

DISSERTATIONES

DCC-17 (Univ. Zagreb)

545.44:547.449.04

Croat. Chem. Acta 37 (1965)**Determination of the Stability Constants of Metal Complexes in Aqueous Solutions. Polarographic Determination of Iron(III), Copper(II) and Uranium(VI) Acetylacetonates**

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The characteristics of polarographic reduction of iron(III), copper(II) and uranium(VI) in aqueous solutions of various concentrations of acetylacetonate, at pH 1 to 7 in a perchlorate medium of a constant ionic strength were investigated.

In the case of iron(III) two separate polarographic steps were obtained, the first caused by the reduction of the bisacetylacetonato complex, and the second by the trisacetylacetonato complex. It was found that the diffusion current of each step was proportional to the equilibrium concentration of the corresponding complex species. The stability constants were calculated from the step heights.

The stability constants of copper(II) acetylacetonates were calculated by two different methods: 1. The shift of the half-wave potential and 2. the a.c. peak heights as functions of the free ligand concentration. The evaluation of the stability constants from the a.c. peak current was possible due to the specific polarographic sensitivity of different copper(II) complex species.

Comparing the results obtained by the mentioned methods it was possible to obtain the stability constants even for an irreversible process.

It was found that the reversibility of the polarographic reduction of uranium(VI) was strongly influenced by the acidity of the solutions i.e. by the free ligand concentration.

The ratio of the stability constants of uranium(VI) and uranium(V) bisacetylacetonato complexes was calculated from the shift of the half-wave potential. The stability constants were calculated from the experimental results: iron(III): $\log K_2 = 8.45$; $\log K_3 = 6.44$; $\log K_2K_3 = 14.95$; copper(II): $\log K_1 = 3.8$; $\log K_2 = 6.9$; $\log \beta_2 = 15.7$; uranium(V): $\log \beta_2 = 8.6$.

Owing to rather different a.c. polarographic sensitivities for uranium(VI) and copper(II) the optimum conditions for quantitative determination of traces of copper in the presence of uranium were found.

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Examiners: Professor B. Težak, Professor I. Filipović, Dr. M. Branica. Oral examination: November 7, 1964; Ph. D. degree conferred: February 13, 1965.

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1. Determination of the Stability Constants of Metal Complexes in Aqueous Solutions. Polarographic Determination of Iron(III), Copper(II) and Uranium(VI) Acetylacetonates

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Complexes
Copper determination in uranium compounds
2,4-Pentanedione, complexes with copper, iron and uranium
Polarography a.c. and d.c.
Stability constants

DCC-18 (Univ. Zagreb)

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Croat. Chem. Acta 37 (1965)**Application of Radionuclides in the Investigations of Physico-Chemical Properties of »Solid-Liquid« Systems**

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Process of heterogeneous exchange on the model systems $\text{AgI} - \text{Ag}^+$ (^{110}Ag) and $\text{AgI} - \text{I}^-$ (^{131}I) has been investigated by the radiometric analysis of distribution of radionuclides ^{110}Ag and ^{131}I in the solid and liquid phase respectively. The influence of the age of the precipitate of AgI particle, of the valency of coagulation ions, of concentration of Ag^+ and I^- ions and of concentration of surface active substance on the heterogeneous exchange process has been analysed.

The obtained data show that the selfdiffusion of the Ag^+ ions in the particles of the AgI precipitate at $p\text{Ag} = 2$ and 3 is responsible for the mechanism of the exchange process of $\text{AgI} - \text{Ag}^+$. From the value of the diffusion coefficient for Ag^+ in the solid AgI it follows that the particles of the precipitate are at these conditions of the cubic structure. It has been found that either the concentration of the coagulation ion and of surface active agent or the valency of the counter ion does not influence either the transformations of the solid phase or the process of heterogeneous exchange.

The investigations on the $\text{AgI} - \text{I}^-$ systems show that the recrystallization is the most probable mechanism determining the heterogeneous exchange process.

It has been found that the process of heterogeneous exchange depends upon the valency of the coagulation ion present, upon the concentration of potential determining coagulation ion, upon the concentration of the surface active agent as well as on the age of the precipitate. AgI was formed by precipitation *in statu nascendi*.

In the systems with dried isoelectric AgI precipitate the exchange process depends on the composition of the liquid phase. In the excess of Ag^+ ions the exchange process is similar to that on the $\text{AgI} - \text{Ag}^+$ systems and in the excess of I^- ions to that on the $\text{AgI} - \text{I}^-$ systems (*in statu nascendi*).

The influences of the investigated parameters upon the kinetics of the heterogeneous exchange process enable the selection of the most economical conditions for anefficient and selective fixation of radionuclides from aqueous solutions.

By radiometric analysis the values for complex solubility of AgI in NaI ($c_{\text{NaI}} = 0.0100 \text{ M}$ to 1.000 M) in the presence of $\text{Co}(\text{NO}_3)_2$ and $\text{Al}(\text{NO}_3)_3$ at 20°C were determined.

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Examiners: Professor B. Težak, Dr. R. Wolf, Dr. C. Đorđević.

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R. DESPOTOVIĆ

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1. The Application of Radionuclides in the Investigations of Physico- Chemical Properties of »Solid-Liquid« Systems

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Exchange processes
Heterogeneous exchange
Precipitates
Radionuclide Application
Systems »Solid-Liquid«

MCC-11

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Master of Science Thesis

Croat. Chem. Acta 37 (1965)

**Investigation of the Electrochemical Reduction of Uranium(VI)
in Carbonate Solutions by Galvanostatic Method**

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Electrochemical reduction of uranium(VI) in 1M sodium carbonate-bicarbonate as supporting electrolyte and in pH range 8.4–12.0 was investigated by chronopotentiometry. It was found that the electrochemical reduction of uranium(VI) to uranium(V) is highly dependent on the free carbonate concentration. At high free carbonate concentration (pH = 12.0) uranium(VI) was reduced to uranium(V). The process of electrochemical reduction is irreversible ($\alpha_n = 0.95$) and controlled by diffusion only. Diffusion coefficient of uranium(VI) calculated from Sand's equation was obtained $D_{25^\circ\text{C}} = (4.35 \pm 0.43) \times 10^{-6}$ (cm²sec⁻¹).

The influence of the disproportionation reaction of the electrochemically generated uranium(V) on reduction of uranium(VI) was observed at low free carbonate concentration (pH = 8.4) only. The disproportionation reaction could be roughly written as:

$2\text{U(V)} \xrightleftharpoons[k]{k} \text{U(IV)} + \text{U(VI)}$. The corresponding overall disproportionation rate constant was calculated as $k^* = 47 \times 10^{-3}$ (Msec⁻¹) using the rate law $-\text{dU(V)}/\text{dt} = k[\text{U(V)}]^2[\text{CO}_3^{2-}]^{-2}$.

Examiners: Professor B. Lovreček, Dr. M. Branica, Dr. M. Herak.
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1. Investigation of the Electrochemical reduction of Uranium(VI) in Carbonate Solutions by Galvanostatic Method

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Carbonate Solutions
Chronopotentiometry
Disproportionation
Electrochemical Reduction
Uranium(VI)