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Experimental (solid + liquid) or (liquid + liquid) phase equilibria of (amine + nitrile) binary mixtures

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Abstract

(Solid + liquid) phase diagrams have been determined for (hexylamine, or octylamine, or 1,3-diaminopropane + acetonitrile) mixtures. Simple eutectic systems have been observed in these mixtures. (Liquid + liquid) phase diagrams have been determined for (octylamine, or decylamine + propanenitrile, or + butanenitrile) mixtures. Mixtures with propanenitrile and butanenitrile show immiscibility in the liquid phase with an upper critical solution temperature, UCST. (Solid + liquid) phase diagrams have been correlated using NRTL, NRTL 1, Wilson and UNIQUAC equations. (Liquid + liquid) phase diagrams have been correlated using NRTL equation.

Keywords: Experimental (solid + liquid) and (liquid + liquid) equilibria; Binary (amine + nitrile) mixtures; Molecular interactions; Correlation

1. Introduction

This paper is a continuation of our systematic study on the interactions between unlike molecules in systems of polar compounds, such as 1-alkanols with amines [1–4] and 1-alkanols with nitriles [5]. The results obtained from our previous study revealed that positive values of V_m^E and H_m^E, observed for (alkan-1-ol + nitrile) mixtures [5], were confirmed by the phase diagrams. Contrary to (amine + alkan-1-ol) mixtures with strong negative excess functions and the congruently melting addition compounds [1–4], weak interactions were observed for (alkan-1-ol + nitrile) mixtures [5]. On the other hand, mixtures of (amine + nitrile) are also known from the literature to show much weaker interactions, than those observed in (amine + alkan-1-ol). The measurements of molar excess volumes, V_m^E [6–8] for (diethylamine, or *s*-butylamine + acetonitrile) and molar excess enthalpies, H_m^E [9] for (aniline, or *n*-butylamine + acetonitrile) systems were presented previously. The (solid + liquid) phase diagram, (SLE) for (decylamine + acetonitrile) system was also presented [10]. Excess molar volumes are relatively small and negative in these mixtures (about $-0.3\ \text{cm}^3 \cdot \text{mol}^{-1}$). Molar excess enthalpies for (aniline + acetonitrile) mixture are negative, about $-300\ \text{J} \cdot \text{mol}^{-1}$, contrary to the values for (*n*-butylamine + acetonitrile) mixture, for which the excess molar enthalpies are positive at about $700\ \text{J} \cdot \text{mol}^{-1}$.

For a better description of the phase diagrams, the basic thermodynamic properties of pure substances – the enthalpy of fusion, the difference in the solute heat capacity between the liquid and solid phase at the melting temperature, determined by the differential scanning calorimetry, DSC for alkan-1-ols (nonan-1-ol, decan-1-ol, and undecan-1-ol) and amines (hexylamine, octylamine, decylamine, and 1,3-diaminopropane) were presented earlier [4].

In the present work, we extended the thermodynamic study to low temperatures where (solid + liquid) and (liquid + liquid) equilibria were measured. In this work, hexylamine, octylamine, decylamine, and 1,3-diaminopropane were chosen in mixtures with acetonitrile, propanenitrile, and butanenitrile. Experimental (solid + liquid) phase equilibria temperatures were measured for (hexylamine, or octylamine, or 1,3-diaminopropane + acetonitrile)

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systems and (liquid + liquid) equilibrium data for {octylamine, or decylamine (1) + propanenitrile (2)} and for {octylamine, or decylamine (1) + butanenitrile (2)} were measured.

2. Experimental

2.1. Materials

The origin of the chemicals and their mass fraction purities were: hexylamine (Fluka, >0.98), octylamine (Fluka, >0.98) decylamine (Aldrich Chemical Co., 0.95) and 1,3-diaminopropane (Aldrich Chemical Co., 0.99); acetonitrile (Aldrich Chemical Co., 0.9993), propanenitrile, (Fluka, >0.99), butanenitrile, (Fluka, >0.99). Amines and nitriles were fractionally distilled over different drying reagents to mass fraction purity better than 0.998 determined by GLC. Liquids were stored over freshly activated molecular sieves of type $4 \cdot 10^{-8}$ (Union Carbide). All compounds were checked by GLC analysis and no significant impurities were found. Analysis, using the Karl–Fischer technique, showed that the water content in solvents was less than 0.02 mass%. The physical properties of the substances used in this work are listed in table 1 together with the literature values.

2.2. Procedure

The (solid + liquid) and (liquid + liquid) phase equilibria, (LLE) temperatures have been determined using a dynamic method that has been described in detail previously [18]. Appropriate mixtures of solute and solvent in a Pyrex glass cell, placed under the nitrogen in a dry box, were heated very slowly (less than $2\ \text{K} \cdot \text{h}^{-1}$ near the equilibrium temperature) with continuous stirring inside a cell. The sample was placed in a glass thermostat filled with water, or acetone with "dry ice". The temperature of the liquid bath was varied slowly until one phase was obtained. The temperature at which the last crystals disappeared was taken as the temperature of the (solid + liquid) equilibrium. The crystal disappearance temperatures were detected visually.

TABLE 1
Physical properties of pure substances: melting temperature, $T_{\text{fus},1}$, enthalpy of fusion, $\Delta_{\text{fus}}H_1$, heat capacity at the melting temperature, $\Delta_{\text{fus}}C_{p,1}$, as determined from the DSC data

Compound	$T_{\text{fus},1}$	$T^{(\text{lit})}_{\text{fus},1}$	$\Delta_{\text{fus}}H_1$	$\Delta_{\text{fus}}C_{p,1}$
	K	K	$\text{kJ} \cdot \text{mol}^{-1}$	$\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
Hexylamine	252.15	251.90[a]	25.04[b]	69.71[b]
Octylamine	273.37	273.15[c]	34.74[b]	72.51[b]
Decylamine	289.16	289.26[d]	42.70[b]	33.40[b]
1,3-Diaminopropane	262.19	262.37[e]	22.36[b]	66.31[b]
Acetonitrile	230.42	231.56[f]	8.167[g]	10.54[g]
Propanenitrile		180.37[h]	5.046[g]	22.25[g]
Butanenitrile		161.30[h]	5.021[h]	

[a] Reference [11].
[b] Reference [4].
[c] Reference [12].
[d] Reference [13].
[e] Reference [14].
[f] Reference [15].
[g] Reference [16].
[h] Reference [17].

In (liquid + liquid) equilibrium measurements, the temperature of disappearance of the second liquid phase on heating was detected visually. The observation of the regime "cloud point" with decreasing temperature was very difficult in these mixtures, and is not presented. The temperature was measured with an electronic thermometer P 550 (DOSTMANN electronic GmbH) with the probe totally immersed in the thermostating liquid. The thermometer was calibrated on the basis of ITS-90. The accuracy of the temperature measurements was judged to be ±0.01 K. The thermometer was calibrated on the basis of ITS-90. The uncertainty of the temperature measurements was ±0.05 K and that of the mole fraction did not exceed ±0.0005.

3. Results and discussion

3.1. SLE and LLE

Experimental temperatures of the (solid + liquid) phase equilibria for (hexylamine, or octylamine, or 1,3-diaminopropane + acetonitrile) systems are recorded in table 2 and are shown in figures 1 to 3. The SLE phase diagram for (decylamine + acetonitrile) system was published earlier [10] and fits very well to ours results what is shown in figure 4. In this study, simple eutectic mixtures with complete miscibility in the liquid phase were observed and complete immiscibility in the solid phase were assumed. For the amines with one functional group –NH_2, the same simple eutectic systems were observed as for 1,3-diaminopropane contrary to the mixtures of (hexylamine, or octylamine, or decylamine, or 1,3-diaminopropane + an alkan-1-ol). For the amines with one functional group –NH_2, a 1:1 congruently melting compound (Am · ROH) was observed [1–3] and for 1,3-diaminopropane a solid compound with the empirical formulae $[\text{Am} \cdot (\text{ROH})_2]$ was formed [4]. In this work, the only difference is that the eutectic point of {1,3-diaminopropane (1) + acetonitrile (2)} system ($T_{\text{eu}} = 221.7$ K; $x_{1,\text{eu}} = 0.1374$) is shifted to the higher mole fraction of acetonitrile in comparison with amines. From figure 4, it is possible to notice that as the number of carbon atoms of amine increases the eutectic point is shifted to the very low mole fraction of acetonitrile. It was possible to measure the eutectic point only in the system {hexylamine (1) + acetonitrile (2)} and the result is: $T_{\text{eu}} = 228.2$ K; $x_{1,\text{eu}} = 0.0426$. The eutectic points were detected, usually graphically, as minima on the crossing of two liquidus curves. The liquidus curves for the octylamine and decylamine were very flat but the immiscibility in the liquid phase was not observed contrary to the systems of {octan-1-ol, or nonan-1-ol, or decan-1-ol, or und-