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Measurement and correlation of solubility of succinic anhydride in pure solvents and binary solvent mixtures

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ABSTRACT

The solubility of succinic anhydride in pure solvents and binary {gamma-butyrolactone (GBL) + tetrahydrofuran (THF)} mixtures was determined at a limited temperature range of (283.15–323.15) K by using a gas chromatography method. The experimental results revealed two aspects. On the one hand, the solubility of succinic anhydride increased monotonically with rising temperature in binary (gamma-butyrolactone + tetrahydrofuran) mixtures when solvent composition remains constant. On the other hand, the solubility of succinic anhydride decreased monotonically with the increasing tetrahydrofuran content when temperature remains constant. The modified Apelblat equation, λh equation, CNIBS/R-K equation and Jouyban-Acree equation were successfully used to correlate the experimental solubility in diverse solution systems. Furthermore, the mixing thermodynamic properties of succinic anhydride in binary solvent mixtures were calculated and discussed. The results indicate that the mixing process of succinic anhydride in the investigated solvents is spontaneous.

1. Introduction

In the chemical industry, succinic anhydride is a pseudo-commodity of remarkable importance, mainly due to its numerous applications as a chemical intermediate [1]. Indeed, one of its main uses is as a starting material for the manufacture of gamma-butyrolactone (GBL) and tetrahydrofuran (THF), which are widely used in chemical industry [2]. It is also employed in the manufacturing of agrochemicals and as a processing aid for production of food and biodegradable polymers [3]. Furthermore, succinic anhydride has a number of primary purposes, such as, a coating additive, a material for synthesis of multifunctional rubbers and an efficient plant growth regulator [4–6].

In this work, GBL, THF and binary (GBL + THF) mixtures are adopted to be particular solvents for succinic anhydride crystallization process. GBL has a wide range of applications, for instance, an environmentally friendly solvent, a circuit board cleaner in electronics and an electrolyte solvent or additive for Li-ion battery applications [1,7–9]. Due to the excellent chemical properties of GBL, a reaction solvent is extensively used in industrial production, which produces succinic anhydride. Simultaneously, GBL and THF are by-products of selective hydrogenation of maleic anhydride to succinic anhydride [10]. Thus, the solubility of succinic anhydride in binary (GBL + THF) solvent mixtures plays a great role in liquid phase selective hydrogenation of succinic anhydride.

At present, limited information is available on the solubility and temperature dependence of the solubility of succinic anhydride. Thus, the target of the research is to explore the solubility of succinic anhydride in the binary mixtures of (GBL + THF) in the temperature range of (283.15–323.15) K. At the same time, our work provides correlation models with meaningful experimental values. The gas chromatography method, which is reliable, simple, time-saving, used extensively, was used to determine the solubility of succinic anhydride in binary (GBL + THF) solvent mixtures. The solubility can be correlated by using the modified Apelblat model, the λh model, the CNIBS/R-K model and Jouyban-Acree model. Besides that, the mixing enthalpy change, the mixing entropy change and the mixing Gibbs energy change can be calculated by the NRTL model.

2. Experimental

2.1. Materials

Succinic anhydride (Fig. 1; $C_4H_4O_3$; CAS RN: 108-30-5; molar mass 100.07 $g \cdot mol^{-1}$) with mass fraction purity higher than 0.997 was purchased from Tianjin Zhiyuan Chemical Regent Co. Ltd., China. Succinic anhydride was stored in a dessicator with

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0021-9614/

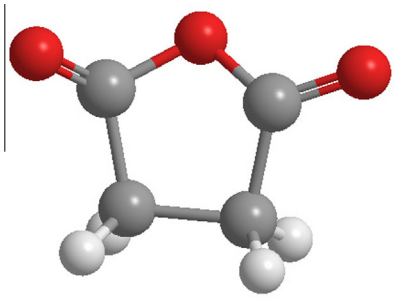

Fig. 1. Chemical structure of succinic anhydride.

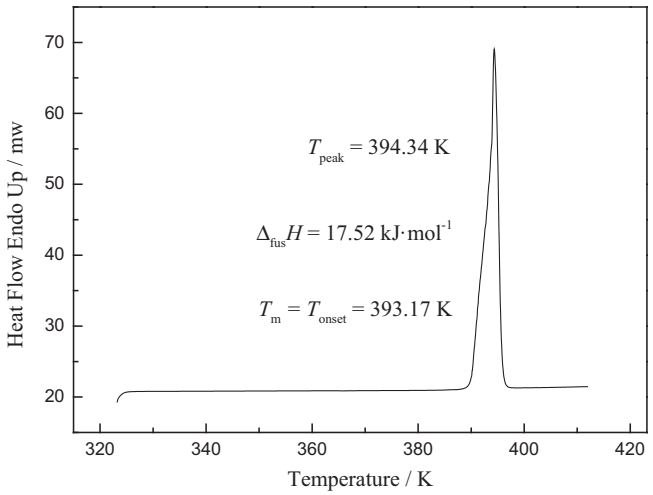

Fig. 2. Thermal analysis (DSC) data of succinic anhydride.

dry silica gel. All the organic solvents (GBL and THF) used in the experiment were analytical grade reagents with purity higher than 0.999 mass fraction which were supplied by Aladdin Regent Co., Ltd. The chemicals were employed without purification. More details about analytical method of solvents along with their CAS registry numbers are listed in Table 1.

2.2. Melting property measurements

The melting temperature T_m and the fusion enthalpy ($\Delta_{fus}H$) of succinic anhydride were obtained by differential scanning calorimetry (DSC) (PerkinElmer Pyris 1 DSC, America) under a nitrogen atmosphere. Approximately 5 mg succinic anhydride was heated at a $T = 10$ K min^{-1} heating rate, and the result are given in Fig. 2.

2.3. Apparatus and procedure

The apparatus for the solubility measurements is similar to that described in the literature [11,12]. A simple equilibrium cell was applied to determine the solubility of solute in the solvent at a known temperature. The apparatus consisted of a magnetic stirrer, a thermostat (type DC 1006, Hengping Scientific Instrument Co., Ltd., Shanghai), a spherical condenser and a cylindrical double-jacketed glass vessel. The thermostat provides circulated water with a thermoelectric controller. The jacketed temperature was kept within ±0.01 K at a desired temperature by water circulated. The succinic anhydride samples were weighted by an electronic analytical balance (type EL104, Mettler Toledo Instrument Co., Ltd., Shanghai) with a standard uncertainty of 0.0001 g. In this work, the gas chromatograph method was used to measure the concentration of succinic anhydride on solid-liquid equilibrium [13,14]. At first, an excess amount of succinic anhydride sample weighted by analytical balance was added into the solvents. A thermostat provided a specific temperature for the solution system. Since the slurry was kept under agitation for 24 h, the solution was guaranteed to have reached solid-liquid equilibrium [15]. The attaining of equilibrium was verified by successive concentration measurements over time. And when the concentration was nearly invariable, that time was considered as the time to reach solid–liquid equilibrium. After standing at least 2 h, the slurry was ready for the separation of solid and liquid at the same temperature. Then the upper clear saturated solutions were filtered by an organic membrane (PTFE, 0.22 μm) and diluted to a certain concentration. This treatment prepared the material for gas chromatograph analysis which was carried out on Agilent 7890B Gas Chromatograph equipped with a Flame Ionization Detector and a HP-ULTRA 2 (25 m × 0.320 mm × 0.52 μm) chromatographic column. The vaporization temperature and detection temperature were both set as 523.15 K. The temperature of the chromatographic column was adjusted to 413.15 K. Five injections of each sample were made and the retention time was determined from the maximum of the symmetric peak. Last but not least, the normalization method was used to measure the mass concentration of succinic anhydride in solution, and the mole fraction solubility of succinic anhydride was obtained by calculation.

To determine the reproducibility of the analytical method, succinic anhydride solution of known concentration was analysed. The relative uncertainty in the mole fraction of the measured solubility values based on error analysis and repeated observations was within 0.05.

The mole fraction solubility of the solute (x_A) in the binary {GBL (B) + THF (C)} solvent mixtures can be obtained as follows:

$$x_A = \frac{w_A/M_A}{w_A/M_A + w_B/M_B + w_C/M_C} \quad (1)$$

$$w'_C = \frac{m_C}{m_C + m_B} \quad (2)$$

in which, w_A, w_B and w_C represent the mass fraction of succinic anhydride, GBL and THF in the ternary mixture (GBL + THF + succinic anhydride), respectively; w'_C, m_B and m_C stand for the mass fraction of tetrahydrofuran in binary solvent mixtures, the mass of GBL and THF, respectively. The M_A, M_B, and M_C are the molar masses of solute, GBL and THF, correspondingly.

Table 1
Provenance and mass fraction purity of the chemical reagent used.

Material	Source	CAS RN	Mass fraction purity	Purification method	Analytical method
Succinic anhydride	Zhiyuan Chemical Regent Co., Ltd.	108-30-5	⩾0.997	None	HPLC[a]
Gamma-butyrolactone	Aladdin Reagent Co., Ltd.	96-48-0	⩾0.999	None	–
Tetrahydrofuran	Aladdin Reagent Co., Ltd.	109-99-9	⩾0.999	None	–

[a] High-performance liquid chromatography.