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Recovery of Phenols Using Liquid Surfactant Membranes Prepared with Newly Synthesized Surfactants

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ABSTRACT

Extraction and stripping equilibrium of phenol, *p*-cresol, and *p*-chlorophenol were studied with an organic solution containing a newly synthesized surfactant and an aqueous alkaline solution as a stripping phase. A cationic surfactant showed the highest extraction ratio of phenol among several surfactants used in this study. The magnitude of phenol extracted from water was in the order phenol < *p*-chlorophenol < *p*-cresol. The stripping of phenol extracted in the organic solution was quantitatively accomplished with an alkaline solution of high concentration except for the case of cationic surfactants. Extraction of phenol and its derivatives by liquid surfactant membranes containing a newly synthesized surfactant as an emulsifier was carried out in a stirred cell. The effects of various parameters (such as a surfactant and alkaline concentration, the kind of surfactant, and the alkali composition) on the extraction efficiency of phenol were examined along with demulsification of W/O emulsions. On the basis of the stability of surfactants

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against alkaline solutions used as a receiving phase, cationic surfactants which did not involve an ester or amide bond in their molecule appeared to be among the best surfactants available for phenol removal in liquid membrane operations. The efficiency of phenol recovery with sodium hydroxide as a stripping agent was much higher than that with sodium carbonate; however, the demulsification efficiency of the emulsions decreased with an increase in the content of sodium hydroxide in the mixed alkaline solutions of sodium hydroxide and sodium carbonate. In the design of an efficient recovery process of phenols by LSMs, the composition of the alkaline solution was one of the key factors. Under optimal conditions, phenolic derivatives could be recovered in a few minutes.

INTRODUCTION

Pollution of the global environment is one the most urgent problems to be solved by mankind. The removal of phenols from industrial wastewater is an approach to protecting the environment from organic pollutants because phenols are highly toxic and resistant to biological treatment. Although phenols are exhausted from coke and petroleum industries and removed by various methods, they are often contained in waters because of their high solubility in water. On the other hand, phenols are important starting materials for the production of phenolic resins, dyes, antiseptics, etc. However, because their price is inexpensive, the cost for the recovery of phenols must be cheap. Thus, the development of an efficient recovery process of phenols is needed.

Separation and concentration processes using liquid surfactant membranes (LSMs) are an innovative separation process, particularly for systems in which the concentration of a target substances is very low or an extraction rate is very slow, because they enable rapid separation and concentration through their very thin liquid membranes and large interfacial areas. The LSM technique has been applied to the separation of various substances [metal ions, organic solutes, and bioproducts (1)] since it was first developed for the separation of hydrocarbons in 1968 (2). Research and development on the practical application of LSMs on a pilot-plant scale have also been conducted extensively, and the LSM process was applied to the recovery of zinc from wastewater at a textile plant in 1986 (3).

Even though many investigations have been carried out with respect to phenol extraction by LSMs, most papers focused on the permeation model of phenol extraction through a liquid membrane. In these studies, only a few commercial surfactants such as Span 80 and PX 100 were used as the emulsifiers. Recently, Gadekar et al. (4) carried out the recovery of nitrophenols using LSMs prepared by the mixed surfactants Span 80 and Tween 80, and they discussed the effects of various parameters, such as hydrophilic lipophilic balance of the surfactants, on the extraction behavior. However, except for this research, few papers have reported the optimum operating conditions and the effect of molecular structure of surfactants on phenol extraction by LSMs. An alkaline solution is required in the recovery process of phenols to concentrate phenols as their phenolate ions into an internal receiving phase of W/O emulsions. There is a large difference between ordinary metal extraction and phenol recovery systems by LSMs, and the use of an alkaline solution often causes several problems including the instability of the surfactant or the difficulty of demulsification.

In this study, the extraction and stripping behavior of phenols in liquid–liquid extraction were investigated by using commercial surfactants and newly synthesized surfactants. The effects of surfactant and pH in aqueous solutions on the extraction and stripping efficiency of phenols are discussed. Based on the results, the recovery of phenol and two phenolic derivatives, which are well known as water pollutants, was carried out in a stirred tank using LSMs prepared with an organic solution involving a commercial or newly synthesized surfactant and aqueous alkaline solutions. The effects of surfactant and alkaline reagent on the extraction of phenols were systematically investigated together with demulsification of the W/O emulsions, and the optimum conditions for the recovery of phenols with LSMs are discussed.

MATERIALS

Figure 1 shows the structures and abbreviations of the surfactants used in this study. The commercial surfactant Span 80 (sorbitan monooleate), purchased from Kishida Chemical Co. (Japan), was used without further purification. Another commercial surfactant PX 100 (polyamine) was purchased from Exxon Chemical Japan Co. and used as received. Nonionic surfactant $2C_{18}\Delta^9GE$, cationic surfactants of $2C_{18}\Delta^9QA$ and $C_{18}/C_{18}\Delta^9QA$, and anionic surfactant DOLPA were synthesized accordingly to the procedure mentioned in previous papers (5, 6). Molar concentrations of Span 80 and PX 100 were determined with their average molecular weights, 604 and 893, respectively, measured by vapor-phase osmometry. Commercially available organic solvent Shellsol 71, which is a hydrocarbon solvent and has a high boiling point, was purchased from Shell Chemicals Japan Co. All the other reagents used in this study were of guaranteed reagent grade.

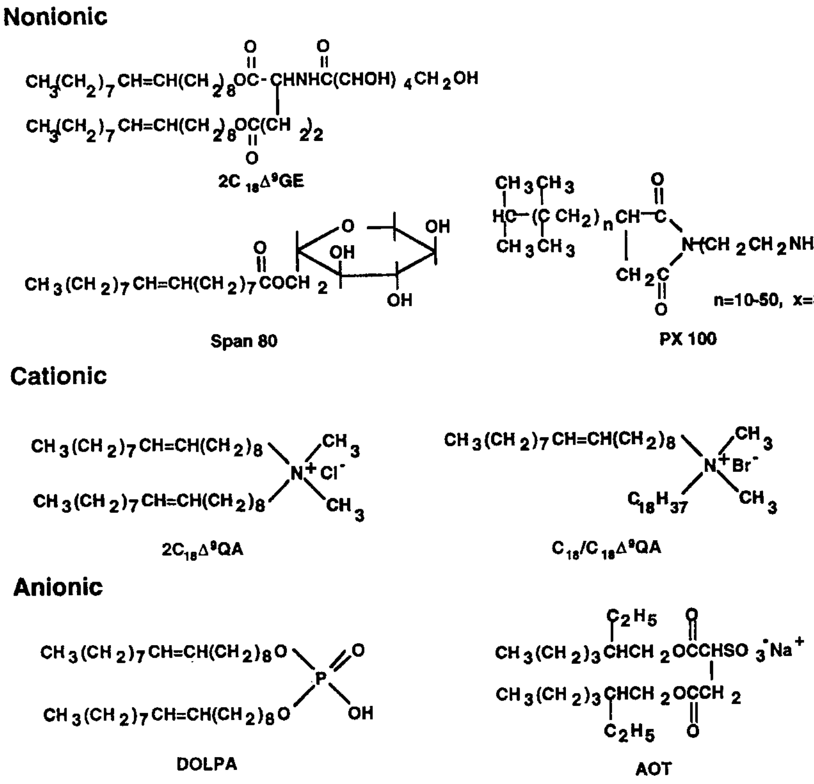

FIG. 1 Molecular structures and abbreviations of surfactants used in this study.

EXPERIMENTAL

Extraction of Phenols

The aqueous solution was prepared by mixing two aqueous solutions containing the same concentration of phenols in a high pH and in a low pH solution. The ionic strength in the aqueous solution was kept constant by adding salts. Shellsol 71 containing a known concentration of surfactants was used as the organic solution. Equal volumes of the aqueous and the organic solutions were shaken in a glass vessel and allowed to attain equilibrium in a water bath thermostated at 303 K. After the solutions were separated, the concentration of phenols in the aqueous solution was analyzed by a UV-VIS absorption spectrophotometry at the maximum wavelength (269.6 nm for phenol, 276.8 nm for *p*-cresol, and 280.0 nm for *p*-chlorophenol).

Stripping of Phenols

Organic phenol solutions were prepared by extracting phenol from deionized water in a glass vessel. Aqueous stripping solutions were prepared by dissolving sodium hydroxide or sodium carbonate in deionized water. The experimental procedure was the same as described above.

Extraction of Phenols by LSM

A batch-type stirred cell (7) equipped with four glass baffles was used for the extraction of phenol and two phenolic derivatives using LSMs. The solution in the tank was stirred with a turbine impeller having six flat blades and a speed controller. The external aqueous solution was prepared by dissolving a known amount of phenols in deionized water. A W/O emulsion was made from equal volumes of an organic solution containing a surfactant and an internal aqueous solution with dissolved alkaline reagents by irradiation with a ultrasonic wave machine (Branson Sonifier 250).

A measured volume of the W/O emulsion was added to the stirred cell containing the external aqueous solution. The cell was placed in a water bath thermostated at 303 K and was stirred at 300 rpm. Samples of about 3–4 cm^3 taken at intervals were settled for a few minutes to separate the external aqueous solution from the emulsions. The concentrations of sodium, a tracer for LSMs' breakup, and phenols in the aqueous solution were determined by atomic absorption spectrophotometry and UV-VIS absorption spectrophotometry, respectively. The detailed experimental conditions are listed in Table 1.

TABLE 1
Standard Experimental Condition for Phenol Extraction by LSMs

Volume of internal and organic solution: 30 mL
Volume of external solution: 300 mL
Internal phase. Stripping reagent: 50–200 mol/m^3
Organic phase. Solvent: Shellsol 71
    Surfactant: Span 80, PX 100, $2C_{18}\Delta^9GE$, $2C_{18}\Delta^9QA$, $C_{18}/C_{18}\Delta^9QA$, DOLPA; 5–50 mol/m^3
External phase. Phenol: 50–600 ppm
Stirring speed: 300 rpm
Temperature: 303 K

A batch-type electrical coalescer used for the demulsification of emulsions was similar to that reported in previous papers (8, 9). A glass-sealed electrode filled with saturated aqueous sodium chloride solution was vertically placed in the demulsifier. A copper disk electrode was set at the bottom and grounded. Demulsification was carried out by applying an alternating current of 15 kV at 60 Hz between the two electrodes at 303 K.

RESULTS AND DISCUSSION

Extraction Equilibrium of Phenols

The distribution ratio of phenols, D, is expressed as Eq. (3) by using the distributing coefficient, K_D, defined in Eq. (1), and the acid dissociation constant, K_a, defined in Eq. (2):

$$K_D = C_{PhOH,org}/C_{PhOH,aq} \tag{1}$$

$$K_a = C_H C_{PhO,aq}/C_{PhOH,aq} \tag{2}$$

$$\begin{aligned} D &= C_{PhOH,org}/(C_{PhOH,aq} + C_{PhO,aq}) \\ &= K_D/(1 + K_a/C_H) \end{aligned} \tag{3}$$

Equation (3) is revised as follows:

$$\log D = \log K_D - \log(1 + K_a/C_H) \tag{4}$$

Figure 2 shows the relation between the distribution ratio of phenols and pH in the aqueous solutions. The distribution ratio was found to be constant in a low pH region; however, it decreased gradually beyond the pH where the acid dissociation of each phenolic derivative proceeds and phenolate ions increased. This pH value is in the order *p*-chlorophenol < phenol < *p*-cresol, and it corresponds to the order of each pK_a value. In addition, the magnitude of the distribution ratio is found to be in the order phenol < *p*-chlorophenol < *p*-cresol, and the order seems to reflect the hydrophobicity of phenols. Based on the results in Fig. 2 and Eq. (4), the values of K_D for phenols can be evaluated as shown in Table 2. In a LSM process, a surfactant is always added to an organic solution, which forms a liquid membrane phase, to stabilize the liquid membrane during operations. Therefore, the effect of surfactants on the extraction equilibrium in phenol extraction should be clarified to understand the permeation behavior of phenols by LSMs. Figure 3 shows the relation between the extraction ratio, E, of phenol and the concentration of several surfactants, C_s. We found that the degree of phenol extraction increased with increasing surfactant concentration, in particular for the cationic surfactants.

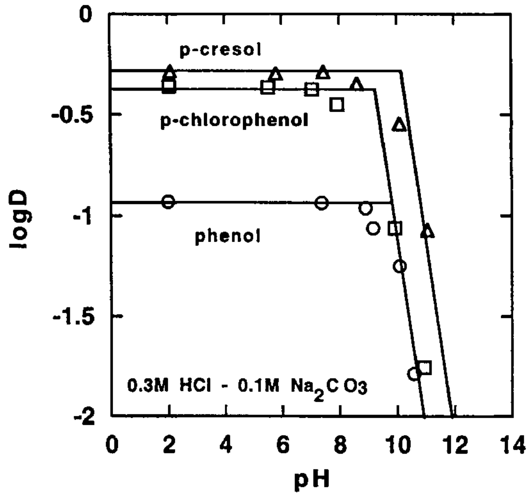

FIG. 2 Distribution coefficient of phenols as a function of pH in aqueous solution.

With respect to phenol extraction using a quaternary ammonium salt, Inoue et al. investigated (10, 11) and reported that the phenols were extracted according to the following equation as in the case of amines:

$$Q^+X^-_{org} + i\mathrm{PhOH} = Q^+X^- \cdot (\mathrm{PhOH})_{i,org} \qquad (5)$$

The physical distribution of phenol between the organic and aqueous phases is considered to be dominant in a low concentration range of the surfactants. The contribution of the chemical reaction between a surfactant and phenol, as shown in Eq. (5), increases in a high concentration range of the surfactant. A slight increase of *E* in a high concentration of the other surfactants, except cationic surfactants, may be due to an increase in

TABLE 2
Distribution Coefficient of Phenols between Shellsol 71L and Water

Materials	K_D [—]
Phenol	0.11
p-Chlorophenol	0.43
p-Cresol	0.51

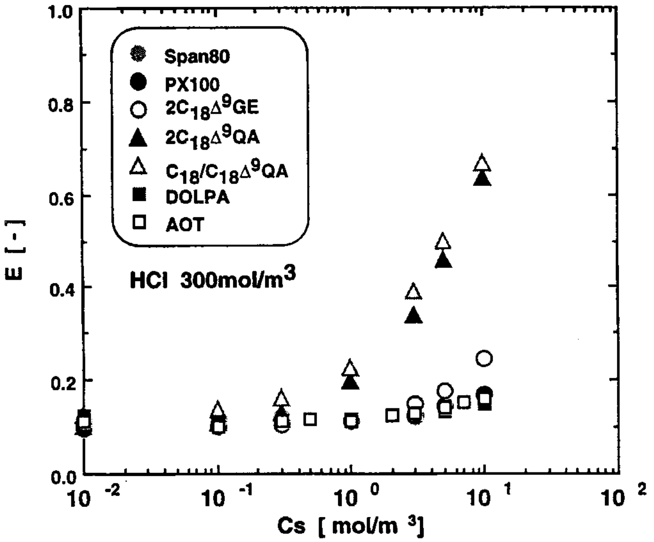

FIG. 3 Degree of phenol extraction as a function of surfactant concentration.

polarity of organic solvents due to adding surfactants to nonpolar media (12). Figure 4 shows the degree of phenol extraction as a function of pH in aqueous solutions. Although a similar tendency as in the case of a surfactant-free system is observed, the degree of phenol extraction in cationic surfactants is much higher than that of a surfactant-free system. These findings mean that cationic surfactants have a high extraction ability for phenol, and this property may enhance the extraction rate of phenols, too. The strange result in anionic surfactant DOLPA may be due to the formation of reversed micelles in the organic phase (13).

Stripping of Phenol

In the design of a recovery process of phenols using LSMs, it is important to clarify the stripping behavior of phenols from an organic phase to an internal phase since extraction and stripping reactions proceed at the same time in LSM operations. Based on the results of extraction equilibrium of phenols, we found that a high pH aqueous solution was suitable for stripping phenols from an organic solution. Therefore, an alkaline reagent would be effective as a stripping agent for phenol recovery. Figure 5 shows the relation between the stripping ratio of phenol and pH in aqueous solutions. In the cases of nonionic and anionic surfactants, stripping of phenol

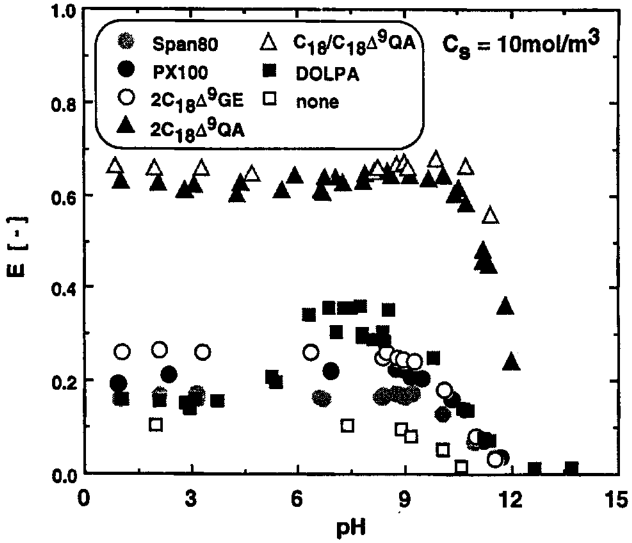

FIG. 4 Relation between extracted ratio of phenol and aqueous pH for various surfactants.

extracted in the organic solution is completed by using an alkaline solution above pH 9. However, in the case of a cationic surfactant, the proper pH region for stripping is narrow. This result means that precise adjustment of pH in an internal aqueous solution as a receiving phase of phenol is required to set up an effective recovery process using LSMs prepared by

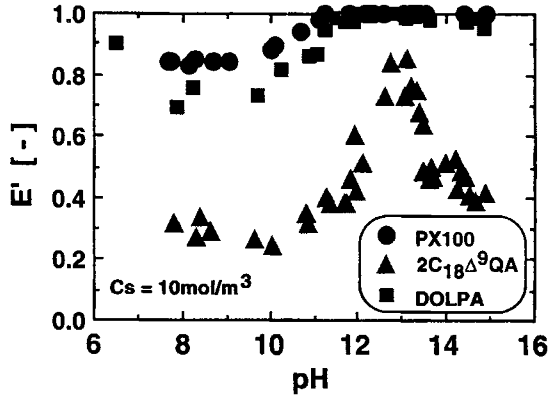

FIG. 5 Relation between stripping ratio and aqueous pH for three surfactants.

a cationic surfactant. The decrease in stripping ratio above pH 13 is presumed to be caused by the change of the extraction mode from the complex formation mechanism shown in Eq. (5) to a solvation mechanism.

Extraction of Phenols by LSMs

Studies on phenol extraction with LSMs have been conducted by many investigators (13–15) since it was first developed by Li (2). However, despite much works on modelings phenol permeation, few studies have examined the optimum conditions for phenol extraction using LSMs. Furthermore, in these reports the conventional, commercially available surfactants Span 80 and PX 100 have been used to form liquid membranes, and little attention has been paid to the synthesis of optimum surfactants for phenol extraction. In LSM systems it is well known that a surfactant plays an important role in the stability and swelling of emulsions (5, 7) and often affects the extraction rate (1, 6, 16). In order to examine these effects, the degree of break-up, ϵ, and the degree of swelling, Y, were defined by the following equations (5, 17):

$$\epsilon = (V_{W,e}C_{Na,e})/(V_{oW,i}C_{oNa,i}) \quad (6)$$

$$Y = V_{W,i}/V_{oW,i} \quad (7)$$

Effect of Surfactant Concentration

In LSMs, the liquid membrane is strengthened by the arrangement of surfactants at the oil–water interface, and the surfactants may affect the permeation rate of solutes through the liquid membrane. In order to design an effective recovery process by LSMs, an appropriate surfactant should be chosen from the viewpoints of both the stability of liquid membranes and the rapid separation of a target material. In previous papers we developed the novel nonionic surfactant $2C_{18}\Delta^9GE$ for copper extraction by LSMs, and reported that the new surfactant could stabilize liquid membranes at a lower concentration than in commercial surfactants such as Span 80 and PX 100 (5, 17). Therefore, we first used the nonionic surfactant and investigated the effect of surfactant concentration on phenol extraction.

Figure 6 shows a typical extraction behavior of phenol as a function of surfactant concentration of $2C_{18}\Delta^9GE$. The extraction rate of phenol was extremely high, and extraction was accomplished in a few minutes. Under the present experimental conditions the liquid membranes formed by this surfactant were relatively stable, and the degree of break-up was about 3% at 5 minutes even at a surfactant concentration of 5 mol/m^3. Much more addition of the surfactant (10 or 20 mol/m^3) lowered the break-up

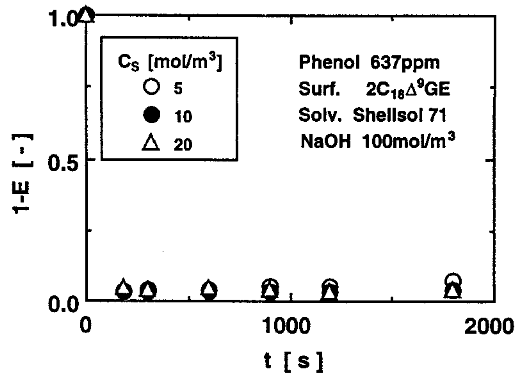

FIG. 6 Effect of the nonionic surfactant concentration on phenol extraction.

of emulsions to less than 1% at 5 minutes. Based on the result in Fig. 6, we found that a several percent break-up of emulsions does not affect the extraction behavior of phenol due to the rapid extraction rate. In metal extractions by LSMs, the extraction rate of metals often decreases with increasing concentration of surfactants because surfactants interrupt a chemical reaction between a carrier and metal ions at the interface (1, 17). However, in phenol extraction, as the permeation behavior of phenol is based on distribution without a chemical reaction, the permeation rate does not seem to be influenced by the adsorption of surfactants at the interface.

Effect of Alkaline Concentration

Figure 7 shows the effect of concentration of sodium hydroxide on the extraction behavior of phenol by LSMs. The extracted ratio of phenol increases with increasing concentration of sodium hydroxide. By raising the concentration to 100 mol/m^3, the extraction efficiency increased significantly because at least 60 mol/m^3 of hydroxide ion is required to neutralize phenol under the present experimental conditions. Further addition of sodium hydroxide to 200 mol/m^3 did not enhance the extraction efficiency. On the other hand, by using sodium carbonate instead of sodium hydroxide (data not shown), the extracted ratio of phenol was very low (about 60%), even when the concentration of sodium carbonate was increased to 200 mol/m^3. An additional increase in the concentration of sodium carbonate caused the emulsions to swell and resulted in a decrease of the recovery efficiency of phenol by LSMs.

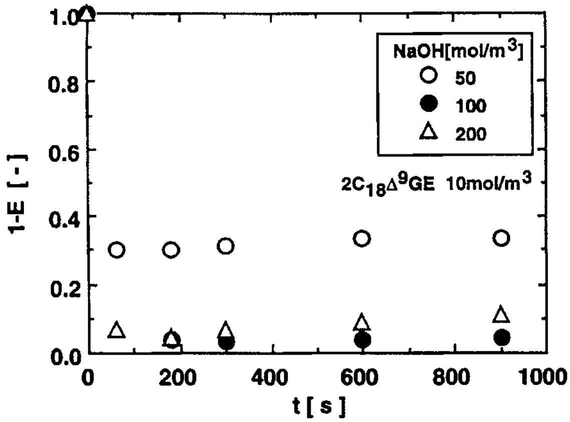

FIG. 7 Effect of the alkaline concentration on phenol extraction.

Effect of Surfactant

As described above, it is very important to select a suitable surfactant for a target material in a LSM process. Therefore, the effect of surfactants was investigated concerning the extraction efficiency of phenol using 100 mol/m^3 sodium hydroxide as an internal aqueous solution. In a stability test of emulsions formed by the seven surfactants shown in Fig. 1, the following results were obtained: 1) anionic surfactant AOT could not form a stable emulsion, 2) PX 100 needed a higher concentration (more than 40 mol/m^3) to form a stable emulsion compared with the other surfactants used in this study, 3) all the surfactants except PX 100 could form a stable emulsion at a concentration of 10 mol/m^3, and the degree of break-up of emulsions was less than 1% at 5 minutes.

Figure 8a shows the change of the swelling ratio with the elapsed time for various kinds of surfactants. In particular, the emulsions prepared by the two nonionic surfactants Span 80 and 2C$_{18}$Δ^{9}GE tend to swell easily compared to those of the other surfactants. It was reported that the commercial surfactant PX 100 is a suitable surfactant from the viewpoint of swelling in metal extraction by LSMs (16). When using the cationic surfactants, the swelling did not proceed and the ratio of swelling was approximately 1 throughout the operations. From the viewpoint of swelling of emulsions, two cationic surfactants and PX 100 are appropriate surfactants for phenol extraction.

Figure 8b shows the effect of surfactants on the extraction behavior of phenol for five kinds of surfactants. Using the nonionic surfactant Span

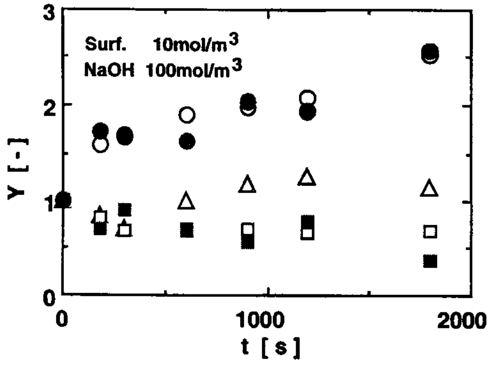

FIG. 8a Effect of surfactants on swelling of emulsions (○, $2C_{18}\Delta^9GE$; △, $C_{18}/C_{18}\Delta^9QA$; □, DOLPA; ●, Span 80; ■, PX 100).

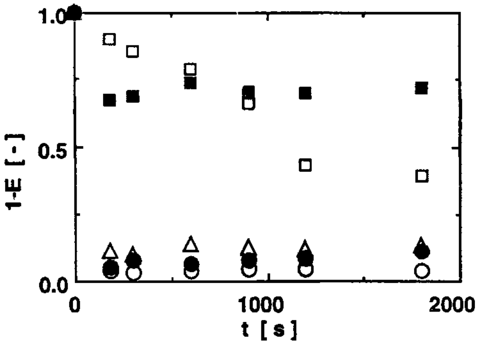

FIG. 8b Effect of surfactants on the efficiency of phenol extraction. Symbols as in Fig. 8a.

80 or $2C_{18}\Delta^9GE$ and the cationic surfactant $C_{18}/C_{18}\Delta^9QA$, more than 90% of phenol was quickly extracted in a couple of minutes. At a concentration of 10 mol/m^3 PX 100, the extracted ratio of phenol was very low due to the break-up of the emulsion; however, almost the same result as in the cationic surfactants was obtained at a concentration of more than 40 mol/m^3 (about 4 wt%). The slow extraction rate in the anionic surfactant DOLPA suggests that permeation of the phenolate ion is interrupted by electric repulsion at the oil–water interface due to adsorption of the anionic surfactants. On the other hand, there might be an acceleration effect in a cationic surfactant for the permeation of phenol. However, the rate was too fast for the effect to be recognized.

In LSMs a surfactant should have a high resistance against a strong alkaline solution because the membrane solutions are used repeatedly. This point is very important in choosing an appropriate surfactant for the phenol recovery process with LSMs. Nemeh and Peteghem (18) reported that Span 80 (which has an ester bond) or PX 100 (which has amide bonds) were unstable in the presence of acids because such ester and amide bonds are easily hydrolyzed by acids. We have investigated the resistance of surfactants against an alkaline solution by FT-IR. It was found that the infrared spectrum strength of the surfactant $2C_{18}\Delta^9QA$ at 1715 and 1736 cm^{-1}, which correspond to two ester bonds in the molecule, decreased considerably by contact with an alkaline solution. This finding indicates that surfactants having an ester bond are easy to break down by alkaline-catalyzed hydrolysis compared with a surfactant having an amide bond like PX 100. Among the surfactants used in the present study, the cationic surfactants, which are specially designed to resist a hazardous aqueous environment, appear to be among the best surfactants currently available for phenol extraction by LSMs.

Demulsification of Emulsion

In the design of an effective LSM process, the efficiency of demulsification is one of the key factors because concentrated solutes must be recovered from the internal aqueous phase of emulsions and the separated liquid membrane phase is used. In contrast to many reports on acid-containing emulsion systems, few studies have examined the demulsification of emulsions which contain aqueous alkaline solutions as an internal phase. Therefore, in this study we focused attention on the effect of alkaline composition on the efficiency of demulsification. Figure 9 shows the effect of alkaline composition on the demulsification rate along with the diameters of the internal water droplets in the emulsions. The abscissa in this figure indicates the volume ratio of a 100 mol/m^3 sodium carbonate solution against a 300 mol/m^3 sodium hydroxide solution. The demulsification rate is defined as the formation rate of producing a water phase in the electric demulsifier (8). Stable W/O emulsions prepared by 5 wt% (45 mol/m^3) PX 100 were employed (9) in the present demulsification experiments. We found that the demulsification of emulsions prepared with an aqueous alkaline solution is difficult compared with those with an aqueous acidic solution. A complete break down of emulsions prepared with sodium hydroxide solution alone was especially impossible, and the demulsification rate of emulsions prepared with a sodium carbonate solution was an order of magnitude higher than that with a sodium hydroxide solution. On the basis of the results in Fig. 9, it was found that the demulsification

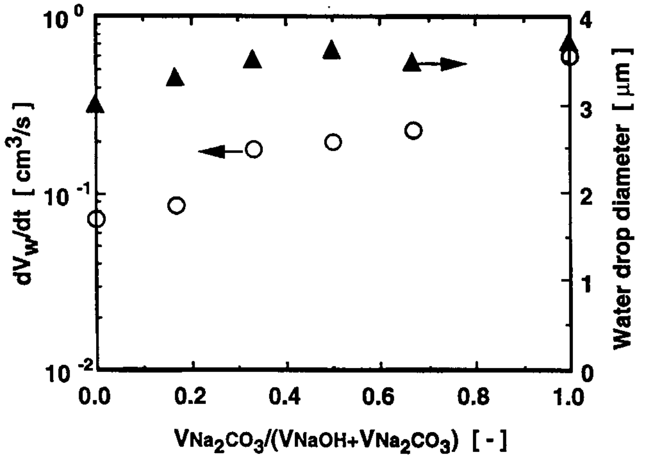

FIG. 9 Effect of alkaline composition in emulsions on the rate of demulsification.

rate of emulsions significantly increased with increasing content of sodium carbonate in aqueous solutions. The increase in the demulsification rate could not be explained by taking into account a change in the droplet size. The increase may be due to interactions between surfactants and alkaline species at the interface. A quantitative treatment on the demulsification behavior with alkaline solutions is now under way. Consequently, although hydroxide solutions gave better extraction efficiency of phenol by LSMs compared with carbonate solutions, a mixed alkaline solution of sodium hydroxide and sodium carbonate was desirable as a receiving phase of emulsions to establish an effective recovery process from the viewpoint of demulsification efficiency. Therefore, in the next section we discuss the optimum composition of alkaline solutions in the extraction of phenols with LSMs.

Effect of Alkaline Composition on Extraction of Phenols

Figure 10 shows the effect of alkaline composition in a mixed alkaline solution of sodium carbonate and sodium hydroxide on phenol extraction by LSMs. The total alkaline concentration was kept constant at 100 mol/m^3. The extraction efficiency increased with increasing content of sodium hydroxide in the alkaline solutions, and the extracted ratio of phenol attained to around 90% at a composition of 1:3 (Na_2CO_3:NaOH). Figure 10 also shows the relation between the breakup ratio of emulsions, ε, and

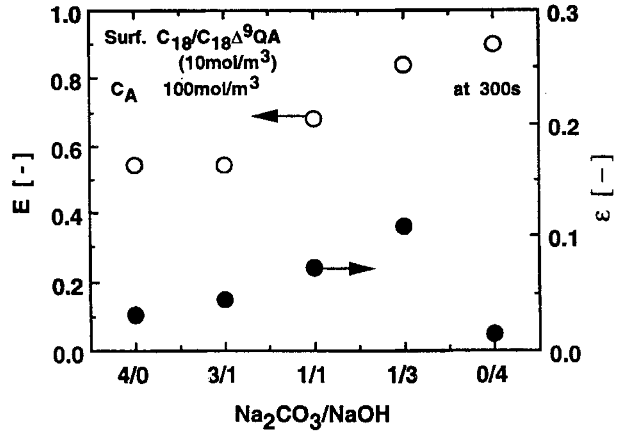

FIG. 10 Effect of alkaline composition on the extraction efficiency of phenol and the breakup of emulsions.

the composition of alkaline solutions. The breakup ratio of the emulsions tends to increase with an increasing fraction of sodium hydroxide. The unexpected stability of an emulsion prepared with sodium hydroxide alone seems to be due to the different preparation method of the emulsion. In the case of sodium hydroxide alone, a stable emulsion could not be prepared by the ordinary method with an ultrasonic wave machine, and a homogenizer was used instead. From the viewpoint of stability, a low sodium hydroxide content is desired. Emulsions with other alkaline agents besides sodium hydroxide and sodium carbonate have not been studied yet. They are a subject for our future studies.

Recovery of Phenols by LSMs

The recovery of two phenol derivatives, *p*-chlorophenol and *p*-cresol, was carried out using LSMs. Figure 11 shows a typical time-course of their extraction behavior with LSMs prepared by the cationic surfactant along with that of phenol. The recovered ratio of the two phenol derivatives reached more than 98% quickly, and extraction was completed in a few minutes. The extraction efficiency of *p*-chlorophenol and *p*-cresol was higher than that of phenol as expected from the distribution coefficients in liquid–liquid extraction. A novel process using the LSMs technique was found to be a promising technology for the recovery of phenols from dilute aqueous solutions.

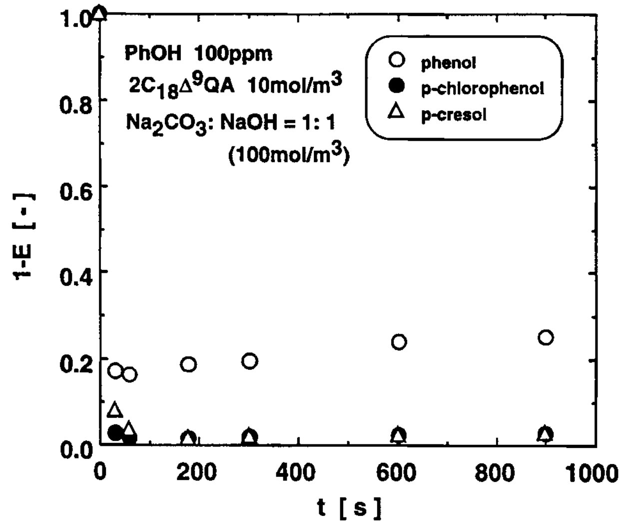

FIG. 11 Recovery of phenolic derivatives using LSMs prepared by the cationic surfactant.

CONCLUSION

Extraction and stripping equilibrium of phenols in liquid–liquid extraction were investigated, and the recovery of phenols using the LSM technique was conducted to find the optimum conditions for the design of an effective recovery process.

In the extraction equilibrium of phenol it was found that cationic surfactants used as emulsifiers in liquid membrane operations had a high extraction ability. In the stripping of phenol the pH value in an alkaline solution was a key factor in obtaining a high stripping ratio. From the viewpoint of the stability of surfactants against strong alkaline solutions, surfactants containing an ester bond seemed to be unsuitable. Based on the results obtained, quaternary ammonium salt-type surfactants appeared to be among the best surfactants currently available for phenol extraction by LSMs. Another important factor was the efficiency of demulsification by an electrical coalescer. The demulsification of emulsions prepared with sodium hydroxide solution alone was very difficult, and a mixed solution of NaOH and Na_2CO_3 was required as the internal aqueous phase of emulsions. More than 90% of phenols could be recovered in a few minutes under optimum conditions. In conclusion, the extraction technique using

LSMs is very effective and is a promising method for the recovery of phenols from dilute aqueous solutions.

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