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Extraction of Thiocyanate Complexes of Metals in the Systems Based on Potassium Bis(alkylpolyoxyethylene) Phosphate and Alkylbenzyldimethylammonium Chloride

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Abstract

The article summarizes the results obtained in the studies of the distribution of thiocyanate acid complexes of iron (III), copper (II), cobalt (II), zinc and cadmium in extraction systems based on technical surfactants – potassium bis(alkylpolyoxyethylene) phosphate (oxyphos B) in the presence of sulphuric acid, alkylbenzyldimethylammonium chloride (catamin AB) in the presence of nitric acid at room temperature or their mixture at 50 °C. It was established that the efficiency of individual surfactants as extractants is conserved both with inorganic salts and acids used as salting-out agents. It is shown that for oxyphos B extractability decreases as a sequence Fe (III) > Co (II) > Zn > Cu (II) > Cd, while for catamine AB the sequence is Cd \approx Zn > Co (II) > Cu (II) > Fe (III), and in the case when a mixture of surfactants is used, oxyphos B is determining, which is confirmed by the extractability sequence: Fe (III) > Co (II) > Zn > Cu (II) > Co (II) > Zn > Cu (II) > Cd. Oxyphos B is an analog of neutral oxygen-containing extractants, it concentrates thiocyanate acid complexes according to the hydrate-solvate mechanism, while catamin AB, anion-exchanging extractant, is more efficient in the extraction of thiocyanate complexes. The use of a mixture of the indicated surfactants allows one to carry out the process in more diluted solutions and to obtain synergetic effects in extraction.

Keywords: liquid extraction, ionic surfactants, anion-exchange extraction, thiocyanate complexes of metals

INTRODUCTION

Extraction of thiocyanate acid complexes of metal ions has won broad application for concentrating metal mixtures and separating them, as well as for metal determination using extractionphotometric methods [1]. A suitable substitute for the extraction of thiocyanate complexes in the system involving water and an organic solvent [2] may be the systems that undergo separation as a consequence of chemical interaction [3]. Another possibility is to use polyethylene glycols as extractants [4-7] or surface-active substances (SAS) in the presence of a salting-out agent [8]. The most thoroughly studied item is the extraction of the thiocyanate complexes of metals by

technical SAS: non-ionic ones (sintanols - monoalkylpolyethyleneglycols, $C_n H_{2n-1} O(C_2 H_4 O)_m H$, where n = 10-18 for sintanol DS-10, n = 12-14for sintanol ALM-10) [9]; anion potassium (bis(alkylpolyoxyethylene)phosphate, $[C_n H_{2n+1} O(C_2 H_4 O)_6]_2 POOK$, where n = 8-10, oxyphos B) [10] and cation (alkylbenzyldimethylammonium chloride, $[C_nH_{2n+1}N^+ (CH_3)_2CH_2C_6H_5]Cl^-$, where n = 10-18, catamin AB) [11] in the presence of inorganic salting-out agents. The indicated SAS may form separating mixtures with inorganic acids but without a salting-out agent (inorganic salt), so the goal of the investigation is to establish the possibility of concentrating thiocyanate acid complexes of metals in the systems based on oxyphos and catamin AB with the use of an inorganic acid as a salting-out agent.

EXPERIMENTAL

The reagents used in the work were oxyethylated anionic SAS – potassium bis(alkylpolyoxyethylene)phosphate (oxyphos B, TU 2484-344-05763441-2001, the content of the major substance was 98 %); alkylbenzylmethylammonium chloride (catamin AB, TU 9392-003-48482528-99, aqueous solution, the content of the major substance was 49-51 %); ammonium thiocyanate NH₄SCN, sulphuric and nitric acids, both Ch. D. A. grade, sulphates of indium, zinc, iron (III), cadmium, cobalt (II), copper (II), thallium oxide of Kh. Ch. grade.

Extraction in the systems Oxyphos B – sulphuric acid – water and catamin AB – nitric acid – water was carried out in a separating funnel. For this purpose, 4.0 mL of catamin AB solution (or 3.6 mL of oxyphos B solution) with the concentration 500.0 g/L, 2.0 mL of the 0.1 M solution of metal salt, calculated amounts of nitric or sulphuric acid and 2.0 M solution of ammonium thiocyanate were poured into the separating flask, and distilled water was added to make the volume equal to 20.0 mL. The result ing mixture was stirred for 3 min, and then the phases were separated from each other after complete layering.

Extraction in the system composed of a mixture of catamin AB and oxyphos B at a ratio of 32.5 : 67.5 (CO-67.5) with water was carried out by pouring the solutions into the volumetric tube: 1.0 g of CO-67.5, 2.0 mL of 0.1 M solution of metal salt, calculated amounts of the solutions of 5.0 M sulphuric acid and 2.0 M ammonium thiocyanate, and then distilled water was added to reach the volume of 20.0 mL. The mixture was thoroughly mixed and kept in a thermostat at 50 $^{\circ}$ C for 30 min, then cooled. The aqueous phase was separated by decanting.

The degree of metal isolation $R_{\rm M}$ (M = Fe, Cu, Co, Zn, Cd) was determined by chelatometric titration of the raffinate. The presence of SAS in the titrated solution did not affect the accuracy of determination.

RESULTS AND DISCUSSION

Due to the instability of thiohydrocyanic acid, extraction is carried out using a mixture of the solutions of ammonium thiocyanate and an inorganic acid. It was established experimentally that the broadest region of separation is observed in the presence of sulphuric acid for Oxyphos B and nitric acid for catamine AB. To determine the optimal conditions that would provide the maximal recovery of the metals under study, the dependences of the degree of metal recovery on the concentrations of ammonium thiocyanate and inorganic acid were plotted for each system.

The system Oxyphos B – sulphuric acid – water

With an increase in the concentration C of ammonium thiocyanate, the degree of metal recovery increases for all metals except copper, however, quantitative recovery is not observed (Fig. 1, *a*). For $C_{\rm NH_4SCN} > 0.1$ mol/L, the degree of iron (III) and zinc recovery exceeds 90 %. The maximal degree of cobalt (II) recovery is observed for $C_{\rm NH_4SCN} > 0.3$ mol/L.

Oxyphos B in the acid medium may be considered as an analogue of neutral oxygen-containing extractants able to concentrate thiocyanate acidocomplexes in the form of complex acids, for example, for iron (III):

 R_2 POOK(o) + 2H⁺(w) = [R_2 POOH]H⁺(o) + K⁺(w) (1) [R_2 POOH]H⁺(o) + [Fe(SCN)₄]⁻(w) =

 $([R_2POOH]H^+)[Fe(SCN)_4]^-(o)$ (2)

where (o) is the organic phase, and (w) is the aqueous phase,

 $\mathbf{R} = \mathbf{C}_{n}\mathbf{H}_{2n+1}\mathbf{O}(\mathbf{C}_{2}\mathbf{H}_{4}\mathbf{O})_{6}, \ n = 8-10.$

For constant $C_{\rm NH4SCN}$ = 0.3 mol/L, the degree of iron (III) recovery is almost independent of $C_{\rm H_2SO_4}$, the maximal zinc recovery is observed for $C_{\rm H_2SO_4} < 0.5$ mol/L, cobalt (II) for $C_{\rm H_2SO_4} < 0.6$ mol/L (see Fig. 1, b).

The studied metals may be arranged as a sequence in the order of decreasing extractability:



Fig. 1. Dependence of the degree of metal ion recovery $(R_{\rm M})$ in the system Oxyphos B – H_2SO_4 – H_2O on concentration, mol/L: a – NH₄SCN ($C_{\rm H_2SO_4}$ = 0.25 mol/L); b – H_2SO_4 ($C_{\rm NH_4SCN}$ = 0.30 mol/L). Here and in Fig. 2, 3: $C_{\rm M}$ = 0.01 mol/L, total volume 20 mL.

Fe (III) > Co (II) > Zn > Cu (II) > Cd, which is identical to the sequence of metals according to their extractability from thiocyanate solutions in

the system Oxyphos B – ammonium sulphate – water [8]. The quantitative recovery of thiocyanate complexes of iron (III), cobalt (II), zinc and



Fig. 2. Dependence of the degree of metal ion recovery $(R_{\rm M})$ in the system catamine AB – HNO₃ – H₂O on concentrations, mol/L: a – NH₄SCN ($C_{\rm HNO_3} = 0.25$ mol/L); b – HNO₃ ($C_{\rm NH_4SCN} = 0.35$ mol/L). For conditions, see Fig. 1.

copper (II) in the system with ammonium sulphate may be explained by its high salting-out capacity.

System Catamine AB — nitric acid — water

The phase diagram of the system Catamine AB – nitric acid – water is characterized by a broad range of separation and the high coefficient of catamine AB distribution [11]. With an increase in $C_{\rm NH4SCN}$ in the system, the recovery degree increases for all the studied metals (Fig. 2, *a*). The quantitative recovery of cobalt, zinc and cadmium is observed for $C_{\rm NH4SCN} > 0.1$ mol/l, copper (II) for $C_{\rm NH4SCN} > 0.25$ mol/L, iron (III) for $C_{\rm NH4SCN} > 0.35$ mol/l.

Catamine AB, which is a salt of the quaternary ammonium base, acts as an anion-exchange extractant concentrating thiocyanate complexes of metals efficiently, which is shown below for iron as an example:

$$\begin{split} & \text{R}_{4}\text{NCl(o)} + [\text{Fe}(\text{SCN})_{4}]^{-}(\text{w}) = \\ & \text{R}_{4}\text{N}[\text{Fe}(\text{SCN})_{4}](\text{o}) + \text{Cl}^{-}(\text{w}) \\ & \text{where } \text{R} = \text{C}_{n}\text{H}_{2n+1}(\text{CH}_{3})_{2}\text{CH}_{2}\text{C}_{6}\text{H}_{5}, \ n = 10\text{----18}. \end{split}$$
(3)

With constant $C_{\rm NH4SCN}$, an increase in $C_{\rm HNO_3}$ causes a decrease in the degree of cobalt (II) recovery for $C_{\rm HNO_3} > 0.75$ mol/L and iron (III) at $C_{\rm HNO_3} > 0.5 \text{ mol/L}$ (see Fig. 2, *b*), which may be connected with an increased competition between nitrate ions and metal acidocomplex for the reagent (see Fig. 2, *b*). The sequence corresponding to a decrease in metal extractability forms the row: Cd \approx Zn > Co (II) > Cu (II) > Fe (III).

Comparing the extraction of thiocyanate complexes in the system Catamine AB – sodium chloride – water [12] with the system studied by us, we are to stress the higher efficiency of the system with nitric acid, which may be due, on the one hand, to the higher salting-out ability of nitrate ions with respect to catamine AB, and on the other hand, to a decrease in the negative effect of chloride ions, which is connected with the suppression of the formation of the chlorides of metal acidocomplexes causing a decrease in the degree of recovery of metal ions under study.

System CO-67.5 - water

Aqueous solutions of the mixtures of catamine AB and oxyphos B, due to the formation of an ionic associate, can get separated at relatively low temperatures, and surfactants are concentrated mainly in the organic phase. In addition, the use of a mixture of surfactants allows achieving syn-



Puc. 3. Dependence of the degree of metal ion recovery (R_M) in the system CO-67.5 – H₂O on concentration, mol/L: a – NH₄SCN ($C_{H_2SO_4} = 0.5 \text{ mol/L}$); b – H₂SO₄ ($C_{NH_4SCN} = 0.25 \text{ mol/L}$). For conditions see Fig. 1.

Optimal concentrations for the extraction of thiocyanate acidocomplexes of metals in the systems based on catamine AB and oxyphos B

| Surfactant | Parameters of extraction | | | Recovery degree | | | | |
|------------|--------------------------|-------------------------------|---------------------|-----------------|--------|--------|-----|-----|
| | Surfactant | H_2SO_4 (HNO ₃) | NH ₄ SCN | Fe(III) | Cu(II) | Co(II) | Cd | Zn |
| | g/L | mol/L | | % | | | | |
| Cataime AB | 100.0 | 0.50 | 0.35 | <99 | <99 | <99 | <99 | <99 |
| Oxyphos B | 90.0 | 0.25 | 0.40 | 98 | 73 | 98 | 51 | 96 |
| CO-67.5 | 50.0 | 0.50 | 0.25 | <99 | 96 | <99 | 80 | 97 |

ergetic effects in extraction, which is demonstrated by the example of the chloride acidocomplexes of metals [13].

In the presence of 0.5 M $\rm H_2SO_4$ iron (III) is recovered quantitatively at $\rm C_{\rm NH_4SCN} > 0.1~mol/L$ and cobalt (II) at $\rm C_{\rm NH_4SCN} > 0.25~mol/L$ in the extraction system (Fig. 3, *a*). The extraction of other metals is not quantitative.

At constant $C_{\rm NH_4SCN} = 0.25$ mol/L, iron (III) is recovered quantitatively within the $C_{\rm H_2SO_4}$ concentration range 0.125–0.5 mol/L and cobalt (II) at $C_{\rm H_2SO_4} = 0.5$ mol/L, the maximal degree of copper (II) recovery is 96 %, zinc 97.3 %, indium 98 % and cadmium 81.5 % (Fig. 3, b). In general, the metals form a sequence with respect to a decrease in their extractability: Fe (III) > Co (II) > Zn > Cu (II) > Cd. This sequence is similar to the system sulfuric acid – oxyphos B – water.

The optimal concentration parameters of the extraction of thiocyanate acidocomplexes in the systems based on catamine AB, oxyphos B and their mixture are shown in Table 1. The use of a mixture of surfactants allows one to enhance the degree of recovery of all the studied metals in comparison with the system based on oxyphos B due to the introduction of a more efficient extractant – catamine AB, and to decrease the concentrations of reagents in the system.

CONCLUSION

Investigations showed that catamine AB, oxyphos B and their mixtures may be used as efficient extragents of the thiocyanate acidocomplexes of metals with inorganic acids applied as salting-out agents. It was shown that catamine AB is more efficient anion-exchange extragent than oxyphos B. The use of the mixture of these surfactants allows one to decrease the concentrations of the reagents. It should also be noted that the proposed systems do not contain expensive, toxic components and are characterized by the low residual content in the raffinate.

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TABLE 1