



Solubility modelling and thermodynamic dissolution functions of phthalimide in ten organic solvents



Renjie Xu, Jian Wang*, Shuo Han, Cunbin Du, Long Meng, Hongkun Zhao

College of Chemistry & Chemical Engineering, YangZhou University, YangZhou, Jiangsu 225002, People's Republic of China

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ABSTRACT

In this work, a high performance liquid chromatography (HPLC) was employed to determine the solubilities of phthalimide in methanol, isopropanol, *n*-propanol, ethyl acetate, acetonitrile, *i*-butanol, *n*-butanol, toluene, acetone and ethanol at temperatures ranging from (283.15 to 318.15) K under 0.1 MPa. The solubility of phthalimide in a fixed solvent increases with an increase in temperature. At a certain temperature, the solubility in different solvents decreases according to the following order: acetone > ethyl acetate > (methanol, isopropanol, *n*-propanol, acetonitrile, *i*-butanol, *n*-butanol, ethanol) > toluene. Four models, modified Apelblat equation, λh equation, Wilson model and NRTL model were employed to correlate the solubility of phthalimide in the solvents studied. The evaluated solubilities provide better agreement with the modified Apelblat equation than the other three models. The four thermodynamic models are all acceptable for correlating the solubility of phthalimide in the solvents studied. Furthermore, the standard dissolution enthalpy and excess enthalpy of the solutions were obtained. The dissolution process of phthalimide in the selected solvents is discussed.

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1. Introduction

Phthalimide is an important chemical intermediate. The use of phthalimide and its derivatives is widely spread in dyestuffs, agriculture, medicine, and many other fields [1–5]. In industry, phthalimide can be prepared by treating phthalic anhydride with ammonia [6–8] or by treating the anhydride with ammonium carbonate or urea [9,10] and or by ammoxidation of ortho-xylene [11]. At present, the commercial preparation method of phthalimide is using phthalic anhydride as raw material. Although the yield of phthalimide is relatively high by this method, the crude product usually contains some unreacted phthalic anhydride. Extreme difficulty is encountered in separating the phthalimide of high purity from the reaction mixture because of the extremely poor solubility of phthalimide in water. With the development of industry, the requirements for product purity are becoming greater. The crude phthalimide restricts its applications in many aspects.

It is well-known that crystallization is an important process during purifying a solid compound. Knowledge of solubility is of significance in designing chemical and pharmaceutical industrial processes. In previous works, some purification methods have been proposed to separate the phthalimide directly with high purity [12,13], however, the cost of these processes is relatively high. To

the best of the authors' knowledge, crystallization is an effective method in phthalimide purification. Unfortunately, values of the solubility of phthalimide in solvents are very scarce in previous publications. Solubility may be employed to optimise the basic design of the crystallization process and improve the purity of phthalimide which is of great significance in the purification procedure of phthalimide via the method of solvent crystallization. Thus, in order to obtain the product with high purity, investigation of the phthalimide solubility in different solvents at various temperatures and the thermodynamic properties of solution are especially necessary in industry.

The purposes of the work are to (1) determine the solubility of phthalimide in methanol, isopropanol, *n*-propanol, ethyl acetate, acetonitrile, *i*-butanol, *n*-butanol, toluene, acetone and ethanol at temperatures ranging from (283.15 to 318.15) K by high performance liquid chromatography (HPLC), (2) correlate solubility data using the Apelblat equation, λh equation, Wilson model and NRTL model, and (3) evaluate the thermodynamic properties for the solutions of phthalimide in different solvents.

2. Experimental

2.1. Materials

Phthalimide having a mass fraction of 0.980 was purchased from Taixing Haoshen Chemical Co., Ltd. It was recrystallized three

* Corresponding author. Tel.: +86 514 87975568; fax: +86 514 87975244.
E-mail address: wjhg@yzu.edu.cn (J. Wang).

times in acetone. The content of phthalimide employed in solubility determination was 0.994 in mass fraction, which was further analysed by a high performance liquid chromatography (HPLC). The solvents were of analytical grade and used without additional purification. The detailed information of the materials employed in this work is tabulated in [table 1](#).

2.2. Solubility determination

In the present work, the solubilities of phthalimide in different solvents are determined by using the high performance liquid chromatography (HPLC), which was described in detail in the previous works [14–16]. The temperature of the experimental systems were controlled by using a smart thermostatic water bath (model: DZKW-4) with a precision of ± 0.01 K. An analytical balance with a precision of 0.0001 g was employed to determine the mass of the solute, solvent and saturated solution.

During the experiment, excessive phthalimide was added into an Erlenmeyer flask (about 50 mL) filled with about 30 mL solvent. The solution was maintained at constant temperature by cycling water from the smart thermostatic water bath through the outside jacket. A mercury thermometer (precision: ± 0.01 K) was inserted the Erlenmeyer flask to display the real temperature of solution, which was stirred continuously for 24 h with a magnetic stirrer. In order to prevent the solvent from volatilising, a condenser was equipped with the Erlenmeyer flask. The liquid phase was got out every one hour using a syringe attached with a 0.2 μm pore filter, and then analysed by HPLC. The system was believed to be in equilibrium if the analytical results did not vary. Results indicated that 15 h is enough for the studied systems to reach equilibrium. Once the system reached equilibrium, the magnetic stirrer was stopped to allow any solid to settle down from the solution. And then the equilibrium liquid phase with about 1 mL (precision: ± 0.01 mL) was got out with a 5 mL syringe attached with a filter (PTFE 0.2 μm) preheated in the smart thermostatic water bath, and put rapidly into a pre-weighed glass bottle of 25 mL. The glass bottle was covered with a rubber stopper to prevent the solvent from evaporating. The mass of the sample was weighed using the analytical balance. The sample was diluted to 25 mL with methanol before testing, and then 1 μL of the solution was taken out to analyse by using high performance liquid chromatography (HPLC).

The mole fraction solubility (x^e) of a solute in pure solvent can be calculated with equation (1),

$$x^e = \frac{m_1/M_1}{m_1/M_1 + m_2/M_2} \quad (1)$$

Here m_1 and M_1 are the mass and molar mass of phthalimide, respectively, and m_2 and M_2 , of solvent.

2.3. Analysis method

The content of phthalimide in equilibrium liquid phase was analysed using a high performance liquid chromatography (HPLC), which comprised of a Waters 717 plus autosampler, a Waters 1525 pump, and a Waters 2487 UV detector. The wavelength of detection was 290 nm. The mobile phase was pure methanol, the flow rate of which was 1 mL \cdot min⁻¹. The chromatographic column used in this study was a Waters C18 reverse phase column (250 mm \times 4.6 mm).

3. Results and discussion

3.1. Solubility values

The mole fraction solubilities determined in this work for phthalimide in methanol, isopropanol, *n*-propanol, ethyl acetate, acetonitrile, *i*-butanol, *n*-butanol, toluene, acetone and ethanol within the temperature range from (283.15 to 318.15) K are tabulated in [table 2](#), and plotted in [figures 1 and 2](#). Furthermore, the van't Hoff plots of $\ln(x)$ versus inverse of absolute temperature in different solvents are graphically shown in [figure 3](#). We can find from [table 2](#) and [figures 1 and 2](#) that, with an increase in temperature, the solubility of phthalimide in different solvents increase. At the same temperature, phthalimide has the largest solubility in acetone. [Figures 1 and 2](#) further demonstrate that the solubility of phthalimide in acetone and ethyl acetate have the strongest positive dependency upon temperature. The solubilities decrease according to the following order: acetone > ethyl acetate > (methanol, isopropanol, *n*-propanol, acetonitrile, *i*-butanol, *n*-butanol, and ethanol) > toluene. For the solvents of methanol, isopropanol, *n*-propanol, acetonitrile, *i*-butanol, and *n*-butanol, when the temperature is greater than 300 K, the order of the solubilities of phthalimide rank as: acetonitrile > isopropanol > *n*-butanol > methanol > *n*-propanol > *i*-butanol.

To elucidate the solubility behaviour of phthalimide in the selected solvents, polarities, dipole moments (μ), dielectric

TABLE 1

Detailed information of the materials used.

Chemicals	Molar mass g \cdot mol ⁻¹	Melting point K	Melting Enthalpy kJ \cdot mol ⁻¹	Density kg \cdot m ⁻³	Molar volume mL \cdot mol ⁻¹	Source	Initial mass fraction purity	Final mass fraction purity	Purification method	Analytical method
Phthalimide	147.13	507.2 ^a	28.6 ^a	1367 ^b		Taixing Haoshen Chemical Co., Ltd.	0.980	0.994	Recrystallization	HPLC ^d
Acetonitrile	41.05				52.86 ^c	Sinopharm Chemical	0.990	0.990		GC ^e
Methanol	32.04				40.4 ^c	Reagent Co., Ltd., China	0.995	0.995		GC
Ethanol	46.07				58.68 ^c		0.997	0.997		GC
<i>n</i> -Propanol	60.06				75.14 ^c		0.990	0.990		GC
Isopropanol	60.06				76.92 ^c		0.997	0.997		GC
Acetone	58.05				73.4 ^c		0.995	0.995		GC
Toluene	92.14				106.85 ^c		0.995	0.995		GC
Ethyl acetate	88.11				98.5 ^c		0.995	0.995		GC
<i>i</i> -Butanol	74.12				92.91 ^c		0.995	0.995		GC
<i>n</i> -Butanol	74.12				91.97 ^c		0.995	0.995		GC

^a Taken from Ref. [15].

^b taken from Ref. [25].

^c taken from Ref. [17].

^d HPLC, high performance liquid chromatography.

^e GC, gas chromatography.

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