Isobaric molar heat capacities of the mixture {p-cymene + ethanol} at several temperatures and atmospheric pressure

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ABSTRACT.

Experimental isobaric molar heat capacities at atmospheric pressure have been determined every 10 K for the mixture {p-cymene (1) + ethanol (2)} in the temperature interval (298.6-328.4) K over the whole composition range with a Calvet type calorimeter. Densities, necessary for calculating heat capacities, have been also measured in the same conditions. Excess molar volumes have been calculated from densities. Excess molar heat capacities have been calculated from the molar heat capacities, their values being positive and increasing as the temperature rises. Excess properties are discussed in terms of intermolecular interactions. The solvation model COSMO-RS has been applied to predict the excess molar heat capacities. The model predicts fairly well the values of the excess heat capacities.

KEYWORDS: (p-cymene + ethanol) mixture, molar heat capacity, density, atmospheric pressure, COSMO-RS

1. Introduction

The thermodynamic behavior of many binary mixtures (alkanol + alkylbenzene) has been often determined and interpreted. In particular, for the mixtures of ethanol + benzene, or + toluene, or + ethyl-benzene, or + cumene, or + xylene, properties such as H^E [1-12], V^E [7, 10, 13, 17-18], G^E [19] and C_p[11, 14, 20] have been measured. An interesting system related with them is the mixture of 1-methyl-4-(1-methyl-ethyl)benzene, usually known as p-cymene, with ethanol, a mixture for which no thermodynamic data have been found in the literature.

p-Cymene is a monocyclic monoterpene that is present in volatile oils from over 100 vegetal species being a major component in the extracts of certain plants such as cumin and thyme. p-Cymene also occurs naturally in more than 200 foodstuffs, such as orange juice, grapefruit, carrots, raspberries, butter, nutmeg, tangerine, oregano, and most any other spice [21]. Some studies have recently proven that p-cymene possesses antinociceptive and anti-inflammatory activity [22] but the commercial importance of p-cymene is due to its utilization as an intermediate in the industrial syntheses of fragrances, flavours, herbicides and, principally, pharmaceuticals.

The relevance of thermophysical data of the mixture of p-cymene with ethanol lies in the information they could add to that already existing about mixtures (alkylbenzene + alkanol) and the corresponding increase of knowledge about the interactions acting in those mixtures. From a more practical point of view, volatile oils containing p-cymene could be extracted from plants by various methods such as maceration with ethanol or advanced separation techniques using supercritical CO_2 and ethanol as cosolvent [23]. Besides, separation of different compounds in the obtained volatile oils could be performed through supercritical antisolvent techniques [24] using ethanolic solutions of those volatile oils. Then, knowledge of the thermodynamic behavior of mixtures (p-cymene + ethanol) is important for designing those processes.

In this work, values of experimental isobaric molar heat capacities for the binary mixtures of p-cymene with ethanol, at four temperatures (298.6, 308.5, 318.5 and 328.4) K and atmospheric pressure over the whole composition range are reported. Densities have been also measured at (298.15, 308.15, 318.15 and 328.15) K and atmospheric pressure over the whole composition range. Then, excess molar volumes and excess molar heat capacities have been calculated for the mixture. The solvation model COSMO-RS [25-27] has been applied in order to evaluate its ability to predict the excess molar heat capacity.

2. Experimental

2.1 Materials

The chemicals used were p-cymene and ethanol. Additionally, water (milliQ quality) was used to perform the measurements. Their description can be found in table 1. Experimental values of density for the pure components at 298.15 K are reported in Table 2 and compared with available bibliographic values [28-33]. In general, a good agreement can be observed between both sets of data. But for p-cymene there are noticeable deviations between our data and those of Ribeiro *et al.* [28] which are lower than ours and also with those of Liao *et al.* [31] which are greater than ours. These differences can be attributed to the different techniques used to determine the density, a pycnometer in the case of Ribeiro *et al.*, a hydrostatic balance in the case of Liao *et al.* and a vibrating tube densimeter in our case. In any case our intermediate values coincide well with those provided by TRC Tables.

TABLE 1

Sample description.

Chemical name	Source	Purity	Purification method	Analysis method
p-Cymene	Aldrich	0.995[a]	None	GC[c]
Ethanol	VWR	0.999[b]	None	GC[c]
Water	Laboratory	MilliQ[d]	None	Electrical resistivity

[a] Mole fraction purity.
[b] Volume fraction purity. Water content < 0.001 (v/v) provided by the supplier.
[c] Gas-Chromatography from the supplier.
[d] 18.2 MΩ·cm

TABLE 2

Experimental and literature densities for the pure liquids at T = (298.15, 308.15, 318.15, 328.15) K and atmospheric pressure p = (0.1 ±0.002) MPa.

Compound	ρ / kg·m^{-3}							
	T/K = 298.15		T/K = 308.15		T/K = 318.15		T/K = 328.15	
	Exp.[a]	Lit.	Exp.[a]	Lit.	Exp.[a]	Lit.	Exp.[a]	Lit.
p-cymene	852.93	852.1[b] 852.26[c] 853.3[d] 853.47[e]	844.89	844.5[b] 844.67[c] 845.59[e]	836.81	837.4[b] 836.87[c] 838.46[e]	828.69	828.88[c]
Ethanol	785.11	784.93[d] 785.01[f] 785.11[g]	776.44	776.34[f] 776.47[g]	767.62	767.53[f] 767.63[g]	758.60	758.57[f] 758.61[g]

[a] Measured with a densimeter Anton Paar DMA 5000 M, Standard uncertainty u is $u(T)$ = ±0.01 K, and the combined expanded uncertainty U_c is $U_c(\rho)$ = 0.7 kg·m^{-3} with 0.95 level of confidence ($k \approx$ 2); [b]Ref [28]; [c]Ref [29]; [d]Ref [30]; [e]Ref [31] [f]Ref [32]; [g]Ref [33]

2.2 Equipments

Heat capacities at atmospheric pressure were determined by means of a Calvet type calorimeter, Setaram C80 (France). A detailed description of the equipment, the method followed

for calorimetric determination as well as the calibration and validation procedure have been previously published [34].

The calorimeter has a measurement and a reference cell which are connected in opposition in such a way that non-desired effects that could affect the measurement cell are cancelled by the reference cell that would be also affected. Referring to the procedure, the incremental temperature mode (step method) was used. Specifically, the temperature was increased 10 K in every step with a heating rate of 0.1 K·min^{-1} followed by an isothermal delay of 9000 s. To carry out a measurement, three runs are necessary. In all of them the reference cell was filled with air at atmospheric pressure. The measurement cell was filled with air in the first run, whereas it was filled with water (milliQ quality) in the second run and with a sample of the liquid (pure compound or mixture) whose heat capacity was to be determined in the third run. Water was chosen as the reference liquid due to the high accuracy with which their heat capacity values are known [35]. Then, molar heat capacity is calculated through the equation

$$C_{P,\mathrm{m,sample}} = C_{P,\mathrm{m,water}} \frac{M_{\mathrm{sample}}\,\rho_{\mathrm{water}}\,(Q_3 - Q_1)}{M_{\mathrm{water}}\,\rho_{\mathrm{sample}}\,(Q_2 - Q_1)} \qquad (1)$$

where $C_{P,\mathrm{m}}$ is the molar heat capacity, M is the molar mass, ρ is the density and Q_1, Q_2 and Q_3 are the heats exchanged in the first, second and third runs, respectively. The equipment was checked by measuring the molar heat capacity of heptane and comparing the results with the values in the critical selection of Zábranský *et al.* [36] and the relative expanded uncertainty (coverage factor $k = 2$) in the molar heat capacity is estimated to be ±0.008.

Densities for water [37] were obtained from the literature whereas densities for p-cymene and its mixtures at 0.1 MPa (atmospheric pressure) were measured by means of a vibrating tube densimeter Anton Paar DMA 5000 M. The expanded uncertainty ($k = 2$) for density is estimated to

be better than ± 0.7 kg·m^{-3}. The densimeter was calibrated using water (Milli-Q quality) and ambient air.

For determining both densities and heat capacities, samples of the mixtures of p-cymene and ethanol were prepared by weighing using a Mettler-Toledo analytical balance, model AB265-S, with a precision of $\pm 10^{-4}$ g. Hence, the expanded uncertainty ($k = 2$) in the mole fraction was estimated to be less than ± 0.0005.

3. Results and discussion

Experimental values of densities, in the whole composition range, for the mixture {p-cymene (1) + ethanol (2)} are gathered in table 3.

TABLE 3

Mole fraction, x_1, density, ρ, for the mixture {p-cymene (1) + ethanol (2)} at $T =$ (298.15, 308.15, 318.15, 328.15) K and atmospheric pressure $p = $ (0.1 ± 0.002) MPa.

	ρ / kg·m^{-3}			
x_1	T/K = 298.15	T/K = 308.15	T/K = 318.15	T/K = 328.15
0	785.11	776.44	767.62	758.60
0.0494	793.49	784.81	775.96	766.90
0.0995	800.72	792.02	783.15	774.08
0.2000	812.35	803.65	794.79	785.71
0.3009	821.26	812.60	803.77	794.75
0.4037	828.42	819.80	811.02	802.06
0.5034	834.18	825.62	816.91	808.04
0.6023	838.73	830.22	821.58	812.79
0.7017	842.86	834.43	825.88	817.21
0.8020	846.53	838.18	829.75	821.21
0.8970	849.61	841.37	833.06	824.68
0.9509	851.34	843.19	834.99	826.74
1	852.93	844.89	836.81	828.69

Standard uncertainty u is $u(T) = \pm 0.01$ K, and the combined expanded uncertainties U_c are $U_c(x_1) = \pm 0.0005$ and $U_c(\rho) = 0.7$ kg·m^{-3} with 0.95 level of confidence ($k \approx 2$).

Excess molar volumes were obtained from these densities by means of the equation

$$V_m^E(p,T) = x_1 M_1 \left(\frac{1}{\rho} - \frac{1}{\rho_1} \right) + x_2 M_2 \left(\frac{1}{\rho} - \frac{1}{\rho_2} \right) \qquad (2)$$

and their values appear represented in figure 1. The estimated expanded uncertainty ($k = 2$) for V_m^E is $\pm 0.008 \cdot 10^6 \, \mathrm{m^3 \cdot mol^{-1}}$. This excess quantity was fitted to the Redlich–Kister equation

$$V_m^E = x_1 (1 - x_1) \sum_{i=0}^{N} A_i (2x_1 - 1)^i \qquad (3)$$

The values of the A_i adjustable parameters are shown in table 4 along with the corresponding standard deviations, σ, defined by equation (4)

TABLE 4

Fitting parameters for the excess molar volumes (equation 3) of the mixture {p-cymene (1) + ethanol (2)} at $T = (298.15, 308.15, 318.15, 328.15)$ K and atmospheric pressure $p = (0.1 \pm 0.002)$ MPa.

	$T / K = 298.15$	$T / K = 308.15$	$T / K = 318.15$	$T / K = 328.15$
$10^6 \cdot A_0 / \mathrm{m^3 \, mol^{-1}}$	0.26	0.44	0.67	0.95
$10^6 \cdot A_1 / \mathrm{m^3 \, mol^{-1}}$	0.46	0.52	0.60	0.68
$10^6 \cdot A_2 / \mathrm{m^3 \, mol^{-1}}$	0.30	0.41	0.51	0.63
$10^6 \cdot A_3 / \mathrm{m^3 \, mol^{-1}}$	0.40	0.51	0.59	0.67
$10^6 \cdot \sigma / \mathrm{m^3 \, mol^{-1}}$	0.004	0.004	0.005	0.005

$$\sigma = \left[\frac{\sum_{j=1}^{m} \left(V_{m,exp}^E - V_{m,cal}^E \right)^2}{m - n} \right]^{\frac{1}{2}} \qquad (4)$$

where the subscripts exp and cal indicate the experimental and calculated values, respectively, m is the number of experimental points, and n is the number of coefficients used in the fitting equation. Fitting curves have been also included in figure 1.
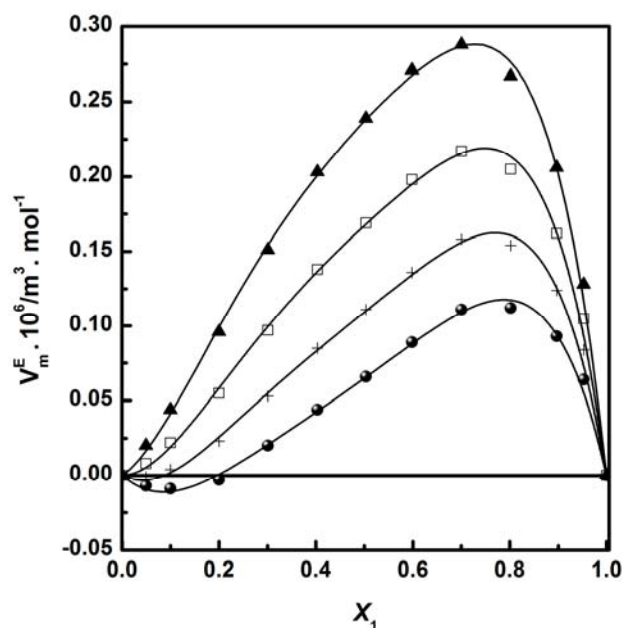
FIGURE 1. Excess molar volumes, V_m^E, for the mixture {p-cymene + ethanol} as a function of p-cymene mole fraction, x_1, at the temperatures: (●) 298.15 K; (+) 308.15 K; (□) 318.15 K; and (▲) 328.15 K along with the curves for the fitting to the mole fraction (equation 3).

The excess volumes of the mixture (p-cymene + ethanol) are sigmoidal at 298.15 and 308.15 K being negative in the zone very rich in ethanol and positive in the remaining composition range. At 318.15 and 328.15 K the excess molar volumes are positive throughout. In general terms, the excess molar volume increases as the temperature rises at a given molar fraction. This volumetric behavior agrees with that observed for the mixtures (benzene + ethanol) [7, 13-14], (toluene + ethanol) [7, 14-16]], (o-xylene or m-xylene + ethanol) [17] and (p-xylene + ethanol) [10, 13, 17] which are also sigmoidal with negative values in the zone rich in ethanol. For the mixture (p-cymene + ethanol) the excess molar volumes are higher than for any of the other aromatic hydrocarbons. On the other hand, for all of these mixtures (excepting those of o-xylene and m-xylene for which only values at 298.15 K have been reported) the effect of the temperature is the same than for (p-cymene + ethanol), that is, the higher the temperature, the greater the excess molar

volume. Then, the volumetric behavior of the mixture (p-cymene + ethanol) is in agreement with that of other mixtures containing benzene or alkylbenzenes. It must be said that there are values reported in the literature for the excess volume of the mixture of cumene ((1-methyl-ethyl)benzene) with ethanol [18] and they do not agree with this general behavior because they are negative over the whole composition range. No account can be given for these results.

On the other hand, values of excess molar enthalpy are positive for the mixtures (benzene + ethanol) [1-5], (toluene + ethanol) [1, 4, 6-7], (o-xylene or m-xylene + ethanol) [17] and (p-xylene + ethanol) [8-10]. Given the close similarity of the mixture (p-cymene + ethanol) with these ones, it can be fairly supposed that its excess molar enthalpy is positive. This means that the prevailing energetic effect in the mixing process is the breaking of interactions existing in the pure compounds, especially of the hydrogen bonds of ethanol. As the breaking of interactions would entail a separation of molecules, that is, positive excess volumes, the occurrence of negative values should be attributed to the packing of molecules within the holes created by the rupture of interactions.

The molar heat capacities for the pure compounds and their mixtures in the temperature range (298.6 - 328.4) K are gathered in table 5 and depicted in figure 2. At each temperature the values of the molar heat capacities were fitted to the mole fraction of p-cymene according to the following equation

$$C_{P,m} = A + Bx_1 + Cx_1^2 + Dx_1^3 \qquad\qquad (5)$$

where A, B, C and D are adjustable parameters whose values can be found in table 6 along with the standard deviation of the fitting, σ, defined in equation 4.
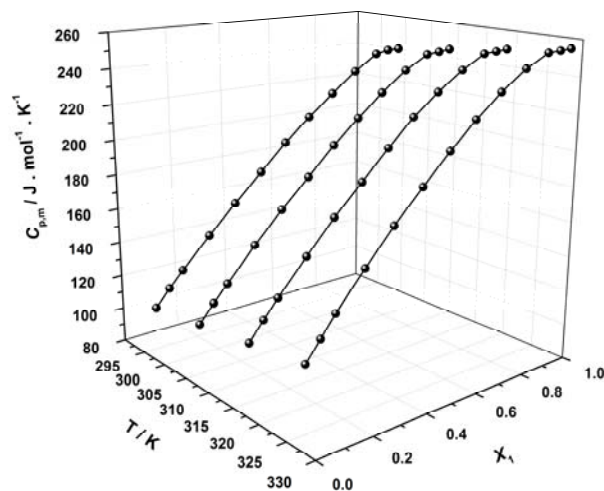
TABLE 5

Mole fraction, x_1, and molar heat capacity, $C_{P,m}$, for the mixture {p-cymene (1) + ethanol (2)} and the pure compounds at $T = (298.6, 308.5, 318.5, 328.4)$ K and atmospheric pressure $p = (0.1 \pm 0.002)$ MPa.

	$C_{p,m}$ / J·mol^{-1}·K^{-1}			
x_1	$T/K = 298.6$	$T/K = 308.5$	$T/K = 318.5$	$T/K = 328.4$
0	112.0	116.4	121.0	125.6
0.0494	121.2	126.1	130.8	135.6
0.0995	130.0	134.7	140.1	145.9
0.2000	146.5	152.2	157.8	163.8
0.3009	162.2	168.5	174.7	181.0
0.4037	177.7	183.8	190.2	197.0
0.5034	192.6	199.0	205.4	211.9
0.6023	205.5	211.8	219.4	225.1
0.7017	217.6	224.3	230.7	236.9
0.8020	229.2	235.3	240.9	247.0
0.8970	238.6	243.1	248.4	253.8
0.9509	240.2	243.9	248.9	254.1
1	240.3	244.7	249.4	254.4

Standard uncertainty u is $u(T) = \pm 0.1$ K, the combined expanded uncertainty U_c is $U_c(x_1) = \pm 0.0005$ and the relative combined expanded

uncertainty U_r is $U_r(C_{P,m}) = \pm 0.008$ with 0.95 level of confidence ($k \approx 2$).

Fitting coefficients in equation (5) along with the corresponding standard deviation, σ, for the mixture {p-cymene (1) + ethanol (2)} at $T = (298.6, 308.5, 318.5, 328.4)$ K and atmospheric pressure $p = (0.1 \pm 0.002)$ MPa.

	$T/K = 298.6$	$T/K = 308.5$	$T/K = 318.5$	$T/K = 328.4$
A / J mol^{-1} K^{-1}	113.00	117.41	121.93	126.53
B / J mol^{-1} K^{-1}	161.10	167.23	174.36	184.49
C / J mol^{-1} K^{-1}	23.01	22.99	18.98	3.20
D / J mol^{-1} K^{-1}	-54.98	-61.76	-64.90	-58.76
σ / J mol^{-1} K^{-1}	1.20	1.01	0.93	0.96

FIGURE 2. Experimental values of molar heat capacity, $C_{p,\mathrm{m}}$, at T = (298.6 , 308.5, 318.5, and 328.4) K and atmospheric pressure for the mixture {p-cymene (1) + ethanol (2)} along with the curves for the fitting to the mole fraction (equation 5).

There are many works reporting isobaric molar heat capacities for ethanol. In figure 3a our present data are compared with the polynomial proposed by Zábranský *et al.* [38] in their critical review of the literature up to 2006. In that figure have been also depicted other bibliographic values reported after 2006 [39-42] including those provided by the authors in an earlier paper [34]. The values reported here are lower than those of García-Miaja *et al.* [39] and Vega-Maza *et al.* [42]. The present values are also lower than those reported in our previous paper [34] with a maximum deviation of -0.4% which is within the uncertainty estimated for the determined molar heat capacities. But they show a good agreement with the data of Anouti *et al.* [40] in their temperature range. The deviations from the values calculated through the polynomial of Zábranský *et al.* [38], which are likely the best ones, range from perfect agreement at 318.5 K to a maximum of -0.3% at 298.6 K. With respect to p-cymene only one work by Huffman *et al.* [43] has reported isobaric molar heat capacities for lower temperatures than those here considered. They are shown in figure

3b along with the present data. It can be seen that the molar heat capacities here determined are slightly higher than those of Huffman et al. [43] but it can be concluded that there is a fair agreement between both set of data.
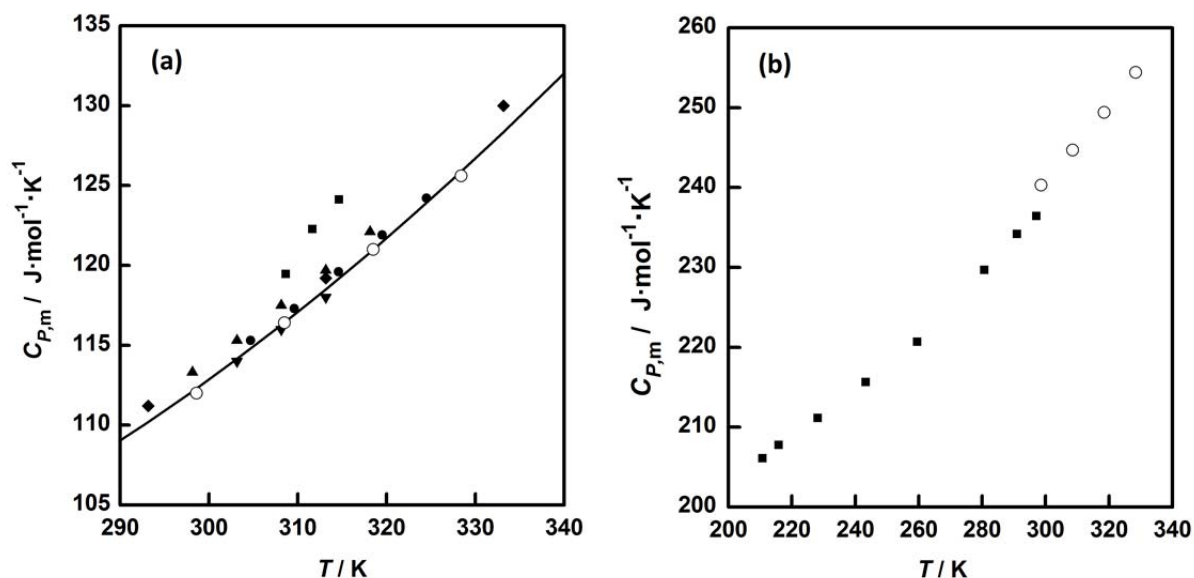

FIGURE 3. (a) Isobaric molar heat capacity for ethanol: (○) this work; (——) polynomial of Zábranský et al. [38]; (●) Martínez-López et al. [34] (▲) García-Miaja et al. [39]; (▼) Anouti et al. [40]; (■) Tripathi [41]; (◆) Vega-Maza et al. [42]. (b) Molar heat capacity for p-cymene: (○) this work; (■) Huffman et al. [43].

Excess molar heat capacities, $C_{p,m}^E$, have been calculated from molar heat capacity data by means of the equation

$$C_{p,m}^E = C_{p,m} - x_1 C_{p,m,1} - x_2 C_{p,m,2}$$ (6)

being $C_{p,m}$ the heat capacity of the mixture, x_i, the mole fraction of pure component i and $C_{p,m,i}$ the molar heat capacity of pure component i. Values of the excess molar heat capacity are represented in figure 4. The excess molar heat capacities are positive over the whole composition range and the

higher the temperature the higher they are. Positive values of excess molar heat capacities have been also observed for the mixtures of benzene [14, 20] and toluene [11, 14] with ethanol and are also expected for the mixture of p-xylene with ethanol whose excess enthalpies increase as temperature increase [8, 9-10]. Supposing that the excess molar enthalpies are positive for the mixture of p-cymene, as stated before, this means that they would increase as the temperature rises and, consequently, that the breaking of interactions would become more and more pronounced for increased temperatures within the range studied. This would be also valid for the mixtures of benzene, toluene and p-xylene with ethanol.
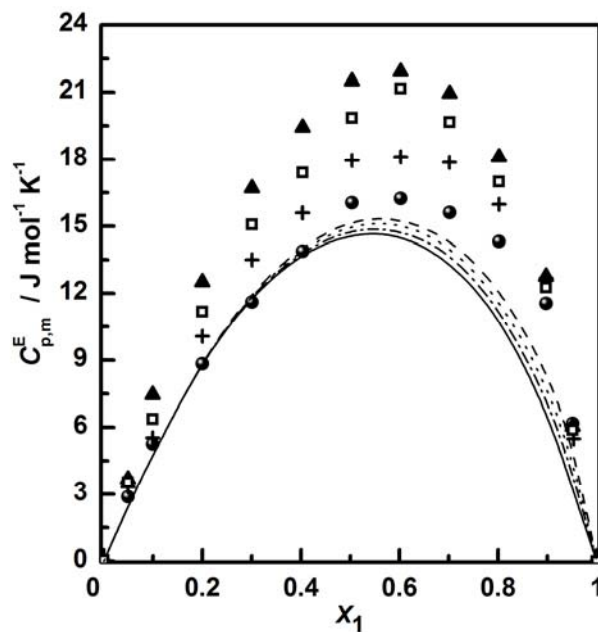
FIGURE 4. Excess molar heat capacity, $C_{p,m}^{E}$, at atmospheric pressure for the mixture {p-cymene (1) + ethanol (2)} at several temperatures: (●) 298.6 K, (+) 308.5 K, (□) 318.5 K and (▲) 328.4 K along with the values of the property predicted by the COSMO-RS model at the same temperatures: (——) 298.6 K, (· · ·) 308.5 K, (- · -), 318.5 K and (——) 328.4 K.

At a given temperature, the variation of the excess heat capacity values over the composition range is quite smooth. The maxima in excess heat capacity are placed at $x_1 = 0.6$. For mixtures (1-alkanol + alkane) this deviation has been attributed [44] to the fact that the structure of the alkanol is not completely broken during the mixing process. This behavior can be likely extended for the mixtures here considered.

In order to predict the excess molar heat capacity of the considered binary mixture the COSMO-RS model has been used. This method allows firstly to estimate values of activity coefficients, γ_i, from which excess molar enthalpies, H_m^E can be obtained, (equation 7).

$$H_m^E = - RT^2 \sum x_i \left(\frac{\partial ln\, \gamma_i}{\partial T} \right)$$ (7)

where R is the constant of ideal gases, T is the absolute temperature, x_i is the molar fraction of the i component, and γ_i is the activity coefficient of component i.

Secondly, the excess molar heat capacities at constant pressure are obtained by the thermodynamics relation showed in equation (8)

$$C_{p,m}^E = \left(\frac{\partial H_m^E}{\partial T} \right)_{p,x}$$ (8)

COSMO-RS, first introduced by Klamt [25] and afterwards refined [26,27], is a method that proceeds in two steps. In a first step, the molecular geometry was optimized for the pure compounds by adjusting the polarization charge density, σ, according to the continuous solvation model COSMO. This is carried out through quantum chemical, specifically DFT (density functional theory) calculations at the BP86/TZVP/DGA1 theory level, that is, functional B88P86 [45-46] with a triple zeta valence polarized (TZVP) basis set [47] and a density fitting function DGA1 [48]. The most stable conformers of p-cymene and ethanol were considered. In the second step, statistical thermodynamics was applied to quantify the molecular interactions in the liquid phase using the

polarization charge densities. For this purpose, the parameterization BP_TZVP_C21_0111 [49] was used. The optimization of the model parameters only requires the vapor pressures of the pure compounds which were obtained from the literature [50]. Excess molar enthalpies and excess molar heat capacities are then obtained from the molecular interactions.

The predicted excess molar enthalpies are positive over the entire composition range and they increase as the temperature rises which is in agreement with the interpretation provided above. According to the model, the main contribution to the excess enthalpy is that of breaking of hydrogen bonds. The results of the predictions for excess molar heat capacities are shown in figure 4. It can be seen that the method reproduces fairly well the values, especially at 298.6 K as well as the position of the maxima. On the other hand, it does not reproduce well the variation with the temperature because the excess heat capacities predicted by COSMO-RS decrease very slightly as the temperature increases in the interval of temperatures considered. It should be said that the reversal of the experimental behavior should be expected at temperatures higher than those here considered because the systems approach the ideal behavior as temperature rises. This reversal has been theoretically predicted by the two-state association (TSAM) model [51] for mixtures of an alkanol with a weak proton acceptor such as alkylbenzene derivatives. In general, the results provided by COSMO-RS are quite acceptable.

Conclusions

The molar heat capacity at atmospheric pressure of the mixture {p-cymene (1) + ethanol (2)} has been determined in the temperature interval (298.6-328.4) K and the whole composition range. Densities have been also experimentally measured for the mixture in the same temperature interval and in the whole composition range. From densities and heat capacity data, the excess molar volumes and the excess molar heat capacities have been calculated, respectively. Excess molar

volumes are positive at all of the temperatures excepting in the zone very rich in ethanol at 298.15 and 308.15 K where they are slightly negative. Excess molar heat capacities are positive in the whole composition range. These properties increase as the temperature rises. These results are in agreement with data reported for mixtures of benzene, toluene and p-xylene with ethanol. Given the values of excess molar enthalpies for these mixtures (aromatic hydrocarbon + ethanol) it can be fairly supposed that the prevailing energetic effect in the mixing process of p-cymene with ethanol is the breaking of interactions existing in the pure compounds, especially of the hydrogen bonds of ethanol. The fact that the excess molar heat capacity increases for rising temperatures indicates that the breaking of interactions would become more and more pronounced for increased temperatures within the range studied. The COSMO-RS model has been applied to predict the excess molar heat capacity of the mixture and provides acceptable predictions.

Acknowledgements

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