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Determination and correlation of solid-liquid phase equilibrium and phase diagram for multicomponent system of mixed dibasic acids. (III) Ternary system of succinic acid + glutaric acid + ethanol system

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ABSTRACT

The solid-liquid phase equilibrium for ternary system of succinic acid + glutaric acid + ethanol was determined by an isothermal saturation method at the three temperatures of (283.15, 303.15 and 313.15) K under atmosphere pressure. Three isothermal phase diagrams were built based on the measured mutual solubility data. There were two pure solids formed in the ternary system at a certain temperature, which corresponded to pure succinic acid and pure glutaric acid and were confirmed by Schreinemaker's method of wet residue and X-ray powder diffraction. The ternary phase diagram included one co-saturated point, two boundary curves, and three crystalline regions. The crystallization region of glutaric acid was smaller than that of succinic acid at each temperature. In addition, two thermodynamic models, NRTL and Wilson were employed to correlate and calculate the mutual solubility data for the ternary succinic acid + glutaric acid + ethanol system. The largest *RMSD* value for the ternary system of succinic acid + glutaric acid + ethanol was 0.43, and the maximum value of *RAD* was 3.0%. The Wilson model and NRTL model may all be employed to describe the mutual solubility behavior for the ternary system of succinic acid + glutaric acid + ethanol at various temperatures. Furthermore, the densities of the equilibrium liquid phase were obtained and correlated with an empirical equation.

1. Introduction

Adipic acid is a large volume commodity chemical used for the production of nylon-6,6, which is a polymeric material used in carpet fibers, tire reinforcement, clothing and many other everyday life fields [1,2]. Both single- and two-step oxidation processes have been described for the production of adipic acid by oxidizing cyclohexane with air and nitric acid [3–5] in the industrial scale. However, in the production process of adpic acid, byproducts comprising glutaric acid and succinic acid are also generated at the same time. After adpic acid is separated from the crude product, the residue is always called the mixed dibasic acids, which composition (mass fraction) is: glutaric acid, 50–75%; adipic acid, 15–35%; and succinic acid, 0–30% [6–8].

As is known to all, pure succinic acid and glutaric acid are also important industrial materials which have wide applications in the pesticides, medicine and food additives [9–11]. Therefore, it is necessary to recover the succinic acid, glutaric acid and adipic acid from the mixed dibasic acids with high purity. Although many separation methods have been put forward in the publications up to yet [6–8,12–17], the recovery and separation procedure are quite complex and very difficult in practicing on a commercial scale at present. Solvent crystallization is an effective method in separating the dibasic acids with low cost and high efficiency. The basis of solvent crystallization is solid-liquid phase equilibrium data. Obviously the fundamental of separating the dibasic acids is based on the phase equilibrium data for quaternary system of succinic acid + glutaric acid + adipic acid + solvent. In our previous investigation [18,19], by comparing the solubility data of succinic acid, glutaric acid and adipic acid in some pure organic solvents reported in the literatures [20–28], we find that ethanol is a proper solvent to separate the dibasic acids mixture. The solubility of pure succinic acid, glutaric acid or adipic acid in ethanol have been reported. Recently, the solid-liquid phase equilibrium and the phase diagram for the ternary adipic acid + glutaric acid + ethanol system [18] and the adipic acid + succinic acid + ethanol systems [19] are determined by our research group at (283.15, 303.15, and 313.15) K. However the existing solubility data of binary systems and ternary systems are not enough for constructing the

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quaternary phase diagram for the adipic acid + glutaric acid + succinic acid + ethanol system.

In order to construct the phase diagram of the quaternary system of adipic acid + glutaric acid + succinic acid + ethanol, the main objectives of this research are to (1) investigate the solid-liquid phase equilibrium by using the isothermal saturation method; (2) construct the phase diagram for the ternary succinic acid + glutaric acid + ethanol system at (283.15, 303.15, and 313.15) K by using the Schreinemakers' method of wet residues [29,30]; (3) correlate and calculate the mutual solubility data for the ternary system with Wilson model [31] and NRTL model [32].

Here the Schreinemaker's method of wet residue was described in briefly. As solid-liquid equilibrium is reached, at least one solid and one liquid phase exist in the equilibrium system. The composition of the solid phase is usually measured indirectly, because it is very difficult to remove small amount of adhering mother liquor from them. Schreinemakers' method of wet residues is used in order to get the composition of pure solid phase. The method is on the basis of the application of the straight line rule: points standing for the liquid phase, wet solid phase and the pure solid phase must lie on a single straight line. If we construct straight lines connecting points that represent the liquid phase and the wet residue for several different initial systems and the identical equilibrium solid phases are formed in the system, the straight lines intersect at the point corresponding to the equilibrium solid phase. In this work the Schreinemakers' method of wet residues was used to construct phase diagrams of the ternary system of succinic acid + glutaric acid + ethanol at different temperatures.

2. Experimental section

2.1. Materials and apparatus

The raw materials, glutaric acid and succinic acid having a mass fraction of 0.985 were purchased from Sinopharm Chemical Reagent Co., Ltd., China. They were re-crystallized two times from $CHCl_3$ and then from water. The final purity employed in solubility determination was confirmed by a high performance liquid chromatography (HPLC, Agilent-1260) in our research laboratory, which were 0.995 and 0.997, respectively. The absolute ethanol was also purchased from Sinopharm Chemical Reagent Co., Ltd., China. Its mass fraction was 0.997, which was confirmed by a gas chromatography (type: Agilent 7890A Infinity GC). It was no further purified and used directly in solid-liquid phase equilibrium determination. The detailed information of the raw materials were collected and presented in Table 1.

The apparatus for determination of solid-liquid phase equilibrium used in this work was given in Fig. 1. It included a 100 ml jacketed glass vessel with a magnetic stirrer and a circulating water system. The temperature of circulating water was kept at a desired value by a smart thermostatic water bath with a model of DZKW-4, which had a standard uncertainty of 0.02 K. A condenser was connected to the jacketed glass vessel to prevent the solvent from volatizing. The real temperature of solution was displayed by a mercury glass micro thermometer (standard uncertainty: 0.02 K) inserted in the inner chamber of the jacket glass vessel. An analytical balance (model BSA224S), which was purchased from Sartorius Scientific Instruments (Beijing) Co., Ltd was used to determine the mass of solute, solvent, equilibrium liquid and equilibrium wet solid in this experiment. The standard uncertainty of analytical balance was 0.0001 g. The equilibrium solid phase was identified by a D8 ADVANCE powder X-ray diffractometer (Bruker AXS, Karlsruhe, Germany).

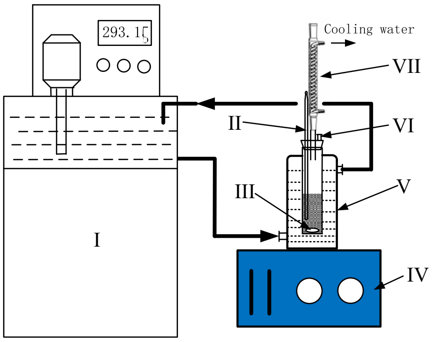

Fig. 1. Schematic diagram of experimental apparatus: I, smart thermostatic water bath; II, mercury-in-glass thermometer; III, magnetic stirrer; IV, stirrer controller; V, jacketed glass vessel; VI, sampling port; VII, condenser.

2.2. Experimental procedure

The solid-liquid equilibrium for the ternary system of succinic acid + glutaric acid + ethanol were obtained by the isothermal saturation method [33–36] at different temperatures under atmosphere pressure, and the high-performance liquid phase chromatograph (HPLC, Agilent-1260) was employed to determine the solubility of succinic acid and glutaric acid in equilibrium liquid phase and wet solid phase.

For the ternary system of succinic acid + glutaric acid + ethanol, initial solutions were prepared as mixtures of excessive amounts of succinic acid and glutaric acid in ethanol with the relevant amounts being chosen to vary the succinic acid/glutaric acid ratio from 0 to 1. The original composition of system was approximately back-calculated based on the "lever rule" and "linking rule". The composition of saturated liquid phase fell in the desired portion of the solubility curve when the constituents were prepared in

Table 1
Sources, purity and properties of materials used in this work.

Chemical name	Source	Initial mass fraction purity	Purification method	Final mass fraction Purity	T_m K	ΔH_m kJ·mol^{-1}	Density (293 K) kg·m^3	Analysis method
Succinic acid	Sinopharm Chemical Reagent Co. Ltd. (China)	0.985	Recrystallization	0.997	457.0[a]	32.95[a]	1572[c]	HPLC[e]
Glutaric acid		0.985	Recrystallization	0.995	371.0[b]	20.90[b]	1424[c]	HPLC[e]
Ethanol		0.997	–	0.997	–	–	789.3[d]	GC[f]

[a] Taken from Refs. [40–43], respectively.
[b] Taken from Refs. [40–43], respectively.
[c] Taken from Refs. [40–43], respectively.
[d] Taken from Refs. [40–43], respectively.
[e] High-performance liquid-phase chromatograph.
[f] Gas chromatography.