Excess Enthalpy, Density, and Speed of Sound for the Mixtures β-Pinene + 2-Methyl-1-propanol or 2-Methyl-2-propanol at Several Temperatures

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Excess enthalpies, densities, and speeds of sound are reported for the binary mixtures β-pinene + 2-methyl-1-propanol at the temperatures (283.15, 298.15, 303.15, 313.15, and 323.15) K and β-pinene + 2-methyl-2-propanol at the temperatures (303.15, 313.15, and 323.15) K. Excess molar volumes have been calculated from the densities and speed of sound deviations, isentropic compressibilities, and excess isentropic compressibilities from speeds of sound. The excess properties and deviations of properties have been fitted to Padé approximants. Excess molar enthalpies and excess molar volumes are positive for both mixtures, whereas speed of sound deviations show both positive and negative values. Also, positive and negative values of excess isentropic compressibility are observed for the mixture β-pinene + 2-methy-1-propanol, but the mixture β-pinene + 2-methyl-2-propanol exhibits positive values only. The excess properties are compared with those of the mixtures of β-pinene with 1-butanol and 2-butanol.

Introduction

In earlier papers,[1−3] 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 several 1- or 2-alkanols of short length. β-Pinene is a common component of essential oils of plants, and our group is also studying the extraction of essential oil from aromatic plants using supercritical carbon dioxide. In this type of extraction, alkanols are commonly employed as modifiers.[4] Thus, information about the thermodynamic behavior of mixtures of β-pinene + alkanol could be of interest for those extraction processes even if the temperature and pressure conditions are rather different.

To complete this study, the thermodynamic properties of mixtures of β-pinene with 2-methyl-1-propanol (isobutanol) or 2-methyl-2-propanol (*tert*-butanol) have been determined. These data along with those obtained for the other isomers of butanol would allow us to know about the effect of both the branching in the hydrocarbon chain and the presence of a tertiary alcohol.

So, excess enthalpy, density, and speed of sound have been measured over the whole composition range for the mixtures β-pinene + 2-methyl-1-propanol at the temperatures (283.15, 298.15, 303.15, 313.15, and 323.15) K and β-pinene + 2-methyl-2-propanol at the temperatures (303.15, 313.15, and 323.15) K. In this case, the temperature range for β-pinene + 2-methyl-2-propanol was selected according to the melting point of the alkanol, and the temperature range for the mixture β-pinene + 2-methyl-1-propanol was chosen in such a way that its results could be compared with those previously reported[1−3] and also with those of β-pinene + 2-methyl-2-propanol. From the experimental density, excess molar volumes have been calculated. From speed of sound values, speed of sound deviations, isentropic compressibilities, and excess isentropic compressibilities have been determined. As far as we know, there are no data for these mixtures. The results for excess molar enthalpies and excess molar volumes are compared with those reported for mixtures of β-pinene with 1-butanol or 2-butanol and cyclohexane (a simpler hydrocarbon similar to β-pinene) + 2-methyl-1-propanol or 2-methyl-2-propanol.

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Experimental

Materials. The compounds used were 1-*S*-(−)-6,6-dimethyl-2-methylenebicyclo[3.1.1]heptane (purity 99 %), 2-methyl-1-propanol (purity +99 %), and 2-methyl-2-propanol (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 4 Å molecular sieves from Fluka. Experimental values of density and speed of sound for the pure components are reported in Table 1 and compared with the available bibliographic values.[5−9] In general terms, a fair agreement can be observed. Significant differences appear for β-pinene, but it must be taken into account that the bibliographic data have been calculated with a correlation equation whose results show uncertainties around 1 kg·m^{-3}. In fact some of the densities[10] used in the correlation correspond to a product of 97 % purity, and all the impurities are compounds less dense than β-pinene itself. This would explain why our values are higher. For a product similar to ours,[6] 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. The calorimeter has been tested with reference to recommended values[11] of the mixture hexane + cyclohexane, the agreement between our data and the bibliographic ones being within ± 1 % of the maximum excess enthalpy value for the reference mixture. Two Shimadzu LC-10ADVP HPLC pumps were used to drive the liquids. The whole procedure is detailed elsewhere.[1−3] Given the uncertainty in the flow rate, the uncertainty in the mole fractions of the mixtures was estimated to be

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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: Comparison with Literature Data

		ρ/kg·m^{-3}			u/m·s^{-1}		
T/K		β-pinene	2-methyl-1-propanol	2-methyl-2-propanol	β-pinene	2-methyl-1-propanol	2-methyl-2-propanol
283.15	exptl	879.07	809.36		1354.7	1238.7	
	lit.	877.95[a]	809.2[c]			1237.48[d]	
			809.27[d]				
298.15	expt.	867.11	798.03		1295.1	1188.0	
	lit.	865.95[a]	797.8[c]			1186.72[d]	
		866.66[b]	797.77[d]				
303.15	expt.	863.17	794.17	775.75	1278.6	1174.3	1101.9
	lit.	861.95[a]	793.8[c]	775.7[c]		1170.08[d]	1104[e]
		862.31[b]	793.87[d]				
313.15	exptl	854.87	786.10	765.05	1236.3	1138.0	1056.4
	lit.	853.95[a]	785.8[c]	764.9[c]			
		854.83[b]					
323.15	exptl	846.75	777.85	754.12	1200.7	1108.2	1015.9
	lit.	845.95[a]	777.6[c]	754.0[c]			

[a] Ref 5. [b] Ref 6. [c] Ref 7. [d] Ref 8. [e] Ref 9.

Table 2. Excess Molar Enthalpies for the Mixtures of β-Pinene + 2-Methyl-1-propanol at (283.15, 298.15, 303.15, 313.15, and 323.15) K and β-Pinene+ 2-Methyl-2-propanol at (303.15, 313.15, and 323.15) K

	H^E/J·mol^{-1}						H^E/J·mol^{-1}				
x_1	283.15 K	298.15 K	303.15 K	313.15 K	323.15 K	x_1	283.15 K	298.15 K	303.15 K	313.15 K	323.15 K
	β-Pinene (1) + 2-Methyl-1-propanol (2)						β-Pinene (1) + 2-Methyl-2-propanol (2)				
0.0529	66	91	115	149	184	0.0562			234	225	426
0.1090	128	184	237	311	351	0.1353			426	434	591
0.2159	253	352	484	590	680	0.2605			679	747	842
0.3175	356	481	643	781	899	0.3731			805	906	987
0.4299	450	588	772	926	1039	0.4910			827	957	1052
0.5331	517	653	835	999	1143	0.5936			840	995	1101
0.6229	543	675	853	1011	1147	0.6788			812	982	1095
0.7198	530	637	798	943	1067	0.7667			732	921	1038
0.8249	464	549	677	804	919	0.8577			626	768	832
0.9096	352	422	518	615	707	0.9279			476	580	616
0.9686	281	360	429	515	588	0.9753			237	260	221

Table 3. Densities and Excess Molar Volumes for the Mixtures of β-Pinene + 2-Methyl-1-propanol at (283.15, 298.15, 303.15, 313.15, and 323.15) K

283.15 K			298.15 K			303.15 K			313.15 K			323.15 K		
	ρ	$10^6 \cdot V^E$		ρ	$10^6 \cdot V^E$		ρ	$10^6 \cdot V^E$		ρ	$10^6 \cdot V^E$		ρ	$10^6 \cdot V^E$
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}	x_1	kg·m^{-3}	m^3·mol^{-1}	x_1	kg·m^{-3}	m^3·mol^{-1}
0.0566	815.77	0.002	0.0481	803.39	0.009	0.0505	799.78	0.011	0.0401	790.45	0.023	0.0547	783.66	0.041
0.1066	820.99	0.010	0.1107	809.85	0.024	0.1044	805.23	0.037	0.1042	796.91	0.063	0.1021	788.33	0.080
0.2011	829.88	0.039	0.2010	818.16	0.064	0.2023	814.23	0.085	0.2004	805.6	0.129	0.2070	797.66	0.174
0.2931	837.56	0.072	0.2969	826.03	0.107	0.2999	822.12	0.142	0.3012	813.68	0.197	0.2989	804.85	0.263
0.3950	845.26	0.096	0.4002	833.57	0.155	0.3929	828.94	0.184	0.3902	820.11	0.251	0.4024	812.32	0.327
0.4928	851.82	0.128	0.4896	839.51	0.186	0.4877	835.22	0.225	0.5100	827.98	0.303	0.5041	818.98	0.377
0.6112	859.03	0.151	0.5856	845.33	0.217	0.6108	842.66	0.255	0.6202	834.55	0.328	0.6074	825.20	0.405
0.6906	863.45	0.161	0.6785	850.56	0.230	0.6829	846.72	0.257	0.6847	838.19	0.324	0.6965	830.27	0.399
0.7939	868.88	0.150	0.7841	856.21	0.206	0.7908	852.45	0.234	0.7768	843.06	0.312	0.8063	836.02	0.381
0.8682	872.61	0.122	0.8875	861.41	0.154	0.8846	857.17	0.185	0.8969	849.21	0.230	0.8887	840.50	0.272
0.9393	876.05	0.078	0.9330	863.62	0.120	0.9299	859.39	0.148	0.9601	852.46	0.140	0.9618	844.41	0.142

± 0.001. The uncertainty in the excess molar enthalpy is ± 2 J·mol^{-1}.

Densities and speeds of sound were obtained by means of a vibrating tube densimeter and sound analyzer (Anton Paar DSA48). Following the proposal of Troncoso et al.,[8] this apparatus is connected to a personal computer through a RS-232 connection. This arrangement was initially claimed[8] to lead to uncertainties for the measured properties of ± 0.01 kg·m^{-3} and ± 0.02 m·s^{-1}. In a recent paper[12] by the same authors, a careful study has been carried out for density measurements with the same arrangement, and they conclude that the repeatability and uncertainty are not worse than ± 0.010 kg·m^{-3} and ± 0.04 kg·m^{-3}, respectively. In these measurements, the composition of the binary mixtures was determined 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

Excess molar enthalpies are listed in Table 2, and densities and excess molar volumes can be found in Tables 3 and 4. Finally, speed of sound, speed of sound deviations, isentropic compressibilities, and excess isentropic compressibilities are gathered in Tables 5 to 7. As an illustration, the excess molar enthalpies for the mixtures β-pinene + 2-methyl-2-propanol have been drawn in Figure 1. The excess molar volumes, V^E, were obtained by means of the equation

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

Table 4. Densities and Excess Molar Volumes for the Mixtures of β-Pinene + 2-Methyl-2-propanol at (303.15, 313.15, and 323.15) K

303.15 K			313.15 K			323.15 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) + 2-Methyl-2-propanol (2)				
0.0534	782.04	0.148	0.0561	771.94	0.143	0.0554	761.34	0.119
0.1048	787.79	0.276	0.1080	777.84	0.283	0.1025	766.94	0.241
0.2017	798.21	0.445	0.2041	788.50	0.445	0.2032	778.49	0.415
0.2814	806.31	0.530	0.2996	798.32	0.553	0.3022	788.82	0.553
0.4041	817.92	0.593	0.4028	808.25	0.609	0.3988	798.40	0.609
0.5042	826.75	0.583	0.5039	817.37	0.607	0.5053	808.25	0.616
0.6025	834.76	0.551	0.5964	825.06	0.590	0.5996	816.33	0.595
0.7042	842.46	0.494	0.6957	832.77	0.544	0.7001	824.27	0.563
0.8048	849.62	0.403	0.7979	840.16	0.476	0.7941	831.23	0.509
0.9007	856.11	0.282	0.8930	846.86	0.345	0.8905	838.16	0.390
0.9495	859.38	0.191	0.9475	850.67	0.233	0.9453	842.10	0.278

Table 5. Speeds of Sound and Speed of Sound Deviations for the Mixtures of β-Pinene + 2-Methyl-1-propanol at (283.15, 298.15, 303.15, 313.15, and 323.15) K

283.15 K			298.15 K			303.15 K			313.15 K			323.15 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}
0.0566	1248.3	3.03	0.0481	1195.7	2.6	0.0505	1181.7	2.1	0.0401	1143.3	1.4	0.0547	1114.2	0.9
0.1066	1257.1	6.03	0.1107	1203.9	4.0	0.1044	1188.4	3.2	0.1042	1150.9	2.7	0.1021	1119.3	1.6
0.2011	1270.2	8.17	0.2010	1214.9	5.4	0.2023	1200.2	4.8	0.2004	1160.9	3.2	0.2070	1129.4	2.0
0.2931	1281.1	8.40	0.2969	1225.1	5.3	0.2999	1210.6	5.0	0.3012	1170.6	3.0	0.2989	1136.8	1.0
0.3950	1292.2	7.68	0.4002	1235.2	4.3	0.3929	1219.2	3.9	0.3902	1178.2	1.9	0.4024	1144.6	−0.8
0.4928	1302.0	6.13	0.4896	1243.9	3.5	0.4877	1227.7	2.5	0.5100	1187.7	−0.4	0.5041	1152.7	−2.1
0.6112	1313.9	4.30	0.5856	1252.2	1.5	0.6108	1238.3	0.3	0.6202	1196.8	−2.1	0.6074	1160.6	−3.8
0.6906	1321.1	2.29	0.6785	1260.4	−0.3	0.6829	1244.6	−0.9	0.6847	1202.2	−3.1	0.6965	1167.7	−4.9
0.7939	1330.7	−0.09	0.7841	1270.1	−1.9	0.7908	1254.4	−2.4	0.7768	1210.2	−4.1	0.8063	1177.1	−5.6
0.8682	1337.7	−1.72	0.8875	1280.4	−2.7	0.8846	1263.9	−2.7	0.8969	1222.1	−4.0	0.8887	1184.7	−5.7
0.9393	1346.2	−1.46	0.9330	1285.2	−2.7	0.9299	1268.9	−2.4	0.9601	1230.5	−1.8	0.9618	1192.6	−4.5

Table 6. Isentropic Compressibilities and Excess Isentropic Compressibilities for the Mixtures of β-Pinene + 2-Methyl-1-propanol at (283.15, 298.15, 303.15, 313.15, and 323.15) K

283.15 K			298.15 K			303.15 K			313.15 K			323.15 K		
x_1	κ_S / TPa^{-1}	κ_S^E / TPa^{-1}	x_1	κ_S / TPa^{-1}	κ_S^E / TPa^{-1}	x_1	κ_S / TPa^{-1}	κ_S^E / TPa^{-1}	x_1	κ_S / TPa^{-1}	κ_S^E / TPa^{-1}	x_1	κ_S / TPa^{-1}	κ_S^E / TPa^{-1}
0.0566	786.7	−5.0	0.0481	870.6	−3.0	0.0505	895.4	−2.1	0.0401	967.8	−0.8	0.0547	1027.9	0.7
0.1066	770.8	−9.2	0.1107	852.0	−4.0	0.1044	879.3	−2.4	0.1042	947.4	−0.8	0.1021	1012.5	1.3
0.2011	746.9	−11.8	0.2010	828.1	−4.4	0.2023	852.6	−2.7	0.2004	921.1	1.0	0.2070	982.8	4.0
0.2931	727.5	−11.4	0.2969	806.6	−3.0	0.2999	830.0	−1.4	0.3012	896.9	3.3	0.2989	961.4	7.9
0.3950	708.5	−9.7	0.4002	786.3	−0.7	0.3929	811.6	1.0	0.3902	878.4	5.9	0.4024	939.6	11.8
0.4928	692.5	−7.1	0.4896	769.8	0.8	0.4877	794.4	3.2	0.5100	856.2	9.5	0.5041	919.0	14.0
0.6112	674.3	−4.3	0.5856	754.4	3.3	0.6108	773.9	5.8	0.6202	836.6	11.2	0.6074	899.7	15.7
0.6906	663.6	−1.8	0.6785	740.1	4.9	0.6829	762.4	6.7	0.6847	825.5	11.6	0.6965	883.3	16.0
0.7939	649.9	0.8	0.7841	724.0	5.7	0.7908	745.5	7.1	0.7768	809.9	11.5	0.8063	863.3	14.7
0.8682	640.4	2.2	0.8875	708.1	5.1	0.8846	730.3	5.8	0.8969	788.4	8.5	0.8887	847.7	12.2
0.9393	629.9	1.8	0.9330	701.0	4.4	0.9299	722.7	4.6	0.9601	774.8	3.9	0.9618	832.6	8.0

where ρ is the density of the mixture; x_i is the mole fraction of component i; and M_i and ρ_i are the molar mass and density of pure component i, respectively.

The speed of sound deviations, Δu, were calculated through the expression

$$\Delta u = u - x_1 u_1 - x_2 u_2 \tag{2}$$

where u is the speed of sound in the mixture and u_i is the speed of sound in pure component i.

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

$$\kappa_S = \frac{1}{\rho u^2} \tag{3}$$

The excess isentropic compressibility, κ_S^E, can be calculated from the definition

$$\kappa_S^E = \kappa_S - \kappa_S^{id} \tag{4}$$

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[13] for binary systems

$$\kappa_S^{id} = \phi_1\left(\kappa_{S,1} + \frac{TV_1\alpha_1^2}{C_{P,1}}\right) + \phi_2\left(\kappa_{S,2} + \frac{TV_2\alpha_2^2}{C_{P,2}}\right) - \frac{T(x_1V_1 + x_2V_2)(\phi_1\alpha_1 + \phi_2\alpha_2)^2}{x_1C_{P,1} + x_2C_{P,2}} \tag{5}$$

where T is the temperature; ϕ_i is the volume fraction of component i in the mixture; and $\kappa_{S,i}$, V_i, α_i, and $C_{P,i}$ are the isentropic compressibility, molar volume, isobaric thermal expansivity, and molar heat capacity at constant pressure of pure component i, respectively. Molar volumes and isobaric thermal expansivities were calculated from our measured densities. Referring to the molar heat capacities, they were obtained from

Table 7. Speeds of Sound, Speed of Sound Deviations, Isentropic Compressibilities, and Excess Isentropic Compressibilities for the Mixtures of *β*-Pinene + 2-Methyl-2-propanol at (303.15, 313.15, and 323.15) K

303.15 K					313.15 K					323.15 K				
	u	Δu	κ_S	κ_S^E		u	Δu	κ_S	κ_S^E		u	Δu	κ_S	κ_S^E
x_1	m·s^{-1}	m·s^{-1}	TPa^{-1}	TPa^{-1}	x_1	m·s^{-1}	m·s^{-1}	TPa^{-1}	TPa^{-1}	x_1	m·s^{-1}	m·s^{-1}	TPa^{-1}	TPa^{-1}
0.0534	1110.0	−1.3	1037.8	6.1	0.0561	1066.4	0.0	1139.1	4.0	0.0554	1027.2	1.1	1244.8	0.8
0.1048	1118.6	−1.8	1014.5	9.7	0.1080	1076.0	0.2	1110.4	6.5	0.1025	1036.7	1.9	1213.2	1.7
0.2017	1135.6	−1.9	971.5	13.3	0.2041	1094.3	1.2	1059.1	8.2	0.2016	1056.6	3.4	1151.2	2.6
0.2814	1150.6	−1.0	936.8	13.2	0.2996	1112.7	2.5	1011.7	8.0	0.3022	1076.4	4.7	1094.1	2.5
0.4041	1173.7	0.4	887.5	11.7	0.4028	1132.3	3.5	965.0	7.1	0.3988	1095.2	5.6	1044.2	1.8
0.5042	1192.6	1.6	850.4	9.5	0.5039	1151.0	4.0	923.5	6.1	0.5053	1115.2	5.9	994.8	1.4
0.6025	1210.5	2.2	817.5	7.6	0.5964	1167.1	3.4	889.8	6.1	0.5996	1132.3	5.6	955.5	1.4
0.7042	1228.3	2.0	786.8	6.1	0.6957	1183.8	2.3	856.9	6.2	0.7001	1149.5	4.3	918.1	2.4
0.8048	1244.8	0.7	759.6	5.4	0.7979	1201.1	1.2	825.0	5.5	0.7990	1165.8	2.3	884.5	3.2
0.9007	1260.2	−0.9	735.5	4.6	0.8930	1216.7	−0.3	797.7	4.7	0.8861	1180.1	0.5	856.9	3.9
0.9495	1268.7	−1.0	722.9	3.2	0.9475	1226.2	−0.6	781.8	3.3	0.9367	1188.6	−0.4	841.4	3.8

Table 8. 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·mol^{-1}	113.0	0.15		
C_P/J·mol^{-1}·K^{-1}	10574.4	−89.9	0.26	−0.0002
		2-Methyl-1-propanol		
$10^6 \cdot V$/m^3·mol^{-1}	88.2	−0.06	$2.5 \cdot 10^{-4}$	
C_P/J·mol^{-1}·K^{-1}	181.8	−0.8	0.003	
		2-Methyl-2-propanol		
$10^6 \cdot V$/m^3·mol^{-1}	54.0	0.14		
C_P/J·mol^{-1}·K^{-1}	−660.8	4.9	−0.006	

the literature for both butanols[14] and *β*-pinene.[15] Values from (280 to 330) K for 2-methyl-1-propanol and values from (300 to 330) K for 2-methyl-2-propanol were fitted to a series of the temperature

$$C_{P,i} = a + bT + cT^2 + dT^3 \tag{6}$$

and then the needed values were interpolated. For *β*-pinene, the procedure has been described in previous papers.[2,3] The adjusting coefficients for molar volumes and heat capacities can be found in Table 8.

The data of the excess properties and also those of the speed of sound deviations have been fitted to the following equation

$$Y = \frac{x_1 x_2 \sum_{i=0}^{p} A_i (2x_1 - 1)^i}{1 + \sum_{j=1}^{q} B_j (2x_1 - 1)^i} \tag{7}$$

that is of the Padé approximant type. The symbol Y denotes the properties 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 9 along with the corresponding standard deviations defined by

$$\sigma = \left[\frac{\sum_m (Y^{\text{exptl}} - Y^{\text{calcd}})^2}{m - n} \right]^{1/2} \tag{8}$$

where Y^{exptl} and Y^{calcd} are the experimental and calculated values of property Y; m is the number of experimental points; and n is

Table 9. Fitting Coefficients, A_i and B_i, and the Standard Deviations, σ, Determined for Equation 7

	T/K	A_0	A_1	A_2	A_3	B_1	B_2	σ
				β-Pinene (1) + 2-Methyl-1-propanol (2)				
H^E/J·mol^{-1}	283.15	2005		−960		−0.494	−0.428	7
	298.15	2555		−1450	−348	−0.409	−0.587	3
	303.15	3313		−2120		−0.294	−0.690	7
	313.15	3955		−2534		−0.260	−0.731	7
	323.15	4489		−2791		−0.255	−0.733	12
$V^E \cdot 10^6$/m^3·mol^{-1}	283.15	0.511	0.467	0.249	0.374			0.003
	298.15	0.763	0.633	0.251	0.369			0.005
	303.15	0.900	0.578	0.350	0.634			0.007
	313.15	1.167	0.598	0.645	0.972			0.010
	323.15	1.492	0.655	0.504	0.904			0.010
Δu/m·s^{-1}	283.15	25.4	−33.7	−5.4	−25.7			0.3
	298.15	12.5	−30.4	−8.8	−26.1			0.2
	303.15	9.7	−34.5	−8.3	−10.4			0.2
	313.15	0.1	−34.9	−9.8	−14.4			0.2
	323.15	−8.6	−24.3	28.2	−8.3	−1.0		0.2
				β-Pinene (1) + 2-Methyl-2-propanol (2)				
H^E/J·mol^{-1}	303.15	3321	85		1334		−0.534	20
	313.15	3886	625		1435		−0.498	18
	323.15	4244	1216		−827		−0.613	29
$V^E \cdot 10^6$/m^3·mol^{-1}	303.15	2.325	−0.506	1.078	1.08			0.010
	313.15	2.420	−0.313	1.334	1.414			0.010
	323.15	2.442	−0.283	1.381	2.151			0.013
Δu/m·s^{-1}	303.15	6.4	15.7	−36.2		−0.6		0.1
	313.15	15.5	−3.4	−24.7		−0.3		0.1
	323.15	23.8	−18.2	−12.6		−0.7		0.1

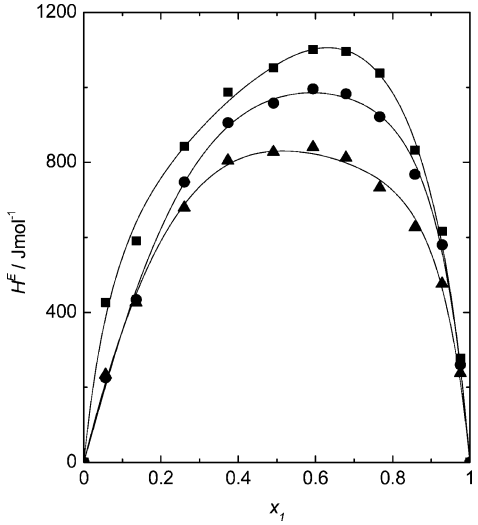

Figure 1. Experimental results and curve fitting (eq 7) for the excess molar enthalpies of the mixture β-pinene (1) + 2-methyl-2-propanol (2): ▲, 303.15 K; ●, 313.15 K; ■, 323.15 K.

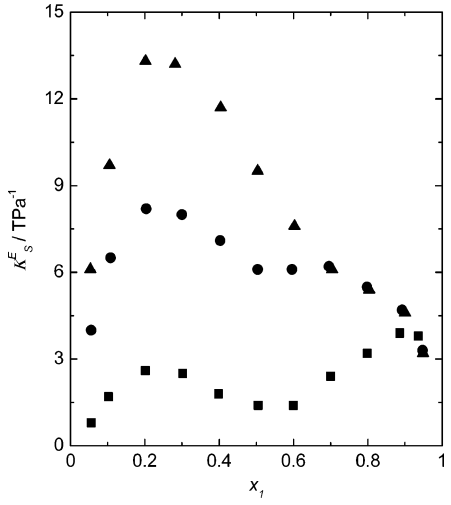

Figure 2. Excess isentropic compressibility for the mixture β-pinene (1) + 2-methyl-2-propanol (2): ▲, 303.15 K; ●, 313.15 K; ■, 323.15 K.

the number of coefficients used in the fitting equation. The curves obtained are also represented in the corresponding figures. It can be observed that eq 7 becomes the well-known Redlich−Kister polynomial when the coefficients in the denominator are zero. But in several cases, especially for excess molar enthalpy, the Redlich−Kister polynomials were not able to fit the data accurately enough and the complete eq 7 should be used.

The excess molar enthalpies and excess molar volumes are positive on the whole composition range for the mixtures of the hydrocarbon β-pinene with both alkanols at all temperatures. For the excess molar enthalpies, the values are quite similar especially in the maxima, whereas for the excess molar volumes, the values for mixtures with 2-methyl-1-propanol are lower than the values for mixtures with 2-methyl-2-propanol. The excess enthalpies for the mixture β-pinene + 2-methyl-2-propanol drawn in Figure 1 show a flat zone in the maximum at 303.15 K. This was observed also for the mixture β-pinene + ethanol[1] and was explained considering that the alkanol, although miscible with β-pinene, is near the limit between miscibility and immiscibility with the hydrocarbon. The behavior of these excess properties has the same basis that was advanced[1−3] for other mixtures of β-pinene + alkanol.

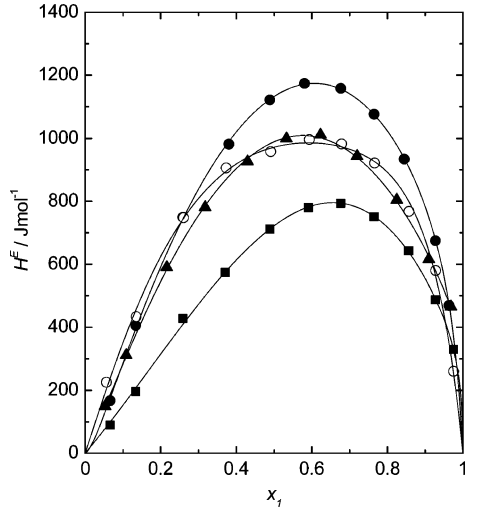

Figure 3. Experimental results and curve fitting (eq 7) for the excess molar enthalpies at 313.15 K of the mixtures: ■, β-pinene + 1-butanol; ●, β-pinene + 2-butanol; ▲, β-pinene + 2-methyl-1-propanol; ○, β-pinene + 2-methyl-2-propanol. β-Pinene is component 1.

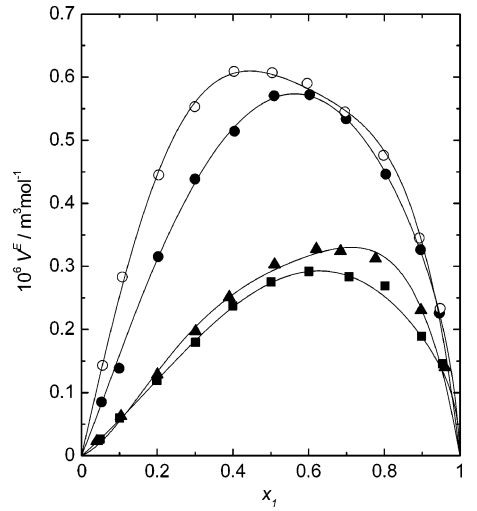

Figure 4. Experimental results and curve fitting (eq 7) for the excess molar volumes at 313.15 K of the mixtures: ■, β-pinene + 1-butanol; ●, β-pinene + 2-butanol; ▲, β-pinene + 2-methyl-1-propanol; ○, β-pinene + 2-methyl-2-propanol. β-Pinene is component 1.

The speed of sound deviations and the excess isentropic compressibilities are sigmoidal for β-pinene + 2-methyl-1-propanol with an exception at 323.15 K where they are positive throughout. It must be said that among the mixtures of β-pinene with the isomers of butanol[2] the system (β-pinene + 2-methyl-1-propanol) is the only one which exhibits negative values of the excess isentropic compressibility. For the mixture with 2-methyl-2-propanol, quite unusual behavior is observed in both speed of sound deviation and excess isentropic compressibility, as shown in Figure 2 for the last property.

To determine the effect on the studied thermodynamic properties of both the branching of the chain and the presence of a tertiary alcohol, the results obtained for the present mixtures at 313.15 K are compared in Figures 3 and 4 with those reported for the mixtures of β-pinene with 1-butanol or 2-butanol[2] at the same temperature. It appears that the excess molar enthalpies for β-pinene + 2-methyl-1-propanol or 2-methyl-2-propanol are placed between those of the mixtures β-pinene + 1-butanol and β-pinene + 2-butanol. Then, the branching of the alkanol chain in 2-methyl-1-propanol leads to an increase of the breaking of hydrogen bonds with respect to the 1-butanol. On the other hand,

the change from a secondary to a tertiary alkanol does not increase the excess molar enthalpy as could be expected from the behavior observed for the change from a primary to a secondary alkanol. This could be due to the fact that 2-methyl-2-propanol is less associated than 2-butanol.[16] As for the excess molar volumes, the behavior is clearly different from that of excess molar enthalpy. For that first property, the primary, secondary, or tertiary character of the alcohols seems to be the main feature. Then, excess molar volumes for β-pinene + 1-butanol and β-pinene + 2-methyl-1-propanol are very similar, being slightly greater when the alkanol is branched.

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) Langa, E.; Mainar, A. M.; Pardo, J. I.; Urieta, J. S. 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. *J. Chem. Eng. Data* **2006**, *51*, 392−397.

(3) Ribeiro, A. F.; Langa, E.; Mainar, A. M.; Pardo, J. I.; Urieta, J. S. Excess Enthalpy, Density, and Speed of Sound for the Mixtures β-Pinene + 1- or 2-Pentanol at (283.15, 298.15, and 313.15) K. *J. Chem. Eng. Data* **2006**, *51*, 1846−1851.

(4) Taylor L. T. *Supercritical fluid extraction*; John Wiley & Sons: New York, 1996.

(5) Wilhoit, R. C.; Hong, X.; Frenkel, M.; Hall, K. R. Thermodynamic properties of organic compounds and their mixtures. Subvolume F: Densities of polycyclic hydrocarbons. *Landolt-Börstein numerical data and functional relationships in science and technology*, Group 4; Springer-Verlag: Berlin, 1999; Vol. 8.

(6) 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.

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

(8) 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.

(9) Venkatesulu, D.; Venkatesu, P.; Rao, M. V. P. Speed of Sound and Isentropic Compressibilities of Trichloroethylene with Branched Alcohols at 303.15 K. *J. Chem. Eng. Data* **1997**, *42*, 1145−1146.

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

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

(12) Sanmamed, Y. A.; González-Salgado, D.; Troncoso, J.; Cerdeiriña, C. A.; Romaní, L. Viscosity-induced errors in the density determination of room temperature ionic liquids using vibrating tube densitometry. *Fluid Phase Equilib.* **2007**, *252*, 96−102.

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

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

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

(16) Pardo, J.; Mainar, A. M.; López, M. C.; Royo, F.; Urieta, J. S. Solubility of gases in butanols IV. Solubilities of nonpolar gases in 2-methyl-2-propanol at 303.15 K and 101.33 kPa partial pressure of gas. *Fluid Phase Equilib.* **1999**, *155*, 127−137.

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