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Thermodynamics of mixtures involving some (benzene derivatives + benzonitrile)

E. Calvo-Iglesias [a,*], R. Bravo [a], M. Pintos [a], A. Amigo [a], A.H. Roux [b], G. Roux-Desgranges [b]

[a] *Departamento de Física Aplicada, Facultad de Física, Universidad de Santiago de Compostela, E-15782 Santiago de Compostela, Spain*
[b] *Thermodynamique des Solutions et des Polymères, UMR CNRS 6003, Université Blaise Pascal, 63177 Aubière cedex, France*

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Abstract

Interactions of binary mixtures involving some benzene derivatives (ethylbenzene, *o*-, *m*-, *p*-xylene, isopropylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, and methoxybenzene) with benzonitrile were investigated in continuation of our previous studies on binary systems (benzene or toluene + benzonitrile). Heat capacities by volume unit, determined with a Picker flow calorimeter at $T = 298.15$ K, and densities, measured by using Picker vibrating densimeters at the temperatures (298.15 and 308.15) K, are reported. Measurements were made over the entire range of mole fraction. From the primary measurements, the corresponding excess quantities V^E and $C^E_{p,m}$ are obtained. The magnitude of these experimental quantities together with H^E literature data is discussed in terms of the nature and type of intermolecular interactions in binary mixtures.

Keywords: Density; Heat capacity; Benzonitrile; Benzene derivatives

1. Introduction

The interactions between aromatic molecules and benzonitrile have been the subject of many investigations, particularly through the analysis of the thermodynamic properties of liquid mixtures [1–9]. The most striking feature in this kind of system is the M-shaped curve of the excess enthalpies as can be observed, for example, in the mixtures of benzonitrile with toluene or benzene [1,5]. This unusual behaviour can be explained by the complex formation between benzonitrile and either benzene or toluene. Most of the benzene derivatives would probably lead to a complex formation with benzonitrile, as suggested by some authors [2,3,9]. The negative values of excess molar enthalpies in the (anisole + benzonitrile) system reported by Viswanathan *et al.* [3] coincide with those reported by Rajkumar *et al.* [9], who concluded that specific interactions between molecules take place in this mixture leading to complex formations with anisole molecules acting as the donor. The formation of charge-transfer complexes in mixtures of benzonitrile with xylene isomers, ethylbenzene and mesitylene was reported by Letcher and Naicker [2]. The excess enthalpies in these mixtures are always positive and their low values indicate a strong association between benzonitrile and the aromatic compounds.

In this work, we report isobaric excess molar heat capacities, $C^E_{p,m}$, at $T = 298.15$ K and excess molar volumes, V^E, at $T = 298.15$ K and $T = 308.15$ K for {benzonitrile + ethylbenzene, *o*-, *m*-, *p*-xylene, isopropylbenzene (cumene), 1,2,4-trimethylbenzene (pseudocumene), 1,3,5-trimethylbenzene (mesitylene), and methoxybenzene (anisole)}. The aim of this research is to compare the modifications of V^E and $C^E_{p,m}$ in binary systems containing different benzene derivatives and to analyze the thermodynamic behaviour of these mixtures while also taking the literature values of excess enthalpies into account.

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* Corresponding author. Tel.: +34 981563100; fax: +34 981520676.
E-mail address: faencina@usc.es (E. Calvo-Iglesias).

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2. Experimental

The origin and purity of the chemical compounds (and their short-name) are shown in table 1 where the measured densities and heat capacities of pure substances are also compared with some selected literature values [7,10–18]. Chemicals were used without further purification other than being kept over molecular sieves to remove water, indispensable with benzonitrile. Before use, the pure compounds were slightly degassed under vacuum to avoid bubble formation. Liquid mixtures for density and heat capacity measurements were prepared by mass. The error in the mole fraction was estimated to be $<10^{-4}$.

Experimental densimetric and calorimetric techniques have been described in detail in previous works [19–23]. Densities, ρ, of pure components and their mixtures were measured with Picker densimeters (models 02D and 03DCss, SODEV, Canada), operated under flow conditions. Before each series of measurements, the instruments were calibrated with vacuum, twice distilled and degassed water [24], and *n*-heptane as secondary reference liquid [19]. The precision of the 02D model, operating at $T = 298.15$ K, has proven greater than $10^{-5}\ \mathrm{g \cdot cm^{-3}}$. Model 03DCss, operating at $T = 308.15$ K, is somewhat less sensitive, the uncertainty of ρ being less than $10^{-4}\ \mathrm{g \cdot cm^{-3}}$. Thermostat stability for the 02D model was greater than 0.005 K. Thermostatic control for the other model proved more difficult and stability of over 0.02 K could not be attained. As a confirmation, the density and refractive index were determined for all the materials and comparison with the literature values was satisfactory.

Volumetric heat capacities were determined using the stepwise procedure [19,20,23] with a Picker flow microcalorimeter (from Setaram) equipped with gold cells, the flow rate being $0.01\ \mathrm{cm^3 \cdot s^{-1}}$. The stability of the thermostat was greater than 0.005 K, and the apparatus was adjusted to obtain a centered temperature of 298.15 K accounting for the increment of temperature imposed by the measuring process. Under these conditions, the apparatus can detect C_p/V differences of $10^{-4}\ \mathrm{J \cdot K^{-1} \cdot cm^{-3}}$. As the primary reference, we selected *n*-heptane for which the density and molar heat capacity at $T = 298.15$ K were taken to be $679.51\ \mathrm{kg \cdot m^{-3}}$ and $224.78\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, respectively [19]. The measured heat capacities by unit volume were converted to molar heat capacities with the use of our measured densities, and subsequently excess molar heat capacities $C_{p,\mathrm{m}}^{\mathrm{E}}$ were calculated.

3. Results and discussion

Experimental densities at temperatures of 298.15 K and 308.15 K, and isobaric excess molar heat capacities at $T = 298.15$ K are summarized in tables 2 and 3, respectively. For each mixture, the excess quantities were fitted with a Redlich–Kister function of the form

$$Y^{\mathrm{E}} = x(1-x)\sum_{i=0}^{N} A_i(2x-1)^i, \tag{1}$$

where either $Y^{\mathrm{E}} = V^{\mathrm{E}}/(\mathrm{cm^3 \cdot mol^{-1}})$ or $Y^{\mathrm{E}} = C_{p,\mathrm{m}}^{\mathrm{E}}/(\mathrm{J \cdot K^{-1} \cdot mol^{-1}})$, and x denotes the benzonitrile mole fraction. The coefficients A_i and standard deviations $s(Y^{\mathrm{E}})$ listed in table 4 were estimated using the unweighted least-squares method. These parameters were used to obtain the calculated curves in figures 1 to 4.

In figures 2 and 4, the experimental and calculated reduced quantities $Y^{\mathrm{E}}/x(1-x)$ are plotted as a function of the mole fraction of benzonitrile. The plot of the reduced functions gives more information than the corresponding

TABLE 1

Source, purity, density, ρ, and molar heat capacity, $C_{p,\mathrm{m}}$, of the pure compounds at the temperature 298.15 K

Compound	Source, purity	$\rho/(\mathrm{kg \cdot m^{-3}})$		$C_{p,\mathrm{m}}/(\mathrm{J \cdot K^{-1} \cdot mol^{-1}})$	
		Experimental	Literature	Experimental	Literature
Benzonitrile	Sigma-Aldrich 99.9% HPLC	1000.25	1000.3[a]	166.415	166.64[b]
Ethylbenzene	Fluka puriss >99% GC	862.41	862.44[c]	185.445	185.572[d]
o-Xylene	Fluka puriss >99%	875.55	875.53[e]	187.282	187.574[f]
m-Xylene	Fluka puriss >99% GC	859.68	859.77[e]	181.379	183.44[d]
p-Xylene	Fluka puriss >99% GC	856.48	856.58[c]	181.734	181.66[d]
Isopropylbenzene (cumene)	Aldrich 99% GC	857.41	857.43[d]	214.746	215.40[g]
1,2,4-Trimethylbenzene (pseudocumene)	Fluka puriss >99% GC	871.56	871.78[h]	213.024	215.03[i]
1,3,5-Trimethylbenzene (mesitylene)	Fluka puriss >99% GC	860.90	861.06[e]	207.425	207.69[j]
Methoxybenzene (anisole)	Aldrich >99% GC	988.98	989.15[e]	191.539	208.57 (32 °C)[d]

[a] Reference [10].
[b] Reference [7].
[c] Reference [11].
[d] Reference [12].
[e] Reference [13].
[f] Reference [14].
[g] Reference [15].
[h] Reference [16].
[i] Reference [17].
[j] Reference [18].