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

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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.

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.

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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].

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 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 [34]. Then, molar heat capacity is calculated through the equation

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

where $C_{P,\text{m}}$ 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. [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

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 $p = (0.1 \pm 0.002)$ 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	852.99	852.1[b]		844.5[b]		837.4[b]		
		852.26[c]	844.94	844.67[c]	836.86	836.87[c]	828.75	828.88[c]
		853.3[d]						
		853.47[e]		845.59[e]		838.46[e]		
propan-1-ol	799.46	799.60[d]						
		799.75[f]	791.36	791.6[f]	783.10	783.3[f]	774.63	774.7[f]
		799.59[g]		791.47[g]		783.12[g]		774.64[g]
		799.60[h]		791.54[h]		783.27[h]		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].