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Cloud-Point Extraction of Organic Compounds from Aqueous Solutions with Nonionic Surfactant

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ABSTRACT

Cloud-point extraction of organic compounds from aqueous solutions by using the nonionic surfactant PONPE10 has been investigated for phenol and three pyridines to clarify the effect of operating factors on its extractability. Phase separation of the surfactant solutions is attained at temperatures above the cloud point, and it is improved by adding NaCl or phenol. Phenol is extracted successfully in a wide pH range from acidic to neutral solutions with and without NaCl, where the extraction efficiency increases with an increase in the surfactant concentration. Backextraction of phenol from the surfactant-rich phase was found to be possible with alkaline solutions. Three pyridine derivatives can also be extracted from the solution under neutral and alkaline conditions, although the efficiencies are somewhat low compared with phenol. Moreover, selective separation of the pyridines from each other could be accomplished because of the difference in their hydrophobicities.

INTRODUCTION

The solubility of a nonionic surface-active agent in aqueous solution is dramatically depressed above a well-defined temperature. This temperature, which can be ascertained by the turbidity of the solution, is known

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as the cloud point (CP). Allowing the surfactant solution to leave above the temperature leads to two distinct phases: one is rich in the surfactant with a small amount of water and the other is the opposite; i.e., the surfactant forms a coacervate phase. Such a clouding phenomenon is attributed to the breaking of a hydrogen bond between a water molecule and the hydrophilic chains of the surfactant (which usually contains the oxyethylene chain) with rising temperature, and hence the surfactant micelle becomes more hydrophobic. CP is influenced by many factors including the hydrophile–liophile balance (HLB) of surfactants and the addition of other surfactants and salts (1–5).

Cloud-point extraction is a relatively new separation method which utilizes partitioning of the solute between surfactant-rich and water phases as a separation field. If an aqueous solution containing a nonionic surfactant and organic compounds is subject to phase separation upon temperature alteration, then the compounds are distributed between the two phases by hydrophobic and/or some specific interactions with the surfactant. Distinct features of CP extraction are solute–surfactant interaction occurring in the homogeneous phase before separation, not at the interface between the phases, phase separation induced by thermal energy, and a surfactant-rich phase containing appreciable amounts of water. Thus the extraction system is similar to an aqueous two-phase partitioning system rather than to solvent extraction. There are some advantages of CP extraction over an aqueous two-phase partitioning system: the high versatility which can be applied not only to macromolecules but also to smaller chemical species, and the smaller amount of surfactant required compared with polymer material for the latter system (6).

A quantitative study on the partitioning of analytical reagents, such as 8-quinolinol, between water and nonionic surfactant-rich phases has been reported by Hoshino et al. (7). Bordier (8) and Ganong et al. (9) also utilized the phase separation of nonionic surfactant solutions for protein separation. Watanabe et al. applied CP extraction to trace analysis of nickel in soils (10) and zinc in tap water (11, 12), wherein the metals were allowed to be hydrophobic by chelation with PAN for zinc and TAN for nickel. Nonionic surfactants used in these studies were isooctylphenoxy polyethoxyethanol (Triton X series), and polyoxyethylene-4-nonyl phenyl ether (PONPE). Moreover, CP extraction of organic compounds with another surfactant has been conducted by Saitoh et al. (6) and Schmid et al. (13), where the former used 3-(nonyl-dimethylammonio) propyl sulfate and the latter permethyl hydroxypropyl-β-cyclodextrin.

To assess the applicability of CP extraction to practical separations, however, there is still lack of information on the phase separation and partitioning of solutes. The present study was conducted to elucidate the effects of operating factors (temperature, time, concentration, etc.) on the CP extraction of water-soluble, organic compounds by using a nonionic surfactant.

EXPERIMENTAL

Reagents

Polyoxyethylene nonyl phenyl ether with an average chain length of 10 oxyethylene units (Tokyo Kasei Kogyo Co., Ltd., abbreviated as PONPE10 hereinafter) was used as a nonionic surfactant without further purification. Phenol and pyridine derivatives were selected as model organic compounds of a weak acid and base, respectively, wherein the latter compounds were pyridine, 3-picoline (3-methylpyridine), and 2,4-lutidine (2,4-dimethylpyridine).

Aqueous stock solutions of the surfactant and the organic compounds were prepared by dissolving the respective solutes in deionized water, and a desired initial solution was obtained by blending them at an appropriate volume ratio. A small amount of HCl or NaOH was added to the solution for pH adjustment in the pH study. All chemicals used were of reagent grade.

Procedure

Cloud point was determined from measurement of the solution temperature at the onset of cloudiness on heating, whereby solution (20 mL) contained in a 25-mL graduated glass tube was heated rather quickly just below the CP, subsequently carefully heated at the rate of about 1°C per every 4 minutes in a thermostatted water bath. After observing CP, the solution was allowed to settle over 12 hours at a prescribed temperature (70°C, except when studying the effect of temperature) in an incubator, then an equilibrium volume of the surfactant-rich phase was determined. History of the coacervation was also measured in the thermostatted water bath.

The cloud-point extraction of organic compounds was carried out as follows. An aqueous solution containing the surfactant and the solute was well mixed at room temperature and allowed to phase-separate over 12 hours at 70°C. After reaching equilibrium, the concentration of the organic compounds in the aqueous phase was determined on a gas chromatography with an FID detector; the amount of the solute distributed in the surfactant-rich phase was then calculated from the mass balance. Determinations of CP and of the volume of the surfactant-rich phase were also made in the presence of the solute as described above. Backextraction (stripping) of the solute from the surfactant-rich phase was carried out by well mixing the coacervate phase (5 mL) with a stripping solution (10 mL) and by phase-separating over 12 hours at 70°C.

RESULTS AND DISCUSSION

Cloud Points and Phase Separation

Figure 1 represents typical CP data for aqueous surfactant solutions as a function of the initial PONPE10 concentration. At temperatures above the CP, the solution is in the state of clouding and ready to be phase separated. The CP of only PONPE10 solution without solute was substantially constant (62°C) over a wide range of the surfactant concentrations, though being a little higher at extremely low concentration.

Addition of salts had a significant effect on the CP: 1 M NaCl allowed it at a temperature as low as 44°C and 2 M as 33°C. With 3 M NaCl, the CP was lowered to 23°C, thus the phase separation could be attained at ambient temperature, though the data are not shown here. The surfactant formed the coacervate as the lower phase with the salt concentration below 1 M, whereas as the upper phase from the solution above 2 M, corresponding to the phase density. Such a salting-out results from the electrolytes weakening the hydrogen bond between the water molecule and the surfactant. This indicates that the control of CP to a desired temperature is possible with the addition of salts to the surfactant system.

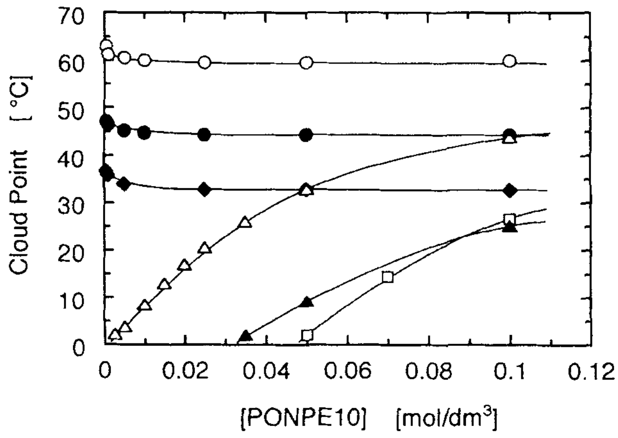

FIG. 1 Effect of addition of NaCl and phenol on cloud point as a function of PONPE10 concentration. (NaCl, phenol) = (0, 0) ○; (1 M, 0) ●; (2 M, 0) ◆; (0, 0.05 M) △; (1 M, 0.05 M) ▲; (0, 0.1 M) □.

In the present system, the presence of phenol also affects the CP at much lower concentrations compared with NaCl, as shown in Fig. 1. With increasing concentration of phenol, the CP was lowered below the ambient temperature and ultimately the freezing point; however, the extent of the lowering is larger at lower PONPE10 concentrations. This implies that there is a strong interaction between the surfactant and phenol.

Figure 2 shows the effect of PONPE10 concentration on the volume ratio of the surfactant-rich phase, $V_S/(V_S + V_W)$, at 70°C. The volume ratio increases with the PONPE10 concentration as a result of an increase in the amount of surfactant in the whole system. For example, when phase separating 20 mL of 0.1 M PONPE10, we obtained 4.9 mL of the surfactant-rich phase containing about 1.28 g PONPE10 and the residue of the aqueous phase. It has been reported (11) that after the phase separation occurred, surfactant concentration of the aqueous phase is approximately equal to the critical micelle concentration; thus, loss of the surfactant is negligible in CP extraction.

Figure 3 shows typical coacervation histories of PONPE10 solutions. By allowing the solution to settle at 70°C, the volume ratio of the surfactant-rich phase decreased with time, and both phases were equilibrated up to 40 minutes for all the observations. The addition of NaCl as well as phenol not only facilitated formation of the coacervate but also decreased the equilibrated volume ratio (also see Fig. 2). Also, a temperature as high as 85°C had a significant effect on phase separation: a volume

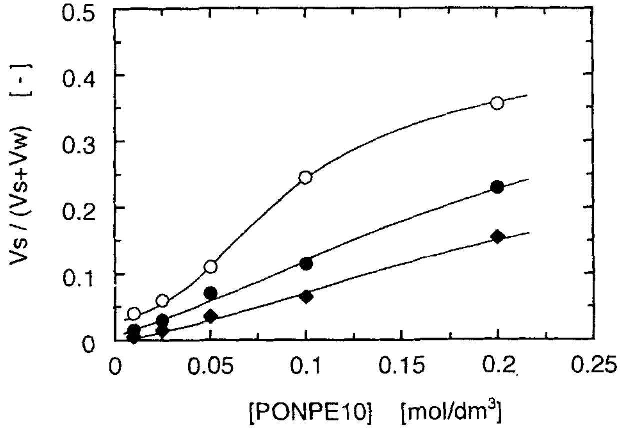

FIG. 2 Effect of PONPE10 concentration on volume ratio of surfactant-rich phase with and without NaCl. [NaCl] = 0 M (○), 1 M (●), 2 M (◆).

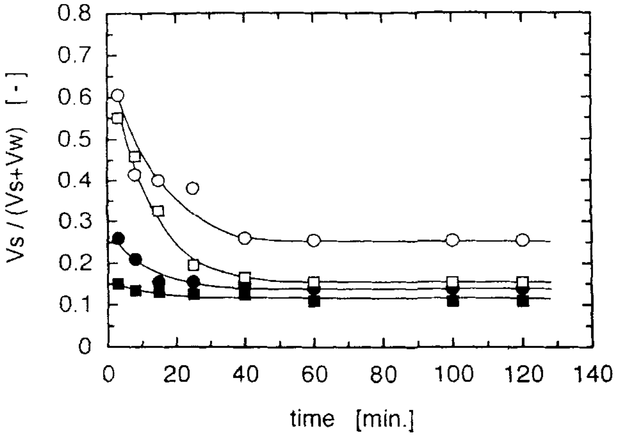

FIG. 3 Coacervation histories of PONPE10 solutions. [PONPE10] = 0.1 M; (NaCl, phenol) = (0, 0) ○; (1 M, 0) ●; (0, 0.05 M) □; (1 M, 0.05 M) ■.

ratio as small as 0.1 was obtained up to 20 minutes, though the data are not shown here. Thus, phase separation of surfactant solutions is relatively fast even without centrifugation. This leads to the expectation that CP extraction could be competed with conventional solvent extraction.

Cloud-Point Extraction of Phenol

If water-soluble organic compounds exist during phase separation of surfactant solution, it would be expected that the solutes are distributed between both phases according to the affinity of the solutes to the surfactant. Here we studied the cloud-point extraction of phenol as a typical organic weak acid.

The results are shown in Fig. 4 as a plot of the percent extraction, E, of phenol against the PONPE10 concentration. The percent extraction is defined as

$$E = 100\,(M_S/(M_S + M_W)) \tag{1}$$

$$M_S = V_S C_S \tag{2}$$

$$M_W = V_W C_W \tag{3}$$

where M and C denote the amount and concentration of phenol, and the subscripts S and W represent the surfactant-rich and aqueous phases, respectively. In the present study, the extent of extraction is given in terms of the amount of the solute instead of the concentration because

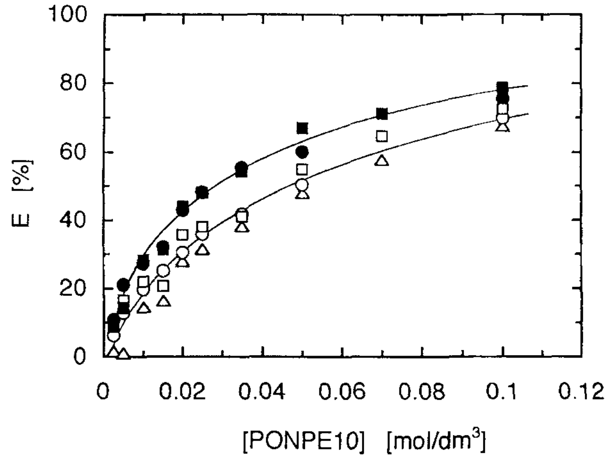

FIG. 4 Relationship between percent extraction of phenol and PONPE10 concentration with and without NaCl. (NaCl, phenol) = (0, 0.1 M) △; (0, 0.05 M) ○; (1 M, 0.05 M) ●; (0, 0.01 M) □; (1 M, 0.01 M) ■.

the volume of the surfactant-rich phase varies under experimental conditions. As Fig. 4 shows, the extraction efficiency increases with an increase in PONPE10 concentration and attains about 70% at 0.1 M of PONPE10, with little dependence on the initial phenol concentration. When plotted against the PONPE10 concentration, the distribution ratio gives a substantially constant value. This indicates that the distribution equilibrium holds in CP extraction in the same manner as in conventional solvent extraction.

The addition of NaCl to the solution tends to somewhat increase the percent extraction of phenol in the whole concentration range of PONPE10 in Fig. 4, accompanied by a lowering of the volume of the surfactant-rich phase. This leads to high phenol recovery in the surfactant-rich phase.

The effect of solution pH on the CP is shown in Fig. 5. For acid to neutral solutions, the CP has a constant value which depends on the concentrations of phenol and NaCl, as described above. A further increase of NaOH causes the CP to rise and approach the inherent value of the PONPE10 solution without phenol. Thus, the effect of the presence of phenol was canceled in the pH region above 12, regardless of its concentration. The same pH effect was also observed for the volume ratio of the surfactant-rich phase, where the ratio increased to the value for the alkaline solution without phenol. Such a pH effect on both the CP and the volume ratio was not observed for the system without phenol. This indi-

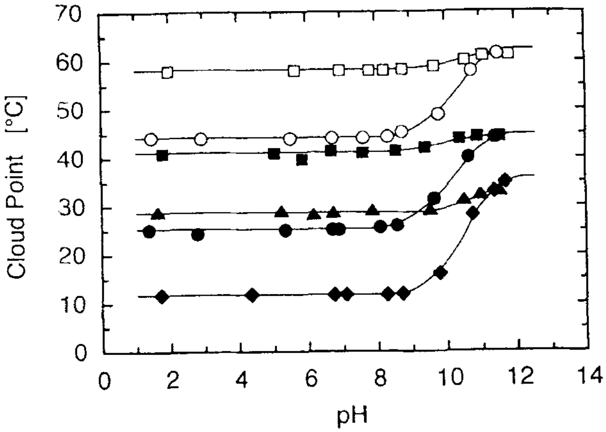

FIG. 5 Effect of solution pH and presence of NaCl on cloud point. [PONPE10] = 0.1 M; (NaCl, phenol) = (0, 0.05 M) ○; (1 M, 0.05 M) ●; (2 M, 0.05 M) ◆; (0, 0.01 M) □; (1 M, 0.01 M) ■; (2 M, 0.01 M) ▲.

cates that pH does not affect the formation of the PONPE10 micelle by itself, as was pointed out by Maclay (1).

Figure 6 shows the percent extraction of phenol as a function of the solution pH. In the pH region below 8, the *E* value becomes constant, depending on the NaCl concentration in the same manner as the CP behavior shown in Fig. 5. Addition of the salt also had a significant effect on

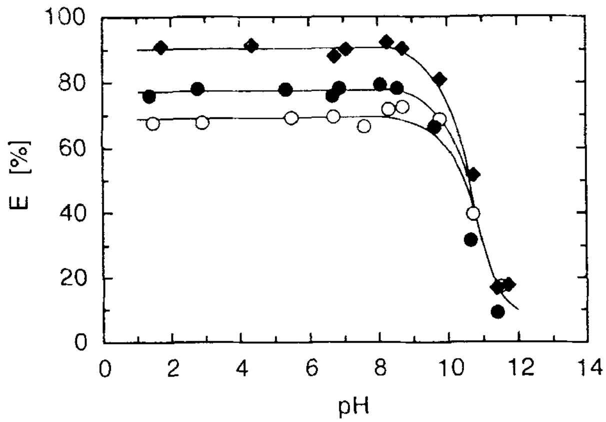

FIG. 6 Effect of solution pH on percent extraction of phenol with and without NaCl. [PONPE10] = 0.1 M; [phenol] = 0.05 M; [NaCl] = 0 M (○), 1 M (●), 2 M (◆).

the extraction efficiency: an E value as high as 90% could be attained with 2 M NaCl. For phenol as a weak acid, the extraction characteristics are affected by the solution pH, so that the percent extraction decreased dramatically near pH 10, corresponding to its pK_a, and little phenol was extracted from the solution above pH 12, irrespective of NaCl concentration. Thus the extraction of phenol is remarkably depressed at high basicities, where phenol is ionized to the less hydrophobic form than the free form. This implies that alkaline solutions have a possibility of backextracting phenol from the surfactant-rich phase.

Here we attempted backextraction from two surfactant-rich phases containing 0.22 and 0.39 M phenol by use of NaOH solutions as stripping solutions; the results are summarized in Table 1. For the surfactant-rich phase with the lower phenol concentration, the percent stripping of phenol, R, could be achieved nearly quantitatively with 0.5 and 1.0 M NaOH, although not more than 65% with 0.1 M NaOH; whereas in the case of the higher phenol concentration, it was somewhat depressed. The R value increases with an increase in the volume ratio of the stripping solution to the loaded coacervate, though the concentration of phenol in the recovery phase becomes lower. In some of the backextraction experiments at lower volume ratios, however, the two phases did not become homogeneous as a result of lowering of the solubility of PONPE10 in aqueous NaOH solution; thus, a complete mixture could not be obtained.

Cloud-Point Extraction of Pyridine Derivatives

The cloud-point extraction of organic weak base such as pyridine derivatives was studied in the same way as was phenol. The CP of PONPE10 solutions containing pyridines and the volume ratio of the surfactant-rich

TABLE 1
Backextraction of Phenol from the Loaded Surfactant-Rich Phases with Aqueous NaOH[a]

M_S (mmol)	NaOH (M)	M_W (mmol)	R^b [%]
1.09	0.10	0.71	65
1.09	0.50	1.10	100
1.09	1.00	1.01	93
1.96	0.10	0.71	36
1.96	0.50	1.50	76
1.96	1.00	1.45	73

[a] V_S = 5 mL, V_W = 10 mL.
[b] $R = 100M_W/M_S$.

phase showed the same behavior as did pure surfactant solutions, unlike the system containing phenol. The difference in the effects of phenol and pyridines may be because the former interacts with the hydrophilic groups of the PONPE10 molecule via the hydrogen bond between its hydroxide group and the ethylene oxide group of the surfactant as well as by hydrophobic interaction. Such a hydrogen bond interaction may make the surfactant micelle more hydrophobic, and hence cause lowering of the CP and the volume ratio. In contrast with phenol, pyridines in each free base form could not interact with the oxygen atom of the ethylene oxide group in PONPE10, and only hydrophobic interaction may be responsible for the partitioning.

Figure 7 shows the effect of initial PONPE10 concentration on the percent extraction of three pyridines. The extraction efficiency increased with an increase in the surfactant concentration. With an increase of the number of methyl groups to the pyridine ring, the hydrophobicity of these compounds increases in the following sequence: pyridine < 3-picoline < 2,4-lutidine. As would be expected, the *E* values increased in the same sequence owing to hydrophobic interaction between the surfactant and each compound. Such extraction behavior is similar to the results reported for the sorption of pyridines onto porous resins in a previous paper (14).

Figure 8 shows the pH dependence of the percent extraction of pyridines. For these weak basic compounds, the highest extraction is attained in each free form at high basicities, whereas there is lower extraction in

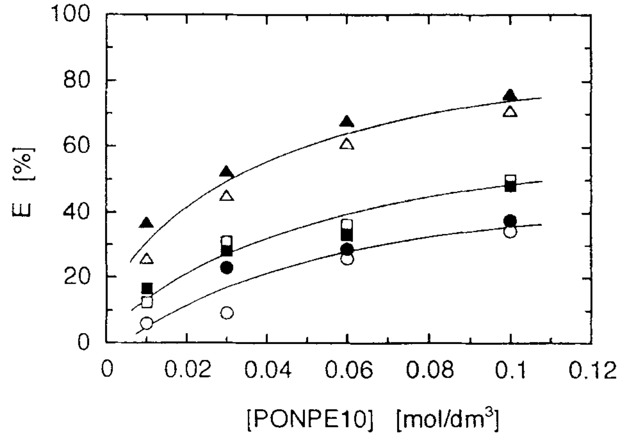

FIG. 7 Relationship between percent extraction of pyridines and PONPE10 concentration with and without NaCl. [Pyridines] = 0.005 M; [NaCl] = 0 M (○□△), 1 M (●■▲), (○●) pyridine, (□■) picoline, (△▲) lutidine.

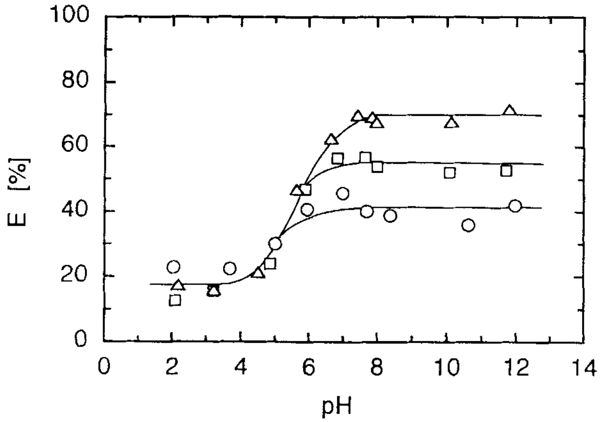

FIG. 8 Effect of solution pH on percent extraction of pyridines. [PONPE10] = 0.1 M; [pyridines] = 0.005 M; (○) pyridine, (□) picoline, (△) lutidine.

the protonated forms at high acidities; the extraction behavior was varied around the pH corresponding to its pK_a (5.22 for pyridine, 5.63 for 3-picoline, and 6.15 for 2,4-lutidine). This leads to the conclusion that back-extraction of pyridines from the surfactant-rich phase is possible by using acid solutions.

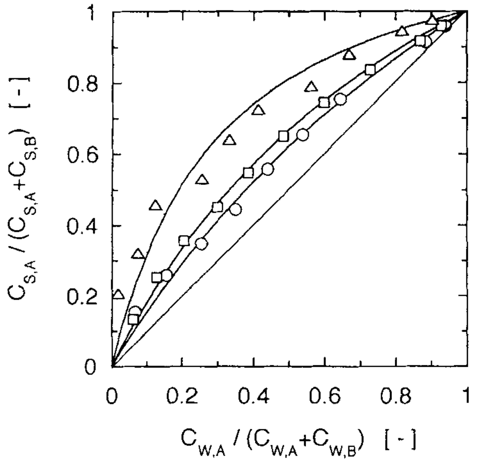

FIG. 9 Relationship between fractional concentrations of pyridines in aqueous and surfactant-rich phases. [PONPE10] = 0.1 M; [pyridines] = 0.005 M; (A, B) = (picoline, pyridine) ○; (lutidine, picoline) □; (lutidine, pyridine) △.

TABLE 2
Separation Factors between Pyridines via Cloud-Point Extraction with and without NaCl, respectively.

A	B	α_{AB}	α_{AB}[a]
Lutidine	Pyridine	4.30	8.03
Lutidine	Picoline	2.01	2.91
Picoline	Pyridine	1.64	2.13

[a] 1.0 M NaCl.

The application of CP extraction to the mutual separation of pyridines was also examined for three binary systems. Figure 9 shows the equilibrium relations between the fractional concentrations of pyridines in both phases as a plot of $C_{S,A}/(C_{S,A} + C_{S,B})$ against $C_{W,A}/(C_{W,A} + C_{W,B})$, where C_S and C_W are concentrations in the surfactant-rich and aqueous phases, respectively. The equilibrium data located on the convex curves indicate a selective extraction of compound A over B; the selectivity is in the same sequence as the hydrophobicities of the pyridines described above.

The separation factor, α_{AB}, is defined as

$$\alpha_{AB} = (C_{S,A}/C_{W,A})/(C_{S,B}/C_{W,B}) \tag{4}$$

We obtained the value of α_{AB} from the data in Fig. 9 by the least-square method, and the results are given in Table 2. In Fig. 9 the solid lines represent the calculations from these values. The mutual separation of pyridines can be attributed mainly to the difference in hydrophobic interactions between the compounds and the surfactant; thus the separation factor for pyridine/lutidine is a higher value than those for the other two binary systems. The addition of NaCl to the system enhances the separation factor and therefore brings about better phase separation as well.

CONCLUSION

Cloud-point extraction of organic compounds was studied using a nonionic surfactant PONPE10, and the following conclusions were obtained.

Cloud-point behavior of aqueous PONPE10 solutions can be improved by adding NaCl as well as organic compounds such as phenol. Phase separation for the solution was completed within 40 minutes at 70°C, although separation is possible even at ambient temperature.

The cloud-point extraction of phenol was successfully attained for PONPE solutions ranging from acidic to neutral, and the extraction efficiency increased with an increase in the surfactant concentration. Back-extraction of phenol from the surfactant-rich phase could be achieved with alkaline solutions.

This extraction method was found to be effective in recovering three pyridine derivatives from neutral and alkaline solutions; however, the extraction efficiency of these compounds is somewhat low compared to that of phenol. For mutual separation of pyridines, selectivity was in the same sequence as the hydrophobicities of their homologues.

NOMENCLATURE

C	concentration (mol/dm^3)
E	percent extraction (%)
M	amount (mol)
R	percent stripping (%)
V	volume (dm^3)
α	separation factor (—)

Subscripts

S	surfactant-rich phase
W	aqueous phase

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