Molar Heat Capacities of the Mixture {1,8-Cineole + Ethanol} at Several Temperatures and Atmospheric Pressure

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ABSTRACT.

Molar heat capacities at atmospheric pressure have been determined every 5 K for the mixture {1,8-cineole (1) + ethanol (2)} in the temperature interval (304.7 to 324.5) K and the whole composition range with a Calvet type calorimeter Setaram C80. From the molar heat capacities, excess molar heat capacities have been calculated, their values being positive and increasing as the temperature rises. The solvation model COSMO-RS has been applied to predict the excess molar heat capacities. The model overestimates the values of the excess heat capacities but predicts well the trend of variation of the excess molar heat capacity with the temperature.

Introduction

Extraction of volatile oils from plants can be carried out by several techniques, among them being hydro-ethanolic maceration and supercritical CO_2 extraction which sometimes requires the addition of alkanols of short chain, usually ethanol, as modifiers in order to improve the extraction of polar compounds [1]. The knowledge of the thermophysical properties of mixtures of (volatile oil + alkanol) would be necessary to optimize the supercritical extraction process and also to treat the liquid mixture obtained after the extraction, either supercritical or hydro-ethanolic. But, being the volatile oils themselves complex mixtures in many cases it is advisable to study the binary mixtures (a major compound of volatile oil + alkanol). For this reason, our research group has been investigating thermophysical properties of liquid mixtures of this kind during the last years.

Among these, the mixture of 1,8-cineole (1,3,3-Trimethyl-2-oxabicyclo[2.2.2]octane) with alkanols has been the subject of an ample investigation in our research group, including properties such as excess molar enthalpy [2], density at low and high pressure [2-4] and (vapor +liquid) equilibrium [5,6]. 1,8-Cineole or eucalyptol, a monoterpenoid, is the main component of the volatile oils obtained from several plants and has many applications in the fields of flavour and fragrances, pharmacy. It also acts as insecticide and insect repellent [7,8].

In order to extend that study on thermodynamic properties, we report in this paper measurements of the molar heat capacity at atmospheric pressure of the mixture {1,8-cineole (1) + ethanol (2)} in the temperature interval (304.7 to 324.5) K and the whole composition range. Then, excess molar heat capacities have been calculated for the mixture and the solvation model COSMO-RS [9-11] has been applied in order to evaluate its ability to predict that excess property. It must be pointed out that, although there are measurements of heat capacity for pure 1,8-cineole and other terpenes, their mixtures have not been studied in this respect. Therefore this study could be of

interest for both fundamental and applied purposes taking into account the special structure of their molecules that are in many cases bicyclic bridged ones.

Experimental

Materials

The chemicals used were 1,8-cineole 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 $T = 298.15$ K are reported in table 2 and compared with available bibliographic values [4,12-15]. A good agreement can be observed between both sets of data.

TABLE 1

Sample description.

Chemical name	Source	Purity	Purification method	Analysis method
1,8-cineole	Aldrich	0.990[a]	None	GC[c]
Ethanol	Scharlau	0.999[b]	None	GC[c]
Water	Laboratory	MilliQ[d]	None	Electrical resistivity

[a] Mole fraction purity.
[b] Volume fraction purity.
[c] Gas-Chromatography.
[d] 18.2 MΩ·cm

TABLE 2

Experimental and literature densities for the pure liquids at $T = 298.15$ K and atmospheric pressure $P = (0.1 \pm 0.002)$ MPa.

	ρ / kg·m^{-3}	
	Experimental[a]	Literature
1,8-Cineole	920.51	920.68[b]
		921.8[c]
		920.29[d]
Ethanol	785.20	784.93[c]
		785.09[e]
		785.49[f]

[a] Measured with a densimeter Anton Paar DSA 5000, $u(T) = \pm 0.01$ K; $U(\rho) = \pm 0.04$ kg·m^{-3} ($k = 2$)
[b] Ref [4]; [c] Ref [12]; [d] Ref [13]; [e] Ref [14]; [f] Ref [15]

Equipment

Heat capacities at atmospheric pressure were determined through a Calvet type calorimeter, Setaram C80 (France). The calorimeter consists of two identical cells of stainless steel, a reference and a measurement one, which are located inside a cylindrical block of high thermal inertia and programmable temperature (software Calisto v1.11. Data Acquisition). When the equipment is working, every difference in temperature between a cell and the block would produce a heat flow that is transformed, via a set of thermocouples, to power data that are, in its turn, integrated (software Calisto v1.11 Processing) to obtain the exchanged heat. Measurement and reference cell 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. These cells, provided by Setaram, are specially designed to avoid the presence of vapor phase in the zone of heat flow and also to ensure that the volume of the cell under control remains constant.

Referring to the procedure, the incremental temperature mode (step method) was used. Specifically, the temperature was increased 5 K in every step with a heating rate of 0.2 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 also 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 [16]. The calorimeter provides the heat flows for a fixed volume of liquid that is always the same because the same measurement cell is used in every experiment. So the molar heat capacity is calculated through the equation

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

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 relative expanded uncertainty (coverage factor $k = 2$) in the molar heat capacity arising from uncertainties for the quantities in equation (1) is estimated to be ±0.003.

The apparatus performance and procedure adequacy were tested by determining the molar heat capacities of ethanol. Densities of water [17] and ethanol [14] for applying equation (1) were obtained from the literature. The values of molar heat capacity obtained for ethanol can be found in table 3. They have been compared with the values provided by the polynomial proposed by Zábranský *et al.* [18], which is based in the critical review of the literature up to 2006. Also, a comparison with other bibliographic values reported after 2006 [19-22] has been done. The values of molar heat capacity for ethanol can be seen in figure 1a whereas the percentage relative deviations of our values from the bibliographic ones at the working temperatures in this paper are plotted in figure 1b, except in the case of the heat capacities of Tripathi [21] that clearly deviate from the rest. The values reported here are placed quite centered between the different literature

heat capacities, being higher than those of Zábranský *et al.* [18] and Anouti *et al.* [20] and lower than those of García-Miaja *et al.* [19] and Vega-Maza *et al.* [22]. The deviations from the values calculated through the polynomial of Zábranský *et al.* [18], which are likely the best ones, range from 0.2% at the higher temperature to 0.4% at the lower one. From this comparison, it can be concluded that the equipment has a good performance.
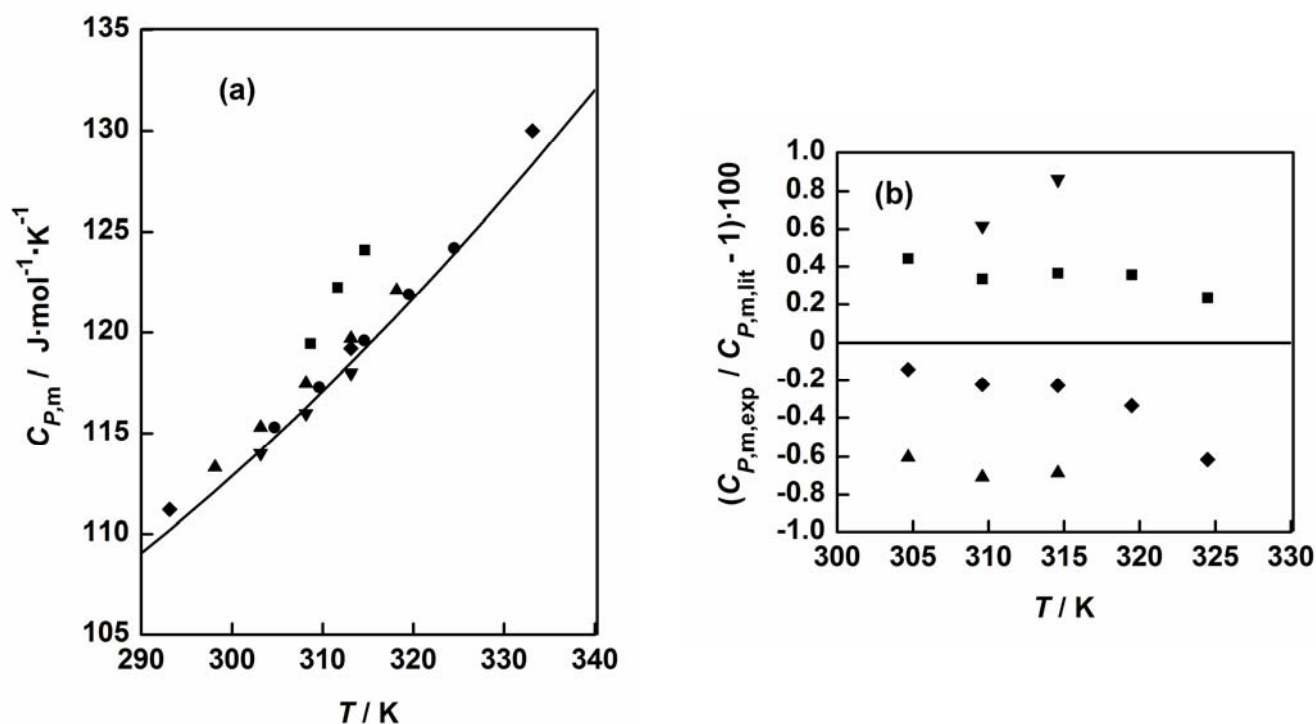

Figure 1. (a) Molar heat capacity for ethanol: (●) this work; (——) polynomial of Zábranský *et al.* [18] (▲) García-Miaja *et al.* [19]; (▼) Anouti *et al.* [20]; (■) Tripathi [21]; (◆) Vega-Maza *et al.* [22]. (b) Percentage relative deviations of experimental molar heat capacities for ethanol from literature ones (interpolated) at the working temperatures in this paper: (■) Zábranský *et al.*, (▲) García-Miaja *et al.*;. (▼) Anouti *et al.*; (◆) Vega-Maza *et al.*

It must be said that the experimental molar heat capacity for ethanol at each temperature is the average of five measurements carried out to test the repeatability, being the highest relative standard

deviation 0.001. The repeatability was also checked by measuring three times the molar heat capacity at each temperature for both 1,8-cineol and a mixture of 1,8-cineole and ethanol in a zone rich in the most volatile compound (mole fraction of 1,8-cineole near 0.3), being the highest relative standard deviations 0.002 and 0.004, respectively. All of these standard deviations are in good agreement with the expanded relative uncertainty estimated when applying equation 1. Given these good results only one measurement was performed for the remaining mixtures. The smooth variation in the molar heat capacities reported below seems to support this procedure.

Samples of the mixtures of 1,8-cineole and ethanol were prepared by weighing with 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.

Molar heat capacities of pure 1,8-cineole obtained in the laboratory of the Group of Applied Thermal Engineering in the Universitat Rovira i Virgili (set II in table 5) were determined with a calorimeter Setaram microDSC-III using a step method. Toluene was used as reference liquid. The uncertainty in molar heat capacity is lower than ± 0.005.

Results and discussion

Molar heat capacities for the pure compounds and their mixtures in the temperature range (304.7-324.5) K are gathered in table 3 and depicted in figure 2. In order to apply equation (1), the densities for water [17], ethanol [14] and 1,8-cineole as well as those of the mixtures (1,8,cineole + ethanol) [3] were obtained from the literature. At each temperature the values of the molar heat capacities were fitted to the mole fraction of 1,8-cineole according to the following equation

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

where A, B and C are adjustable parameters whose values can be found in table 4 along with the standard deviation of the fitting, σ, defined by

$$\sigma = \left[\frac{\sum\limits_{j=1}^{m} \left(C_{P,m,exp} - C_{P,m,cal} \right)^2}{m - n} \right]^{\frac{1}{2}} \qquad (3)$$

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 (three in this case). The fitting curves appear in figure 2.
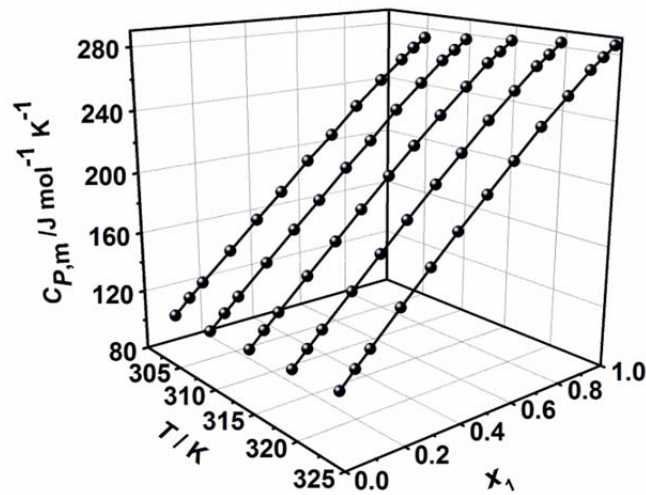

Figure 2. Experimental values of molar heat capacity, $C_{P,m}$, at atmospheric pressure for the mixture {1,8-cineole (1) + ethanol (2)} along with the curves for the fitting to the mole fraction (equation 2).

TABLE 3

Mole fraction, x_1, and molar heat capacity, $C_{P,m}$, for the mixture {1,8-cineole (1) + ethanol (2)} and the pure compounds at $T = (304.7, 309.6, 314.6, 319.5, 324.5)$ K and atmospheric pressure $P = (0.1 \pm 0.002)$ MPa.

	$C_{P,m}$ / $J \cdot mol^{-1} \cdot K^{-1}$				
x_1	$T/K = 304.7$	$T/K = 309.6$	$T/K = 314.6$	$T/K = 319.5$	$T/K = 324.5$
0	115.3	117.3	119.6	121.9	124.2
0.0506	123.9	126.2	128.6	131.1	133.5
0.0990	132.0	134.6	137.1	139.7	142.1
0.1999	149.0	151.8	154.6	157.1	160.0
0.3007	166.0	169.0	171.8	174.9	177.7
0.3956	181.7	184.9	188.1	191.1	194.1
0.5002	199.4	202.5	205.5	208.5	211.3
0.5975	214.3	217.4	221.5	224.5	227.4
0.7017	231.6	235.1	238.0	241.2	244.1
0.8065	247.2	250.5	253.6	256.7	259.3
0.8964	259.8	263.7	267.0	269.9	272.5
0.9501	267.0	269.9	273.4	275.8	279.0
1	273.3	276.4	279.5	282.6	285.1

$U(x_1) = \pm 0.0005$ $(k = 2)$; $u(T) = \pm 0.1$ K; $U_r(C_{P,m}) = 0.003$ $(k = 2)$

TABLE 4

Fitting coefficients in equation (2) along with the corresponding standard deviation, σ, for the mixture {1,8-cineole (1) + ethanol (2)} at $T = (304.7, 309.6, 314.6, 319.5, 324.5)$ K and atmospheric pressure $P = (0.1 \pm 0.002)$ MPa.

	$T/K = 304.7$	$T/K = 309.6$	$T/K = 314.6$	$T/K = 319.5$	$T/K = 324.5$
A / J mol^{-1} K^{-1}	114.65	116.81	119.04	121.38	123.76
B / J mol^{-1} K^{-1}	178.50	181.90	185.0	187.30	189.10
C / J mol^{-1} K^{-1}	-19.00	-21.3	-23.5	-25.20	-26.8
σ / J mol^{-1} K^{-1}	0.68	0.74	0.67	0.67	0.60

Values of molar heat capacities have been previously reported for 1,8-cineole by Aparicio et *al.* [23] and Štejfa et *al.* [24] at several temperatures. But, it is the case that they are very different one from each other as the values provided by Aparicio et *al.* range from 300 J·mol^{-1}·K^{-1} at 298.15 K to 328.15 J·mol^{-1}·K^{-1} at 328.15 K. . A comparison of the molar heat capacities of 1,8-cineole here measured, called set I and collected in table 3, with those mentioned shows a good agreement with Štejfa *et al.* and, consequently, a great deviation from the values of Aparicio *et al.* Then, our data corroborate the results of Štejfa *et al.* To fully ascertain this point, an independent determination of molar heat capacities of the 1,8-cineole used in this work was carried out in the laboratory of the Group of Applied Thermal Engineering of Dr. Coronas in the Universitat Rovira i Virgili. The results obtained and called set II are listed in Table 5. The values of the property, experimental and bibliographic, are represented in figure 3a and the percentage relative deviations for our two set of data from those of Štejfa *et al.* can be found in figure 3b. Deviations range from -0.2 to 0.3%. So, the molar heat capacities of Štejfa *et al.* (and those here reported) for 1,8-cineole seem to be correct.

TABLE 5

Molar heat capacity of 1,8-cineole (set II) at several temperatures and atmospheric pressure $P = (0.1 \pm 0.002)$ MPa determined by the Group of Applied Thermal Engineering.

T / K	$C_{P,\mathrm{m}}$ / J·mol^{-1}·K^{-1}
293.26	266.9
303.48	273.0
313.71	279.5
323.93	285.2
334.16	290.8
344.38	297.7

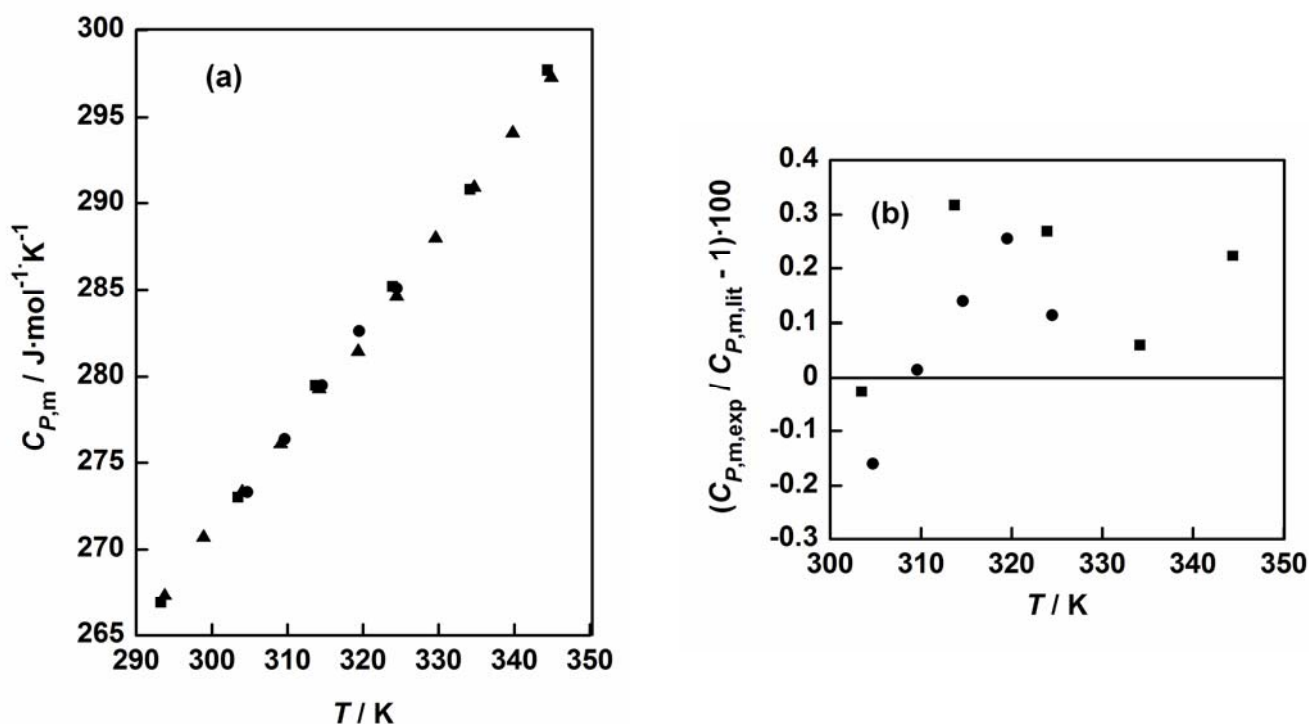$u(T) = \pm 0.02$ K; $U_r(C_{P,\mathrm{m}}) = \pm 0.005$

Figure 3. (a) Molar heat capacity for 1,8-cineole: (●) set I (Universidad de Zaragoza); (■) set II (Universitat Rovira i Virgili); (▲) Štejfa *et al.*[24]. Percentage relative deviations of experimental molar heat capacities for 1,8-cineole: (●) set I (Universidad de Zaragoza); (■) set II (Universitat Rovira i Virgili) from those of Štejfa *et al.* (interpolated) at the working temperatures in this paper:

On the other hand, the molar heat capacity of 1,8-cineole extrapolated at 298.15 K is comparable to those of several monoterpenes [25,26] of similar molar mass and bicyclic structure as can be seen in table 6. In any case, the molar heat capacity of 1,8-cineole is quite large and a significant part of it can be attributed to the presence of two rings fused forming a bridge, a feature that would bring about a remarkable structural strain. That this is the case can be corroborated by the calculation of the heat capacity of 1,8-cineole through the method of Rùzicka and Domalski [27,28] that gives a value of 215.61 $J \cdot mol^{-1} \cdot K^{-1}$ at 298.15 K. The heat capacity is clearly

underestimated by this group contribution method although strain ring contributions have been introduced by supposing that the cineole molecule is formed by two tetrahydropyran and one cyclohexane rings. Probably the strain ring contributions in the method are for independent rings and not for bridged ones that would add additional strain.

However, a new and improved group contribution method [29] that takes into account specific contributions for carbon atoms in cycles and also for carbon atoms pertaining to two rings provides much better results. The heat capacity predicted for 1,8-cineole at $T = 298.15$ K are 271.0 J·mol^{-1}·K^{-1} in the non-hierarchic approach and 253.6 J·mol^{-1}·K^{-1} in the hierarchic approach. Then, this new method is a powerful tool to calculate heat capacities.

TABLE 6

Molar mass and molar heat capacities at 298.15 K of 1,8-cineole and several compounds.

Compound	M / g·mol^{-1}	$C_{P,\mathrm{m}}$ / J·mol^{-1}·K^{-1}
1,8-Cineole	154.25	268.6[a]
		269.8[b]
		270.0[c]
(+)-Fenchone	152.23	269.2[d]
(-)-Verbenone	150.22	268.3[e]
α-Pinene	136.24	251.9[e]
β-Pinene	136.24	242.7[e]

[a]Extrapolated from this work (set I); [b]Interpolated form this work (set II); [c]Interpolated from values of ref.[29]; [d]Interpolated from values of ref.[30]; [e]Interpolated from values of ref. [31]

From the molar heat capacity data, the excess molar heat capacities, $C_{P,\mathrm{m}}^{\mathrm{E}}$, have been calculated by means of the equation

$$C_{P,\mathrm{m}}^{\mathrm{E}} = C_{P,\mathrm{m}} - x_1\, C_{P,\mathrm{m},1} - x_2\, C_{P,\mathrm{m},2} \tag{4}$$

being $C_{P,\mathrm{m}}$ the heat capacity of the mixture, x_i, the mole fraction of pure component i and $C_{P,\mathrm{m,i}}$ is the molar heat capacity of pure component i. As an example, values of the excess molar heat capacity corresponding to the temperatures (304.7, 314.6, and 324.5) K are represented in figure 4 along with the uncertainty in the form of error bars at 324.5 K, being the error the same for all of the temperatures. The excess molar heat capacities are positive over the whole composition range, a result that agrees with the fact that the excess molar enthalpy for the mixture increases when temperature increases in the temperature interval comprised between (298.15 and 313.15) K [2] and, according to our values of excess heat capacity, would continue increasing at the higher temperatures considered in this work. As the positive values of excess molar enthalpy indicate that there is a breaking of interactions, mainly the hydrogen bonds in ethanol, in the mixing process, the
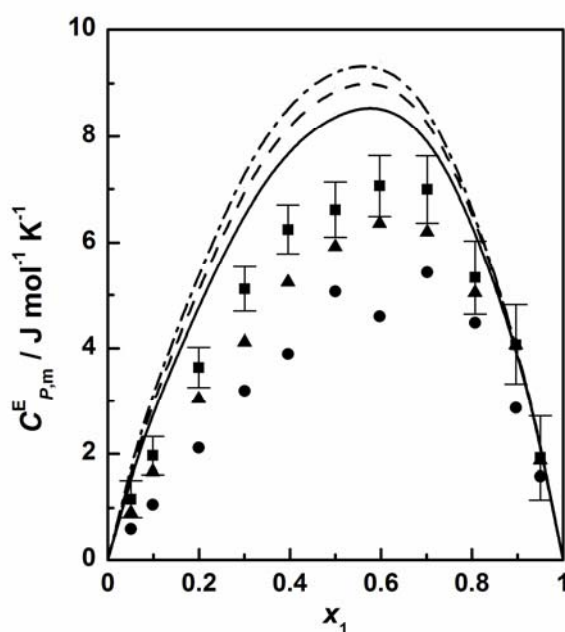

Figure 4. Excess molar heat capacity, $C_{P,\mathrm{m}}^{\mathrm{E}}$, at atmospheric pressure for the mixture {1,8-cineole (1) + ethanol (2)} at several temperatures: (●) 304.7 K, (▲) 314.6 K, (■) 324.5 K; along with the values of the property predicted by the COSMO-RS model at the same temperatures: (—) 304.7 K, (— —) 314.6 K, (— · —) 324.5 K. Error bars are shown at 324.5 K, being equal for the other temperatures.

positive values of excess heat capacities show that the breaking would increase with rising temperatures. Besides, given that the higher the temperature the higher the excess heat capacities, the breaking of interactions would become more and more pronounced for increased temperatures within the range studied. The variation of the excess heat capacity data over the composition range is quite smooth but a trend towards a W shaped behavior can be observed at the lower temperature. The maxima in excess heat capacity are placed at $x_1 = 0.6$ as also occurred for the excess enthalpies [2]. For mixtures (1-alkanol + alkane) this deviation has been attributed [30] 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 used to predict the excess molar heat capacity of the mixture. This method allows the calculation of the excess molar enthalpies from which the excess molar heat capacities at constant pressure are obtained by derivation with respect to the temperature

$$C_{P,m}^{E} = \left(\frac{\partial H_m^E}{\partial T} \right)_{P,x} \tag{6}$$

COSMO-RS, first proposed by Klamt [9] and subsequently refined [10,11], 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, 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 [31,32] with a triple zeta valence polarized (TZVP) basis set [33] and a density fitting function DGA1 [34]. The most stable conformers of 1,8-cineole 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_C11_0101 [35] was used. The optimization of the model parameters [10] only requires the vapor pressures of the pure

compounds which were obtained from the literature [5]. Excess molar enthalpies and excess molar heat capacities are then obtained from the molecular interactions.

The results of the predictions are shown in figure 4 for the temperatures (304.7, 314.6, and 324.5) K. The method overestimates the values of the excess heat capacities but the results are quite acceptable. It predicts well the trend of variation of the excess molar heat capacity with the temperature.

Conclusions

The molar heat capacity at atmospheric pressure of the mixture {1,8-cineole (1) + ethanol (2)} has been measured in the temperature interval (304.7 to 324.5) K and the whole composition range. For this purpose a calorimeter Setaram C80 has been used after being checked with ethanol. The molar heat capacity values for 1,8-cineole have led to corroborate the data previously reported by Štejfa *et al.* The molar heat capacity of 1,8-cineole is quite high but the values are comparable with those of similar compounds such as fenchone, verbenone and pinenes. The molar heat capacity of the mixture {1,8-cineole (1) + ethanol (2)} for each temperature can be adjusted to a polynomial of second order in the mole fraction. From the heat capacity data, the excess molar heat capacities have been calculated, being positive in the whole composition range, a fact which is in agreement with measured excess molar enthalpies for this mixture. 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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