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A Systematic Study on the Complexation of Quaternary Ammonium Salts and Neutral Phenols

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Complexation of quaternary ammonium salts (Q^+X^-) and undissociated, neutral phenols (ArOH) in homogeneous organic solutions was systematically investigated to afford a reliable quantitative basis for a new model of anionic potentiometric response to neutral phenols, displayed by organic liquid membranes based on Q^+X^-. IR, ^{1}H- and ^{13}C-NMR, and UV studies indicated complexation of Q^+X^- and ArOH in 1 : 1 stoichiometry in nonpolar organic solvents such as benzene and chloroform. The stability constant (K_s) of the complex was affected by the acidity and lipophilicity of the ArOH component as well as the size of X^- of the Q^+X^- component; stronger complexes were formed by ArOH with a lower pK_a and higher log P_{oct}, as well as by Q^+X^- with a smaller ionic radius for X^-. These results suggest that the major driving force for complexation is hydrogen bonding interactions between X^- and the phenolic OH. The K_s values were found to be parallel with the magnitudes of anionic potentiometric responses by membranes based on Q^+X^-, indicating that the complexation of ArOH by Q^+X^- plays an important role in the anionic potentiometric responses. The significance of proton dissociation from the $Q^+X^- \cdot$ArOH complex was also discussed.

Key words neutral phenolic compound; quaternary ammonium salt; complexation; organic solution; hydrogen bonding; proton dissociation

Complexation between a quaternary ammonium or phosphonium salt (Q^+X^-) and a neutral phenolic compound (ArOH) through hydrogen bonding between the anionic component X^- and the phenolic OH has been studied in order to understand the nature of such interactions in organic solutions,[2−5)] micellar systems[6)] or the gaseous phase,[7)] and to utilize an activated fluoride ion of Q^+F^- for increasing the nucleophilicity of phenolic OH in organic synthesis.[8)] Recently, we have found a novel significance of the complexation of Q^+X^- and ArOH in relation to membrane potential changes.[9,10)]

Changes in membrane potentials (potentiometric responses) induced by ionic species contribute to the principle of ion-selective electrodes (ISEs), which provide an important sensing method for a variety of chemical analyses.[11)] In contrast to the responses to ionic (charged) species, "potentiometric" responses to "neutral" molecules afford an intrinsically puzzling problem, but involve a significant question concerning how uncharged species can influence charge separation across the membrane interface and induce potentiometric responses. Based on the previous findings of Kimura *et al.*[12)] that a macrocyclic polyamine forms stable complexes with neutral catecholic guests in aqueous solutions, we have examined potentiometric responses to various phenolic compounds by poly(vinyl chloride) (PVC) matrix liquid membranes based on lipophilic macrocyclic polyamines (*e.g.*, **1**; Fig. 1)[13)] and related compounds.[9,10)] The latter includes lipophilic quaternary ammonium or phosphonium salts (Q^+X^-) that are intrinsically cationic,[9)] as well as lipophilic aliphatic or heteroaromatic amines (B) that acquire a cationic property by protonation.[10)] With these membranes, a number of phenols induced anionic potentiometric responses under pH conditions in which they exist almost exclusively as their undissociated, neutral forms (ArOH).

The potentiometric selectivities of these membranes were found to reflect the acidity (hydrogen bond donor activity) and lipophilicity (extractability) of ArOH, as well as the size of the anionic component X^- of the quaternary onium salts Q^+X^- or the protonated amine salts BH^+X^-.[9,10)] The mechanism of these anionic responses was explained on the basis of a decrease in the charge separation of the lipophilic cation (Q^+ or protonated amines BH^+) and its counteranion (X^-) across the membrane interface. Possible processes leading to a decrease in the charge separation between the cation and X^- are complexation between ArOH and Q^+X^- or BH^+X^-, followed by proton dissociation and concomitant ejection of HX into the aqueous phase.[9,10)] Although the whole process occurs in a two phase system, fundamental studies on the complexation of Q^+X^- (BH^+X^-) and ArOH in homogeneous organic solutions will afford an important quantitative basis to understand the potentiometric response mechanism.

In this paper, we describe the nature of the interactions between Q^+X^- and ArOH in homogeneous organic solutions on the basis of IR, ^{1}H- and ^{13}C-NMR, and UV spectroscopic results, together with the stability constants of 1 : 1 complexes. Although a number of studies based on mid[2−4)] or far[4,5)] IR and NMR[2,3,6)] spectroscopy have been carried out on the interactions of ammonium salts and ArOH in organic solutions, a systematic investigation, particularly that based on quaternary ammonium salts (Q^+X^-) with invariable charge regardless of pH, is necessary to afford a reliable quantitative basis for a new model of potentiometric response to neutral phenols.[9)]

Results and Discussion

The interactions between Q^+X^- and ArOH were investigated in nonpolar organic solvents, using Q^+X^- with different Q^+ and/or X^- components (**2**—**6**) and ArOH with different acidity and/or lipophilicity (**7**—**10**). Nonphenolic compounds **11**—**13** were used for compar-

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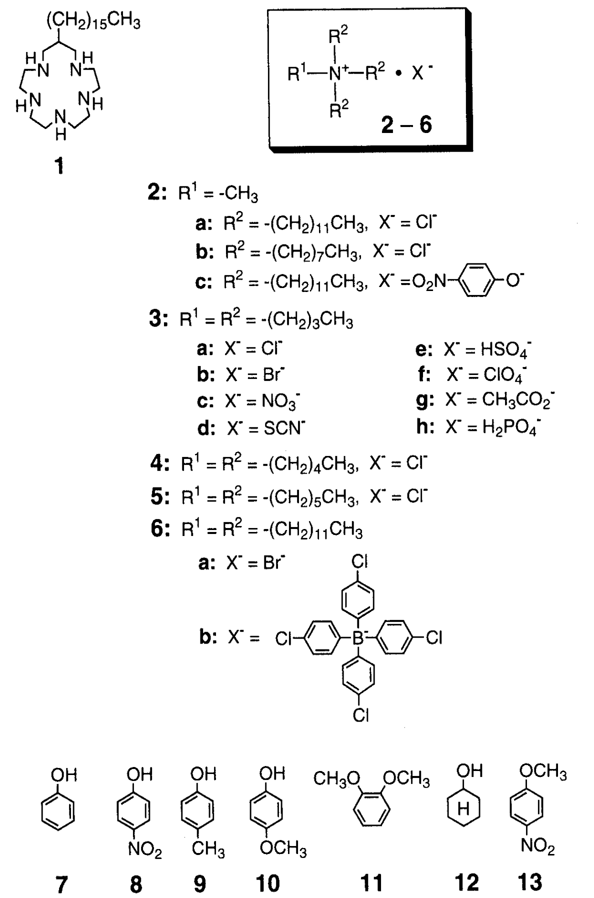

Fig. 1. Chemical Structures of Lipophilic Macrocyclic Pentaamine **1**, Quaternary Ammonium Salts **2**—**6**, and Phenol and Related Compounds (**7**—**13**)

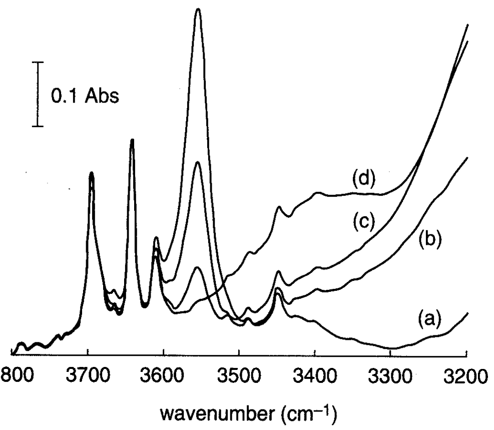

Fig. 2. IR Spectra of Phenol (**7**; 0.16 M) in the Presence or Absence of $(C_{12})_3C_1N^+ \cdot Cl^-$ (**2a**) in Benzene at Room Temperature (*ca.* 25 °C)

The concentration of **2a** is (a) 0, (b) 0.04, (c) 0.08, and (d) 0.16 M.

ison. The structures of all compounds are shown in Fig. 1. As possible interactions between Q^+X^- and ArOH, formation of the complex $Q^+X^- \cdot ArOH$ and the ion pair Q^+ArO^- was considered.

Interactions between Quaternary Ammonium Salts and Phenolic Compounds in Organic Solutions Interactions between Q^+X^- and ArOH in organic solutions was investigated with IR, ^1H- and ^{13}C-NMR, and UV spectra.

(a) IR Studies: Fig. 2 shows the OH stretching region in the IR spectra of phenol (**7**) in the presence or absence of $(C_{12})_3C_1N^+ \cdot Cl^-$ (**2a**) in benzene. With increasing molar ratio of **2a**, the intensity of the initial band at 3555 cm^{-1} decreased and that of a new band around 3400 cm^{-1} increased. It has been reported previously that complexation of undissociated phenols (ArOH) by quaternary ammonium or phosphonium salts (Q^+X^-) in nonpolar organic solvents (*e.g.*, CH_2Cl_2, CCl_4) induces a lower-frequency shift of the OH stretching band of ArOH.[2-4] The complexation also induces a higher-frequency shift of the band of Q^+X^- at *ca.* 110 cm^{-1} in the far IR region.[4,5] These IR spectral changes were ascribed to hydrogen bonding between the phenolic OH and the anion component X^- of the onium salt. Considering these results, the shift of the OH stretching band at 3555 cm^{-1} to the lower frequency region suggests the formation of the complex $Q^+X^- \cdot ArOH$ between **2a** and undissociated **7** by hydrogen bonding through the phenolic OH. The alternative mode of interaction involving proton dissociation and ion pair formation ($Q^+ \cdot ArO^-$) does not agree with the above results.

(b) NMR Studies: ^1H- and ^{13}C-NMR spectra of phenols (**7**—**10**) and related compounds (**11**, **12**) were measured at room temperature (*ca.* 25 °C) in the presence or absence of quaternary ammonium salt **2a**. In ^1H-NMR spectra in benzene-d_6, **2a** induced marked downfield shifts of the OH signals of the phenols. For example, the changes in the chemical shift of **7** (3×10^{-1} M), **8** (2×10^{-3} M), **9** (9×10^{-3} M), and **10** (9×10^{-3} M) in the presence of an equimolar amount of **2a** were 4.79→10.61 ppm, 4.00→11.92 (broad) ppm, 3.72→10.42 ppm, and 3.60→9.67 ppm, respectively. Since a nuclear Overhauser effect was observed for the ortho proton signals by irradiation of the downfield-shifted signals, the latter can be assigned to phenolic OH signals that are still undissociated and involved in hydrogen bonding. These results are consistent with those of the IR study described above.

Downfield shifts were also induced to the aromatic signals, particularly to the ortho proton and ipso carbon with respect to the OH group. For example, the downfield shifts of the signals of **8** (50 mM) induced by **2a** (50 mM) in benzene-d_6 were 6.02→7.47 ppm ($\Delta\delta = +1.45$ ppm) for H_{ortho} and 161.22→165.34 ppm ($\Delta\delta = +4.12$ ppm) for C_{ipso}. The downfield shifts of the ^1H-NMR signals of the OH as well as the aromatic protons of phenols upon complexation with quaternary ammonium salts are consistent with the reported observations in CH_2Cl_2 solutions[2] and in micellar systems.[6] On the other hand, changes in ^1H- and ^{13}C-NMR spectra in the presence of an equimolar amount of **2a** in benzene-d_6 were very small for **12** and negligible for **11**. All of the above results support the mode of complexation between Q^+X^- and ArOH involving the phenolic OH.

(c) UV Studies: Fig. 3 shows the absorption spectra of 7.41×10^{-5} M **8** in the presence or absence of **2a** in benzene. With increasing concentration of **2a**, the initial absorbance at 300 nm shifted to a longer wavelength and eventually reached 321 nm. An isosbestic point was observed at 305 nm, indicating the formation of a single complexed species in benzene. The stoichiometry of the complex of **8** and **2a** was confirmed to be 1 : 1 by the continuous variation method (Job's plot; Fig. 4). Since the wavelength

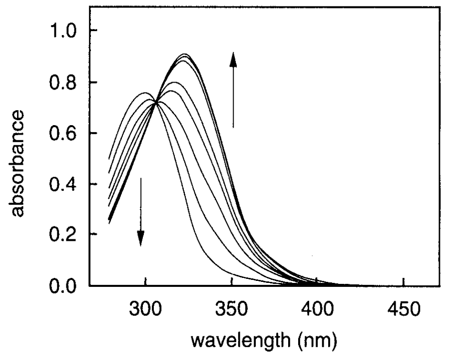

Fig. 3. Absorption Spectra of *p*-Nitrophenol (**8**; 7.4×10^{-5} M) in the Presence or Absence of $(C_{12})_3C_1N^+ \cdot Cl^-$ (**2a**) in Benzene at Room Temperature (*ca.* 20 °C)

The concentration of **2a** was increased successively from 0 to 1.9×10^{-5}, 3.7×10^{-5}, 5.6×10^{-5}, 7.4×10^{-5}, 1.5×10^{-4}, 2.2×10^{-4}, and 3.0×10^{-4} M. The direction of the spectral change with increasing concentration of **2a** is indicated with an arrow.

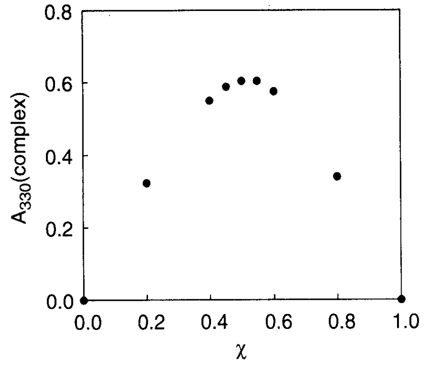

Fig. 4. The Absorbance at 330 nm of the Complex of *p*-Nitrophenol (**8**) and $(C_{12})_3C_1N^+ \cdot Cl^-$ (**2a**), Plotted against the Mole Fraction χ of **2a**

The sum of the concentrations of **8** and **2a** was kept constant at 1.4×10^{-4} M.

Table 1. Complexation Constants (K_s), Acid Dissociation Constants (pK_a), and Partition Coefficients (log P_{oct}) of Phenols and Related Compounds

ArOH	K_s (M^{-1})[a]	pK_a[b]	log P_{oct}[c]
p-Nitrophenol (**8**)	1.3×10^5	7.15	1.91
p-Cresol (**9**)	1.5×10^4	10.26	1.93
p-Methoxyphenol (**10**)	7.9×10^3	10.20	1.34
Cyclohexanol (**12**)	7.4×10^1	*ca.* 16	1.23
1,2-Dimethoxybenzene (**11**)	NC[d]	—	—
p-Nitroanisole (**13**)	NC[e]	—	—

a) The stability constants of the 1 : 1 complexes with $(C_{12})_3C_1N^+ \cdot Cl^-$ (**2a**) were determined in benzene at room temperature by either UV (**8**; *ca.* 20 °C), ^{1}H-NMR (**9**, **10**; *ca.* 25 °C), or ^{13}C-NMR (**12**; *ca.* 25 °C). See the Experimental for details. *b*) Acid dissociation constants (pK_a) at 25 °C, taken from reference 14. *c*) Partition coefficients for 1-octanol/water system (log P_{oct}) at room temperature, taken from reference 15. *d*) Negligible change in ^{1}H-NMR spectra. *e*) Negligible change in UV spectra.

of 321 nm is much shorter than that of the dissociated form of **8** [λ_{max} = 414 nm for $(C_{12})_3C_1N^+ \cdot NPO^-$ (**2c**) in benzene], the involvement of the neutral form of a phenolic compound in the complexation with **2a** is further supported. In contrast to **8**, no shift was observed for the corresponding *O*-methyl compound (**13**), indicating again that a phenolic OH group plays an essential role in the complexation with a quaternary ammonium salt in a homogenous solution.

Solvent Effect The complexation between Q^+X^- and ArOH was shown to be subject to a solvent effect. In ^{13}C-NMR studies, upon addition of an equimolar amount of **2a** or **2b**, the C_{ipso} signal of **7** (0.12—0.3 M) in benzene-d_6 shifted downfield from 156.47 to 159.39 ($\Delta\delta = +2.92$ ppm) and from 156.26 to 159.37 ppm ($\Delta\delta = +3.11$ ppm), respectively. A similar magnitude of downfield shift was also observed in $CDCl_3$. In contrast, the downfield shift was negligible (<0.2 ppm) in more polar solvents such as dimethyl sulfoxide-d_6 and methanol-d_4. Also in UV studies, the magnitude of the bathochromic shift for **8**, induced by complexation with **2a**, decreased with increasing polarity of the solvent; the band of **8** shifted by *ca.* 20 nm in benzene (*vide supra*), by 10 nm in chloroform (from 309 to 319 nm), and no shift was observed in ethanol. Addition of a small amount of water to benzene led to a decrease in the stability of the complex, as manifested by a decrease in the stability constant of the 1 : 1 complex of **8** and **3a** ($K_s = 1.9 \times 10^5\,M^{-1}$ in dry benzene and $5.8 \times 10^4\,M^{-1}$ in water-saturated benzene). Such solvent effects are characteristic of interactions involving polar groups and hence support the involvement of the phenolic OH group in the interaction with a quaternary ammonium salt.

Nature of Interactions in Homogenous Solutions For more quantitative discussions, the stability constants for the 1 : 1 complexes of phenols with different pK_a's and quaternary ammonium salts (Q^+X^-) with different cation (Q^+) and anion (X^-) components were determined in benzene. The K_s values were calculated by a non-linear curve-fitting method carried out with ^{1}H-NMR, ^{13}C-NMR, or UV titration.

(a) Effect of the Phenol Structure: Table 1 lists the stability constants (K_s) of the 1 : 1 complexes of **2a** and phenols or related compounds (**8**—**13**) in benzene, together with the pK_a[14)] and log P_{oct}[15)] values for the latter. The results indicate that the stability (K_s) of the complex $Q^+X^- \cdot$ArOH reflects the acidity and lipophilicity of ArOH. The greater K_s values for **8** against **9** and **9** against **10** show, respectively, the effects of acidity and lipophilicity. In contrast to the phenolic compounds, the complexation of **2a** with cyclohexanol (**12**) was very weak and that with 1,2-dimethoxybenzene (**11**) and *p*-nitroanisole (**13**) was negligible.

(b) Effect of the Structure of Quaternary Ammonium Salt: The stability constants (K_s) in benzene for the 1 : 1 complexes of **8** and a series of Q^+X^- with different X^- or Q^+ components are listed in Table 2. In all cases, the UV spectra of **8** in the presence of a large excess of Q^+X^- showed absorption maxima at 314—324 nm, indicating complexation that involves undissociated **8**. This is consistent with the observations in the IR, NMR, and UV spectra described earlier. The stability of the complex with **8** was found to be greatly affected by X^- (markedly different K_s values for **3a**—**f** and **6a**, **b**) but not by Q^+ (similar K_s values for **2a**, **3a**, **4**, and **5**). These results support, on a quantitative basis, the notion that the major factor for the complexation is the interaction between an undissociated phenolic OH and the anionic component X^- of Q^+X^-.

Table 2. Stability Constants (K_s) in Benzene for the 1 : 1 Complexes of *p* Nitrophenol (**8**) and a Series of Quaternary Ammonium Salts (Q^+X^-), together with Ionic Radii of X^-

Q^+X^-	K_s (M^{-1})[a]	r_x^* (Å)[b]
$(C_4)_4N^+\cdot Cl^-$ (**3a**)	1.9×10^5	1.80
$(C_4)_4N^+\cdot Br^-$ (**3b**)	5.2×10^4	1.95
$(C_4)_4N^+\cdot NO_3^-$ (**3c**)	2.0×10^4	2.03
$(C_4)_4N^+\cdot SCN^-$ (**3d**)	1.5×10^4	2.08
$(C_4)_4N^+\cdot HSO_4^-$ (**3e**)	1.1×10^3	—
$(C_4)_4N^+\cdot ClO_4^-$ (**3f**)	NC	2.28
$(C_{12})_4N^+\cdot Br^-$ (**6a**)	5.7×10^4	1.95
$(C_{12})_4N^+\cdot$T*p*ClPB$^-$ (**6b**)[c]	NC	—
$(C_{12})_3C_1N^+\cdot Cl^-$ (**2a**)	1.3×10^5	1.80
$(C_5)_4N^+\cdot Cl^-$ (**4**)	2.1×10^5	1.80
$(C_6)_4N^+\cdot Cl^-$ (**5**)	2.1×10^5	1.80

a) Stability constants (K_s) of the 1 : 1 complexes of *p*-nitrophenol (**8**) and quaternary ammonium salts (Q^+X^-), determined by UV titration in benzene at room temperature (*ca.* 20 °C). See the Experimental for details. *b*) Ionic radius of X^-,[16a] calculated from the molal volume of ion from the partial volume at infinite dilution.[16b] *c*) T*p*ClPB = tetrakis(*p*-chlorophenyl)borate. NC: Negligible complexation.

The stability of the complex with respect to X^- was in the order of Cl^- (**3a**) > Br^- (**3b**, **6a**) > NO_3^- (**3c**) ≥ SCN^- (**3d**) ≫ ClO_4^- (**3f**), T*p*ClPB$^-$ (**6b**) (no interaction). This order is parallel to that of the ionic radius of X^- calculated[16a] from its molal volume[16b] (r_x^*; see Table 2) and is also consistent with that of the hydration energies of some anions in the gaseous phase ($Cl^- > Br^- > NO_3^-$).[7b,c] Such a tendency, which can be considered to reflect hydrogen bonding (and/or charge-dipole) interactions between X^- and ArOH, has previously been observed for complexation of Q^+X^- and ArOH in nonpolar solvents, manifested by the stability constants of 1 : 1 complexes[3] and the force constants of the $OH\cdots X^-$ interactions in IR spectra.[4,5] A similar tendency was observed in nonpolar solvents for the stability constants of the dimers of quaternary ammonium salts[16a] and of the complexes between quaternary ammonium salts and aliphatic alcohols.[17]

These results confirm the view that the interaction between an undissociated phenolic OH and the anionic component X^- of Q^+X^- by hydrogen bonding is essential for the complexation of Q^+X^- and ArOH, as demonstrated previously by other groups on the basis of IR[2-5] and NMR[2,3] studies. Furthermore, the K_s values are found to be parallel with the magnitudes of anionic potentiometric responses by membranes based on Q^+X^-,[9] indicating that the complexation of ArOH by Q^+X^- plays an important role in the anionic potentiometric responses.

Proton Dissociation and Ion Pair Formation in Homogenous Organic Solutions In our new model for the potentiometric response to neutral phenols by organic liquid membranes based on Q^+X^-,[9] not only initial complexation ($Q^+X^- + ArOH \rightarrow Q^+X^-\cdot ArOH$) but also subsequent proton dissociation and ion-pair formation ($Q^+X^-\cdot ArOH \rightarrow Q^+ArO^- + HX$) are regarded as the key processes for the anionic potentiometric response. The latter process is generally unfavorable because, in many cases, it involves the formation of a stronger acid in an acid-base equilibrium. In addition, the stronger acid formed is generally less soluble in nonpolar organic solvents, and this contributes as an additional unfavorable factor.

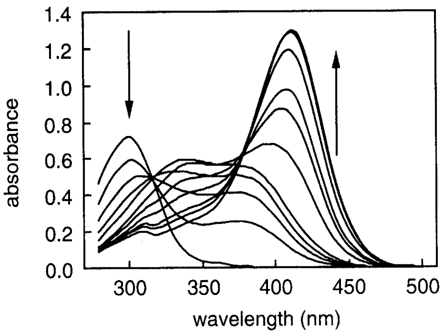

Fig. 5. Absorption Spectra of *p*-Nitrophenol (**8**; 7.4×10^{-5} M) in the Presence or Absence of $(C_{12})_3C_1N^+\cdot AcO^-$ (**3g**) in Benzene at Room Temperature (*ca.* 20 °C)

The concentration of **3g** was increased successively from 0 to 1.9×10^{-5}, 3.7×10^{-5}, 5.6×10^{-5}, 7.4×10^{-5}, 1.5×10^{-4}, 2.2×10^{-4}, 3.0×10^{-4}, 4.4×10^{-4}, 5.5×10^{-4}, and 7.4×10^{-4} M . The direction of the spectral change with increasing concentration of **3g** is indicated with an arrow.

However, we found that proton dissociation and ion pair formation occurred by adding a large excess of **3g** ($X^- = AcO^-$) to a solution of **8** in benzene. In this case, the acid formed (AcOH, $pK_a = 4.756$)[14] is relatively weak though still stronger than **8** ($pK_a = 7.15$).[14] By increasing the concentration of **3g**, the initial λ_{max} at 300 nm for undissociated **8** shifted first to *ca.* 340 nm (**8**: $Q^+X^- = 1:1$ molar ratio) and further to 410 nm as shown in Fig. 5. The latter λ_{max} value corresponds to the dissociated form of **8** in benzene, as observed for **2c** ($\lambda_{max} = 414$ nm). The presence of a large excess of Q^+X^- seems to stabilize the Q^+ArO^- ion pair sufficiently to enable the liberation of relatively weak acid. Such a proton dissociation in a homogeneous solution was not observed for the X^- with a weaker basicity and/or a poorer solubility in nonpolar organic solvents ($X^- = Cl^-$, Br^-, NO_3^-, SCN^-, ClO_4^-, and T*p*ClPB$^-$).

However, when a particular driving force is available, the formation of a stronger acid in an acid-base equilibrium is possible even for X^- with weak basicity. It was reported that the formation of a stronger acid by proton dissociation of a phenolic compound occurred in a cationic micellar system[18] and also in a homogeneous solution under a strongly cationic environment generated by a multiply protonated macrocyclic polyamine.[19] Interestingly, we found that the ArOH, extracted and complexed by Q^+X^- in an organic solvent, underwent proton dissociation with concomitant ejection of HX to the aqueous phase.[9] The driving force of this process is dissolution of HX to the aqueous phase. Such a process, inherent with a two phase system, allows the formation of a stronger acid even for X^- with a weak basicity and/or a poor solubility in nonpolar organic solvents, such as the ones described above.[20] We have shown that consideration of the second process involving proton dissociation and acid ejection, in addition to the first process involving simple complexation (*vide supra*), is essential for explaining the anionic potentiometric responses to neutral phenols.[9]

Conclusion

Spectroscopic measurements (IR, ^{1}H- and ^{13}C-NMR, UV) and quantitative investigations based on the stability constants of the complex $Q^+X^- \cdot ArOH$ clearly showed that the complexation of Q^+X^- and ArOH occurs in homogenous organic solutions by hydrogen bonding interactions between X^- and the phenolic OH group. The K_s values were found to be parallel to the magnitudes of anionic potentiometric responses by membranes based on Q^+X^-,[9] indicating that hydrogen bonding through a phenolic OH group plays an important role not only in the complexation between Q^+X^- and ArOH in a homogeneous organic solution but also in a potentiometric response, which involves chemical processes occurring at a membrane/aqueous solution interface.

Experimental

^{1}H- and ^{13}C-NMR spectra were measured on a JNM-A500 Fourier transform NMR spectrometer (500 and 125 MHz, respectively; JEOL, Tokyo, Japan). Chemical shifts are reported in δ values in ppm downfield of tetramethylsilane (TMS, 0.1%) as the internal standard. IR spectra were recorded on a Model 1720-X Fourier transform infrared spectrometer (Perkin-Elmer, Norwalk, CT, U.S.A.). UV-visible spectra were recorded on a UV-240 spectrophotometer (Shimadzu, Kyoto, Japan).

Chemicals The following compounds were purchased and used without further purification: Tridodecylmethylammonium chloride (**2a**) (Aldrich Chemical, Milwaukee, WI, U.S.A.), methyltrioctylammonium chloride (**2b**) (Tokyo Kasei Kogyo, Tokyo, Japan), tetrabutylammonium chloride (**3a**) (Aldrich Chemical), tetrabutylammonium bromide (**3b**) (Tokyo Kasei Kogyo), tetrabutylammonium nitrate (**3c**) (Aldrich Chemical), tetrabutylammonium thiocyanate (**3d**) (Tokyo Kasei Kogyo), tetrabutylammonium hydrogensulfate (**3e**) (Tokyo Kasei Kogyo), tetrabutylammonium perchlorate (**3f**) (Tokyo Kasei Kogyo), tetrabutylammonium acetate (**3g**) (Aldrich Chemical), tetrabutylammonium dihydrogenphosphate (**3h**) (Aldrich Chemical), tetrapentylammonium chloride (**4**) (Wako Pure Chemical, Osaka, Japan), tetrahexylammonium chloride (**5**) (Kanto Chemical, Tokyo, Japan), tetradodecylammonium bromide (**6a**) (Sigma Chemical, St. Louis, MO, U.S.A.), and tetradodecylammonium tetrakis(*p*-chlorophenyl)borate (**6b**) (Fluka, Buchs, Switzerland). The purities of these quaternary ammonium salts were above 97%, as checked by ^{1}H-NMR. Tridodecylmethylammonium *p*-nitrophenolate (**2c**) was prepared according to our previous paper.[9]

The following phenol and related compounds were of the highest quality grade commercially available and used without further purification: Phenol (**7**), *p*-nitrophenol (**8**), *p*-cresol (**9**), and *p*-nitroanisole (**13**) from Tokyo Kasei Kogyo; *p*-methoxyphenol (**10**), 1,2-dimethoxybenzene (veratrole, **11**), and cyclohexanol (**12**) from Wako Pure Chemical.

IR Measurements Sample solutions were prepared from appropriate stock solutions of **2a** (0.57 M) and/or **7** (0.22 M) in benzene. Quaternary ammonium salt **2a** was used after drying under vacuum, and **7** and benzene were used after drying over molecular sieves 5A. IR spectra were recorded with a resolution of 4 cm^{-1} at room temperature (*ca.* 25 °C). The sample solution (100 μl) was set in an IR liquid cell with NaCl windows, and spectra were measured with a triglycine sulfate (TGS) detector operated under dry air.

^{1}H- and ^{13}C-NMR Measurements ^{1}H- and/or ^{13}C-NMR spectra of phenolic or related compound **7** (40 or 160 mM), **8** (2.0 or 50 mM), **11** (20 or 80 mM), or **12** (20 mM) in the presence or absence of an equimolar amount of **2a** were measured in benzene-d_6, $CDCl_3$, DMSO-d_6, or CD_3OD. Similar measurements were made with a mixture of **7** and **2b** in benzene-d_6 or $CDCl_3$. All measurements were carried out at room temperature (*ca.* 25 °C). The stability constants (K_s) of the complexes of **2a** and **9**, **10** or **12** were determined by a nonlinear least-squares curve fitting method, applied to the chemical shift of the ortho proton (with respect to the phenolic OH) with varying concentrations of **2a** (0 to 4 eq) relative to **9** or **10** (10^{-3}—10^{-2} M). The K_s value of the complex of **2a** and **12** was determined in a similar manner, calculating from the changes in the chemical shift of the ipso carbon (with respect to the phenolic OH) with varying concentrations of **2a** (0 to 4 eq) relative to **12** (5.0×10^{-2} M). ^{1}H-NMR spectral change was negligible for **11** (2×10^{-2} M) in the presence of **2a** (up to 4 eq).

UV Measurements Sample solutions were prepared from appropriate stock solutions of phenolic or related compound (**8** or **13**, 1 mM) and/or quaternary ammonium salts (1—8 mM) in benzene, chloroform, or ethanol. Chloroform was used after passing through a basic alumina column. The stoichiometry of the complex of **8** and **2a** was determined at room temperature (*ca.* 20 °C) by the continuous variation method (Job's plot), plotting the absorbance at 330 nm of the complex of **8** and **2a** against the mole fraction of **2a** in benzene. The sum of the concentrations of **8** and **2a** was kept constant at 1.4×10^{-4} M. The stability constants (K_s) of the complexes of quaternary ammonium salts and **8** were determined at room temperature (*ca.* 20 °C) by a nonlinear least-squares curve fitting method at the absorbance of 330 nm with varying concentrations of quaternary ammonium salt (0 to 50 eq) relative to **8** (7.4×10^{-5} M). UV spectral change was negligible for **13** (9.7×10^{-5} M) in the presence of a large excess of **2a**.

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20) Similar UV spectral changes indicating proton dissociation and ion pair formation were observed when a large excess of **3h** ($X^- = H_2PO_4^-$) was added to a solution of **8** in benzene. Since precipitates (phosphoric acid) were formed in this case, the driving force for the formation of a stronger acid (H_3PO_4, $pK_a = 2.148$)[14] from a weaker one (**8**, $pK_a = 7.15$)[14] is considered to be separation of the acid from the equilibrium in addition to possible stabilization of the Q^+ArO^- ion pair by a large excess of Q^+X^-.