CCA-306

543.253:546.791.6:547.442.3:661.185
Original Scientific Paper

Square Wave Polarography of Uranium(VI). II. Influence of Surface Active Agents

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Received April 12, 1963

The influence of surface active agents on the square wave polarographic behaviour of uranyl acetylacetone was investigated. Tritone-X-100 decreases specifically the S.W. peak height of each uranyl-acetylacetonato species, *i.e.* the adsorption layer is specifically penetrable by each one. From this specific depression the over-all stability constant of uranyl acetylacetonato complexes, in 1 *M* sodium perchlorate, was calculated as log $\beta_2 = 12.5$. This is in agreement with earlier obtained results[3]. Electrocapillary curves for T-X-100 and acetylacetone are also presented.

INTRODUCTION

The addition of small quantities of surface active agents in solution exerts a marked influence on the electrochemical processes at the mercury drop, ranging from suppressing polarographic maxima, shifting of the half-wave potential, decreasing the limiting current, causing the appearance of minima, splitting of a wave down to complete elimination. The precise reasons for these effects are not fully understood. Schmid and Reilley[1] described different types of adsorption of surface active agents (SAA) on the mercury drop by forming an adsorption film in the boundary between two phases. Kolthoff and Okinaka[2] described the »penetration current« through such adsorbed film of SAA in accordance with Frumkin's theory.

In an earlier paper[3] it was shown that higher concentrations of acetylacetone have a remarkable specific effect on the uranyl S.W. peak height, depending on the ionic state of the uranyl ion in aqueous solution. It is likely that this effect is due to an adsorption of acetylacetone molecules forming an adsorption layer on the mercury surface.

If this assumption is valid lower concentrations of SAA should have the same effect on the uranyl S.W. peak height as acetylacetone has in higher concentrations. To explain the possible mechanism of this effect, the influence of Triton-X-100 and Thymol on the uranyl S.W. peak height has been considered. The possibility of applying such an adsorption »sieve« of SAA on the surface of the mercury drop for the determination of stability constants of uranyl acetylacetonato-complexes in aqueous solution has been studied.

EXPERIMENTAL

Polarographic measurements were made using Barker's Mervyn-Harwell Square Wave Polarograph Mark III. Electrocapillary curves were obtained by Radiometer Polariter type PO4d. *p*H was measured with a glass and a calomel electrode and a Radiometer *p*H Meter Type PHM4. Solutions of Thymol (recrystallized »Merck«) and Triton-X-100 (»Röhm & Haas«) were prepared by dilution with quadruply distilled water. All preparations of stock solutions and techniques of measurement were the same as described in the previous paper[3].

RESULTS AND DISCUSSION

The dependence of uranyl S.W. peak height on the concentration of Thymol $[(CH_3)(C_3H_7)\ C_6H_3OH]$ and Triton-X-100(T-X-100) $[C_8H_{17}(C_6H_4)(OCH_2CH_2)_{9-10}OH]$ is shown in Fig. 1. With the increase in SAA concentration the uranyl S.W. peak height diminishes. The observed effect is the same as in the case of increasing acetylacetone concentrations for solutions where the UO_2^{++} and $UO_2Acac_2^0$ species are predominant[3]. Lower concentrations of T-X-100 are required to produce the same effect as with tymol. The influence of T-X-100 on the uranyl S.W. peak height in dependence on the free ligand concentration (*p*H of the solution) was further investigated. In this way numerous experimental curves were obtained, and from each curve only the »critical« point of the T-X-100 concentration was considered. As the »critical« point of the T-X-100 concentration the point of 50% depression of the original uranyl S.W. peak height was taken. However, the irregular shape of depression curves obtained by using thymol gave no reproducible »critical« points. At a given concentration T-X-100 shows different effects upon the S.W. peak height for the free uranyl ion (UO_2^{++}), the uranyl mono-acetylacetonato (UO_2Acac^+) and uranyl bis-acetylacetonato ($UO_2Acac_2^0$) complexes.

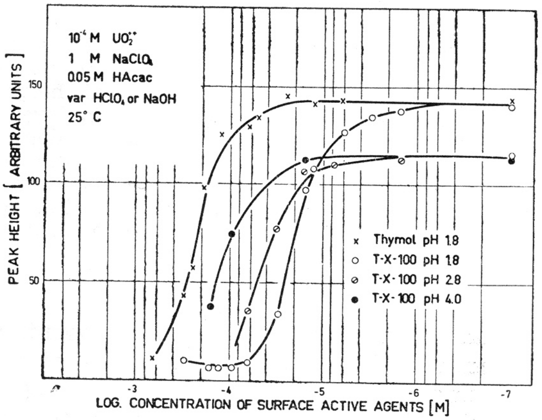

Fig. 1. Square Wave peak height (at 1/32 maximum sensitivity) against log. concentration of SAA, *i.e.* T-X-100 and thymol[M] of solutions: $10^{-4}M$ $UO_2(NO_3)_2$, 1 M $NaClO_4$, 0.05 *M* acetylacetone, pH varied by adding NaOH or $HClO_4$.

Fig. 2 represents the »critical« points of the T-X-100 concentrations against the logarithm of the concentration of free acetylacetone ions (*p*H + log [HAcac]). Obtained results are represented by two straight lines with the intersection point at pH_{max} + log [HAcac] = 2.7. This result is in agreement with published data[3] on the influence of acetylacetone concentration on the uranyl S.W. peak height. The value pH_{max} + log (HAcac) = 2.7 indicates the point in which the

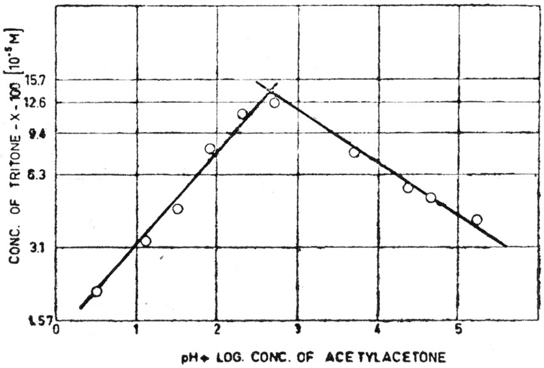

Fig. 2. »Critical« point of T-X-100 concentration which diminishes uranyl S.W. peak height to 50% of the original value against pH + log [HAcac]. Composition of solutions: $10^{-4}M$ $UO_2(NO_3)_2$, 1 M $NaClO_4$, 0.05 M acetylacetone, pH adjusted by adding NaOH or $HClO_4$, and various concentrations of T-X-100

UO_2Acac^+ species is at the maximum concentration. The concentrations of UO_2^{++} and $UO_2Acac_2^0$ are equal at the same point.

From the equation:

$$\log \beta_2 = \log K_1 \cdot K_2 = 2pK_A - 2(pH_{max} + \log [HAcac]) \qquad (1)$$

(using as the average value of the dissociation constant of acetylacetone $pK_a = 8.95$[4]) and from the experimental results one obtains:

$$\log \beta_2 = 2\,(8.95 - 2.7) = 12.5$$

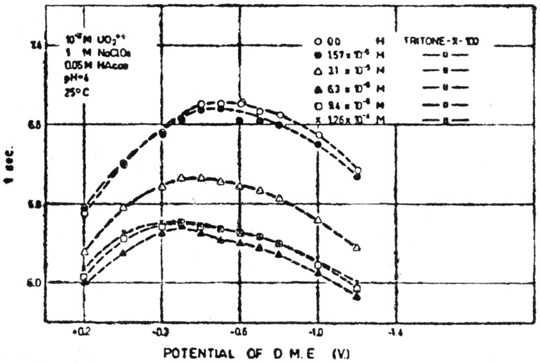

Fig. 3. Drop time [Sec] of the dropping mercury electrode, at H = 50 cm, against potential [V] $vs.$ S.C.E. in solutions of: $10^{-4}M$ $UO_2(NO_3)_2$, 1 M $NaClO_4$, 0.05 M acetylacetone, pH = 4.0, and various concentrations of T-X-100.

The result for the overall stability constant, log β_2, is the same as obtained earlier[3] from the specific influence of acetylacetone.

This effect is probably due to specific transport conditions for various uranyl species through the adsorption layer of SAA on the mercury drop. This mechanism was tested by investigating the dependence of the adsorption on the SAA concentration and on the acetylacetone concentration. The electrocapillary curves obtained for various concentrations of T-X-100 are shown in Fig. 3, and those for different concentrations of acetylacetone in Fig. 4. With the increase of concentration the drop time of D.M.E. decreases, *i.e.* the adsorption of T-X-100 and acetylacetone at the mercury drop occurs. Adsoption of T-X-100 and acetylacetone on the mercury surface begins at the concentration of 10^{-5} *M* T-X-100 or 0.1 *M* acetylacetone, respectively. This is the same concentration range in which the diminishing effect on the uranyl S.W. peak height begins. The results for the decrease of the uranyl S.W. peak height with increasing acetylacetone[3] and T-X-100 concentration (Fig. 1) show that this effect is due to the formation of an adsorbed film of acetylacetone or T-X-100 molecules on mercury surface. The adsorption layer of acetylacetone and T-X-100 is specifically penetrable for different ionic specia: the free uranyl ion (UO_2^{++}), the uranyl mono-acetylacetonato (UO_2Acac^+) and the uranyl bis-acetylacetonato ($UO_2Acac_2^0$) complexes.

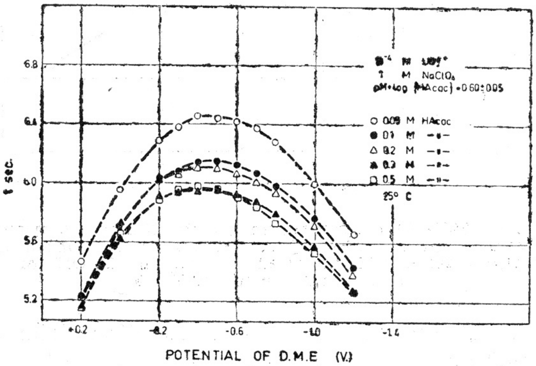

Fig. 4. **Drop time of the dropping mercury electrode against potential [V]** *vs.* **S.C.E. in** solutions of: 10^{-4} *M* $UO_2(NO_3)_2$ 1 *M* $NaClO_4$, *p*H + log [HAcac] = 0.60 + 0.05, (*p*H adjusted by **adding $HClO_4$), and** various concentrations of acetylacetone.

In the course of our further investigation the possibility of a general application of this sort of specific penetration for different ionic specia through the SAA adsorption layer for stability constant determination of different metal complexes were examined. Making use of maximum sensitivity of the S.W. polarograph the ionic state of metallic ions in concentrations lower than 10^{-5}*M* may be determined by the proposed method.

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IZVOD

Pravokutno-valna polarografija urana(VI). II. Utjecaj površinsko aktivnih tvari

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Ispitivane su karakteristike pravokutno-valnih polarograma uranil-acetilacetonato-kompleksa u vodi uz prisutnost površinsko aktivnih supstanci (PAS). Kao PAS bili su ispitivani T-X-100, timol i acetilaceton. Prikazane elektrokapilarne krivulje za triton-X-100 i acetilaceton pokazuju da nastaje adsorpcija ovih supstanci na živinoj kapi, kod istih koncentracija kod kojih nastaje i njihovo djelovanje na pravokutno valni polarogram uranil-iona. Triton-X-100 stvara adsorpcioni sloj na površini živine kapi koji je specifično propustan, kao i acetilaceton, za pojedine uranil-acetilacetonato-vrste u otopini. Utjecaj tritona-X-100 na smanjenje pravokutno-valne polarografske stepenice je veći za otopine koje sadrže pretežno slobodne uranil (UO_2^{++}) i uranil bis-acetilacetonato ($UO_2Acac_2^0$) vrste nego na otopine koje sadrže uranil mono-acetilacetonato (UO_2Acac^+) vrstu. Na osnovu ovako različitog ponašanja određena je konstanta stabiliteta uranil-acetilacetonato-kompleksa u otopinama $1\,M$ $NaClO_4$: $\log \beta_2 = 12.5$. Ova vrijednost se dobro slaže sa objavljenim rezultatom[3].

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ZAGREB

Primljeno 12. travnja 1963.