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Solubility of succinic acid, glutaric acid and adipic acid in propionic acid + ε-caprolactone mixtures and propionic acid + cyclohexanone mixtures: Experimental measurement and thermodynamic modeling

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ABSTRACT

By dynamic laser method, the solubilities of succinic acid, glutaric acid and adipic acid in propionic acid + ε-caprolactone mixtures and propionic acid + cyclohexanone mixtures were determined under atmospheric pressure. The experimental temperature ranged from 283.95 to 340.45 K, and the mass fraction of propionic acid in the solvent mixtures ranged from 0.00 to 1.00 respectively. It was found that when the solvent composition is constant, the solubilities of succinic acid, glutaric acid and adipic acid would increases with the increase of the temperature. What is more, at constant temperature, with the mass fraction of propionic acid in mixtures increasing, the solubilities of glutaric acid and adipic acid increase gradually, on the contrary, the solubility of succinic acid decrease gradually. The experimental data were correlated by the modified Apelblat equation and the modified nonrandom two-liquid (NRTL) activity coefficient models. The maximum value of average relative deviation was 3.015%, which shows the values of the solubility calculated showed good agreement with the experimental observations. Furthermore, the thermodynamic functions including dissolution enthalpy, entropy and Gibbs energy were obtained from the solubility data by using the van't Hoff equation.

1. Introduction

ε-Caprolactone, as an important intermediate of organic synthesis, is widely used as an intermediate in degradable material [1–4], environmental protection [5] and medical fields [6–9] because of its biocompatibility, nontoxicity, medicine permeability and biological degradability [10–15]. Commercially, the majority of ε-caprolactone is manufactured from cyclohexanone by the typical Baeyer-Villiger oxidation [16,17]. During the process of oxidation, the perpropionic acid, as one of the most the preferred oxidant, is usually used because of its high oxidation efficiency and its economic advantages in the industrial production [18], and cyclohexanone is usually regarded as reactants, ε-caprolactone is the major product, and propionic acid, succinic acid (SA), glutaric acid (GA) and adipic acid (AA) are the unfavorable byproducts. Therefore, to obtain ε-caprolactone with a high purity, it is necessary to crystallize the SA, GA and AA from propionic acid + ε-caprolactone + cyclohexanone mixtures. Sequentially, the solid-liquid equilibria (SLE) of SA, GA and AA in propionic acid + ε-caprolactone + cyclohexanone mixtures are indispensable to design the process and optimize the separation conditions.

In recent works, some relevant solubilities of SA, GA and AA in pure or mixed solvents could be obtained in the literatures. The solubility of SA in various solvent systems such as ε-caprolactone + acetic acid (HAc) mixtures [19], ε-caprolactone + cyclohexanone mixtures [19], GA + cyclohexanone and GA + acetic acid mixtures [20], urea + diethyleneglycol mixtures [21], pure water and water + ethanol mixtures [22], AA + ethanol mixtures [23], AA + GA + acetone mixtures [24], HAc + water mixtures [25], HAc + cyclohexanone mixtures [25], methanol + water, ethanol + water and binary aqueous ethanol solvents [26], cyclohexanone, cyclohexanol, and their mixed solvents [27] has been reported. The solubility of GA in ε-caprolactone + HAc mixtures [29], ε-caprolactone + cyclohexanone mixtures [29], HAc + cyclohexanone mixtures [28], HAc, cyclohexanone, cyclohexanol, cyclohexane + cyclohexanol mixtures, cyclohexane + cyclohexanone mixtures, cyclohexanone + cyclohexanol mixtures, and cyclohexanol + cyclohexanone + cyclohexane mixtures [30–32] has been measured. What is more, most relevant solubility of AA could be obtained in the literatures. Like the solubility of AA in HAc + water mixtures, HAc + cyclohexane mixtures [33], water, ethanol, chloroform, n-butanol and acetone [34], acetone, chloroform and toluene [35], glutaric acid + acetone mixtures [36], cyclohexanone, cyclohexanol, HAc, DMF, DMAC, and DMSO [37], HAc, cyclohexanol and cyclohexanone [38] has been measured also.

Unfortunately, no reports about experimental equilibrium data for SA, GA and AA in ε-caprolactone + propionic acid + cyclohexanone solvent mixtures could be available. And the corresponding SLE data is lacking for the particular conditions of temperature and composition

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Table 1
Supplier and mass fraction purity of materials.

Compound	Molecular formula	Mass fraction	Analysis method	Suppliers
Succinic acid	$C_4H_6O_4$	≧0.995	HPLC[a]	Aladdin Chemistry Co.
Glutaric acid	$C_5H_8O_4$	≧0.990	HPLC[a]	Aladdin Chemistry Co.
Adipic acid	$C_6H_{10}O_4$	≧0.990	HPLC[a]	Aladdin Chemistry Co.
Propionic acid	$C_3H_6O_2$	≧0.995	HPLC[a]	Sinopharm Chemical Reagent Co.
ε-Caprolactone	$C_6H_{10}O_2$	≧0.990	GC[b]	Aladdin Chemistry Co.
Cyclohexanone	$C_6H_{10}O$	≧0.995	GC[b]	Sinopharm Chemical Reagent Co.

[a] High-performance liquid chromatography: Agilent 1100 LC.
[b] Gas chromatography: Shimadzu GC-2010 plus.

required in a particular program. Hence, it is essential to measure and correlate the solubilities of SA, GA and AA in ε-caprolactone + propionic acid + cyclohexanone solvent mixtures. When suitable data are lacking, the desired equilibrium data could be estimated from some appropriate correlation by interpolating or extrapolating these SLE data.

In this work, the solubilities of SA, GA and AA in propionic acid + ε-caprolactone mixtures and propionic acid + cyclohexanone mixtures at (283.95 to 340.45 K)would been measured. The modified Apelblat equation and the modified NRTL activity coefficient model would be applied to correlate the experimental values. Then thermodynamic functions including dissolution enthalpy, entropy and Gibbs energy would be calculated from the solubility data by using the van't Hoff equation.

2. Experiments

2.1. Materials

SA, GA, AA, ε-caprolactone, propionic acid and cyclohexanone were obtained from Aladdin Chemistry Company and Sinopharm Chemical Reagent Company, whose major information was given in Table 1.

2.2. Apparatus and procedure

The determination of solubility was carried out by the method of laser dynamics, which is commonly used in the literature [27,36]. The experimental device consists of SLE machine, laser detection system, temperature control monitoring device and magnetic stirring system, as shown in Fig. 1. And it could be obtained in our previous work [19,28–30,39]. Briefly, the experiment was implement in a 100 ml glass bottle with a magnetic stirrer and a jacket linked up with the thermostatic water-circulator bath. The thermoelectric controlling system was used to determine and control the temperature of the solution continuously. To prevent effectively the evaporation of ε-caprolactone, propionic acid, cyclohexanone and other ingredient, the bottle was sealed by the reflux condenser with a rubber stopper. The laser-detecting system mainly contained a semiconductor laser emitter of 25 mW, a photoelectric transformer and a computer equipped with the Kingview software that was applied to display and record the real-time temperature and laser intensity value.

In each experiment, firstly the preweighed amounts of SA, GA or AA and a certain amount of solvent were carefully added into the SLE bottle carried on stirring continuously in the meantime so as to ensure the presence of the solute particles in the solution. Secondly, the thermostatic water-circulator bath was turned on and the equilibrium bottle was heated in a stepwise fashion (1.5 $K\cdot h^{-1}$) until the SA(GA, AA) was going to dissolve. Near the SLE temperature (more than 1 K below), the temperature of the solution increase was less than 0.2 $K\cdot h^{-1}$. During a steady laser beam went through the solute and solvent mixtures continuously, the unsolved SA(GA, AA) particle would block the laser beam and weaken the intensities of transmitted laser. When the SA(GA, AA) particle disappeared exactly, the intensities of transmitted laser would reach the maximum. Just then, the SLE would be achieved and the corresponding solution temperature was the saturated dissolving temperature. Moreover, the saturated mole fraction solubility of SA (GA, AA)could be calculated as follows:

$$x_i = \frac{m_i/M_i}{m_i/M_i + m_A/M_A + m_B/M_B + m_C/M_C} \tag{1}$$

where m_i, m_A, m_B and m_C are the mass of SA(GA or AA), propionic acid, ε-caprolactone and cyclohexanone; M_i, M_A, M_B and M_C are the molecular weights of SA(GA or AA), propionic acid, ε-caprolactone and cyclohexanone.

2.3. Verfication of the experimental methods

The solubilities of SA, GA and AA in pure cyclohexanone were measured and compared with the published data [19,20,27,29,30,32,37,38] respectively to verify the reliability and accuracy of the experimental apparatus and method. The results were also shown graphically in Figs 2 to 4. Our results agree well with the published data

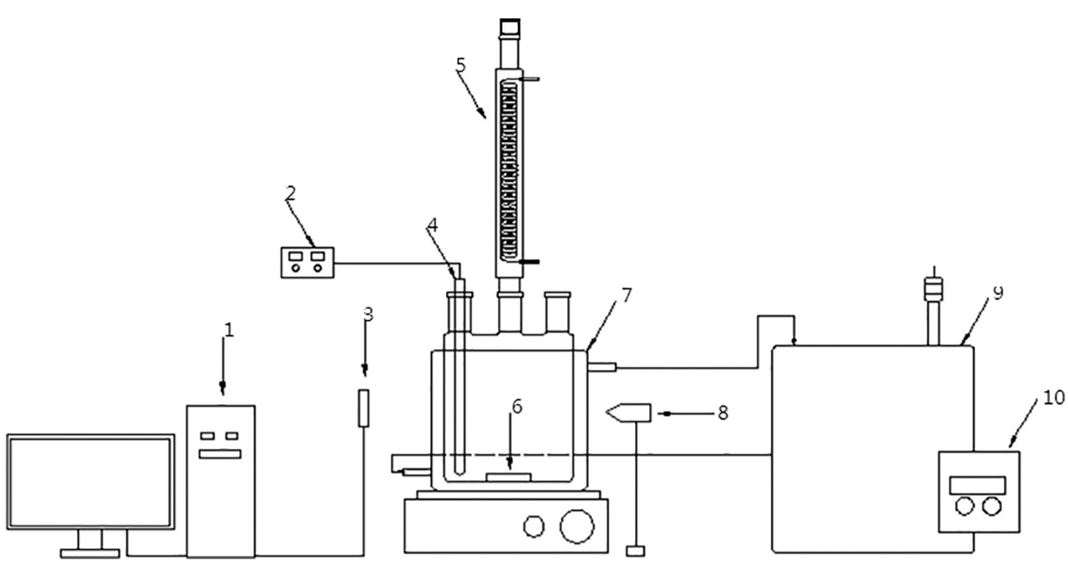

Fig. 1. The Devices for Measuring the Solubility of SLE: 1, computer monitoring center; 2, temperature display panel; 3, a photoelectric transformer; 4, Pt100 temperature sensor; 5, reflux condenser; 6, magnetic stirring system; 7, a jacketed equilibrium glass bottle; 8, semiconductor laser emitter; 9, thermostatic water-circulator bath; 10, temperature programmed controller.