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Excess Molar Enthalpies of Mixtures of (±)-Linalool with Several Alkanols

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ABSTRACT: Excess molar enthalpies are reported for mixtures of (±)-2,6-dimethyl-2,7-octadien-6-ol (linalool) with ethanol, propan-1-ol, propan-2-ol, and butan-1-ol at the temperatures (283.15, 298.15, 313.15, and 328.15) K and atmospheric pressure, covering the whole composition range. The values of excess molar enthalpy at each temperature have been fitted using approximants of Padé. Most of the mixtures show negative values of the excess enthalpy, indicating the formation of attractive interactions, mainly hydrogen bonds, between the molecules of linalool and molecules of the different alkanols.

INTRODUCTION

In the last few years, our research group has carried out a study of the thermophysical behavior of mixtures consisting of an alkanol and a compound present in essential oils from plants as is the case of β-pinene,[1−4] 1,8-cineole,[5−7] or (±)-linalool.[8,9] The information about these kind of mixtures is important with regard to the modeling of processes of extraction with supercritical carbon dioxide of essential oils from plants. The ability of supercritical carbon dioxide to dissolve polar compounds is quite limited, but it can be significantly improved with the addition of small amounts of polar compounds which would act as cosolvents. For this purpose, short-chain alkanols such as ethanol and propan-1-ol[10] are among the most suitable candidates. With regard to the essential oils, which in many cases are quite complex mixtures, their behavior when mixed with those alkanols can be fairly approximated by selecting their major component.

Following that research line, we report in this paper the excess molar enthalpies of the mixtures of (±)-2,6-dimethyl-2,7-octadien-6-ol (linalool) + ethanol, propan-1-ol, propan-2-ol, and butan-1-ol. The excess enthalpies have been measured over the whole composition range at (283.15, 298.15, 313.15, and 328.15) K and atmospheric pressure. Linalool is a monoterpene that constitutes the main component of the essential oil of several plants. The values of the excess enthalpy of the mixtures with ethanol and propan-1-ol would provide information about the linalool—alkanol interactions and, consequently, about the extracting power of those alkanols. Also, mixtures of linalool with propan-2-ol and butan-1-ol have been studied to achieve a more complete view of the effect of branching and chain length on the linalool—alkanol interactions.

EXPERIMENTAL SECTION

Materials. The chemicals used were (±)-linalool (purity 98.1 %), propan-1-ol (purity 99.9 %), and butan-1-ol (purity better than 99.8 %) by Aldrich and ethanol and propan-2-ol (purity 99.9 % for both compounds) by Scharlab (Barcelona, Spain). The stated purities of the chemicals were checked by gas chromatography analysis. No further purification was attempted. Experimental values of density for the pure components at 298.15 K are reported in Table 1 and compared with the available bibliographic values.[8,11−14] These densities were obtained by means of a vibrating-tube densimeter Anton Paar DSA 5000, their uncertainty being ± 0.04 $\text{kg}\cdot\text{m}^{-3}$. A good agreement can be observed between both sets of data.

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 uncertainty in the measurement of the temperature is estimated to be ± 0.01 K. The calorimeter has been tested with reference to recommended values[15] of the mixture of hexane with 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. As described in detail elsewhere,[1−3] the calibration was made by determining through a Sartorius analytical balance with a precision of ± 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) $\text{cm}^3\cdot\text{min}^{-1}$). A determination was made every 0.025 $\text{cm}^3\cdot\text{min}^{-1}$. 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 for each composition at several total flow rates of mixture to determine the best total flow rate, which is that leading to the highest absolute value of excess enthalpy. The uncertainty in the excess molar enthalpy is less than 2.7 %.

RESULTS AND DISCUSSION

The values of the excess molar enthalpy for the mixtures can be found in Table 2. They were correlated at each temperature

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Table 1. Comparison Between the Experimental and the Bibliographic Values of Density, ρ, of the Pure Compounds at 298.15 K

	$\rho/\mathrm{kg\cdot m^{-3}}$	
compound	expt	lit.
(±)-linalool	857.00	856.9[a] 857.60[b]
ethanol	785.46	784.93[c] 785.09[d] 785.49[e]
propan-1-ol	799.56	799.60[c] 799.75[d]
propan-2-ol	781.23	781.26[c,d]
butan-1-ol	805.71	805.75[c] 806.0[d]

[a] Reference 8. [b] Reference 11. [c] Reference 12. [d] Reference 13. [e] Reference 14.

using the approximants of Padé

$$H_m^E = \frac{x_1 x_2 \sum_{i=0}^{p} A_i (2x_1 - 1)^i}{1 + \sum_{j=1}^{q} B_j (2x_1 - 1)^j} \qquad (1)$$

where H_m^E is the excess molar enthalpy, x_i is the mole fraction of component i, and A_i and B_j are adjustable coefficients that were determined using a Levenberg–Marquardt algorithm. This equation can correlate quite asymmetric as well as sigmoidal shaped sets of data. Coefficients A_i and B_j are listed in Table 3 along with the corresponding standard deviations that were calculated through the following relation

$$\sigma = \left[\frac{\sum_m (H_m^{E,\,exp} - H_m^{E,\,cal})^2}{m - n}\right]^{1/2} \qquad (2)$$

where $H_m^{E,exp}$ and $H_m^{E,cal}$ are the experimental and calculated values of the excess molar enthalpy, 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 Figure 1a–d. It can be observed that eq 1 becomes the well-known Redlich–Kister polynomial when the coefficients in the denominator are zero.

The values of the excess molar enthalpies are negative over the whole composition range for the mixtures of (±)-linalool with ethanol and propan-1-ol as well as for the mixtures of (±)-linalool with butan-1-ol at the higher temperatures (313.15 and 328.15) K. For the remaining systems, that is, mixtures of (±)-linalool with butan-1-ol at (283.15 and 298.15) K and mixtures of (±)-linalool with propan-2-ol, the data fit to a sigmoidal-shaped curve corresponding the positive values to the (±)-linalool-rich regions with the only exception of the mixture of (±)-linalool with propan-2-ol at 328.15 K for which the negative values are limited to mole fractions of (±)-linalool lower than 0.1. The values of the excess molar enthalpy increase in the series

ethanol < propan-1-ol < butan-1-ol < propan-2-ol

Table 2. Excess Molar Enthalpies, H_m^E, for the Mixtures of (±)-Linalool with Alkanols at Several Temperatures

	$H_m^E/\mathrm{J\cdot mol^{-1}}$			
x_1	T/K = 283.15	T/K = 298.15	T/K = 313.15	T/K = 328.15
	(±)-Linalool (1) + Ethanol (2)			
0.047	−153	−153	−175	−173
0.094	−310	−337	−351	−334
0.190	−600	−630	−660	−600
0.290	−770	−830	−850	−750
0.387	−800	−870	−890	−790
0.481	−750	−800	−830	−740
0.585	−640	−690	−710	−640
0.695	−460	−510	−540	−480
0.780	−311	−390	−420	−366
0.895	−140	−177	−198	−172
0.946	−69	−88	−104	−97
	(±)-Linalool (1) + Propan-1-ol (2)			
0.048	−169	−164	−179	−172
0.096	−323	−329	−329	−292
0.188	−540	−570	−560	−470
0.290	−640	−700	−680	−550
0.383	−650	−700	−680	−550
0.491	−600	−620	−600	−500
0.584	−510	−520	−510	−420
0.693	−370	−380	−390	−325
0.794	−246	−257	−287	−240
0.894	−113	−130	−149	−127
0.945	−58	−68	−80	−69
	(±)-Linalool (1) + Propan-2-ol (2)			
0.024	−33	−31	−24	−8
0.048	−46	−49	−38	−10
0.097	−59	−62	−48	−3
0.195	−73	−73	−45	26
0.292	−78	−72	−35	55
0.392	−82	−68	−23	77
0.490	−82	−56	−7	90
0.592	−73	−37	8	92
0.693	−50	−12	20	77
0.796	−19	6	19	55
0.894	3	9	7	24
0.948	2	3	3	11
	(±)-Linalool (1) + Butan-1-ol (2)			
0.042	−13	−30	−30	−22
0.085	−21	−60	−66	−92
0.174	−22	−95	−146	−220
0.265	−12	−101	−195	−303
0.359	−1	−91	−215	−343
0.457	9	−76	−213	−350
0.559	24	−57	−187	−326
0.661	40	−28	−147	−261
0.771	57	3	−92	−184
0.884	59	26	−31	−88
0.943	44	22	−8	−37

Table 3. Fitting Coefficients, A_i and B_j, Determined for Equation 1 along with the Corresponding Standard Deviations, σ, Calculated through Equation 2

T	A_0	A_1	A_2	A_3				σ
K	$\mathrm{J \cdot mol^{-1}}$	$\mathrm{J \cdot mol^{-1}}$	$\mathrm{J \cdot mol^{-1}}$	$\mathrm{J \cdot mol^{-1}}$	B_1	B_2	B_3	$\mathrm{J \cdot mol^{-1}}$
			(±)-Linalool (1) + Ethanol (2)					
283.15	−2976	2106	535	−1081				11
298.15	−3210	2148	344	−1401				17
313.15	−3299	2101	108	−1323				14
328.15	−2928	1799	−24	−805				7
			(±)-Linalool (1) + Propan-1-ol (2)					
283.15	−2371	1636	−184					9
298.15	−2487	2125	−244	−966				10
313.15	−2414	1893	−579	−785				11
328.15	−1966	1335	−686					8
			(±)-Linalool (1) + Propan-2-ol (2)					
283.15	−328	−65	354	361	0.63	−0.24		3
298.15	−209	142	345	150	0.93			2
313.15	−16	337	−111			0.42	1.14	2
328.15	363		−503	127	−0.250	−0.636		2
			(±)-Linalool (1) + Butan-1-ol (2)					
283.15	63	253	106	307	−0.12	−0.22		1
298.15	−278	532			−0.25	−0.42		3
313.15	−826	−98	829		0.68	−0.34		6
328.15	−1371	−746	738		0.96			4

for each temperature except for 283.15 K where butan-1-ol and propan-2-ol exchange their places in the sequence.

Referring to the variation of the excess molar enthalpy with the temperature, it is remarkably complex because it changes depending on the system considered. For the mixture of (±)-linalool with propan-2-ol, the excess molar enthalpy increases as the temperature increases, whereas the opposite behavior is observed for the mixture of (±)-linalool with butan-1-ol. For the mixture of (±)-linalool with ethanol, the excess molar enthalpy decreases in the range from (283.15 to 313.15) K and then increases when the temperature rises to 328.15 K. A similar pattern can be observed for the mixture of (±)-linalool with propan-1-ol, but in this case the excess molar enthalpy decreases when passing from (283.15 to 298.15) K and then increases when the temperature rises. This complexity would depend on the differences in the variation with the temperature of the strength of the bonds both in the pure components and in the mixtures as well as the change of the densities with the temperature.

The excess enthalpy data fully ascertain the interpretation advanced by Torcal et al.[8] and García-Abarrio et al.[9] to explain the reported data of excess molar volume that were measured for mixtures of (±)-linalool with ethanol, propan-1-ol, and propan-2-ol at the same temperatures considered in this work. For all of the mixtures they obtained negative excess volumes that are attributed to the formation of hydrogen bonds between the molecules of linalool and alkanol. Lan et al.[16] also obtained negative excess volumes at 303.15 K for mixtures of (±)-linalool with ethanol, propan-1-ol, and butan-1-ol. It should be indicated that there is a quite good agreement between all of the values reported in those papers.

The prevailing exothermic behavior of the mixtures points to the formation of specific interactions between different molecules. All of the pure alkanols interact through hydrogen bonds, and the same could be expected of linalool that has an OH group in its molecule. When mixing, these hydrogen bonds would break to a certain extent, but they would be replaced by new hydrogen bonds linking linalool molecules with alkanol molecules. In the case, at least, of butan-1-ol, new bonds could be also established between the OH group of the alkanol and the π-clouds on the double bonds of linalool.[17]

The trend in the values of excess enthalpy is closely related to the size and shape of the alkanol. This is expected because the lower the size of the molecules, the better they could fit among the molecules of (±)-linalool and then more easily would orient to form the hydrogen bonds. This would account for the behavior observed for alkan-1-ols. But the shape of the alkanol is also important as is shown by the mixture of linalool with propan-2-ol. This alkan-2-ol has one methyl group at each side of the OH group in such a way that once formed the hydrogen bond the structure will be quite rigid whereas the hydrocarbon chains of propan-1-ol and butan-1-ol are more flexible and can likely conform to the free space around them. Thus, the position of OH group in propan-2-ol would hinder the formation of bonds between its molecules and those of linalool with the subsequent higher values of excess enthalpy.

The values of the excess molar volumes[8,16] increase for each mixture ((±)-linalool + alkanol) following the same sequence as the excess molar enthalpies. This is to be expected because the more exothermic the mixture is, the shorter would be the distance between molecules due to the formation of bonds and, consequently, the lower would be the volume occupied. But the fact that the excess volumes are always negative indicate that steric factors (such as the proposed accommodation of the

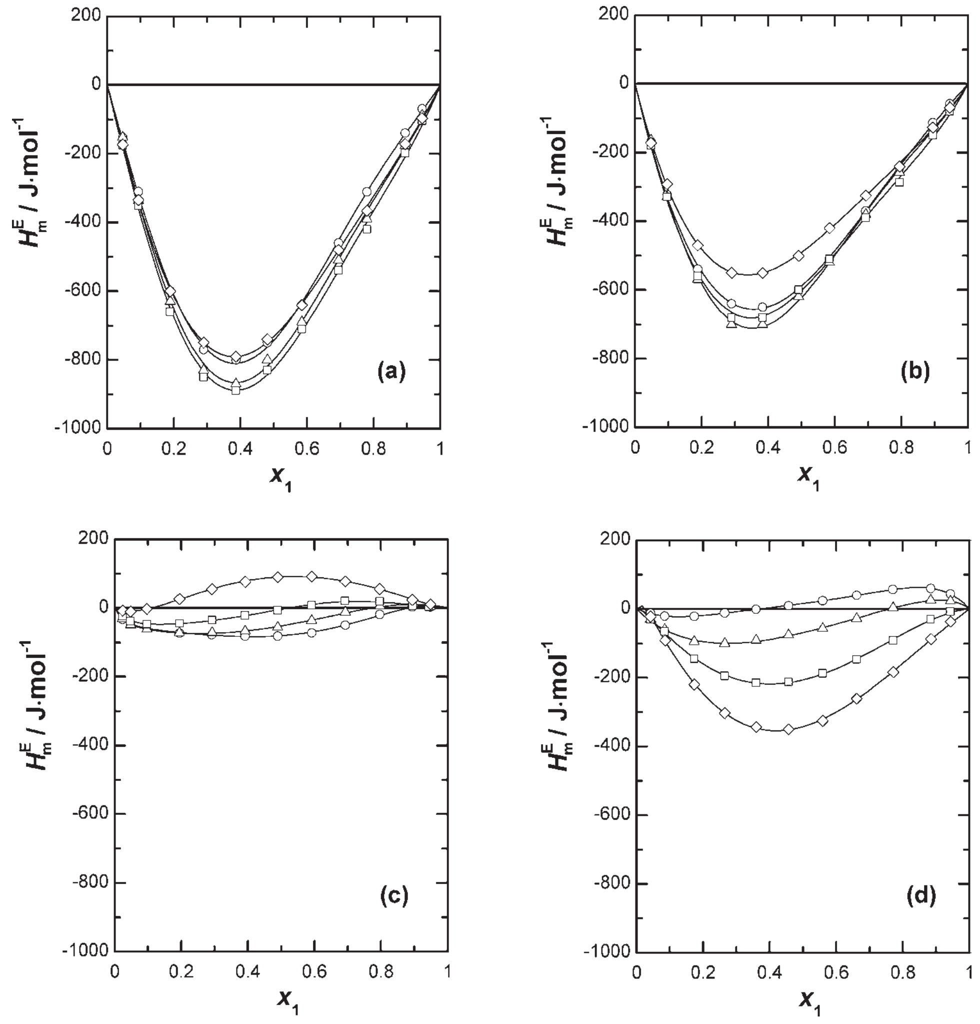

Figure 1. Excess molar enthalpies of the mixtures of (±)-linalool with (a) ethanol, (b) propan-1-ol, (c) propan-2-ol, and (d) butan-1-ol along with the corresponding fitting curves at several temperatures: ○, 283,15 K; △, 298.15 K; □, 313.15 K; and ◇, 328.15 K.

molecules of the alkanols among the molecules of linalool) are relevant in the volumetric behavior of these mixtures.

The variation of the excess molar volumes of some of the mixtures[8,9] with temperature reflects that of the excess enthalpies. Thus, the excess molar volumes of the mixture of (±)-linalool with propan-2-ol increases as temperature rises, whereas for the mixture of (±)-linalool with propan-1-ol the excess molar volume decreases between (283.15 and 313.15) K and then slightly increases at 328.15 K. But no inversion in the trend with temperature is observed for the mixture of (±)-linalool with ethanol whose excess volume decreases as temperature increases. Then the enthalpic and volumetric behavior of the mixtures of (±)-linalool with alkanols is the result of a quite complex combination of bonding sites, sizes, and shapes of the molecules involved.

In relation with the use of these alkanols as cosolvents in the supercritical extraction with carbon dioxide of essential oils whose major component is linalool, the excess enthalpy data confirm the adequacy of ethanol and propan-1-ol as they would strongly bind with that component. But for the overall process the ease of the subsequent separation of (±)-linalool and alkanol should be considered. Then a study of the vapor−liquid equilibria involved is necessary, which we are currently carrying out.

■ CONCLUSIONS

The excess molar enthalpy has been measured over the whole composition range for mixtures of (±)-linalool with ethanol, propan-1-ol, propan-2-ol, and butan-1-ol at at (283.15, 298.15, 313.15, and 328.15) K and atmospheric pressure. The measured values are always negative for the mixtures of (±)-linalool with ethanol and propan-1-ol at all of the temperatures and for the mixture of (±)-linalool with butan-1-ol at (313.15 and 328.15) K. The excess molar enthalpies are sigmoidal shaped for the mixtures of (±)-linalool with propan-2-ol and butan-1-ol showing positive values at high mole fractions of linalool. The excess enthalpy increases in the series: ethanol, propan-1-ol, butan-1-ol, and propan-2-ol. The variation of the excess enthalpy with the temperature is complex, changing from one mixture to another. The prevailing negative values of the excess enthalpy can be attributed to the formation of hydrogen bonds between the molecules of linalool and alkanol.

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