Correlation of solubility and calculation of thermodynamic properties of guanidine nitrate in different solvents

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ABSTRACT

To realize the rapid solvent screening and further crystallization process optimization, experimental determination of accurate solubility data of target solute in potential solvents is necessary. Using a gravimetric method, solubilities of guanidine nitrate in water, methanol, ethanol, n-propanol and acetone at temperature ranging from 278.05 K to 332.85 K at pressure $p = 0.1$ MPa were experimentally measured. Melting temperature, T_m, and fusion enthalpy, ΔH_f, of guanidine nitrate were determined using differential scanning calorimetry. Subsequently, Apelblat equation, van't Hoff equation, λh equation, and Wilson model were used to correlate the measured solubility data, respectively. Dissolution of guanidine nitrate in all examined solvents was found to be endothermic and entropically favorable. Moreover, the measured solubility data were combined with calculated ideal solubility data to calculate activity coefficients at infinite dilution based on the assumption of $\Delta C_p = 0$, which were then fitted to a van't Hoff like regular solution equation.

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1. Introduction

Guanidine nitrate (GN, $CH_6N_4O_3$, CAS Registry No. 506-93-4) is well known as a high energy fuel used in some gas generator and solid rocket propellant applications. Moreover, it is also an important intermediate for synthesizing sulfa and pyrimidine nitrate drugs such as sulfadiazine and 2-amino-4-chloro-6-methoxypyrimidine. Especially, the latter drugs have broad spectrum, high selectivity and low toxicity, and are often used for the treatment of malignant lymphoma, lung cancer, etc. [1]. The chemical structure of GN is shown in Fig. 1.

In industrial, GN is mainly produced by condensation reaction of urea and ammonium nitrate or fusion reaction of dicyandiamide and ammonium nitrate [1]. In any case, the raw product is refined by solution crystallization. The experimental determination of its accurate solubility in potential solvents is then crucial for rapid solvent screening and further crystallization process optimization.

Moreover, as one of the most fundamental physicochemical properties, solubility of materials in given system also provided valuable information for the preference crystallization of target polymorphic forms and estimation of crystallization efficiency [2,3]. However, the few available solubility data of GN in different pure solvents have been reported at the beginning of last century and show no systematic [4,5]. The present papers concerning about GN mainly focused on the investigation on synthetic process and thermal stability [6,7].

In this work, gravimetric method was used to determine the solubility of GN in water, methanol, ethanol, n-propanol and acetone at temperature ranging from 278.05 K to 332.85 K at pressure $p = 0.1$ MPa. Melting temperature and fusion enthalpy were measured using differential scanning calorimetry (DSC). With these thermodynamic properties, Apelblat equation, van't Hoff equation, λh equation, and Wilson model were used to correlate the measured solubility data, respectively. To obtain sufficient information for the selection of crystallization apparatus and optimization of crystallization process, detailed and systematic thermodynamic properties of GN such as dissolution enthalpy, ΔH_{sol}, and dissolution entropy, ΔS_{sol}, were calculated. Moreover,

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Nomenclature

A, B, C	Empirical constant in Eq. (4)
ΔC_p	Difference in heat capacity of the solute between solid and liquid
h, λ	Parameters in Eq. (9)
m_1	Mass of the solute, g
m_2	Mass of the solvent, g
M_1	Corresponding molar mass of the solute, g/mol
M_2	Corresponding molar mass of the solvent, g/mol
MAPD	Mean absolute percentage deviation
N	Number of experimental point
R^2	Coefficient of correlation
R	Gas constant, J/mol K
T	Absolute temperature, K
T_m	Melting temperature, K
ΔH_f	Enthalpy of fusion at melting point, kJ/mol
ΔH_{mix}	Enthalpy of mixing, kJ/mol
ΔH_d	Enthalpy of dissolution, kJ/mol
ΔH_d^{0-app}	Apparent standard dissolution enthalpy change, kJ/mol
$\overline{H}_1^{E,\infty}$	Limiting partial excess enthalpy, kJ/mol
ΔS_f	Entropy of fusion at melting point, J/mol K
ΔS_{mix}	Entropy of mixing, J/mol K
ΔS_d	Entropy of dissolution, J/mol K
ΔS_d^{0-app}	Apparent standard dissolution entropic change, J/mol K
$\overline{S}_1^{E,\infty}$	Limiting partial excess entropy, J/mol K
ΔG_d^{0-app}	Apparent standard dissolution Gibbs energy change, kJ/mol
x_1^{id}	Ideal solubility of the solute, mol/mol
x_1	Experimental solubility of the solute, mol/mol
γ_1	Activity coefficient of the solute in solution
$\lambda_{12} - \lambda_{11}$	Cross interaction energy parameter in Eq. (12)
$\lambda_{21} - \lambda_{22}$	Cross interaction energy parameter in Eq. (13)
v_1	Molar volume of solute
v_2	Molar volume of solvent

the activity coefficients at infinite dilution were estimated based on the assumption of $\Delta C_p = 0$, which were then fitted to a van't Hoff like regular solution equation to calculate the mixing enthalpy, ΔH_m, and mixing entropy, ΔS_m.

2. Theory

The following thermodynamic relationship was usually used to describe the temperature dependence of mole fraction equilibrium solubility of crystalline in liquid solvent [8]:

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

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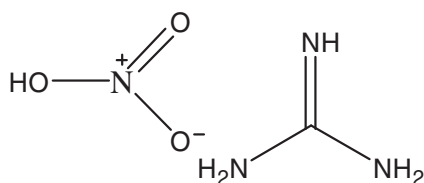

Fig. 1. Molecular structure of guanidine nitrate.

The ideal solubility shown in Eq. (1) is defined by

$$\ln x_1^{id} = \left[\frac{\Delta H_f}{RT_m} - \frac{\Delta C_p}{R}(1 + \ln T_m) \right]$$
$$+ \left[\left(\frac{\Delta C_p T_m}{R} - \frac{\Delta H_f}{R} \right) \right] \frac{1}{T} + \frac{\Delta C_p}{R} \ln T \tag{2}$$

where T, T_m and R refer to the absolute solution temperature, melting temperature and gas constant, respectively. ΔH_f is the molar fusion enthalpy of the pure solute at the melting point. ΔC_p refers to the difference between the molar heat capacity of the crystalline form and the hypothetical supercooled liquid form at their melting point.

As to the activity coefficient in Eq. (1), it is usually assumed to follow a van't Hoff-like equation within a narrow temperature range [8]:

$$\ln \gamma_1 = \frac{\overline{H}_1^{E,\infty}}{RT} - \frac{\overline{S}_1^{E,\infty}}{R} = \frac{\Delta H_{mix}}{RT} - \frac{\Delta S_{mix}}{R} \tag{3}$$

where $\overline{H}_1^{E,\infty}$ and $\overline{S}_1^{E,\infty}$ represent the limiting partial excess enthalpy and entropy, ΔH_{mix} and ΔS_{mix} are the mixing enthalpy and entropy. All these parameters are assumed to be temperature-independent.

2.1. Apelblat equation

Substituting Eqs. (2) and (3) into Eq. (1) gives

$$\ln x_1 = A + B/T + C \ln T \tag{4}$$

where A, B and C are parameters. Referring to the equations mentioned previously, the above parameters can be written as

$$A = \frac{\Delta H_f}{RT_m} - \frac{\Delta C_p}{R}(1 + \ln T_m) + \frac{\Delta S_{mix}}{R} \tag{5}$$

$$B = \frac{\Delta C_p T_m}{R} - \frac{\Delta H_f - \Delta H_{mix}}{R} \tag{6}$$

$$C = \frac{\Delta C_p}{R} \tag{7}$$

Eq. (4) is known as Apelblat equation, which was originally proposed by Apelblat and Manzurola and is frequently used to correlate solubility [9]. The parameters can be regressed from the temperature dependence of solubility data. However, the activity coefficient cannot be easily obtained due to the fact that the differential heat capacity is difficult to be experimentally measured or regressed from the values of $C = \Delta C_p/R$. The detailed information concerning about Apelblat equation can be consulted from numbers of published papers [10,11].

2.2. Van't Hoff equation

In the case of non-ideal solution, van't Hoff equation was usually applied to correlate the experimentally measured solubility data [12,13]. The van't Hoff equation can be expressed in the form:

$$\ln x_1 = -\frac{\Delta H_d}{RT} + \frac{\Delta S_d}{R} \tag{8}$$

As shown in Eq. (8), the dissolution enthalpy, ΔH_d, and dissolution entropy, ΔS_d, can be estimated by plotting the $\ln x_1$ versus reciprocal of temperature ($1/T$).