

Binding of Phenol Derivatives to Nonionic Surfactant Micelles as Studied by Capillary Zone Electrophoresis

Toshio Takayanagi* **and Shoji Motomizu**

Department of Chemistry, Faculty of Science, Okayama University, 3-1-1 Tsushimanaka, Okayama 700-8530

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Binding constants of 13 kinds of phenols as neutral and anionic species to nonionic surfactant micelles were determined using their mobility changes in capillary zone electrophoresis. Electrophoretic mobility of the phenolate ions at alkaline regions decreased with increasing the concentrations of nonionic surfactant. Analyzing such mobility decreases provided the binding constants of the ions ($K_{B,A}$). The $K_{B,A}$ values are larger in the anions which are more hydrophobic. Binding constants of the phenols as their neutral species to nonionic surfactant micelles ($K_{B,HA}$) were also determined by using the difference in acid dissociation constants between in the absence of and in the presence of nonionic surfactant micelles: in the presence of the surfactant, the apparent pK_a values became larger, which indicates that the neutral species are more likely bound to the micelles. The $K_{B,A}$ and $K_{B,HA}$ values determined were compared with each other on the basis of hydrophobicity, basicity, and position of the substituents.

Since the development of Micellar Electrokinetic Chromatography (MEKC),[1] various types of surfactant micelles have been utilized in capillary zone electrophoresis (CZE) for the resolution improvement of analytes.[2,3] It has been noticed that the resolution improvement is introduced by the binding/distribution phenomena of the analytes to the surfactant micelles. Quantitative analyses of binding reactions have been investigated by using the electrophoretic mobility in anionic[4–6] and cationic[7] surfactant micelles, as well as in mixed micelles.[8,9] Binding of neutral compounds to cationic and anionic surfactant micelles has also been analyzed by micellar liquid chromatography.[10] Luminescence quenching was also utilized for the binding analysis of phenolate ions to cetyltrimethylammonium micelle,[11] and NMR spectroscopy was also utilized for phenols and phenolate ions to cationic micelles.[12]

Nonionic surfactants (NIS) have also been utilized in MEKC separations.[13–16] However, analyses of the reactions of binding to the NIS micelles are very scarce.[16] In dealing with neutral compounds, analysis of the binding reaction to NIS micelles is quite difficult even using the electrophoretic measurements, because no difference in the electrophoretic mobility between neutral and the bounded species can be observed; both of them have zero electrophoretic mobility. Only potentiometric method[17] and micellar-enhanced ultrafiltration[18,19] allowed one to analyze the binding reaction.

In this paper, we propose a simple and reliable method for the analysis of binding reactions of acidic compounds as neutral species to NIS micelles by a CZE measurement. Electrophoretic migration of the acidic compounds can be schematically illustrated as in Fig. 1. The characteristic of the proposed method is the determination of acid dissociation constants (pK_a) both in the absence and presence of NIS micelles, where electrophoretic mobility of the analytes was measured at various pHs. In the presence of NIS micelles, the acid dissociation constant of a given analyte observed would change depending on the binding strength of neutral and anionic species, $K_{B,HA}$ and $K_{B,A}$, respectively. The difference between the pK_a value and the apparent pK_a value in the presence of NIS micelle can be utilized for the reaction analysis. In the proposed CZE method, low concentrations of analytes down to 10^{-5} M levels are allowed when analyzing the reactions, and multiple analytes can be treated simultaneously through the CZE separation. Phenol derivatives including positional isomers were adopted as model substances and used as analytes in CZE; Brij 35, Brij 58, and Brij 78 were used as NIS to form NIS micelles, which can be considered as pseudo-homogeneous hydrophobic media. Binding constants of the phenols were determined and compared with each other on the basis of hydro-

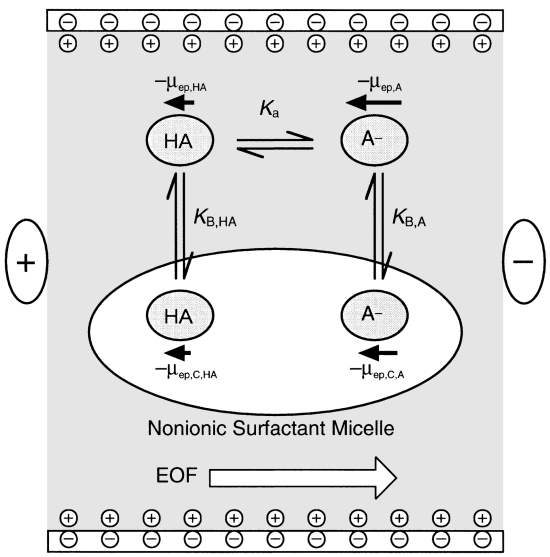

Fig. 1. Schematic illustration for binding of phenol derivatives to nonionic surfactant micelles.

phobicity, basicity, and position of the substituents.

Experimental

Apparatus. A Hewlett Packard ^{3D}CE was used as a capillary electrophoresis system. A fused silica capillary purchased from Hewlett Packard was attached to the system; the capillary was 64.5 cm in total length, 56 cm in effective length from the sample injection point to the UV detector, and had a 50 μm inner diameter. A Hewlett Packard ChemStation was used for recording and analyzing the electropherograms. A Corning Ion Analyzer M-250, calibrated daily with standard pH solutions, was used to measure the pH values.

Reagents. As the components of pH buffers in a separation solution, KH_2PO_4–Na_2HPO_4, sodium tetraborate (borax), and NaOH were used. Nonionic surfactants of polyoxyethylene (23) dodecyl ether (Brij 35, Wako), polyoxyethylene (20) hexadecyl ether (Brij 58, Wako), and polyoxyethylene (20) octadecyl ether (Brij 78, Aldrich) were used to prepare the NIS micelles which provided the hydrophobic medium. These NIS were added to the separation solution at the concentration ranges from 0 to 1.4%(w/v). Various kinds of phenol derivatives including positional isomers were adopted as analytes; these included phenol (P), 2-cresol (2MeP), 3-cresol (3MeP), 4-cresol (4MeP), 2-chlorophenol (2ClP), 3-chlorophenol (3ClP), 4-chlorophenol (4ClP), 4-ethylphenol (4EtP), 2-nitrophenol ($2NO_2P$), 3-nitrophenol ($3NO_2P$), 4-nitrophenol ($4NO_2P$), 1-naphthol (1N), and 2-naphthol (2N). These acids were used after being neutralized with an equivalent amount of sodium hydroxide. De-ionized and distilled water was used.

Procedure for the CZE Measurement. Separation solutions were prepared by using the pH buffers with their concentrations of 5 or 10 mM (1 M = 1 mol dm^{-3}) and known amounts of nonionic surfactants. A small amount of HCl or NaOH was added to the buffers to adjust their pH values. An appropriate amount of sodium chloride was also added to the separation solutions to adjust the ionic strength to 0.05 M. The separation solutions thus prepared were transferred into both a cathodic and an anodic reservoir, as well as into a capillary by the pressure system. A sample solution containing 13 kinds of analytes at the concentration of 5×10^{-5} M was injected into the capillary from the anodic end for 3 s by applying pressure (150 mbar·s). Then a voltage of 15 kV was applied, and electrophoresis was started. The analytes were photometrically detected at 210 nm. Throughout the experiments, the temperature of the capillary, as well as that of the vials, was controlled at 25 °C. To evaluate the velocity of the electroosmotic flow (EOF), 3%(v/v) ethanol was added to the sample solution to detect it. Electrophoretic mobility of the analytes was calculated in the ordinary manner.

Results and Discussion

Determination of Acid Dissociation Constants by Using Mobility Change in CZE. For the investigation of the binding reaction of neutral species to NIS micelles, changes in ionization properties, an acid dissociation reaction in this case, can be utilized. In the presence of the NIS micelles, the acid dissociation reaction should occur at higher pHs than those in the absence of the micelles, because less charged species will be more likely bound or distributed to the micelles.

Prior to the analysis of the binding constants, we have to clarify the acid dissociation property of phenol derivatives. The mobility change of the phenol derivatives by varying pHs of the separation buffers was investigated; the separation buffers used were 10 mM phosphate (pH range: 6–8), 5 mM borax –HCl or –NaOH (pH range: 8–10), or 1–20 mM NaOH (pH range: 11–12.3). Typical electropherograms for the phenols are shown in Fig. 2. At a neutral pH region, most of the phenol derivatives migrated along with the EOF; only nitrophenols and chlorophenols migrated as partially anionic species, as is seen in the electropherogram in Fig. 2a. As the separation solution become more alkaline, the phenols became anionic, and the migration time became longer, as is shown in Figs. 2b and c.

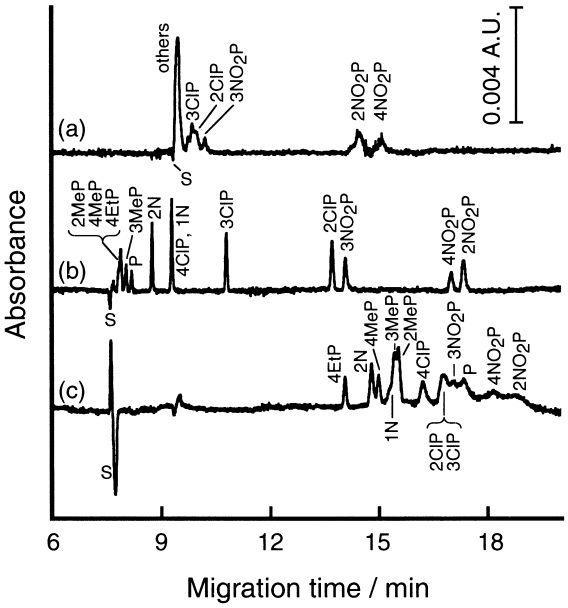

Fig. 2. Typical electropherograms for 13 kinds of phenol derivatives at different pH conditions. CZE conditions: applied voltage, 15 kV; detection wavelength, 210 nm; capillary temperature, 25 °C; injection period, 3 s (150 mbar·s). Separation solution: (a), 10 mM phosphate + 40 mM NaCl (pH 7.10); (b), 5 mM borax + 40 mM NaCl (pH 9.21); (c), 10 mM NaOH + 40 mM NaCl (pH 11.96). Sample solution: 5×10^{-5} M 13 kinds of phenol derivatives + 3%(v/v) ethanol. S: ethanol (EOF marker).

The changes in the electrophoretic mobility of the phenol derivatives by varying the pHs of the separation solutions are shown in Fig. 3. The electrophoretic mobility ($-\mu_{ep}'$) of all the phenols increased with increasing pH of the separation solution; the plots of $-\mu_{ep}'$ against pHs are in a similar sigmoid curve. Acid dissociation constants of the phenols can be determined by analyzing such sigmoid curves of the mobility changes. The acid dissociation reaction and its equilibrium are written as in Eqs. 1 and 2, respectively.

$$HA \rightleftarrows H^+ + A^- \quad (1)$$

$$K_a = [H^+][A^-]/[HA] \quad (2)$$

where HA and A^- denote neutral phenols and phenolate ions, respectively, and K_a is an acid dissociation constant. Apparent electrophoretic mobility of a certain phenol, $-\mu_{ep}'$, is attributed to the ionized species, A^-, and written as in Eq. 3, where

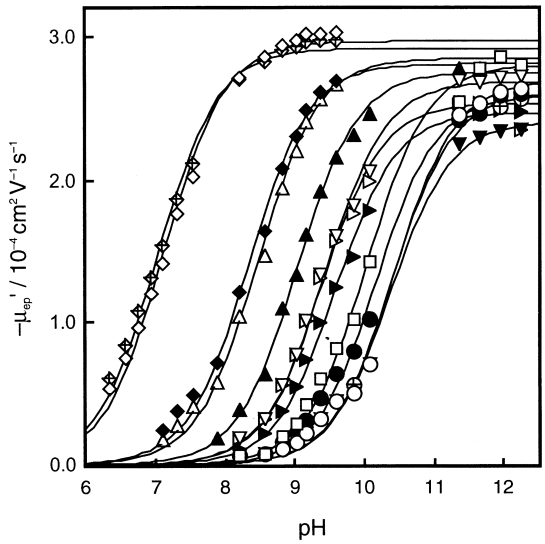

Fig. 3. Mobility change of phenol derivatives as a function of pH. CZE conditions and the sample solution are the same as in Fig. 2. Separation solution: 10 mM phosphate, 5 mM borate or NaOH buffer + NaCl (I = 0.05).

mass balance for the phenol and the equilibrium constant is considered.

$$-\mu_{ep}' = \frac{[H^+]/K_a}{[H^+]/K_a+1}(-\mu_{ep,HA}) + \frac{1}{[H^+]/K_a+1}(-\mu_{ep,A}). \quad (3)$$

In Eq. 3, the values of $(-\mu_{ep,HA})$ and $(-\mu_{ep,A})$ are the electrophoretic mobility of neutral phenols and their ionized ones, respectively. A non-linear least-squares analysis method[20] was applied to the analysis of the mobility change, where the value of $-\mu_{ep,HA}$ was considered to be zero from non-charged HA species. The solid curves in Fig. 3 are the results simulated by calculating with the values of $-\mu_{ep,A}$ and K_a. The pK_a and the $-\mu_{ep,A}$ values obtained are summarized in Table 1. The pK_a values obtained agreed well with the reported values.[21,22] It can be noticed from the values of $-\mu_{ep,A}$ in Table 1 that larger ions possess smaller electrophoretic mobility, as is commonly known, and that small differences among the isomers are seen which reflected the differences in ionic molecular volume or the degree of hydration. The errors for pK_a and $-\mu_{ep,A}$ values obtained seem to be relatively large, which should attributed to the analysis method used. The non-linear least-squares method has advantages that it can treat small changes in the electrophoretic mobility and that all the data can be operated equivalently. When the analysis method was applied to the acid dissociation reaction and to the conditions where the acidic species are major, the electrophoretic mobility close to zero value should be also used. The deviation of the electrophoretic mobility close to zero value comes to be relatively large, and the analysis would have caused serious errors.

Table 1. Acid Dissociation Constants Determined in This Study

Compound	pK_a		$-\mu_{ep,A}$[c)]
	This study[a)]	Reference[b)]	
P	10.02 ± 0.23	9.89	2.73 ± 0.51
2MeP	10.42 ± 0.30	10.20	2.65 ± 0.33
3MeP	10.16 ± 0.26	10.01	2.59 ± 0.38
4MeP	10.39 ± 0.30	10.17	2.57 ± 0.32
4EtP	10.36 ± 0.31	10.0	2.42 ± 0.28
2ClP	8.45 ± 0.18	8.48	2.78 ± 0.19
3ClP	9.02 ± 0.12	9.02	2.72 ± 0.34
4ClP	9.42 ± 0.18	9.38	2.65 ± 0.41
$2NO_2P$	7.10 ± 0.17	7.17	2.97 ± 0.18
$3NO_2P$	8.32 ± 0.21	8.28	2.74 ± 0.29
$4NO_2P$	7.01 ± 0.16	7.15	2.92 ± 0.17
1N	9.38 ± 0.17	9.35	2.52 ± 0.36
2N	9.58 ± 0.17	9.51	2.48 ± 0.41

a) Error: 3σ.
b) Reported values cited from Refs. 21 and 22.
c) Dimension: 10^{-4} cm^2 V^{-1} s^{-1}. Error: 3σ.

Analysis of Binding Reactions of Phenolate Ions to NIS Micelles. In previous paper,[16] we have investigated binding reactions of aromatic carboxylate and sulfonate ions to nonionic surfactant micelles at pH 9.2. In the analysis of phenolate ions, however, the investigation must be carried out at higher pH conditions. The binding reactions of phenolate ions were investigated at more alkaline pH region (20 mM NaOH; pH = 12.3), where the species of the phenols are all dissociated and anionic. Typical electropherograms for the anions are shown in Fig. 4. As is shown in Fig. 4b, migration times of the anions became closer to that of the EOF by the addition of NIS, Brij 35, in the separation solution, whereas the EOF was almost unchanged. These results indicate that the electrophoretic mobility of the anions decreased as the result of the reaction of the analytes with NIS micelles. The migration order of the anions

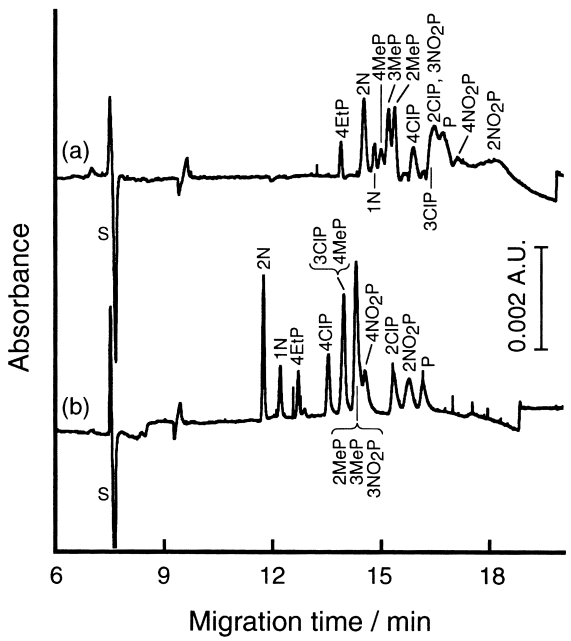

Fig. 4. Typical electropherograms for 13 kinds of phenolate ions in the absence and presence of nonionic surfactant. CZE conditions and the sample solution are the same as in Fig. 2. Separation solution: (a), 20 mM NaOH + 30 mM NaCl (pH 12.36); (b), 20 mM NaOH + 30 mM NaCl + 1.0%(w/v) Brij 35 (pH 12.34). S: ethanol (EOF marker).

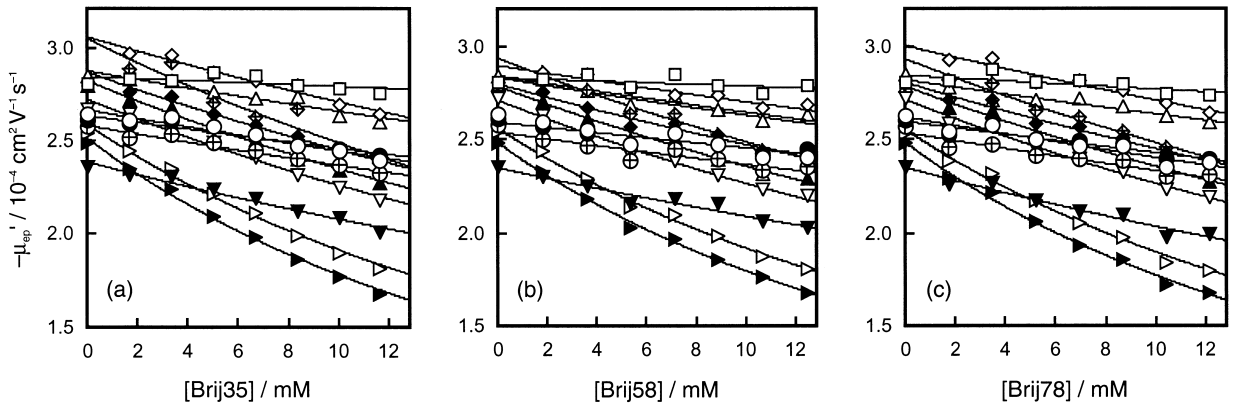

Fig. 5. Mobility change of phenolate ions with increasing concentrations of nonionic surfactant. CZE conditions, the sample solution, and the separation solutions are the same as in Fig. 4, except for the concentration of the surfactant. Nonionic surfactant: (a), Brij 35; (b), Brij 58; (c), Brij 78. Symbols: □, P; ○, 2MeP; ●, 3MeP; ⊕, 4MeP; ▼, 4EtP; △, 2ClP; ▲, 3ClP; ▽, 4ClP; ◇, $2NO_2P$; ◆, $3NO_2P$; ⟡, $4NO_2P$; ▷, 1N; ▶, 2N.

in the presence of Brij 35 was different from that in the absence of NIS micelles. Such a difference should be attributed to the difference in the reactivity of the anions with the micelles. Changes in the electrophoretic mobility by varying the concentrations of NIS are shown in Fig. 5. The electrophoretic mobility of the phenolate ions decreased with increasing the concentrations of NIS, which can be explained from the increase in the apparent molecular mass/volume of the analytes.

The binding reaction of the anions and its equilibrium constant, $K_{B,A}$, are expressed as in Eqs. 4 and 5, respectively.

$$A^- + (NIS)_m \rightleftarrows A^- - (NIS)_m \tag{4}$$

$$K_{B,A} = \frac{[A^- - (NIS)_m]}{[A^-][(NIS)_m]}, \tag{5}$$

where $[(NIS)_m]$ is the concentration of NIS micelles calculated from the concentration of NIS, its critical micelle concentration (c.m.c.), and its aggregation number.[23] The aggregation numbers used are: 40 for Brij 35 and 70 for Brij 58.[23] The binding constants were calculated by applying a non-linear least-squares analysis method[16] to the mobility change; the values obtained are summarized in Table 2. The binding constants of the phenolate ions based on the concentration of the surfactant molecule ($K_{B,A(mon)}$), as is defined in Eqs. 6 and 7, are also summarized in Table 2 for comparison.

$$A^- + NIS \rightleftarrows A^- - NIS \tag{6}$$

$$K_{B,A(mon)} = \frac{[A^- - NIS]}{[A^-][NIS]}. \tag{7}$$

Table 2 shows that the binding constant is larger with such anions as are more bulky ones and that the type of the surfactants showed small differences in binding properties of the anions. The results are similar to our previous study on aromatic carboxylate and sulfonate ions.[16] In the comparison of the position of the substituents on benzene ring, 4-substituted ones are most reactive, 2-substituted ones being the least reactive, except for cresolate ions. The selectivity of the surfactant micelles toward the isomers seems to have some relationship with the basicity of the anions; a more basic isomer is much more reactive with the micelle in the cases of cresols, chlorophenols, and naphthols. However, the nature of this selectivity is not certain at this stage.

The binding constants of monovalent carboxylate or sulfonate ions to the NIS micelles were not determined in the previous study,[16] so we cannot compare the reactivities of the phenolate ions with them. However, the constants for naphtholate ions are very close to those obtained with naphthalenecarboxylate and naphthalenesulfonate ions. Among the 1-substituted naphthalene derivatives, such as 1-naphtholate, naphthalene-1-carboxylate, and naphthalene-1-sulfonate ions, 1-naphtholate ion showed the highest reactivity, naphthalene-1-carboxylate ion being the lowest, whereas the reactivities of the 2-substituted naphthalene derivatives were almost equal.

Analysis of Binding Reactions of Phenols to NIS Micelles as Neural Species. The binding reactions of the neutral phenols and their equilibria, $K_{B,HA}$, are expressed as in Eqs. 8 and 9, respectively.

$$HA + (NIS)_m \rightleftarrows HA - (NIS)_m \tag{8}$$

$$K_{B,HA} = \frac{[HA - (NIS)_m]}{[HA][(NIS)_m]}. \tag{9}$$

In the analysis of the binding reaction of the neutral compounds to NIS micelles, direct measurement of the binding reaction is quite difficult by the electrophoretic method, because the change in electrophoretic mobility from neutral species to neutral complex is still zero in each analyte. In this study, therefore, the differences in acid dissociation constants between those in the absence and those in the presence of NIS micelles were utilized for the analysis of the binding reaction. The apparent acid dissociation constants (pK_a') should become larger in the presence of NIS micelles, because neutral species would be more easily bound to the micelle than the anionic species, as is schematically illustrated in Fig. 1. Electrophoretic mobility of the phenols was measured at various pHs in the presence of 1.0%(w/v) NIS micelles (Fig. 6) to obtain apparent

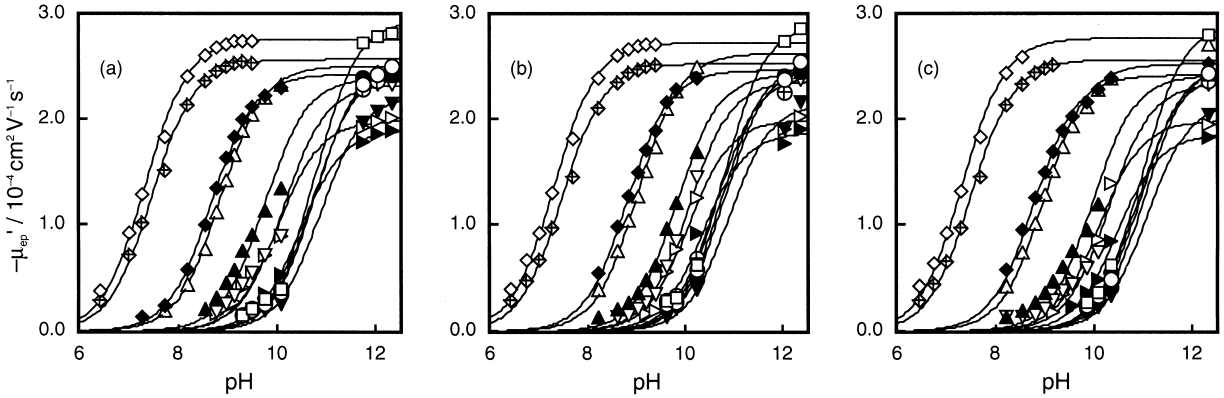

Fig. 6. Mobility change of phenol derivatives as a function of pH in the presence of 1.0%(w/v) nonionic surfactant. CZE conditions, the sample solution, and the separation solutions are the same as in Fig. 3, except for the concentration of the surfactant. Nonionic surfactant: (a), Brij 35; (b), Brij 58; (c), Brij 78. Symbols: □, P; ○, 2MeP; ●, 3MeP; ⊕, 4MeP; ▼, 4EtP; △, 2ClP; ▲, 3ClP; ▽, 4ClP; ◇, 2NO_2P; ◆, 3NO_2P; ⊕, 4NO_2P; ▷, 1N; ▶, 2N.

acid dissociation constants (pK_a'). The apparent acid dissociation constant is written in Eq. 10

$$K_a' = \frac{[H^+][A^-]_T}{[HA]_T}, \quad (10)$$

where $[HA]_T$ and $[A^-]_T$ are the total concentrations of HA and A^- species, respectively. The pK_a' values of the phenols were determined by using the mobility change with the non-linear least-squares analysis method in a similar manner to that used in the pK_a determinations; the pK_a' values obtained are summarized in Table 3. In Table 3, the pK_a' values for phenol, cresols, and 4-ethylphenol were less reliable, because adequate pH buffers could not be found in the required pH ranges from 10 to 11, where the compounds would display the transition of the mobility from neutral ones to anionic ones.

In the relation of the pK_a' values with the $K_{B,HA}$ values, Eq. 10 is connected to Eq. 11 on the basis of the mass balances for the species and the binding constants.

$$K_a' = \frac{[H^+][A^-](1+K_{B,A})}{[HA](1+K_{B,HA})} = \frac{K_a(1+K_{B,A})}{(1+K_{B,A})}. \quad (11)$$

From Eq. 11, Eq. 12 can be derived.

$$K_{B,HA} = \frac{K_a}{K_a'}(1+K_{B,A})-1. \quad (12)$$

When K_a' value is determined experimentally at certain conditions, we can determine $K_{B,HA}$ values by using Eq. 12 and the known values of K_a and $K_{B,A}$. The binding constants of neutral phenols on the basis of the concentration of the surfactant, $K_{B,HA(mon)}$, were also determined in a similar manner as in $K_{B,HA}$ using Eq. 13 and the known values of K_a and $K_{B,A(mon)}$

$$K_{B,HA(mon)} = \frac{K_a}{K_a'}(1+K_{B,A(mon)})-1. \quad (13)$$

Values of $K_{B,HA}$ and $K_{B,HA(mon)}$ determined are also summarized in Table 3. The $K_{B,HA}$ values are in the order of phenol < cresols < nitrophenols < chlorophenols < naphthols. The order should be attributed to the increasing hydrophobicity of the phenol derivatives.

Comparison of $K_{B,HA}$ and $K_{B,A}$ Values. Binding constants of $K_{B,HA}$ and $K_{B,A}$ are compared with each other. It can be seen from the values in Tables 2 and 3 that $K_{B,HA}$ values are larger than the corresponding $K_{B,A}$ values in the order of 0.22–0.96 in logarithmic units. Such results can be easily understood if one supposes that hydrophobic micelles would bind less charged substances, as is mentioned in the previous study.[24]

We have already reported the binding of ion associates of aromatic carboxylate and sulfonate ions ($K_{B,IA}$).[24] We can compare the binding constants with each other, though anionic groups substituted on benzene and naphthalene rings are different. Logarithmic values of $K_{B,IA}$ are 3.13, 3.32, 3.33, and 3.33 for naphthalene-1-carboxylate, naphthalene-2-carboxylate, naphthalene-1-sulfonate, and naphthalene-2-sulfonate ions, respectively, when tetrabutylammonium ion was used a pairing cation, and Brij 35 as NIS micelles. It can be seen from the comparison that $K_{B,HA}$ values are slightly larger than $K_{B,IA}$ values, which means that ion associates are not completely neutral as in the protonated species, but are in the state where the positive and negative charges remain in the ion associates.

Conclusion

Binding phenomena of neutral phenols, as well as their anionic species, to nonionic surfactant micelles were clarified by analyzing the mobility change in capillary zone electrophoresis. The utilization of apparent acid dissociation constants and binding constants of phenolate ions helped simple analysis of the reactions. The equilibrium constants obtained were reasonably explained from the viewpoint of distribution of anions or neutral species between aqueous and pseudo-homogeneous hydrophobic media. The proposed method would serve as a powerful technique for the reaction analysis in micelle solubilization, cloud point extraction, and permeation of substances through lipid bilayer.

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Table 2. Binding Constants of Phenolate Ions Determined by the Electrophoretic Method[a)]

	log K_B[b)]												
Surfactant	P	2MeP	3MeP	4MeP	4EtP	2ClP	3ClP	4ClP	$2NO_2P$	$3NO_2P$	$4NO_2P$	1N	2N
Brij 35	1.85	2.55±0.23	2.45±0.29	2.55±0.16	2.77±0.15	2.51±0.28	2.90±0.08	2.91±0.15	2.71±0.12	2.38±0.07	2.95±0.25	3.14±0.08	3.21±0.06
	(0.25)	(0.95)	(0.85)	(0.95)	(1.17)	(0.91)	(1.30)	(1.31)	(1.11)	(1.23)	(1.35)	(1.54)	(1.61)
Brij 58	2.04	2.72±0.34	2.59±0.52	2.70±0.46	2.94±0.20	2.71±0.36	3.10±0.11	3.14±0.08	2.70±0.18	2.96±0.16	3.10±0.12	3.36±0.07	3.43±0.05
	(0.19)	(0.88)	(0.74)	(0.85)	(1.09)	(0.86)	(1.26)	(1.29)	(0.85)	(1.12)	(1.25)	(1.52)	(1.58)
Brij 78	—[c)]	—	—	—	—	—	—	—	—	—	—	—	—
	(0.42)	(0.95±0.30)	(0.83±0.36)	(0.93±0.31)	(1.19±0.20)	(0.84±0.28)	(1.26±0.10)	(1.29±0.11)	(1.03±0.18)	(1.16±0.12)	(1.26±0.10)	(1.54±0.09)	(1.60±0.07)

a) Surfactant concentration: 0.0–1.4%(w/v).
b) Error: 3σ. Values in parentheses are the constants based on the surfactant molecule ($K_{B,A(mon)}$).
c) Aggregation number was not provided so that $K_{B,A}$ values were not determined.

Table 3. Apparent pK_a and log $K_{B,HA}$ Values Determined by the Electrophoretic Method

	pK_a'[a)]												
Surfactant	P	2MeP	3MeP	4MeP	4EtP	2ClP	3ClP	4ClP	$2NO_2P$	$3NO_2P$	$4NO_2P$	1N	2N
Brij 35	10.78±0.31	10.78±0.27	10.77±0.36	10.73±0.27	10.88±0.26	8.85±0.08	9.75±0.39	10.13±0.41	7.33±0.18	8.67±0.08	7.47±0.20	10.02±0.35	10.47±0.16
Brij 58	10.79±0.22	10.77±0.24	10.82±0.27	10.64±0.24	10.90±0.38	9.03±0.12	9.83±0.14	10.08±0.09	7.30±0.16	8.81±0.12	7.47±0.17	10.07±0.27	10.37±0.32
Brij 78	10.96±0.36	10.95±0.15	11.03±0.17	10.88±0.14	11.07±0.21	8.99±0.18	9.96±0.35	10.30±0.37	7.32±0.18	8.78±0.16	7.50±0.20	10.10±0.24	10.47±0.15

	log $K_{B,HA}$[a,b)]												
Surfactant	P	2MeP	3MeP	4MeP	4EtP	2ClP	3ClP	4ClP	$2NO_2P$	$3NO_2P$	$4NO_2P$	1N	2N
Brij 35	2.78	2.94	3.11	2.91	3.31	2.94	3.65	3.63	2.95	3.19	3.42	3.79	4.11
	(1.18)	(1.34)	(1.50)	(1.31)	(1.71)	(1.34)	(2.05)	(2.03)	(1.35)	(1.59)	(1.82)	(2.19)	(2.51)
Brij 58	2.99	3.11	3.31	2.98	3.50	3.33	3.93	3.81	2.92	3.47	3.57	4.07	4.23
	(1.15)	(1.26)	(1.46)	(1.13)	(1.66)	(1.49)	(2.09)	(1.97)	(1.07)	(1.63)	(1.73)	(2.22)	(2.38)
Brij 78	—[c)]	—	—	—	—	—	—	—	—	—	—	—	—
	(1.48)	(1.51)	(1.76)	(1.46)	(1.92)	(1.42)	(2.22)	(2.19)	(1.27)	(1.64)	(1.76)	(2.27)	(2.50)

a) Error: 3σ.
b) Surfactant concentration: 1.0%(w/v). Values in parentheses are the constants based on the surfactant molecule ($K_{B,HA(mon)}$).
c) Aggregation number was not provided so that $K_{B,HA}$ values were not determined.

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