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Thermodynamics of mixtures containing amines. XVI. C_{pm}^{E} of 1-butanol, 1-octanol or 1-decanol + benzylamine systems at (298.15, 308.15, 318.15 and 333.15) K

Ricardo Páramo, Juan Antonio González *, Isaías García de la Fuente, Carlos Casanova, José Carlos Cobos

G.E.T.E.F., Departamento de Física Aplicada, Facultad de Ciencias, Universidad de Valladolid, Paseo de Belén, 7, 47011 Valladolid, Spain

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ABSTRACT

Molar isobaric heat capacities, C_{pm}, and molar excess isobaric heat capacities, C_{pm}^{E}, are reported for 1-butanol, 1-octanol or 1-decanol + benzylamine systems at (293.15, 308.15, 318.15, 333.15) K. C_{pm}^{E} values were measured with a Setaram Micro DSC II microcalorimeter using a scanning method. The investigated mixtures are characterized by large and positive $C_{pm}^{E}(x_1 = 0.5)$ values at 298.15 K, which remarks that self-association and/or solvation effects are predominant in such solutions. The C_{pm}^{E} curves are skewed towards higher mole fractions of the alcohol, which suggests that alcohol-amine interactions are more probable in that region. In addition, for a given 1-alkanol, $C_{pm}^{E}(x_1 = 0.5)$ decreases when temperature increases, due to alcohol dissociation is larger at elevated temperatures. The lower self-association of longer 1-alkanols and lower solvation effects may explain that the $C_{pm}^{E}(x_1 = 0.5)$ change with temperature is sharper for the solutions with the mentioned alcohols. The observed decrease of $C_{pm}^{E}(x_1 = 0.5)$ with the increasing of the chain length of the alcohol at enough high temperatures may be explained in similar terms.

1. Introduction

We are engaged in a systematic study of mixtures containing amines. Thus, previously we have investigated systems with linear secondary amines [1]; *N,N,N*-trialkylamines [2,3]; cyclic amines [4,5] or mixtures including some of the following aromatic amines: aniline [6],*o*-toluidine [7], *N*-methylaniline [8,9], or pyridines [10–13]. In fact, this type of solutions has been treated in the framework of the DISQUAC [14]; ERAS [15]; or Flory [16] models, and by means of the Kirkwood–Buff [17] or concentration–concentration structure factor [18] formalisms. In addition, we have also provided data on molar excess volumes; liquid–liquid equilibrium (LLE) and/or excess molar enthalpy (H_{m}^{E}) for mixtures containing some of the mentioned amines and hydrocarbons. Regarding solutions involving benzylamine, the database on thermodynamic properties of mixtures with this amine is very limited [19,20]. In the preceding papers, we have reported C_{pm}^{E} data for the benzylamine + heptane system at 293.15 K and for methanol, 1-propanol or 1-pentanol + benzylamine mixtures at (293.15–308.15) K [21], and LLE measurements for benzylamine + alkane systems [22]. As continuation of these studies, we provide now C_{pm} and C_{pm}^{E} data for 1-butanol, or 1-octanol or 1-decanol + benzylamine mixtures at (298.15, 308.15, 318.15 and 333.15) K and at 0.1 MPa. The investigation on C_{pm}^{E} of systems containing organic liquids is a common method to gain insight into the interactions of the studied mixtures and on their structure [18,23].

2. Experimental

2.1. Materials

Table 1 shows the main characteristics of pure compounds used in the present work including source, purity, water contents, determined by the Karl-Fischer method, density (ρ) and molar isobaric heat capacities, C_{pm}. The chemicals were used without further purification. The experimental values of ρ and C_{pm} of the pure compounds are in good agreement with those available in the

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* Corresponding author. Tel.: +34 983 423757; fax: +34 983 423136.
E-mail address: jagl@termo.uva.es (J.A. González).

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Table 1
Densities, ρ, and isobaric molar heat capacities, C_{pm}, of pure compounds at temperature 298.15 K and 0.1 MPa[a].

Compound	Source	Initial mole fraction	ρ/kg m^{-3}		C_{pm}/J mol^{-1} K^{-1}		Water content[b]
			Exp.	Lit.	Exp.	Lit.	
Benzylamine	Fluka	≥0.99	978.337	981[c] 977.7[e]	207.31	207.18[d]	680×10^{-6}
1-Butanol	Sigma–Aldrich	≥0.995	805.901	805.75[f]	177.50	176.86[h]	290×10^{-6}
1-Octanol	Fluka	≥0.995	821.72	821.57[f]	304.25	304[h]	140×10^{-6}
1-Decanol	Sigma–Aldrich	≥0.99	826.58	826.44[i]	370.16	372.98[g]	330×10^{-6}

[a] Standard uncertainties: $u(T) = \pm 0.01$ K; $u(P) = \pm 0.1$ kPa; $u() = \pm 0.02$ kg m^{-3}; $u(C_{pm}) = 0.01\ C_{pm}$ J mol^{-1} K^{-1}.
[b] In mass fraction.
[c] [45].
[d] [46].
[e] Extrapolated value from data reported in [19].
[f] [37].
[g] [47].
[h] [48].
[i] [49].

literature (Table 1). Densities were measured using a vibrating-tube densimeter and a sound analyser, Anton Paar model DSA-5000. The ρ uncertainty is $\pm 1 \times 10^{-2}$ kg m^3, and its precision is $\pm 1 \times 10^{-3}$ kg m^{-3}. Uncertainty of C_{pm} is given below.

2.2. Procedure

Binary mixtures were prepared by mass in small vessels of about 10 cm^3, using an analytical balance HR-202 (weighing accuracy $\pm 0.1 \times 10^{-6}$ kg), with all weighings corrected for buoyancy effects. Caution was taken to prevent evaporation. The error in the final mole fraction is estimated to be less than ±0.0001. Molar quantities were obtained using the relative atomic mass Table of 2006 issued by IUPAC [24].

Measurements were developed with a Setaram Micro DSC II microcalorimeter using a scanning method, with the reference cell filled with undecane. The apparatus has been described in detail previously, including the design of the hermetic vessels used to avoid leaks, the required calibrations of the apparatus, and the working principle [21,25]. Temperature calibration was performed using a Pt-1000 probe, calibrated on the basis of the ITS-90 scale of temperature using the triple point of the water and the fusion point of Ga (uncertainty ±0.01 K) embedded in a stainless steel block of the same geometry that the vessels, and at different scanning rates. The estimated uncertainty of temperature is ±0.03 K for the scanning mode. A calorimetric calibration is also needed to obtain the proportionality constant between the output signal and the total heat flow rate. The calibration was developed by means of Setaram vessels specially designed to produce electrical heating of known power with the EJ2 power source, also from Setaram. The uncertainty of C_{pm} is estimated to be 1% for pure compounds. This value is estimated from the comparison of our data over the temperature range (270–360) K with those from the literature for hexane, heptane, decane, dodecane, cyclohexane, benzene, toluene, methanol or 1-butanol. Note that the differences between experimental C_{pm} values listed in Table 1 and those from the literature are within this uncertainty. The uncertainty of C^E_{pm} is estimated to be better than 4% at the central range of concentration. At the extremes of the concentration range, the low C^E_{pm} values are very sensitive to the values used for the C_{pm} of the pure compounds.

3. Results

Results for C_{pm} and C^E_{pm} for the 1-butanol, or 1-octanol or 1-decanol + benzylamine systems at the four temperatures considered are collected in Table 2. The data were fitted by unweighted least-squares polynomial regression to the equation:

$$C^E_{pm} = x_1(1 - x_1)\sum_{i=0}^{k-1} A_i(2x_1 - 1)^i \quad (3)$$

The number of coefficients k used in Eq. (3) for each mixture was determined by applying an F-test [26] at the 95% confidence level. Table 3 lists the parameters A_i obtained in the regression, together with the standard deviations, σ, defined by:

$$\sigma\left(C^E_{pm}\right) = \left[\frac{1}{N - k}\Sigma\left(C^E_{pm,cal} - C^E_{pm,exp}\right)^2\right]^{1/2} \quad (4)$$

where N is the number of direct experimental values. Results are shown graphically in Figs. 1–3. No data have been encountered in the literature for comparison.

4. Discussion

Below, we are referring to the molar excess functions at equimolar composition and 298.15 K.

We note that regarding the excess molar heat capacity at constant pressure, the main features of the investigated solutions are: (i) the large and positive values of this magnitude at 298.15 K; (ii) the shape of the corresponding curves, shifted to higher mole fractions of the alcohol (x_1); (iii) C^E_{pm} of mixtures containing a given 1-alkanol decreases for increasing values of the temperature; (iv) at enough high temperatures, C^E_{pm} decreases with the increasing of the alcohol size. The large and positive C^E_{pm} values at 298.15 K reveal that this magnitude is mainly determined by effects related to self-association of the alcohols and/or solvation between the system components. 1-Alkanol + alkane mixtures, where self-association of the alcohols plays a dominant role, show low positive H^E_m values and large positive C^E_{pm} values. Thus, for the 1-butanol + heptane system, $H^E_m = 647$ J mol^{-1} [27] and $C^E_{pm} = 11.1$ J mol^{-1} K^{-1} [28]. A weakening of effects related to alcohol self-association leads to larger H^E_m and C^E_{pm} values, as in the case of 2-butanol + heptane solution, for which the mentioned magnitudes are 907 J mol^{-1} [29] and 15.22 J mol^{-1} K^{-1} [30], respectively. 1-Alkanol + oxaalkane mixtures are characterized by the existence of dipolar interactions, which in the case of polyether solutions are rather relevant [31,32], and this leads to an increase of the H^E_m values and to a decrease of C^E_{pm} values in comparison to those of 1-alkanol + alkane systems. For example; H^E_m/J mol^{-1} = 840 (1-butanol + dibutyl ether) [33]; 1222 (1-propanol + 2,5,8-trioxanonane)