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Rapid and Efficient Admicelle-Mediated Extraction of Chlorophenols in Water

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Cetyltrimethylammonium chloride was sorbed on silica gels and formed stable admicelles at pH 9. The extractabilities of chlorophenols were greater than those to sodium dodecyl sulfate–γ-alumina admicelles. Because the admicelles were floatable, the flotation was found to be useful for the rapid and efficient recovery of admicelles.

Recently, we found that surfactant-coated solids (admicelles or hemi-micelle) were floatable on water. This phenomenon may be ascribed to the somewhat hydrophobic property of admicelles that can stick to air bubbles. In the present study, the admicelle-flotation technique was studied to clarify the feasibility of designing a rapid and efficient method for collecting organic pollutants in water. The concept includes the solid-phase extraction of organic pollutants to admicelles and the subsequent collection of admicelles by flotation. The combination of solid sorbent and surfactant as well as those optimal amounts were investigated.

Admicelles that have mainly been utilized for analytical purposes are alumina-based ones composed of an anionic surfactant and γ-alumina. Many fundamental studies about the formation and solute-solubilization of alumina-based admicelles have been performed.[1–10] However, their uses are limited in acidic pHs because of the requirement of sufficient positive charge of alumina for the stable formation of admicelles. The sorption of SDS on 1.5 g of γ-alumina at different pH is shown in Fig. 1. At pH 2, the sorption was quantitative up to ca. 200 mg of SDS. The extent of the sorption became constant by adding excess SDS, because of the saturation of alumina surfaces. The saturation is clearly indicated by the zeta-potential of γ-alumina. The sharp knee of the curve indicates quite stable binding of SDS. On the other hand, the curve gradually increased with increasing the amount of SDS added at higher pHs, indicating a decrease in the strength of SDS sorption. The decrease in the stability of admicelles lowers the extent of solute incorporation.

Silica gel has a lower isoelectric point (pI 2–4),[11–13] and hence is negatively charged in the neutral pH region. Additionally, it is well known that cationic surfactants such as CTAC strongly adsorb on silica surfaces.[14,15] Cooperative adsorptions of some organic compounds on CTAC-coated silica surfaces have also been reported in the literature.[16–19] These facts suggest the formation of CTAC–silica admicelle. The extent of CTAC sorption onto 1.0 g of silica gel at pH 7 and 9 are shown in Fig. 2. The sorption increased with increasing pH and the amount of CTAC added. Stable sorption was obtained at pH 9.

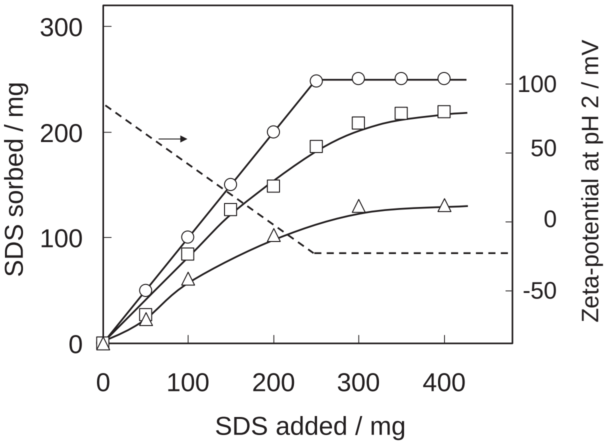

Fig. 1. Sorption of SDS on 1.5 g of γ-alumina at pH 2 (○), 4 (□), and 6 (△).

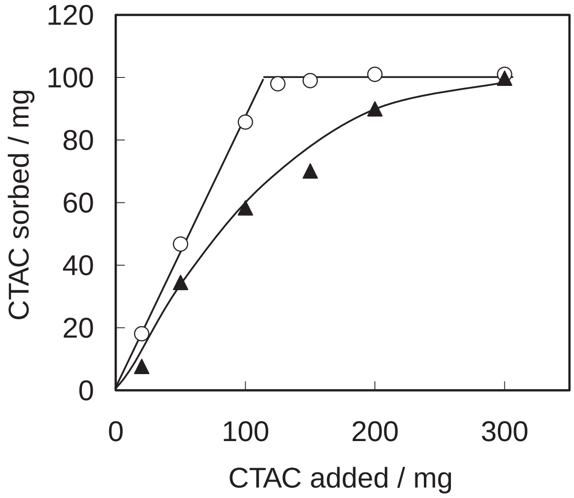

Fig. 2. Sorption of CTAC on 1.0 g of silica gel at pH 7 (▲) and 9 (○).

Comparing spectra of certain molecular probes has extensively been performed for evaluating the microscopic solvent properties of macromolecules or micelles.[20–23] As previously reported,[24] *N*-phenyl-1-naphthylamine (PN) was a good fluorescence probe for evaluating the solvent properties of alumina-based admicelles. In the present study, it was also successfully employed for characterizing the CTAC–silica system. Figure 3 shows the correlation of relative permittivity and the wavelength of the maximum emission ($\lambda_{\max}$) of PN in some solvent systems. The value of $\lambda_{\max}$ shifted to shorter wavelengths with decreasing solvent polarity.

The values for SDS and CTAC micellar solution (arrows A and C) indicate that these micelles provide hydrophobic media contrary to water and have solvent properties corresponding to hygro-alcohols. On the other hand, those for SDS–alumina

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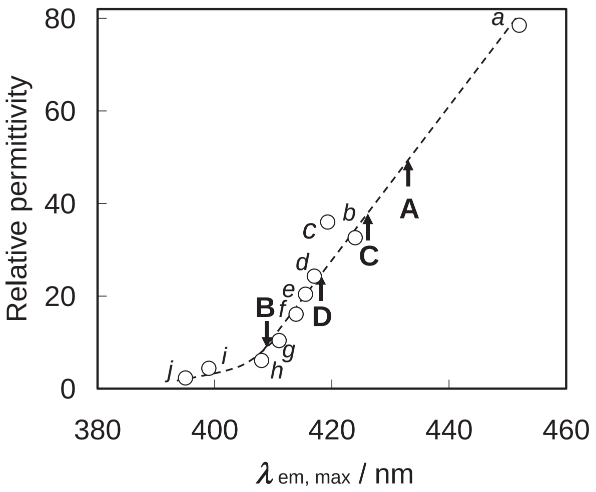

Fig. 3. Relationship of relative permittivity and the maximum wavelength (λ_{max}) of the emission of PN. Solvent: (*a*) water, (*b*) methanol, (*c*) acetonitrile, (*d*) ethanol, (*e*) 1-propanol, (*f*) 1-butanol, (*g*) 1-octanol, (*h*) ethyl acetate, (*i*) diethyl ether, (*j*) benzene. Arrow: (A) 20 mM SDS (SDS micelle), (B) 1 mM SDS, 0.1% (w/v) γ-alumina (SDS–alumina admicelle), (C) 5 mM CTAC (CTAC micelle), (D) 0.65 mM CTAC, 0.1% (w/v) silica gel (CTAC–silica admicelle).

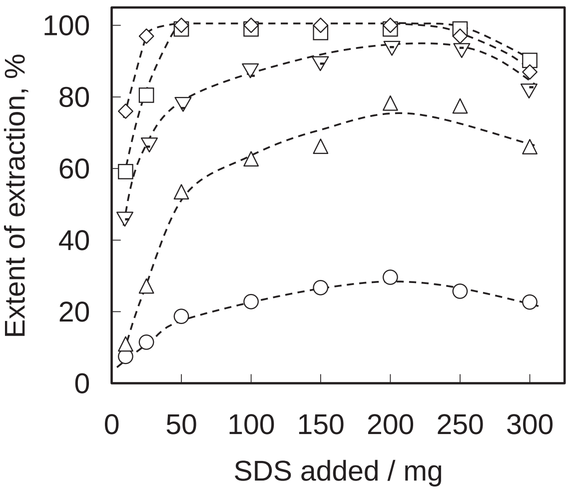

Fig. 4. Extraction of chlorophenols from 50 mL of aqueous solution (pH 2) to SDS–γ-alumina admicelle. γ-Alumina: 1.5 g, Chlorophenols: (10 µM). ○: 2-chlorophenol, △: 2,4-dichlorophenol, ▽: 2,3,4-trichlorophenol, □: 2,3,4,6-tetrachlorophenol, ◇: pentachlorophenol.

or CTAC–silica systems (arrows B and D) shifted to shorter wavelengths. Evidently, CTAC molecules cooperatively sorbed on silica surfaces and aggregated to form CTAC–silica admicelles. Similar to the case of SDS–alumina admicelle, CTAC–silica admicelle provided somewhat hydrophobic media rather than CTAC micelles.

Extraction of chlorophenols to SDS–alumina admicelles at different amounts of SDS are shown in Fig. 4. The extent of extraction increased with increasing the amount of SDS. This is explained by the increasing formation of SDS-admicelles. Highly hydrophobic tetrachlorophenol and pentachlorophenol were almost quantitatively extracted. However, chlorophenols having less chloro-substituents were insufficiently recovered. Hydrophobic interaction plays an important role in solute incorporation. On the other hand, the extraction was decreased by adding excess SDS, due to the formation of normal SDS micelles in the bulk aqueous solution. The extractabilities were almost the same as those obtained by a batch method.[8]

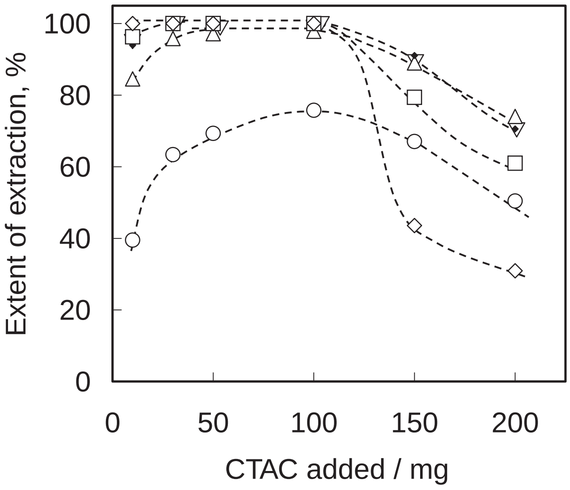

Fig. 5. Extraction of chlorophenols from 50 mL of aqueous solution (pH 9) to CTAC–silica gel admicelle. Silica gel: 1.0 g, [chlorophenols] = 10 µM. Marks are the same as those in Fig. 4.

A similar tendency was obtained in the extraction to CTAC–silica admicelles (Fig. 5). However, the extractabilities of chlorophenols were greater than those in the SDS–alumina system. Chlorophenols having more than 3 chloro-substituents were quantitatively extracted to CTAC–silica admicelles. The extraction of dichlorophenol was also satisfactory. Such extractabilities seem to be also greater than those previously obtained in the batch extraction to Aerosol OT–γ-alumina admicelles.[9] Therefore, CTAC–silica admicelles were good separation media for chlorophenols. Pramauro et al.[25] reported that cationic micelles can strongly incorporate halophenols compared to anionic micelles. The contribution of the aromatic moiety of halophenol is substantially greater in cationic than anionic micelles. In addition, according to the acid dissociation constants of chlorophenols ($\mathrm{p}K_{\mathrm{a}} = 8.52$ for 2-chlorophenol, 7.09 for 2,4-dichlorophenol, 6.97 for 2,3,4-trichlorophenol, 5.22 for 2,3,4,6-tetrachlorophenol, and 4.74 for pentachlorophenol),[26] they exist as chlorophenolate ions in the present study. The electrostatic interaction to cationic surfactant aggregates could greatly enhance their extractabilities. The extraction was decreased by further addition of CTAC. Similar to the SDS–alumina system, the decrease in extraction can be ascribed to the formation of normal CTAC micelles in the bulk aqueous solution.

Finally, flotation was attempted for easy and rapid collection of admicelles involving concentrated chlorophenols. An aqueous suspension of SDS–alumina admicelles was prepared by mixing 0–400 mg of SDS and 1.5 g of γ-alumina, while the preparation of CTAC–silica admicelles was performed by mixing 0–300 mg of CTAC and 1.0 g of silica gel. The suspension was added to an aqueous solution (pH 7–9) containing 2.0×10^{-5} M respective of chlorophenols that was precedently placed in a column having 300 mm length, 19 mm diameter, and a sintered glass filter (5–10 µm pore size) at the bottom. The total volume of the solution system was 50 mL. Air bubbles were introduced from the bottom of the column to mix the solution and to float the admicelles. The extents of the extraction of chlorophenols were estimated from their HPLC determination in the residue aqueous solution.

In the absence of SDS, γ-alumina particles hardly floated even with a high feed rate of air bubbles. In contrast, the particles became floatable by the addition of the appropriate amount (50–150 mg) of SDS. In this condition, the positive charge of γ-alumina significantly decreased by the sorption of negatively charged SDS (Fig. 1). SDS molecules can bind their hydrophilic head groups on alumina surfaces, and hence, tend to orientate their hydrophobic tails outward. The good floatability of alumina particles is ascribable to the decrease in charge and the increase in the hydrophobicity of alumina surfaces. However, the flotation hardly occurred by the addition of further amounts of SDS. The decrease in floatability is ascribable to the decrease in hydrophobicity of admicellar surfaces. In addition, the air/water interfaces of air bubbles would be occupied by excess SDS, and hence, hardly work to float admicelles.

Similar to the SDS–alumina system, silica gel particles negligibly floated on water in the absence or the presence of an excess amount of CTAC. On the other hand, they became floatable in the presence of the appropriate amount of CTAC (30–75 mg for 1.0 g of silica gel). The CTAC sorbed decreased the negative charge on silica surfaces and increased their hydrophobicity. Under the optimum conditions, the floatation was complete within 1 min. The appropriate combination of surfactant and solid sorbent as well as optimal surfactant–solid ratio were important for obtaining admicelles that can be effectively floated.

In conclusion, the admicelles could be rapidly recovered as compact precipitates from the water surface. CTAC–silica admicelle was a good selection for the extraction of chlorophenols in water and collection by flotation. The chlorophenols extracted were easily eluted with a small amount of polar organic solvents such as acetonitrile. The combination of admicelle-mediated extraction and the subsequent floatation of the admicelle is a useful concept for designing a rapid and efficient method for separating organic pollutants in water.

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