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Metal Concentration by Reversed Micelles

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ABSTRACT

A new method of metal concentration by reversed micelles is described. It differs from traditional solvent extraction concentration in the procedure of metal stripping from an organic phase. Reversed micelles are broken by heating or by adding a polar organic diluent. A concentrated metal solution is produced at surfactant disaggregation; there is no need to use a water-stripping solution. Coefficients of concentration for Fe(III), Pt(IV), and Pd(II) chloride complexes as high as 150 to 1800 have been seen when nonionic oxyethylated surfactants are used.

INTRODUCTION

The problem of metal concentration is common in both analytical chemistry and hydrometallurgy for treating low-concentration processing solutions and wastewaters. Among the commonly used methods, the sorptional ones are characterized by high concentration coefficients ($\sim 10^3$) and low throughput. On the other hand, low concentration coefficients (50–100) and high throughput are typical of liquid–liquid extraction systems (1). Recently, there has been increasing interest in using new, nontraditional systems for separation and concentration of substances such as multiple emulsions (2), microemulsions and micellar solutions (3), three-phase systems (4), and supercritical extraction systems (5).

This work investigates the possibility of using micellar solutions for metal concentration. Micellar solutions are considered to be systems with surfactant aggregates (micelles) with sizes no more than 10 nm (6). Micellar solutions have extremely high specific surface areas; therefore, many heterogeneous processes [i.e., micellar catalysis (7)] proceed most effectively in micelles.

The phenomenon of micellation is quite common in solvent metal extraction, since many extractants show surface-active properties. Micellation usually leads to a decrease in thermodynamic activity of extractants and, finally, to deterioration of extraction performance [decrease in metal capacity, selectivity, etc. (8, 9)]. However, research now appears more frequently on micellar solutions and microemulsions for the extraction of metals (10, 11) and organic substances (12, 13).

The approach to be proposed for metal concentration is based on the assumption that if a metal interacts with an oil-soluble surfactant at the liquid–liquid interface, then its concentration in a surface layer will be higher than in the bulk water phase, i.e., positive adsorption occurs. Since a spherical micelle is a closed monolayer (6), then, during contact of the micellar phase with the feed solution, metal passes into reversed micelles. The concentration of metal in the micelles will be higher than in the water phase as there is so little water in the core of the micelle. The solubilized solution is separated from an organic phase by disaggregation of surfactants (micelle breaking). Note that micellar concentration differs from extraction which uses a water-stripping solution. With micellar concentration, there is no need to use a water-stripping solution. The micellar solution can be regenerated and used repeatedly. The proposed concentration scheme has been examined for a series of model systems.

EXPERIMENTAL

Oxyethylated isononylphenol of oxyethylation degree 4 was used as the micellation surfactant (Trademark "Neonol APh_9-4"). The surfactant was synthesized by the Diagnosticum Company, Belgorod, Russia, with a content of 99.8% purity. The solvents were reagent grade *n*-decane and chloroform.

Extraction of chlorocomplexes of iron(III), platinum(IV), and palladium(II) was investigated from acid chloride and sulfate media of the following composition: 4 mol/L NaCl + 1.5 mol/L HCl, and saturated Na_2SO_4 + 3 mol/L H_2SO_4 in distilled water. Salts were all reagent grade or better. The volume of feed solution has varied between 250 and 50 mL; the water/oil phase ratio usually was 5:1. The phases were contacted for 15 minutes using gentle stirring. The aqueous solution was the continuous phase in all the experiments.

Neonol APh_9-4 forms reversed micelles only in nonpolar solvents like saturated hydrocarbon. Therefore, to break micelles and separate the solubilized solution, chloroform (polar solvent) or a mixture of chloroform with *n*-decane was added to the micellar phase. The procedure was performed in a conical bottomed flask whose walls were covered with hydrophobic material. The time for separation has varied from a few minutes to several hours, depending on feed solution composition. In some cases, micelles were broken when heated at 80°C for 30 minutes. The maximum degree of metal backextraction from micelles did not exceed 90%.

Interfacial tension at the liquid–liquid interface was determined by the "hanging drop" method with Garkins–Brown corrections (14). To measure low interfacial tensions, the "spinning drop" method was applied using a tensiometer by Kruss Company, Germany.

RESULTS AND DISCUSSION

The scheme for micellar metal concentration is shown in Fig. 1. For effective concentration of metals in the micelles, surfactant–metal extraction takes place only at surfactant concentrations exceeding the critical micelle concentration (CMC). Figure 2 shows a plot of the logarithm of the distribution coefficient D [= equilibrium Fe(III) concentration in organic phase/equilibrium Fe(III) concentration in the water phase] and a plot of interfacial tension (σ) vs the logarithm of the APh_9-4 concentration in *n*-decane. Substantial metal recovery into the organic phase begins at surfactant concentrations exceeding CMC (a break in the isotherm of interfacial tension corresponds to the beginning of micelle formation). At lower surfactant concentrations, the metal recovery is virtually nil.

The micellar extraction mechanism is also suggested by the fact that no extraction occurs with polar solvents like chloroform, carbon tetrachloride, benzene, or toluene in which APh_9-4 micellation does not occur; metal recovery into the organic phase is virtually nil. Similar results were also obtained for saturated hydrocarbons when carrying out extraction at high temperatures.

Extraction isotherms at surfactant concentrations higher than CMC are curves (Fig. 3) that resemble Langmuir adsorption isotherms.

With chloroform and micellar solution, the backextraction step is accomplished with solubilized solution separation only in a certain range of volume ratios of surfactant:*n*-decane:chloroform. The region of backextraction is determined experimentally for each of the metals (Fig. 4.). Best

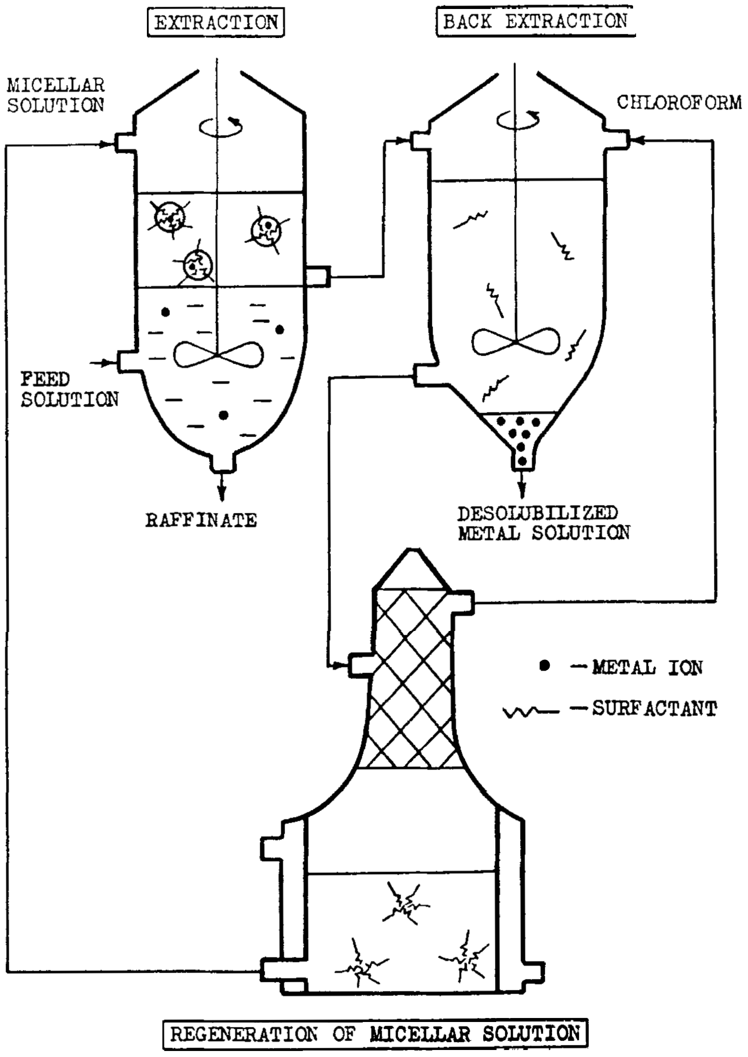

FIG. 1 Schematic diagram of the micellar metal concentration.

results were obtained when one micellar solution volume was added to nine volumes of *n*-decane/chloroform mixture (2 : 1) for Fe(III) backextraction; to four volumes of *n*-decane/chloroform mixture (3 : 1) for Pt(IV); and to 0.5 volume of chloroform for Pd(II).

Typical results are given in Table 1. The search for optimal extraction conditions has not been performed. Further experiments have shown that

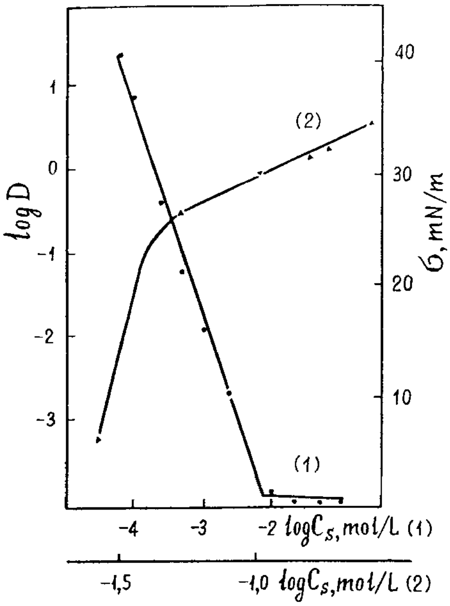

FIG. 2 Effect of surfactant concentration (C_S) on the Fe(III) distribution coefficient (Curve 2), and interfacial tension (Curve 1). The initial Fe(III) concentration in the water phase is 2×10^{-4} mol/L.

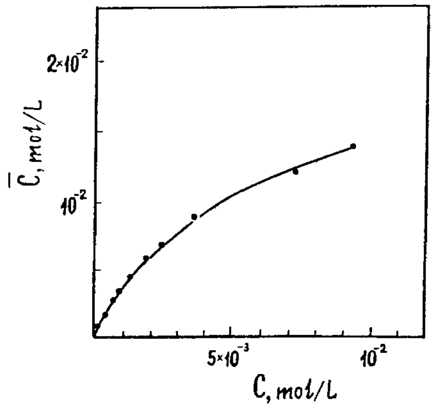

FIG. 3 Extraction isotherm of Fe(III) from acid chloride media. $\bar{C}$, C-equilibrium Fe(III) concentrations in organic and water phases, respectively.

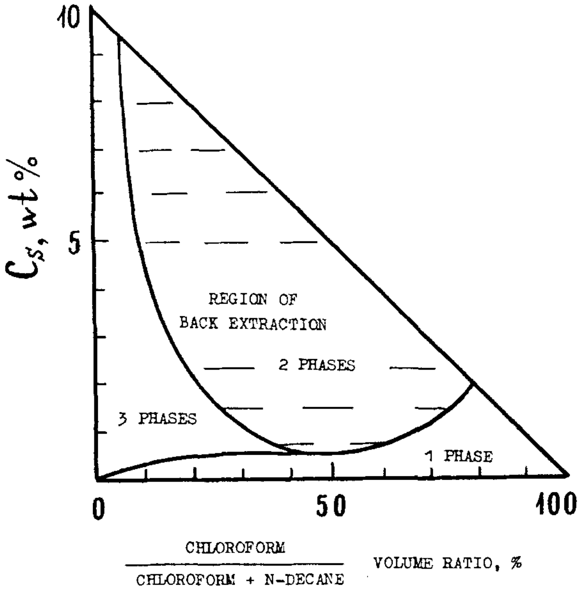

FIG. 4 Phase diagram of Fe(III) backextraction.

metal recovery could be increased (at high coefficients of concentration) by changing the water-phase composition. The possibility for micellar concentration in a closed cycle has been demonstrated for Pt(IV) extraction. Chloroform was distilled upon the solubilized solution separation; the micellar solution was used repeatedly. Ten cycles were conducted, and the extraction and concentration parameters did not deteriorate.

TABLE 1
Results of Micellar Metal Concentration with 10 wt% Solution of APh$_9$-4 in *n*-Decane

Metal initial concentration (mol/L)	Feed solution	Extraction (%)	Backextraction (%)	Coefficient of concentration[a]
Fe(III), 2×10^{-4}	Chloride	45	86	150 [370]
Pd(II), 4×10^{-4}	Sulfate	65	70	200
Pt(IV), 2×10^{-4}	Sulfate	77	90	650 [1800]

[a] Data in brackets were obtained for organic solutions saturated in metal.

CONCLUSIONS

A new method for concentrating metals by reversed micelles has been proposed. The method combines the advantages of concentration by extraction and sorption.

The surfactant–metal interaction mechanism and the resulting selectivity were not considered. The cause of metal adsorption at the liquid–liquid interface could be chemical, ion-electrostatic [ionic exchange in a double electric layer (15)], or van-der-Waals interactions. When using oxyethylated surfactants in acid media, similar to oxygen-containing extractants, the chemical interaction of protonated oxyethylated groups with anionic metal chlorocomplexes are likely to be involved. It is evident that as surfactant oxyethylation degree grows, the distribution coefficient increases. Under the same conditions, non-oxyethylated isononylphenol reveals no extractive capacity. In addition to the metals used in this article, one could expect similar results at concentrations from acid media of other metals which generate anionic metal chlorocomplexes.

Finally, the oxyethylated surfactants could also be used as traditional extractants in concentrations of metals by solvent extraction. Therefore, there is an opportunity to separate the metal in the backextraction step into the water phase at virtually any composition by breaking the micelles with heat or by polar organic additives.

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