Fluid Phase Equilibria 367 (2014) 1–6

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Measurement and correlation of the solubility of maleic anhydride in different organic solvents

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ARTICLE INFO

Article history:
Received 18 September 2013
Received in revised form 2 January 2014
Accepted 7 January 2014
Available online 20 January 2014

Keywords:
Maleic anhydride
Solubility
Gravimetric method
Purification

ABSTRACT

Data on corresponding solid–liquid equilibrium of maleic anhydride in different organic solvents are essential for industrial design and further theoretical studies. In this study, the solubilities of maleic anhydride were measured in DMF, methanol, acetic acid, acetonitrile, acetone, ethyl acetate, 2-propanol and n-butyl alcohol with the temperature range of 278.15–323.15 K by the analytical stirred-flask method under atmospheric pressure. The experiment results indicated that the solubility of maleic anhydride was highest in DMF and followed by methanol, acetic acid, acetonitrile, acetone, ethyl acetate, 2-propanol and n-butyl alcohol. For the temperature range investigated, the solubilities of maleic anhydride in the organic solvents increased with increasing temperature. Results of these measurements were well-correlated with the modified Apelblat equation, the Buchowski–Ksiazaczak λh equation and the van't Hoff equation. The calculated solubilities showed good agreement with the experimental data. The modified Apelblat equation was found to regress the solubility data is higher accuracy than the Buchowski–Ksiazaczak λh equation. The experimental data and model parameters would be useful for optimizing the process of purification of maleic anhydride in industry.

1. Introduction

Maleic anhydride ($C_4H_2O_3$, CASRN: 108-31-6, shown in Fig. 1) also called maleic acid anhydride is a white crystalline solid, which is widely used as an important raw material for many other organic substances applied in the field of resins, pesticides, paints, additives and surfactants [1,2]. The solubilities of organic compounds in different solvents play an important role in their separation and purification application. To determine proper solvents and to design an optimized production process, it is necessary to know the solubilities of maleic anhydride in different organic solvents [3].

Unfortunately, limited date is available on the solubility and temperature dependence of the solubility of maleic anhydride. The aim of this study is to explore the solubilities of maleic anhydride in eight solvents, this is, DMF, methanol, acetic acid, acetonitrile, acetone, ethyl acetate, 2-propanol and n-butyl alcohol in the temperature range 278.15–323.15 K and to provide accurate data correlation model [4,5].

In the present study, the solubilities of maleic anhydride in eight solvents were measured by a static method, the modified Apelblat equation and the Buchowski–Ksiazaczak λh equation were used to correlate and predict the solubility of maleic anhydride in pure solvents. The standard enthalpy, standard entropy and Gibbs energy charge of solution of maleic anhydride were calculated from the solubility data by the van't Hoff equation.

2. Experimental

2.1. Materials

Maleic anhydride ($C_4H_2O_3$) with a purity of >99.0% was supplied by Aladdin. Its purity was measured by high performance liquid chromatography (HPLC type DIONEX P680 DIONEX Technologies), and its melting temperature was found to be 325.95 K measured by different scanning calorimeter (Netzsch DSC 204), and a series of literature reported its melting temperature [325.75 K, procedures in ice calorimetry; 326.00 K, adiabatic calorimeter for determination of cryoscopic data; 325.15–326.15 K, the rate of reaction of maleic anhydride with 1,3-dienes as related to diene conformation; 325.15 K, F.E. Rogers, S.W. Quan, J. Phys. Chem. 77 (1973) 828]. All of the organic solvents for dissolving were purchased from Shanghai Shenbo Chemical Co., Ltd., China. The purities of the solvents were

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http://dx.doi.org/10.1016/j.fluid.2014.01.008

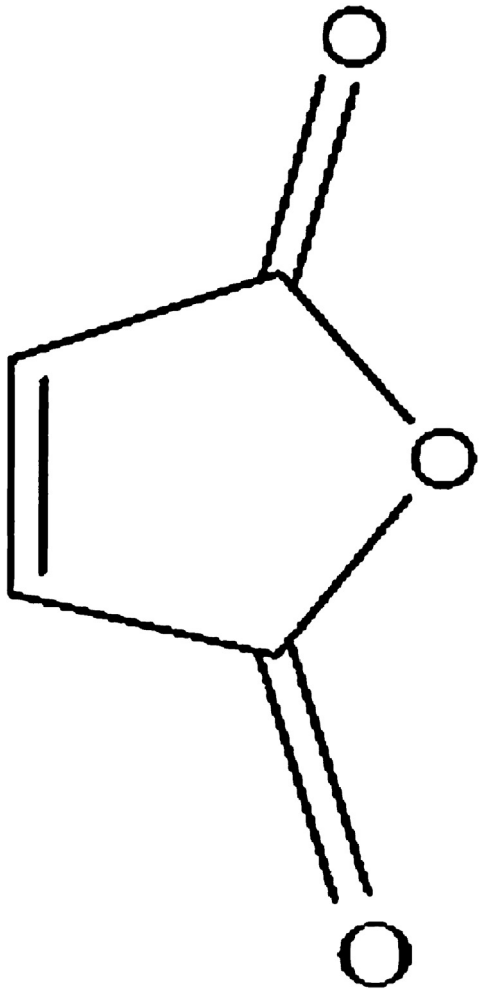

Fig. 1. Chemical structure the maleic anhydride.

Table 1
Provenance and purity of the materials used.

Compound	Provenance	Mass fraction purity
Maleic anhydride	Aladdin	>0.990
DMF	Shenbo Chemicals	≥0.995
Methanol	Shenbo Chemicals	≥0.997
Acetic acid	Shenbo Chemicals	≥0.992
Acetonitrile	Shenbo Chemicals	≥0.995
Acetone	Shenbo Chemicals	≥0.990
Ethyl acetate	Shenbo Chemicals	≥0.995
2-Propanol	Shenbo Chemicals	≥0.997
n-Butyl alcohol	Shenbo Chemicals	≥0.990

determined in our laboratory by gas chromatography and all chemicals were used received without further purification (Table 1).

2.2. Apparatus and procedure

The solubilities of maleic anhydride in different organic solvents were determined by the analytical stirred-flask method and the compositions of the saturated solutions were measured using the gravimetric method. Saturated solutions of maleic anhydride were prepared in a spherical, 10 mL Pyrex glass flask. The flask was maintained at the desired temperature through circulating water. The water temperature was controlled by a thermostat within ±0.1 K that was provided from a constant-temperature water bath (type HWC-52, ShangHai Cany Precision Instrument Co., Ltd.) through the jacket of the cell. For each measurement, an excess amount of maleic anhydride was added to a known volume of solvent. Continuous stirring was achieved for fully mixing the suspension using a magnetic stirrer at the required temperature. The stirring was kept for about 12 h to ensure the solid–liquid equilibrium and the solution was allowed to settle for at least 3 h before sampling [6–8]. The upper portion was taken, filtered, and poured into a volumetric flask preweighed by using an analytical balance (Sartorius, BS210s, Germany) with a resolution of ±0.1 mg. All the experiments were conducted three times, and the mean values were used to calculate the mole fraction solubility.

The saturated mole fraction solubility of the solute (x) in solvents is obtained as follow:

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

where m_1 represents the mass of maleic anhydride which is obtained after solvent evaporation and m_2 represents the mass of solvents, respectively. M_1 is the molecular mass of maleic anhydride; M_2 is the molecular mass of solvents, correspondingly.

3. Results and discussion

3.1. Solubility data

The measured mole fraction solubilities of maleic anhydride in DMF, methanol, acetic acid, acetonitrile, acetone, ethyl acetate, 2-propanol and n-butyl alcohol with the temperature range of 278.15–323.15 K are showed in Table 2 and graphically displayed in Fig. 2, it could be found that solubility is a function of temperature, which increased with the increasing temperature. (The experimental data of X are the solubilities of maleic anhydride removing the maleic acid.) Fig. 2 clearly showed that solubility decreased according to the following order: DMF > methanol > acetic acid > acetonitrile > acetone > ethyl acetate > 2-propanol > n-butyl alcohol. Meanwhile, we could find that maleic anhydride had the largest solubility in DMF, and methanol and acetic acid showed the strongest positive dependency on temperature. The result suggested that the polarity of the organic solvent is the important factor to determine the solubility of maleic anhydride.

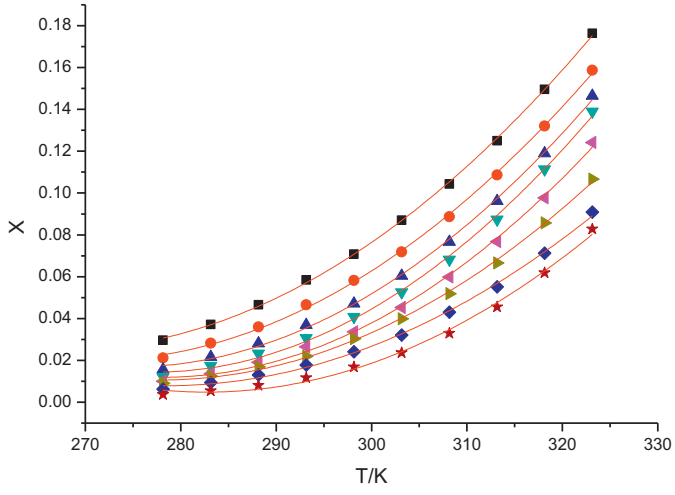

Fig. 2. Mole fraction solubility (x) of maleic anhydride versus temperature (T) in the selected organic solvents: ■, DMF; ●, methanol; ▲, acetic acid; ▼, acetonitrile; ◀, acetone; ▶, ethyl acetate; ◆, 2-propanol; ★, n-butyl alcohol.