

COMMUNICATION

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USE OF LIQUID EXTRACTION IN ELECTRO-CHEMICAL PROCESSES FOR SELECTIVE EXTRACTION OF METALS

In implementing the processes of separation, concentration purification of the natural and processed solutions the most widely used is the electroionite method, based on the application of solid resins and membranes [1]–[2]. An inadequate specificity of the latter membranes, however limits their application,

Hence, it is advisable to use liquid extraction membranes and characterized by a high selectivity which may be easily adjusted by introducing different chelating and highly selective complexing agents. It should be noted that the combination of the processes of electrodialysis with specific interaction of liquid organic extracting agents, at a (featuring ion-exchange properties with medium) constant electric field offers many advantages since it allows to adjust the selectivity and completeness of extraction or separation of metal ions depending not only on the nature of the extracting agent, but also on the direction and intensity of the current flowing through the system [5]–[6].

For the systems containing several types of ions and subject to separation, the effectiveness of application of liquid extraction membranes is determined by their selectivity of absorption of ions from the solution and by ion mobility within the membrane. In the processes of separation and extraction of ions requiring the usage of electric current the membrane permeability for individual type of ions is characterized by the transference number. This in turn, depends both on the composition and electro-chemical properties of the liquid membrane and on the composition of the aqueous solution [7]–[8]. An ion largely absorbed by the membrane has higher transference numbers only when its mobility within the membrane itself is high. If however the selectivity of the membrane is accompanied by a substantial decrease in the mobility of one of the ions being separated, then the first ion to be transferred through the liquid membrane during electrodialysis will be mobile, although less absorbable one.

The introduction of highly specific organic complexing agents into the liquid extraction membrane allows to change the mechanism of ion motion within the membrane by associating one of the penetrating ions either into a weakly dissociating or a neutral complex. Consequently the ratio of concentrations of penetrating ions in the liquid membrane is much higher than in the aqueous solution. These procedures employed to adjust the ion selectivity and permeability of liquid extraction membranes in electrochemical processes allow to achieve a high effectiveness of concentration, separation and extraction of metals from aqueous solutions of various compositions.

The experimental data on the electrochemical transfer of the ReO_4^- , VO_3^- , $[\text{RuCl}(\text{H}_2\text{O})]^{-2}$, MoO_4^{-2} ions through the liquid extraction membrane are given in fig. 1. The liquid membrane was formed by a thin (2 mm) layer of the 5% solution of tri-*n*-octylamine in the amyl alcohol between two cellophanepartitions. The latter separated two aqueous solutions, of which one contained metal ions. To avoid a possible

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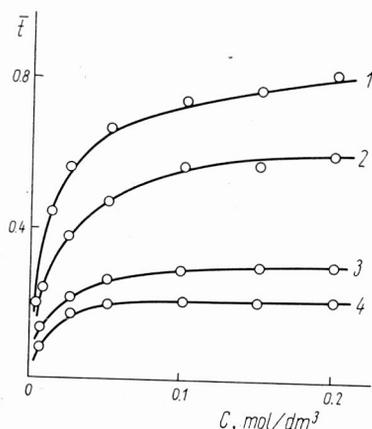


Fig. 1. Transference numbers of anions vs. their concentration in 0.5 M solution of $(\text{NH}_4)_2\text{SO}_4$, pH = 5; $i = 5.0 \text{ ma/cm}^2$ 1 - ReO_4^- ; 2 - VO_3^- ; 3 - $[\text{RuCl}_5(\text{H}_2\text{O})]^{-2}$; 4 - MoO_4^{-2}

penetration of the products of electrolysis into the circummembrane space, as well as the change in the composition and pH of aqueous media, the electrodes were separated additionally by inert partitions.

As can be seen from fig. 1, the transference numbers of the ions investigated increase with the concentration of salt in the solution. In all the curves two segments can be distinguished. The first appears in the region of low concentrations of salt (up to 0.05 mol/dm^3) where the transference numbers increases very intensely, while the second one appears at high concentrations, where the dependence of transference numbers on the concentration of salt is weaker. It may be of interest to note that the amount of current transferred by the anions under investigation compared with other foreign ions, mainly sulphate ions is quite large. This is the more so that the transport process takes place in a relatively high concentration (0.5 M) of ammonium sulphate. It should be noted, however, that the differences in the transference numbers of metal anions investigated are not large enough to apply a single electrodialysis with the liquid extraction membrane as a sufficiently workable procedure for separation of the given ions.

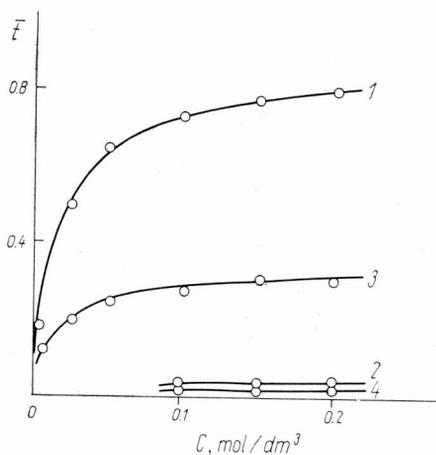


Fig. 2. Transference numbers of anions vs. their concentration for a liquid membrane with the addition of thiooxyn 10^{-3} M , pH = 5; $i = 5.0 \text{ ma/cm}^2$. The notations are the same as in fig. 1

One of the factors capable of effecting considerable and selective changes in the mobility of the given anions is a change in the composition of the liquid membrane, in particular, by the introduction of the 8-mercaptochinoline (thiooxyn) [9] as the organic complexing agent. Indeed, the addition of thiooxyn in the concentration of the order of 10^{-2} – 10^{-4} mol/dm³ results in the pronounced decrease in the transference numbers of vanadium and molybdenum anions, leaving the transference numbers of rhenium and ruthenium anions almost unchanged (fig. 2). This allows the concentration of the anions of rhenium and ruthenium and at the same time their separation from vanadium and molybdenum made in the course of electro dialysis with the liquid membrane modified by thiooxyn. Thus, the separation and extraction of ions from the aqueous solutions of complex compositions, which take place in electro dialysis with the liquid membrane, may be effected in a sufficiently workable manner by adjusting the composition of the membrane. Moreover, this procedure does not result in the contamination of aqueous solutions with organic impurities, which is the case when we deal with the extraction processes. The latter circumstance is of major importance in the treatment of wastewaters and natural solutions.

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