



Solubility of L-asparagine monohydrate in water and water-isopropanol mixed solvents: Measurements and thermodynamic modelling



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ARTICLE INFO

Article history:

Received 24 September 2015

Received in revised form

10 December 2015

Accepted 21 December 2015

Available online 24 December 2015

Keywords:

L-asparagine monohydrate

Iso-propanol

Water

Solubility

UNIQUAC model

NRTL model

Solid-liquid equilibrium

ABSTRACT

The solubility of L-asparagine monohydrate (LAM) in pure water and various water-isopropanol mixtures is determined in the temperature range from 298.15 K to 333.15 K using gravimetric method. The solubility of LAM increases with increasing temperature at a given solvent composition within the temperature range studied, and decreases with increasing isopropyl alcohol (IPA) ratio over the same temperature range for water-IPA mixture. The NRTL and UNIQUAC framework with adjustable binary parameters were used to correlate the experimental solubility data and the computed solubilities are in good agreement with experimental observations. The heat of fusion for LAM was considered as an additional parameter for both the models and was estimated along with binary parameters using experimental solubility data and a nonlinear regression method. The dissolution enthalpy and dissolution entropy of the solution of LAM in pure water and water-IPA mixtures were also obtained using van't Hoff equation.

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1. Introduction

The experimental determination of solubility in pure or mixed solvents is usually a time consuming procedure and therefore, calculation of solubility using validated thermodynamic models is an attractive option and receiving much attention currently. Several thermodynamic models that have been successfully used to correlate liquid-liquid phase equilibrium can also be used to correlate solid-liquid equilibrium, such as Wilson equation [1,2], Universal quasi chemical (UNIQUAC) [3–5], Non random two liquid (NRTL) [5–7] and UNIQUAC Functional-group Activity Coefficients (UNIFAC) [8–10] models. The UNIFAC model uses the chemical structure of the molecule and group contribution method to predict the solid-liquid equilibrium. But Wilson, NRTL and UNIQUAC are semiempirical models and require experimental data to estimate few adjustable parameters. The calculation of solid-liquid equilibrium by thermodynamic models is in its early stage compared to calculation of vapour-liquid or liquid-liquid equilibrium situation.

The solubility study of amino acids has received considerable attention, particularly from pharmaceutical and food industries. Several studies have correlated the solubility of amino acids with well known thermodynamic models, such as Wilson equation [11,12], NRTL equation [13], UNIQUAC model [14,15], UNIFAC model [16,17]. It is reported that UNIQUAC model gives the best fit in describing the temperature dependence of solubility of L-phenylalanine in pure water, water-ethanol mixture, and water-acetone mixture [15]. The calculation of solubility depends heavily on the computation of activity coefficient which in turn is a function of temperature and the weight fraction of acetone or ethanol in the solution. Besides, UNIQUAC-Debye-Huckel approach has also been successfully used to correlate the solubility data of amino acids in aqueous solution [14]. Among all these models, the UNIQUAC model is often used to correlate the solubility data as it has fewer adjustable parameters and also has a good theoretical basis. L-asparagine is an important non-essential amino acid that plays a significant role in human metabolism. Only the L-stereoisomer participates in the biosynthesis of mammalian proteins. There is also a growing interest in L-asparagine monohydrate (LAM) crystals as it shows good non-linear optical property due to the presence of pi bonds. LAM can be crystallized from its aqueous solution by

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cooling or by addition of isopropyl alcohol (IPA) as antisolvent. LAM can also be crystallized from its aqueous solution by combined cooling and antisolvent crystallization where IPA can be considered as a good antisolvent. Combining these two modes of operation is beneficial as it offers greater degree of control over the crystallization process. However, such a mode of operation will require the knowledge of solubility of LAM as a function of temperature and solvent composition. In literature, the solubility of LAM is reported only for pure water over a range of temperatures [18,19]. Also, the solubility of LAM in (water-IPA) mixture is available only at a particular temperature of 298.15 K [20,21] and no solubility data is reported in other temperatures. In this work, we report experimentally determined solubility of LAM in pure water and water-IPA mixture in the temperature range from 298.15 K to 333.15 K using gravimetric method. We also used two activity coefficient models UNIQUAC and NRTL with adjustable parameters to correlate the experimental solubility data and the model correlate very well with experimental observations. Furthermore, the dissolution enthalpy and dissolution entropy of the solution of LAM in pure water and (water-IPA) mixtures were calculated using van't Hoff equation. The concerned binary interaction parameters of the UNIQUAC and NRTL models are not available in open literature and are estimated here from the experimental solubility data using an optimization method. To the best of our knowledge, measurement and thermodynamic modelling of solubility of LAM in various water-IPA mixtures over a range of temperatures have not been reported in open literature.

2. Solid–liquid equilibrium

When a solid phase is in equilibrium with a liquid phase, the relationship between the fugacities of the solute in the two phases for nonideal solutions is given by Refs. [14,22].

$$\ln\left(\frac{f_i^L}{f_i^S}\right) = \frac{\Delta H_{fus}}{RT_m} \left(\frac{T_m}{T} - 1\right) - \frac{\Delta C_p}{R} \left(\frac{T_m}{T} - 1\right) + \frac{\Delta C_p}{R} \ln \frac{T_m}{T} \quad (1)$$

where the superscript i refers to the solute, f_i^L is the fugacity of the solute in the liquid phase, f_i^S is the fugacity of the solute in the solid phase, ΔH_{fus} is the enthalpy of fusion of the solute, and R is the ideal gas constant. T and T_m are the experiment temperature and triple point temperature of the solute which can be considered as melting point of solute, respectively. ΔC_p is the difference in heat capacities of the solid and the liquid at temperature T . At equilibrium, the fugacities in solid and liquid phase are related by

$$x_i \gamma_i = \frac{f_i^S}{f_i^L} \quad (2)$$

where γ_i is the activity coefficient of the solute i in the real solution and x_i is the solute mole fraction at equilibrium. Combining Eqs. (1) and (2) yields

$$\ln\left(\frac{1}{x_i \gamma_i}\right) = \frac{\Delta H_{fus}}{RT_m} \left(\frac{T_m}{T} - 1\right) - \frac{\Delta C_p}{R} \left(\frac{T_m}{T} - 1\right) + \frac{\Delta C_p}{R} \ln \frac{T_m}{T} \quad (3)$$

For ideal solutions, the activity coefficient of solute is unity, and the general expression for ideal solubility can be written as

$$\ln\left(\frac{1}{x_i^{ideal}}\right) = \frac{\Delta H_{fus}}{RT_m} \left(\frac{T_m}{T} - 1\right) - \frac{\Delta C_p}{R} \left(\frac{T_m}{T} - 1\right) + \frac{\Delta C_p}{R} \ln \frac{T_m}{T} \quad (4)$$

Generally speaking, the first term of right hand side of Eq. (4) has the largest effect, and the last two terms with opposite signs are of little importance as they tend to cancel each other [15,23].

The Eq. (4) can thus be rewritten as

$$\ln(x_i^{ideal}) = \frac{\Delta H_{fus}}{R} \left(\frac{1}{T_m} - \frac{1}{T}\right) \quad (5)$$

The saturation mole fraction of solute in an ideal solution (x_i^{ideal}) and the experimental mole fraction (x_i) are related by

$$x_i = \frac{x_i^{ideal}}{\gamma_i} \quad (6)$$

For nonideal solutions, γ_i must be estimated from experimental data or a liquid solution model.

3. The UNIQUAC model theory

The UNIQUAC model to predict the activity coefficient of a solute in a solvent is given by Ref. [24].

$$\ln \gamma_i = \ln \frac{\phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_{j=1}^k x_j l_j - q_i' \ln \sum_{j=1}^m \theta_j' \tau_{ji} + q_i' - q_i' \sum_{j=1}^m \frac{\theta_j' \tau_{ji}}{\sum_{k=1}^m \theta_k' \tau_{kj}} \quad (7)$$

where θ_i and θ_i' are the area fractions and ϕ_i is the segment fraction of component i . z is the coordination number which is frequently considered as 10 for all the components.

$$\phi_i = \frac{r_i x_i}{\sum_{j=1}^m r_j x_j}, \theta_i = \frac{q_i x_i}{\sum_{j=1}^m q_j x_j}, \theta_i' = \frac{q_i' x_i}{\sum_{j=1}^m q_j' x_j} \quad (8)$$

$$l_i = \frac{z}{2} (r_i - q_i) - (r_i - 1) \quad (9)$$

$$\tau_{ij} = \exp\left(\frac{-a_{ij}}{T}\right), \tau_{ji} = \exp\left(\frac{-a_{ji}}{T}\right) \quad (10)$$

The UNIQUAC equation consists of two interaction parameters a_{ij} and a_{ji} which can be estimated from experimental solid–liquid equilibrium data. r_i , q_i and q_i' are the pure component structural parameters and can be calculated from the van der Waals molar volume and area [22].

$$r_i = \frac{Q_{vdwi}}{15.17} \quad (11)$$

$$q_i = \frac{R_{vdwi}}{2.5 \times 10^9} \quad (12)$$

Here R_{vdwi} and Q_{vdwi} are the van der Waals molar area and volume of the molecule i , respectively. If the parameters r_i and q_i are unknown, a functional group approach as proposed by Fredenslund et al. [25] can be used to calculate the above mentioned parameters as follows

$$r_i = \sum_{i=1}^N n_i R_i \quad (13)$$

$$q_i = \sum_{i=1}^N n_i Q_i \quad (14)$$

where N is the number of functional groups of molecule i that occurs n_i times. R_i and Q_i are the dimensionless van der Waals area

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