Salts of high–molecular alkylamines have found wide use for the extraction of acids and acidocomplexes of metals. The literature data [1, 2] show that a great influence on their extraction properties is exerted by organic solvents (diluents) for amines. The polarity of the molecular structure of the amine salts is the basic factor determining this influence. In relatively nonpolar, nonsolvating solvents with a low dielectric constant, these salts are poorly soluble, remain in solution in a nondissociated state, and, as a rule, are substantially polymerized.

Most solvents possess more or less pronounced acid–base properties [3]. They are capable of specific solvation, i.e., of the formation of hydrogen bonds (or relatively unstable complexes with charge transfer) with anions or cations of amine salts [2]. Solvation leads to an increase in the solubility of these salts and their depolymerization. Ultimately polymerization and specific solvation of the amine salts determine their thermodynamic activity in the organic solvent and, consequently, their extraction properties.

In this work we studied the influence of solvating solvents (haloderivatives of hydrocarbons, aromatic hydrocarbons, alcohols, ethers) on the extraction of niobium from concentrated solutions of hydrochloric acid with solutions of certain secondary and tertiary alkylamines.

**EXPERIMENTAL METHOD**

Trioctylamine (TOA), dinonylamine (DNA), and dioctylamine (DOA) were used as the extraction reagents; CCl₄ and decane were used as the "inert," nonsolvating diluents for the amines.

Solutions of niobium were prepared by dissolving a weighed sample of the pentoxide in a mixture of (NH₄)₂SO₄ and H₂SO₄ (1 ml of H₂SO₄ and 0.3 g (NH₄)₂SO₄ per 50 mg of Nb₂O₅), followed by dilution with conc. HCl. The extraction of niobium was monitored using the radioisotope Nb⁹⁵. Volumes of the phases 5 ml, time of shaking 5 min.

In the case of extraction from conc. solutions of HCl, interfacial exchange of the chloride ions of the amine salt for anionic chloride complexes of niobium (NbOCl⁻ₙ, NbOCl⁻ₙ⁻) is the step determining the equilibrium:

\[
\text{NbOCl}^-\text{aq} + (n - 3) \text{AmHCl}^-\text{org} \rightleftharpoons \text{NbOCl}^-\text{Am}^-\text{org} + (n - 3) \text{Cl}^-\text{aq}
\]  

Since the hydrochloric acid concentration is constant, the equilibrium concentration of chloride ions, as well as the activity coefficients of chlorine and niobium in the aqueous phase (\(\gamma_{\text{Nb}^{aq}}, \gamma_{\text{Cl}^-\text{aq}}\)) will be constant. If the concentration of the amine salt in the organic phase is also kept constant in this case, and it is far greater than the total niobium concentration, it is not difficult to establish the relationship between the distribution coefficient of niobium (D) and the activity coefficients of the extraction reagent and the extractable complex in the organic phase from the equilibrium (1):

\[
\lg D = \lg K' + \lg \frac{\gamma_{\text{AmHCl}^-\text{org}}}{\gamma_{\text{Nb}^{aq}}}
\]
Fig. 1. Dependence of the distribution coefficient of Nb in extraction with a 0.025 M solution of TOA in mixtures of CCl₄ with CHCl₃ on the CHBr₃ (1) and CHCl₃ (2) content. C_HCl = 11 M, C_Nb = 10⁻⁴ g-atom/liter.

Fig. 2. Dependence of the logarithm of the distribution coefficient of Nb in extraction by 0.05 M solutions of amines in mixtures of CCl₄ and CHCl₃ on the chloroform content: 1) TOA; 2) DNA. C_HCl = 11.3 M, C_Nb = 10⁻³ g-atom/liter.

Fig. 3. Dependence of the degree of extraction of Nb (R) on the content of the organic solvent in extraction by 0.025 M solutions of amines in mixtures of decane with p-xylene (1 and 2) and chlorobenzene (3 and 4). C_HCl = 11.1 M, C_Nb = 10⁻⁴ g-atom/liter.

Here K' considers the constancy of the equilibrium constant (K_ex) and all the quantities independent of the nature of the organic solvent (the activity of HCl and the activity coefficient of Nb in the aqueous phase, concentration of the amine salt in the organic phase).

Any solvating interaction of the solvent with the amine salt or with the extractable complex of the metal leads to a decrease in their activity coefficients in the organic phase. In this case, as can be seen from Eq. (2), a decrease in the distribution coefficient of niobium will occur when the extraction reagent (amine chloride) is more strongly solvated than the extractable complex of niobium.

Acid solvents (CHCl₃, alcohols) specifically solvate the anion of the amine salts Am⁺...Cl⁻...HCCl₃. The volumes of the complex anions of niobium NbOCl₃⁻, NbOCl₅²⁻ significantly exceed the volume of the chloride anions. Consequently, the electron density and basic properties of these anions are weaker than those of the chloride anion. Then solvation by solvents with acid properties should be stronger for simple chloride anions and should lead to a decrease in the value of γ_AmHClorg/γ_Nborg in Eq. (2), i.e., to a deterioration of the extraction. For solvents of the same class, this effect should be related at least qualitatively to a change in the acid properties of the solvent.

Haloderivatives of Hydrocarbons. Figure 1 shows the dependence of the distribution coefficient of niobium on the content of CHCl₃ and CHBr₃. The acid properties of CHCl₃ are more pronounced than those of CHBr₃. The electronegativity of the halogen (eV), which is equal to 3.0 for chlorine and 2.8 for bromine, can be used as a quantitative characteristic of these properties. Consequently, CHCl₃ should solvate the amine salt and decrease the extraction of niobium to a little greater degree than CHBr₃, which is also evident from the shape of the curves of Fig. 1.

Figure 2 shows the dependence of the logarithm of the distribution coefficient of niobium in the case of extraction of its chloride complexes by solutions of the tertiary (TOA) and secondary (DNA) amines in mixtures of CHCl₃, depending on the content of CHCl₃. TOA·HCl, a salt of a stronger base, is of a more polar character than DNA·HCl. Consequently, the electron donor capacity of the chloride anion in TOA·HCl should be higher, solvation by chloroform stronger, and the decrease in the extraction capacity greater than in DNA·HCl [2]. The shape of the curves in Fig. 2 shows the opposite relationship. In this case apparently the influence of the polarity of the amine salt during solvation is compensated by other factors. It may be assumed that the chloride anion in the salt of the secondary amine is sterically more accessible for solvation by CHCl₃, since it is shielded by the alkyl chains to a lesser degree than for the tertiary amine.