J. Chem. Eng. Data **2000,** *45,* 1179−1181 **1179**

Solubility of *o*- and *p*-Aminobenzoic Acid in Ethanol + Carbon Dioxide at 308.15 K to 318.15 K and 15 bar to 85 bar

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The solubility of *o*- and *p*-aminobenzoic acid in ethanol + carbon dioxide (CO_2) was determined at 308.15 K and 318.15 K in the pressure range from 15 bar to 85 bar. The mole fraction of CO_2 in the liquid phase increases with pressure and decreases with temperature. The solubility of the solutes decreases with pressure and increases with temperature.

Introduction

It is well-known that some gases, such as carbon dioxide, can dissolve in many organic solvents in the pressure range from 10 bar to 100 bar, which results in a reduction of the solvency of the organic solvents.[1] As a result, precipitation of the dissolved solutes occurs, and fine particles with narrow size distribution can be obtained.[2−4] This process is termed the gas or supercritical antisolvent process (GAS or SAS) based on the state of the antisolvent.

So far, the GAS or SAS process has been successfully used to recrystallize organic compounds,[5,6] to separate mixtures,[7,8] and to produce finely comminuted particles of high explosives and solid propellants[5] and polymers.[9−12] However, their focuses have been mainly on the effects of operating parameters on the properties of the products, while the knowledge of the solubilities of solids in liquids with gas antisolvents is very limited. There have been several papers on phase equilibria involved in GAS found in the literature,[13−16] and a few systems have been investigated. With the development of GAS or SAS, it becomes important to study the phase equilibria involved in these processes.

In this paper, the solubility of *o*-aminobenzoic acid (*o*-ABA) and *p*-aminobenzoic acid (*p*-ABA) in ethanol + carbon dioxide mixtures was studied. Solubility data of these two chemicals in organic solvents + CO_2 have not been found in a literature survey. This work aims at the effect of CO_2 on the solubility of these two isomers in the liquid phase, which can provide basic data for recrystallizing the two chemicals or separating their mixtures.

Experimental Section

Materials. CO_2 was from Huanxin Gas Co. with a purity of 99.995%. Ethanol was from Beijing Chemical Reagent Plant with a purity of 99.9%. The solutes, *o*- and *p*-ABA, from Beijing Chemical Reagent Plant (AR grade) with purities of 99.5%, were used without further purification.

Apparatus and Procedures. The apparatus and procedures for determining the solubility of *o*- and *p*-ABA in ethanol + CO_2 were described in detail in a previous work.[17] Briefly, the apparatus consisted of a CO_2 cylinder, a high-pressure pump, a solenoid-operated circulating pump, a liquid sample bomb, a view cell, a pressure gauge, a constant-temperature bath, and valves and fittings. A typical experiment was composed of three steps: equilibration, sampling, and sample analysis. The accuracy of the pressure and temperature measurements was ±0.25 bar in the pressure range of 0 bar to 200 bar and within ±0.1 K, respectively. The accuracy of the amount of CO_2 was better than ±0.5 wt %, and that of the solute solubility was within ±0.2 wt %.

Table 1. Experimental Compositions of the Liquid Phase at the Solid−Liquid−Vapor Equilibrium in the System CO_2 (1) + Ethanol (2) + *o*-ABA (3)

pressure/bar	x_1	x_3	pressure/bar	x_1	x_3
		T = 308.15 K			
14.73	0.0799	0.094	47.00	0.272	0.060
25.78	0.124	0.089	53.12	0.315	0.049
36.24	0.179	0.084	59.72	0.408	0.041
36.94	0.192	0.078	66.29	0.533	0.033
41.84	0.213	0.071	67.88	0.626	0.024
		T = 318.15 K			
15.60	0.058	0.100	60.73	0.325	0.065
22.54	0.104	0.099	74.24	0.451	0.039
34.28	0.157	0.093	76.22	0.477	0.038
37.68	0.183	0.090	81.88	0.588	0.031
53.44	0.265	0.073	83.82	0.643	0.028

Table 2. Experimental Compositions of the Liquid Phase at the Solid−Liquid−Vapor Equilibrium in the System CO_2 (1) + Ethanol (2) + *p*-ABA (3)

pressure/bar	x_1	x_3	pressure/bar	x_1	x_3
		T = 308.15 K			
19.03	0.0918	0.037	61.19	0.487	0.013
35.14	0.199	0.036	67.53	0.808	0.0017
39.49	0.233	0.031	68.18	0.814	0.00084
48.43	0.319	0.024	68.42	0.876	0.00072
55.60	0.385	0.019			
		T = 318.15 K			
16.72	0.061	0.047	76.82	0.555	0.011
32.48	0.163	0.042	80.82	0.688	0.0067
46.02	0.242	0.039	81.14	0.825	0.0020
65.87	0.403	0.022			

Results and Discussion

The solubility of *o*- and *p*-ABA in ethanol + CO_2 was determined at 308.15 K and 318.15 K in the pressure range from 15 bar to 85 bar. All experiments were conducted at conditions where the system consists of three phases: vapor phase, liquid phase, and solid phase. There are three components in the liquid phase. This work focuses on the

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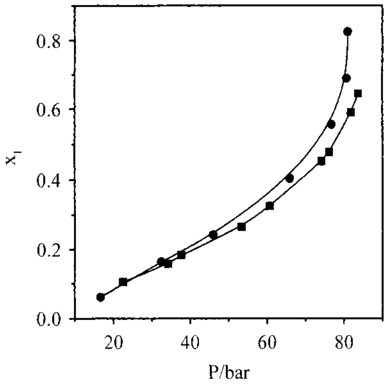

Figure 1. Effect of solutes on the mole fraction of CO_2 (x_1) in the liquid phase at 318.15 K: (■) *o*-ABA; (●) p-ABA.

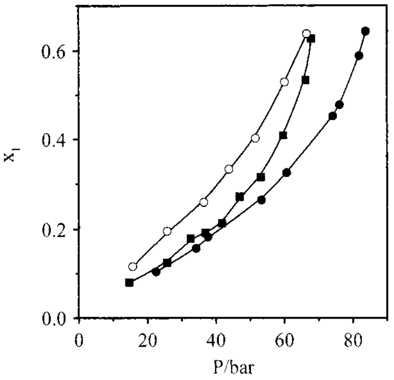

Figure 2. Mole fraction of CO_2 in the liquid phase: (■) with *o*-ABA as the solute at 308.15 K; (●) with *o*-ABA as the solute at 318.15 K; (○) without solute at 308.15 K (ref 18).

effect of temperature and pressure on the composition of the liquid phase. The results are listed in Tables 1 and 2 and shown in Figures 1−5. In the figures and tables, x_1 represents the mole fraction of CO_2 in the liquid phase and x_3 the solubility of solutes in the liquid phase.

Mole Fraction of CO_2 in the Liquid Phase. Figure 1 shows the dependence of the mole fraction CO_2 in the liquid phase on pressure and different solutes. The mole fraction of CO_2 increases with pressure. *o*-ABA and *p*-ABA are isomers, which have the same molecular weight and different molecular structure. The figure also indicates that the solute affects the mole fraction of CO_2, especially at higher pressures.

In Figure 2, the effect of temperature on the CO_2 mole fraction in ethanol with *o*-ABA demonstrates that the mole fraction of CO_2 in the liquid phase decreases with temperature. The figure also compares the effect of solute on the mole fraction of CO_2 in the liquid phase.

Solubility of the Solutes in the Liquid Phase. The solubility of *o*-ABA in ethanol + CO_2 is shown graphically in Figure 3 as a function of pressure at 308.15 K and 318.15 K. The solubility decreases with an increase in pressure, which is caused by the reduction of solvent power of ethanol for the solute because of the increase in the mole fraction of CO_2 in the liquid phase. So, recrystallization of the solute can be carried out by tuning the pressure in a gas antisolvent process.

Figure 3 demonstrates that the solubility of *o*-ABA at 308.15 K is lower at fixed pressure than at 318.15 K. This can be explained from two aspects. In general, the solubility of a solute in a solvent is less at lower temperatures. There is another important reason in the GAS process. The mole fraction of CO_2 in the liquid phase increases at fixed pressure as the temperature decreases, which results in a reduction of the solvating power of the solvent, and thus the solubility of a solute in the liquid phase decreases as the temperature decreases. So, a decrease in temperature is favorable to recrystallizing or precipitating the compound. The effect of temperature on *p*-ABA solubility in the liquid phase shows behavior similar to that on *o*-ABA.

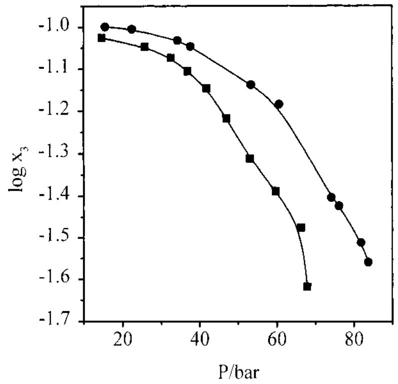

Figure 3. Solubility of *o*-ABA in the liquid phase: (■) 308.15 K; (●) 318.15 K.

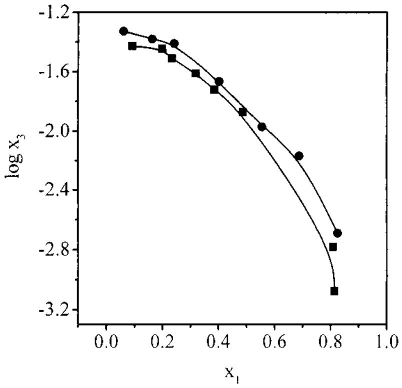

Figure 4. Effect of the mole fraction of CO_2 on the solubility of *p*-ABA: (■) 308.15 K; (●) 318.15 K.

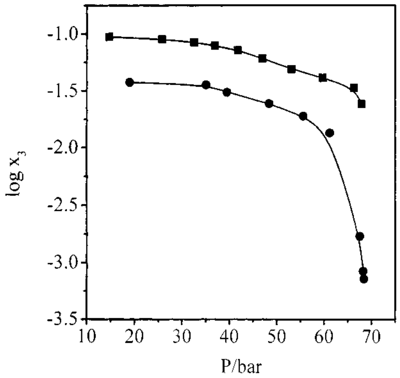

Figure 5. Solubility of *o*- and *p*-ABA in the liquid phase at 308.15 K: (■) *o*-ABA; (●) p-ABA.

Figure 4 shows the effect of the mole fraction of CO_2 on the solubility of *p*-ABA in the liquid phase. It indicates that the solute solubility in the ethanol + CO_2 mixture decreases with an increase in the mole fraction of antisolvent.

Figure 5 shows the solubility curves for *o*- and *p*-ABA at 308.15 K, which indicates that the solubility of *o*-ABA is higher than that of *p*-ABA. The differences in their structures make them behave differently. *o*-ABA can form an intramolecular hydrogen bond, which makes it more soluble in ethanol, so it is expected to be more soluble in ethanol + CO_2 than *p*-ABA. It is expected that the difference in their solubilities should enable them to be separated from a mixture by a CO_2 antisolvent process.

Acknowledgment

The authors are grateful to the National Natural Science Foundation of China for financial support (Grants 29725308 and 29633020).

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Received for review June 20, 2000. Accepted August 24, 2000.

JE000186H