

S.O.Kenzhetayeva¹, S.Sh.Abdygalimova²

¹Ye.A.Buketov Karaganda State University;

²Zh.N.Abishev Chemical-Metallurgical Institute, Karaganda
(E-mail: kenzhetaeva58@mail.ru)

Investigation of influence of colloids formation process on parameters of rare metals extraction

It was established that the introduction of aliphatic alcohols into the extraction system as a modifier during the extraction of rare metals led to structural changes in the organic phase. It was shown that structural reorganization of the organic phase led to a decrease in metal recovery and reduction of the process selectivity with increasing concentrations of alcohol. It was found that metal extractability increased at a certain ratio of the concentration of alcohol/extractant.

Key words: extraction, rare metals, modifier, colloidal structures, aliphatic alcohols.

The extraction method has received the great practical importance in recent years. There are many works devoted to its application for solving various problems of analytical chemistry and chemical technology. Extraction is a complex physical-chemical process. Rational practical use of extraction is not possible without understanding the chemical basis of the method. You can responsibly say that now an understanding of chemistry of the main extraction processes is achieved. Moreover, there are significant opportunities of priori estimate of the behavior of metals in extraction systems.

Research on liquid-liquid extraction widely used in hydrometallurgy of nonferrous, rare and rare earth metals is carried out at the Chemical and Metallurgical Institute (National Center on complex processing of mineral raw materials). Technological schemes are elaborated. However, disintegration of the organic phase into two immiscible liquids in the extraction process is observed in a number of cases. From the standpoint of the process, the formation of the third phase leads to difficulties in the work of extraction equipment designed for the homogeneity of the organic phase. As a consequence, modifiers are introduced to eliminate these negative phenomena in the extraction system.

The influence of certain substances introduced as the third component on the mutual solubility of liquids and the solubility of solids in liquids is described in the literature. The action of the third component that improves the solubility is known as solubilization. According to the theory of Winsor, the effectiveness of a solubilizing additive depends on the R (the relations of affinity) which is equal A_{co}/A_{cw} , where A_{co} is the value expressing affinity for supplements to low-polarity phase; A_{cw} is affinity of the additive to the more polar phase.

According to Winsor, the maximum increase in solubility per mole of introduced additives is achieved if the R value is close to one, i.e. when the affinity of the third component added to both phases is the same. If two liquids both polar and non-polar are not mixed and R value for the added third substance is greater than one, the substance when added to the system proceeds to a greater extent in the non-polar phase and dissolution of the polar substance occurs predominately in a non-polar phase. When $R < 1$ dissolution of the non-polar phase substance occurs in the polar phase as adding a solubilizing agent. Thus the amount of additive required to homogenize the system for $R < 1$ and $R > 1$ is greater than at $R = 1$.

Recent publications [1] suggest that the colloids formation process can occur in such extraction systems if modifiers, having surface-active properties, are introduced into the system for better separation of the organic and aqueous phases in the extraction process. In the process of application of such modifiers can be realized a so-called «micelle» extraction mechanism, comprising transferring the extracted component into the organic phase as a part of colloids particles.

This paper is restricted to reveal laws of micellar mechanism and establish the effect of the resulting colloidal structures on technological parameters of the extraction of rare metals (rhenium) by amines. In studies performed by us previously [2, 3] to prevent the third phase formation, the extraction of rhenium by amines was carried out in the presence of fatty alcohols. Aliphatic alcohols used are surfactants, their surface activity $g = -(\partial\tau/\partial s) > 0$. According to the Duclos-Traube's rule surface activity in homologous series of alcohols in an aqueous medium at the solution-air interface is increased by 3.2 times at increasing the hydro-

carbon chain by one CH_2 -group [4]. In the organic phase the surface activity of alcohols decreases with increasing length of the hydrocarbon radical (reversing the Duclos-Traube's rule).

Investigation of the rhenium extraction by synthesized amines [5, 6] in the presence of various aliphatic alcohols allowed making several conclusions: extracting of a metal depends on the structure of the modifier added, and the concentration of the latter. If we display a graphic dependence of the distribution coefficient of rhenium on the molar ratio of the initial concentrations of alcohol and extractant $U = [\text{alcohol}]_{\text{ref.}} / [\text{extractant}]_{\text{ref.}}$ at the extraction from the sulfuric acid solutions (Fig. 1), it is possible to visually follow the differences in behavior of modifiers depending on the length of their hydrocarbon radicals.

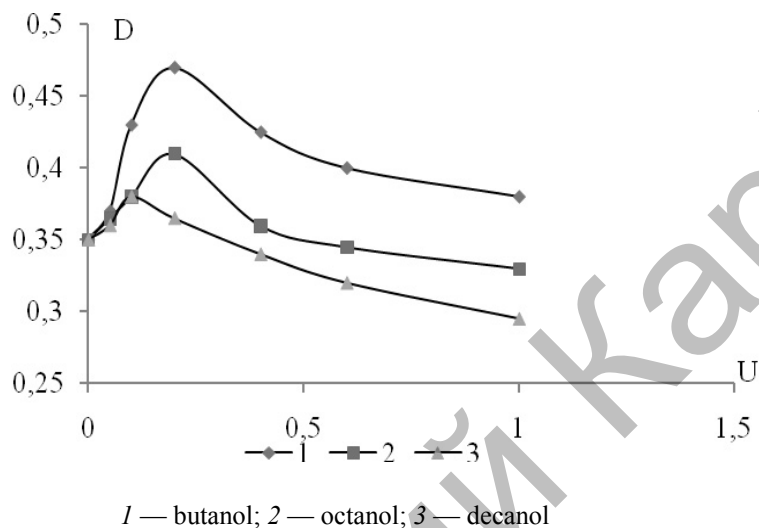


Figure 1. The dependence of the distribution coefficient of rhenium at the extraction by amines on the molar ratio of the starting concentrations of alcohols and the extractant

So, for butanol and octanol $U_{\text{opt.}} = 0.2$, for decanol $U_{\text{opt.}} = 0.1$, i.e. with a decrease in surface activity in a non-aqueous medium, the maximum increment of the distribution coefficient decreases. It should be noted that the dependence of the distribution coefficient U passes through a maximum in all cases, which is apparently due to the associative processes in the organic phase.

The obtained dependences on the physico-chemical parameters (conductivity and viscosity) on the ratio of U (Fig. 2, 3) are an indirect confirmation of the structural changes in the organic phase.

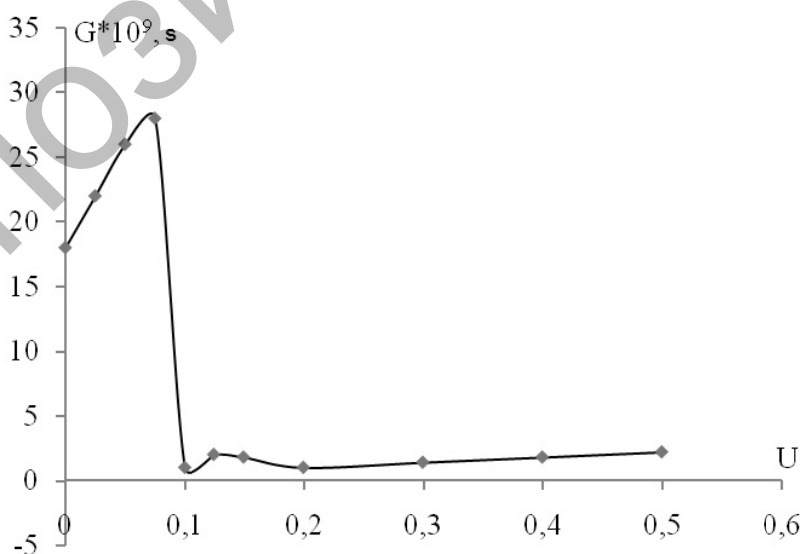


Figure 2. The dependence of the electrical conductivity of the system on the concentration of octanol

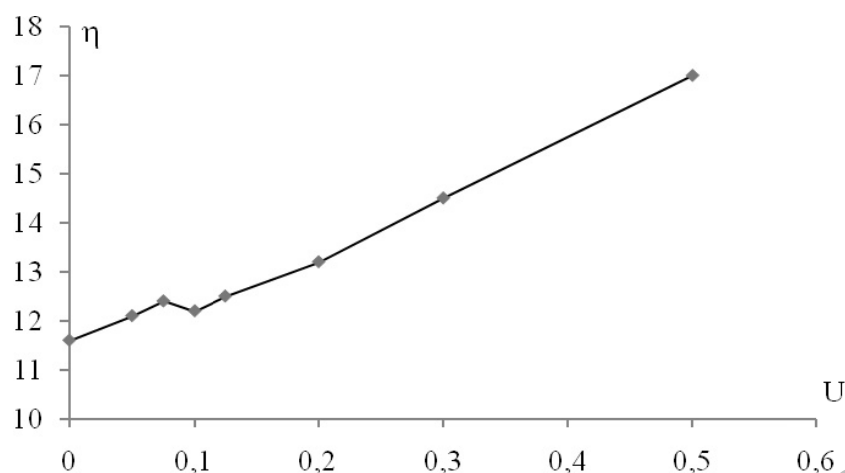


Figure 3. The dependence of viscosity on the concentration of octanol

The inflection point, corresponding to the maximum of metal recovery is obvious on the provided dependence of the system conductivity at different contents of alcohol. It should be noted that the effect of concentration of alcohol is clearly exhibited. The observed facts can be explained by the existence of associates with low-order chain structure at low concentrations of alcohol in the organic phase. Increasing the size of the associates determines the increase in conductivity. From this we can expect a further increase in the conductivity of the solution, however, drop in conductivity indicating clear trend of conversion of chain associates in a complex structures or a microemulsion (micelles) or vesicles. Results of the study of viscous properties of the system are in good agreement with the above structural changes. Given that the viscosity is a structure-sensitive characteristic of the system, there is an acute narrow maximum in the dependence $\eta = f(U)$ indicates the structural reorganization of the organic phase.

Thus, it can be argued that in practical extraction systems in the presence of aliphatic alcohols colloids formation is possible. If at low concentrations of alcohol associates produced in the extract stimulate metal recovery, then a picture changes at increasing the modifier concentration. Experimental data shows that, apparently, the transition into a more complex structure leads to a deterioration in the metal recovery. Apparently resulting particles contain a large fraction of the molecules of the extractant and partially molecules of the extracted compound.

Next, we tried to find out the distribution of the alcohol both in aqueous and organic phases at introduction of the aliphatic alcohol into the extraction system. As it turned out, the concentration of octanol introduced had values exceeding its solubility in water (see Table).

Table

Distribution of the modifying additive at the extraction of rhenium by amines from solutions

U	$C_{\text{octanol}}, \text{ mol/l}$	$C_{\text{octanol}} \cdot 10^3, \text{ mol/l},$ organic medium	$C_{\text{octanol}} \cdot 10^3, \text{ mol/l},$ aqueous medium
0,10	0,01	7,81	2,19
0,20	0,02	15,89	4,11
0,30	0,03	23,85	6,15
0,40	0,04	31,79	8,21

It is believed that the transition of alcohol into the aqueous phase is not due to its solubility. It is due to formation of direct micelles in the aqueous phase. Therefore an increase in the metal distribution coefficient is not only because of solubilization of metal inside the polar core of the inverse colloidal structures formed, but also due to changes of the transfer mechanism in the result of formation of colloidal structures as in the organic and aqueous phases.

To elucidate the role of the nature of alcohols considered on the speed of the extraction process kinetic curves were obtained (Fig. 4). Comparison of the results allowed explaining the high rate of extraction in the presence of butanol because of its high surface activity.

As regards addition of octanol into the extraction system, this fact of an accelerating action should be associated with the ability of this alcohol to stronger «loosen» the interfacial area due to the size of the hydrocarbon radical. We can note that all investigated systems achieve the equilibrium state quickly, and the rate of mass transfer increases in the presence of additives. In our opinion, the adsorption of alcohols at the interface involves reducing the concentration of metal in the interfacial region. In the leaching solutions of raw rhenium-containing material along with these ions concomitant iron ions are present. Elucidation of solubilization effect on the activity of these metals indicated that the separation factor at $C_{Re} = 0,1$ mol/l, $C_{Fe(III)} = 0,01$ mol/L in the presence of butanol decreases from $\beta = 12,98$ (when $U = 0,025$) to $\beta = 8,91$ (when $U = 0,05$), i.e. the difference in position of U_{opt} is leveled.

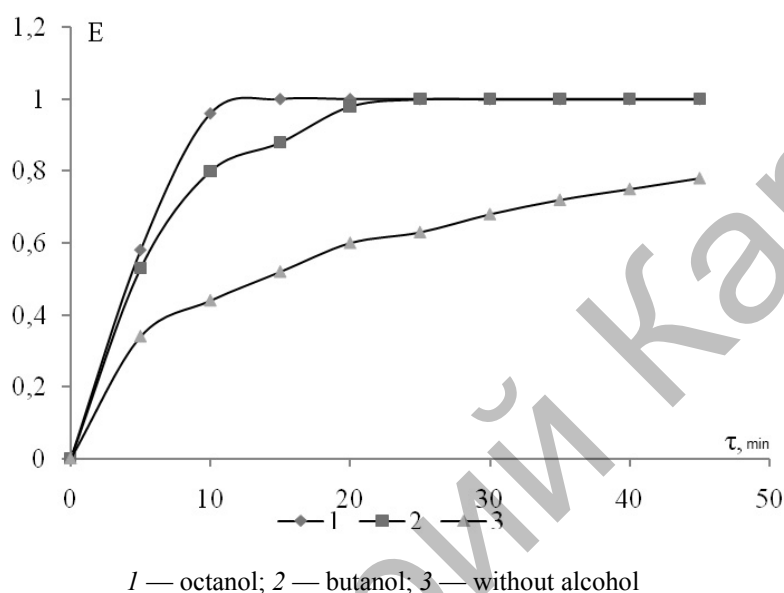


Figure 4. Kinetic curves of rhenium extraction by amines in the presence of modifying additives

It follows that the iron ions can solubilize in a polar nucleus of a micellar unit without dehydration. As it is well known [7], the limiting stage of a typical extraction of iron (III) is a dehydration step of a metal aqua complex. A similar effect of butanol is possible due to its surface activity, which is the highest value among the alcohols used in the work (reversing the Duclos-Traube's rule). Being adsorbed at the interface, butanol facilitates formation of reverse micelles in the organic phase. Obviously, an alcohol, forming hydrogen bonds with water, carries it into the organic phase. The presence of water in the organic phase is one of the essential aspects of the formation of colloidal structures. Consequently, it is not possible to achieve a high rate of separation coefficient at the micellar extraction, a metal target will be contaminated with impurity ions. The use of alcohol with longer hydrocarbon radical, e.g. octanol which activity will decrease at the interface, leads to a reduction in the amount of water entrained by an alcohol molecule. However, as already indicated above, not only different structures of modifiers added, but also their concentrations affect the extractability of the metal. Increasing the concentration of alcohol reduces the separation factor, which is probably due to increased solubilization of extractable metal ions. In this connection it is advisable the presence of a small amount of alcohol ($U = 0,025$) in the extraction system, where separation of metals is possible.

Summarizing all the above data, it can be concluded that at the extraction of rare metals introduction of modifying additives into the extraction system, in particular the aliphatic alcohols leads to structural changes in the organic phase, affecting the distribution coefficients. It is found that the kinetics of the extraction process is dependent on the structure of the modifier and its concentration.

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С.О.Кенжетаева, С.Ш.Әбдіғалымова

Сирек металдарды экстракциялау параметрлеріне коллоид түзілу үрдістерінің әсерін зерттеу

Сирек металдарды бөліп алуға экстракциялайтын жүйеге модификатор ретінде алифаттық спирттерді енгізу органикалық фазадағы құрылымдық өзгерістерге әкелетіні анықталды. Спирттің концентрациясы артқан сайын органикалық фазаның құрылымдық өзгерістері металдың бөліп алынуын төмендететіні, сонымен қатар үрдістің селективтігі төмендейтіні көрсетілді. Спирт/реагент концентрациясының белгілі ара қатынастарында металдың экстракциялануы артатыны анықталды.

С.О.Кенжетаева, С.Ш.Абдығалимова

Исследование влияния процессов коллоидообразования на параметры экстракции редких металлов

Установлено, что введение алифатических спиртов в качестве модификатора в экстракционную систему при извлечении редких металлов приводит к структурным изменениям в органической фазе. Показано, что с увеличением концентрации спирта структурные реорганизации органической фазы приводят к уменьшению извлечения металла, а также к снижению селективности процесса. Доказано, что при определенном соотношении концентрации спирт/экстрагент возрастает экстрагируемость металла.