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Equilibrium Distribution of Aromatic Compounds between Aqueous Solution and Coacervate of Nonionic Surfactants

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ABSTRACT

Studies have been made of the equilibrium distribution of aromatic compounds between an aqueous solution and a coacervate of a nonionic surfactant, polyoxyethylene nonyl phenyl ether, which has an average ethylene oxide number of 10. Phase separation of the surfactant solution was attained by allowing it to settle at a temperature above the cloud point, and then the aromatic compounds were partitioned into the surfactant-rich phase from the solution in a form of the neutral species. The extraction behavior could be interpreted in terms of the acid dissociation constant as a function of the solution pH. It was found that organics which lower the cloud point to larger extent can attain higher extraction. Furthermore, the cloud-point extraction of phenol in a mixed surfactant system has been examined.

INTRODUCTION

Increased attention has been given in recent years to the utilization of surface-active agents for the separation and purification of various compounds, e.g., bioproducts and environmental pollutants, from aqueous

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streams. There are some advantages in surfactant-based separation technologies: availability of various surfactants, possibility of designing a desirable surfactant, flexibility of the process, and nontoxicity and biodegradability of most surfactants (1). Cloud-point extraction is a water-based separation method which utilizes coacervation characteristics of some classes of nonionic surfactants.

Aqueous solutions of nonionic surfactants turn cloudy at a definite temperature on heating, and this temperature is referred to as the cloud point (CP). Such a clouding phenomenon is caused by the decreased solubility of a surfactant in aqueous media as a result of weakening of hydrogen bonding between a water molecule and the hydrophilic moiety of the surfactant due to heating. By allowing the solution to settle at a temperature above the CP, the surfactant aggregates to make a small coacervate phase; in other words, the solution is phase-separated into water and surfactant-rich phases. If water-soluble organic compounds are present in a nonionic surfactant solution and phase-separated by heating, the solutes may be partitioned between the two phases according to their affinity to the surfactant. Nonionic surfactants containing oxyethylene units in their molecules usually reveal such phenomena as clouding and coacervation.

Cloud-point extraction has been applied for separating several compounds, e.g., water-soluble organics (2–5), membrane proteins (6, 7) and metals (8–10), from aqueous media. In a previous paper (11) we studied the CP extraction of phenol and pyridine derivatives from aqueous solution, and we found that these compounds are partitioned successfully in the coacervate phase and that the addition of NaCl has positive effects on both the recovery and phase-separation characteristics. The present study has been conducted to elucidate the extraction mechanism for several aromatic compounds in connection with dissociation and to assess the possibility of using a mixed surfactant system for CP extraction.

EXPERIMENTAL

Reagents

Polyoxyethylene nonyl phenyl ethers with an average chain length of 10 and 7.5 oxyethylene units (abbreviated as PONPE10 and PONPE7.5, respectively) were obtained as nonionic surfactants from Tokyo Kasei Kogyo Co. and used without further purification. Aromatic compounds investigated as extracts were phenol, benzenesulfonic acid, aniline, benzoic acid, *p*-phenolsulfonic acid, *o*-nitrophenol, *o*-cresol (1-methylphenol), catechol (1,2-dihydroxybenzene), resorcinol (1,3-dihydroxybenzene), hydroquinone (1,4-dihydroxybenzene), *o*-aminophenol, and salicylic acid (1-hydroxybenzoic acid). All chemicals used were of reagent grade.

Procedure

A desired initial solution (aqueous feed) was obtained by blending two aqueous stock solutions of the surfactants and organic compounds which were prepared by dissolving the respective solutes in deionized water at an appropriate volume ratio. A small amount of HCl or NaOH was added to the solution for pH adjustment, and an appropriate amount of NaCl was added in the study on the effect of salt. Typical concentrations of the surfactant and organics in an aqueous feed are 5.0 wt% and 0.01 M, respectively.

An aqueous feed (20 mL) contained in a 25-mL graduated glass tube was heated rather quickly just below the CP, followed by slow heating in a controlled temperature water bath until the solution became turbid at the CP temperature. After observing the CP, the solution was subjected to overnight gravity-settling for phase separation in an incubator at 70°C (unless otherwise specified), and the equilibrium volumes of both the surfactant-rich and aqueous phases were measured. An aliquot of the aqueous phase (upper phase) was subsequently withdrawn, and the concentration of organic compounds was determined by means of gas chromatography with an FID detector or by UV spectrophotometry; that of the surfactant-rich phase was calculated from the mass balance. The surfactant concentration of the aqueous phase was determined by spectrophotometry at 277 nm.

RESULTS AND DISCUSSION

Cloud Point Extraction of Phenol

The solution temperature must be raised above the CP to attain phase separation; thus, it is desirable to lower the CP temperature in order to extract heat-sensitive substrates and to reduce costs. With a decrease in the ethylene oxide number of a nonionic surfactant molecule, the CP of its aqueous solution is lowered because of the increased hydrophobicity of the surfactant. Figure 1 shows the effect of the weight fraction of PONPE7.5 to the mixed surfactant with PONPE10 on the CP of aqueous solutions. At a temperature above the CP, the solution is in a state of clouding and ready for phase separation. The CP for the mixed surfactant system is positioned intermediate between the results obtained for each single system of PONPE10 and PONPE7.5, where the former was about 63°C and the latter below the freezing point in the absence of NaCl and

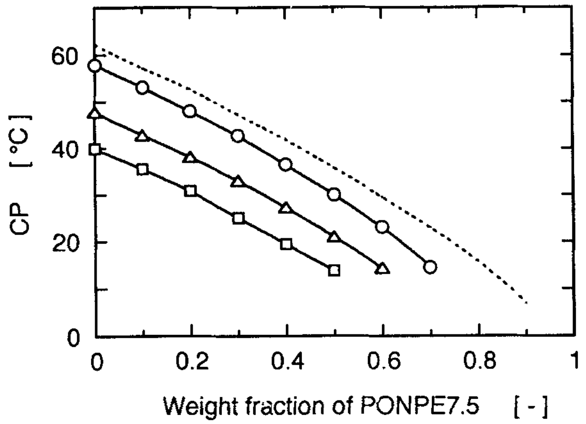

FIG. 1 Effect of weight fraction of PONPE7.5 on cloud point of mixed surfactant solutions with PONPE10. [PONPE10 + PONPE7.5] = 5 wt%; (NaCl, phenol) = - - - (0, 0), ○ (0, 0.01 M), △ (0.5 M, 0.01 M), □ (1.0 M, 0.01 M).

phenol. With an increasing fraction of PONPE7.5, the CP decreases gradually, and it is possible to attain phase separation at a lower settling temperature. However, a disadvantage in using the mixed system comes from a rise in the solution viscosity with an increase in PONPE7.5.

The addition of phenol or NaCl also gives rise to a significant lowering of the CP, as reported in a previous paper (11), whereby phase separation can be attained at ambient temperature. This indicates that CP may be adjusted to a desired temperature through a combination of salt and a mixed surfactant system.

Figure 2 shows the results for the CP extraction of phenol in a mixed surfactant system (total surfactant content of 5 wt%) at 70°C as a function of the weight fraction of PONPE7.5 to the two surfactants. The distribution ratio, D, is defined by

$$D = C_S/C_W \tag{1}$$

where C denotes the concentration of phenol and the subscripts S and W refer to the surfactant-rich and aqueous phases, respectively. The distribution ratio is substantially independent of the PONPE7.5 content. This indicates that a difference in the ethylene oxide number has no significant effect on phenol extraction under the experimental conditions.

The distribution ratio increases with increasing NaCl concentration, but the amount of phenol partitioned into the surfactant-rich phase was almost

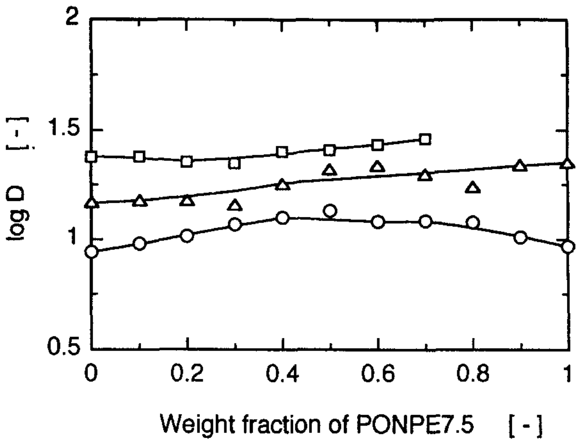

FIG. 2 Effect of weight fraction of PONPE7.5 on distribution ratio of phenol for mixed surfactant system at 70°C. [PONPE10 + PONPE7.5] = 5 wt%; [phenol] = 0.01 M; NaCl = 0 M (○), 0.5 M (△), 1.0 M (□).

the same, corresponding to ca. 70% of that in the feed. The effect of the salt concentration is attributable to the decrease in the volume of the surfactant-rich phase: the volume varied from 15 to 25% of the feed solution in the absence of NaCl to ca. 10% for an NaCl solution of 1.0 M. When the weight fraction of PONPE7.5 was over 0.7, however, phase separation of the solution with 1.0 M NaCl was incomplete owing to the close densities of the two phases. Henceforth, a PONPE10 solution of 5 wt% was used in this study.

The effect of solution pH on the CP is represented in Fig. 3. It is evident that the CP gives a constant temperature over a wide pH range from acid to neutral solutions at a NaCl concentration. For alkaline solutions the CP goes through a maximum with increasing pH; however, the presence of phenol has no significant effect in the pH region above 11. This implies that the interaction between phenol and PONPE10 is weaker in alkaline solution than in the lower pH region.

Figure 4 shows the relationship between the distribution ratio of phenol and the equilibrium solution pH in CP extraction with PONPE10 at 70°C, indicating that phenol is extracted from the solutions in a wide pH range from acidic to neutral, where the distribution ratio increases with an increase in NaCl concentration, as also in Fig. 2. A further increase in pH gives rise to a dramatic effect on extraction; for an alkaline solution without NaCl, the concentration of phenol in both phases is nearly equal.

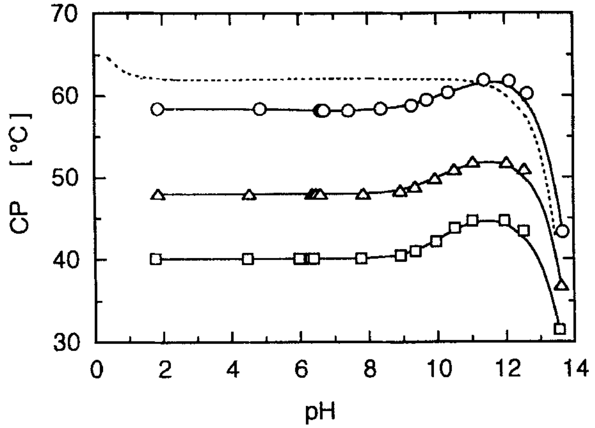

FIG. 3 Effect of solution pH and presence of NaCl or phenol on cloud point. [PONPE10] = 5 wt%, (NaCl, phenol) = --- (0, 0), ○ (0, 0.01 M), △ (0.5 M, 0.01 M), □ (1.0 M, 0.01 M).

Phenol, a weak acid, is dissociated in aqueous solution as

$$PhOH \rightleftharpoons PhO^- + H^+ \tag{2}$$

and the dissociation constant is defined as

$$K_a = [PhO^-][H^+]/[PhOH] \tag{3}$$

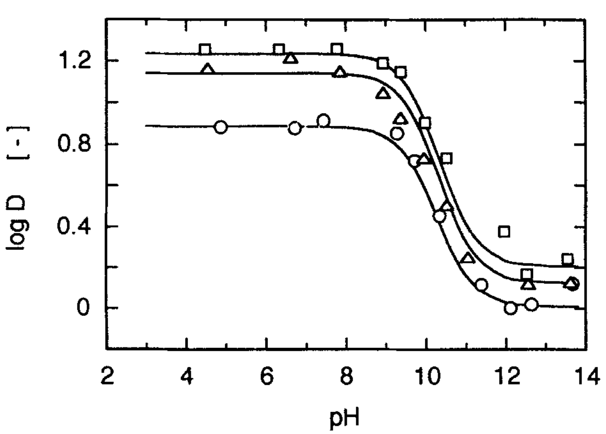

FIG. 4 Effect of solution pH and presence of NaCl on distribution ratio of phenol at 70°C. [PONPE10] = 5 wt%; [phenol] = 0.01 M; NaCl = 0 M (○), 0.5 M (△), 1.0 M (□).

The overall distribution ratio can be expressed by the following equation, provided that phenol is distributed between the two phases in the form of neutral and dissociated species.

$$
\begin{aligned}
D = \frac{C_S}{C_W} &= \frac{\overline{[\mathrm{PhOH}]} + \overline{[\mathrm{PhO^-}]}}{[\mathrm{PhOH}] + [\mathrm{PhO^-}]} = \frac{\overline{[\mathrm{PhOH}]}}{[\mathrm{PhOH}]}\left(\frac{1}{1 + K_a/[\mathrm{H^+}]}\right) \\
&\quad + \frac{\overline{[\mathrm{PhO^-}]}}{[\mathrm{PhO^-}]}\left(\frac{1}{1 + [\mathrm{H^+}]/K_a}\right) \qquad (4) \\
&= D_1\left(\frac{1}{1 + K_a/[\mathrm{H^+}]}\right) + D_2\left(\frac{1}{1 + [\mathrm{H^+}]/K_a}\right)
\end{aligned}
$$

where the overbar denotes the surfactant-rich phase. The term D_1 ($\overline{[\mathrm{PhOH}]}/[\mathrm{PhOH}]$) in Eq. (4) represents the distribution ratio of phenol as the neutral species and can be determined from experimental data at low pH, whereas the term D_2 ($\overline{[\mathrm{PhO^-}]}/[\mathrm{PhO^-}]$) is for the dissociated species at high pH. The values of D_1 and D_2 obtained in a variety of NaCl concentrations are presented in Table 1 together with the pK_a of phenol (12). In Fig. 4 the solid lines represent the results calculated from Eq. (4) with the values of D_1 and D_2; it is found that there is close agreement with the experimental data. The value of D_1 larger than D_2 comes from the fact that the neutral species is more liable to be extracted than the ionic species since it is less hydrophilic. Thus, it is considered that phenol is partitioned in the surfactant-rich phase through hydrogen bonding between the hydroxyl group of phenol and the ethylene oxide of the surfactant as well as the hydrophobic interaction between these molecules.

The distribution ratio of PONPE10 itself was also examined at a prescribed temperature for phase separation, and the results are plotted in Fig. 5 against the feed concentration. Although the distribution ratio increases with the addition of NaCl or an increase in the settling temperature, it is substantially independent of PONPE10 concentration. More-

TABLE 1
Values of D_1 and D_2 for Cloud-Point Extraction of Phenol

	NaCl (M)	pK_a	D_1	D_2
Phenol (PH)	0	9.82	7.72	1.02
Phenol (PH)	0.5	9.82	13.86	1.33
Phenol (PH)	1.0	9.82	17.21	1.59

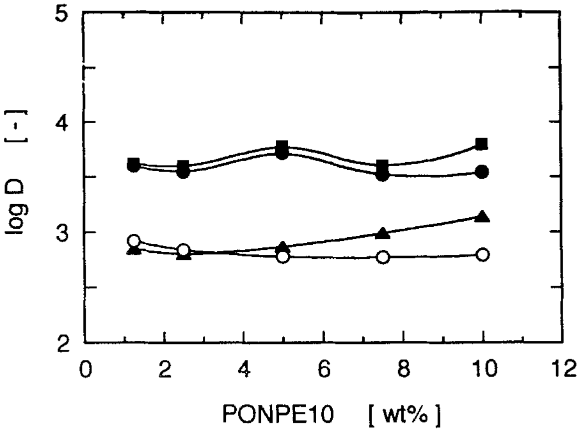

FIG. 5 Relationship between distribution ratio and feed concentration of PONPE10 after phase separation. (NaCl, temperature) = ○ (0, 70°C), ▲ (0.5 M, 60°C), ● (0.5 M, 70°C), ■ (0.5 M, 80°C).

over, the PONPE10 concentration of the aqueous phase after separation was found to be only severalfold of the CMC, whereas the water content of the surfactant-rich phase was ca. 80%. This finding leads to the conclusion that the CP extraction loss of the surfactant may be negligible in practical situations.

Cloud Point Extraction of Aromatic Compounds

Quantitative evaluation of the CP extraction of organic compounds was also attempted for several aromatics in the same way as for phenol in the previous section.

Figure 6 shows the results for the CP extraction of four monosubstituted benzene derivatives with PONPE10 at 70°C as a plot of log D versus the equilibrium solution pH. The partitioning of benzoic acid (abbreviated BA in Fig. 6) has a behavior similar to phenol (PH), though the D value begins to decrease at a much lower pH corresponding to its pK_a than that for phenol. The partitioning of aniline (AN) as a weak base also favors its free species at high basicities, and becomes lower for its protonated species at high acidities; hence the extraction behavior also varies near the pH corresponding to its pK_a. Benzenesulfonic acid (BSA) is a strong acid and hence is dissociated in the whole pH region studied, thus the extraction provides a low distribution ratio independent of the solution pH. The

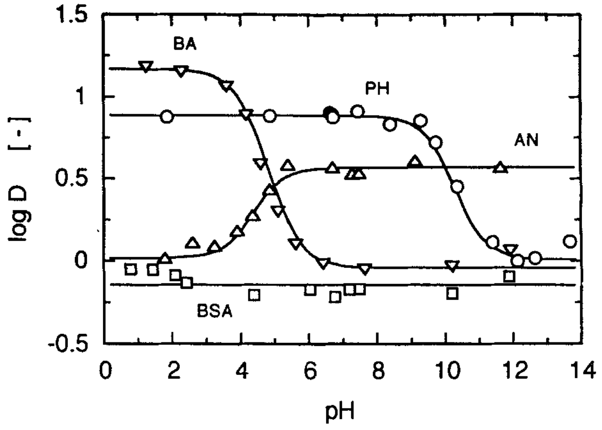

FIG. 6 Cloud-point extraction of monosubstituted benzene derivatives at 70°C. [PONPE10] = 5 wt%; [solute] = 0.01 M; [NaCl] = 0 M.

values of D_1 and D_2 for these aromatics were also evaluated on the basis of the experimental data (Table 2). The solid lines in Fig. 6 represent the calculated results. Note that in all runs a lowering of the CP was brought about in the pH region which gives the highest extraction for each solute.

Figure 7 shows the results for the CP extraction of disubstituted benzene derivatives with PONPE10 at 70°C. The distribution ratio of cresol (CR)

TABLE 2
Values of D_1, D_2, and D_3 for Cloud-Point Extraction of Benzene Derivatives

Solute	pK_{a1}	pK_{a2}	D_1	D_2	D_3
Benzenesulfonic acid (BSA)	—	—	0.89	—	—
Aniline (AN)	4.65	—	1.04	3.70	—
Benzoic acid (BA)	4.20	—	14.72	0.91	—
Phenolsulfonic acid (PA)	8.66	—	1.37	0.97	—
Nitrophenol (NP)	7.05	—	13.50	0.85	—
Cresol (CR)	10.28	—	21.24	1.31	—
Catechol (CA)	9.23	13.00	5.29	1.03	0.77
Resorcinol (RE)	9.30	11.06	4.85	0.65	0.47
Hydroquinone (HQ)	9.91	12.04	2.72	0.65	0.32
Aminophenol (AP)	4.74	9.87	1.30	2.93	0.82
Salicylic acid (SA)	2.81	13.40	23.38	0.52	1.93

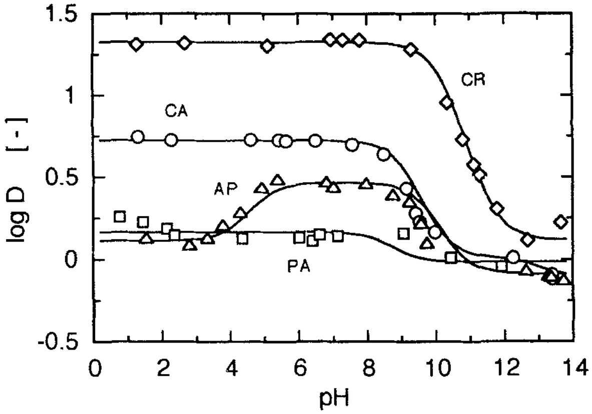

FIG. 7 Cloud-point extraction of disubstituted benzene derivatives at 70°C. [PONPE10] = 5 wt%; [solute] = 0.01 M; [NaCl] = 0 M.

is higher than that of phenol, as expected from its low solubility in water, so the ratio also decreases near the pK_a but has a significant value even at an extreme high pH. The values of D_1 and D_2 are also given in Table 2 together with those of phenolsulfonic acid (PA) and nitrophenol (NP).

Catechol (CA), a dibasic acid, gave a two-step extraction curve as in Fig. 7, although it is obscure in the higher pH region. By assuming the existence of three species of the compound, we define the distribution ratio as

$$\begin{aligned} D = {} & D_1\left(\frac{1}{1 + K_{a1}\cdot K_{a2}/[\mathrm{H}^+]^2 + K_{a1}/[\mathrm{H}^+]}\right) \\ & + D_2\left(\frac{1}{1 + [\mathrm{H}^+]/K_{a1} + K_{a2}/[\mathrm{H}^+]}\right) \\ & + D_3\left(\frac{1}{1 + [\mathrm{H}^+]^2/K_{a1}\cdot K_{a2} + [\mathrm{H}^+]/K_{a2}}\right) \end{aligned} \tag{5}$$

where D_1, D_2 and D_3 denote the respective distribution ratios of the three forms: neutral, mono-, and divalent species in Table 2. The D_1 value for catechol is a little lower than that of phenol because the former acid has two hydroxyl groups and hence is more hydrophilic. For the extraction curve of aminophenol (AP), the rise near pH 4.7 and the fall near pH 9.8 are attributable to the deprotonation of the amino group and of the hydroxyl group, respectively; the *D* value for its neutral species in neutral solution is higher than those in acid and alkaline solutions.

The *D* values for resorcinol (RE), hydroquinone (HQ), and salicylic acid (SA) are also listed in Table 2. At a lower pH, where the neutral species is dominant, salicylic acid gave a much higher D_1 value than phenol although it has a hydrophilic carboxyl group as well as a hydroxyl group. At an extremely high pH, on the other hand, a small rise of the distribution ratio, viz., D_3, was found. This behavior in SA extraction cannot be explained reasonably.

As stated in the previous section, the CP temperature of nonionic surfactant solutions was lowered in the presence of aromatic compounds. In Fig. 8 the distribution ratios for various solutes are plotted as a function of the CP difference in PONPE10 solutions with and without solute. The larger the difference, the higher the distribution ratio becomes; a linear relationship between them is found in Fig. 8. The incorporation of organic compounds into the surfactant micelle may make the micelle more hydrophobic and hence cause a lowering of the CP. Thus, we conclude that the extent of extraction is predictable from CP lowering, as in Fig. 8.

Smaller values of log *D* are found to be around 0 for almost all compounds in Figs. 6 and 7, where the solutes are partitioned equally between the two phases rather than excluded from the surfactant-rich phase. This indicates that backextraction is not efficient in recovering the solutes, and possibly raises problems. We are presently investigating more efficient recovery of solutes from the surfactant-rich phase.

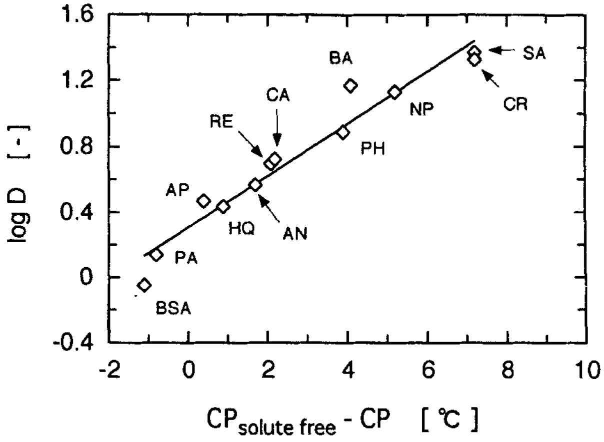

FIG. 8 Effect of difference in cloud points of surfactant solutions with and without solute on distribution ratio at 70°C. [PONPE10] = 5 wt%; [solute] = 0.01 M; [NaCl] = 0 M.

CONCLUSION

Cloud-point extraction of aromatic compounds from aqueous solutions using a nonionic surfactant, PONPE10, was studied, and the following results were obtained.

Phase separation of the surfactant solution was attained by settling it at a temperature above the CP, and phenol was partitioned into the surfactant-rich phase over a wide pH range from acid to neutral solutions. In the case of a mixed surfactant system with PONPE7.5, the CP could be lowered without reducing the extractability of phenol. The amount of surfactant remaining in the aqueous phase was so small that the loss of surfactant in CP extraction is negligible.

Cloud-point extraction of aromatic compounds was attained in the form of the neutral species; the distribution ratio could be expressed in terms of the acid dissociation constant. It was found that there is a linear relationship between the distribution ratio and the lowering of the CP induced by the presence of aromatics.

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