Solubility of Benzoic Acid in Aqueous Solutions Containing Ethanol or *N*-Propanol

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The solubility of benzoic acid in water−ethanol and water−*n*-propanol mixtures at temperatures between (303.5 and 333.7) K has been measured by using an apparatus in our laboratory. Experiments were carried out employing different concentrations of alcohol. Addition of alcohol in water results in a large increase in acid solubility. Owing to a lack of available literature data, no results comparison could be done for systems containing *n*-propanol. Furthermore, the predicted results of solubility for the systems studied over a range of temperatures indicated that both modified equations tested can fairly be used to predict solid−liquid equilibrium for alcoholic aqueous solutions at several temperatures.

Introduction

Solubility data of acid compounds have a broad application and importance in the pharmaceutical industry.[1,2] A variety of pure solvents, including water and solvent mixtures, can usually be employed in a particular crystallization process during manufacturing of pharmaceuticals.[2] Measurements of acid solubilities in water and aqueous solutions have been receiving a growing interest.[3−6] Although there are some experimental phase equilibrium data in aqueous solutions of acids compounds,[3−6] very little are available for no aqueous media.

Benzoic acid is used as a perfume intermediate, dye intermediate, cosmetic flavoring, and preservative.[4] Enhancing the aqueous solubility of benzoic acid and others is of interest because of the challenges in extracting them due to the extremely low aqueous solubilities of these acids. Understanding molecular thermodynamic interactions of acid molecules will help the pharmaceutical and chemical industry with improved separation processes.[7−10] This paper deals with the study of the improvement in acid solubility through the addition of an alcohol to the aqueous medium. Ethanol and *n*-propanol are fully water miscible, and at the same time they help this acid dissolution.

Although the binary water + alcohol is completely miscible with the addition of a third component, acid or salt, a two-liquid-phase region could be formed. In this work, no second-phase formation was observed. Therefore, new systematic data were measured for the solubility of benzoic acid in temperatures ranging between (303.5 and 333.7) K in mixtures of ethanol with water and *n*-propanol with water when no second liquid phase was visually observed.

Experimental Section

Materials. Redistilled deionized water was used throughout. Benzoic acid (99.5 % pure) was purchased from Dinâmica Reagentes Analiticos LTDA. Ethanol and *n*-propanol used were obtained from Isofar and Vetec Química LTDA, respectively. Alcohol products were more than 99.5 % pure. All chemicals were used without further purification.

Experimental Procedure. Investigations on the solubility of benzoic acid in water + ethanol and water + *n*-propanol, in temperatures ranging between (303.5 and 333.7) K, have been carried out.

Data solubilities were measured by using an equilibrium cell, as described in Oliveira et al. (2007), recently. The temperature was measured by using a calibrated thermometer with 0.1 K resolution. The cell was charged gravimetrically with acid and solvents with a precision of ± 0.0001 g. In each temperature, acid solubility was determined by observing no second liquid-phase formation.

Acid-saturated solutions were prepared with varying mass fractions of ethanol and *n*-propanol in bidistilled deionized water. These solutions were allowed to reach equilibrium with excess acid while in the jacketed glass cell where the temperature was controlled by circulating thermostatted water. The equilibrium was sped up by stirring the samples on a magnetic stirrer. After 1 h of stirring and 2 h of decanting, samples were analyzed using Oliveira's procedure.[3] Each experiment was repeated three times. Differently from Oliveira et al., the samples were titrated with standardized 0.01 M NaOH solution. The average relative error of the solubility determination was less than 2 %. In this way, the solubility of benzoic acid, in molality, was obtained with an accuracy (δ_m) between [0.001 and 0.022] $\text{mol}\cdot\text{kg}^{-1}$.

Results and Discussion

The experimental solubilities of benzoic acid with standard deviation obtained in this work are reported in Tables 1 and 2, and consequently, measurements for the two systems, with ethanol (EtOH) and *n*-propanol, are also presented.

From the results shown in Table 1, it is noticed, in general, that increasing alcohol concentration, at the same temperature, favors the dissolution of benzoic acid. A similar performance was observed by Oliveira et al. (2007), who worked with very low concentrations of ethanol in the mixture. It seems that the presence of the alcohol decreases hydrophobic repulsion between water and acid molecules. It was also observed that benzoic acid is more soluble in water with the addition of *n*-propanol compared to the ethanol−water mixtures.

Particularly, in the mixtures examined in this work, no second liquid phase was formed. For all systems with an alcohol

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Table 1. Solubilities of Benzoic Acid in Molalities in Several Mass Fractions of Ethanol (W_1) as a Function of Temperature[a]

W_1	T/K	$m_3 \pm \delta_m$/mol·kg^{-1}
0.0300	303.0	0.0468 ± 0.001
0.0542	303.5	0.0451 ± 0.003
0.0500	302.0	0.0453 ± 0.007
0.0699	304.2	0.0496 ± 0.003
0.0992	304.3	0.0565 ± 0.004
0.1300	303.0	0.0542 ± 0.001
0.1300	304.0	0.0640 ± 0.004
0.0300	313.0	0.0608 ± 0.003
0.0540	313.3	0.0732 ± 0.005
0.0500	314.0	0.0850 ± 0.007
0.0710	314.1	0.0766 ± 0.003
0.0997	314.4	0.0916 ± 0.007
0.1300	313.0	0.0760 ± 0.002
0.1300	313.2	0.0913 ± 0.004
0.0300	324.0	0.0854 ± 0.003
0.0549	323.6	0.1006 ± 0.010
0.0500	323.1	0.1110 ± 0.013
0.0710	323.6	0.1182 ± 0.010
0.0994	323.9	0.1187 ± 0.010
0.1300	323.4	0.1261 ± 0.012
0.1300	323.2	0.1540 ± 0.001
0.0300	333.2	0.1078 ± 0.005
0.0548	333.3	0.1343 ± 0.012
0.0500	334.0	0.1280 ± 0.022
0.0698	333.7	0.1373 ± 0.015
0.1000	333.7	0.2056 ± 0.020
0.1300	333.2	0.2709 ± 0.012
0.1300	333.2	0.2862 ± 0.015

[a] W_1 = Ethanol mass fraction in an acid-free solvent mixture; m_3 = solubility of acid, in molality.

Table 2. Solubilities of Benzoic Acid in Several Mass Fractions of *n*-Propanol (W_1) as a Function of Temperature

W_1	T/K	$m_3 \pm \delta_m$/mol·kg^{-1}
0.0298	303.8	0.0434 ± 0.004
0.0502	303.7	0.0475 ± 0.005
0.0705	304.1	0.0546 ± 0.003
0.0296	313.7	0.0576 ± 0.004
0.0500	313.5	0.0685 ± 0.005
0.0700	313.8	0.0833 ± 0.007
0.0310	323.5	0.0865 ± 0.007
0.0504	322.8	0.1062 ± 0.013
0.0710	323.3	0.1288 ± 0.012
0.0300	333.3	0.1180 ± 0.012
0.0502	332.5	0.1737 ± 0.022
0.0704	332.7	0.1985 ± 0.022

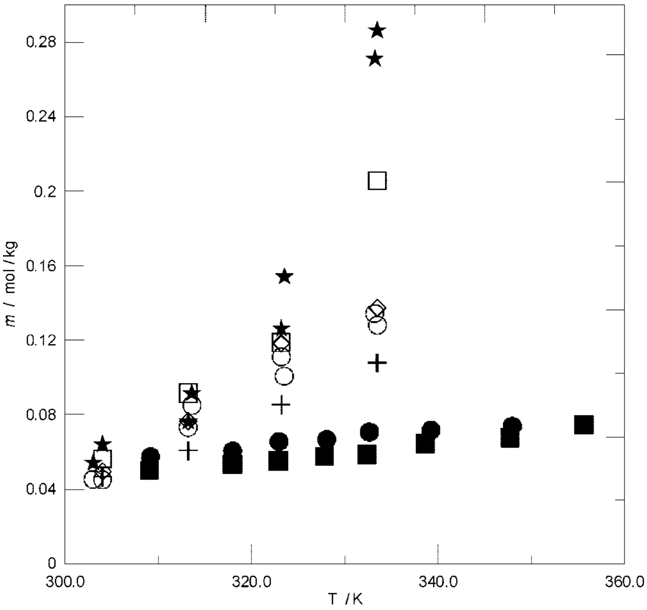

Figure 1. Solubility of benzoic acid in ethanol + water at different temperatures. +, 3 % EtOH; ○, 5 % EtOH; ◇, 7 % EtOH; □, 10 % EtOH; ★, 13 % EtOH; ■, Oliveira et al., 3.2 % EtOH; ●, Oliveira et al., 5.4 % EtOH.

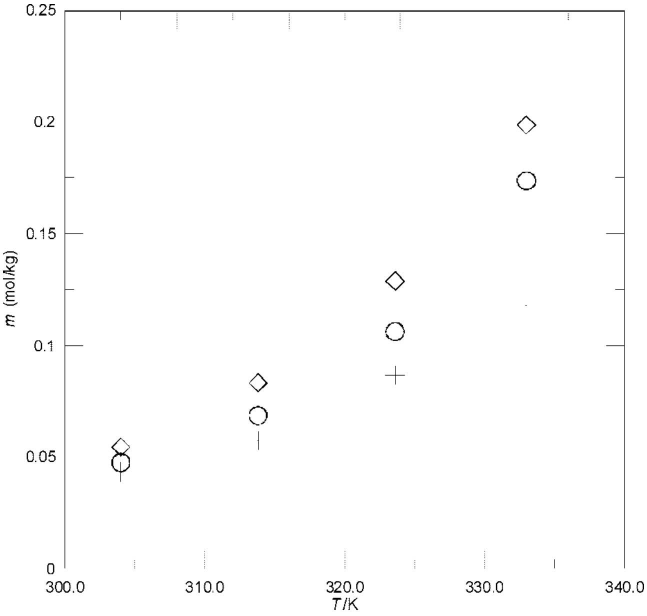

Figure 2. Solubility of benzoic acid in *n*-propanol−water mixtures at different temperatures. +, 3 % *n*-propanol; ○, 5 % *n*-propanol; ◇, 7 % *n*-propanol.

Table 3. Calculated Parameters for Each Equation Used

	parameters eq 1			parameters eq 2		
system	A	B·10^{-3}	C	A'	B'·10^{-3}	C'·10^{-5}
benzoic acid + ethanol + water	4.7130	3.5405	1.4552	4.70	2.2523	9.92827
benzoic acid + *n*-propanol + water	9.4606	3.7026	1.5133	9.45	2.3151	10.30527

concentration higher than 3 %, the acid solubility increases rapidly with rising temperature. Figures 1 and 2 illustrate this behavior and can also show that the effect is less pronounced in *n*-propanol mixtures than in those containing ethanol. To emphasize the differences in the solubilities and solvent compositions, tables have been built using molality (m) units and the standard deviation (δ_m).

Finally, as shown in Figures 1 and 2, at temperatures around 305 K, the influence of alcohol concentration on the solubility data is small and could be essentially neglected. For water−*n*-propanol mixtures, large increases in solubility result from relatively small temperature changes. This observation is clearly confirmed observing the water−ethanol mixtures in the last temperature measured as shown in Figure 2.

According to Figure 1, there is a discrepancy between this work and Oliveira et al. The experimental solubility determined by Oliveira et al. was lower than the one found in this work. There may be two possible reasons for the experimental mistakes. First, it could be due to the solvent (ethanol) loss effect. Probably, the data were taken with the opened cell, and so ethanol vaporization would probably be the main cause of discrepancy between our results and Oliveira's. Second, the titration end-point was not reached effectively. Different from Oliveira et al., in our work, the titration was carried out by using 0.01 NaOH solution which provided a more accurate result while doing the titration.

Regression Analyses. The complete equilibrium equation for the solid−liquid equilibrium is well-described in the literature.[11]

Table 4. Predicted Results for Comparison of the Equations Performance

	this work			eq 1			eq 2		
system	T/K	m_3	δ_m	$\bar{T}$/K	$\Delta\bar{m}$	$(\mathrm{R.D.})_1$	$\bar{T}$/K	$\Delta\bar{m}$	$(\mathrm{R.D.})_2$
benzoic acid + EtOH + water	302.0 to 334.0	0.0451 to 0.2862	0.001 to 0.022	303.0	0.0035	6.8	303.0	0.0034	6.6
				313.0	0.0073	9.1	313.0	0.0073	8.9
				323.0	0.0098	8.3	323.0	0.0099	8.4
				333.0	0.0340	17.7	333.0	0.0340	17.1
benzoic acid + *n*-propanol + water	303.7 to 333.3	0.0434 to 0.1985	0.004 to 0.022	all range	0.006	5.4	all range	0.006	5.9

From this equation, some models or modified equations have been created and support reliable calculations for solubility. For example, expressions given by Heidman et al. (1985) and Yaws et al. (1993) were modified by considering the first constant as a function of the alcohol concentration. Thus

$$\ln m = Aw_1 + \frac{B}{T} + C \ln T \qquad (1)$$

$$\log m = A' w_1 + \frac{B'}{T} + \frac{C'}{T^2} \qquad (2)$$

where m is the solute molality, T (K) is the temperature, and A, B, C, A', B', and C' are the unknown parameters.

For each system, there are 28 and 12 experimental points (m^{expt}, T). These points are fitted via linear regression using eqs 1 and 2. Consequently, parameters are obtained, and the absolute (Δm) and relative deviation $(\mathrm{R.D.})_i$ are calculated as follows

$$(\mathrm{R.D.})_i = 100\frac{m^{\mathrm{expt}} - m^{\mathrm{Eq}(i)}}{m^{\mathrm{expt}}} = 100\frac{\Delta m}{m^{\mathrm{expt}}} \qquad (3)$$

where $m^{\mathrm{Eq}(i)}$ is the molality given by the equation "i". Figures 1 and 2 show the experimental and predicted results for all cases studied here.

Tables 3 and 4, respectively, present the parameters fitted and the absolute and relative deviations for all systems regarded in this article at three or more different compositions of alcohol. According to Table 4, both equations can be used equally to correlate the experimental data for the system in the temperature employed.

Equations 1 and 2 showed that both of them can represent the data with little deviation. However, increasing ethanol composition, the deviation calculated has become unacceptably high.

On one hand, it is noted that for mixtures containing ethanol, as the composition increases, the relative deviation increases. On the other hand, for mixtures containing *n*-propanol, this behavior was not observed.

Conclusions

The apparatus recently presented by Oliveira et al. has been successful in the acid solubility measurements in mixed solvents. However, no comparison or confirmation could be done for systems containing *n*-propanol due to lack of available data.

The results indicate that adding ethanol or *n*-propanol in water can result in a large increase in acid solubility. Ethanol vaporization would probably be the main cause of discrepancy between our results and those of Oliveira et al.

Summing up, the procedure used to achieve the solubility measurements in this publication produces reliable experimental data, and both equations predict results which are also applied in the engineering field.

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