Solubility of Benzoic Acid in Mixed Solvents

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Benzoic acid solubility has been measured in pure water and in the binary mixtures containing different solvents including water, *N,N*-dimethylformamide (DMF), ethanol, or 1,4-dioxane. The experiments were carried out employing the cell used in Oliveira's dissertation. The temperature dependence of the solubility of an acid in two solvents could be evaluated. There was similar influence of the temperature in the solubility of benzoic acid in mixtures of water + DMF and water + 1,4-dioxane. An increase in acid solubility was observed with temperature in all mixtures. Addition of more ethanol in water favors the solubilization of benzoic acid.

Introduction

The chemical industry has produced benzoic and phthalic acids in large quantities.[1,2] It is widely known that several of their ester derivatives are used as intermediates in the preservation of foods, fats, and fruit juices as well in the preparations of resins, plasticizers, dyes, inks, and pharmaceutical products.[3] Because of the property to form toxic metal–benzene polycarboxilic ligands, they are of great interest in the environmental chemistry.

New technologies for separating acid from water solutions may significantly lower the cost of producing and purifying benzoic acid and others. To study this and to perform design calculations of each process, experimental data for liquid–liquid (LLE) and solid–liquid (SLE) equilibrium need to be known.

Many researchers have obtained and published solubility data of acid compounds in water[3,4] and in DMF.[3] Investigations in different areas involving separation process[6–8] are very important as a result of determining equilibrium data for designing and operating industrial equipment.[9,10]

Understanding and obtaining solubility data of benzoic acid and other compounds will help the chemical industry with improvements in separation processes.[1,7,11] The focus of this work is to study the effects of temperature and the addition of an organic solvent in benzoic acid solubility. As well as pure water, more three different organic solvents were employed: ethanol and 1,4-dioxane, which are fully miscible with water, and DMF (*N,N*-dimethylformamide), which is partially miscible with water.

Experimental Section

Materials. In all experiments, bidistilled and deionized water was used. All chemicals were purchased from VETEC Química Fina LTDA. Benzoic acid was more than 99.9 % pure, and organic solvents (ethanol, DMF, and 1,4-dioxane) with a minimum purity of 99.5 % were employed with no further purification.

Procedure and Equipment. The vessel (cell) used is presented in Figure 1. The mixture (acid + solvents) was added in the internal sealed dual-wall flask. Between the outer and inner walls
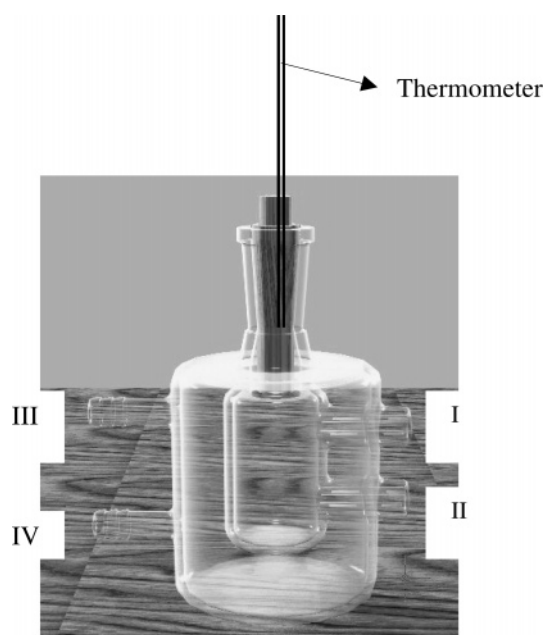

Figure 1. Experimental setup for solubility measurements.

of the flask, water at constant temperature was circulated. The temperature was controlled by a cell thermostated bath (± 0.1 °C). Cell temperature was monitored with a calibrated chromel–alumel thermocouple (± 0.1 °C).

The method consists of the preparation of a saturated solution at constant temperature. The cell was charged with known quantities (± 0.1 mg) of all components. (ADA 210/L, Adam Equipment Co LTDA). In order to reach solution equilibrium conditions, stirring is carried out for at least 1.5 h at constant working temperature. When the same mixture were agitated by a magnetic stirrer for (1, 2, and 3) h, for each time, samples were taken and analyzed; similar values were obtained showing that the equilibrium was achieved within 1 h using the dynamic mixture. Then the solution is settled at least 2 h or more before sampling.

Samples of the solution were withdrawn in two sample points (I, II) using a glass heated syringe with a slightly higher temperature than the solution temperature to avoid any precipi-

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Table 1. Solubility of Benzoic Acid in Water as a Function of Temperature[a]

T^m/K	m^{EXP}/mol·kg^{-1}	T^m_{APE}/K	m^{APE}/mol·kg^{-1}
303.65	0.0300	281.15	0.0173
312.75	0.0431	295.65	0.0297
318.25	0.0482	300.15	0.0340
323.25	0.0554	305.15	0.0398
328.35	0.0595	309.65	0.0407
333.65	0.0677	318.15	0.0594
338.35	0.0728	333.15	0.0976
343.15	0.0779	337.15	0.1210

[a] APE, ref 5.

Table 2. Solubility of Benzoic Acid in Water + DMF at Various Temperatures

x^{DMF}: 2 %		x^{DMF}: 3.4 %	
T^m/K	m/mol·kg^{-1}	T^m/K	m/mol·kg^{-1}
303.65	0.0554	304.20	0.0876
313.31	0.0492	313.73	0.1114
318.10	0.0595	318.34	0.1725
322.60	0.0595	323.06	0.1804
327.66	0.0574	328.46	0.2943
332.25	0.0584	333.07	0.4015
342.20	0.0533	342.80	0.7205

Table 3. Solubility of Benzoic Acid in Water + 1,4 Dioxane at Various Temperatures

$x^{DIOXANE}$: 2 %		$x^{DIOXANE}$: 3.4 %	
T^m/K	m/mol·kg^{-1}	T^m/K	m/mol·kg^{-1}
303.95	0.0740	304.35	0.1180
313.75	0.0990	313.85	0.1685
323.25	0.1663	323.05	0.2500
332.85	0.2150	332.65	0.4600
342.75	0.3193	342.80	0.5570

Table 4. Solubility of Benzoic Acid in Water + Ethanol at Various Temperatures

$x^{ETHANOL}$: 3.2 %		$x^{ETHANOL}$: 5.4 %	
T^m/K	m/mol·kg^{-1}	T^m/K	m/mol·kg^{-1}
309.05	0.0502	309.15	0.0574
317.95	0.0533	317.95	0.0605
322.85	0.0554	322.95	0.0656
327.85	0.0574	328.05	0.0666
332.35	0.0584	332.65	0.0707
338.65	0.0646	339.25	0.0718
347.75	0.0677	347.95	0.0738
355.65	0.0748		

tation. The samples were titrated with standardized 0.1 M NaOH solution. The solubility of benzoic acid was determined by measuring the volume of standard solution added to reach neutralization.

Results and Discussion

The results from the solubility measurements for benzoic acid are given in Tables 1 to 4. In these tables, the following nomenclature was used: m, experimental molality of solute (mol·(kg of solvent)$^{-1}$); x^{SOLV}, mole fraction of solvent (SOLV: DMF, dioxane, or ethanol); and T^m, temperature of the mixture (K).

As indicated in Table 1 and better visualized in Figure 2, the solubility of benzoic acid increased by raising the temperature. Beside it, our results are in good agreement with Apelblat et al.[4] For higher temperatures, a slight disagreement was observed. However, this observation has also been reported in Figure 4 from ref 4, whose data are in disagreement with two references: Yukhno and Bukkulov and Rathousky et al. (cited in Apelblat's work[4]).
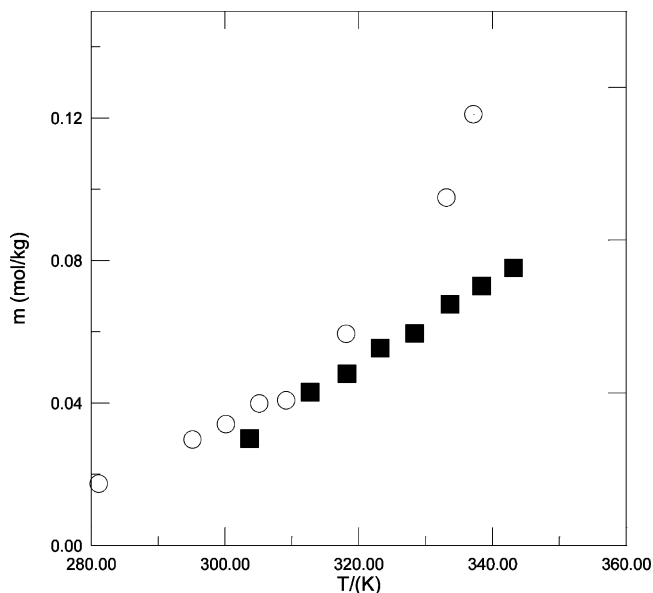
Figure 2. Solubility of benzoic acid in water as a function of temperature: ○, ref 4; ■, this work.
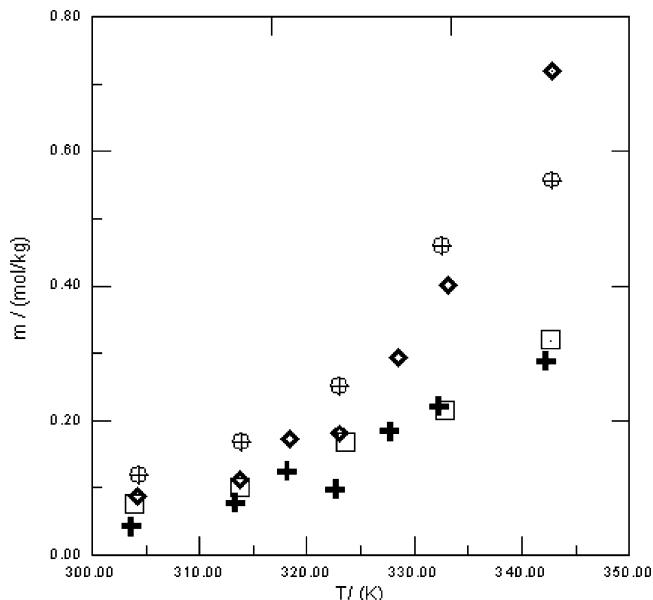
Figure 3. Solubility of benzoic acid in solvent mixtures: +, 2 % in DMF; □, 2 % in dioxane; ◇, 3.4 % in DMF; ⊕, 3.4 % dioxane.

The enthalpy of fusion of benzoic acid (ΔH^f) was determined by fitting the experimental data with the simplified basic equation[7] properly written in Sandler[12] and Cheng et al.[13] for predicting the saturation mole fraction of a diluted solid (x) in a liquid as follows:

$$\ln(x_i\gamma_i^\infty) = \frac{\Delta H_i^f}{R}\left[\frac{1}{T_0} - \frac{1}{T}\right] \quad (1)$$

where T_0 is the temperature of fusion; γ_i is the activity coefficient; R is the gas constant; and for a solute in water, the mole fraction (x) is related to molality (m) as

$$x = \frac{0.018m}{1 + 0.018m} \quad (2)$$

The enthalpy of fusion was regressed using least-square method with eqs 1 and 2 and experimental data reported in Table 1. The activity coefficient was estimated by using Cheng's
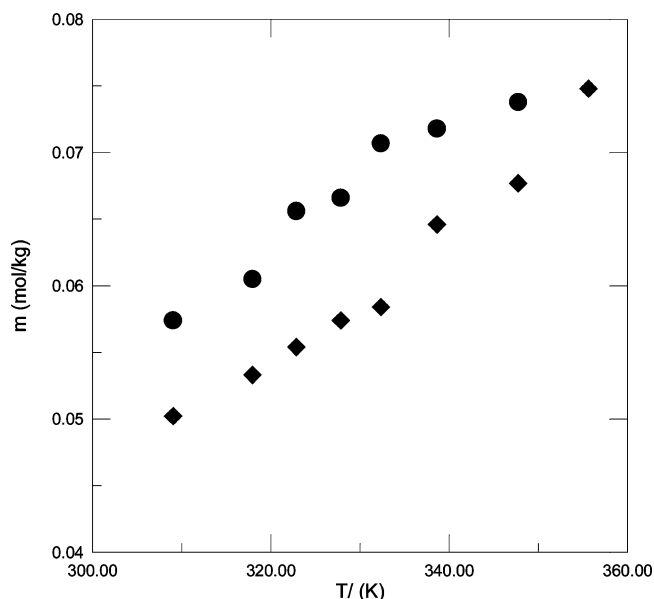
Figure 4. Benzoic acid solubility in mixtures containing ethanol: ◆, 3.2 % in ethanol; ■, 5.4 % in ethanol.

model.[13] For this model (m-DA model), the molecular surface area and volume parameters could be found in Gmehling et al.,[14] and the other parameters were considered for *n*-acid compounds listed in Cheng's Table 2.[13] From the correlated result, 17.2 kJ·mol^{-1} was obtained. Our value is in good agreement with literature[1,2] (15.9 < ΔH_{fusion} < 17.4 kJ·mol^{-1}).

For the ternary systems, there was no data set found for comparison. In Tables 2 and 3, the measured solubility between (303.65 and 342.80) K for benzoic acid in water + DMF and water + 1,4-dioxane solvents are shown. First, it was observed that the solubility increased at the range of temperature studied. Second, if the amount of organic solvent is increased, the solubility will rise in the same way. From Figure 3, it can be observed more easily. Furthermore, the addition of DMF (or 1,4-dioxane) caused significant changes in acid solubility. This behavior was noted when we measured acid solubility in the presence of ethanol. Besides, this effect was strongly noticed as the temperature increase.

In our work, we noticed that the higher the temperature was, the liquid−liquid equilibrium of DMF (or 1,4-dioxane) could be achieved in the vessel. In this sense at the temperature of 342.80 K (for x^{DMF} or $x^{DIOXANE}$ = 3.4 %), a second liquid phase was formed, and then only the result of acid concentration in the aqueous phase was reported in Tables 2 and 3.

The solubility of benzoic acid in water + ethanol mixtures behaved very close to the one in pure water. The values in Table 4 were very similar especially in higher temperatures if we compare them to the ones in pure water. As can be seen, in Figure 4, there was an increasing in acid solubility when the concentration of ethanol in the mixture was increased.

Conclusions

In this work new data were measured for the solubility of benzoic acid in pure water and in mixtures of an organic solvent (DMF, ethanol, and 1,4 dioxane) with water in the temperature range from (303.65 to 355.65) K.

Adding more organic solvent to the mixture, significant changes in acid solubility in mixtures of DMF + water, ethanol + water, and 1,4-dioxane + water were verified. Therefore, the addition of an organic solvent to water favored the solubilization of benzoic acid. There were similarities between the effect of temperature on the solubility of benzoic acid in pure water and in organic solvent−water mixtures.

Further studies are necessary in order to determine the solubility data of solutions when a second phase is formed. It will be possible carrying out experiments in temperatures higher than 342.8 K in water + DMF or water + 1,4-dioxane mixtures.

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