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EXTRACTION OF URANILE-IONS OUT OF WATER SOLUTIONS BY THE CHLORINATED NAPHTHENIC ACIDS**S.R.Mamedova***M.Nagiev Institute of Catalysis and Inorganic Chemistry NAS of Azerbaijan**nuriyeva.1963@mail.ru*

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The extraction of the small quantities of uranile-ions out of water solutions has been studied. It is established that chlorinated naphthenic acids are effective extragents of uranium from water solutions containing great quantities of salts of alkaline metals. $pH_{1/2}$ extraction considerably shifts into acid (in the presence of chlorides) or alkaline sphere (in the presence of sulphates) depending on ammoniac composition of salts and their concentration that permits to increase choiceness of extracting uranium. Effectivity of extracting uranium is considerably improved in the presence of minimum quantities of aniline or that of other amines. High effectiveness of extraction of uranium in the presence of aniline and under relative constancy of extraction in a wide interval of acidity of water phase served as foundation for working out the method of determining small quantities of uranium chlorinated by naphthenic acids.

Keywords: *extraction, uranile-ions, organic reagents, water phase, alkaline metals.*

Extraction of uranium by the organic reagents or solvents in order to extract it out of water solutions of different composition, its separation from other elements and purification got the wide application both in technological processes and in analytical practice.

At present a great deal of well-known papers are devoted to extraction of uranium out of acidic, neutral solutions [1–5] by the alkylphosphorous acids, oxygen-containing organic solvents (ethers, ketones, aldehydes etc.), as well as by highmolecular amines [6]. That's why the old twels are taken and sent to the retirement: they are dissolved in the acid or alkali and by the method of extraction the uranium is extracted out of the solvent. The uranium easily creates extractional complexes and transfers into organic phase; the mixtures, which are necessary to escape, drop out in the water solution. The uranium is extracted from organic phase practically by the sahie methods as those while obtaining it from the ore [6, 7].

In this paper there have been presented the results of investigation on creation of the conditions for extraction of the small quantities of uranium out of strongly concentrated solutions of chlorides and sulphates, alkaline and alkaline earth elements. As an extragent for the first time there were used chlorinated naphthenic acids (CNA). These are optimum condi-

tions of extraction, concentration, separation of uranium from the number of attendant elements.

The uranium determination in the corresponding phases after their arrangement in layers has been made by the colorimetric method [8].

As an extragent there has been used 1.0 M solution of CNA (average molecular weight is 232) in kerosene.

In the separate experiments as a diluent we have taken pure hydrocarbons – heptene, benzol and tetrachloromethane.

We have studied the extraction of uranile-ions 1.0 M by the solutions of naphthenic acids (NA) and CNA in order to compare them in the identical conditions. The results have been presented in Figure 1.

As is seen in Figure 1, the extraction of uranile-ions 1.0 M by CNA solution starts at $pH=1.8$, and at $pH=4-6$ they completely transfer into organic phase. Under the same conditions the extraction of uranile-ions NA starts only when $pH=3.4$ and their optimuml extraction is observed at $pH=5.2$. It should be mentioned that in the same conditions the curve of uranile-ions extraction by NA is shifted to one unit of pH into the alkaline field. The further pH increase in the water solution leads to consequent decrease in the coefficient of distribution, the emulsion appears on the boundary of the phases, in consequence the border between the phases loses its sharpness.

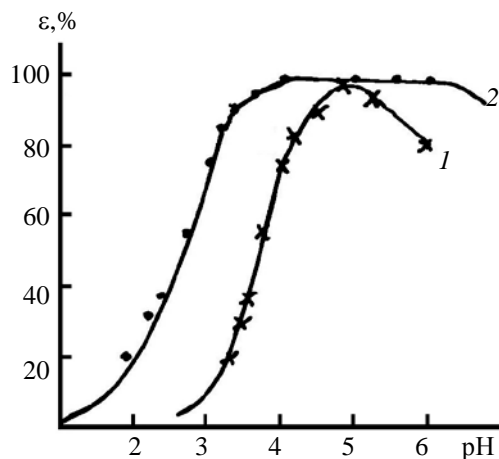


Fig.1. Dependence of uranile-ions extraction by chlorinated naphthenic acids (1) and by naphthenic acids (2) on pH sphere.

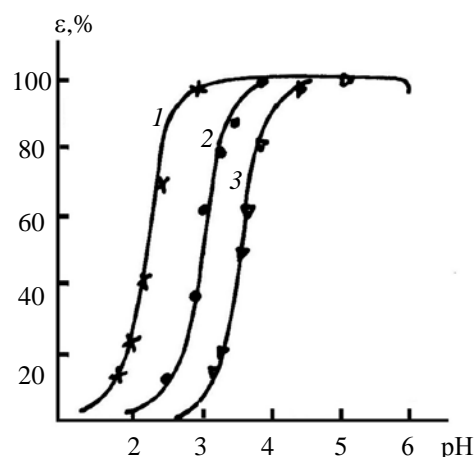


Fig.3. Dependence of uranile-ions extraction by chlorinated naphthenic acids on pH sphere in the presence of sulphate-ions: 1 - 2, 2 - 1, 3 - 0.5 N Na₂SO₄.

When $\text{pH} > 7$ the phases get shifted, besides, the created emulsion strongly blocks the division of phases, and thus reduces the coefficient of distribution. The emulsion is easily destructed while adding the minimum quantity of higher alcohols into the organic phase. The division of phases is much improved when using the solution of caustic kali, as well as the demanded significance of pH water solution is created.

The influence of (NaCl, Na₂SO₄) salts concentration on extraction of uranile-ions from the solutions of chloride and sulphuric acid sodium of different concentrations, dependent on pH is shown in Figures 2 and 3.

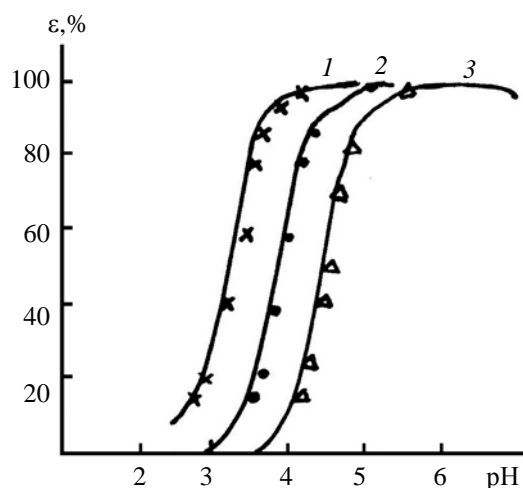


Fig.2. Dependence of uranile-ions extraction by chlorinated naphthenic acids on pH sphere in the presence of chlorine-ions: 1 - 2, 2 - 1, 3 - 0.5 N NaCl.

As it is seen (in Figure 2) while uranile-ions extraction out of such solutions, as distinct from the cases when the mentioned above salts are absent in the solution with a very little change of pH, the coefficient of distribution grows quickly, and the optimal extraction is noticeably shifted to acidic field. With the rise of chloride sodium concentration, the shifting becomes more noticeable and the optimal extraction takes place at pH of the balanced water solution < 2 . Thus, if without chloride sodium, when pH of balanced water phase is 2.8 the uranil-ions extraction is just 45%, with its presence (2, 1, and 0.5 N NaCl) at the corresponding value of water solution pH, it achieves more than 98%.

A noticeable increase of uranile-ions extraction is observed in case of existence of sulphuric-acid sodium in the water solution. Depending on the concentration of the latter in solution, the curve of the extraction as distinct from the chloric sodium solutions, is shifted to more alkaline field (Figure 3). For example, among the other equal conditions, the significance of pH in balanced water solution, where 50% of uranile-ions are extracted, compiles:

$$2.5 \leftarrow \text{NaCl} \quad 3.6 \xrightarrow{\text{Na}_2\text{SO}_4} 4.2.$$

Another important factor which influences the uranile-ions extraction is the concen-

tration of the CNA in the organic phase, because, as it is supposed, the uranile-ions are extracted from the solution in the type of the uranile-chlor naphthenate.

As it is evident in Figure 4, where dependence of uranile-ions extraction on the ratio CNA/UO_2^{2+} is displayed, the optimal extraction of uranile-ions takes place at the ratio $CNA/UO_2^{2+} > 6$. The further increase in this ratio nearly doesn't influence the rise of the distribution coefficient.

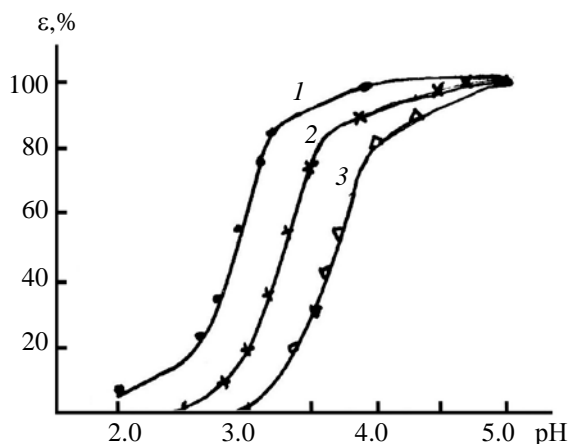
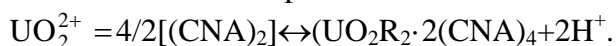


Fig.4. Dependence of uranile-ions extraction on pH sphere at the different concentrations of the chlorinated naphthenic acids: 1 – 1.0, 2 – 0.5, 3 – 0.25 M CNA.

Proceeding from this fact we can suppose that the extraction is the result of a secondary reaction between the salt (that is obtained during the interaction of uranile-ion with CAN) and free CNA. Thus, one of the basic factors, providing the effectiveness of the extractational process is a surplus quantity of the chloric naphthenic acids.

While studying the distribution of the chlorinated naphthenic acids between the different organic solvents and water, it has been found out the existance of dimer form of these acids in the inert diluters.

In accordance with it, the reaction of uranile-ions extraction by the chlorinated naphthenic acids can be expressed as follows:



In fact, the uranile-chlor naphthenate obtained by the preparative way (deposited from *n*-heptene solution) is very little dissolved in the ordinary diluters. The addition of chlor naphthenic acids into the organic solvent leads to the sharp increase in solubility of chlor naphthenate uranile. Apparently, such scheme of creation the soluble salt is typical for the most of naphthenates (UO_2^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Fe^{2+} etc.) the solubility of which after deposition from the organic phase by the corresponding precipitators is sharply reduced.

There also have been carried out the experiments on extraction of the uranium by the chlor naphthenic acids in the presence of aniline and other low-molecular amines. Besides, the equilibrium is established at once, the phases are separated exactly, and in the wide interval of pH in water phase the coefficient of distribution sharply rises, achieving 10^4 – 10^5 .

Such a high effectiveness of extraction in the presence of aniline at the relative constancy of these data in the wide interval of the water phase acidity permits us to suppose the creation of a new extracted product – aminate complex of uranile, that is interacting with the chlorinated naphthenic acids and its transfer into the organic phase.

The additional information about the character and composition of the product extracted in the indicated conditions has been obtained with the heft of spectrum of absorbing the extracts which were taken at spectrophotometer SPh-5 in the field of 350–560 $m\mu$ (Figure 5).

The taken spectrum has been compared with the spectrum of absorption of the nitric acid uranile in the water solution. The stripes of absorption, typical for uranile in extractions have been shifted on 10–12 $m\mu$ to the longwaving field.

As for extraction obtained in the presence of aniline, there aren't any typical stripes in the visible part, and the swamped maximum is strongly shifted to a more hot wiring field.

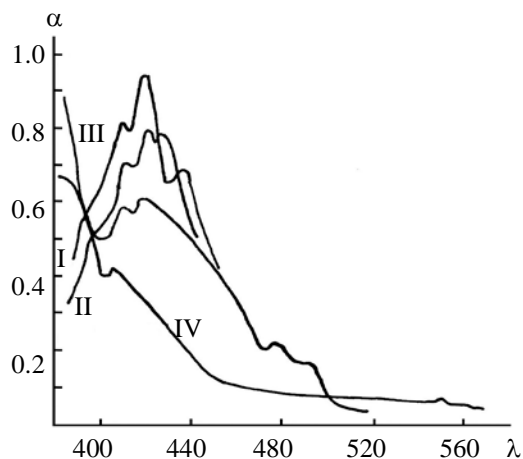


Fig.5. Spectrum of absorption of the aminate complex of uranile chlornaphthenate: I – water solution $UO_2(NO_3)_2$, II – solution of uranile chlornaphthenate in kerosene, III – solution of uranile chlornaphthenate in benzol, IV – aminate complex of uranile chlornaphthenate.

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ЭКСТРАКЦИЯ УРАНИЛ-ИОНОВ ИЗ ВОДНЫХ РАСТВОРОВ ХЛОРИРОВАННЫМИ НАФТЕНОВЫМИ КИСЛОТАМИ

С.Р.Мамедова

Изучено экстракционное извлечение небольших количеств уранил-ионов из водных растворов. Установлено, что хлорированные нафтенновые кислоты являются эффективными экстрагентами урана из водных растворов, содержащих большие количества солей щелочных металлов; $pH_{1/2}$ экстракции в зависимости от анионного состава солей и их концентрации значительно смещается в кислую (в присутствии хлоридов) или щелочную (в присутствии сульфатов) области, что позволяет повысить избирательность экстракции уранил-ионов. Эффективность экстракции уранил-ионов значительно улучшается в присутствии в органической фазе минимальных количеств анилина или других низших аминов. Высокая эффективность экстракции уранил-ионов в присутствии анилина при относительно постоянстве извлечения в широком интервале кислотности водной фазы послужила основанием для разработки метода определения малых количеств урана хлорированными нафтенновыми кислотами.

Ключевые слова: экстракция, уранил-ионы, органические реагенты, водная фаза, щелочные металлы.

URANİL-İONLARININ SULU MƏHLULLARDAN XLORLAŞDIRILMIŞ NAFTEN TURŞULARI İLƏ EKSTRAKSİYASI

S.R.Məmmədova

Az miqdarda olan uranil-ionların sulu məhlullardan ekstraksiya yolu ilə çıxarılması öyrənilmişdir. Müəyyən edilmişdir ki, xlorlaşdırılmış naften turşuları sulu məhlullardan uranın çıxarılması üçün effektiv ekstragentdir. Qələvi metal duzlarının iştirakında uranil-ionlarının ekstraksiyası, götürülmüş duzun anion tərkibindən və onların qatılığından asılılığı öyrənilmişdir. $pH_{1/2}$ az miqdarda turşu və ya qələvi mühitə yerini dəyişir, bu da uranil-ionlarının seçici olaraq ekstraksiyasına imkan verir. Üzvi fazaya az miqdarda kiçik molekullu amin əlavə edilməsi uranın ekstraksiyasının az miqdarda yaxşılaşdırır. Lakin uranil-ionlarının ekstraksiyasının yüksək effektivliyi anilin iştirakında olur. Su fazasının turşuluğunun nisbətən geniş intervalda xlorlaşdırılmış naften turşuları ilə uranil-ionlarının çıxarılması imkan verir ki, uranın məhlullarda az miqdarını təyin metodikası işlənib hazırlansın.

Açar sözlər: ekstraksiya, uranil-ionları, üzvi reagentlər, su fazası, qələvi metallar.