Solubility of Benzoic Acid in Pure Solvents and Binary Mixtures

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The solubility of benzoic acid has been determined in ethanol, toluene, heptane, cyclohexane, pentane, and chloroform and in binary mixtures of ethanol + heptane and ethanol + toluene, in the temperature range of (278.15 to 323.15) K. The solubility is high in ethanol, reasonably high in chloroform, lower in toluene, and quite low in the remaining three pure solvents. In the binary mixtures the solubility of benzoic acid increases with increasing concentration of ethanol. The solubility of benzoic acid increases with increasing temperature.

Introduction

In industry, solubility data in different solvents and temperatures are routinely collected across many different scientific disciplines to enable efficient isolation of a product or an intermediate by crystallization. The solubility properties determine the method of supersaturation generation in crystallization and the yield and productivity of the process. The most common crystallization operations are cooling crystallization, antisolvent crystallization, or a combination of the two. A suitable solvent system amenable for isolation by crystallization should at the starting condition provide a sufficiently high solubility to completely dissolve the product without dramatically increasing the solution volume but also allow for a significant reduction in solubility at the end of the process to reduce product losses and increase process yield. To fulfill these requirements, it is desired to use a solvent system where the effect of temperature on solubility is great (in cooling crystallizations) and/or where the solubility difference between the co- and antisolvent is significant (in antisolvent crystallizations).

Benzoic acid and its salts are used mainly as food preservatives against yeast and mold. It is used to make a large number of chemicals such as phenol, benzoate plasticizers, and so forth. Benzoic acid is also used as a bacteriostatic and bactericidal agent and acts as an antiseptic stimulant and also an ingredient in Whitfield's ointment in the treatment of ringworm. It is also used in cosmetics, resin preparation, plasticizers, and so forth.

In this paper the solubility of benzoic acid in pure ethanol, toluene, heptane, cyclohexane, pentane, and chloroform at different temperatures, (278.15 to 323.15) K, has been investigated. In addition, the solubility has also been determined in binary mixtures of ethanol + toluene and ethanol + heptane. Solubility data of benzoic acid in some pure and binary mixtures are available in the literature.[1−3,6−8] However, there are no experimental data available in the literature for the solubility in heptane, pentane, and chloroform and neither for the solubility in the binary mixtures of ethanol + toluene and ethanol + heptane.

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Experimental Work

Materials. Benzoic acid (CAS No. 65-85-0) of 99.7 % purity was purchased from Merck and was used without further purification. Ethanol (CAS No. 64-17-5) of 99.7 % purity was purchased from Solveco Chemicals, heptane (CAS No. 142-82-5 and purity 99 %), cyclohexane (CAS No. 110-82-7 and purity 99.5 %), and pentane (CAS No. 109-66-0 and purity ≥ 95 %) from VWR, and toluene (CAS No. 108-88-3 and purity (99 to 99.4) %) and chloroform (CAS No. 67-66-3 and purity (99 to 99.4) %) from Merck.

Solubility Measurements. The solubility of benzoic acid was determined by the gravimetric method[4] in pure ethanol, heptane, toluene, cyclohexane, pentane, and chloroform, in a temperature range of (278.15 to 323.15) K. The solubility was also determined in the binary mixtures of ethanol + heptane and ethanol + toluene, in the range of (0 to 50) % by mass of ethanol in the mixture. The solvent mixtures were prepared by weighing the desired amount of each solvent. Benzoic acid saturation was reached by dissolution from a surplus of solid benzoic acid added to the solution. The bottles were placed at a certain temperature, and the solution concentration was recorded over time up to 1 week. The attaining of equilibrium was verified by continuous concentration measurements over time and when there was no change in concentration, that time was considered as the time to reach equilibrium (i.e., 2 h). The temperature was controlled by thermostat baths, and the true temperature was validated by using a calibration mercury thermometer (Thermo-Schneider, Wertheim, Germany, uncertainty of ± 0.01).

The solubility is determined in temperature steps starting at 278.15 K. The bottle with solvent or solvent mixture is initially cooled to 278.15 K at which an amount of benzoic acid is added. The solution is stirred by magnetic stirrer for 2 h and is then turned off to allow the suspended solid phase to settle down for 30 min. Syringes (10 mL) with needles are used to sample (2 to 5) mL of the clear solution from the bottles. Then a filter (PTFE 0.2 μm) is mounted on the syringe through which the solution is transferred into preweighed glass vials. The weight of the glass vial with the saturated solution is recorded. The samples are then dried in ventilated laboratory hoods at room temperature (293.15 K). The solid sample mass is recorded

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Table 1. Mole Fraction Solubility of Benzoic Acid in Pure Solvents[a]

	x					
T/K	ethanol	chloroform	toluene	cyclohexane	pentane	heptane
278.15	0.128 (0.0014)	0.074 (0.0002)	0.035 (0.0001)		0.004 (0.0001)	0.005 (0.0001)
283.15	0.139 (0.0021)	0.086 (0.0002)	0.043 (0.0003)	0.006 (0.0001)	0.005 (0.0001)	0.006 (0.0001)
293.15	0.166 (0.0011)	0.114 (0.0001)	0.062 (0.0005)	0.009 (0.0001)	0.007 (0.0002)	0.010 (0.0001)
303.15	0.196 (0.0002)	0.151 (0.0005)	0.089 (0.0006)	0.015 (0.0001)	0.011 (0.0003)	0.015 (0.0002)
313.15	0.234 (0.0011)	0.196 (0.0013)	0.128 (0.0003)	0.025 (0.0001)		0.022 (0.0002)
323.15	0.276 (0.0021)	0.253 (0.0012)	0.178 (0.0002)	0.039 (0.0005)		0.033 (0.0002)

[a] The average of four samples; the standard deviation is in parentheses.

Table 2. Mole Fraction Solubility of Benzoic Acid in Binary Solvent Mixtures of Ethanol (2) + Heptane (1)[a]

	100 w_1					
T/K	0	10	20	30	40	50
	x					
278.15	0.128 (0.0014)	0.121 (0.0008)	0.112 (0.0005)	0.102 (0.0003)	0.092 (0.0002)	0.079 (0.0002)
283.15	0.139 (0.0021)	0.132 (0.0007)	0.123 (0.0005)	0.111 (0.0022)	0.101 (0.0003)	0.087 (0.0002)
293.15	0.166 (0.0011)	0.158 (0.0003)	0.147 (0.0011)	0.135 (0.0009)	0.124 (0.0006)	0.107 (0.0005)
303.15	0.196 (0.0002)	0.188 (0.0009)	0.178 (0.0007)	0.164 (0.0016)	0.145 (0.0007)	0.132 (0.0007)
313.15	0.234 (0.0011)	0.227 (0.0007)	0.216 (0.0002)	0.203 (0.0005)	0.187 (0.0021)	0.165 (0.0005)
323.15	0.276 (0.0021)	0.271 (0.0007)	0.261 (0.0005)	0.246 (0.0007)	0.224 (0.0012)	0.203 (0.0009)

[a] The average of four samples; the standard deviation is in parentheses. w_1 = the mass fraction of heptane in ethanol on a solute-free basis.

Table 3. Mole Fraction of Benzoic Acid in Binary Solvent Mixtures of Ethanol (1) + Toluene (2)[a]

	100 w_2					
T/K	0	10	20	30	40	50
	x					
278.15	0.128 (0.0014)	0.127 (0.0004)	0.125 (0.0004)	0.123 (0.0002)	0.119 (0.0003)	0.112 (0.0002)
283.15	0.139 (0.0021)	0.138 (0.0005)	0.137 (0.0003)	0.133 (0.0006)	0.129 (0.0003)	0.122 (0.0002)
293.15	0.166 (0.0011)	0.163 (0.0008)	0.161 (0.0009)	0.157 (0.0005)	0.152 (0.001)	0.145 (0.0001)
303.15	0.196 (0.0002)	0.194 (0.0002)	0.191 (0.0009)	0.186 (0.0003)	0.181 (0.0003)	0.172 (0.0001)
313.15	0.234 (0.0011)	0.231 (0.0004)	0.227 (0.0011)	0.222 (0.0005)	0.214 (0.0013)	0.203 (0.0001)
323.15	0.276 (0.0021)	0.273 (0.0015)	0.266 (0.0012)	0.262 (0.0011)	0.254 (0.0004)	0.243 (0.0008)

[a] The average of four samples; the standard deviation is in parentheses. w_2 = the mass fraction of toluene in ethanol on a solute-free basis.

repeatedly throughout the drying process to establish the point where the mass remained constant. The mass of the final dry sample is then used for the calculation of the solubility. The balance used during the experimental work has a resolution of ± 0.0001 g. For each data point an average of four measurements are reported, two samples each from two equal experimental solutions. After taking the samples from the saturated solution at 278.15 K, the solution is heated to 283.15 K, then to 293.15 K, and so on up to 323.15 K for further measurements, of course always assuring that solid benzoic acid is present at equilibrium. To sample the solution at high temperatures of (293.15 to 323.15) K, preheated syringes are used to avoid crystallization in the syringes. The uncertainty of the solubility values based on the repeated observations is within 1 % for all of the solubilities in pure solvents and mixtures.

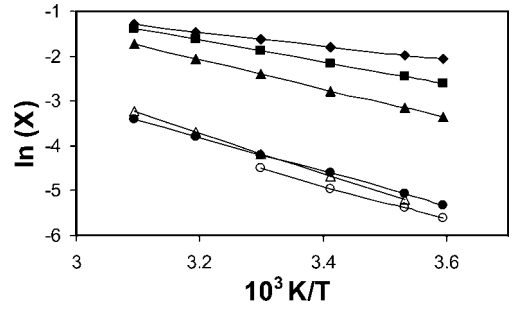

Figure 1. Solubility (moles of solute/moles total) of benzoic acid in pure solvents between (278.15 and 323.15) K (average of four samples): ♦, ethanol; ■, chloroform; ▲, toluene; △, cyclohexane; ●, heptane; ○, pentane. Lines are calculated using eq 1.

Results and Discussion

The mole fraction solubility of benzoic acid in the pure solvents is shown in Table 1. The mole fraction solubility of benzoic acid in the binary solvent mixtures is reported in Tables 2 and 3. Since the melting temperature of cyclohexane is 279.15 K and the boiling temperature of pentane is 309.15 K, the data for these solvents do not cover the entire temperature range. By converting the experimental solubility into mole fraction solubility, x, a so-called van't Hoff plot can be established and is shown in Figure 1 for the pure solvents. The mole fraction solubility in each binary solvent system is given in Figure 2 and 3. As expected, the solubility in heptane and toluene is much lower than in ethanol, and in the binary mixtures the solubility decreases nonlinearly with the increasing fraction of the nonpolar solvent. The solubility difference between the cosolvent (i.e., ethanol) and the antisolvent (i.e., heptane and toluene) increases as the temperature is reduced, and this leads to that the curves in Figure 2 and 3 diverge somewhat at increasing antisolvent concentration.

In the current contribution, the solubility of benzoic acid has been determined as a function of temperature in a total of six pure solvents and 10 binary solvent mixtures. The solubility of benzoic acid is low in all pure solvents besides ethanol and chloroform. The molar solubility decreases in the order ethanol, chloroform, toluene, heptane, cyclohexane, and pentane. The solubility of benzoic acid is decreasing with the increasing fraction of toluene or heptane, respectively, in the binary mixtures. With increasing temperature the solubility of benzoic acid increases for all solvents and solvent mixtures. The

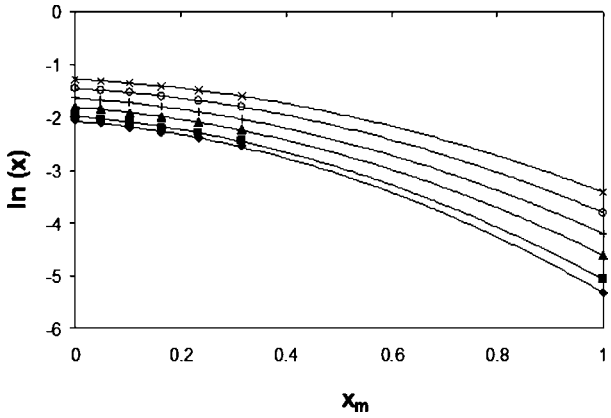

Figure 2. Mole fraction solubility of benzoic acid in mixtures of heptane + ethanol (x_m is specified as the mole fraction of heptane in the solvent mixture on a solute-free basis) between (278.15 and 323.15) K (average of four samples). ♦, 278.15 K; ■, 283.15 K; ▲, 293.15 K; +, 303.15 K; ○, 313.15 K; ×, 323.15 K. Lines are calculated using eq 2.

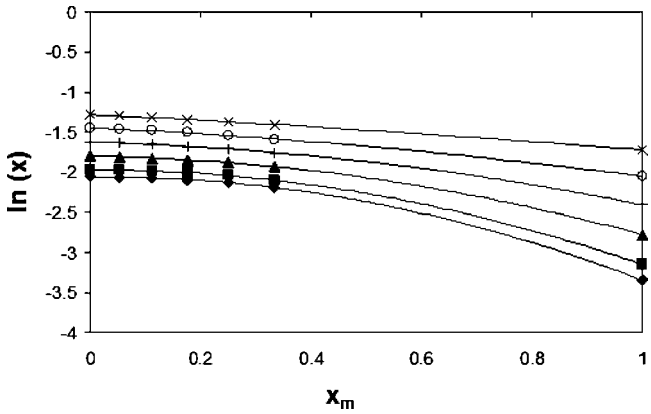

Figure 3. Mole fraction solubility of benzoic acid in mixtures of toluene + ethanol (x_m is specified as the mole fraction of toluene in the solvent mixture on a solute-free basis) between (278.15 and 323.15) K (average of four samples). ♦, 278.15 K; ■, 283.15 K; ▲, 293.15 K; +, 303.15 K; ○, 313.15 K; ×, 323.15 K. Lines are calculated using eq 2.

relationship between solubility and temperature has been explored in detail in previous contributions for a number of organic compounds.[1,4,5] The general rule is that the lower the mole fraction solubility the higher is the temperature dependence, that is, the higher is the van't Hoff enthalpy of solution. This relationship can be readily observed in Figure 2. At 298.15 K the solubility of benzoic acid in ethanol and toluene (0.5839 and 0.1034) is in good agreement with the values given in the literature (0.584 and 0.106).[6] The solubility of the benzoic acid in toluene and cyclohexane is shown in Figure 4.[7,8] The values for the solubility of benzoic acid in toluene given in the literature[7] are lower than the values given in this work. The literature work was done almost 90 years ago, and the experimental procedure has ignored some errors. The solubility of benzoic acid and cyclohexane is shown in Figure 4 and is in good agreement with the literature values.[8]

The temperature dependence of the solubility can be well-correlated by the nonlinear equation

$$\ln x = A(T/\mathrm{K})^{-1} + B + C(T/\mathrm{K}) \qquad (1)$$

where x is the mole fraction solubility, T is the absolute temperature, and A, B, and C are regression coefficients that are listed in Tables 4, 5, and 6. Overall, for all of the correlations

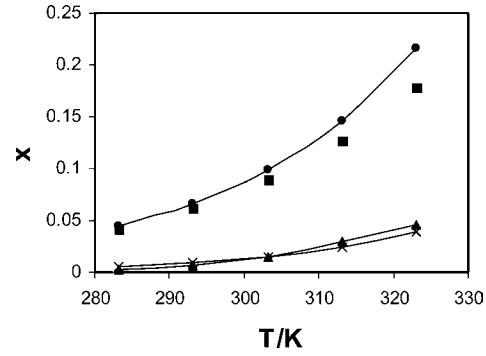

Figure 4. Comparison of the solubility of benzoic acid in toluene (●, experimental; ■, literature) and cyclohexane (×, experimental; ▲, literature).

Table 4. Regression Coefficients of Equation 1 for the Solubility of Benzoic Acid in Pure Solvents in the Temperature Range of (278.15 to 323.15) K

solvent	10^{-2} A	B	10^{2} C
ethanol	−1.0231	−6.1372	1.599
chloroform	−14.9275	−0.2008	1.066
toluene	−19.2702	−0.4993	1.466
cyclohexane	−16.8388	−7.9394	3.071
pentane	4.4493	−20.9245	4.932
heptane	−38.0341	8.4537	−0.032

Table 5. Regression Coefficients of Equation 1 for the Solubility of Benzoic Acid in Ethanol + Heptane Mixtures in the Temperature Range of (278.15 to 323.15) K and Solvent Composition in Mass Fraction of Heptane (1) + Ethanol (2) on a Solute-Free Basis

100 w_1	10^{-2} A	B	10^{2} C
0	−1.0231	−6.1372	1.599
10	1.4762	−8.0981	1.961
20	4.6488	−10.5239	2.396
30	6.1357	−11.8822	2.657
40	−0.5766	−7.5864	1.942
50	3.6213	−10.8402	2.515

Table 6. Regression Coefficients of Equation 1 for the Solubility of Benzoic Acid in Ethanol + Toluene in the Temperature Range of (278.15 to 323.15) K and Solvent Mass Fraction of Toluene (2) + Ethanol (1) on a Solute-Free Basis

100 w_2	10^{-2} A	B	10^{2} C
0	−1.0231	−6.1372	1.599
10	1.0134	−7.4855	1.818
20	−1.3948	−5.8245	1.527
30	1.6961	−7.9302	1.877
40	1.8489	−8.0594	1.893
50	1.4659	−7.9388	1.878

the correlation coefficient (R^2) exceeds 0.9996. For pure solvents the solubilities calculated with eq 1, with parameters in Table 4, are shown in Figure 1 and for binary mixtures in Tables 5 and 6.

At a constant temperature, the dependence of the solubility on solvent composition in the binary mixtures of ethanol + heptane and ethanol + toluene is well-described by a second-order polynomial:

$$\ln(x) = Dx_m^{\,2} + Ex_m + F \qquad (2)$$

where x is the mole fraction solubility and x_m is the mole fraction on solute-free basis of the nonpolar solvent in the solvent binary mixture. D, E, and F are regression coefficients at each temperature and are listed in Tables 7 and 8. Overall, for all of the correlations, the correlation coefficient (R^2) exceeds 0.9992.

Table 7. Regression Coefficients of Equation 2 for the Solubility of Benzoic Acid in Ethanol (2) + Heptane (1) Binary Mixtures on a Solute-Free Basis at Different Temperatures

T/K	*D*	*E*	*F*
278.15	−2.4718	−0.7744	−2.0703
283.15	−2.2985	−0.7855	−1.9833
293.15	−2.0535	−0.7433	−1.8068
303.15	−1.8902	−0.6747	−1.6343
313.15	−1.8166	−0.5303	−1.4552
323.15	−1.649	−0.4861	−1.2814

Table 8. Regression Coefficients of Equation 2 for the Solubility of Benzoic Acid in Ethanol (1) + Toluene (2) Binary Mixtures on a Solute-Free Basis at Different Temperatures

T/K	*D*	*E*	*F*
278.15	−1.3395	0.0536	−2.062
283.15	−1.1829	0.0055	−1.9739
293.15	−0.8723	− 0.104	−1.8023
303.15	−0.5929	−0.1891	−1.628
313.15	−0.2943	−0.3157	−1.4475
323.15	−0.1092	−0.3344	−1.2831

The solubilities calculated with eq 2, with parameters in Tables 7 and 8 are shown in Figures 2 and 3.

Conclusions

The solubility of benzoic acid in the pure solvents of the present work is low with exception for chloroform and ethanol. The molar solubility decreases in the order of ethanol, chloroform, toluene, heptane, cyclohexane and pentane. In binary solvent mixtures with ethanol, the solubility of benzoic acid decreases with increasing concentration of heptane and toluene, respectively. The solubility increases with increasing temperature for all of the solvents and solvent mixtures of the work.

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