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Solubility determination and thermodynamic modeling of 5-nitro-8-hydroxyquinoline in ten organic solvents from T = (278.15 to 313.15) K and mixing properties of solutions



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ABSTRACT

The solubility of 5-nitro-8-hydroxyquinoline in ten organic solvents including methanol, ethanol, acetone, acetonitrile, acetic acid, n-propanol, toluene, isopropanol, ethyl acetate and 1-butanol was determined experimentally by using the isothermal saturation method over a temperature range from (278.15 to 313.15) K under 101.3 kPa. For the temperature range studied, the solubility of 5-nitro-8hydroxyquinoline in the solvents increased with a rise of temperature. In general, they obeyed the following order from high to low in different solvents: acetone > ethyl acetate > toluene > acetic acid > acetonitrile > 1-butanol > (n-propanol, ethanol) > isopropanol > methanol. The acquired solubility data of 5-nitro-8-hydroxyquinoline in the solvents studied were correlated by using the modified Apelblat equation, λh equation, Wilson model and NRTL model. The maximum values of root-mean-square deviation (*RMSD*) and relative average deviation (*RAD*) were 1.10×10^{-4} and 1.39%, respectively. Generally, the RAD values acquired with the modified Apelblat equation were smaller than those with the other three models for a certain solvent. Generally, the four thermodynamic models were all acceptable for the systems of 5-nitro-8-hydroxyquinoline in these solvents. Furthermore, the mixing Gibbs energy, mixing enthalpy, mixing entropy, activity coefficient at infinitesimal concentration (γ_1^{∞}) and reduced excess enthalpy $(H_1^{E_{\infty}})$ were obtained. The solution process of 5-nitro-8-hydroxyquinoline was spontaneous and endothermic in the studied solvents. The obtained solubility and thermodynamic studies would be very helpful for optimizing the purification process of 5-nitro-8-hydroxyquinoline.

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1. Introduction

5-Nitro-8-hydroxyguinoline (CAS No. 4008-48-4) is an important pharmaceutical intermediate. It shows antibacterial activity to Gram-negative and Gram-positive bacteria and is also effective relating to certain fungi (e.g. the *Candida* strain) [1]. Comparison with other 8-hydroxyquinoline derivates, 5-nitro-8hydroxyquinoline is quickly absorbed from the gastro-intestinal tract and excreted unchanged by the kidneys [2]. It is also effective to microflora resistant to other antibacterial agents [3-5]. Several methods have been proposed to produce 5-nitro-8hydroxyquinoline in the literature [1,6–11]. The commercial preparation method of 5-nitro-8-hydroxyquinoline is by nitration of 8-hydroxyquinoline [6-11]. The direct nitration of 8hydroxyquinoline in an acid medium produces a large amount of

* Corresponding author. *E-mail address:* hkzhao@yzu.edu.cn (H. Zhao). side products 8-hydroxy-5,7-dinitroquinoline and 8-hydroxy-7nitroquinoline. With the development of pharmaceutical industry, the requirement for product purity is becoming higher. The crude 5-nitro-8-hydroxyquinoline restricts its applications in many aspects. The by-products must be removed from the crude product before use.

It is well-known that solvent crystallization is commonly used as an important separation and purification step in the production process. The solubility of solid in different solvents is an important physicochemical property which plays an important role for understanding the (solid + liquid) equilibrium (SLE) or phase equilibrium in the development of a crystallization process. More particularly, the knowledge of accurate solubility is needed for the design of crystallization process. Solvent crystallization is an effective method for 5-nitro-8-hydroxyquinoline purification. In previous publications, the purification method of 5-nitro-8hydroxyquinoline is recommended via a twofold recrystallization from ethanol [12], or recrystallization from acetone [1]. Although the solubility data are of great significance in the purification procedure of 5-nitro-8-hydroxyquinoline via the method of solvent crystallization where the accurate solubility values of 5-nitro-8hydroxyquinoline are essential, to the best of the authors' present knowledge, no solubility data are reported in the previous works. In order to acquire high purity 5-nitro-8-hydroxyquinoline, the knowledge of 5-nitro-8-hydroxyquinoline solubility in different solvents at various temperatures and the thermodynamic properties of solution is a necessary procedure.

The purposes of the work are to (1) determine the solubility of 5-nitro-8-hydroxyquinoline in ethanol, isopropanol, *n*-propanol, 1-butanol, methanol, ethyl acetate, toluene, acetone, acetonitrile and acetic acid at temperatures ranging from (278.15 to 313.15) K by using the isothermal saturation method; (2) correlate the solubility data with different thermodynamic models; and (3) calculate the mixing properties for the solution process of 5-nitro-8-hydroxyquinoline in different solvents.

2. Solid-liquid phase equilibrium models

In order to find suitable models to describe the solubility behavior of 5-nitro-8-hydroxyquinoline in the studied solvents, in this work, four models are used to correlate the solubility data, which correspond to the modified Apelblat equation [13,14], λh equation [15], Wilson model [16] and NRTL model [17].

2.1. Modified Apelblat equation

The dependence of mole fraction solubility on the absolute temperature T can be described by using the modified Apelblat equation [13,14], which is a semi-empirical equation, and expressed as Eq. (1).

$$\ln x = A + \frac{B}{T} + C \ln T \tag{1}$$

with

$$A = \frac{\Delta_{\text{fus}}H}{RT_{\text{t}}} + \frac{\Delta C_{\text{p}}}{R} (1 + \ln T_{\text{t}}) - a \tag{2}$$

$$B = -\left[b + \left(\frac{\Delta_{\text{fus}}H}{RT_{\text{t}}} + \frac{\Delta C_{\text{p}}}{R}\right)T_{\text{t}}\right]$$
(3)

$$C = -\frac{\Delta C_{\rm p}}{R} \tag{4}$$

where *x* is the mole fraction solubility of 5-nitro-8-hydroxyquinoline in ten organic solvents, $\Delta_{fus}H$ is the melting enthalpy of 5-nitro-8-hydroxyquinoline, ΔC_P is the difference of heat capacity of 5-nitro-8-hydroxyquinoline between in liquid and solid state, *T* is the absolute temperature in Kelvin, *T*_t is the triple point temperature of 5-nitro-8-hydroxyquinoline, *a* and *b* are constant parameters, and *R* is the universal gas constant. *A*, *B* and *C* are the adjustable equation parameters, and may be acquired by correlating the experimental solubility.

2.2. λh equation

The λ hequation is another model to describe the solid–liquid equilibrium behavior of 5-nitro-8-hydroxyquinoline in solvents. It is first proposed by Buchowski and expressed as Eq. (5) [15]. The Buchowski–Ksiazaczak λ h equation has two parameters λ and h, and can well be used to correlate the experimental solubility values for many solid–liquid equilibrium systems.

$$\ln\left[1 + \frac{\lambda(1-x)}{x}\right] = \lambda h\left(\frac{1}{T} - \frac{1}{T_{\rm m}}\right) \tag{5}$$

The λ and h are adjustable equation parameters, T_m denotes the melting temperature of 5-nitro-8-hydroxyquinoline in Kelvin. The λ value relates to the non-ideality of solution, which is considered as the association number of solute molecules in associating system, and h is relating to the excess enthalpy of solution.

2.3. Wilson model

If liquid–solid phase equilibrium is established at a given temperature and pressure, on the basis of the traditional theory of (solid–liquid) phase equilibrium, the solubility of a solid in pure solvent can be described in a very universal manner as Eq. (6) [18].

$$\ln(x \cdot \gamma) = \frac{\Delta H_{tp}}{R} \left(\frac{1}{T_{tp}} - \frac{1}{T} \right) - \frac{\Delta C_p}{R} \left(\ln \frac{T_{tp}}{T} - \frac{T_{tp}}{T} + 1 \right) - \frac{\Delta V}{RT} (p - p_{tp})$$
(6)

where $\Delta C_{\rm p}$ and ΔV stand for the difference of heat capacity and volume between solid phase and liquid phase at melting temperature, respectively; γ denotes the activity coefficient of solute. Under a fixed pressure, the values of ΔV and $\Delta C_{\rm p}$ are too small and are negligible [19]. The $\Delta H_{\rm tp}$ denotes melting enthalpy at triple point temperature $T_{\rm tp}$. The melting temperature $T_{\rm m}$ is almost equal to the triple point temperature $T_{\rm tp}$. So, substituting $T_{\rm tp}$ and $\Delta H_{\rm tp}$ with $T_{\rm m}$ and normal melting enthalpy $\Delta_{\rm fus} H$, respectively, the dependence of solute solubility in solvents upon temperature can be derived and described as Eq. (7) [18].

$$\ln(x \cdot \gamma) = \frac{\Delta_{\text{fus}} H}{R} \left(\frac{1}{T_{\text{m}}} - \frac{1}{T} \right)$$
(7)

For a binary system, the logarithm of activity coefficient described by the Wilson model is expressed as Eqs. (8)-(11) [16].

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1} \right]$$
(8)

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) + x_1 \left[\frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1} - \frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} \right]$$
(9)

$$\Lambda_{12} = \frac{V_2}{V_1} \exp\left(-\frac{\lambda_{12} - \lambda_{11}}{RT}\right) = \frac{V_2}{V_1} \exp\left(-\frac{\Delta\lambda_{12}}{RT}\right) \tag{10}$$

$$\Lambda_{21} = \frac{V_1}{V_2} \exp\left(-\frac{\lambda_{21} - \lambda_{11}}{RT}\right) = \frac{V_2}{V_1} \exp\left(-\frac{\Delta\lambda_{21}}{RT}\right) \tag{11}$$

Here V_i denotes the molar volume of component I; $\Delta \lambda_{ij}$ are the interaction parameters (J·mol⁻¹) relating to interaction energy between the components *i* and *j*. The values of $\Delta \lambda_{ij}$ can be obtained by regressing from the experimental solubility.

2.4. NRTL model

The NRTL model [17] was put forward according to the local composition concept. It is widely used in liquid–solid phase equilibrium. For a component *i*, the activity coefficient described by the NRTL model can be expressed with Eqs. (12)–(15).

$$\ln \gamma_{i} = \frac{\sum_{j=1}^{N} \tau_{ji} G_{ji} x_{j}}{\sum_{i=1}^{N} G_{ij} x_{i}} + \sum_{j=1}^{N} \frac{x_{j} G_{ij}}{\sum_{i=1}^{N} G_{ij} x_{i}} \left[\tau_{ij} - \frac{\sum_{i=1}^{N} x_{i} \tau_{ij} G_{ij}}{\sum_{i=1}^{N} G_{ij} x_{i}} \right]$$
(12)

$$G_{ji} = \exp(-\alpha_{ji}\tau_{ji}) \tag{13}$$

$$\alpha_{ij} = \alpha_{ji} \tag{14}$$

$$\tau_{ij} = \frac{g_{ij} - g_{jj}}{RT} = \frac{\Delta g_{ij}}{RT}$$
(15)

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