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Solid–liquid equilibrium of dicyandiamide in different solvents

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ABSTRACT

Solubilities of dicyandiamide in five different solvents including water, methanol, ethanol, glycol and acetone were determined at temperature ranging from 273.15 to 338.95 K at atmospheric pressure using a gravimetric method. Fusion enthalpy, ΔH_f, melting temperature, T_m, and the difference in molar heat capacity of the liquid and solid form of dicyandiamide, ΔC_p, were determined by differential scanning calorimetry. On this basis, the ideal solubility of dicyandiamide was calculated, and validity of heat capacity assumptions (specifically, $\Delta C_p = 0$) in predicting the ideal solubility has been evaluated. Further, the measured solubility data was used with the calculated ideal solubility to obtain activity coefficients, which were then fitted to a van't Hoff like regular solution equation.

1. Introduction

As a low-cost, high-efficiency separation and purification process, crystallization is widely used in fine chemical, pharmaceutical, biological as well as environmental industries. Accurate solubility data are required for process design to obtain products with desired qualities.

Solubility of materials is one of the most fundamental physiochemical properties, which depends several factors such as chemical composition, temperature, the pH, the presence of additional species in the solution and the use of different solvents [1]. Especially when dealing with organic species (or inorganics in nonaqueous solvents) a wide variety of solvents and solvent mixtures can be employed. Although there is a vast amount of literature reporting the solubility of many binary and ternary systems in aqueous solution [2–5], many more combinations of solvent and solute remain to be investigated. This is because the measurement of solubility using the current experimental method is time consuming and usually requires large amount of pure solute which is often unavailable or can be very expensive.

The cyano substituted quinidine, dicyandiamide (molecular weight 84.08), is widely used as a slow fertilizer. Moreover, it can be used as a latent curing agent in heat-cured epoxy resins for laminates or prepreg fabrication, coatings and adhesives [6,7]. Fig. 1 shows the chemical structure of dicyandiamide. In industrial manufacturing, dicyandiamide goes through several purification and separation processes to purify it; in such processes, solution crystallization and further recrystallization are the key steps. The determination of its solubility in different solvents is then essential for rapid design and optimization of isolation, purification and formulation processes in industry. A literature survey on available solubility data of dicyandiamide in different solvents reveals no systematic study [8,9]. The present papers relating to dicyandiamide are mainly concerned with its production and application. Given this situation, to ascertain the suitable solvent, a systematic determination of the solubility of dicyandiamide in potential solvents is necessary.

In the present work, experimental solubility data for dicyandiamide in five different solvents, water, methanol, ethanol, glycol and acetone, were determined at temperatures ranging from 273.15 to 338.95 K at atmospheric pressure using a gravimetric method. Additionally, the melting temperature, enthalpy change of fusion and differential molar heat capacity at the melting point of dicyandiamide were measured using differential scanning calorimetry (DSC). Further, these data were used to calculate the ideal solubility of dicyandiamide and estimate its activity coefficient in different solvents.

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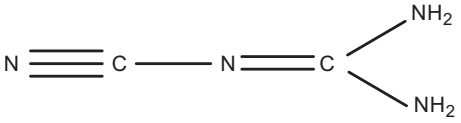

Fig. 1. Molecular structure of dicyandiamide.

2. Theory

The temperature dependence of mole fraction equilibrium solubility of crystalline can be described by the following thermodynamic relationship [10]:

$$\ln\ x_1 = \ln\ x_1^{id} - \ln\ \gamma_1 \tag{1}$$

where x_1, x_1^{id} and γ_1 represent the mole fraction solubility of the solute 1, ideal mole fraction solubility of the solute and activity coefficient of the solute in solution, respectively.

The ideal solubility of a crystalline solute in liquid solvent in Eq. (1) is given by

$$\ln\ x_1^{id} = \frac{-\Delta H_f}{R}\left(\frac{T_m - T}{T_m T}\right) + \frac{\Delta C_p}{R}\left(\frac{T_m - T}{T}\right) - \frac{\Delta C_p}{R}\ln\ \frac{T_m}{T} \tag{2}$$

where ΔH_f refers to the molar enthalpy of fusion at the melting point of the pure solute. T_m is the absolute melting temperature, T is the absolute solution temperature, R is the ideal gas constant, and ΔC_p refers to the difference between the molar heat capacity of the crystalline form and the molar heat capacity of the hypothetical supercooled liquid form at their melting point, which is included in this expression to acknowledge the influence of these heat capacity effects on the enthalpy required to dissolve the crystalline material.

To the last term in Eq. (1), over a narrow temperature range, the activity coefficient, $\ln \gamma_1$, is usually assumed to follow a van't Hoff-like equation [10]:

$$\ln\ \gamma_1 = \frac{\bar{H}_1^E}{RT} - \frac{\bar{S}_1^E}{R} = \frac{\Delta H_m}{RT} - \frac{\Delta S_m}{R} \tag{3}$$

where $\bar{H}_1^E$, $\bar{S}_1^E$, ΔH_m and ΔS_m represent the partial excess enthalpy, partial excess entropy, enthalpy of mixing and entropy of mixing, respectively, are assumed to be temperature-independent.

Referring to Eq. (1), to determine the values of $\ln \gamma_1$, the ideal mole fraction solubility, x_1^{id}, must be estimated from ΔH_f, T_m and ΔC_p (Eq. (2)). Among them, the melting temperature, T_m, and molar enthalpy of fusion, ΔH_f, can be readily determined using DSC. With respect to the differential molar heat capacity, ΔC_p, an assumption has been made [11–13]:

ΔC_p is negligible and can be considered to be zero. Then, Eq. (2) has been simplified to be

$$\ln\ x_1^{id} = \frac{-\Delta H_f}{R}\left(\frac{T_m - T}{T_m T}\right) \tag{4}$$

The previous equation has been employed in the investigation of different systems [13–15]. The results show that the effect of these ΔC_p values on the prediction of the ideal solubility cannot be neglected.

In this work, the values of ΔH_f, T_m and ΔC_p have been measured experimentally using DSC. On this basis, the ideal molar solubility of dicyandiamide has been calculated and validity of the assumptions in predicting the ideal solubility has been evaluated. Moreover, the solubility of dicyandiamide in different solvents has been measured experimentally to obtain the values of the activity coefficient, $\ln \gamma_1$, using Eq. (1).

3. Experimental

3.1. Materials

Dicyandiamide (supplied by Ningxia Beilite Chemical Industry Co., Ltd., China) was recrystallized one time from double-distilled water by cooling crystallization. Its purity was analyzed by a HPLC equipped with a UV detector (HP 1100 America) and the mass fraction purity is >0.95. The standard uncertainty for mass fraction is ±0.005. The methanol, ethanol, glycol and acetone used for experiments were of analytical reagent grade, all supplied by Shanghai Chemical Reagent Co., China and used without further purification for experiments. Their mass fraction purities are greater than 99.0% (Table 1).

3.2. Procedure

3.2.1. Solubility measurement

The solubility of dicyandiamide in different solvents was measured using gravimetric method. The experiments were carried out in a 100 ml-vessel with a double jacket through which oil from a thermostated oil bath (FT 32, Julabo Labortechnik, Gmbh, Germany) was circulated and the process temperature was measured by a probe with an accuracy of ±0.05 K. Mixing was provided by a magnetic stirrer rotating at 300 rpm. Then, excess amount of dicyandiamide was suspended in corresponding solvent at a certain temperature under stirring for at least 12 h, the stirring was stopped, and the solution was kept still for 2 h to allow complete sedimentation of the fine crystals. Three samples of 10 ml each were carefully withdrawn from the clear solution using a 10 ml pipettes equipped with a filter on top so as to make sure that fine crystals were completely removed and preserved in the weighted watch glass. Further, the watch glass was weighted to record the mass of solution and then the solvent was dried for more than 12 h under vacuum circumstance at 323.15 K. After drying, the watch glass was reweighed to determine the mass of residue solid (m_1) and the evaporated solvent (m_2). The mean values of three samples were used to calculate the mole fraction solubility x_1 of dicyandiamide in different solvents. The relative uncertainty of the experimental solubility values is within 0.02% [16]. The mole fraction solubility of the solute (x_1) in different pure solvents can be calculated by the following equation:

$$x_1 = \frac{m_1/M_1}{m_1/M_1 + m_2/M_2} \tag{5}$$

Table 1
Sample table.[a]

Chemical name	Source	Mass purity	Purification method	Analysis method
Dicyandiamide	Ningxia beilite chemical	0.95	Recrystallized	HPLC
Methanol	Shanghai chemical	0.99	None	HPLC
Ethanol	Shanghai chemical	0.99	None	HPLC
Glycol	Shanghai chemical	0.99	None	HPLC
Acetone	Shanghai chemical	0.99	None	HPLC

[a] Standard uncertainty for mass fraction u is $u(c) = \pm 0.005$.