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Experimental solid–liquid equilibria for systems containing alkan-1-ol + 1,3-diaminopropane
Heat capacities of alkan-1-ols and amines—Thermodynamic functions of dissociation and enthalpies of melting of the congruently melting compounds for the systems (alkan-1-ol + amine)

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Abstract

Solid–liquid phase diagrams (SLE) have been determined for (octan-1-ol, or nonal-1-ol, or decan-1-ol, or undecan-1-ol + 1,3-diaminopropane) mixtures. Solid addition compounds form with the empirical formulae: $\{(C_8H_{17}OH)_2{\cdot}C_3H_{10}N_2\}$, $\{(C_9H_{19}OH)_2{\cdot}C_3H_{10}N_2\}$, $\{(C_{10}H_{21}OH)_2{\cdot}C_3H_{10}N_2\}$, $\{(C_{11}H_{23}OH)_2{\cdot}C_3H_{10}N_2\}$. All these compounds are congruently melting compounds. Compound formation is attributed to a strong A–B interaction. An alkan-1-ol and amine are associated by formation O–H···O and N–H···N hydrogen bonds. Strong cross association between the hydroxyl and the amine group ($OH\cdots NH_2$) is the dominant effect and a 2:1 congruently melting solid compound is formed at low temperatures. Standard thermodynamic functions of the dissociation of the compound have been calculated.

The paper includes 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, 1,3-diaminopropane). The values of the enthalpies of fusion of congruently melting compounds in the binary systems (an alkan-1-ol + amine) are also presented.

Keywords: Experimental solid–liquid equilibria; Alkan-1-ol + 1,3-diaminopropane; Heat capacity; Enthalpy of fusion of congruently melting compound; Molecular interactions

1. Introduction

This work is the continuation of our systematic study on thermodynamic properties and phase equilibria of (alkan-1-ol + amine) binary systems. In this series of papers [1–3] our general aim was to confirm the interactions between unlike molecules in systems that exhibit very strong negative deviations from Rault's law from solid–liquid equilibria (SLE) measurements.

It is very well known that in the pure state the alcohol and the amine are associated by the formation O–H···O and N–H···N hydrogen bonds, respectively. From vapour pressure and spectroscopic measurements it has been shown that the dimerisation energy and the energy for the formation of higher oligomers are nearly the same, 8.5–13.5 kJ mol^{-1} for the amines and 20–25.1 kJ mol^{-1} for the alcohols [4]. Usually, it is assumed that in amines one kind of hydrogen bond, probably a linear bond, occurs, and that in alcohols two kinds of hydrogen bonds, leading to cyclic dimmers and linear higher oligomers, depending on the length of the alcohol chain are present. Two-constant models for the association of alcohols within a wide range of concentrations are not used for the hexan-1-ol and longer chain alcohols [4]. Mixtures of alcohols and amines show high negative values of excess molar volumes, V_m^E and excess molar enthalpies,

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H_m^E. Strong intermolecular interactions between the hydroxyl group and the amine group lead to the strongest negative values found for organic mixtures in the literature [5–10]. The excess molar volumes, V_m^E and excess molar enthalpies, H_m^E for (1-propanol + 1,3-diaminopropane) were also found to be negative [8].

In the systems under study, the strong intermolecular hydrogen bonds O–H···N predominance the O–H···O and N–H···N bonds. Thus, the dominant effect in this kind of mixtures is cross association instead of self-association. Values of a cross hydrogen bonding energy between $-32\,\mathrm{kJ\,mol^{-1}}$ and $-45\,\mathrm{kJ\,mol^{-1}}$ have been determined exceeding significantly the corresponding values of the self-association of alcohols and amines [5]. In the present work, we extended the thermodynamic study to the low temperatures, where the solid–liquid equilibria was measured for the mixtures (an alkan-1-ol + 1,3-diaminopropane). The dynamic method of the observation of the disappearance of the last crystal has been used. In this work octan-1-ol, nonan-1-ol, decan-1-ol and undecan-1-ol were chosen as a continuation of our previous work [1–3]. For the interpretation of the results obtained in this work and presented previously [1–3], the enthalpy of fusion, the difference in the solute heat capacity between the liquid and solid phase at the melting temperature were 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, 1,3-diaminopropane). The enthalpies of fusion of the congruently melting compounds formed between alkan-1-ols and amines were also estimated.

2. Experimental

The origin of the chemicals and their mass fraction purities were: hexylamine (Fluka, >98%), octylamine (Fluka, >98%), decylamine (Aldrich Chemical Co., 95%), 1,3-diaminopropane (Aldrich Chemical Co., 99%), octan-1-ol (Aldrich Chemical Co., >99%), nonan-1-ol (Fluka, >98%), decan-1-ol (Aldrich Chemical Co., 99%) and undecan-1-ol (Fluka, >98%). Amines and alcohols were fractionally distilled over different drying reagents to a mass fraction purity better than 99.8 mass% determined by GLC. Decylamine was used immediately after distillation under low pressure, and samples were kept for 2–3 h before the experiment in a desiccator. Liquids were stored over freshly activated molecular sieves of type 4Å (Union Carbide).

The solid–liquid equilibria temperatures were determined using a dynamic method [11]. Appropriate mixtures of solute and solvent were heated very slowly (less than $5 \times 10^{-2}\,\mathrm{K\,min^{-1}}$ near the equilibrium temperature) with continuous stirring inside a Pyrex glass cell which was placed in a glass thermostat filled with acetone and dry ice. The temperature at which the last crystals disappeared (or disappearance of solution cloudiness) was taken as the temperature of the solid–liquid equilibria. The crystal disappearance temperatures, detected visually, were 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. Mixtures were prepared by mass and the errors did not exceed $\delta x_1 = 0.0002$ and δT_1 (K) = 0.05 in the mole fraction and temperature, respectively. The uncertainties of the method were ±0.1 K and ±0.0005 for the equilibrium temperature and concentration, respectively.

The enthalpy of fusion for hexylamine, octylamine, decylamine, 1,3-diaminopropane, nonan-1-ol, decan-1-ol, undecan-1-ol was measured using a differential scanning microcalorimetry (DSC) at the $5\,\mathrm{K\,min^{-1}}$ scan rate with the power sensitivity of $16\,\mathrm{mJ\,s^{-1}}$ and with the recorder sensitivity of 5 mV. The instrument (Perkin–Elmer Pyris 1) was each time calibrated with a 99.9999 mol percent purity indium sample. The calorimetric accuracy was ±1%, and the calorimetric precision was ±0.5%.

The heat capacity per unit volume of melting was measured under atmospheric pressure by means of differential scanning calorimeter TG-DSC 111 (Setaram) based on the Calvet principle. The heat capacity measurements were made during the heating process. The range depends on the melting point of the investigated compound. The measurements were carried out the "by step with reference" method with a scanning rate of $0.5\,\mathrm{K\,min^{-1}}$ in a wide range of temperature. As reference sample Al_2O_3 of known heat capacity was used.

3. Results and discussion

3.1. SLE

Experimental solid–liquid equilibria liquidus temperatures for {an alkan-1-ol (1) + 1,3-diaminopropane (2)} are recorded in Table 1 and are shown in Figs. 1–4. The molecular addition compounds melting congruently were observed in every system. The authors attributed the compound formation to a strong intermolecular interaction between an alcohol and 1,3-diaminopropane. A solid compound with the empirical formulae [$(ROH)_2$·Am] was formed. The most interesting result, obtained in this work is the composition of the congruently melting compound in comparison with binary systems of the same alkan-1-ols and hexylamine [1], octylamine [2] and decylamine [3]. For the amines with one functional group $-NH_2$, a 1:1 congruently melting compound (ROH·Am) was observed [1–3].

The equilibrium temperatures T were fitted using a least-squares method to the Ott equation [12]:

$$T = T^* \left\{ 1 + \sum_{j=1}^{n} a_j (x - x^*)^j \right\} \quad (1)$$