

CHARACTERIZATION OF URANIUM(VI) SPECIES IN SEAWATER

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Summary

Uranyl complexes were characterized in artificial seawater and model solutions in dependence of the medium's pH. Results were compared with theoretically derived distribution curves. Agreement of our experiments and the theoretical speciation of uranium(VI) in seawater was satisfactory.

Resume

Les complexes uranyl ont été caractérisés dans l'eau de mer artificielle et dans les solutions modèles en dépendance du pH du medium. Les résultats obtenus ont été comparés aux courbes de distribution dérivées théoriquement. On a trouvé un accord satisfaisant de nos expériences et de la spéciation théorique de l'uranium(VI) dans l'eau de mer.

Increasing energy demands and the large quantity of uranium available in seawater brought its recovery from the ocean into the focus of interest (1). The evaluation of possible recovery techniques requires the knowledge both of the concentration and the physico-chemical state of uranium in seawater. However, in spite of extensive literature on the subject, the ionic uranium species in seawater have, as yet, not been unambiguously experimentally determined. The majority of the uranium species distributions published so far, were obtained on the basis of carbonate and hydroxo complexation constants derived from thermodynamic data (2).

The distribution of ionic uranium species in artificial seawater (3) and acidic, neutral and weakly alkaline model solutions was investigated using sensitive electrochemical (sampled d.c. and differential pulse polarography) and spectrophotometric methods.

Polarographic measurements in model solutions enabled us to follow the gradual coordination of the hydrated uranyl ion with carbonate ligands.

Logarithmic analyses of uranyl reduction waves in media of pH 5 have shown the process to be a single electron reversible reduction. Increasing the pH causes the process to become quasi-reversible and beyond pH 7 the reduction is completely irreversible (4). From pH 5 onwards the process displays a kinetic character caused by the

establishing of a homogeneous equilibrium in the bulk of the solution which precedes the electrode reaction (equilibrium between uranyl tricarbonate and bicarbonate forms). Beyond the pH value of 5.5 the reaction is strongly influenced by the formation of the uranyl tricarbonate complex.

Judging by the dependence of the $E_{1/2}$ displacement on the free carbonate concentration, we came to the conclusion that the predominating uranium(VI) forms are the following: $UO_2CO_3^0$ from pH 4 - 4.5; $UO_2(CO_3)_2^{2-}$ in the pH range 4.5 - 5.0 and $UO_2(CO_3)_3^{4-}$ in more alkaline surroundings. At pH 8 uranyl hydroxo complexes start to form.

Polarographic results were compared with the theoretical pH dependent distribution curves, which were constructed on the basis of published stability constants, and the Pytkowicz model of seawater (5).

Spectrophotometric measurements confirmed our concept of uranium(VI) species distribution.

As our experiments were done in solutions very closely approaching the composition of seawater, we believe that the above mentioned distribution would also be valid in a natural marine environment. Moreover, various extraction procedures for uranium from seawater may involve a change in local pH conditions, so that our distribution over a comparatively broad pH range may help to explain the fate of different uranium species under such circumstances.

References

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Djogić, R., Sipos, L., Branica, M.

"Characterization of uranium (VI) species in seawater"

Paper presented by R. Djogić (Yugoslavia)

Discussion

- V. Žutić: a) What is the equilibrium distribution of U(VI) at the pH of real seawater?

b) Using electroanalytical techniques it is possible to obtain not only the equilibrium distribution of species but also their reactivity (kinetic properties).

Is it justified to conclude that $\text{UO}_2(\text{CO}_3)_3^{4-}$ is also in seawater a relatively inert complex and $\text{UO}_2(\text{OH})_3^-$ a very mobile species?

R. Djogić:

a) On the basis of the program developed (based on published stability constants) at pH-8 and a concentration of $\text{U} = 10^{-8} \text{ mol l}^{-1}$ the equilibrium distribution of U species in the seawater is:

87.16%	$\text{UO}_2(\text{CO}_3)_3^{4-}$
0.83%	$\text{UO}_2(\text{CO}_3)_2^{2-}$
11.88%	$\text{UO}_2(\text{OH})_3^-$

b) On our d.c. polarographic curves we were not able to detect the $\text{UO}(\text{OH})_3^-$ reduction process, but on differential pulse polarograms we found the reduction wave which might be of the $\text{UO}_2(\text{OH})_3^-$ species showing a kinetic character, as a labile species.

P. Valenta:

From your $E_{1/2}$ dependence v.s. concentration of CO_3^{2-} you have deduced the existence of two equilibria of U(VI) with one and two carbonate ligands respectively just from 4 points. It is rather uncertain to use the "slope approach" for this. Why did you not use the De Ford-Hume approach?

R. Djogić:

In our diagram showing $E_{1/2}$ dependence, vs. pH we represented only 4 points. We however deduced the existence of two equilibria of U(VI) on the basis of a greater number of experimental points. The De Ford-Hume approach could not be applied because the reduction product forms of uranyl-complexes with our experimental conditions do not form an amalgam.

