Collection of Metal(II) - 1-(2-Pyridylazo)-2-naphthol Complexes in Nonionic Surfactant Assembly Adsorbed on Silica Gel

Kotaro Bessho, Koichi Saitoh,* and Norio Teramae
Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980-77

(Received April 18, 1995)

The nonionic surfactant phase adsorbed on silica gel is proposed as a new medium for the separation and concentration of trace metal chelates. The 1-(2-pyridylazo)-2-naphthol chelates of Ni(II) and Zn(II) can be concentrated into the nonionic surfactant phase on silica gel. It was found that these hydrophobic compounds were collected by dissolution into the surfactant assembly formed at the silica / water interface.

Molecular assemblies such as micelles have been paid much attention in analytical chemistry.[1] Micelles are usually considered as microscopic organic solvents dispersed in aqueous solution, and hydrophobic species can be distributed into the micellar pseudo phase. Metal species also can be concentrated into the micellar phase by formation of hydrophobic chelates.[2] But the isolation of micellar phase is difficult, so the application of micelles in the separation chemistry is almost restricted to chromatography.[3,4] A few studies were reported for the isolation of micelles by ultrafiltration[5] or by aggregation at a temperature above cloud point.[6] These methods, however, are complicated and need delicate procedures.

Recently, it was found that nonionic surfactants containing oxyethylenic groups were adsorbed on silica gel and formed micelle-like molecular assemblies at the silica / water interface.[7,8] These surfactant phases can be easily isolated with silica gel by filtration or centrifugation. The easiness of isolation is an advantageous property which cannot be attained in case of micelles dispersed in solution.

In this report, the nonionic surfactant phase on silica gel is proposed as a new medium for the separation and concentration of trace metal ions. The method consists of two important steps. In the first step, sample solution is added to the nonionic micellar solution dissolving hydrophobic chelating reagents. In this solution, trace metal ions react with ligands to form hydrophobic species which are concentrated into micellar phase. In the second step, the solution is shaken with a small amount of silica gel. Nonionic surfactants are adsorbed on silica gel, and simultaneously hydrophobic compounds such as neutral chelates are expected to be collected in the surfactant assembly formed on silica gel.

The nonionic surfactant and the chelating reagent used in this study are polyoxyethylene(9.5) octylphenyl ether (Triton X-100) and 1-(2-pyridylazo)-2-naphthol (Hpan), respectively. Hpan is little soluble in pure water, but considerably in dilute aqueous solution of Triton X-100. Ni(II) and Zn(II) were chosen as the metal ions.

At first, the formation of metal(II)-pan complexes in a Triton X-100 micellar solution was investigated by UV-visible absorption spectrometry. Since Hpan alone cannot dissolve in aqueous solution, 2%(v/v) methanol is used as a solvent. The concentrations of Triton X-100, Hpan, and Ni(II) or Zn(II) were 1.0×10^{-2} M (1 M = 1 mol dm^{-3}) , 1.0×10^{-4} M, and 1.0×10^{-5} M, respectively. The ionic strength of the solution was adjusted to 0.1 M with sodium perchlorate.

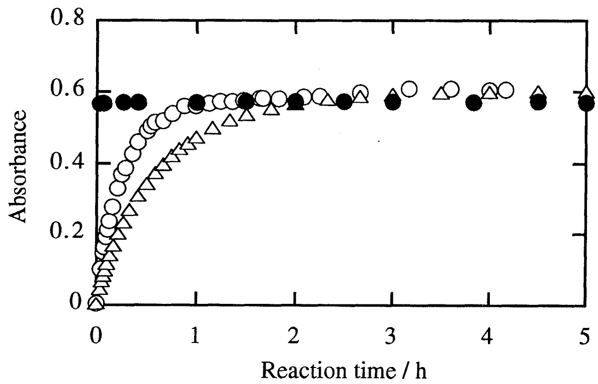

Figure 1. Effect of the reaction time on the formation of $Ni(pan)_2$ or $Zn(pan)_2$ complexes in aqueous Triton X-100 solution.
Triton X-100 1.0×10^{-2} M, Hpan 1.0×10^{-4} M, Ni(II) or Zn(II) 1.0×10^{-5} M, I=0.1 M $NaClO_4$, 2%(v/v) methanol, pH 6.8 (○●) or pH 5.2 (△). Wavelength : Ni(II) ○△ 568 nm, Zn(II) ● 555 nm. Path Length : 1 cm.

After the equilibration, the absorbance values of the Ni(II)-pan complexes at 568 nm and that of Zn(II)-pan complexes at 555 nm were constant at pH above 3.5 and 6, respectively. The complexes formed in this pH region can be considered as neutral forms, $Ni(pan)_2$ and $Zn(pan)_2$, judging from their absorption spectra. The above complexes are expected to be concentrated into micelle phase or adsorbed surfactant phase depending on their hydrophobicity. The effect of the reaction time on the chelate formation are shown in Figure 1. Zn(II) reacted rapidly at pH 6.8, and the absorbance of $Zn(pan)_2$ reached constant value within 1 min. On the other hand, Ni(II) reacted slowly, and the quantitative reaction needed about 1 h at pH 6.8, and 2 h at pH 5.2. It is found that the reaction time of Ni(II) is very fast compared with the case of solvent extraction, in which the complete reaction needs more than 40 h.[9] This advantageous feature relates to the dispersive properties and high specific surface area of micelle phase.

The adsorption of Triton X-100 on silica gel and the collection of neutral solutes into the adsorbed surfactant phase were examined by shaking a mixture of silica gel and the aqueous Triton X-100 solution containing Hpan and $Zn(pan)_2$. The silica gel used was high-purity Kieselgel 60HR (Merck), with a particle size ranging 5 - 40 μm, and an average pore diameter 60 Å. The initial solution contained 1.0×10^{-2} M or 2.0×10^{-2} M Triton X-100, 1.0×10^{-4} M Hpan, and 1.0×10^{-5} M Zn(II). The pH of the solution was adjusted to 6.8-7.0. Under these conditions, Zn(II) quantitatively exists in the form of $Zn(pan)_2$, in other words, the solution contains 8.0×10^{-5} M Hpan and 1.0×10^{-5} M $Zn(pan)_2$. The 10 cm^3 of the above solution was shaken with 0 - 0.6 g of silica gel for 0 - 120 min. After shaking, the concentrations of the constituents in the solution phase were determined by measuring the absorbance at 277 nm for Triton X-100, 471 nm

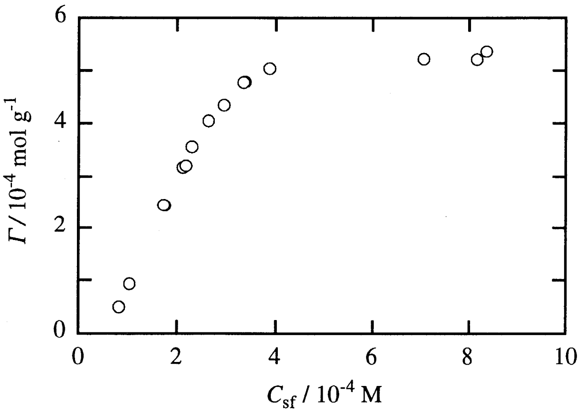

Figure 2. Adsorption isotherm of Triton X-100 on silica gel at 25 °C. Silica gel : Kieselgel 60HR (Merck). Aqueous phase : I = 0.1 M $NaClO_4$, 2%(v/v) methanol, pH 6.8 - 7.0.

for Hpan, and 555 nm for $Zn(pan)_2$. The amount of each constituent retained on silica gel was calculated from the variation of the concentration in the solution phase.

The adsorption of Triton X-100 onto silica gel proceeded fast and attained equilibrium within 3 min. The adsorption isotherm of Triton X-100 on silica gel is shown in Figure 2. It was found that the adsorbed amount of Triton X-100 on unit weight of silica gel (Γ) increased with the equilibrium concentration of Triton X-100 (C_{sf}), and reached saturation under the condition of C_{sf} above the critical micelle concentration of Triton X-100 (2.6×10^{-4} M). The adsorption capacity of Triton X-100 was determined to be about 5.6×10^{-4} mol g^{-1} under the experimental conditions.

The collection of Hpan and $Zn(pan)_2$ on silica gel occurred simultaneously with the adsorption of Triton X-100. Relationship between the adsorption of each constituent and the amount of silica gel is shown in Figure 3. It is found that the collection of Hpan and $Zn(pan)_2$ depend not only on the amount of silica gel but on the initial concentration of Triton X-100. Hpan and $Zn(pan)_2$ are collected quantitatively under the condition that Triton X-100 is adsorbed quantitatively. However, when the amount of silica gel is not large enough for quantitative adsorption of Triton X-100, the collection of either Hpan or $Zn(pan)_2$ cannot occur completely because of the formation of micelles in aqueous solution and the distribution of these compounds into the micelles. These results imply that the most important factor on the collection of Hpan and $Zn(pan)_2$ is the quantitative adsorption of Triton X-100, and these hydrophobic compounds are collected by dissolution into the surfactant assembly on the silica surface. The collection behavior of $Ni(pan)_2$ can be considered to be similar to that of $Zn(pan)_2$ taking into account the chemical properties of these complexes, such as 1:2 metal chelates and electrically neutral forms.

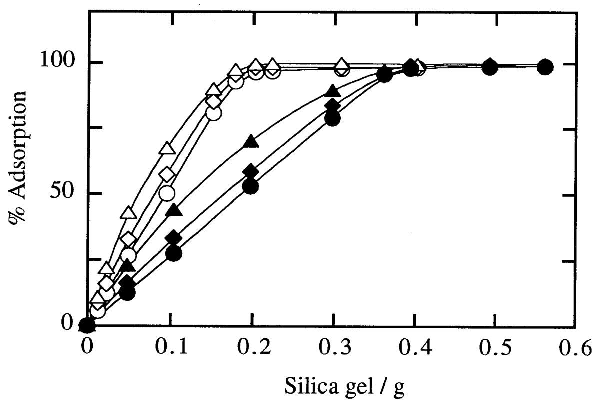

Figure 3. Effect of the amount of silica gel on the adsorption of Triton X-100, Hpan, and $Zn(pan)_2$. Triton X-100 ○●, Hpan ◇◆, $Zn(pan)_2$ △▲ . Silica gel : Kieselgel 60HR (Merck). Aqueous phase ($10 cm^3$) : Triton X-100 1.0×10^{-2} M(○◇△) or 2.0×10^{-2} M (●◆▲), Hpan 8.0×10^{-5} M, $Zn(pan)_2$ 1.0×10^{-5} M, I=0.1 M $NaClO_4$, 2%(v/v) methanol, pH 6.8 - 7.0.

In conclusion, trace metal ions can be concentrated selectively into the nonionic surfactant phase adsorbed on silica gel in the forms of hydrophobic chelates. In the proposed method, water-insoluble chelating reagents can be used, and the chelate formation in micellar solution and the collection on silica gel take place in a short time. The metal chelates retained on silica gel can be eluted quantitatively with a small amount of methanol. Therefore, the proposed method can be used as a preconcentration technique for the determination of trace metal ions in aqueous samples. The nonionic surfactant adsorbed on silica gel is expected to be applicable to the separation and concentration of various compounds, as well as trace metal ions.

References and Notes

1 E. Pelizzetti and E. Pramauro, *Anal. Chim. Acta*, **169**, 1 (1985).
2 H. Watanabe, *Talanta*, **21**, 295 (1974).
3 D. W. Armstrong and F. Nome, *Anal. Chem.*, **53**, 1662 (1981).
4 S. Terabe, K. Otsuka, K. Ichikawa, A. Tsuchiya, and T. Ando, *Anal. Chem.*, **56**, 111 (1984).
5 E. Pramauro, A. B. Prevot, E. Pelizzetti, R. Marchelli, A. Dossena, and A. Biancardi, *Anal. Chim. Acta*, **264**, 303 (1992).
6 H. Watanabe and H. Tanaka, *Talanta*, **25**, 585 (1978).
7 M. Lindheimer, E. Keh, S. Zaini, and S. Partyka, *J. Colloid Interface Sci.*, **138**, 83 (1990).
8 D. C. McDermott, J. R. Lu, E. M. Lee, R. K. Thomas, and A. R. Rennie, *Langmuir*, **8**, 1204 (1992).
9 M. Nakagawa and H. Wada, *Nippon Kagaku Zasshi*, **84**, 639 (1963).