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Extraction Equilibria of Benzoic Acid with Tributyl Phosphate in Kerosene and 1-Octanol

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Liquid−liquid equilibrium data of benzoic acid in the systems water + solvent, with tributyl phosphate as extractant and kerosene as diluent, and water + pure 1-octanol are presented. The total benzoic acid concentration in the organic phase increases with an increase of tributyl phosphate concentration, and the extractability of benzoic acid with 1-octanol is equivalent to that with 30 vol % tributyl phosphate in kerosene. Most benzoic acids exist as dimers in the organic phase of tributyl phosphate + kerosene except for the organic phase of pure tributyl phosphate. On the basis of the mass action law and suitable assumptions, the distribution coefficient for benzoic acid with tributyl phosphate is derived, and the apparent equilibrium constants, K_{11} and K_{12}, are evaluated by nonlinear regressions.

Introduction

Recovery of organic chemicals in dilute solution can be achieved by solvent extraction,[1] and this method has received increasing attention. Organic solvents used for extraction can be classified into three major types: (1) conventional oxygen-containing and hydrocarbon solvents, (2) phosphorus-bonded oxygen-containing extractants, and (3) higher molecular weight aliphatic amines.[1] For carboxylic acid, the first type of solvents such as ketones and alcohols give rather low distribution coefficients especially for those with short carbon chains,[2] while the second and the third types of solvents, which have a higher distribution coefficient, such as tributyl phosphate (TBP),[3,4] trialkyl phosphine oxide (TRPO),[5] and aliphatic amines,[2,4,6] have been used in the extraction of carboxylic acid, acetic acid,[2,5−7] lactic acid,[6,8] propionic acid,[6,9] butyric acid,[6] succinic acid,[10] and so forth.

Benzoic acid is an important chemical, commonly used in human foods, animal feed additives, and pharmaceuticals, and used as the intermediate for production of phenol and caprolactam. Generally, the industrial effluent resulting from the production of benzoic acid by oxidating toluene also contains about 0.3 mol·L^{-1} benzoic acid.[11] Since benzoic acid is a medium−strong acid (pK_a = 4.20[12]) and has a higher hydrophobicity (1.87[13]) than most carboxylic acids, all types of solvents could be used for recovering benzoic acid from dilute solution according to the reactive extraction rules and the physical extraction rules; for example, kerosene is used as the standard solvent, commonly used in the study of extraction behaviors in extractors. However, an evaluation of all types of solvent for extraction of benzoic acid, especially the phosphorus-bonded oxygen-containing extractant, is not available in the literature.

In this work, liquid−liquid equilibrium data of benzoic acid in the systems water + solvent, with tributyl phosphate as extractant and kerosene as diluent, and water + pure 1-octanol are measured, and a mathematical model based on mass action law is determined to describe the results.

Materials and Methods

Chemicals. Benzoic acid, tributyl phosphate, and 1-octanol used from Beijing Chemical Co. are analytical reagents, and the extractant tributyl phosphate has a purity > 99 mass %. The diluent kerosene was obtained from Petrochemical China, contained more than 98.3 mass % alkane, and was pretreated first with 98 mass % sulfuric acid, solid NaOH, and distilled water successively in use. The physical properties of the solvents obtained from the manufactures are listed in Table 1. The mixed extractant of tributyl phosphate and kerosene has a tributyl phosphate molar concentration from 0.365 mol·L^{-1} (10 vol % tributyl phosphate + 90 vol % kerosene) to 3.653 mol·L^{-1} (pure tributyl phosphate).

Extraction Experiments. All extraction experiments were conducted with 50 mL flasks at 25 ± 2 °C. Solvent (15 mL) and 15 mL of the benzoic acid solution without adjusting the solution pH were added to each flask. The flask containing the mixture was shaken for about 20 min by hand in air, and then the mixture was left to equilibrate for 2−4 h, followed by separation of the two phases. An aqueous-phase sample was then taken from the bottom layer (aqueous phase) using a syringe with a long needle for pH and solute concentration analyses at room temperature (25 ± 2 °C).

It was noted that, after extraction, no significant volume change was observed, as the initial benzoic acid concentration in the aqueous phase was low.

Sample Analysis. The molar concentrations of benzoic acid in the aqueous phase, C_{aq}, were measured using a HP-8452 UV spectrometer at 270 ± 2 nm. The concentrations of benzoic acid in the organic phase, C_{org}, were calculated by material balance. The preliminary experiment of stripping of the organic phase indicated that the deviation of calculating values of benzoic acid concentrations in the organic phase was within 2%. The pH value of the aqueous phase was determined with a pH meter (Hanna pH 201 model) with a deviation of ±0.02.

Results and Discussion

Results. The equilibrium data at various tributyl phosphate concentrations are given in Table 2 and Figure 1 and

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Table 1. Physical Properties of the Solvents

name	formula	avg MW	viscosity η/Pa·s	density ρ/g·cm^{-3}
tributyl phosphate	$(C_4H_9O)_3PO$	266.37	0.00332 (25 °C)	0.973 (25 °C)
kerosene		170−310 °C[a]	0.00194 (20 °C)	0.752 (20 °C)
1-octanol	$CH_3(CH_2)_7OH$	130.23	0.01064 (15 °C)	0.826 (20 °C)

[a] Distillation range.

Table 2. Equilibrium Data of Benzoic Acid between Water and Tributyl Phosphate in Kerosene

		total equil conc of benzoic acid	
init TBP conc	equil pH in aq phase	10^3(conc in aq phase)	conc in org phase
mol·L^{-1}		mol·L^{-1}	mol·L^{-1}
0.365	4.27	0.929	0.013
0.365	4.03	1.253	0.028
0.365	3.84	1.777	0.055
0.365	3.72	2.145	0.069
0.365	3.65	2.551	0.084
0.365	3.64	3.370	0.109
0.365	3.49	5.102	0.162
0.365	3.32	10.305	0.272
0.731	3.65	1.310	0.054
0.731	3.61	1.384	0.063
0.731	3.50	2.289	0.091
0.731	3.52	2.645	0.112
0.731	3.40	4.066	0.165
0.731	3.31	7.394	0.254
1.096	3.80	1.245	0.053
1.096	3.78	1.310	0.065
1.096	3.75	1.503	0.077
1.096	3.68	1.544	0.105
1.096	3.59	2.170	0.157
1.096	3.44	3.845	0.262
1.826	3.78	0.921	0.072
1.826	3.75	1.056	0.093
1.826	3.69	1.212	0.114
1.826	3.65	1.503	0.159
1.826	3.52	2.375	0.274
2.740	4.01	0.264	0.026
2.740	3.76	0.363	0.054
2.740	3.70	0.402	0.065
2.740	3.64	0.452	0.080
2.740	3.59	0.527	0.103
3.653	3.82	0.123	0.026
3.653	3.81	0.227	0.050
3.653	3.78	0.283	0.067
3.653	3.76	0.364	0.082
3.653	3.74	0.461	0.107
3.653	3.68	0.679	0.164
3.653	3.62	1.331	0.282

show that the equilibrium benzoic acid concentration in the organic phase increases with an increase of tributyl phosphate concentration. This is similar to the equilibrium behavior of carboxylic acid with trialkyl phosphine oxide and trioctylamine.[14,15] It has been reported that tributyl phosphate associates a carboxyl group with the hydrogen bond,[16] so this tributyl phosphate concentration effect could be explained by the extractant concentration effect alone.

Similarly, the extraction equilibrium of benzoic acid with 1-octanol is shown in Table 3 and Figure 1. Since 1-octanol is a polar solvent and the value of the hydrophobicity of benzoic acid is high enough, the extractability of benzoic acid with 1-octanol is higher than that of most carboxylic acids and is equivalent to the extractability of benzoic acid with 30 vol % tributyl phosphate (1.096 mol·L^{-1} tributyl phosphate).

Stoichiometry of Complex Formation of Tributyl Phosphate and Benzoic Acid. Most organic acids, also benzoic acid, exist as dimers in the organic phase because of their strong intermolecular hydrogen bonding, especially in nonpolar solvents, for example, kerosene.[1,16] The stoichiometry of complex formation of tributyl phosphate and benzoic acid in the organic phase is determined first by the following method, similarly as in ref 17.

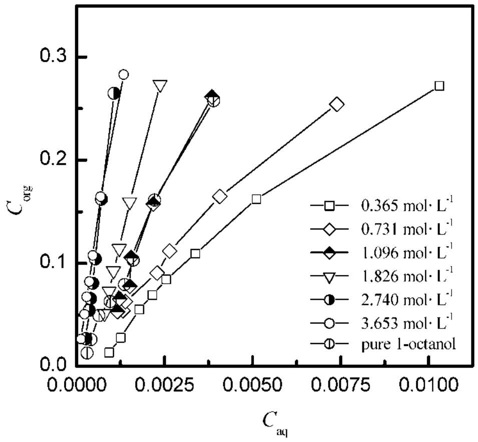

Figure 1. Equilibrium data of benzoic acid between water and tributyl phosphate or 1-octanol.

Table 3. Equilibrium Data of Benzoic Acid between Water and 1-Octanol

	total equil conc of benzoic acid	
	10^3(conc in aq phase)	conc in org phase
equil pH in aq phase	mol·L^{-1}	mol·L^{-1}
4.12	0.291	0.067
3.98	0.414	0.034
3.80	0.631	0.063
3.73	0.946	0.081
3.67	1.364	0.102
3.65	1.609	0.133
3.55	2.215	0.209
3.38	3.890	0.334

Using the mass action law[1] and neglecting physical partitioning of benzoic acid between kerosene and water because of the low distribution coefficient ($D \sim 1$), the extraction equilibrium for benzoic acid can be written as a reaction of one molecule of tributyl phosphate (TBP) and p molecules of benzoic acid (HA) to form a (1, p) complex. With respect to the apparent equilibrium constants, K_{1p}

$$\mathrm{TBP}_{\mathrm{org}} + p\mathrm{HA} \xleftrightarrow{K_{1p}} \mathrm{TBP}{\cdot}p\mathrm{HA}_{\mathrm{org}} \tag{1}$$

where the organic phase is denoted by the subscript org.

The distribution coefficient, D, is defined as the total molar concentration of benzoic acid (all forms) in the organic phase, divided by that in the aqueous phase. With appropriate material balances, D can be expressed as

$$D = \frac{[\mathrm{TBP}{\cdot}p\mathrm{HA}]_{\mathrm{org}}}{[\mathrm{HA}] + [\mathrm{A}^-]} = \frac{pK_{1p}S_0[\mathrm{HA}]^{p-1}}{(1 + K_{1p})[\mathrm{HA}]^p} \tag{2}$$

where S_0 is the initial molar concentration of tributyl phosphate in the organic phase.

The extraction equilibrium constant, K_{1p}, is evaluated from eq 2 by the regression of the experimental data. As shown in Table 4, the p value for various extractants is

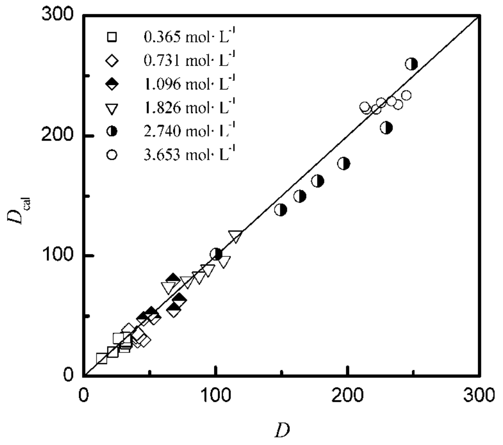

Figure 2. Comparison of calculated D_{cal} and the experimental distribution coefficient *D*.

Table 4. Model Parameters for the Equilibrium Data of Benzoic Acid in the System Water + Tributyl Phosphate in Kerosene

init TBP conc S_0/mol·L^{-1}	p	K_{11}/mol·L^{-1}	K_{12}/mol·L^{-1}
0.365	1.251	88	100
0.731	1.096	50	55
1.096	1.395	50	180
1.826	1.511	50	200
2.740	1.481	50	800
3.653	0.997	88	0

between 0.997 and 1.511. The value of p can be explained by the fact that the stoichiometries of complex formation of tributyl phosphate and benzoic acid are 1,1 and 1,2.

Equilibrium Description. On the basis of mass action law and the above stoichiometry analysis of complex formation of benzoic acid and tributyl phosphate, the extraction equilibrium can be described by a set of equilibria involving the dissociation equilibrium of benzoic acid in the aqueous phase, the formation of two types of complexes (1,1) and (1,2) with tributyl phosphate and benzoic acid in a stepwise association manner, and the extraction taking place at the organic-aqueous interface. The distribution coefficient can be derived as

$$D = \frac{S_0(K_{11} + 2K_{11}K_{12}[\mathrm{HA}])}{(1 + K_{11}[\mathrm{HA}] + K_{11}K_{12}[\mathrm{HA}]^2)(1 + 10^{\mathrm{pH}-\mathrm{p}K_a})} \quad (3)$$

K_{11} and K_{12} represent the apparent equilibrium constants of the (1:1) and (1:2) complexes, respectively.

The two constants, K_{11} and K_{12}, are obtained by fitting the experimental data to eq 3 using nonlinear regressions. As shown in Figure 2, the predicted curves superimpose the data very well. Thus, the model is valid in representing the extraction equilibrium of benzoic acid with tributyl phosphate + kerosene. The K_{11} and K_{12} fitted are listed in Table 4 and show that K_{11} and K_{12} depend on the initial tributyl phosphate concentration in the organic phase. The tendency of K_{12} with S_0 is similar to that of the p values; that is, most benzoic acids exist as dimers in the organic phase of tributyl phosphate + kerosene except for the organic phase of pure tributyl phosphate, which could be explained by the effect of the polar solvent on the organic acid dimer. For the K_{11} dependence on S_0, maybe it results from the interfacial sorption of tributyl phosphate in a nonpolar diluent of kerosene.[18]

Conclusions

This work has shown the equilibrium data of benzoic acid in the system water + extractant with tributyl phosphate in kerosene, and the data of pure 1-octanol. The total benzoic acid concentration in the organic phase increases with an increase of the concentration of total benzoic acid in the aqueous phase and tributyl phosphate. The extractability of benzoic acid with 1-octanol is equivalent to that with 30 vol % tributyl phosphate. On the basis of the mass action law and suitable assumptions, the distribution coefficient for benzoic acid with tributyl phosphate is derived, and K_{11} and K_{12} are evaluated by nonlinear regressions. Most benzoic acids exist as dimers in the organic phase of tributyl phosphate + kerosene except for the organic phase of pure tributyl phosphate.[18]

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