Solvent Extraction and Association of Nitrophenols with Trioctylphosphine Oxide in Cyclohexane

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Synopsis. Extraction of phenol and nitrophenols into cyclohexane and association of these phenols with trioctylphosphine oxide (TOPO) in the organic phase were investigated at 298 K. A linear relation was found between the logarithm of the partition coefficient of the phenols and the logarithm of their association constant with TOPO.

In the course of a study on solvent extraction of mono- and dinitrophenols with trioctylphosphine oxide (TOPO) in cyclohexane, we found that the extractability of these nitrophenols depends on the position of the nitro group. This was explained in terms of a difference in the partition of these phenols between water and cyclohexane and in the formation of hydrogen-donor–acceptor complexes with TOPO in the organic phase. Since cyclohexane is an inert solvent, the interactions with water may be reflected in the partition coefficient of the phenols. The association constant of the phenols with TOPO should reflect the degree of hydration of the phenols in the aqueous phase because water is a hydrogen-bond acceptor though it is weaker than TOPO. In what follows, phenol and the nitrophenols are called "acids".

Experimental

The nitrophenols and TOPO were purified by recrystallization. Phenol and cyclohexane were of reagent grade. All the experiments were carried out in a room thermostated at 298 K. A prescribed amount of the acid was dissolved in an aqueous 1 mol dm^{-3} hydrochloric acid. Five to seven milliliters of the aqueous solution and the same volume of a cyclohexane solution containing a weighed amount of TOPO were placed in a stoppered glass tube (capacity 20 cm^3). The two phases were mechanically agitated for 15 min and centrifuged. The concentration of the acid in both phases was determined by spectrometry. A cyclohexane solution containing TOPO and one of the acids was also prepared in a stoppered polypropylene tube. The UV spectrum of the solution was measured with a Hitachi U-3400 spectrophotometer at 298 K.

A chemical species in the organic phase is indicated below by the subscript "org". The acid and TOPO are denoted by HA and B, respectively. The partition coefficient of the acid is written as K_d=$[HA]_{org}/[HA]$. The association equilibrium of the aicd with the base in the organic phase is expressed as follows:

$$HA_{(org)} + B_{(org)} \rightleftharpoons BHA_{(org)} \tag{1}$$

$$K_{as} = [BHA]_{org}/[HA]_{org}[B]_{org} \tag{2}$$

Since the aqueous phase is 1 mol dm^{-3} hydrochloric acid, the dissociation of HA is assumed to be negligible. Thus, the distribution ratio D of HA is given by

$$D = ([HA]_{org} + [BHA]_{org})/[HA]$$

$$= K_d(1 + K_{as}[B]_{org}) \tag{3}$$

Since TOPO is scarcely soluble in the aqueous phase, the following equations are approximately established.

$$[B]_{org,i} = [B]_{org} + [BHA]_{org} \tag{4}$$

$$[B]_{org} = [B]_{org,i}/(1 + K_d K_{as}[HA]) \tag{5}$$

The subscript "i" represents a quantity in the initial state. When the volume of the two phases is the same, the following equation is established.

$$[HA]_i = [HA] + [HA]_{org} + [BHA]_{org}$$

$$= [HA](1 + K_d + K_{as}[B]_{org}) \tag{6}$$

From Eqs. 2—6 a quadratic equation of D is obtained as Eq. 7 with a solution given by Eq. 8;

$$D^2 + bD - c = 0 \tag{7}$$

$$D = (-b + \sqrt{b^2+4c})/2 \tag{8}$$

where

$$b = 1 - K_d\{1 + K_{as}([B]_{org,i} - [HA]_i)\}$$

$$c = K_d\{1 + K_{as}([B]_{org,i} + K_d[HA]_i)\}$$

The value of K_d can be obtained by separate experiments and then the value of K_{as} can be determined by a successive approximation computer program on the basis of Eq. 8.

Results and Discussion

The solvent extraction data of the acids are displayed in Fig. 1. The partition coefficients and association constants were calculated from these data and are listed in Table 1. The association constant of 2-nitrophenol could not be determined since the distribution ration changed scarcely by the addition of TOPO. The values of partition coefficient obtained in the present study agree with the literature values,[1,2] though the values for 2,5- and 2,6-dinitrophenol are not found in the literature. The UV spectra of cyclohexane solutions of phenol containing various amounts of TOPO are depicted in Fig. 2 as an example of the spectometric data. The presence of isosbestic points seen in Fig. 2 ensures the validity of the equilibrium given by Eq. 1. When TOPO was added to a solution of phenol, the absorption maxima shifted to longer wavelengths. It is known that an ionized phenol shows a peak at around 400 nm but its hydrogen-bonded complex exhibits only a small shift from the original peak.[3,4] In view of this, the associates formed in the present study may essentially be the hydrogen-bonded ones.

From the spectrometric data, the association constants were calculated by a successive approximation method.5) The results are also listed in Table 1. The change in the spectra of 2-nitrophenol solutions by the addition of TOPO was too small to determine the association constant. With a few exceptions, a somewhat smaller association constants were obtained from the spectrometric data than from the solvent extraction data. Using water-saturated cyclohexane solutions of phenol and TOPO, the value log K_as=4.00±0.06 was obtained by spectrometry and this agreed well with that obtained by the solvent extraction method. Thus, the difference in the values obtained by the two methods should mainly be caused by the water in the organic medium although the role of this water is not yet clear. For this reason, the values of association constant obtained spectrometrically are used in the discussion below.

As seen from Table 1, values of K_as are not necessarily parallel with those of K_a, the acid dissociation constant in aqueous solutions.6–9) The value of K_a is used in several

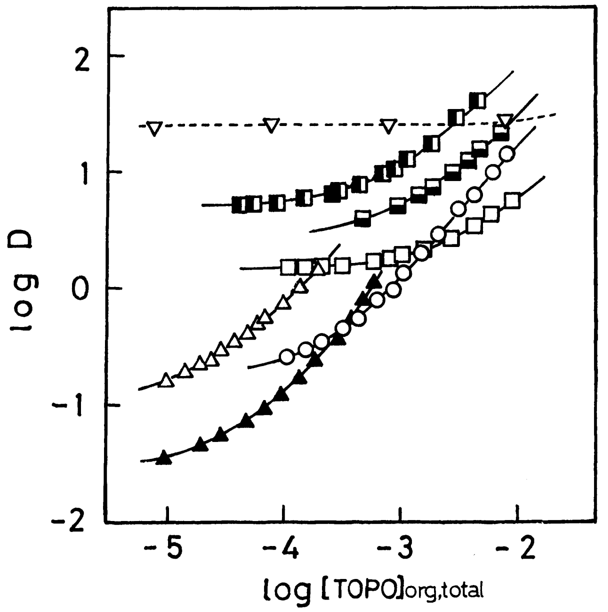

Fig. 1. Distribution ratio of phenol and nitrophenols between aqueous 1 mol dm^{-3} hydrochloric acid and cyclohexane as a function of the initial TOPO concentration in the organic phase. The compounds (initial concentration in mol dm^{-3}) are phenol (○, 8.98×10^{-4}), 2-nitrophenol (▽, 1.04×10^{-4}), 3-nitrophenol (△, 1.02×10^{-3}), 4-nitrophenol (▲, 1.54×10^{-3}), 2,4-dinitrophenol (⬓, 5.11×10^{-5}), 2,5-dinitrophenol (◧, 1.06×10^{-4}), and 2,6-dinitrophenol (□, 1.49×10^{-3}). Solid lines are theoretical ones according to Eq. 8 using the constants in Table 1. Broken line is the assumed distribution of 2-nitrophenol for log K_as=0.7.

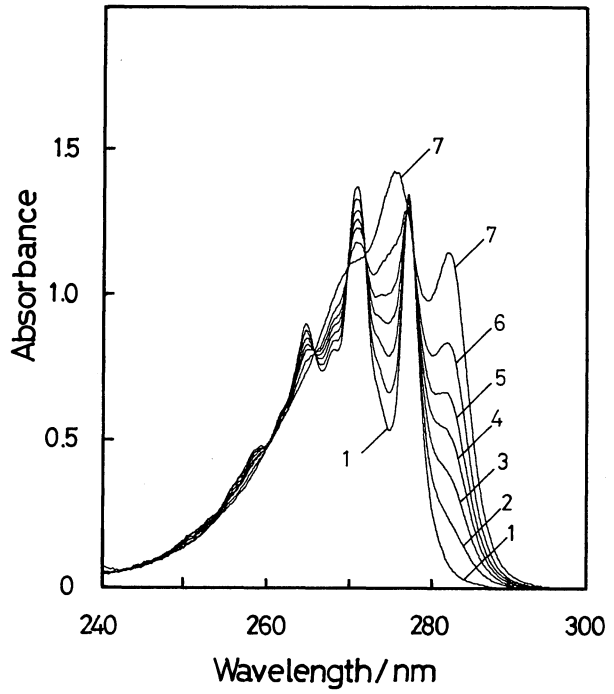

Fig. 2. UV spectra of cyclohexane solutions of phenol (6.01×10^{-4} mol dm^{-3}) containing various amounts of TOPO. TOPO concentrations are 0, 1.04×10^{-4}, 2.08×10^{-4}, 3.33×10^{-4}, 4.16×10^{-4}, 6.25×10^{-4}, and 3.33×10^{-3} mol dm^{-3} for (1) through (7), respectively.

Table 1. Partition Coefficient of Phenol and Nitrophenols between Cyclohexane and 1 mol dm^{-3} HCl, and Their Association Constant with TOPO in Cyclohexane at 298 K

Substance number	Nitro group position	pK_aa)	log K_d	log K_as		
				Solvent extraction	Spectrometry	Calcd with Eq. 9b)
1	—	9.94	−0.73	3.99±0.04	3.70±0.12	
2	2-	7.21	1.41	Nil	Nil	0.7
3	3-	8.35	−1.58	5.70±0.18	5.66±0.27	5.6
4	4-	7.15	−2.02	5.76±0.25	5.55±0.13c)	5.6
5	2,4-	4.09	0.45	2.97±0.06	2.55±0.03	2.6
6	2,5-	5.22	0.69	3.18±0.08	2.62±0.14	2.6
7	2,6-	3.71	0.17	2.48±0.03	2.63±0.07	2.6
8	2,4,6-	0.40	−0.82d)	4.12d)	4.16d)	4.5

a) Taken from Ref. 10. b) Using the parameter θ=−3.0 for the nitro group at the 2-position and +1.9 at other positions. c) Taken from Ref. 5. d) Taken from Ref. 11; in Table 1 of Ref. 11 the value of K_d should be as is given in the present Table and pK_a should be −0.16.

papers for discussing the acidity of a substance in nonaqueous solutions. However, the use of association constants may be more appropriate to find out the acid strength in nonpolar solvents. In view of this, the log K_{as} values in Table 1 were treated on the basis of the linear free-energy relationship; the log K_{as} value of a nitrophenol can be given by the sum of the each value which represents the contribution of a nitro group at the substituting position. The relation thus found obeys the following equation.

$$\log K_{as} = 3.7 + \Sigma\theta \qquad (9)$$

The value 3.7 is employed as the log K_{as} of the mother compound, phenol. The parameter θ represents the contribution of a nitro group on the phenol ring and it was estimated to be −3.0 for nitro substitution at the 2-position and +1.9 for the substitution at other positions. The log K_{as} values thus obtained on the basis of Eq. 9 are given in the final column of Table 1.

The log K_d of the acids are plotted against log K_a in Fig. 3a and against log K_{as} in Fig. 3b. As seen from Fig. 3a, the acids with a nitro group at the 2-position have much larger K_d than those which have no nitro group at this position. It is clear from Fig. 3b that the K_d is larger when the K_{as} is smaller, irrespective of the presence or absence of a nitro group at 2-position. This suggests that the hydrogen bonding with water, which exerts a large effect on the partition of phenols between water and cyclohexane, should take place to an extent in similar order to the formation of the hydrogen-bonded complexes with TOPO in cyclohexane.

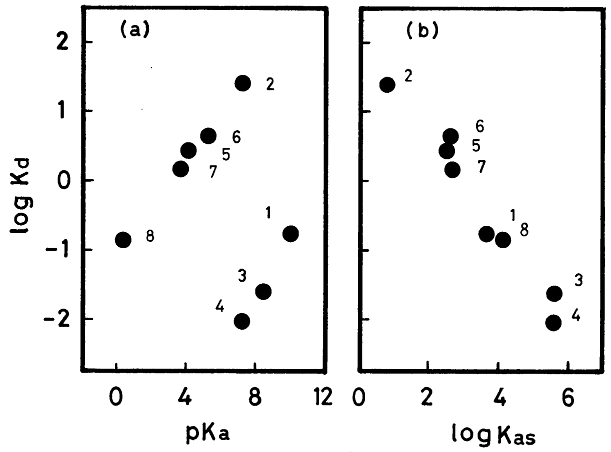

Fig. 3. Partition coefficient of phenol and nitrophenols between cyclohexane and 1 mol dm^{-3} hydrochloric acid plotted against (a) the acid dissociation constant in aqueous solutions and (b) the association constant with TOPO in cyclohexane obtained spectrometrically. The value of log K_{as} for 2-nitrophenol is a calculated one. The substance numbering is the same as in Table 1.

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