	1276.4	−8.4	728.2	11.0	0.5024	1220.6	−10.3	807.8	13.9
0.6034	1335.1	−7.9	652.2	9.4	0.6021	1277.9	−9.1	721.8	11.6	0.5976	1221.2	−10.8	802.3	14.5
0.7014	1337.8	−8.0	645.9	9.2	0.6960	1279.6	−9.5	716.0	11.8	0.6977	1222.1	−10.9	796.6	14.8
0.8036	1341.4	−7.3	638.8	8.2	0.8066	1283.0	−8.4	707.9	10.3	0.7991	1224.3	−9.8	789.3	13.3
0.9009	1346.2	−5.3	631.0	5.7	0.8952	1286.9	−6.4	700.5	7.9	0.9066	1228.6	−6.7	779.2	9.1
0.9481	1349.3	−3.5	626.6	3.7	0.9528	1291.0	−3.6	694.1	4.6	0.9468	1231.0	−4.7	774.4	6.4
						β-Pinene (1) + 2-Pentanol (2)								
0.1040	1291.4	−2.3	726.8	4.4	0.1056	1235.0	−4.3	806.5	7.5	0.1069	1170.1	−5.3	913.0	10.5
0.2047	1295.3	−5.2	716.2	8.9	0.2051	1238.6	−6.9	795.0	12.1	0.1981	1173.2	−8.4	901.0	16.3
0.3071	1299.3	−8.2	706.0	12.9	0.3052	1241.5	−10.3	785.0	17.2	0.3039	1177.7	−11.1	886.4	21.0
0.3997	1303.5	−10.2	696.5	15.3	0.4038	1245.8	−12.2	773.8	19.8	0.4034	1182.2	−13.4	872.8	24.4
0.4964	1308.8	−11.5	686.1	16.5	0.5068	1251.5	−13.0	761.0	20.5	0.5067	1188.2	−14.5	857.4	25.4
0.6058	1316.2	−11.4	673.3	15.9	0.6010	1257.8	−12.7	748.4	19.4	0.6023	1195.1	−14.1	841.7	24.1
0.6929	1323.1	−10.4	662.5	14.1	0.6950	1265.0	−11.4	735.2	17.1	0.7005	1203.4	−12.5	824.5	20.9
0.8016	1332.7	−8.2	648.5	10.7	0.8014	1273.7	−9.4	720.2	13.6	0.7975	1212.8	−9.7	806.4	15.9
0.9040	1342.4	−5.4	635.2	6.7	0.9001	1282.7	−6.6	705.8	9.2	0.8956	1223.2	−6.0	787.7	9.7
0.9454	1346.8	−3.8	629.5	4.6	0.9499	1288.2	−4.2	697.5	5.8	0.9497	1229.6	−3.3	776.7	5.3

α_i, and $C_{P,i}$ 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. For the determination of isobaric thermal expansivities, the molar volumes were considered as a linear function of the temperature. Referring to the heat capacities, they were obtained from the literature for both pentanols[7] and β-pinene.[13] 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 through the equation

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

then extrapolated. There was a value at 313.15 K, but it deviated so markedly from the remaining that it was not used neither directly nor in the fitting. Nevertheless, the inclusion of that value would have a negligible influence on the excess isentropic compressibility. The adjusting coefficients for molar volumes and heat capacities can be found in Table 5.

The speed of sound deviations and the excess isentropic compressibilities have been fitted to Redlich−Kister equations as well as the excess molar volumes of the mixture β-pinene + 2-pentanol, but the remaining data, excess molar enthalpies and excess molar volumes of the mixture β-pinene + 1-pentanol, cannot be fitted to that equation because the standard deviations obtained are too high and consequently the equation does not lead to a reliable reproduction of experimental data. Then, they have been adjusted to the following equation

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

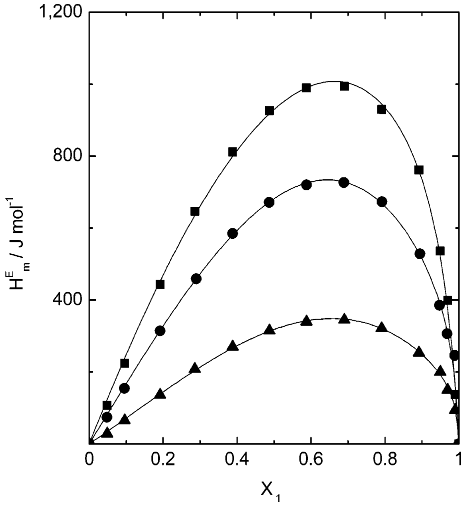

Figure 1. Excess molar enthalpies H^E_m for the mixture β-pinene (1) + 1-pentanol (2): ▲, 283.15 K; ●, 298.15 K; ■, 313.15 K.

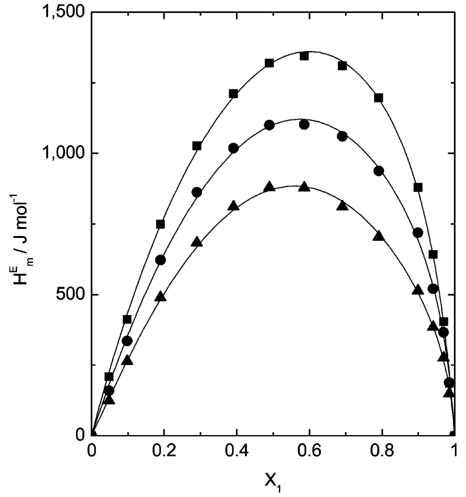

Figure 2. Excess molar enthalpies H^E_m for the mixture β-pinene (1) + 2-pentanol (2): ▲, 283.15 K; ●, 298.15 K; ■, 313.15 K.

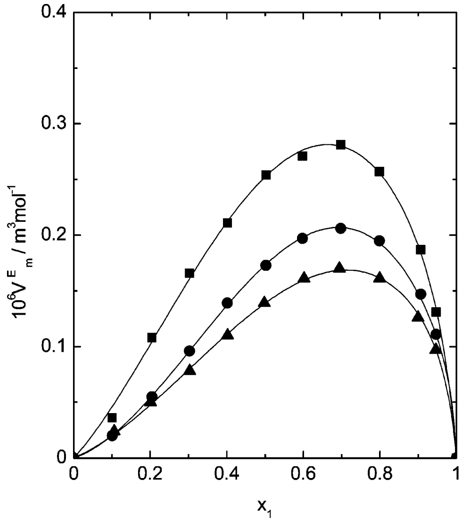

Figure 3. Excess molar volumes V^E_m for the mixture β-pinene (1) + 1-pentanol (2): ▲, 283.15 K; ●, 298.15 K; ■, 313.15 K.

that is of the type Padé approximant. The symbol Y denotes the properties H^E_m/J·mol^{-1}, $V^E_m/10^6$ m^3·mol^{-1}, x_i is the mole fraction of component i, and A_i and B_j are adjustable coefficients. The fitting for both Redlich−Kister equation and Padé approximants 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

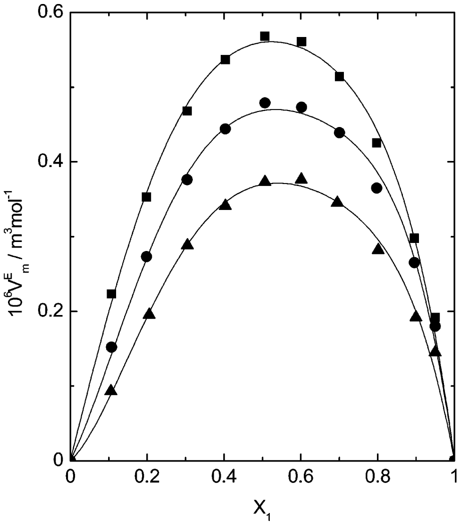

Figure 4. Excess molar volumes V^E_m for the mixture β-pinene (1) + 2-pentanol (2): ▲, 283.15 K; ●, 298.15 K; ■, 313.15 K.

Table 5. Fitting Coefficients of Molar Volume, V_m, and Molar Heat Capacity, C_P, for Pure Compounds Determined for Equation 5

	a	*b*	*c*	*d*
	β-Pinene			
$10^6 \cdot V_m$/m^3·mol^{-1}	113.5	0.15		
C_P/J·mol^{-1}·K^{-1}	10574.4	−89.9	0.26	−0.0002
	1-Pentanol			
$10^6 \cdot V_m$/m^3·mol^{-}	79.4	0.1		
C_P/J·mol^{-1}·K^{-1}	41.0	0.55		
	2-Pentanol			
$10^6 \cdot V_m$/m^3·mol^{-1}	76.7	0.11		
C_P/J·mol^{-1}·K^{-1}	25.3	0.58	0.0005	

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

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 results obtained for excess molar enthalpies, excess molar volumes, and excess 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 + 2-pentanol than those for the mixtures with 1-pentanol and, as usually occurs near room temperature and atmospheric pressure in mixtures containing 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-pentanol and at $x_1 = 0.6$ for the system containing 2-pentanol. An exception is found in the excess isentropic compressibility of the mixtures β-pinene + 2-pentanol that exhibits a quite symmetrical behavior. In general terms, the results for the mixture β-pinene + 1-pentanol show a remarkable resemblance to those for the mixture of β-pinene + 1-butanol[2] and the same can be said of the mixtures β-pinene + 2-pentanol and β-pinene

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	A_4	B_1	B_2	σ
				β-Pinene (1) + 1-Pentanol (2)					
H_m^E/J·mol^{-1}	283.15	1274	−517	−41			−0.981		5.3
	298.15	2749	−1314	−883			−0.994		11.3
	313.15	3724	−1598	−396			−0.914		15.9
10^6·V_m^E/m^3·mol^{-1}	283.15	0.492		−0.225			−0.902	−0.048	0.002
	298.15	0.695		−0.526			−0.912	−0.085	0.002
	313.15	1.009		−0.469			−0.662	−0.212	0.006
Δu/m·s^{-1}	283.15	−28.0	−20.9	−2.7	−11.8	−17.5			0.1
	298.15	−33.3	−25.0	0.9	−13.5	−22.0			0.1
	313.15	−41.1	−12.9	−22.6	−24.8				0.2
κ_S^E/TPa^{-1}	283.15	33.7	20.1	10.9	13.4				0.2
	298.15	43.8	25.1	−6.2	26.9	28.3			0.2
	313.15	55.5	17.4	27.7	39.2				0.3
				β-Pinene (1) + 2-Pentanol (2)					
H_m^E/J·mol^{-1}	283.15	3493		−2153			−0.203	−0.719	12.9
	298.15	4396		−2046			−0.246	−0.631	19.2
	313.15	5282		−1363			−0.292	−0.485	19.7
10^6·V_m^E/m^3·mol^{-1}	283.15	1.509	0.224	−0.396	0.848	0.943			0.008
	298.15	1.923	0.210	−0.381	0.992	1.575			0.008
	313.15	2.286	0.182	−0.105	0.597	1.508			0.008
Δu/m·s^{-1}	283.15	−46.1	−10.3	23.3	−20.2	−30.6			0.1
	298.15	−52.4	−4.7	20.1	−21.6	−47.8			0.2
	313.15	−57.8	−9.2	15.36	6.8	−30.5			0.1
κ_S^E/TPa^{-1}	283.15	66.2	3.7	−26.0	23.0	31.9			0.2
	298.15	82.6	−4.0	−27.2	31.2	61.9			0.3
	313.15	101.7	0.3	−20.8	−7.7	47.4			0.1

+ 2-butanol.[2] The speed of sound deviations are negative over the composition range with the values for systems with the secondary alcohol being lower.

The main cause of the observed behavior would be the same as that proposed[1,2] for the other mixtures of β-pinene + alkanols, that is, the breaking of the hydrogen bonds of the later compounds that leads to an endothermic mixing process and a subsequent expansion of the mixture. The likely existing attractive interactions between the OH group of alcohol and the π cloud of the double bond in β-pinene are far weaker than the original broken hydrogen bonds. 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.

The results for the systems containing the isomers of pentanol corroborate the conclusions advanced in an earlier paper[2] about the effect of both the chain length of 1-alcohols and the shift from primary to secondary alcohols on the excess properties. On one hand, the hypothesis[2] that the place, terminal or not, of the OH group is the feature which mainly determines the value of the excess molar enthalpy is supported by the clear-cut existing between the mixtures involving primary alcohols and those containing 2-alkanols which exhibit quite higher values as can be seen in Figure 5 for the excess molar enthalpies. The same is observed for the other excess properties. On the other hand, the variation of the chain length of 1-alkanols has little effect in the values of the excess properties. Nevertheless, it can be noticed in Figure 5 that the excess molar enthalpy of the mixture of β-pinene + 1-pentanol is clearly larger. This perhaps implies a change in the effect of chain length for higher alkanols, a change that would lead to greater hydrogen bond breaking. That difference in excess molar enthalpy is not transferred to excess molar volume or excess isentropic compressibility that are very similar for all of the systems containing 1-alkanols including 1-pentanol. This is due to the well-known fact that the volumetric behavior is not completely determined by the energetic one.

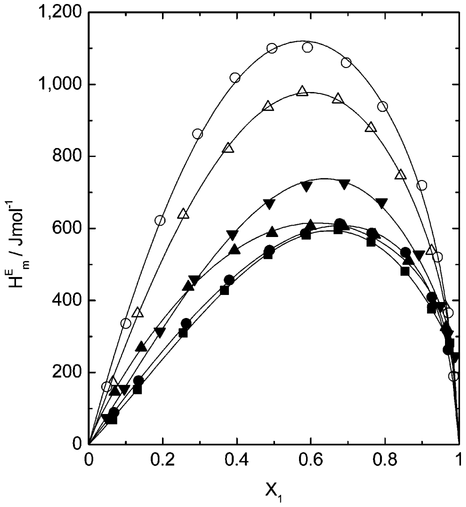

Figure 5. Excess molar enthalpies H_m^E at 298.15 K for the mixtures: ▲, β-pinene + ethanol; ●, β-pinene + 1-propanol; ■, β-pinene + 1-butanol; ▼, β-pinene + 1-pentanol; △, β-pinene + 2-butanol; ○, β-pinene + 2-pentanol. β-Pinene is component 1.

As has been discussed in previous papers,[1,2] an interesting comparison can be made with mixtures that contain cyclohexane instead of β-pinene given that β-pinene is mainly constituted by a six carbon atom ring as occurs with cyclohexane. In the case of the isomers of pentanol, only the data of Hiroyuki[3] for the mixture cyclohexane + 1-pentanol can be compared directly for the three temperatures. The systems show a behavior that agrees with the previous observations,[1,2] namely, the excess molar volume is far lower when the hydrocarbon is β-pinene.

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