# Thermophysical and volumetric study of mixtures {p-cymene + propan-1-ol} at several temperatures and atmospheric pressure. Modeling with COSMO-RS.

*José F. Martínez-López*[1,]*, *Juan I. Pardo*[2], *Sichen Liu*[2], *Ana M. Mainar*[2]

[1] Group of Applied Thermodynamics and Surfaces (GATHERS), Aragon Food Institute (IA2), Universidad de Zaragoza, Facultad de Ciencias, Zaragoza 50009, Spain

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

CORRESPONDING AUTHOR FOOTNOTE Email: jfmarti@unizar.es. Fax: +34 976 761 202. Phone +34 629 573 446

ABSTRACT

Experimental isobaric molar heat capacities at atmospheric pressure have been determined for the mixture {p-cymene + propan-1-ol} every 10 K in the temperature interval (298.8-328.5) K and over the entire composition range with a Calvet type calorimeter. Densities, necessary for calculating heat capacities, have been also measured in similar conditions. Excess molar volumes have been calculated from densities. They are positive at (318.15 and 328.15) K and sigmoidal at (298.15 and 308.15) K with negative values in the zone very rich in propan-1-ol. Excess molar heat capacities have been calculated from the molar heat capacities and show positive values. Both excess molar properties increase as the temperature rises at a given molar fraction. Excess properties are discussed in terms of intermolecular interactions. The solvation model COSMO-RS has been applied to predict the excess molar heat capacities, being the quantitative predictions rather poor.

KEYWORDS: (p-cymene + propan-1-ol) mixture, molar heat capacity, density, atmospheric pressure, COSMO-RS

## 1. Introduction

The thermodynamic study of binary mixtures of short chain alkanols such as ethanol or propan-1-ol with the main component of a vegetable extract results interesting for the design of extraction processes with supercritical $CO_2$ as those alkanols are added as cosolvents to $CO_2$ for increasing the polarity of the final solvent [1]. For this reason, in an earlier paper [2] we reported values of isobaric heat capacities and densities at atmospheric pressure for the binary mixtures of p-cymene with ethanol. In this respect, it would be interesting to extend these studies to the mixture of p-cymene with propan-1-ol.

p-Cymene (1-methyl-4-(1-methyl-ethyl)benzene) 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 [3]. At present the main economic importance of this compound lies in its use as an intermediate in the industrial syntheses of fragrances, flavours, herbicides and, principally, pharmaceuticals. Besides, some studies have recently proven that p-cymene possesses antinociceptive as well as anti-inflammatory activity [4], a fact which can widen its field of applications.

In addition to the interest of thermodynamic properties for the extraction processes mentioned above, there are several studies in the literature about the thermodynamic behavior of binary mixtures of an alkanol with alkylbenzenes. So, for binary mixtures of propan-1-ol with benzene or alkylbenzenes (toluene or cumene or xylene isomers) excess molar enthalpies [5,6 -13], excess molar volumes [6,14 -22], excess molar Gibbs energies [5,9] and isobaric molar heat capacities [9] have been determined. New data for the mixture of p-cymene with propan-1-ol would provide a more complete knowledge about this kind of mixtures.

Therefore, in this work values of experimental isobaric molar heat capacities for the binary mixtures of p-cymene with propan-1-ol, at four temperatures (298.8, 308.7, 318.6 and 328.5) K and atmospheric pressure over the entire composition range are reported. Besides, densities have been measured at (298.15, 308.15, 318.15 and 328.15) K and atmospheric pressure also over the entire composition range. Then, excess molar volumes and excess molar heat capacities have been calculated for the mixture. The solvation model COSMO-RS [23-25] has been applied in order to evaluate its ability to predict the excess molar heat capacity. In this way useful information would be added for practical purposes as well as for basic knowledge of mixtures of alkylbenzene with alkanol.

## 2. Experimental

### *2.1 Materials*

The chemicals used were p-cymene and propan-1-ol. Also, water (milliQ quality) was used to perform the measurements. Their descriptions are shown in table 1. Experimental values of density for the pure components at the working temperatures are reported in Table 2 and compared with available bibliographic values [26 -32]. In general, a good agreement can be observed between both sets of data. As pointed out in a previous paper [2] for p-cymene there are noticeable deviations between our data and those of Ribeiro *et al.* [26] which are lower than ours and also with those of Liao *et al.* [29] which are greater than ours. An inspection of the purities of p-cymene in those papers, 0.9985 for Ribeiro *et al*. and 0.9917 for Liao *et al*., show that the purity can play a role in the discrepancies as the lower the purity the higher is the density. Ribeiro *et al.* state that the impurities in p-cymene are mainly α-pinene and β-pinene which have both higher densities than p-cymene. Also, these differences can be explained in base of 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 [27].

**TABLE 1**

Sample description.

| Chemical name | Source | Purity | Purification method | Analysis method |
|---|---|---|---|---|
| p-Cymene | Aldrich | 0.995[a] | None | GC[c] |
| Propan-1-ol | Aldrich | 0.999[b] | None | GC[c] |
| Water | Laboratory | MilliQ[d] | None | Electrical resistivity |

[a] Mole fraction purity.

[b] Volume fraction purity. Water content: 0.006 % (Karl Fischer assay provided by the supplier)

[c] Gas-Chromatography from the supplier.

[d] 18.2 MΩ·cm

**TABLE 2**

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

| Compound | $\rho$ / 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 | 852.99 | 852.1[b]<br>852.26[c]<br>853.3[d]<br>853.47[e] | 844.94 | 844.5[b]<br>844.67[c]<br>845.59[e] | 836.86 | 837.4[b]<br>836.87[c]<br>838.46[e] | 828.75 | 828.88[c] |
| propan-1-ol | 799.46 | 799.60[d]<br>799.75[f]<br>799.59[g]<br>799.60[h] | 791.36 | 791.6[f]<br>791.47[g]<br>791.54[h] | 783.10 | 783.3[f]<br>783.12[g]<br>783.27[h] | 774.63 | 774.7[f]<br>774.64[g]<br>774.76[h] |

[a] Measured with a densimeter Anton Paar DMA 5000 M, Standard uncertainties $u$ are $u(T) = \pm 0.01$ K, and $u(P) = \pm 0.002$ MPa, 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 [26]; [c]Ref [27]; [d]Ref [28]; [e]Ref [29] [f]Ref [30]; [g]Ref [31]; [h]Ref [32]

### *2.2 Equipments*

A Calvet type calorimeter, Setaram C80 (France), were used for the experimental determination of molar heat capacities at atmospheric pressure. A detailed description of the equipment, the method followed for calorimetric determination as well as the calibration and validation procedure have been previously reported [33].

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. Concerning 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 $\mathrm{K{\cdot}min^{-1}}$ 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 [34]. Then, molar heat capacity is calculated through the equation

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

where $C_{P,\mathrm{m}}$ is the molar heat capacity, $M$ is the molar mass, $\rho$ 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.* [35] and the relative expanded uncertainty (coverage factor $k$ = 2) in the molar heat capacity is estimated to be ±0.008.

Densities for water [36] were obtained from the literature whereas densities for p-cymene, propan-1-ol and their 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 propan-1-ol were prepared by weighing using a Mettler-Toledo analytical balance, model AB265-S, with a precision of ±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 entire composition range, for the mixture {p-cymene (1) + propan-1-ol (2)} are reported in table 3.

**TABLE 3**

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

| | $\rho$ / kg·m$^{-3}$ | | | |
|---|---|---|---|---|
| $x_1$ | $T$/K = 298.15 | $T$/K = 308.15 | $T$/K = 318.15 | $T$/K = 328.15 |
| 0 | 799.46 | 791.36 | 783.10 | 774.63 |
| 0.0499 | 804.92 | 796.73 | 788.38 | 779.80 |
| 0.1007 | 809.80 | 801.54 | 793.11 | 784.46 |
| 0.2029 | 818.12 | 809.76 | 801.22 | 792.47 |
| 0.3021 | 824.80 | 816.37 | 807.78 | 798.98 |
| 0.4032 | 830.42 | 821.98 | 813.38 | 804.59 |
| 0.5045 | 835.28 | 826.83 | 818.25 | 809.51 |
| 0.6044 | 839.47 | 831.05 | 822.51 | 813.82 |
| 0.6974 | 842.95 | 834.57 | 826.09 | 817.49 |
| 0.8035 | 846.57 | 838.26 | 829.87 | 821.37 |
| 0.8989 | 849.61 | 841.39 | 833.10 | 824.75 |
| 0.9508 | 851.22 | 843.07 | 834.88 | 826.65 |

| | | | | |
|---|---|---|---|---|
| 1 | 852.99 | 844.94 | 836.86 | 828.75 |

Standard uncertainties $u$ are $u(T)$ = ±0.01 K and $u(P)$ = ±0.002 MPa, and the combined expanded uncertainties $U_c$ are $U_c(x_1)$ = ±0.0005 and $U_c(\rho)$ = 0.7 kg·m$^{-3}$ with 0.95 level of confidence ($k \approx 2$).

Excess molar volumes, $V_m^E$ were obtained from these densities by means of the equation

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

being $x_i$ the mole fraction of pure component i and their values appear represented in figure 1. The estimated expanded uncertainty ($k \approx 2$) for $V_m^E$ is ± 0.008·10$^6$ m$^3$·mol$^{-1}$. This excess quantity was fitted to the Redlich–Kister equation

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

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

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

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.

**TABLE 4**

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

| | $T$ / K = 298.15 | $T$ / K = 308.15 | $T$ / K = 318.15 | $T$ / K = 328.15 |
|---|---|---|---|---|

| | | | | |
|---|---|---|---|---|
| $10^6 \cdot A_0$ / m$^3$ mol$^{-1}$ | 0.34 | 0.56 | 0.82 | 1.14 |
| $10^6 \cdot A_1$ / m$^3$ mol$^{-1}$ | 0.60 | 0.65 | 0.70 | 0.76 |
| $10^6 \cdot A_2$ / m$^3$ mol$^{-1}$ | -0.04 | -0.04 | 0.03 | 0.15 |
| $10^6 \cdot A_3$ / m$^3$ mol$^{-1}$ | 0.54 | 0.64 | 0.73 | 0.82 |
| $10^6 \cdot A_4$ / m$^3$ mol$^{-1}$ | 0.59 | 0.71 | 0.76 | 0.75 |
| $10^6 \cdot \sigma$ / m$^3$ mol$^{-1}$ | 0.005 | 0.005 | 0.005 | 0.004 |

Standard uncertainties $u$ are $u(T) = \pm 0.01$ K, and $u(P) = \pm 0.002$ MPa, the combined expanded uncertainty $U_c$ is $U_c(\rho) = 0.7$ kg·m$^{-3}$ with 0.95 level of confidence ($k \approx 2$)

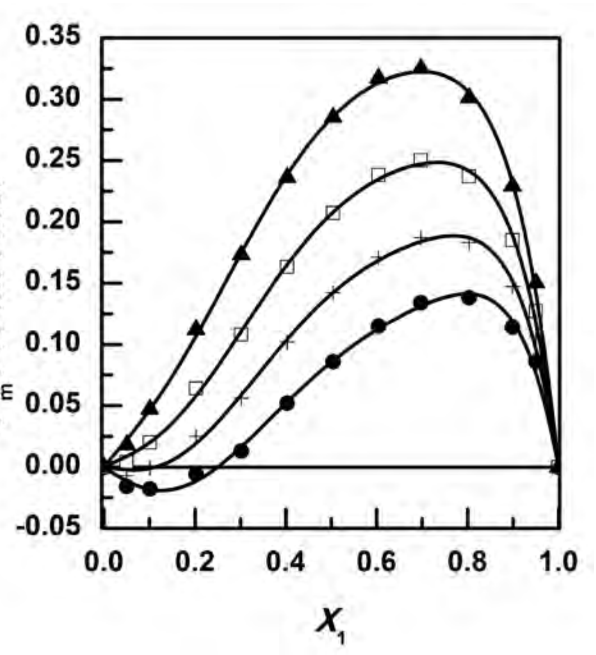

**FIGURE 1**. Excess molar volumes, $V^E_m$, for the mixture {p-cymene (1) + propan-1-ol (2)} as a function of p-cymene mole fraction, at the temperatures: ( ● ) 298.15 K; ( + ) 308.15 K; ( □ ) 318.15 K; and (▲) 328.15 K along with the curves for the fitting to the mole fraction (equation 3).

The excess molar volumes for the mixture of p-cymene with propan-1-ol are sigmoidal at 298.15 and 308.15 K showing negative values in the zone very rich in propan-1-ol and positive ones in the remaining composition range whereas their values are positive throughout at 318.15 and 328.15 K. In general terms, the excess molar volume increases as the temperature rises at a given molar fraction. This volumetric behavior is very similar to that observed for the mixture of p-cymene with ethanol [2] although the values are higher for propan-1-ol. In fact, the same behavior has been reported for mixtures of several alkylbenzenes with ethanol [2] as well as for mixtures of propan-1-ol with benzene [8,15,17,21], or toluene [8,15,18,19,21], or cumene (1-methylethylbenzene) [20], or the three isomers of xylene [8,-16,21]. But the excess molar volumes are higher for p-cymene than for any of the other aromatic hydrocarbons. Besides, for all of these mixtures the effect of the temperature is the same than for the mixture of p-cymene + propan-1-ol, that is, the higher the temperature, the greater the excess molar volume. In this way, the excess molar volume from being sigmoidal shaped becomes positive throughout for the mixtures of propan-1-ol with benzene at 303.15 K [21], or toluene at 323.15 K [19]. Then, the volumetric behavior of the mixture of p-cymene with propan-1-ol fully agrees with that of other mixtures containing benzene or alkylbenzenes as occurred when the alkanol was ethanol [2].

In sight of this agreement, it is fair to suppose that the excess molar enthalpy for the mixture of p-cymene with propan-1-ol would be positive because it is also positive for the mixtures of propan-1-ol with benzene [5,8,10,12,13], or toluene [8,10,12,13], or the three isomers of xylene [7,8,10,11,13,14] as was also supposed on a very similar basis for the mixture of p-cymene with ethanol [2]. Then, for all of the mixtures of benzene or alkylbenzene with ethanol or propan-1-ol the prevailing thermal effect in the mixing process is the breaking of interactions in the pure compounds (especially of hydrogen bonds in the alkanol), a breaking which is not compensated by the $\pi$-OH interactions between aromatic compounds and alkanol. But, in spite of this breaking of interactions, the mentioned $\pi$-OH interactions along with molecular packing would account for the negative values observed for the excess molar volume in the zone rich in alkanol [14,15,20].

Although there is not a perfect correlation between excess properties (likely due to the packing effects affecting the volume), it can be said, in general terms, that the excess molar enthalpies and the excess molar volumes are higher for the mixtures of benzene or alkylbenzene with propan-1-ol than for their mixtures with ethanol. Then, the higher excess molar volumes of the mixture of p-cymene with propan-1-ol with respect to those with ethanol would point to higher values of excess molar enthalpies for the first mixture.

The molar heat capacities for the pure compounds and their mixtures in the temperature range (298.8 - 328.5) 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

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

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, $\sigma$, defined in equation 4.

**TABLE 5**

Mole fraction, $x_1$, and molar heat capacity, $C_{P,\mathrm{m}}$, for the mixture {p-cymene (1) + propan-1-ol (2)} and the pure compounds at $T$ = (298.8, 308.7, 318.6, 328.5) K and atmospheric pressure $p$ = (0.1 ± 0.002) MPa.

| | $C_{p,\mathrm{m}}$ / J·mol$^{-1}$·K$^{-1}$ | | | |
|---|---|---|---|---|
| $x_1$ | $T$ / K = 298.8 | $T$ / K = 308.7 | $T$ / K = 318.6 | $T$ / K = 328.5 |
| 0 | 144.5 | 150.9 | 157.4 | 164.5 |
| 0.0499 | 151.2 | 158.5 | 165.9 | 173.4 |
| 0.1007 | 159.6 | 166.5 | 173.5 | 180.7 |
| 0.2029 | 174.5 | 182.2 | 188.4 | 195.4 |
| 0.3021 | 186.9 | 194.0 | 201.2 | 208.3 |
| 0.4032 | 198.6 | 206.1 | 213.2 | 220.7 |
| 0.5045 | 210.6 | 217.2 | 223.9 | 231.2 |
| 0.6044 | 221.0 | 227.2 | 233.3 | 240.2 |
| 0.6974 | 229.1 | 235.0 | 240.8 | 246.8 |
| 0.8035 | 237.6 | 242.8 | 248.1 | 253.4 |
| 0.8989 | 242.2 | 246.2 | 250.4 | 254.5 |
| 0.9508 | 242.4 | 245.3 | 248.8 | 252.6 |
| 1 | 240.9 | 244.8 | 249.4 | 254.6 |

Standard uncertainties $u$ are $u(T)$ = ±0.1 K and $u(P)$ = ±0.002 MPa, the combined expanded uncertainty $U_c$ is $U_c(x_1)$ = ±0.0005 and the relative combined expanded uncertainty $U_r$ is $U_r(C_{P,\mathrm{m}})$ = ±0.008 with 0.95 level of confidence ($k \approx 2$).

**TABLE 6**

Fitting coefficients in equation (5) along with the corresponding standard deviation, $\sigma$, for the mixture {p-cymene (1) + propan-1-ol (2)} at $T$ = (298.8, 308.7, 318.6, 328.5) K and atmospheric pressure $p$ = (0.1 ± 0.002) MPa.

| | $T$ / K = 298.8 | $T$ / K = 308.7 | $T$ / K = 318.6 | $T$ / K = 328.5 |
|---|---|---|---|---|
| A / J mol$^{-1}$ K$^{-1}$ | 144.91 | 151.45 | 158.18 | 165.16 |
| B / J mol$^{-1}$ K$^{-1}$ | 138.67 | 146.41 | 150.18 | 155.14 |
| C / J mol$^{-1}$ K$^{-1}$ | 13.85 | -4.40 | -14.66 | -27.45 |
| D / J mol$^{-1}$ K$^{-1}$ | -55.26 | -47.51 | -43.52 | -38.24 |
| $\sigma$ / J mol$^{-1}$ K$^{-1}$ | 1.12 | 1.01 | 0.59 | 0.29 |

Standard uncertainties $u$ are $u(T)$ = ±0.1 K and $u(P)$ = ±0.002 MPa, the combined expanded uncertainty $U_c$ is $U_c(x_1)$ = ±0.0005 and the relative combined expanded uncertainty $U_r$ is $U_r(C_{P,\mathrm{m}}) =$ ±0.008 with 0.95 level of confidence ($k \approx 2$).

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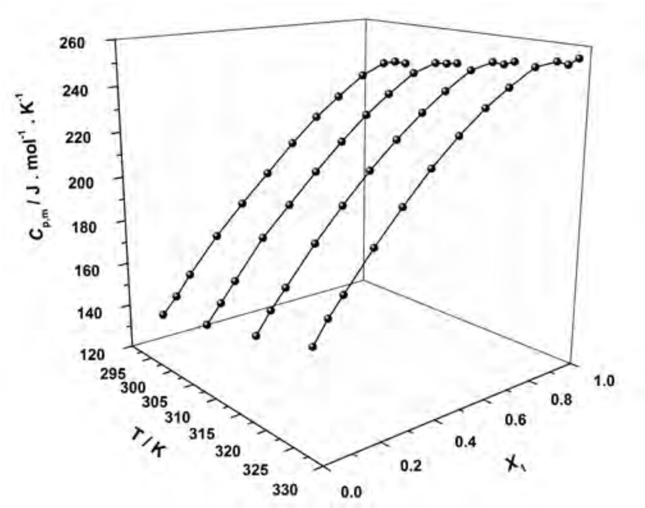

**FIGURE 2**. Experimental values of molar heat capacity, $C_{p,\mathrm{m}}$, at $T$ = (298.8 , 308.7, 318.6, and 328.5) K and atmospheric pressure for the mixture {p-cymene (1) + propan-1-ol (2)} along with the curves for the fitting to the mole fraction (equation 5).

There are many works reporting isobaric molar heat capacities for propan-1-ol. In figure 3 our present data for propan-1-ol are compared with the polynomial proposed by Zábranský *et al.* [37]. Furthermore, in that figure, other bibliographic values have been depicted as well [38-41]. It can be seen that the molar heat capacities here reported are in good agreement with the literature data. The major deviations appear with respect to the data of Counsell *et al.* [38] and with the polynomial of Zábranský *et al.* [37] at the higher temperatures. In any case those deviations are always within the estimated uncertainty for the molar heat capacities. For p-cymene, as was already commented in a previous paper [2], the values of isobaric molar heat capacities are slightly higher than those of Huffman *et al.* [42] that is the only one reference found that provides values of this property for p-cymene.

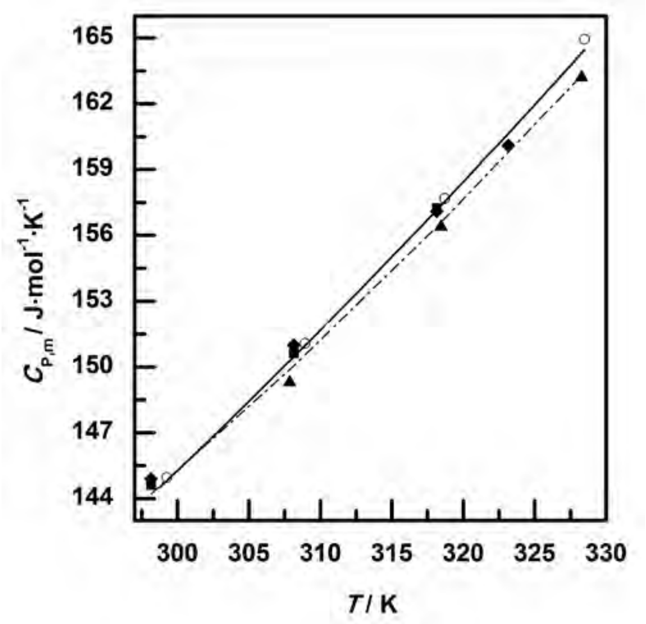

**FIGURE 3**. (a) Isobaric molar heat capacity for propan-1-ol: this work (──); polynomial of Zábranský et *al.* [37] (—•—); Counsell *et al.* [38] (▲); van Miltenburg et *al.* [39] (○); Comelli et *al.* [40] (◆); Peleteiro et *al.* [41] (■).

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

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

being $C_{p,\mathrm{m}}$ the heat capacity of the mixture and $C_{p,\mathrm{m,i}}$ 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 entire composition range and increase as the temperature rises in fact, as occurred with the excess molar volumes, this trend of the molar heat capacities with the temperature is in agreement with that of the mixture of p-cymene with ethanol as well as with those of the mixtures of benzene or alkylbenzene compounds with both ethanol [2] and propan-1-ol. For example, positive values of excess molar heat capacities have been reported [9] for the mixtures of benzene with propan-1-ol. Moreover, the available data of excess molar enthalpies show that they are higher at higher temperatures for the mixtures of propan-1-ol with toluene [11,12], or isomers of xylene [7,11,13], a fact which would lead to positive values of excess molar heat capacities. Therefore, taking into account the similarity between both mixtures the explanation proposed for the mixture of p-cymene with ethanol would be applicable to the mixture with propan-1-ol (and could be extended to other mixtures of ethanol or propan-1-ol with alkylbenzenes): considering that the excess molar enthalpies are positive, as stated before, the breaking of interactions, mainly hydrogen bonds, would become more and more pronounced for increased temperatures within the range studied. It must be pointed out that the increase in the excess molar heat capacity could be reversed at higher temperatures as has been observed for mixtures of propan-1-ol with benzene [9] which shows that reversal between 308.15 K and 313.15 K. This behavior is expected because all mixtures would approach in the end the ideality as temperature rises.

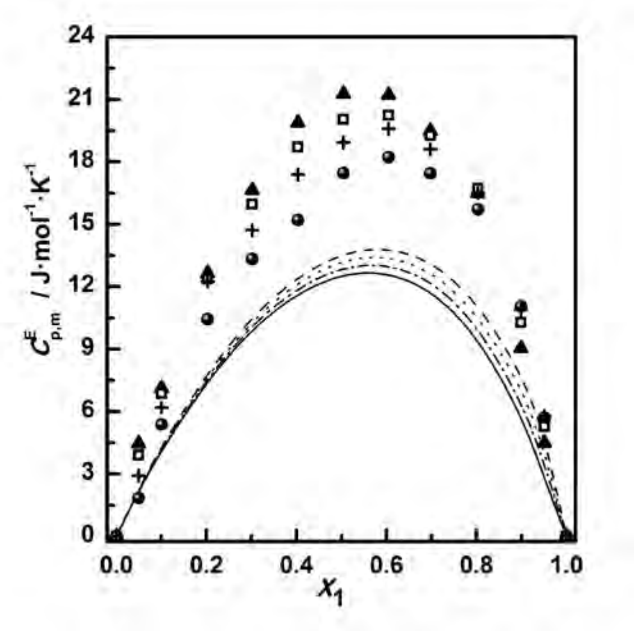

**FIGURE 4**. Excess molar heat capacity, $C_{p,\mathrm{m}}^{\mathrm{E}}$, at atmospheric pressure for the mixture {p-cymene (1) + propan-1-ol (2)} at several temperatures: ( ● ) 298.8  K, ( + ) 308.7 K, ( □ ) 318.6 K and (▲)

328.5 K along with the values of the property predicted by the COSMO-RS model at the same temperatures: (——) 298.8 K, ( · · · ) 308.7 K, ( - · - ), 318.6 K and (—) 328.5 K.

At a given temperature, the variation of the excess molar heat capacity values over the entire composition range is quite smooth and show the maxima placed at $x_1 = 0.6$, both features were also observed for the mixtures of p-cymene with ethanol. For mixtures (alkan-1-ol + alkane) the deviation of the maxima from equimolar composition has been attributed [43] 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.

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

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

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

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

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

In particular the excess molar enthalpies calculated at the working temperatures were adjusted to a second order polynomial equation with respect to the temperature. Then, the polynomial was analytically differentiated to determine the excess molar heat capacity.

COSMO-RS, first introduced by Klamt [23] and afterwards refined [24,25], is a method that proceeds in two steps. In the first one, the molecular geometry was optimized for the pure compounds by adjusting the polarization charge density, $\sigma$, 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 [44-45] with a triple zeta valence polarized (TZVP) basis set [46] and a density fitting function DGA1 [47]. 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 [48] was used. The optimization of the model parameters only requires the vapor pressures of the pure compounds which were obtained from the literature [49].

The results are quite similar to those found for the mixture of p-cymene with ethanol [2]. As occurred in that case, the predicted excess molar enthalpies for the mixture with propan-1-ol are positive over the entire composition range which is in agreement with the interpretation provided above. Besides, the model indicates that the main contribution to the excess enthalpy comes from the breaking of hydrogen bonds. The results of the predictions for excess molar heat capacities are shown in figure 4. Their values are positive because the predicted excess molar enthalpies increase as the temperature rises. It is remarkable that the values of excess heat capacity predicted are lower for the mixture with propan-1-ol than for the mixture with ethanol, although the experimental values are quite similar. Then the prediction is somewhat worse for the mixture with propan-1-ol and, consequently, rather poor. A feature that share the predictions for the mixtures with ethanol and propan-1-ol, is that COSMO-RS predicts a slight decrease in the excess molar heat capacity as the temperature increases in the interval of temperatures considered which is the behavior opposite to the observed one. But, as was advanced in the discussion this is expected and has even theoretically predicted by the two-state association (TSAM) model [50] for mixtures of an alkanol with a weak proton acceptor such as alkylbenzene derivatives. Furthermore, COSMO-RS reproduces fairly well the position of the maxima for excess molar heat capacities which are placed at $x_1 = 0.6$ as was observed for the excess molar heat capacities obtained from experimental molar heat capacities. In general terms, the results provided by COSMO-RS method should be considered as acceptable when comparing with the results reported for other similar systems.

## Conclusions

The molar heat capacity at atmospheric pressure of the mixture {p-cymene (1) + propan-1-ol (2)} has been determined in the temperature interval (298.8-328.5) K and the whole composition range. Densities have been also experimentally measured for the mixture in the same temperature interval for the entire composition range. From densities and molar 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 propan-1-ol at 298.15 and 308.15 K where they are slightly negative. Excess molar heat capacities are positive in the whole composition range. Both properties increase as the temperature rises. These results are in agreement with data reported on the one hand for mixtures of p-cymene with ethanol and on the other hand for mixtures of benzene, toluene and p-xylene with propan-1-ol. As the values of excess molar enthalpies for these mixtures (aromatic hydrocarbon + propan-1-ol) are always positive 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 propan-1-ol. 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 of p-cymene with propan-1-ol providing rather poor quantitative results although the model is able to reproduce both the position of the maxima for excess molar heat capacities, which are placed at $x_1 = 0.6$, and the positive sign experimentally observed for excess molar heat capacities at all temperatures and compositions.

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