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Solubility determination and modelling for phthalimide in mixed solvents of (acetone, ethyl acetate or acetonitrile + methanol) from (278.15 to 313.15) K

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ABSTRACT

The solubilities of phthalimide in mixed solvents of (acetone + methanol), (ethyl acetate + methanol) and (acetonitrile + methanol) were determined experimentally by using the isothermal dissolution equilibrium method within the temperature range from (283.15 to 318.15) K under atmospheric pressure (101.1 kPa). For the three systems of (acetone + methanol), (ethyl acetate + methanol) and (acetonitrile + methanol), at a fixed composition of acetonitrile, acetone or ethyl acetate, the solubility of phthalimide increased with an increase in temperature; however, at the same temperature, they increased at first and then decreased with the increase in mass fraction of acetonitrile, acetone or ethyl acetate. At the same temperature and mass fraction of acetonitrile, acetone or ethyl acetate, the mole fraction solubility of phthalimide in (acetone + methanol) was greater than those in the other mixed solvents. The solubility values obtained were correlated with Jouyban-Acree model, van't Hoff-Jouyban-Acree model, modified Apelblat-Jouyban-Acree model and CNIBS/R-K model. The maximum values of relative average deviations (*RAD*) and root-mean-square deviations (*RMSD*) between the experimental and calculated solubility were 5.64×10^{-2} and 11.56×10^{-4}, respectively. The CNIBS/R-K model proved to provide the best representation of the experimental results. In addition, the standard dissolution enthalpies of the dissolution process were calculated on the basis of the measured solubility. Dissolution of phthalimide in these mixed solvents is an endothermic process.

1. Introduction

Imides are monomers to prepare polyimides that contain repeating imide groups. Aromatic polyimides have better resistance to high temperatures and corrosion than linear polyimides. Phthalimide is commonly used as plastic modifiers to improve heat-resistant, antioxidant and antifoulant properties. It is an important intermediate for the synthesis of cross-linking agents [1], pesticides [2], dyes [3] and corrosion inhibitors [4]. Phthalimide is also a useful compound in the synthesis of primary amines and amino acids for the application in the field of medicine and biological research [5]. At present, the industrial preparation method of phthalimide is employing phthalic anhydride as raw material. It can be prepared by treating phthalic anhydride with ammonium carbonate or urea [9,10] or by treating the anhydride with ammonia [6–8] and or by ammoxidation of ortho-xylene [11]. The yield of phthalimide is relatively high via this method; however the crude product usually contains a little amount of unreacted phthalic anhydride. Great difficulty is encountered in separating the phthalimide with high purity from the reaction mixture because the solubility of phthalimide in water is very poor. In order to extend the application of phthalimide, the requirements for product purity are becoming greater and greater. The crude phthalimide restricts its applications in several aspects. It is needed to isolate and purify the crude product. In previous publications, some purification methods have been proposed to separate the phthalimide with high purity [12,13]. Nevertheless, the cost of these procedures is relatively high.

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 thermodynamic parameters, especially accurate solubility is needed for the design of crystallization process and determination of suitable solvents via solvent

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crystallization. Knowledge of the solubility enables discovery of the appropriate solvent system for purifying phthalimide via the crystallization method. In order to design an optimized production process, it is necessary to know the solubility of phthalimide in binary solvent mixtures. The solubilities of phthalimide in ten pure solvents have been determined by Xu and co-workers [14]. However, no work has been published that determine the solubility of phthalimide in mixed solvents. Solubility alteration of solid is essential in many industrial applications, and the solvent mixing is one of the most frequent and feasible methods employed in the industry. By using different ratios of the solvents, a wide range of solubility for a given compound can be achieved. So there is a strong need to determine the phthalimide solubility in mixed solvents and build better models for describing their behaviour, especially in the cases of non-ideal systems. According to the previous studies [14], the solubility of phthalimide is greater in acetone and ethyl acetate than in methanol. The mixed solvents can change the solubility of phthalimide. The knowledge of phthalimide solubility in different binary solvents at various temperatures and the thermodynamic properties of solution is a necessary procedure.

This paper is the continuation of the previous work [14]. The purposes of this work are to (1) determine the solubility of phthalimide in (acetone + methanol), (ethyl acetate + methanol) and (acetonitrile + methanol) at temperatures ranging from (283.15 to 318.15) K by using the isothermal dissolution equilibrium method; (2) correlate the solubility with different models; (3) calculate the standard dissolution enthalpy for the solution process of phthalimide in different binary solvents. For the reason that the temperature of solvent-assisted crystallization of phthalimide lies almost within the temperature range from 280 K to 320 K, the temperatures selected are within the range from T = 283.15 K to T = 318.15 K.

2. Solubility models

In addition to the experimental efforts to determine solubility of solids in mixed solvents, several solubility models have been proposed to correlate the results. In this work, four models are used to correlate the solubility of phthalimide in binary solvent mixtures of (acetone + methanol), (ethyl acetate + methanol) and (acetonitrile + methanol) at different temperatures, which correspond to Jouyban-Acree model [15,16], a combination of Jouyban-Acree model with van't Hoff equation [17,18], a combination of Jouyban-Acree model with modified Apelblat equation [17,18] and CNIBS/R-K model [19–21].

2.1. Jouyban-Acree model

The Jouyban-Acree model is an accurate mathematical description for the dependence of solubility on both temperature and solvent composition for binary and ternary mixed solutions [15,16], and is described as Eq. (1).

$$\ln x_{w,T} = w_1 \ln x_{1,T} + w_2 \ln x_{2,T} + \frac{w_1 w_2}{T} \sum_{i=0}^{2} J_i (w_1 - w_2)^i \quad (1)$$

In Eq. (1), $x_{w,T}$ is the solubility of solute in mole fraction in the binary solvents at temperature T in Kelvin; w_1 and w_2 represent the mass fraction of solvents 1 (acetone, ethyl acetate or acetonitrile) and 2 (methanol) in the absence of the solute (phthalimide), respectively; $x_{1,T}$ and $x_{2,T}$ are the solute solubility in mole fraction in pure solvent, and J_i are the Jouyban-Acree model parameters. The model needs the solute solubility in pure solvent at the lowest and highest temperatures to calculate the model parameters.

2.2. Van't Hoff-Jouyban-Acree model

A linear van't Hoff equation is used for providing precise predictions of a solute dissolved in a solvent at a limited temperature range. It is expressed as Eq. (2), which describes the dependence of the natural logarithm of the mole fraction solubility on the reciprocal of absolute temperature [22].

$$\ln x = A + B/T(\mathrm{K}) \quad (2)$$

Here A and B are equation constants. Substituting Eq. (2) into Eq. (1), the Van't Hoff-Jouyban-Acree model can be obtained and expressed as Eq. (3) [17,18].

$$\ln x_{w,T} = w_1 \left(A_1 + \frac{B_1}{T/\mathrm{K}} \right) + w_2 \left(A_2 + \frac{B_2}{T/\mathrm{K}} \right) + \frac{w_1 w_2}{T/\mathrm{K}} \sum_{i=0}^{2} J_i (w_1 - w_2)^i \quad (3)$$

A_1, B_1, A_2, B_2 and J_i are the model constants.

2.3. Modified Apelblat-Jouyban-Acree model

The modified Apelblat equation is employed to correlate the solute solubility against temperature at the same solvent composition. It is a semi-empirical model, described as Eq. (4) [23].

$$\ln x = A + \frac{B}{T/K} + C \ln(T/K) \quad (4)$$

Substituting Eq. (4) into Eq. (1), the Apelblat-Jouyban-Acree model is acquired and expressed as Eq. (5) [17,18].

$$\ln x_{w,T} = w_1 \left[A_1 + \frac{B_1}{T/\mathrm{K}} + C_1 \ln(T/K) \right] + w_2 \left[A_2 + \frac{B_2}{T/\mathrm{K}} + C_2 \ln(T/K) \right] + \frac{w_1 w_2}{T/\mathrm{K}} \sum_{i=0}^{2} J_i (w_1 - w_2)^i \quad (5)$$

A_1, B_1, C_1, A_2, B_2, C_2 and J_i are the constants in the Apelblat-Jouyban-Acree model.

2.4. CNIBS/R-K model

The CNIBS/R-K model [19–21] is employed to describe the relationship between solubility and composition of binary mixed solvents at certain temperature, which is regarded as one of the most appropriate models for binary solvent systems. The simplified CNIBS/R-K model is described as

$$\ln x = B_0 + B_1 x_2 + B_2 x_2^2 + B_3 x_2^3 + \ldots + B_4 x_2^4 \quad (6)$$

where x is the mole fraction solubility of solute in mixed solvents; x_2 is the initial composition in mole fraction of acetone, ethyl acetate or acetonitrile in binary solvent mixtures in the absence of solute; and B_0 to B_4 are model parameters.

3. Experimental

3.1. Materials and apparatus

Phthalimide having a mass fraction of 0.980 was provided by Taixing HaoshenChemical Co., Ltd. It was purified several times via recrystallization in methanol. The purified sample had a mass fraction purity of 0.994, which was confirmed by a high-performance liquid phase chromatograph (HPLC, Agilent-1260). The solvents of methanol, acetone, ethyl acetate and acetonitrile with analytical grade were provided by Sinopharm Chemical Reagent Co., Ltd., China. The mass fraction purities of these solvents were all greater than 0.990, which were determined by a gas chromatography (FULI 9790, China). These solvents were used