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Molar Volume Effect of Pyridylazophenols and Their Metal Chelates on Their Distribution between Aqueous Micellar Pseudophases in Triton X-100 Micellar Solutions

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The distribution constants of 2-(2-pyridylazo)phenol (PAP), 2-(2-pyridylazo)-5-methylphenol (PAP-5Me), and metal chelates with PAP and PAP-5Me between aqueous micellar psuedophases were evaluated in aqueous micellar solutions of Triton X-100. The distribution constants were found by measurement of equilibrium shifts in acid-base and complexation reactions in the presence of micelles at an ionic strength of 0.1 ((Na^+, H^+) ClO_4^-) and at 293±1 K. The metal chelates (vanadium(V), nickel(II), and iron(II)) had a linear correlation between their logarithmic distribution constants and their van der Waals volumes. PAP and PAP-5Me had a different kind of correlation from the metal chelates did. These results were explained by the difference in the part of the micelles into which hydrophobic chelates and hydrophilic chelating reagents were incorporated.

The analytical separation of organic compounds by micellar chromatography[1)] and micellar electrokinetic chromatography has been reported.[2)] In micellar chromatography, the distribution of a solute between aqueous micellar pseudophases is introduced into the mobile phase. In micellar electrokinetic chromatography, micelles act as the stationary phase. In these micellar-mediated separations, the distribution constants of metal chelates between aqueous micellar pseudophases are critical if chromatograms of metal chelates are to have good resolution.

Some authors have begun to compile distribution constants of chelating reagents and their metal chelates between the phases by measuring equilibrium shifts in acid-base and complexation reactions in micellar solutions.[3—7)] Yotsuyanagi et al.[6)] have pointed out that, for all chelating reagents and metal chelates, the distribution constants in a micellar solution of Triton X-100 increases with increasing van der Waals volume (molar volume), but levels off above a value near 110 $cm^3\,mol^{-1}$.

We have calculated the distribution constants of metal chelates with several chelating reagents between two phases separated from a micellar solution of poly(oxyethylene)-4-nonylphenyl ether (average number of ethylene oxides; 7.5) above the cloud point.[8)] The distribution constants of chelating reagents had good correlation with those obtained by solvent extraction with *n*-octanol. The free-energy relationship in the distribution constants of chelates was not linear.

These results suggest that chelating reagents and their chelates are distributed differently. Thus, the molar volume effect of chelates on the distribution between the aqueous micellar pseudophases seems to be different from that of chelating reagents. This study is concerned with the distribution equilibria of metal chelates between aqueous micellar pseudophases in Triton X-100 micellar solutions. The chelates tested are 1 : 1 vanadium(V) chelates and 1 : 2 metal chelates (nickel(II) and iron(II)) with 2-(2-pyridylazo)phenol (PAP) and 2-(2-pyridylazo)-5-methylphenol (PAP-5Me).

Experimental

Apparatus. A Hitachi 320 double-beam spectrophotometer with 1-cm quartz cells was used for measurements of absorbance. A Toa HM-60S pH meter was used for pH measurements. All experiments were carried out in a water bath thermostated at 293±0.1 K with a Yamato Coolnics instrument (CTR220/CTE220).

Reagents. In our previous study,[9)] PAP and PAP-5Me were synthesized as reported elsewhere.[10,11)] Their solutions (0.02 $mol\,dm^{-3}$) were prepared by dissolving the respective compounds in a sodium hydroxide solution (0.02 $mol\,dm^{-3}$). An aqueous solution of Triton X-100 (20.0% (w/w)) was prepared. Other reagents used were of analytical grade. All aqueous solutions were prepared with deionized distilled water purified by a Millipore Milli-Q system.

Procedure. Prescribed amounts of a sodium perchlorate solution (1.0 $mol\,dm^{-3}$), the Triton X-100 solution, the chelating reagent solution, and a perchloric acid solution (1.0 $mol\,dm^{-3}$) were mixed together in a beaker. The solution was diluted to 200 cm^3 with water. The ionic strength was kept at 0.1 ((Na^+, H^+), ClO_4^-). In testing of the distribution equilibria of metal chelates, a specified metal ion solution was also added before the dilution with water. If necessary, L-ascorbic acid (100 $mg\,dm^{-3}$) or sodium periodate (20 $mg\,dm^{-3}$) was added. The former was to prevent oxidation of iron(II), and the latter was to maintain the valence of vanadium(V). The solution was kept at 293±0.1 K and then titrated by the dropwise addition of saturated sodium hydroxide solution with a micropipet, with stirring. After equilibration, absorbances at an appropriate wavelength and pH were measured.

Results and Discussion

Distribution Equilibria of PAP and PAP-5Me. The distribution constants were evaluated according to the aqueous-micellar distribution model shown in Fig. 1. The concentrations of species in the micellar phase are denoted by subscript m and those in the aqueous phase

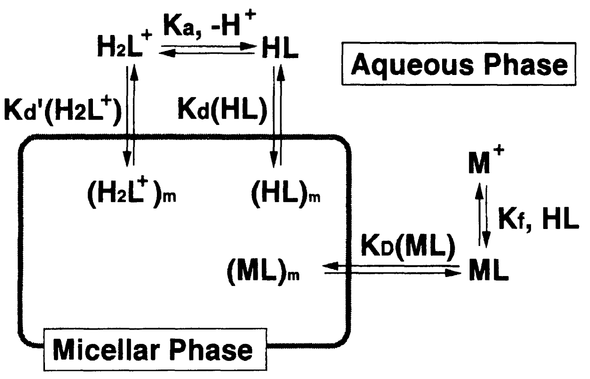

Fig. 1. Aqueous-micellar two-phase distribution model.

by subscript w. The apparent acid dissociation constant (K'_a) of a chelating reagent (HL) in an aqueous micellar solution is given by Eq. 1.

$$K'_a = [H^+](\phi_w[HL]_w + \phi_m[HL]_m)/(\phi_w[H_2L^+]_w + \phi_m[H_2L^+]_m) \qquad (1)$$

Here, ϕ_w and ϕ_m are the volume fraction of each phase. The volume fraction of the micelles (ϕ_m) was calculated by the method of Robson and Dennis,[12] as a function of the Triton X-100 concentration. The distribution constant (K_d) of HL and the conditional distribution constant, K'_d, of H_2L^+ are defined by Eqs. 2 and 3, respectively.

$$K_d(HL) = [HL]_m/[HL]_w \qquad (2)$$

$$K'_d(H_2L^+) = [H_2L^+]_m/[H_2L^+]_w \qquad (3)$$

Combining Eq. 1 with Eqs. 2 and 3, we can obtain Eq. 4.

$$(1 - K_a/K'_a)(\phi_w/\phi_m) = K_d(HL)(K_a/K'_a) - K'_d(H_2L^+) \qquad (4)$$

where the aqueous K_a values (acid dissociation constant) of PAP and PAP-5Me were taken from a previous paper.[9]

The K'_a values were found spectrophotometrically as functions of pH and the Triton X-100 concentration. A plot of the left-hand term in Eq. 4 against (K_a/K'_a) should give a straight line with a slope and intercept of K_d (HL) and $-K'_d$ (H_2L^+), respectively. The plot is linear (Fig. 2). The K_d (HL) and K'_d (H_2L^+) values thus obtained are summarized in Table 1.

Distribution Equilibria of Metal Chelates. The distribution constants of metal chelates with PAP and PAP-5Me can also be found by measurement of the absorbance of the metal chelate as a function of pH and the Triton X-100 concentration. The absorbance–pH curve is then analyzed according to the model in Fig. 1, in which the complexation of vanadium(V) ($VO_2^+ = M^+$) with a chelating reagent is shown as an example. The distribution constant of a 1 : 1 vanadium(V) chelate (ML) between the two phases and its conditional stability constant in the aqueous phase are defined by Eqs. 5 and 6, respectively.

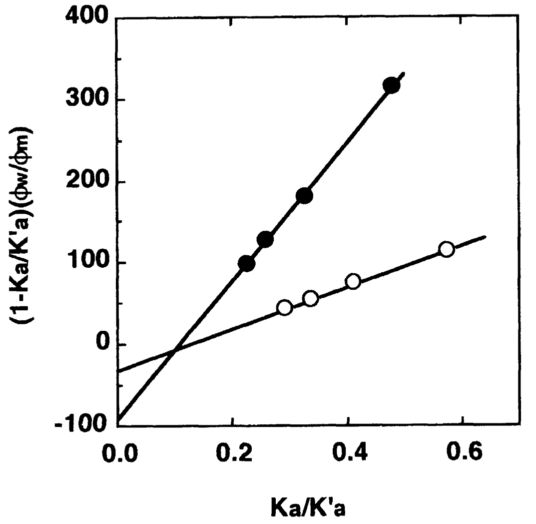

Fig. 2. Plots of $(1-K_a/K'_a)(\phi_w/\phi_m)$ vs. K_a/K'_a for PAP and PAP-5Me. (○) PAP, (●) PAP-5Me.

$$K_D(ML) = [ML]_m/[ML]_w \qquad (5)$$

$$K_f = [ML][H^+]/[M^+][HL] \qquad (6)$$

Thus, the relation of absorbance A with the concentration of hydrogen ions can be expressed by an equation similar to that for 1 : 2 chelate.[6]

$$\log Y = pH + \log(K_f(\phi_w + \phi_m K_D(ML))) \qquad (7)$$

where

$$Y = \frac{A\phi_w((\phi_w + \phi_m K'_d(H_2L^+))[H^+]/K_{a1} + \phi_w + \phi_m K_d(HL))}{(C_M - A/\varepsilon)(C_L - A/\varepsilon)}$$

Here, ε, C_M, and C_L are the molar absorptivity, and the total concentrations of a metal ion and a chelating reagent, respectively. The K_f values have been published.[9] Plots of log Y versus pH are given in Fig. 3 for the vanadium(V) chelate with PAP-5Me at fixed and various concentrations of Triton X-100. From the intercept of the plots, K_D can be calculated. The distribution constants of the other metal chelates, nickel(II) and iron(II), were obtained in a similar way. The distribution constants thus obtained are listed in Table 1.

Table 1 shows that PAP-5Me and its metal chelates have lager distribution constants than those of PAP and its chelate. The distribution constant of the 1 : 1 vanadium(V) chelate with PAP is almost half of the distribution constants for 1 : 2 chelates with PAP. PAP-5Me chelates are in the same relationship. These results are consistent with those predicted by the regular solution theory:[13] The greater the molar volume, the higher the distribution constant. However, the distribution constants of the vanadium(V) chelates are even smaller than those of the corresponding chelating

Table 1. Logarithmic Distribution Constants of PAP, PAP-5Me, and Their Metal Chelates

	$\log K_d$ and $\log K'_d$		$\log K_D$		
Reagent	H_2L^+	HL	VO_2^+	Fe^{2+}	Ni^{2+}
PAP	1.44±0.02	2.40±0.05	0.93±0.05	2.38±0.10	1.87±0.01
PAP-5Me	1.67±0.02	2.79±0.07	1.24±0.14	2.78±0.03	2.80±0.03

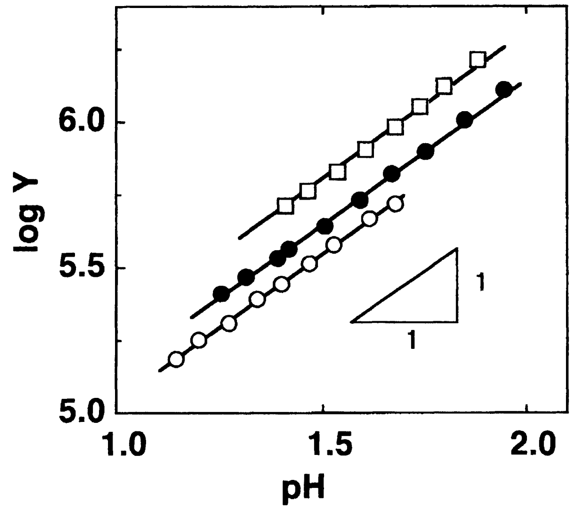

Fig. 3. Plots of log Y vs. pH for vanadium(V)–PAP-5Me mixture. Concentration of Triton X-100, % (w/w): (○) 1.0, (●) 2.0, (□) 3.0.

reagents. This finding cannot be explained by a difference in the molar volume. We next tested the relationship between the molar volume and the distribution constant.

Molar Volume and Distribution Constant. Plots of the logarithmic distribution constant ($\log K_D$) against molar volume (V_w) are shown in Fig. 4. The molar volume of the chelating reagents was calculated by the method of Bondi.[14] The chelates (ML_n) were assumed to have an n-fold volume of PAP or PAP-5Me, where n is the number of the chelating reagent bound in the chelates. In Fig. 4, the dotted line is that reported by Yotsuyanagi et al.,[6] on the basis of the distribution constants of three nitrophenols, five thiazolylazophenols, and one iron(II) chelate with 2-(2-thiazolylazo)-4-methylphenol.

Our data for PAP and PAP-5Me are arranged linearly and are at points close to the levelling-off of K_d, but those of the chelates are not on the line. The plot for the metal chelates yielded a different correlation from that of the chelating reagents. This difference is probably due to the difference in the distribution mechanism of the chelating reagents and the chelates. That is, the chelating reagents are distributed mainly into the hydrophilic part of the micelles by interaction through hydrogen bonding between the hydroxyl group of PAP (or PAP-5Me) and the oxyethylene part of Triton X-100. Hydrophobic chelates are likely to be incorporated into the hydrophobic core of the micelles.

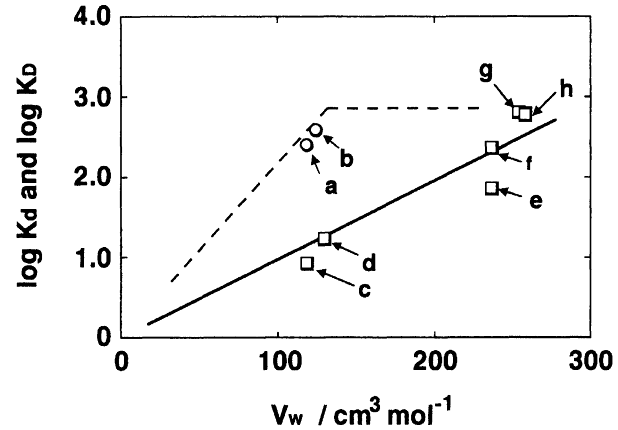

Fig. 4. Correlation between logarithmic distribution constant and molar volume. The dotted line is the correlation reported by Yotsuyanagi et al.,[6] and the solid line was obtained by the least-squares method from the data of metal chelates tested in this work. Compounds: (a) PAP, (b) PAP-5Me, (c) $[VO_2(pap)]$, (d) $[VO_2(pap\text{-}5Me)]$, (e) $[Ni(pap)_2]$, (f) $[Fe(pap)_2]$, (g) $[Ni(pap\text{-}5Me)_2]$, (h) $[Fe(pap\text{-}5Me)_2]$.

In general, metal chelates do not always give well resolved chromatograms in micellar reversed-phase high performance liquid chromatography (RP-HPLC). Separation of metal chelates from a free chelating reagent is difficult.[15] These facts are due to the slight difference in the distribution constants.[6] In this respect, PAP is a promising chelating reagent in derivatization of metal ions before micellar RP-HPLC. As is evident in Table 1, the difference in the distribution constants of PAP and its vanadium(V) chelate is large, and PAP also gives 1 : 2 chelates with different distribution constants.

In conclusion, the correlation between K_D and V_w of the chelates was different from that of the chelating reagents. This difference was attributable to the difference in sites of micelles into which hydrophobic chelates and hydrophilic chelating reagents were incorporated.

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