



Thermodynamics of mixtures containing aromatic nitriles



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ARTICLE INFO

Article history:

Received 28 March 2017
Received in revised form 21 September 2017
Accepted 22 September 2017
Available online 23 September 2017

Keywords:

LLE
Aromatic nitrile
Proximity effects
Dipolar interactions
DISQUAC

ABSTRACT

The coexistence curves of liquid-liquid equilibrium (LLE) for the mixtures: phenylacetoneitrile + heptane, + octane, + nonane, + cyclooctane, or + 2,2,4-trimethylpentane and for 3-phenylpropionitrile + heptane, or + octane are reported. Aromatic nitrile + alkane, + aromatic hydrocarbon or + 1-alkanol systems are investigated using a set of thermophysical properties: phase equilibria (solid-liquid, SLE, vapour-liquid, VLE and LLE), excess molar functions, enthalpies (H_m^E), isochoric internal energies ($U_{V,m}^E$), isobaric heat capacities ($C_{p,m}^E$) and volumes (V_m^E), and the Kirkwood's correlation factor. Due to proximity effects between the phenyl and the CN groups, dipolar interactions between molecules of aromatic nitriles are stronger than those between molecules of isomeric linear nitriles. Dipolar interactions become weaker in the order: 3-phenylpropionitrile > phenylacetoneitrile > benzonitrile. Benzonitrile + aromatic hydrocarbon mixtures are characterized by dispersive interactions and structural effects. The latter are more important in systems with phenylacetoneitrile. Structural effects are also present in benzonitrile + *n*-alkane, or + 1-alkanol + mixtures. The systems mentioned above have been studied using DISQUAC. Interaction parameters for contacts where the CN group in aromatic nitriles participates are given. DISQUAC describes correctly any type of phase equilibria, $C_{p,m}^E$ of benzonitrile + hydrocarbon mixtures and H_m^E of benzonitrile + cyclohexane, or 1-alkanol systems. Large differences encountered between theoretical H_m^E values and experimental data for some solutions are discussed. 1-Alkanol + benzonitrile mixtures are also investigated by means of the ERAS model. ERAS represents well H_m^E of these systems. The V_m^E curves of solutions with longer 1-alkanols are more poorly described, which has been explained in terms of the existence of structural effects.

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1. Introduction

Aromatic nitriles, $C_6H_5-(CH_2)_{n-1}CN$ ($n = 1$ (benzonitrile); $n = 2$ (phenylacetoneitrile); $n = 3$ (3-phenylpropionitrile)) are rather polar compounds as it is indicated by their high dipole moments (μ) [1]: 3.87 D ($n = 1$); 3.50 D ($n = 2$); 3.29 D ($n = 3$). They are good solvents and are used as starting materials in the synthesis of fungicides, fragrances and pharmaceuticals, as analgesics or antihistamines. Recently, the mixture formed by 3-phenylpropionitrile and supercritical CO_2 has received attention as the miscibility of these type of systems is a relevant condition for polymer processes [2].

It is well known that the existence of two groups (X, Y) of the same or different nature within the same molecule leads to an enhancement of the dipolar interactions between the mentioned molecules. For example, the 1-butanol + heptane mixture is

miscible at any concentration at 298.15 K and, at equimolar composition, its excess molar enthalpy, H_m^E , is 575 J·mol⁻¹ [3]. In contrast, the 2-methoxyethanol (isomeric molecule of 1-butanol) + heptane system is characterized by a moderately high UCST (319.74 K [4]), what has been typically ascribed to proximity effects between the –O– and –OH groups within the alkoxyethanol [5]. It is also known, that the application of group contribution methods to systems characterized by proximity effects between two given groups X,Y leads to erroneous results when one uses interaction parameters for the (X/Y) contacts obtained from solutions with X and Y belonging to different molecules [6]. In fact, proximity effects can drastically change the interaction parameters of the applied model. Thus, in terms of UNIFAC (Dortmund version) specific main groups have been defined for aniline or phenol for a better representation of the thermodynamic properties of mixtures involving these compounds [7]. We are engaged in a systematic research on proximity effects between the phenyl group C_6H_5- and a polar group as carbonyl, aldehyde, alkanoate, amine,

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alkanol or oxygen. At this end, we have provided LLE measurements for systems formed by one alkane and a polar aromatic compound such as: $C_6H_5-(CH_2)_{n-1}COCH_3$ ($n = 1, 2, 3$) [8–10]; C_6H_5-CHO [11]; $C_6H_5-CH_2OCOCH_3$ [9,10]; $C_6H_5-CH_2NH_2$ [12]; $C_6H_5-CH_2OH$ [13], or $C_6H_5-O-CH_2CH_2OH$ [14]. These data together with measurements available in the literature on VLE or H_m^E for these or related compounds, aniline or phenol, e.g., have been employed for the characterization of aromatic polar compound + organic solvent mixtures [8–16] in terms of the DISQUAC group contribution model [17]. Here, we continue with this research line and report LLE data for the systems: $C_6H_5-CH_2CN$ + heptane, or + octane, or + nonane, or + cyclooctane, or + 2,2,4-trimethylpentane, and for $C_6H_5-CH_2CH_2CN$ + heptane, or + octane. In addition, aromatic nitrile + organic solvent mixtures are characterized using DISQUAC and the interaction parameters for a number of contacts, CN/aliphatic; CN/aromatic and CN/OH, are provided. UNIFAC (Dortmund) and DISQUAC interaction parameters for the contacts CN/aliphatic and CN/OH in systems involving linear nitriles are available in the literature [7,18,19]. The mixtures 1-alkanol + linear nitrile or + benzonitrile have been investigated by means of the Flory theory [20], and the ERAS model [21] has been applied to 1-alkanol + benzonitrile systems [22]. On the other hand, due to high μ values of aromatic nitriles, one may expect the existence of strong dipolar interactions between nitrile molecules in solutions where these compounds participate. An interesting question arises from the concentration dependence of H_m^E of benzonitrile + benzene, or + toluene systems. Some authors have reported M-shaped H_m^E curves for these mixtures [23,24]. Such anomalous concentration dependence of H_m^E has been explained by invoking charge-transfer complex formation between benzonitrile and the aromatic hydrocarbon [23]. However, it must be remarked that other researchers have not observed the mentioned trends for benzonitrile mixtures [25]. This matter will also be considered along the work.

2. Experimental

2.1. Materials

Table 1 shows some properties of the pure chemicals used along the experimental part of this investigation: source, purity, water contents, determined by the Karl-Fischer method, and density (ρ). The reagents were employed without further purification. Density values were determined by means of a vibrating-tube densimeter and a sound analyser, Anton Paar model DSA-5000. The repeatability of the ρ measurements is $5 \cdot 10^{-3} \text{ kg} \cdot \text{m}^{-3}$, while their relative standard uncertainty is 0.0012. From the values collected in Table 1, we can conclude that there is a good agreement between our density results and those reported in the literature.

2.2. Apparatus and procedure

Mixtures were prepared by mass in small Pyrex tubes (0.009 m i.d. and about 0.04 m length, with a free volume of the ampoule $\approx 1.17 \cdot 10^{-6} \text{ m}^3$). The tubes were immediately sealed by capping at 0.1 MPa and 298.15 K. Weights were determined by means of an analytical balance Sartorius MSU125p (weighing accuracy 10^{-8} kg). Mole fractions were calculated using the relative atomic mass Table of 2015 issued by the Commission on Isotopic Abundances and Atomic Weights (IUPAC) [26].

The coexistence curves of liquid-liquid equilibrium were determined by a method of turbidimetry, i.e., by means of the observation of the turbidity produced on cooling when a second phase takes place. Details on the experimental technique have been pre-

viously reported [14]. Particularly, we remark that mixtures are slowly cooled ($1.2 \text{ K} \cdot \text{h}^{-1}$) under continuous stirring. Due to the equilibrium times are much longer in the two-phase region than those in the one-phase region, this procedure is suitable to prevent supercooling and gravity effects in systems with compositions far from the critical one [27]. The equilibrium temperatures were measured using a Pt-1000 resistance, calibrated, according to the ITS-90 scale of temperature, against the triple point of the water and the fusion point of Ga. The precision of the equilibrium temperature measurements is $\pm 0.001 \text{ K}$. The estimated standard uncertainty is 0.1 K in the flat region of the coexistence curves, and outside of this region is 0.2 K. The standard uncertainty of the equilibrium mole fraction is 0.0005. This value of composition uncertainty takes into account that the more volatile component is partially evaporated to the mentioned free volume of the ampoule.

3. Experimental results

Table 2 lists the directly measured liquid-liquid equilibrium temperatures, T , vs. x_1 , the mole fraction of the aromatic nitrile, for the systems: phenylacetonitrile + n -C₇, or + n -C₈, or + n -C₉, or + cyclooctane, or + 2,3,4-trimethylpentane, and for 3-phenylpropionitrile + n -C₇, or + n -C₈. A literature survey shows that there are no data available for comparison. Some experimental results are also represented in Fig. 1.

For the considered systems, the LLE curves are characterized by a rather flat maximum and become progressively skewed towards higher x_1 values when the number of C atoms of the n -alkane is increased. In addition, the upper critical solution temperature, UCST, of the studied solutions increases with the n -alkane size. These features are also encountered in many others systems previously investigated as those formed by n -alkane and acetophenone [8], or phenylacetone [9], or benzaldehyde [11], or aromatic alcohols [13], or aromatic amines, or linear organic carbonate, or acetic anhydride, or alkoxyethanol, or linear polyether (see reference [9] for the source of experimental data).

The experimental (x_1, T) pairs obtained for each system were correlated with the equation [28]:

$$T/K = T_c/K + k|y - y_c|^m \quad (1)$$

where

$$y = \frac{\alpha x_1}{1 + x_1(\alpha - 1)} \quad (2)$$

$$y_c = \frac{\alpha x_{1c}}{1 + x_{1c}(\alpha - 1)} \quad (3)$$

In Eqs. (1)–(3), m , k , α , T_c and x_{1c} are the parameters which must be adjusted against the experimental data. Particularly, (x_{1c}, T_c) stand for the coordinates of the critical point. It should be remarked that, when $\alpha = 1$, Eq. (1) is similar to [29–31]:

$$\Delta\lambda = B\tau^\beta \quad (4)$$

In Eq. (4), $\Delta\lambda_1 = \lambda_1' - \lambda_2''$ may be any density variable in the conjugate phase (order parameter). In this investigation, $\lambda_1 = x_1$. On the other hand, $\tau (=T_c - T)/T_c$ denotes the reduced temperature and β is the critical exponent linked to $\Delta\lambda_1$. The critical exponent β value depends on the theory applied to its determination [29–32].

The adjustment of the m , k , α , T_c and x_{1c} parameters was conducted by means of the Marquardt algorithm [33] with all the points weighted equally. Final values of m , k , α , T_c and x_{1c} and of the standard deviations for LLE temperatures, $\sigma(T)$, are given in Table 3. The corresponding $\sigma(T)$ values are calculated from:

$$(\sigma(T)/K) = \left[\sum (T_{\text{exp}}/K - T_{\text{calc}}/K)^2 / (N - n) \right]^{1/2} \quad (5)$$

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