THE ADSORPTION OF URANYL-IONS ON ION EXCHANGERS

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It is well-known, that the affinity of the uranyl ions to the sulphate ions is great, they form uranyl-sulphate and by SO_4^{--} excess, complex anions together, therefore it is possible to bind uranyl ions from sulphuric acid solutions on anion exchangers.

Possibly, in the solutions there exists the following equilibrium [1]:

$$UO_2^{2+} + n \cdot SO_4^{2-} \rightleftharpoons UO_2SO_4 + (n-1)\, SO_4^{2-} \rightleftharpoons UO_2(SO_4)_n^{2-2n}$$

Besides the ions and salts here mentioned, there are hydrosulphate ions present too. The value of n may be 2 or 3.

By our experiments we wanted to solve the following questions:

1. What is the effect of the composition of the solution on the binding of uranyl-ions on anion exchangers, and

2. how may this behaviour be influenced by the choice of the most successful exchanger-type.

For our investigations we used strongly basic anion exchangers, which hold on polystyrene-divinylbenzene co-polymerizate network only one type of ammonium-group.

The investigated exchangers were:

1. Dowex 1. (Dow Chemical Co). Active group:

$$R-N^+(CH_3)_3-Cl^-$$

2. Dowex 2. (Dow Chemical Co). Active group:

$$R-N^+(CH_3)_3CH_2CH_2OH-Cl^-$$

3. Mykion PA (Research Institute for Plastic Materials, Budapest). Active group the same as 2.

4. Ethyl-exchanger (Research Institute for Plastic Materials, Budapest) Active group:

$$R-N^+(C_2H_5)_2-CH_2CH_2OH-Cl^-$$

The four exchangers showed in $OH^- - SO_4^{--}$ exchange approximately of the same capacity.

We performed the investigations also with porous Mykion PA. For increasing the porosity, instead of the well-known method of modifying the divinylbenzene-styrene ratio of the resin, we used "diluted polymerization" (J. MIKES' report on the macromolecular symposion of IUPAC, Praha, 8—15. Sept. 1957). This method gives a greater porosity by using great cross-linking component content; the exchanger has a greater mechanical resistance, therefore, it withstands the mechanical requirements of exchange and regeneration.

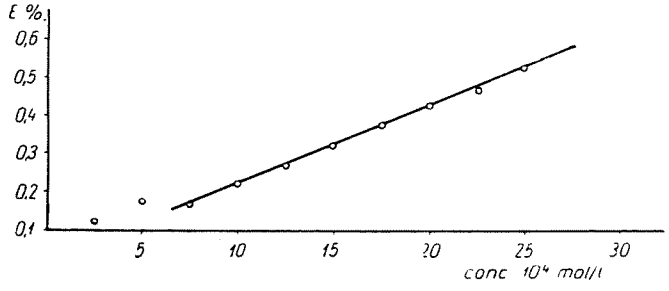

Fig. 1

For the control of measurements we had to look for suitable uran-analysis. The known methods were not suitable for series investigations because they require too much time, and in the presence of SO_4^{--}-ions the solutions changed their colour by standing, and so we could not use photometric methods.

The substance of the used method is the following:

A suitably diluted sample of a well-selected quantity of H_2O_2 and NaOH was held for one hour between 80 and 85° C, then, after 12—18 hours standing the solution is determined with Pulfrich Photometer, filter S—47 (465 mμ). The calibration curve is shown in Fig. 1. By the courtesy of the Central Chemical Research Institute made it possible for us to perform the measurements with an C$\varnothing$—4 spectrophotometer (made in USSR). We determined the readings at 413 mμ wavelength (Fig. 2). The method is applicable in $7 \cdot 10^{-4}$—$30 \cdot 10^{-4}$ mol/l concentration-range; by application of the spectrophotometer the fault of the method is $\pm$ 0,6%. The control-measurements were performed by the Bacon and Milner method [2].

We experimented with the radioactive measurement method too, but in connection with ion exchange it was not applicable.

The concentration of our solutions was $5 \cdot 10^{-3}$ mol/l for uranyl-ion, because ion exchange is used for uran-binding in this concentration-range.

We know from the literature that with strongly basic anion-exchangers tenfold increase in concentration is obtained [3].

The results of our measurements are the following :

The results of the dynamic, performed with column-method measurements are shown in Fig. 3. The ratio length/diameter is 10 : 1. The resins used were : Dowex 1, Mykion PA and ethyl-exchanger. Rate of flow : 0,85 ml/g min.

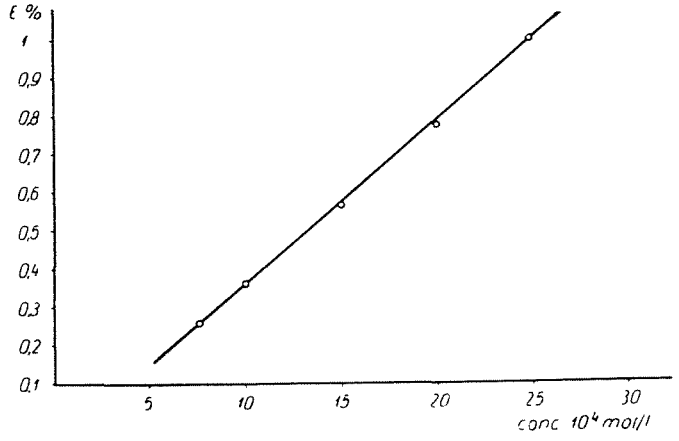

Fig. 2

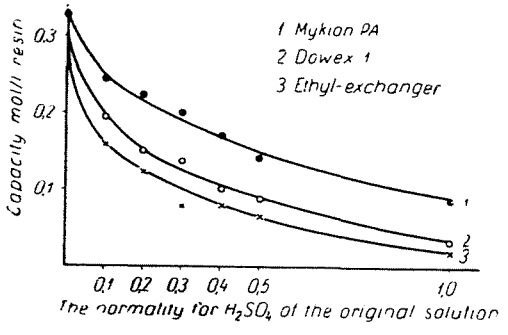

Fig. 3

In a column with the same capacity, rate of flow and granular size with Dowex 1 we obtained a ninefold increase, on the column filled with Mykion PA a thirteenfold increase in concentration. The capacity of the columns were 1,6 mmol for uranyl-ion. The results of the measurements are shown in Fig. 4.

With the column filled with Mykion PA one can work with the same rate of flow in adsorption and elution, but with the column filled with Dowex 1

one has to work in elution with a slower rate of flow to obtain the mentioned tenfold increase in concentration.

By Mykion PA the break-through capacity is a much greater part of the full capacity than by Dowex 1.

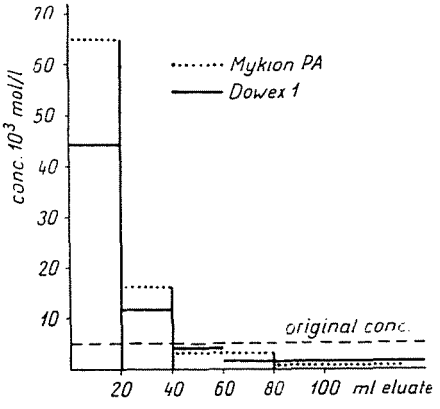

Fig. 4

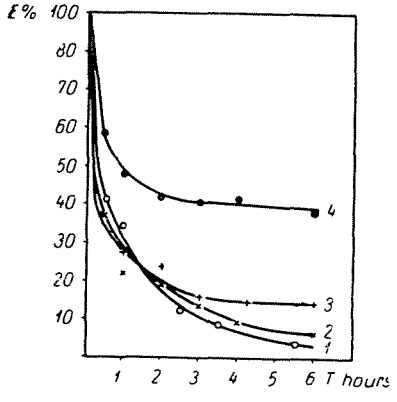

Fig. 5

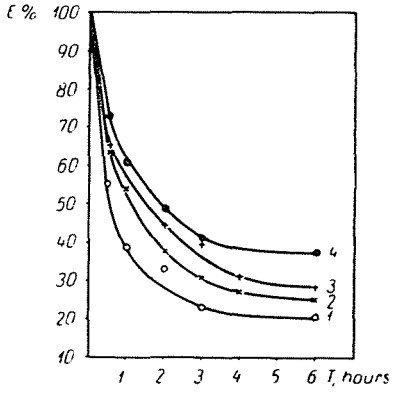

Fig. 6

The capacity of the ethyl-resin was so small for UO_2^{++}, that static measurements were not made.

Performing measurements in static system, we came to the following results :

Figures 5, 6, 7 and 8.

On the figures we plotted the extinction of the solution remaining after adsorption in the percentage of the original extinction against time of contact (hours).

From the results of the measurements we can ascertain that in dilute solutions the rate and quantity of uran-adsorption decrease with decreasing pH. We suppose that the reason for this is 1. the larger quantity SO_4^{--} and HSO_4^- adsorbed and 2. by lowering the pH the quantity of $U_2O_5(SO_4)_3^{4-}$ increases and the diffusion of this ions in the resin phase is slower than that of the $UO_2(SO_4)_3^{4-}$ and $UO_2(SO_4)_2^{2-}$ ions.

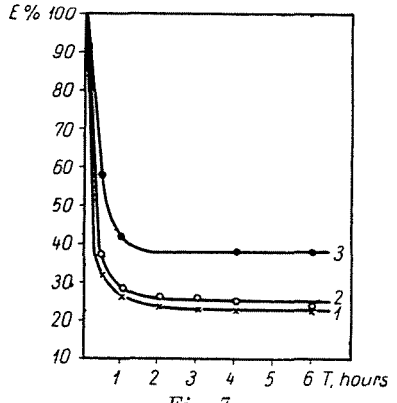

Fig. 7

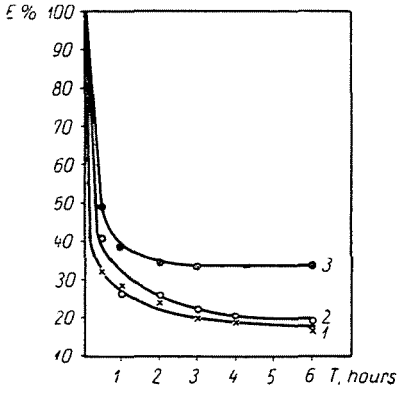

Fig. 8

The rate of adsorption is the greatest, if we use porous Mykion PA resin and the solution contains no sulfuric acid. From this result we suppose that the rate determining step is the diffusion of the ions in the resin-phase. In less porous resins we attained the equilibrium slower, because the diffusion of the ions in the resin phase was delayed by the diminished porosity, while the supply was rapid and the binding of the ions was supposed to be momentary.

The above experiences established that under laboratory conditions the Mykion PA porous anion exchanger seems to be the most suitable for binding uranyl-ions from sulphuric-acid solutions.

We are grateful for the co-operation to *G. Fássy* laboratory assistant.

Summary

We compared Dowex 1 and Dowex 2 ion exchangers used in the western countries for uran-binding with strongly basic anion exchangers produced in the laboratories of the Research Institute for Plastic Materials, Budapest. We came to the conclusion that under laboratory conditions the porous Mykion PA strongly basic exchanger was to be held as the most suitable for binding uranyl-ions from sulfuric acid solutions. The velocity-determining step is the diffusion of the ions in the exchanger phase.

References

1. KUNIN—PREUSS: Ion Exchange in the Atomic Energy Program. Ind. and Eng. Chem 1956. VIII.
2. BACON—MILNER: The Determination of Uranium by High Precision Spectrophotometry. The Analyst **81**, 456 (1956).
3. A-Ore on the Plateau. C and Eng. June, 1956.

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