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Extraction-Electrophoretic Concentration of Gold by Reverse Mixed Micelles of Triton N-42 and AOT

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A new method of gold concentration with a total enrichment factor of $\sim 10^4$ has been developed. The method includes a liquid-liquid extraction of $AuCl_4^-$ by reverse micelles; reduction of gold (III) to Au nanoparticles (with hydrazine monohydrate as a reducing agent) in the extracts and an electrophoretic concentration of the particles in a cell with parallel-plane electrodes. With increasing sodium sulfate concentration in the feed there was a decrease of water content for ordinary micelles and an increase of gold extraction. At a constant acid-salt background (3 mol/L HCl + 3.5 mol/L Na_2SO_4) concentration, AOT introduction into micelles led to a decrease in extraction. The obtained regularities are consistent with a hydrate-solvate mechanism. The electrophoretic mobility of gold nanoparticles in extracts has been determined. When AOT was introduced into the extracts after the stage of reduction the electrophoretic mobility of nanoparticles was considerably increased (from -1.8×10^{-11} to $1.8 \times 10^{-10}\,m^2/(V \times s)$) which made possible an additional stage of electrophoretic concentration with an enrichment factor of $\sim 1.5 \times 10^3$.

Keywords concentration; electrophoresis; nanoparticles; reverse micelles; solvent extraction

INTRODUCTION

Concentration of noble metals is of great interest today both for separation science and technology as it allows lean raw materials to be put into use (1). The aim of this work was to combine the extraction and electrophoretic methods of concentration on the basis of reverse micelles in a single process. Reverse micelles of surfactants effectively extract complex ions of metals from aqueous media (2). On the other hand, they are widely recognized reactors for the synthesis of nanoparticles with a predetermined size and shape (3). So far, no attempts have been made to make use of both of these properties simultaneously. The extraction concentration is the most often used method of pre-concentration both in the analytical chemistry (4) and technology (5) but it has low enrichment factors (50–100) (6). By the reduction of metal ions in extracts to nanoparticles it is possible to perform an additional stage of electrophoretic concentration with considerably higher enrichment factors ($\sim 10^3$) which can widen the possibilities of the extraction method (7). In addition to this, from the cathode concentrates, which have molar concentrations of metals one, it will be easy to prepare highly dispersed metal particles with a pre-determined size and morphology.

Reverse micelles make possible realization of a variety of processes, such as extraction of ions, synthesis of nanoparticles, and electrophoresis which becomes possible due to the unique structure of reverse micelles and mainly the peculiar properties of micellar water.

Extraction

The association of the widely used extractants in the organic phase during the liquid-liquid extraction of metals is a well-known phenomenon (8). Usually it was considered as undesirable since the formation of micelles leads to a reduction of extractant activity, losses in selectivity, and a considerable solubilization of the aqueous phase into the organic phase.

Attempts to use the reverse micelles for the separation and concentration of metals were determined by the existence of a well-developed interface between the organic solution and the aqueous pseudo-phase and by the high mobility of micelles. The micelles used in these studies were those of the well-known surfactants. Sodium bis(2-ethylhexyl)sulfocuccinate (AOT) in saturated hydrocarbons was the most often used surfactant. Cetyltrimethylammonium bromide (CTAB) and sodium dodecylsulfate (DDSNa) in CCl_4 and $CHCl_3$ or in saturated hydrocarbons in the presence of a co-surfactant and nonionic oxyethylated surfactants were used less often. The solubilization of alkali and alkali-earth metals by AOT micelles in isooctane has been studied (9). A model has been developed which took into account the local changes of the dielectric permeability in the micellar water core and the charge and size of the hydrated cation. The extraction of Cu^{2+} by AOT micelles is considered by the authors to proceed through its adsorption into the micellar surface layer according to

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Stern model of electric double layer (10). By controlling the $W_0 = [H_2O]/[\text{surfactant}]$ parameter in AOT micelles in isooctane it was possible to effectively separate Cu^{2+} and Fe^{3+} (the extraction of the trivalent metals turned out to be better than that of the one- and bivalent metals) (11). It has been shown by the Monte Carlo method that the large cations K^+ and Cs^+ can be exchanged for Na^+ in AOT micelles (12). At the same time, the highest selectivity of the AOT micelles was towards Li^+ ions. The extraction of copper and the solubilization of water by AOT micelles in isooctane impregnated by three extractants: *anti*-2-hydroxy-5-nonylbenzophenone oxime (HNBPO), Versatic 10, and di(2-ethylhexyl)dithiophosphoric acid (DEHDTPA) has been studied (13). The addition of DEHDTPA increased the solubilization of water by mixed micelles; in the case of HNBPO the solubilization was almost unchanged and decreased in the case of Versatic 10. The effect of neutral ligands (of the type of carbamoylmethylphosphine oxides) on the extraction of lanthanides (III) from nitric acid media by a microemulsion of AOT has been studied (14). At low surfactant and ligand concentrations (2×10^{-3} mol/L) there was a considerable synergic effect and an improvement in selectivity.

The extraction of copper into micelles of different surfactants (CTAB, DDSNa, and hexa-oxyethylene glycol dodecyl ether ($C_{12}EO_6$)) impregnated by a series of 6-(alkylamino)-methyl-2-(hydroxymethyl)pyridines has been studied (15,16). Two possible mechanisms of complexation (on the interface and in the bulk) have been discussed. The complexation in the aqueous phase was found to make the predominant contribution in the case of ionic micelles. For the oxyethylated surfactants, interface interactions must also be taken into consideration. The extraction by impregnated micelles of $C_{12}EO_6$ was more effective. The extraction of copper from aqueous solutions by microemulsions of nonionic surfactant in n-decane impregnated with benzoylacetone was carried out with and without a buffer. In this case 26 v/v% of the sulfuric acid was solubilized into the micelles (17) which allowed the extraction by microemulsions to be considered as a variant of the liquid-membrane extraction with higher mass transfer rates as compared with the normal emulsion membranes.

We are developing a new approach to the concentration, which is based on the use of various micellar structural transitions. A new method for the concentration of anionic complexes of metals has been developed (18) which differs from the traditional one by the presence of a stage of back extraction. The micellar structure was destroyed by chloroform or by heating and then the aqueous phase containing the metal solubilized at the stage of extraction was isolated into a separate phase of a small volume. The concentration of the anionic complexes of metals (Fe(III), Pt(IV), Pd(II)) was $\sim 1.5 \times 10^3$ which is an order of magnitude higher than in the case of the traditional extraction systems (19). The extraction of anionic complexes of metals by oxyethylated surfactants was shown to proceed by a hydrate-solvate mechanism (20). The concentration of gold (III) from acid sulfate-chloride media by oxyethylated nonylphenol (Triton N-42) micelles (2) and mixed Triton N-42 + dioctylsulfide (DOS) micelles has been performed (21). The distribution coefficient increased from 200 to 1000 as the DOS concentration increased from 0 to 0.25 mol/L (a positive synergic effect). An analysis of the extraction equilibriums indicated that the determining contribution to the extraction of gold (III) is made by the mixed micelles (as compared with the micelles of Triton N-42 and molecular species of DOS in n-decane).

Synthesis of Gold Nanoparticles and Electrophoresis

Nanoparticles of metallic gold were prepared in micelles of AOT in n-heptane and studied by atomic force microscopy (22). The mean micellar radius was found to be dependent on the micellar size which allowed the authors to suggest stabilization of nanoparticles by adsorbed layers of AOT. The particles were prepared by the reduction of the respective salts with hydrazine in methanol after which they were recovered into a hydrocarbon phase. The possibility of using *t*-octylphenoxypolyethoxyethanol (Triton X-100) and AOT micelles for the synthesis of minute-size particles of gold has been investigated (23). It was found that the mean size of Au nanoparticles (3 nm) prepared in reversed micelles of Triton X-100 in the presence of sodium sulfite was much smaller than in microemulsions of AOT. This is explained by the fact that gold clusters are formed in the micellar shell rather than in the aqueous pool and there they are stabilized by Triton X-100 oxyethyl groups. The synthesis of nanoparticles of gold in reverse micelles of nonionic oxyethylated surfactants and their hydrophobization by alkanthiols with a hydrocarbon radical length of C_6 to C_{18} have been reported (24). Two- and three-dimensional arrays of such nanoparticles were obtained. The reduction kinetics of gold (III) in micelles of AOT (with sodium citrate as a reducing agent) (25) and Triton N-42 (with hydrazine as reduction agent) (26) has been studied as a function of the content of aqueous pseudo-phase. It has been shown (27) that the growth of the clusters of gold occurs as a result of surface reduction until the micellar polar nanocavity becomes filled completely. No coagulation takes place in the process of growth. The system turns unstable when the nanoparticle radius begins to exceed a certain critical value determined by the interaction energy of the particles.

A brief review of the works on the electrophoresis of nanoparticles in aqueous and non-aqueous media is given in (7) together with a method for the electrophoretic concentration in reverse micelles where the micelles with nanoparticles are electrophoretically separated from the "empty" ones. AOT was used as the micelle-forming surfactant. The high electrokinetic potential of the gold nanoparticles (43 mV) formed as a result of reduction ensured a high rate of concentration.

However, in the case of AOT (an anion-active surfactant), the distribution coefficient of $AuCl_4^-$ in the extraction from sulfate-chloride media is small which does not allow one to conduct an additional concentration at the stage of extraction. In the case of Triton N-42 the extraction is more effective (21) (the distribution coefficient reaches 10^3) but the electrophoretic mobility of the nanoparticles is small (27) so that considerably more time is required for electrophoresis.

It appears that a solution to this problem may be the use of the advantages of both systems simultaneously in the form of mixed AOT + Triton N-42 micelles.

It should be noted that in our previous papers (2,21,26) the stage of the extractive concentration ends with the gold precipitation (by coagulation) in the form of an ultra-dispersed powder. The use of electrophoretic concentration instead of precipitation provides a more promising procedure with considerably higher concentration coefficients which would also allow the final product to be obtained as a liquid coagulation-stable concentrate with nanoparticles of the metal. In the liquid hydrophobic concentrate the nanoparticles of gold are not linked to each other and can be used in different nanotechnologies without a re-dispersion required in the case of the ultra-dispersed powders.

EXPERIMENTAL

Materials

Oxyethylated nonylphenol ($C_9H_{19}C_6H_4(OCH_2CH_2)_4OH$) with a degree of oxyethylation of 4 (Triton N-42) from Sigma and an anionic AOT (Aldrich, 96%) were used as the micelle-forming surfactants. For the formation of mixed micelles two types of solution were prepared:

1. 0.25 mol/L AOT + x mol/L Triton N-42 (with AOT as the base surfactant)
2. 0.25 mol/L Triton N-42 + x mol/L AOT (Triton N-42 as the base surfactant) in n-decane.

The maximum concentration of the surfactant was also 0.25 mol/L. The surfactant was kept over Al_2O_3 for 2 to 3 months to remove the water; n-decane ($\geq$98.0%) used as the solvent was dried for a prolonged time and distilled twice.

Hydrazine monohydrate (20 mol/L) was used as the reducing agent. The hydrochloric acid (11 mol/L) and sodium sulfate ($\geq$99.5%) were used for the preparation of the feed, which had a constant concentration of the acid (3 mol/L HCl), the Na_2SO_4 concentration varied from 0 to a saturated solution ($\sim$3.5 mol/L).

Methods

The IR spectra in the intermediate region (4000 – 940 cm^{-1}) were recorded on a Scimitar FTS 2000 Fourier transform spectrometer (32 scans, resolution 4 cm^{-1}) in a CaF_2 cell with a thickness 0.11 mm. A preliminary processing of the spectra included subtraction of the absorption by the solvent (n-decane), by AOT using stretching vibrations of carbonyl (1740 cm^{-1}) and sulfonate (1050 cm^{-1}) groups and by Triton N-42 molecules using the bands of the phenyl ring (1611 and 1580 cm^{-1}) so that the areas of the over- and undercompensated parts of the spectra were equal to each other (28). From the integral absorption areas of the ν(OH) stretching vibrations (3800 – 3000 cm^{-1}) the concentrations of water in micellar solutions after extraction were calculated. The calibration dependence was obtained for the micellar solutions of ordinary and mixed micelles by an injection solubilization of water ($A = 352.96 \times [H_2O]$, $R^2 = 0.99$, where A is the area of O-H stretching band of water, $[H_2O]$ is the water concentration (mol/L)).

The hydrodynamic radius of the micelles was determined by the photon-correlation spectroscopy (PCS). The effective hydrodynamic radii of micelles were calculated from the diffusion coefficients for spherical particles of equal size (fitting of experimental values of the autocorrelation function of one exponent). The measurement of the hydrodynamic radius was performed at an angle of 30° with sampling times of 20 or 40 μs; the collection time was several minutes. No angular dependence of the hydrodynamic radius was found in the studied systems at angles from 15° to 90°. For each system the hydrodynamic radius was determined as the mean of 10 measurements. The measurement error was 10%. Prior to the measurements, the micellar solutions were dedusted by filtering in a closed box through a glass filter with a pore diameter of 5.1 μm. The aqueous solutions were filtered through a membrane filter with a pore size of 0.12 μm.

The extraction of Au (III) was performed by micellar solutions of Triton N-42 and AOT and mixed Triton N-42 + AOT micelles in n-decane from a sulfate-chloride solution. The ratio of the volumes of the aqueous and organic phase was equal to 50 and 10 at the stage of extraction. The gold content of the feed after the extraction was determined by a flame variant of the atomic-absorption method on a Perkin-Elmer spectrophotometer (Model 303).

The electronic absorption spectra of the initial solutions of gold (III) in the aqueous feed and in the extract and the spectra of the solutions of nanoparticles of gold (0) were recorded on a Shimadzu 1700 spectrophotometer in a 0.5 cm thick quartz cell. The reduction of Au (III) to

Au (0) was performed by injecting into the extract an aqueous solution of hydrazine monohydrate (20 mol/L). For the formation of mixed micelles with nanoparticles certain amounts of dry AOT were dissolved in the extract after reduction. The electrophoretic mobility of the nanoparticles was measured on the next day.

Determination of the electrokinetic potential of nanoparticles in micellar systems and the electrophoretic concentration were carried out in a cell similar to that described elsewhere (7) with the only difference that the velocity of the layer of nanoparticles was recorded not visually but photometrically as it was done when studying the kinetics of electrophoretic concentration. The relative error of determination was 10%.

RESULTS AND DISCUSSION

Extraction

First of all, to determine the optimum conditions for the extraction, the distribution coefficient of gold (III) was studied as a function of sodium sulfate concentration in the feed at a constant concentration of HCl (3 mol/L) for ordinary Triton N-42 and AOT micelles. In both cases the extraction isotherms had the form of curves ending in a saturation plateau. At low gold concentrations the dependences were linear. In the extraction by AOT micelles (Fig. 1) the distribution coefficient of $AuCl_4^-$ sharply increased with the increasing sodium sulfate concentration. The dependence for Triton N-42 had a maximum with a value of ~500 at a 1 mol/L concentration of Na_2SO_4 (2).

In the mixed micelles when oxyethylated Triton N-42 was added to AOT micelles the distribution coefficient increased to ~10^2 at equal concentrations of the surfactants (Fig. 2, curve 1) and vice versa with the increasing concentration of AOT at a constant concentration of Triton N-42 the distribution coefficient decreased (Fig. 2, curve 2) to the same value.

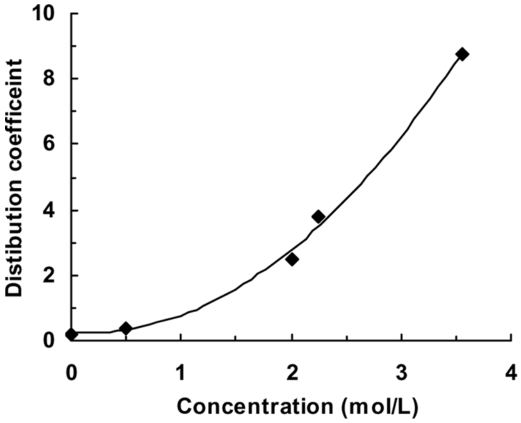


FIG. 1. Dependence of the distribution coefficient of gold (III) on the sodium sulfate concentration in the extraction by ordinary AOT micelles.

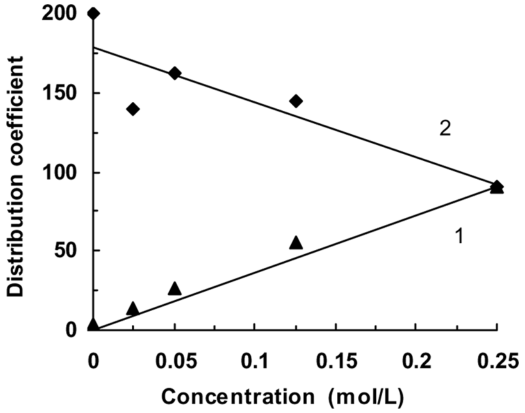


FIG. 2. Dependence of the distribution coefficient on the concentration of the co-surfactant: Triton N-42 (1), AOT (2).

Thus the possibility of an extraction transfer of gold (III) into the micellar phase has been demonstrated. The micelles of Triton N-42 turned out to be more effective extractants than the AOT micelles. This evidence is quite predictable and justified: a molecule of Triton N-42 has four ether groups and an alcohol group. So Triton N-42 can be considered as a neutral oxygen-containing an extractant (29). What is surprising is the extraction of $AuCl_4^-$ by micelles of AOT (although with low distribution coefficients). AOT is an anionic surfactant and has demonstrated its preference for the exchange of cations (14,30). In mixed micelles the recovery of gold was less effective than in ordinary micelles of Triton N-42.

Thus the use of Triton N-42 allows the achievement of a 50-fold concentration of gold at the stage of extraction while with the mixed micelles the concentration was only 10-fold with a recovery of gold from the feed of ~90%.

Water Content in the Extracts

The water content in the extracts is determined both by the extractive ability of micelles and the stability of micellar systems with gold nanoparticles after the reduction. The effect of the composition of the aqueous feed on the water content in reverse micellar solutions of Triton N-42 in the extraction from acid sulfate-chloride solutions has been studied as a function of sodium sulfate concentration at a constant acidity (3 mol/L HCl). With increasing sodium sulfate concentration in the feed there was a decrease in the water content (by approximately 7 times) of the micellar phase and a reduction of the micellar hydrodynamic radius (Fig. 3). In the extraction from solutions with a Na_2SO_4 concentration below 0.5 mol/L the IR spectra could not be recorded because of the high water contents of the extracts.

The effect of micellar solution composition on the water content in the extraction from sulfate-chloride media of a

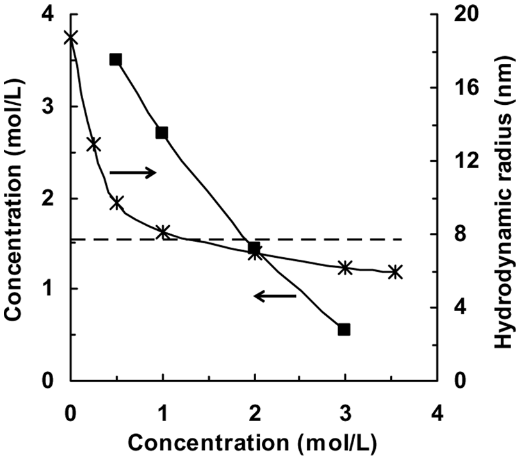


FIG. 3. The concentration of water and the hydrodynamic radius of Triton N-42 micelles as a function of sodium sulfate concentration in the feed.

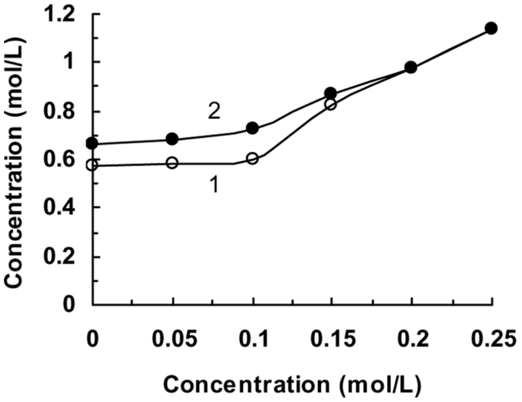


FIG. 4. The concentration of water in the micellar solutions in the extraction by mixed micelles of Triton N-42 and AOT as a function of AOT (1) and Triton N-42 (2) co-surfactant concentration.

constant composition (3 mol/L HCl +3.5 mol/L Na_2SO_4) has been studied for two types of mixed micelles:

1. 0.25 mol/L Triton N-42 + x mol/L AOT
2. 0.25 mol/L AOT + x mol/L Triton N-42.

In both cases with the increasing concentration of the co-surfactant the total content of water in the extracts was increasing by approximately a factor of 1.5 to 2 (Fig. 4).

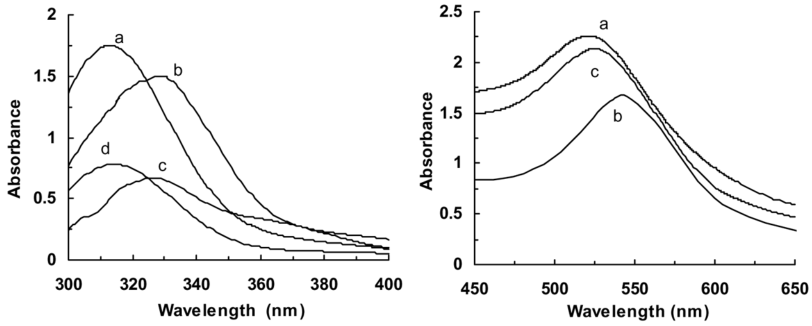
Thus, the content of Na_2SO_4 in the feed has a much greater influence on the water content of the micelles than does the concentration of the surfactant (in the studied regions).

$AuCl_4^-$ Localization in Micelles

Figure 5a shows the electronic absorption spectra of gold (III) in the feed and the extract. In the case of ordinary Triton N-42 micelles there is a considerable batochromic shift of the absorption band maximum. According to the crystal field theory, this shift (31) can be treated as arising from a breakdown of symmetry of the complex tetrahedral $AuCl_4^-$ anion occurring under the influence of the hydrated proton. This, in turn, is indicative of the preferred localization of the anion in the surface layer of the surfactant, most probably near the hydroxyl group since it is the first to be protonated (32). In the micelles of AOT there was a small hypsochromic effect which appears to be due to the $HAuCl_4$ localization in the central part of the AOT micelle. In mixed micelles the value of this shift is close to that obtained for Triton N-42 suggesting a localization analogous to that of the complex anion in ordinary Triton N-42 micelles.

Extraction Mechanism

Spectrophotometry, IR spectroscopy, photon correlation spectroscopy data, and the observed behavior of the distribution coefficients allow some conclusions to be made as to the mechanism of extraction. Within the



(a) (b)

FIG. 5. The electronic absorption spectra of a chloride complex of gold (III) (a) and gold nanoparticles (b) in AOT (a), Triton N-42 (b), Triton N-42 + AOT (c) micelles, and in a 3 mol/L aqueous solution of HCl (d). [AOT] = [Triton N-42] = 0.25 mol/L, $[H_2O] = 0.52$ mol/L.

framework of a hydrate-solvate mechanism, the extraction of gold by Triton N-42 micelles is describable by ordinary reactions of protonation and subsequent anionic exchange (26):

The extraction of gold (III) by AOT micelles can be explained in two ways. In strongly acidic media there may occur protonation of the oxygen of the AOT ether groups to form an anion-exchange complex and the extraction will proceed by an anion-exchange mechanism. It is, however, more probable that there will be an attack by a proton on an AOT sulfonate group to produce a poorly dissociating acid AOTH and this appears to be more realistic (34,35). Gold (III) gets into the aqueous core of the AOT micelle as $HAuCl_4$ and the extraction occurs by the mechanism of a ordinary physical distribution.

In the extraction with mixed micelles, the addition to Triton N-42 micelles of molecules of AOT decreases the extraction of gold. The reasons for this decrease may be

1. an increase of the water content (Fig. 4);
2. a decreased concentration of the counter-ions capable of undergoing anion-exchange.

The latter variant (which seems to be more preferable) can, in turn, be explained by the following: a portion of the hydrated protons protonating the Triton N-42 hydroxyl group may jump over to a sulfonate group of the anionic AOT.

As a result the concentration of the counter-ions (Cl^- or SO_4^{2-}) capable of exchanging with $AuCl_4^-$ decreases and the distribution coefficient decreases as more AOT is added. Of course, further experimental tests are needed to verify these assumptions.

Judging by the solvatochromic effects, at noticeable concentrations of Triton N-42, $AuCl_4^-$ in mixed micelles is mainly localized at the hydrated proton of Triton N-42 molecules. The main contribution to the extraction by mixed micelles is made by Triton N-42 and the extraction proceeds by a hydrate-solvate mechanism.

Nanoparticle Synthesis and Stability

The next task was to prepare nanoparticles of gold in the extracts. The extracts used were those obtained in the extraction by ordinary and mixed micelles from a feed containing 3 mol/L HCl; 3 mol/L HCl + 1 mol/L Na_2SO_4 and 3 mol/L HCl + saturated Na_2SO_4. Stable nanoparticles of gold could be obtained only in the extracts from a feed containing 3 mol/L HCl +saturated Na_2SO_4. In all other cases, in the course of the reduction by hydrazine, the color was rapidly changing from yellow to red and then to blue, an evidence indicative of the occurrence of a fast coagulation after the reduction. After coagulation, a highly dispersed black powder was deposited on the bottom of the test-tube with a content of gold of ~96%. The absorption spectra of gold nanoparticles in stable systems are shown in Fig. 5b. The nanoparticles that formed in the AOT micelles ($\lambda_{\max} = 520\,\text{nm}$) were smaller than those formed in the micelles of Triton N-42 ($\lambda_{\max} = 540\,\text{nm}$), in agreement with the literature data (36). In all of the extracts (except for the mixed micelles) stable systems could be obtained only after prolonged heating (for several hours) at ~60°C to remove the excessive aqueous pseudo-phase and to reduce the micellar size. Thus, stable systems with nanoparticles are obtained only in systems containing micelles of a small size.

To explain the obtained regularities the energy of the particle pair interaction according to the DLVO-theory has been calculated using the equations that had been adapted to micellar systems (27,36):

$$\begin{aligned}
E_{total} &= E_{el} + E_{osm} + E_{vdW} \\
E_{el} &= \frac{4\pi\varepsilon\varepsilon_0\, R^2\psi_o^2}{h + 2R} \\
E_{vdW} &= -\frac{A^*}{6}\left[\frac{2R^2}{h_c^2 - 4R^2} + \frac{2R^2}{h_c^2} + \ln\left(\frac{h_c^2 - 4R^2}{h_c^2}\right)\right] \\
E_{osm} &= \frac{4\pi R k_B T}{V_{solv}}\phi^2\left(\frac{1}{2} - \chi\right)\left(l - \frac{1}{2}\right)^2
\end{aligned}$$

where Ψ_0 is the surface potential of nanoparticles, k_B is the Boltzmann constant, T is the absolute temperature, φ is the volume occupied by a surfactant molecule, ϕ_{solv} is the molecular volume of the solvent, χ is the Flory-Huggins parameter, A^* is the complex Hamaker constant, h is the surface-to-surface separation of the particles, $h_c = h + 2R$ is the center-to-center separation. The calculations were performed on a model system: spherical nanoparticles of gold of radius R covered with a layer of adsorbed surfactant molecules of thickness l. The complex Hamaker constant A^* was calculated from the Hamaker constants for gold (45.3×10^{-20} J) (36) and n-decane (6.86×10^{-20} J) (37) by the formula: $A^* = (A_1{}^{1/2} - A_2{}^{1/2})^2$. It was assumed that the Hamaker constant for the adsorbed layer of the surfactant coincides with that for decane. The electrostatic interaction was calculated using an approximation formula neglecting the shielding of the surface potential by counter-ions (38) and the approximation: $\Psi_0 \approx \zeta$. The electrokinetic potential was calculated from the values of electrophoretic mobility by the Huckel formula:

$$\zeta = \frac{3}{2} \times \frac{\eta \times V_{el}}{\varepsilon\varepsilon_0 \times H}$$

where V_{el} is the particle velocity, η is the dynamic viscosity, H is the electric field force, ε is the relative dielectric permeability of the medium (n-decane), ε_0 is the dielectric constant. The use of the Huckel formula implies that the

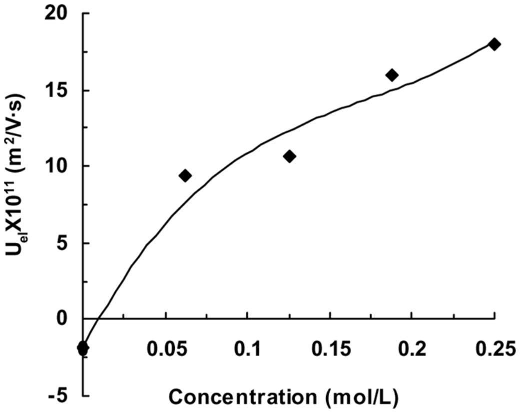


FIG. 6. Electrophoretic mobility of gold nanoparticles in mixed micelles as a function of AOT concentration in the extract. $C_{Au} = 2.1 \times 10^{-4}$ mol/L.

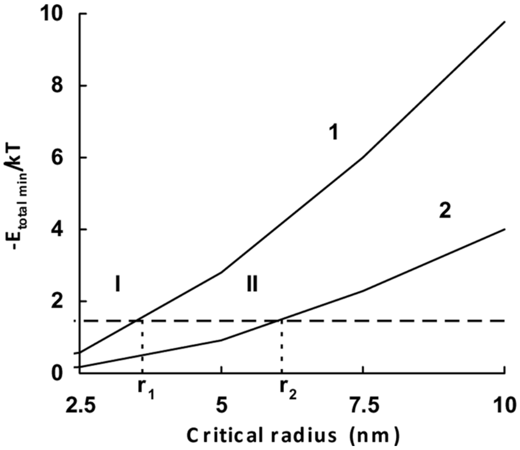
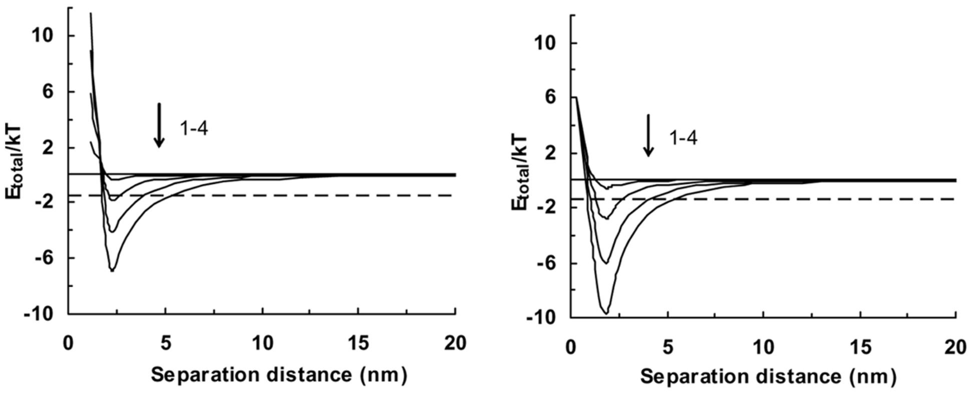


FIG. 8. Stability zones for gold nanoparticles in ordinary micelles of AOT (I) and Triton N-42 (II). The critical radius is equal to 3.7 and 6.1 nm, respectively.

nanoparticle radius is much smaller than the thickness of the double electric layer (39). Measurements have shown that in the Triton N-42 extract the electrophoretic mobility of the gold nanoparticles was close to zero but sharply increased with the addition of AOT (Fig. 6). The calculations were performed for nanoparticles in micelles of Triton N-42 ($l = 1.6$ nm (27), $\Psi_0 = -1$ mV) and AOT ($l = 1$ nm, $\Psi_0 = 8$ mV). The dependences of the particle interaction energy have a minimum whose position depends on the thickness of the micellar adsorption layer (Fig. 7). The larger the particle, the greater is the depth of the potential well. The sharp growth of the energy of interaction at small separations is determined by the repulsion of the adsorption layers (40). At potential well depths greater than $3/2\ kT$ the particle interaction energy exceeds that of the heat interaction and coagulation takes place in the system. At these values of the surface potential the electrostatic interaction begins to make a contribution to the total energy only for large particles. From the depths of the potential well, as a function of particle size and adsorption layer thickness, the critical radii and stability zones of micellar systems with gold nanoparticles were found. For micelles of Triton N-42 the critical radius was equal to 6.1 nm and for the micelles of AOT to 3.6 nm (Fig. 8); for the mixed micelles (with parameters varying within: $l = 1.6$–1.0 nm, $\Psi_0 = -1$–8 mV) intermediate values were obtained. These calculations are only an estimation. Along with the aggregation there take place processes of desaggregation and for an accurate description the coagulation kinetics should also be studied (41). Nevertheless, even such rough estimations give an understanding of the impossibility of obtainment of stable micellar systems with nanoparticles in the extracts from solutions with a low content of salts. Only in solutions with a high content of salt will the radius of the micelle polar cavity be smaller than



(a)

(b)

FIG. 7. The energy of the pair particle interaction as a function of the radius of gold nanoparticles in the ordinary micelles of Triton N-42 ($\Psi_0 = 0$ mV, $l = 1.6$ nm) (a) and AOT ($\Psi_0 = 8$ mV, $l = 1$ nm) (b): 2.5 (1), 5 (2), 7.5 (3), 10 (4) nm.

the critical radius of the nanoparticle (the critical hydrodynamic radius equal to 7.7 nm (6.1 + 1.6) is shown in Fig. 3 by the dash line). At lower sodium sulfate concentrations the extract is to be subjected to an additional thermal treatment to remove the water and a reduction in the size of the micelles.

Thus, in the synthesis of nanoparticles it is the content of the aqueous pseudo-phase in micelles that determines the size of the forming nanoparticles and allows obtainment of systems with stable nanoparticles. In the extracts of ordinary Triton N-42 and AOT micelles stable nanoparticles could be obtained without any difficulties by making use of smaller micelles (which was achieved by heating or by increasing the background electrolyte concentration).

In mixed systems stable solutions of nanoparticles were not obtainable at all. Probably, this is also associated with the growing content of the aqueous pseudo-phase (and hence the growth of the micellar size) with the increasing concentration of the co-surfactant) (Fig. 4). However, in this case attempts to reduce the micellar size by removing the excessive aqueous phase by heating the extract turned out to be of no help. What was the matter? When considering the problem of stability no attention has been given to what was the growth mechanism of nanoparticles in the process of reduction. In a previous study (27) it was found that during the micellar synthesis seeds of gold nanoparticles are first formed which grow as a result of reduction ions on their surfaces (by an autocatalytic mechanism) until the polar cavity is completely filled. The size of the polar cavity is given by the content of the aqueous pseudo-phase. But the growing particle may "extend" the adsorption layer of the micelle (as a result of a swelling of the micelle which may be accompanied by an increase in the area per a surfactant molecule or of the association with other micelles at a constant area per molecule) (42). Such a possibility is confirmed by the fact that in the micellar synthesis of nanoparticles of metals (including gold) the size of the forming particles generally exceeds the size of the polar cavity of "empty" micelles (43). To explain this evidence, some workers use the notion of a "rigidity" of the micelle adsorption layer (44). By "rigidity" is meant the ability of the layer to withstand the expansion. In our case, such a behavior may be associated with a decreased rigidity of the adsorption layer of two surfactants. No doubt, that it is connected with the interface tension of the surface layer: the greater the tension the higher is the rigidity. It is well known (45) that with the formation of a mixed adsorption layer (especially in the case of a combination of an ionic and a non-ionic surfactant) the interface tension may be substantially decreased to very low values sometimes passing through a maximum.

The Final Scheme of the Concentration of Gold

Taking into account the obtained results, the following scheme has been chosen for the concentration of gold:

1. extraction by micelles of Triton N-42;
2. reduction of gold in the Triton N-42 extract;
3. addition to the micellar solutions of nanoparticles of a dry AOT to produce mixed micelles and to increase the electrophoretic mobility of the gold nanoparticles;
4. electrophoretic concentration in the mixed micelles.

At the stage of extraction, extraction of gold from the feed has been performed which contained 3 mol/L HCl + saturated Na_2SO_4 and 2.8×10^{-5} mol/L $AuCl_4^-$. The volume of the aqueous phase was 100 mL, that of the organic phase was 10 mL; the extraction of gold was 91%. Then stable micellar systems with gold nanoparticles were prepared by the injection solubilization of hydrazine monohydrate into the extract. Then by dissolving dry AOT in the extract (to a concentration of 0.25 mol/L) the electrokinetic potential of the nanoparticles was increased to 8 mV which made it possible to perform an effective additional electrophoretic concentration. The maximum concentration that could be achieved at the stage of the electrophoresis was equal to 1.6×10^3 and the total concentration, including the 10-fold concentration at the stage of extraction, was equal to 1.6×10^4 at a 90% recovery of gold from the feed.

CONCLUSIONS

Thus the possibility of an extraction-electrophoretic concentration of gold from acid sulfate-chloride media by mixed micelles of Triton N-42 and AOT with a total enrichment factor of $\sim 10^4$ has been demonstrated. In the studied processes the determining role is played by the water content of extracts. During the extraction, the decrease in the content of water leads to a decrease in the extent of hydration of ions in micelles and an increase of the extraction of gold (III). During the reduction (in ordinary micelles) it is the content of the aqueous pseudo-phase that determines the size of the forming particles and the zones of stability.

With the use of the electrophoretic concentration, the possibilities of the extraction concentration could be widened considerably. At the stage of the extraction concentration, along with the oxyethylated surfactants it will also be possible to use traditional extractants (tributyl phosphate, di(2-ethylhexyl)phosphoric acid, alkyl sulfides, and so on). After the extraction, AOT is added to the extracts and the reduction of ions to nanoparticles is performed and then the electrophoretic concentration is carried out. This variant is applicable to practically all metals as objects of analysis (and to all of the known extractants and extraction schemes) and makes it possible to use the vast body of the available experimental material on the liquid extraction of metals. The high values of the enrichment factor obtainable with the extraction-electrophoretic concentration allow a considerable improvement of sensitivity for the instrumental methods of analysis.

Apart from the importance of the concentration for "analytical" purposes, the search for new sources of raw materials for the preparation of nanoparticles of noble metals (Au, Ag, Pt, Pd and so on) is also of great interest. They are attracting attention because of their unique optical, electrical, and chemical properties and the wide prospects for use in medicine, biology, and catalysis (46). At the present time, nanoparticles of gold and other noble metals are prepared from commercial materials ($HAuCl_4$, $AgNO_3$, H_2PtCl_6 and so on), or pure metals. Therefore, the development and a scientific substantiation of a process in which the concentration of metal ions from diluted aqueous solutions is directly followed by synthesis of nanoparticles without the stage of preparation of the massive metal would be of great interest for a cheaper preparation of nanoparticles.

As compared with the extraction-precipitation procedure (2,21,26), the extractive-electrophoretic method allows the nanoparticles to be obtained as a liquid concentrate with a metal concentration of 1–2 mol/L. It should be noted that such systems cannot be obtained in a purely synthetic way: the high concentrations of the metal lead to immediate coagulation already during the process of reduction. The concentrates are more convenient for use than the powders as there is no need in re-dispersion and an additional stabilization.

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