THEORY OF METAL IONS ACCUMULATION BY THE SYNERGISTIC ADSORPTION AT MERCURY ELECTRODES

Marina MLAKAR[a], Milivoj LOVRIĆ[a] and Marko BRANICA[b]

[a] *Center for Marine Research Zagreb,*
"Rudjer Bošković" Institute, POB 1016, Zagreb 41001, Yugoslavia and
[b] *Center for Marine Research Zagreb,*
"Rudjer Bošković" Institute, Zagreb 41001, Yugoslavia and
Institute of Applied Physical Chemistry,
Nuclear Research Center, POB 1913, D-5170 Jülich, F.R.G.

Received January 10, 1989
Accepted May 4, 1989

The synergistic adsorptive accumulation of metal ions at the surface of mercury electrodes is described. The basic thermodynamic relationships between the ionic species involved in the synergistic adsorption are developed and analysed. The method is compared with the simple anion-induced adsorption. The synergistic adsorption of uranyl ions in the system salicylic acid–tributylphosphate is reported.

The phenomenon of anion-induced adsorption of metal ions at a mercury electrode surface has been recognized long ago[1–3]. It appears in the presence of compounds which are surface active and form complexes with metal cations. Many organic ligands form thermodynamically very stable complexes with metal ions and induce their strong adsorption[4–15]. The adsorptive accumulation can be applied as a preconcentration step of electroanalytical methods for the quantitative determination of metal ions in traces. It is especially valuable in the cases when the amalgam formation cannot be used for the preconcentration[4,5,7,9,10,12–15]. The accumulation may be combined with different voltammetric stripping techniques, such as linear scan[4,5,9,13,15], alternating current[4], pulse[8,11,14], differential pulse[7,10,12] and square-wave voltammetry[13].

Recently, an alternative method, named synergistic adsorptive accumulation, has been proposed[14,15]. It was applied to the concentration measurements of uranyl in seawater samples. The method is based on principles of synergistic solvent extractions. The phenomenon of synergism is described as the manyfold enhancement of the metal ion extraction from the aqueous phase to the organic phase by the system of two ligands forming hydrophobic complex species[16–25]. The first ligand forms an uncharged chelate complex with the metal ion. The complex is partially hydrated and moderately hydrophilic. The other ligand is hydrophobic and reacts with the complex ML_1 substituting all, or almost all water molecules from the coordinative sphere of the metal ion. The mixed complex ML_1L_2 is hydrophobic and get extracted in the organic phase. The hydrophobic surface of the mercury drop electrode may serve as a good replacement for the organic phase. If it is covered by the adsorbed monolayer of the hydrophobic, neutral ligand, and if the chelating ligand is added to the electrolyte, the mixed metal complex of highly hydrophobic characteristics can be formed in the adsorption layer. In the adsorbed state, the metal ions remain to be electroactive and respond well to the voltammetric excitation signals. The synergistic effects were observed in solvent extractions of many metal ions, such as those of uranium[17-20,25], plutonium, neptunium, thorium, americium, europium, copper[21], manganese[22], cadmium[23], calcium, thulium, curium[24], vanadium, cobalt, strontium, nickel and neodymium[16]. For this reason we believe that the synergistic adsorptive accumulation method may obtain wide application.

In the present communication the basic thermodynamic relationships between the ionic species involved in the synergistic adsorption will be analysed. The method will be compared with the simple anion-induced adsorption. The experiments performed with uranyl ions in the system salicylic acid–tributylphosphate will be also reported.

EXPERIMENTAL

The pulse polarographic and the linear scan voltammetric measurements were performed with Princeton Applied Research (PAR) model 174/A polarographic analyzer connected to an HP 7045 A x-y recorder (Hewlett-Packard). For the alternating current voltammetry the PAR 170 polarographic system was used. The pH of the solutions was measured with an MA-5723 pH-meter (Iskra). Measurements were performed in an EA 875-20 electroanalytical cell (Metrohm) using a three-electrodes system. The working electrodes were either the dropping mercury electrode, or the hanging mercury drop electrode. The reference was a saturated silver/silver chloride electrode and a platinum wire was the auxiliary electrode.

All solutions were prepared from analytical grade chemicals. Supporting electrolytes were prepared by dissolving appropriate amounts of salts in doubly distilled water. A stock solution of the disodium salt of salicylic acid was prepared by dissolving the appropriate amounts of salicylic acid (H_2Sal) and NaOH. The tri-1-butyl phosphate (TBP) was purified by the conventional method[14] and dissolved in doubly distilled water to a concentration of 10^{-3} mol/dm^3. Solution samples were prepared in volumetric flasks and equilibrated for about 12 hours at room temperature. Prior to the measurements the solutions were deaerated in the polarographic cell for 20 minutes with extra pure nitrogen. pH was adjusted with supra-pure perchloric or hydrochloric acids.

THEORETICAL

Simple Model

The model is developed under the following simplifying assumptions: (i) the electrode surface is totally covered solely by the neutral, hydrophobic ligand B. (ii) the chelating ligand L neither adsorbs directly to the mercury surface, nor reacts with the adsorbed ligand B, (iii) no complexes of the type MB_n^+ appear either in a solution, or at the electrode surface, and (iv) the equilibrium is established and the concentrations of M^+, ML and L^- are uniform throughout the space (Eqs (*A2*)–(*A7*), see Appendix).

The surface complexation reaction:

$$B_{ads} + (ML)_{x=0} \rightleftarrows (BML)_{ads} \qquad (I)$$

is defined by the equilibrium and the mass balance equations:

$$K_2 = \gamma_{BML}/(\gamma_B c_{ML,x=0}) \qquad (1)$$

$$f_{BML}\gamma_{BML} + \gamma_B = \gamma_{B,max}\,. \qquad (2)$$

The assumption (iv) implies that $c_{ML,x=0} = c^*_{ML}$. The conversion factor f_{BML} is introduced in order to relate the surface concentration of the complex to the maximum surface concentration of the ligand D. It is equal to[2]:

$$f_{BML} = \gamma_{B,max}/\gamma_{BML,max}\,. \qquad (3)$$

The list of symbols is given. Combining Eqs (*1*) and (*2*) one obtains:

$$\gamma_{BML} = K_2\gamma_{B,max}c^*_{ML}/(1 + f_{BML}K_2c^*_{ML})\,. \qquad (4)$$

In a common case the concentration c^*_{ML} is defined by Eq. (*A4*). If, however, ligand L is in a large excess, it is defined by Eq. (*A7*) and Eq. (*4*) reduces to:

$$\gamma_{BML} = K_1K_2\gamma_{B,max}c^*_{L,tot}c^*_{M,tot}/(1 + K_1c^*_{L,tot} + f_{BML}K_1K_2c^*_{L,tot}c^*_{M,tot})\,. \qquad (5)$$

If the chelate complex is rather strong, the condition $1 \ll K_1c^*_{L,tot}$ may be satisfied in the excess of the ligand L and Eq. (*4*) may be further reduced to:

$$\gamma_{BML} = K_2\gamma_{B,max}c^*_{M,tot}/(1 + K_2f_{BML}c^*_{M,tot})\,. \qquad (6)$$

Eq. (*6*) can be transformed to:

$$f_{BML}K_2c^*_{M,tot} = \gamma_{BML}/((\gamma_{B,max}/f_{BML}) - \gamma_{BML})\,. \qquad (7)$$

Common Solution

The assumptions (iii) and (iv) remain, but the surface activity of the chelating ligand L is included in the consideration. The bulk concentrations of both ligands L and B are variables. The electrode surface is not totally covered by the adsorbed species. The following interactions between the adsorbed and the dissolved ionic species are considered:

a) the synergistic adsorption (Eq. (*1*)). Considering Eq. (*1*) and the condition (iv) one obtains:

$$\gamma_{BML} = K_2 c^*_{ML} \gamma_B \; ; \tag{8}$$

b) the simple, anion-induced adsorption (Eq. (*A-II*)). Considering Eq. (*A8*) and (iv):

$$\gamma_{ML} = \lambda_1 c^*_{M^+} \gamma_L \; ; \tag{9}$$

c) the partial solvation of the ligand L by the ligand B, regarded as the formation of one-to-one complex BL at the electrode surface:

$$L_{x=0} + B_{ads} \rightleftarrows (BL)_{ads} \tag{II}$$

$$\gamma_{BL} = K_3 c^*_L \gamma_B \, . \tag{10}$$

This reaction is assumed because of some experimental evidences that the chelating ligand salicylic acid can be solvated by the neutral ligand tributylphosphate[27]. The surface concentrations γ_B and γ_L as well as the free electrode surface S^* are defined by the competitive adsorption equations:

$$\beta_B c^*_B = \gamma_B / S^* \tag{11}$$

$$\beta_L c^*_L = \gamma_L / S^* \tag{12}$$

$$S^* = \gamma_{max} - \gamma_B - \gamma_L - \gamma_{BL} - \gamma_{BML} - \gamma_{ML} \, . \tag{13}$$

For the simplicity, the maximal surface concentrations of all adsorbed species are assumed to be equal. The concentration c^*_B is a variable and the concentrations $c^*_{M^+}$, c^*_L, and c^*_{ML} are defined by Eqs (*A2*)–(*A4*). The combination of Eqs (*8*)–(*13*), after several transformations, results in:

$$\gamma_B = \beta_B c^*_B \gamma_{max} / Z \tag{14}$$

$$\gamma_L = \beta_L c^*_L \gamma_{max} / Z \tag{15}$$

$$Z = 1 + \beta_L c^*_L (1 + \lambda_1 c^*_{M^+}) + \beta_B c^*_B (1 + K_3 c^*_L + K_2 c^*_{ML}) \, . \tag{16}$$

The surface concentration of the adsorbed complex BML is defined by Eqs (*8*), (*14*), and (*16*) straightforwardly.

Synergistic Adsorptive Accumulation

The equilibrium conditions assumed in the preceding paragraphs can be established only through the mass transfer. This process requires a certain time to be completed. The time depends on the nature of the mass transfer: whether it is obtained solely by the diffusion, or by the convection and the diffusion. At real electrodes the voltammetric measurements are frequently performed before the equilibrium is established.

Diffusion only. The adsorption–time relationship will be developed assuming the conditions which justify the application of Eq. (*6*): $c_\mathrm{L}^* = c_\mathrm{L,tot}^*$ and $c_\mathrm{ML}^* = c_\mathrm{M,tot}^*$ (see Eq. (*A7*) for $K_1 c_\mathrm{L,tot}^* \gg 1$). These are the optimal experimental conditions. The diffusion towards the spherical stationary electrode surface can be described by the differential equation:

$$\partial(r c_\mathrm{M,tot})/\partial t = D \partial^2 (r c_\mathrm{M,tot})/\partial r^2 \,. \tag{17}$$

It has to be solved under the following initial and boundary conditions:

$$t = 0,\, r \geqq r_0\colon c_\mathrm{M,tot} = c_\mathrm{M,tot}^*,\, \gamma_\mathrm{BML} = 0 \tag{a}$$

$$t > 0,\, r \rightarrow \infty\colon c_\mathrm{M,tot} \rightarrow c_\mathrm{M,tot}^* \tag{b}$$

$$r = r_0\colon D(\partial c_\mathrm{M,tot}/\partial r)_{r=r_0} = \mathrm{d}\gamma_\mathrm{BML}/\mathrm{d}t \tag{c}$$

$$f_\mathrm{BML} K_2 c_{\mathrm{M,tot},r=r_0} = \gamma_\mathrm{BML}/((\gamma_\mathrm{B,max}/f_\mathrm{BML}) - \gamma_\mathrm{BML}) \,, \tag{d}$$

where r_0 is the radius of the spherical electrode. The solution of Eq. (*17*) can be obtained by the numerical integration[26,28], but here it is not important. The analytical solution of Eq. (*17*) can be obtained if the relationship between $c_{\mathrm{M,tot},r=r_0}$ and γ_BML is approximated by the linear isotherm:

$$t > 0,\, r = r_0\colon \gamma_\mathrm{BML} = K_2 \gamma_\mathrm{B,max} c_{\mathrm{M,tot},r=r_0} \,. \tag{e}$$

The approximation is justified if the total metal concentration is very low (see Eq. (*6*) for $K_2 f_\mathrm{BML} c_{\mathrm{M,tot},x=0} \ll 1$). The solution of Eq. (*17*) under the condition (*e*) is still rather involved[29]:

$$\gamma_\mathrm{BML} = K_2 \gamma_\mathrm{B,max} c_\mathrm{M,tot}^* (1 - (1 - 4z/r_0)^{-1/2} ((1 - D^{1/2}/r_0 y_1)\, F(y_1 t^{1/2}) - \\ - (1 - D^{1/2}/r_0 y_2)\, F(y_2 t^{1/2}))) \,, \tag{18}$$

where:

$$y_1 = (D^{1/2}/z)(1 + (1 - 4z/r_0)^{1/2})/2 \,; \quad y_2 = (D^{1/2}/z)(1 - (1 - 4z/r_0)^{1/2})/2 \,;$$
$$z = K_2 \gamma_\mathrm{B,max} \quad \text{and} \quad F(y_i t^{1/2}) = \exp(y_i^2 t)\, \mathrm{erfc}(y_i t^{1/2}) \quad (i = 1, 2) \,.$$

If $r_0 \to \infty$, Eq. (*18*) reduces to:

$$\gamma_{\mathrm{BML}} = K_2 \gamma_{\mathrm{B,max}} c^*_{\mathrm{M,tot}} (1 - \exp(DtK_2^{-2} \gamma_{\mathrm{B,max}}^{-2}) \operatorname{erfc}((Dt)^{1/2}/K_2 \gamma_{\mathrm{B,max}})) \,. \tag{19}$$

Eq. (*19*) is the solution of the differential equation for the semiinfinite, stationary planar diffusion:

$$\partial c_{\mathrm{M,tot}}/\partial t = D(\partial^2 c_{\mathrm{M,tot}}/\partial x^2) \tag{20}$$

under the initial and boundary conditions (*a*)–(*c*) and (*e*).

Convection and diffusion. If the solution is stirred with a magnetic stirrer during the accumulation period, the equilibrium conditions can be established earlier. The stirring induces a formation of a diffusion layer of nonuniform thickness near the surface of a mercury drop electrode. The adsorption depends on an average diffusion layer thickness (δ). Inside the layer, the concentration of the complex ML is a linear function of a distance from the electrode surface:

$$\partial c_{\mathrm{M,tot}}/\partial x = (c^*_{\mathrm{M,tot}} - c_{\mathrm{M,tot},x=0})/\delta \tag{f}$$

and outside the layer it is constant: $c_{\mathrm{M,tot},x>\delta} = c^*_{\mathrm{M,tot}}$. The expression for the adsorption–time relationship can be obtained if the conditions (*c*) and (*f*) are combined either with the condition (*d*), or with the condition (*e*). The combination (*c*), (*e*) and (*f*) (the linear isotherm approximation) can be solved analytically and the solution reads:

$$\gamma_{\mathrm{BML}} = K_2 \gamma_{\mathrm{B,max}} c^*_{\mathrm{M,tot}} (1 - \exp(-Dt\delta^{-1} K_2^{-1} \gamma_{\mathrm{B,max}}^{-1})) \,. \tag{21}$$

The combination (*c*), (*d*), and (*f*) can be solved only numerically. The solution is presented in Appendix.

Faradaic Reaction

The accumulation is followed by a voltammetric excitation signal by which the metal ions from the adsorbed mixed complex are reduced. During the reduction, the condition (*c*) must be replaced by:

$$D(\partial c_{\mathrm{M,tot}}/\partial x)_{x=0} = \mathrm{d}\gamma_{\mathrm{BML}}/\mathrm{d}t + i/nFS \,. \tag{g}$$

The condition describes the planar, stationary diffusion and applies to Eq. (*20*). Here S stays for the electrode surface area.

The product of the redox reaction may either dissociate from the electrode surface, or may stay adsorbed in the form of the mixed complex BPL, or in some other form.

The differential equation:

$$\partial c_{\mathrm{P,tot}}/\partial t = D_{\mathrm{P}}(\partial^2 c_{\mathrm{P,tot}}/\partial x^2) \tag{22}$$

must be solved under the following initial and boundary conditions:

$$t = 0, x \geqq 0: c_{\mathrm{P,tot}} = 0 \tag{h}$$

$$t > 0, x \to \infty: c_{\mathrm{P,tot}} \to 0\,. \tag{i}$$

At the electrode surface either:

$$D_{\mathrm{P}}(\partial c_{\mathrm{P,tot}}/\partial x)_{x=0} = -i/nFS\,, \tag{j}$$

if the product does not adsorb, or:

$$D_{\mathrm{P}}(\partial c_{\mathrm{P,tot}}/\partial x)_{x=0} = \mathrm{d}\gamma_{\mathrm{BPL}}/\mathrm{d}t - i/nFS \tag{k}$$

$$\gamma_{\mathrm{BPL}} = K_{\mathrm{BPL}}\gamma_{\mathrm{B,max}}c_{\mathrm{P,tot},x=0}\,, \tag{l}$$

if it stays adsorbed as a mixed complex BPL and the initial bulk concentration $c^*_{\mathrm{M,tot}}$ is very low (condition (*e*)). Besides, a relationship between P and the ligand L must be defined, similarly as in Eq. (*A7*). If the association and the dissociation of the complexes ML and PL are very fast, the mass transfer of M and P must be calculated by the consideration of all ionic species ($c_{\mathrm{M,tot}}$ and $c_{\mathrm{P,tot}}$), but if they are very slow, only the complexes may be considered (c_{ML} and c_{PL}). It is assumed that the ligand L is in a large excess and its diffusion is neglected ($c_{\mathrm{L},x\geqq 0} = c^*_{\mathrm{L,tot}}$).

Equations (*20*) and (*22*) are connected by the equations for a charge transfer. If the redox reaction is reversible and the product adsorbs:

$$(\mathrm{BML})_{\mathrm{ads}} + \mathrm{e} \rightleftarrows (\mathrm{BPL})_{\mathrm{ads}} \tag{III}$$

$$\gamma_{\mathrm{BML}} = \gamma_{\mathrm{BPL}} \exp(\sigma_1)\,, \tag{m}$$

where: $\sigma_1 = \sigma_0 + \ln(K_2K_1/K_{\mathrm{BPL}}K_{\mathrm{PL}})$, $\sigma_0 = nF(E - E^0)/RT$, K_{BPL} and K_{PL} are stability constants of complexes BPL and PL ($1 \ll K_1c^*_{\mathrm{L,tot}}$ and $1 \ll K_{\mathrm{PL}}c^*_{\mathrm{L,tot}}$) and E^0 is a standard potential of a simple redox reaction $\mathrm{M}^+ + \mathrm{e} \rightleftarrows \mathrm{P}$ (here M^+ is only a symbol for any M^{n+}, so the charge of the product P is omitted).

If the product does not adsorb, two reactions are possible:

(i)

$$(\mathrm{BML})_{\mathrm{ads}} + \mathrm{e} \rightleftarrows \mathrm{B}_{\mathrm{ads}} + \mathrm{PL} \tag{IV}$$

$$\gamma_{\mathrm{BML}} = \gamma_{\mathrm{B,max}}c_{\mathrm{PL},x=0} \exp(\sigma_2)\,, \tag{n}$$

where $\sigma_2 = \sigma_0 + \ln(K_2K_1/K_{PL})$. The conditions (*e*) and (*l*) imply that $\gamma_B = \gamma_{B,max}$.

(ii)

$$(BML)_{ads} + e \rightleftarrows B_{ads} + P + L^- \qquad (V)$$

$$\gamma_{BML} = \gamma_{B,max}c^*_{L,tot}c_{P,x=0}\exp(\sigma_3)\,, \qquad (o)$$

where $\sigma_3 = \sigma_0 + \ln(K_2K_1)$.

The reaction schemes (*IV*) and (*V*) are frequently irreversible because the reoxidation of the ionic species P and PL can be significantly hindered by the monolayer of the adsorbed ligand B. In that case, the conditions (*m*)–(*o*) must be replaced by:

$$i/nFS = k_{s1}\exp(-\alpha_1\sigma_1)(\gamma_{BML} - \gamma_{BPL}\exp(\sigma_1)) \qquad (p)$$

$$i/nFS = k_{s2}\exp(-\alpha_2\sigma_2)(\gamma_{BML} - \gamma_{B,max}c_{PL,x=0}\exp(\sigma_2)) \qquad (q)$$

$$i/nFS = k_{s3}\exp(-\alpha_3\sigma_3)(\gamma_{BML} - \gamma_{B,max}c^*_{L,tot}c_{P,x=0}\exp(\sigma_3))\,, \qquad (r)$$

where k_{si} and α_i ($i = 1, 2, 3$) are the standard reaction rate constants and the transfer coefficients of the reactions (*III*)–(*V*).

The solutions of Eqs (*20*) and (*22*) for the adsorption and the redox reaction of simple, electroactive, surface-active substances are numerous[26,28,30–40]. They can be applied to the synergistic adsorption if the proper parameters are included. The solutions were obtained for the linear scan[30], the alternating current[31,32] and the square-wave voltammetry[33,34], as well as for the pulse[28,35,36] and the differential pulse polarography[37,38]. There are also several approximative solutions[39,40]. If the adsorption of the reactant follows a non-linear isotherm, the solution can be obtained only if the redox reaction is reversible and the product does not adsorb[26,28,30–32,35,37]. If the adsorptions of both the reactant and the product follow linear isotherms, Eqs (*20*) and (*22*) can be solved for a quasireversible charge transfer, as a general case[28,33,34,36,38].

RESULTS AND DISCUSSION

The surface concentration of the synergistically adsorbed metal ions, γ_{BML}, is a complex function of many parameters (see Eqs (*8*), (*14*), and (*16*)). However, under optimal experimental conditions, which can be easily obtained, the relationship between γ_{BML} and the total metal bulk concentration $c^*_{M,tot}$ becomes rather simple and resembles the Langmuirian type isotherm (see Eqs (*5*)–(*7*)). The hydrophobic ligand B is usually adsorbed much stronger than the chelating ligand L. If B is added in a proper concentration, it will cover the electrode surface totally, displacing the ligand L. The chelate complexes ML are usually very stable. If the ligand L is added to the electrolyte in not too large excess, it will complex almost all metal ions, leaving virtually no free metal ions M^+ (see Eqs (*A6*) and (*A7*)). The titration curves $c^*_{ML} - \log(c^*_{L,tot})$ and $\gamma_{BML} - \log(c^*_{L,tot})$ are shown in Figs 1*a* and 1*b*. The curves can be described by Eqs (*4*) and (*A4*), but at their plateaus Eqs (*A6*), (*A7*), and (*6*) apply and γ_{BML} becomes independent of $c^*_{L,tot}$.

The firmness of the synergistic adsorption depends on the parameters $f_{BML}K_2$ and $\gamma_{B,max}/f_{BML}$ (Eq. (7)). The maximal surface concentration of the ligand B ranges between $1 \, . \, 10^{-10}$ and $3 \, . \, 10^{-10}$ mol/cm^2. Therefrom, the values of K_2 can range from $10^7 - 10^4$ dm^3/mol. The value of the K_2constant defines the total metal concentration range in which the relationship between γ_{BML} and $c^*_{M,tot}$ can be approximated by the linear Eq. (*e*). The linear approximation can be applied if $K_2 f_{BML} c^*_{M,tot} < 0{\cdot}1$, i.e. if less than 10% of the surface is covered by the $(BML)_{ads}$ (see Eqs (*6*) and (7)). If $K_2 = 10^7$ dm^3/mol, the condition is satisfied if $c^*_{M,tot} < 10^{-8}$ mol/dm^3, but if $K_2 = 10^4$ dm^3/mol, the concentration range extends to $c^*_{M,tot} < 10^{-5}$ mol/dm^3. This is the basis for the application of the synergistic adsorption for the quantitative determination of metal ion traces.

The γ_{BML} independence of $c^*_{L,tot}$ in the range of a large chelating ligand excess is the main difference between the synergistic and a simple, anion-induced adsorption. The relationship between the surface concentration of the adsorbed complex ML and metal and ligand bulk concentrations is expressed by Eq. (*A10*). This equation can be transformed to:

$$f_{ML}\lambda_1(1 + K_1 c^*_{L,tot})^{-1} c^*_{M,tot} = \gamma_{ML}/((\gamma_{m,L}/f_{ML}) - \gamma_{ML}) , \qquad (23)$$

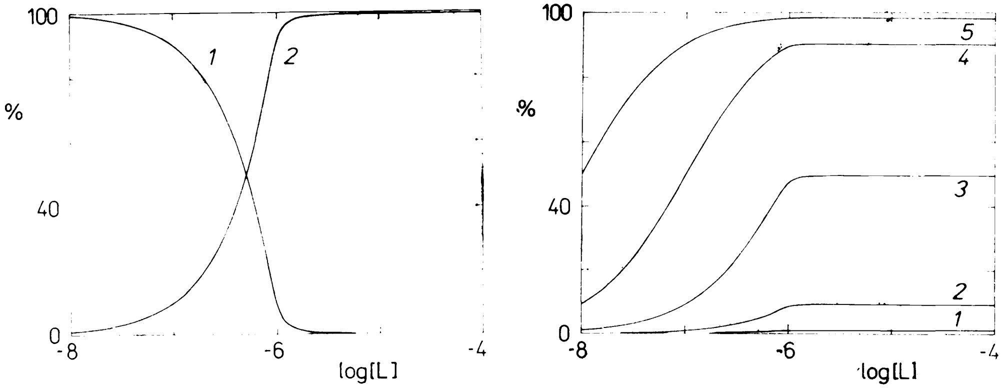

FIG. 1

Normalized ionic species distribution in a solution (*a*) ($c^*_{M^+}/c^*_{M,tot}$ (curve *1*) and $c^*_{ML}/c^*_{M,tot}$ (curve 2)) and at an electrode surface (*b*) ($\gamma_{BML}/\gamma_{B,max}$ (curves *1*—*5*)). The electrode surface is totally covered by the adsorbed species B and BML (Eqs (*4*) and (*A4*)). $K_1 = 10^8$ dm^3/mol, $c^*_{M,tot} = 10^{-6}$ mol/dm^3, $f_{BML} = 1$. K_2 (dm^3/mol) $= 10^4$ (*1*); 10^5 (2); 10^6 (*3*); 10^7 (*4*) and 10^8 (*5*) where $\gamma_{m,L}$ is the maximal surface concentration of the ligand L. It is obvious that the firmness of the simple, anion-induced adsorption depends on the ligand L concentration. The consequence is the displacement of the adsorbed complex $(ML)_{ads}$ by the adsorbed ligand $(L)_{ads}$ in the range of the highest ligand concentrations[26]. Besides, the simple, anion-induced adsorption does not depend solely on the stability of the adsorbed complex (λ_1), but on the ratio of the stabilities of the adsorbed and the dissolved complexes (λ_1/K_1). The synergistic adsorption constant K_2 is independent of both K_1 and $c^*_{L,tot}$. This difference can be seen in Figs 2*a*–2*c*. The nor-

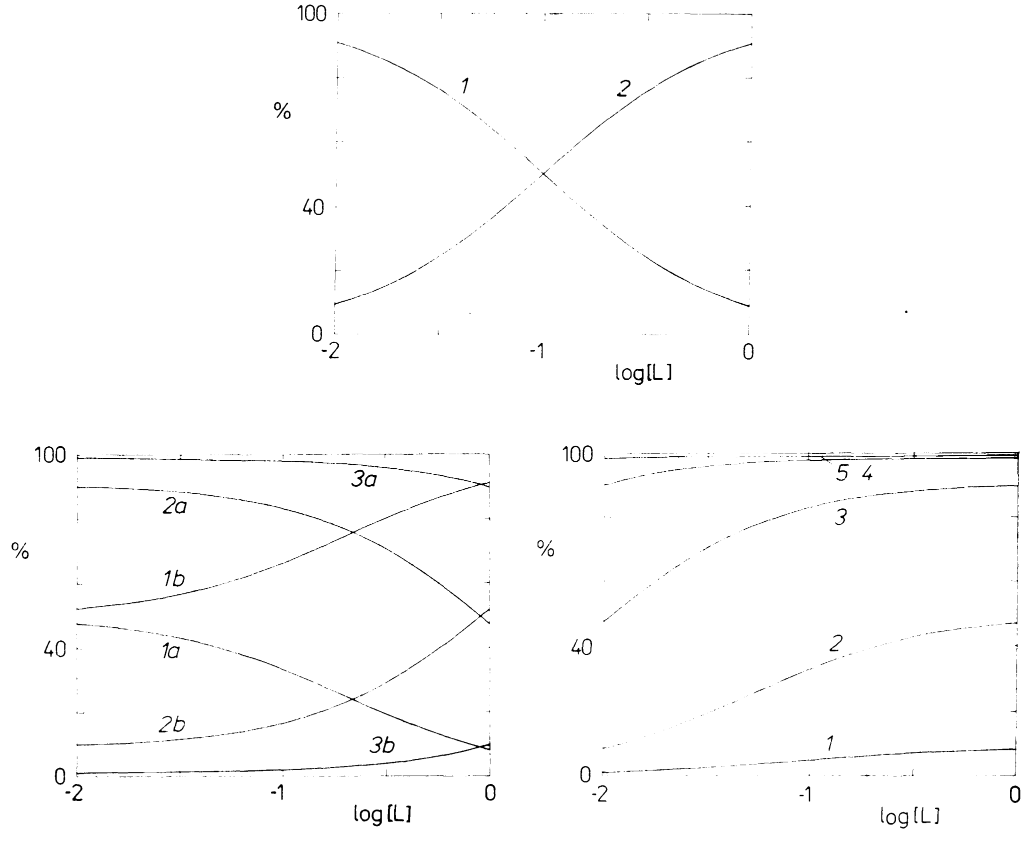

FIG. 2

Normalized ionic species distribution in a solution (*a*) ($c^*_{M^+}/c^*_{M,tot}$ (curve *1*) and $c^*_{ML}/c^*_{M,tot}$ (curve *2*)) and at an electrode surface for simple, anion-induced adsorption (*b*) ($\gamma_{ML}/\gamma_{m,L}$ (curves *1a*–*3a*) and $\gamma_L/\gamma_{m,L}$ (curves *1b*–*3b*)) and for synergistic adsorption (*c*) ($\gamma_{BML}/\gamma_{B,max}$ (curves *1*–*5*)). The electrode surface is totally covered for both types of adsorption. *b*: $K_1 = 10\ dm^3/mol$, $c^*_{M,tot} = 10^{-4}\ mol/dm^3$, $f_{BML} = 1$, $f_{ML} = 1$, $\lambda_1/(dm^3/mol) = 10^4$ (*1a*, *1b*); 10^5 (*2a*, *2b*) and 10^6 (*3a*, *3b*). *c*: $K_2/(dm^3/mol) = 10^3$ (*1*); 10^4 (*2*); 10^5 (*3*); 10^6 (*4*) and 10^7 (*5*) malized distribution of a free metal ions M^+ and a rather weak complex ML in the bulk of the solution is presented by Fig. 2*a*. The simple, anion-induced adsorption of the complex ML is shown in Fig. 2*b*. The surface concentration γ_{ML} follows the distribution curve of $c^*_{M^+}$ in the solution and decreases as the ligand concentration increases (e.g.: curves *1a* and *2a*). The displacement of $(ML)_{ads}$ by $(L)_{ads}$ is inversely proportional to the stability of the adsorbed complex (compare curves *1a* and *3a*). The synergistic adsorption of metal ions in the form of the surface complex $(BML)_{ads}$ is shown in Fig. 2*c*. The surface concentration γ_{BML} follows the distribution of the dissolved complex ML and no displacement occurs. This fact enables the synergistic adsorptive accumulation to be performed in the large excess of the chelating ligand L without loosing the efficiency. However, if the excess is too large, the complication may arise from the solvation of the ligand L by the adsorbed ligand B. This possibility can be explored by the application of Eqs (*8*)–(*16*). The normalized surface distribution of adsorbed species in the non-ideal case is shown in Fig. 3. The figure displays the titration curve $\gamma_{BML} - \log(c^*_B)$ in the presence of a large excess of the chelating ligand L. The surface activity of the ligand L and its possible interaction with the adsorbed ligand B were taken into consideration. The parameters were chosen arbitrarily. The ligand B displaces the ligand L from the electrode surface because of much stronger adsorption. The synergistically adsorbed complex $(BML)_{ads}$ follows the surface concentration of $(B)_{ads}$ in the ratio defined by Eq. (*8*). The adsorbed complex $(BL)_{ads}$ occupies a part of the electrode surface and decreases the efficiency of the adsorptive accumulation of metal ions. It is obvious that the optimal experimental conditions require that $\beta_B \gg \beta_L$ and $K_3 \to 0$, i.e. that the ligands B and L do not react significantly. Besides, the measurements must be done in a large excess of both ligands. If the chelating ligand L is in a large excess and if its surface activity is neglected ($1 \gg \beta_L c^*_{L,tot}$ and $1 \gg K_3 c^*_{L,tot}$), Eqs (*8*), (*14*), and (*16*) may be transformed to:

$$\gamma_{BML} = K_2 c^*_{M,tot} \beta_B c^*_B \gamma_{B,max} / (1 + \beta_B c^*_B (1 + K_2 c^*_{M,tot})) \,, \tag{24}$$

because $c^*_{ML} = c^*_{M,tot}$ and $\gamma_{max} = \gamma_{B,max}$. If $1 \ll \beta_B c^*_B$, Eq. (*24*) turns to Eq. (*6*).

At real electrodes the amount of synergistically adsorbed metal ions depends on the duration of the accumulation. The relationship between γ_{BML} and the accumulation time is rather complicated and depends on the nature of the mass transfer. If the total metal concentration is very low and the mass transfer is obtained solely by diffusion, the accumulation rate depends on the parameter $D^{1/2} K_2^{-1} \gamma_{B,max}^{-1}$ (see Eq. (*19*)). The function $\exp(x) \,.\, \mathrm{erfc}(x)$ tends to zero if the variable x tends to the infinity. So, the adsorption equilibrium will be established earlier if the adsorption is weaker (i.e. the product $K_2 \gamma_{B,max}$ smaller). At spherical electrodes the accumulation rate is higher due to the sphericity effects (see Eq. (*18*): the parameters y_1 and y_2 depend on $D^{1/2} K_2^{-1} \gamma_{B,max}^{-1}$ and on the ratio $K_2 \gamma_{B,max} / r_0$). This rate can be significantly increased if the convection is introduced (the solution is stirred). The accumulation time needed to approximate equilibrium within 5% of error ($\gamma_{\text{BML}} = 0{\cdot}95 K_2 \gamma_{\text{B,max}} \cdot c^*_{\text{M,tot}}$) can be calculated from Eq. (*21*). The condition is:

$$\exp\left(-D t_{\text{accum}} \delta^{-1} K_2^{-1} \gamma_{\text{B,max}}^{-1}\right) = 0{\cdot}05 \qquad (25)$$

and the solution reads:

$$t_{\text{accum}} = -\ln\left(0{\cdot}05\right) D^{-1} \delta K_2 \gamma_{\text{B,max}} \qquad (26)$$

For parameters from Fig. 4, $t_{\text{accum}} = 150$ s what is rather long time and proves that the voltammetric measurements which follow the adsorptive accumulation can oftenly be made before the equilibrium with the bulk of the solution is established. Besides, in the range of higher total metal concentrations, the accumulation rate depends on $c^*_{\text{M,tot}}$, as can be seen from Fig. 4. The adsorption equilibrium is established sooner if the ratio $c^*_{\text{M,tot}}/\gamma_{\text{B,max}}$ is higher. The results of voltammetric measure-

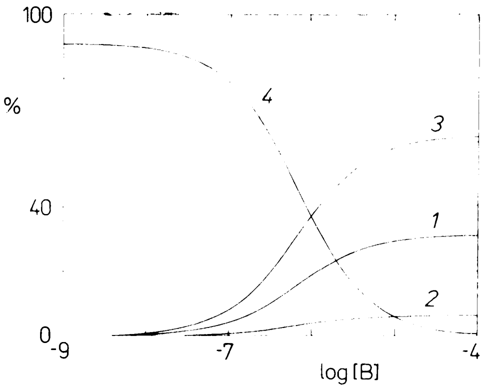

FIG. 3

Dependence of the normalized ionic species distribution at the electrode surface on the bulk concentration of the hydrophobic ligand B. The synergistic adsorption complicated by the adsorption of the chelating ligand L (Eqs (*8*)–(*16*)): *1* $\gamma_{\text{BML}}/\gamma_{\text{max}}$; *2* $\gamma_{\text{BL}}/\gamma_{\text{max}}$; *3* $\gamma_{\text{B}}/\gamma_{\text{max}}$; *4* $\gamma_{\text{L}}/\gamma_{\text{max}}$. $K_1 = 10^8$ dm^3/mol, $c^*_{\text{M,tot}} = 10^{-6}$ mol/dm^3, $c^*_{\text{L,tot}} = 10^{-4}$ mol/dm^3, $\beta_{\text{B}} = 10^7$ dm^3/mol, $\beta_{\text{L}} = 10^5$ dm^3/mol, $K_2 = 5 \cdot 10^5$ dm^3/mol and $K_3 = 10^3$ dm^3/mol

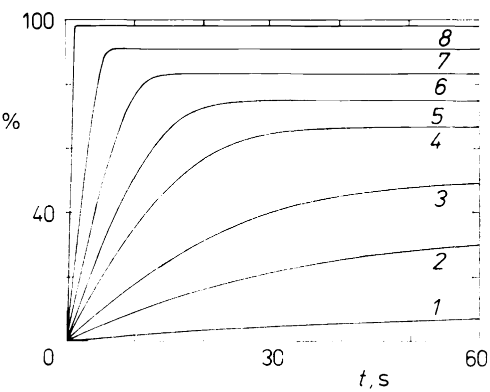

FIG. 4

Synergistic adsorptive accumulation of the mixed complex (BML)$_{\text{ads}}$ from the stirred solution. The dependence of $f_{\text{BML}}\gamma_{\text{BML}}/\gamma_{\text{B,max}}$ on the accumulation time (Eq. (*A17*)). $(2D/\delta) = 4 \cdot 10^{-3}$ cm/s, $K_2\gamma_{\text{B,max}} = 0{\cdot}1$ cm, $c^*_{\text{M,tot}} f_{\text{BML}}/\gamma_{\text{B,max}}$ (cm^{-1}) is: *1* 1; *2* 5; *3* 10; *4* 20; *5* 30; *6* 50; *7* 100; *8* 500 ments performed with the constant accumulation time, but different total metal concentrations should not be analysed according to the well known expression:

$$\gamma_{\mathrm{BML}}^{-1} = (f_{\mathrm{BML}}/\gamma_{\mathrm{B,max}}) + (K_2\gamma_{\mathrm{B,max}})^{-1}\,(c^*_{\mathrm{M,tot}})^{-1} \qquad (27)$$

because the recorded γ_{BML} values do not belong to the same isotherm. However, for electroanalytical purposes, when synergistic adsorptive accumulation is used for the determination of metal ions in traces, one can neglect the dependence of the accumulation rate on the total metal concentration. If γ_{BML} depends linearly on $c^*_{\mathrm{M,tot}}$ in the equilibrium, then similar linear relations exist during the accumulation as well, but the proportionality factors depend on the accumulation time, as can be seen from Eqs (*18*), (*19*), or (*21*).

The lowest detection limit which can be achieved by the application of the synergistic adsorptive accumulation depends on the intensity of the surface complexation reaction (*I*), on the reversibility of redox reactions (*III*), (*IV*) and (*V*) and on the characteristics of the applied voltammetric technique. The limit can be roughly estimated for several simpler cases. If the reaction (*III*) is reversible and the linear scan voltammetry is applied, the relationship between the LSV peak current and the amount of the adsorbed reactant γ^0_{BML} reads[39,40]:

$$i_{\mathrm{p}} = n^2F^2S\gamma^0_{\mathrm{BML}}v/(4RT)\,, \qquad (28)$$

where v is the scan rate. Eq. (*28*) was developed under the assumption that during the voltammetric measurement the contribution of the mass transfer could be neglected. Assuming that the minimum peak current which can be confidently detected equals 10 nA, the reactant surface concentration which is required for this faradaic response can be estimated from Eq. (*28*). If $S = 0{\cdot}05\ \mathrm{cm}^2$, $n = 1$ and $v = 0{\cdot}1$ V/s, the required γ^0_{BML} equals $2\,.\,10^{-12}\ \mathrm{mol/cm^2}$. The total metal bulk concentration which equilibrates this surface concentration can be calculated from the linear isotherm:

$$\gamma^0_{\mathrm{BML}} = K_2\gamma_{\mathrm{B,max}}c^*_{\mathrm{M,tot}} \qquad (29)$$

If the surface complex is very stable, the product $K_2\gamma_{\mathrm{B,max}}$ can be equal to 1 cm. In that case the lowest metal concentration which can be detected is equal to $2\,.\,10^{-9}\ \mathrm{mol/dm^3}$. This detection limit can be obtained only by the prolonged accumulation from the stirred solution. There is no reason why the product $K_2\gamma_{\mathrm{B,max}}$ could not be higher than 1 cm. In the classical adsorption, the product $\beta\gamma_{\mathrm{max}}$ is usually lower than 1 cm (ref.[40]), but the synergistic adsorptive accumulation is not a simple adsorption, but the surface complexation reaction.

Similar detection limit can be obtained if the reactions (*III*)–(*V*) are totally irreversible and the square-wave voltammetry is applied. The following relationship exists[33]:

$$i_p = 500n^2FS\alpha af\,\Delta E\gamma^0_{BML}\,, \qquad (30)$$

where a is the amplitude, f the frequency and ΔE the step increment of the SW signal, while α is the transfer coefficient. For the standard parameters ($S = 0{\cdot}05$ cm^2, $n = 1$, $\alpha = 0{\cdot}5$, $a = 0{\cdot}01$ V, $f = 100$ s^{-1} and $\Delta E = 0{\cdot}005$ V) the faradaic response $i_p = 10$ nA can be obtained if $\gamma^0_{BML} = 1{\cdot}6 \,.\, 10^{-12}$ mol/cm^2, what is in the equilibrium with $c^*_{M,tot} = 1{\cdot}6 \,.\, 10^{-9}$ mol/dm^3 if $K_2\gamma_{B,max} = 1$ cm. If the redox reaction (*III*) is quasireversible, the square-wave response may be 9 times higher and the detection limit can be lowered to $2 \,.\, 10^{-10}$ mol/dm^3. If the reactions (*IV*) and (*V*) are reversible, the square-wave responses are 4 times higher than those of totally irreversible reactions and the detection limit is $4 \,.\, 10^{-10}$ mol/dm^3.

Very high ratio between the faradaic response and the reactant surface concentration exists in normal pulse polarography of totally irreversible redox reactions (*III*)–(*V*) (ref.[28]):

$$i_p = nFS\gamma^0_{BML}/t_p\,. \qquad (31)$$

If $S = 0{\cdot}05$ cm^2, $n = 1$ and $t_p = 0{\cdot}05$ s, the response $i_p = 10$ nA requires only $\gamma^0_{BML} = 10^{-13}$ mol/cm^2. This surface concentration can not be obtained by the corresponding equilibrium bulk concentration $c^*_{M,tot} = 10^{-10}$ mol/dm^3 (for $K_2\gamma_{B,max} = 1$ cm) because the accumulation time is restricted to the drop life-time. However, the detection limit can be lowered if the signal is applied to the hanging mercury drop electrode (the normal pulse voltammetry) which enables the arbitrarily long accumulation from the stirred solution[14]. This technique can be recommended for totally irreversible redox reactions (because a non-productive current substraction is avoided), while for the reversible and the quasireversible reactions the square-wave voltammetry should be the optimal choice.

System U(VI)–H$_2$Sal–TBP

The redox reaction of uranyl ion in the presence of salicylic acid (H_2Sal) and tributyl phosphate (TBP) has been the subject of the previous communication[14]. The formation of the adsorbed mixed complex $(UO_2(HSal)_2TBP(H_2O))_{ads}$ has been demonstrated. Its reduction is totally irreversible. The product UO_2^+ is electroinactive under these conditions. Some additional evidences for this mechanism were obtained by the pulse polarography and the linear scan and the alternating current voltammetries. The pulse polarogram of the redox couple UO_2^{2+}/UO_2^+ in 0·7 mol/dm^3 $NaClO_4$, pH 3·6, is a reversible wave. It is displayed as curve *1* in Fig. 5. On the addition of H_2Sal to the electrolyte, two waves appear (curve *2*). The first wave corresponds to the reduction of the dissolved UO_2^{2+}, catalyzed by the disproportionation of U(V) under the influence of H_2Sal (ref.[41]). The second wave has a form of a peak and corresponds to the reduction of the adsorbed complex $(UO_2(HSal)_2)_{ads}$. The nature of the second wave can be prooved by the results of tensametric measurements which are displayed in Fig. 6. Salicylic acid adsorbs only weakly (curve *2*), but in the presence of UO_2^{2+} ions (curve *3*) its adsorption is much stronger. The very high peak which appears at −0·28 V vs Ag/AgCl is of faradaic origine. Its maximal current increases if the phase angle is decreased. Its potential corresponds well to the second pulse polarographic wave. In the presence of TBP, pulse polarograms are marked by an extensive maximum of capacitive nature (curve *3*, Fig. 5). Its nature is proved by the corresponding tensametric peak which appears on the curve *4* in Fig. 6. The redox reaction of UO_2^{2+}/UO_2^{+} couple becomes irreversible if the electrode surface is covered by the adsorbed TBP (ref.[42]). It can be seen from the curve *3* in Fig. 5. After the minimum at −0·3 V vs Ag/AgCl, the faradaic response of UO_2^{2+} reduction developes, but it is totally irreversible. The presence of both H_2Sal and TBP, but without UO_2^{2+}, causes in pulse polarography the development of a capacitive peak at about −0·2 V (curve *4*, Fig. 5). That peak appears also in the linear

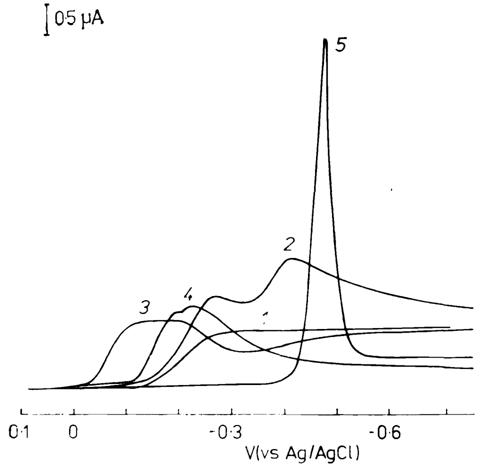

FIG. 5

The pulse polarograms of the systems: *1* UO_2^{2+}; *2* $UO_2^{2+} + H_2Sal$; *3* UO_2^{2+} + TBP; *4* H_2Sal + TBP; *5* $UO_2^{2+} + H_2Sal$ + TBP. 0·7 mol/dm³ $NaClO_4$, pH 3·6. DME, t_d = = 1 s, t_p = 57 ms. $[UO_2^{2+}]$ = 6·2 . . 10^{-5} mol/dm³, $[H_2Sal]$ = 7·2 . 10^{-4} mol/ /dm³, [TBP] = 2 . 10^{-4} mol/dm³ (where applies)

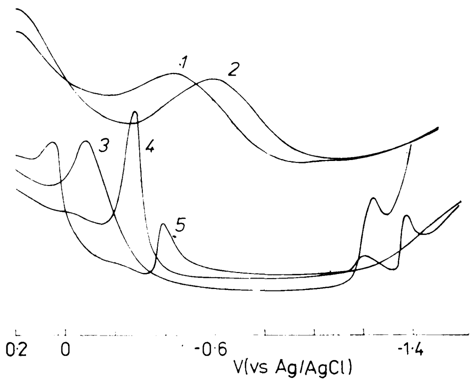

FIG. 6

Alternating current voltammograms of the systems: *1* 0·7 mol/dm³ $NaClO_4$ (supporting electrolyte, pH 3); *2* H_2Sal; *3* UO_2^{2+} + H_2Sal; *4* TBP; *5* $UO_2^{2+} + H_2Sal$ + TBP. HMDE, $f_{a.c.}$ = 230 Hz, $a_{a.c.}$ = 10 mV, $\varphi_{a.c.}$ = 90°, dE/dt = 20 mV/s, $[UO_2^{2+}]$ = = 6·2 . 10^{-4} mol/dm³. Concentrations of H_2Sal and TBP as in Fig. 5

scan and alternating current voltammetry and can be assigned to the solvation of H_2Sal by the adsorbed TBP (refs[14,27]). Finally, if UO_2^{2+} ions are added to the solution of H_2Sal and TBP, the synergistically adsorbed mixed complex $(UO_2(HSal)_2.TBP(H_2O))_{ads}$ appears at the electrode surface (curves *5*, Figs 5 and 6). This complex displaces complexes $(UO_2(HSal)_2)_{ads}$ and $(TBP.H_2Sal)_{ads}$ from the electrode surface. The first complex is probably displaced by the adsorption of TBP which is immediately followed by the formation of a mixed, adsorbed complex. The evidence for the displacement is a rather flat residual current between 0 V and −0·4 V (curve *5*, Fig. 5) and the capacitance pit in this potential range (curve *5*, Fig. 6). In the pulse polarography (PP), the adsorbed mixed complex is reduced at −0·48 V vs Ag/AgCl, giving rise to a sharp maximum which is followed by a heavily depressed limiting current. These characteristics are in agreement with the theory of pulse polarography of adsorbed reactants[28,35,36]. The PP maximum current depends almost linearly on

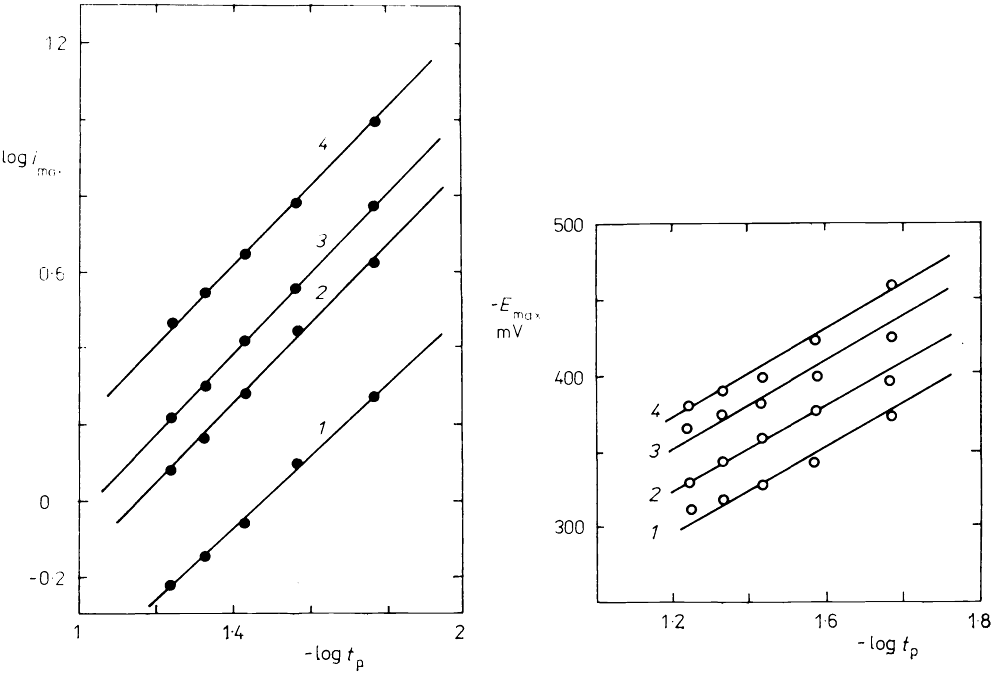

Fig. 7

Pulse polarography of UO_2^{2+} + H_2Sal + TBP system. The dependence of the logarithms of peak currents (*a*) and peak potentials (*b*) on the logarithms of pulse duration times. 6·2 . 10^{-5} mol/dm^3 UO_2^{2+} + 7·2 . 10^{-4} mol/dm^3 H_2Sal + 2 . 10^{-4} mol/dm^3 TBP in 0·7 mol/dm^3 $NaClO_4$, pH 3. DME, t_d(s): *1* 0·5; *2* 1; *3* 1·5; *4* 2 the mercury drop life-time ($\Delta \log(i_p)/\Delta \log(t_d) = 0{\cdot}91 \pm 0{\cdot}02$) what is rather unusual, but agrees well with the results of berberine measurements[36]. The dependences of the logarithms of PP maximum currents and of the potentials of PP maxima on the logarithms of the pulse duration time are shown in Figs 7*a* and 7*b*. The relationships between $\log(i_{\max})$ and $\log(t_p)$ and $E_{\max}$ and $\log(t_p)$ are both linear with the slopes -1 and 143 ± 3 mV/d.u., respectively. According to the theory[28,36], such relationships indicate a totally irreversible charge transfer from the adsorbed state. From the slope $\Delta E_{\max}/\Delta \log(t_p)$ the transfer coefficient of that reduction can be calculated: $\alpha = 0{\cdot}41 \pm 0{\cdot}1$.

Linear scan voltammograms of the synergistically adsorbed mixed complex exhibit a very sharp cathodic peak at −0·35 V vs Ag/AgCl. The peak current is linearly proportional to the scan rate. The dependence of the uranyl peak currents on the bulk concentrations of H_2Sal and TBP are displayed in Figs 8*a* and 8*b*. The voltammograms were recorded at the HMDE, but without any deliberate accumulation prior to the scan. The results are in agreement with the theoretical predictions (Figs 1*b* and 3).

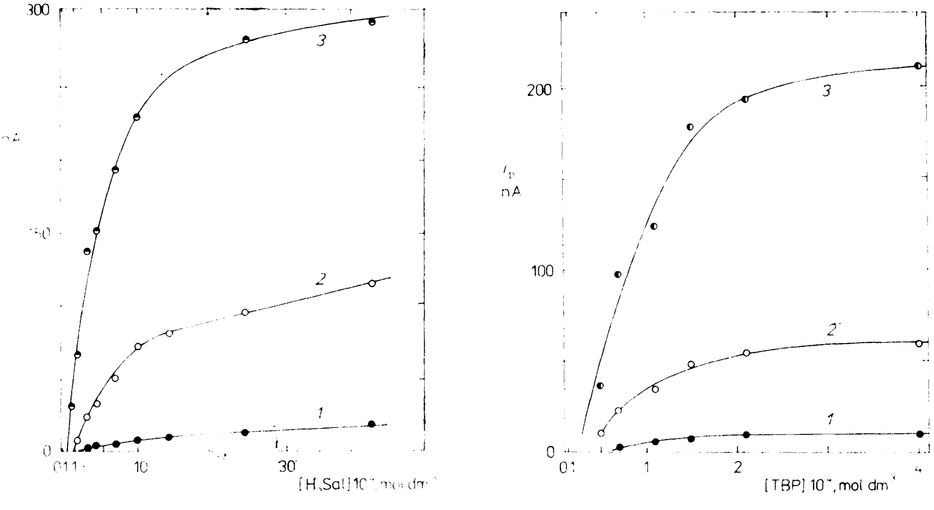

FIG. 8

The linear scan voltammetry of the system UO_2^{2+}–H_2Sal–TBP in 0·7 mol/dm³ $NaClO_4$, pH 3·2. The dependence of peak currents on the concentrations of H_2Sal (*a*) and TBP (*b*). [UO_2^{2+}] (mol dm^{-3}): *1* 6·2 . 10^{-6}; *2* 6·2 . 10^{-5}; *3* 6·2 . 10^{-4}. [TBP] = 2 . 10^{-4} mol/dm³ (*a*); [H_2Sal] = = 7·2 . 10^{-4} mol/dm³ (*b*). HMDE; no accumulation; $E_{\text{init}} = -0{\cdot}1$ V vs Ag/AgCl; scan rate −20 mV/s

APPENDIX

Equilibria in the Bulk of Solution

If only one complex species is formed:

$$\mathrm{M}^+ + \mathrm{e} \rightleftarrows \mathrm{ML} \qquad (A\text{-}I)$$

the equilibrium and the mass balance equations are:

$$K_1 = c^*_{\mathrm{ML}}/(c^*_{\mathrm{M}^+} c^*_{\mathrm{L}}) \qquad (A1)$$

$$c^*_{\mathrm{M}^+} + c^*_{\mathrm{ML}} = c^*_{\mathrm{M,tot}} \qquad (A2)$$

$$c^*_{\mathrm{ML}} + c^*_{\mathrm{L}} = c^*_{\mathrm{L,tot}} \qquad (A3)$$

The ionic species distribution is defined by:

$$c^*_{\mathrm{ML}} = (b - (b^2 - 4c^*_{\mathrm{L,tot}}c^*_{\mathrm{M,tot}})^{1/2})/2\,, \qquad (A4)$$

where: $b = c^*_{\mathrm{L,tot}} + c^*_{\mathrm{M,tot}} + K_1^{-1}$.

If a ligand is in a large excess:

$$c^*_{\mathrm{L}} = c^*_{\mathrm{L,tot}} \qquad (A5)$$

$$c^*_{\mathrm{M}^+} = c^*_{\mathrm{M,tot}}/(1 + K_1 c^*_{\mathrm{L,tot}}) \qquad (A6)$$

$$c^*_{\mathrm{ML}} = K_1 c^*_{\mathrm{L,tot}} c^*_{\mathrm{M,tot}}/(1 + K_1 c^*_{\mathrm{L,tot}})\,. \qquad (A7)$$

Simple, Anion-Induced Adsorption

A large excess of ligand is assumed. The electrode surface is assumed to be totally covered by the adsorbed species. The surface complexation reaction[3,26]:

$$\mathrm{M}^+_{x=0} + \mathrm{L}_{\mathrm{ads}} \rightleftarrows (\mathrm{ML})_{\mathrm{ads}} \qquad (A\text{-}II)$$

is defined by the equilibrium and the mass balance equations:

$$\lambda_1 = \gamma_{\mathrm{ML}}/(\gamma_{\mathrm{L}} c_{\mathrm{M}^+,x=0}) \qquad (A8)$$

$$\gamma_{\mathrm{L}} + \gamma_{\mathrm{ML}} f_{\mathrm{ML}} = \gamma_{\mathrm{m,L}}\,, \qquad (A9)$$

where: $f_{\mathrm{ML}} = \gamma_{\mathrm{m,L}}/\gamma_{\mathrm{m,ML}}$. The equilibrium is established when the diffusion stops and $c_{M^+,x=0} = c^*_{M^+}$, defined by Eq. (*A6*). The surface distribution is then defined by:

$$\gamma_{ML} = \lambda_1 \gamma_{m,L} c^*_{M,tot}/(1 + K_1 c^*_{L,tot} + \lambda_1 f_{ML} c^*_{M,tot}) \qquad (A10)$$

$$\gamma_L = (1 + K_1 c^*_{L,tot})\,\gamma_{m,L}/(1 + K_1 c^*_{L,tot} + \lambda_1 f_{ML} c^*_{M,tot})\,. \qquad (A11)$$

It has been shown[26] that the same relationship is obtained if the mechanism is regarded as a competitive adsorption of L and ML.

Accumulation of the Mixed Complex at the Electrode Surface in the Case of the Synergistic Adsorption from the Stirred Solution

The conditions (*c*) and (*f*) may be combined to:

$$D(c^*_{M,tot} - c_{M,tot,x=0})/\delta = d\gamma_{BML}/dt\,. \qquad (A12)$$

If the condition (*d*) is introduced to Eq. (*A12*), one obtains:

$$(S_1 - \gamma_{BML})(d\gamma_{BML}/dt) - \omega(S_1 - \gamma_{BML}) + z\gamma_{BML} = 0\,, \qquad (A13)$$

where $S_1 = \gamma_{B,max}/f_{BML}$, $z = D(\delta K_2 f_{BML})^{-1}$ and $\omega = Dc^*_{M,tot}/\delta$. By the substitution $y = (S_1 - \gamma_{BML})/S_1$ (where $y_0 = 1$ for $t = 0$) Eq. (*A13*) can be transformed to the integral equation:

$$y^2 + 2S_1^{-1}(\omega + z)\int_0^t y\,dt = 2ztS_1^{-1} + 1\,. \qquad (A14)$$

For the purpose of numerical integration, the time is divided in finite increments *d*. During one time increment the function *y* is constant:

$$y_k^2 + 2dS_1^{-1}(\omega + z)\,y_k = 2zkdS_1^{-1} + 1 - 2dS_1^{-1}(\omega + z)\sum_{i=1}^{k-1} y_i\,. \qquad (A15)$$

The solution of Eq. (*A15*) reads:

$$y_k = (-b + (b^2 - 4c_k)^{1/2})/2\,, \qquad (A16)$$

where $b = (2dD/\delta)\,(c^*_{M,tot} f_{BML} \gamma^{-1}_{B,max} + (K_2 \gamma_{B,max})^{-1})$ and

$$c_k = (2dD/\delta)\,k(K_2\gamma_{B,max})^{-1} + 1 - b\sum_{i=1}^{k-1} y_i\,.$$

The normalized surface concentration is equal to:

$$f_{BML}(\gamma_{BML})_k/\gamma_{B,max} = 1 - y_k\,. \qquad (A17)$$

This study is a contribution to the joint project of the Institute of Applied Physical Chemistry, Nuclear Research Center, Jülich, and Center for Marine Research Zagreb, "Rudjer Bošković" Institute Zagreb. Financial support by the International Bureau of KFA, Jülich, within the frame of the bilateral research agreement between S.F.R. Yugoslavia and F.R.G. is gratefully acknowledged.

In addition it was partially supported by the US National Science Foundation and Self-Management Council for Scientific Research of S.R. Croatia through funds made available from the US-Yugoslav Joint Board on Scientific and Technical Cooperation under the project JFP Nr 679.

LIST OF SYMBOLS

$c^*_{M^+}$, c^*_L, c^*_{ML}	the bulk concentrations of M^+, L^- and ML
c^*_B	bulk concentration of ligand B
$c_{M,tot}$, $c_{P,tot}$	total concentrations of the metal and the product of its redox reaction
$c^*_{M,tot}$, $c^*_{L,tot}$	total bulk concentrations of the metal and the ligand L
$c_{M^+,x=0}$, $c_{ML,x=0}$, $c_{P,x=0}$, $c_{PL,x=0}$	concentrations of M^+, ML, P and PL at the electrode surface
$c_{M,tot,x=0}$, $c_{M,tot,r=r_0}$, $c_{P,tot,x=0}$	total concentrations of the metal and the product at the electrode surface
D, D_P	diffusion coefficients
F	Faraday constant
f_{BML}, f_{ML}	conversion factors of the adsorbed complexes $(BML)_{ads}$ and $(ML)_{ads}$
i/nFS	normalized current density
K_1	stability constant of the dissolved complex ML
K_2	stability constant of the adsorbed mixed complex $(BML)_{ads}$
K_3	stability constant of the adsorbed complex $(BL)_{ads}$
n	number of electrons
r_0	radius of the mercury drop electrode
S	electrode surface area
t_{accum}	adsorptive accumulation time
α	transfer coefficient
β_B, β_L	adsorption constants of the ligands B and L
δ	diffusion layer thickness
γ_B, γ_L	surface concentrations of the adsorbed ligands B and L
γ_{BML}, γ_{ML}, γ_{BL}	surface concentrations of the adsorbed complexes $(BML)_{ads}$, $(ML)_{ads}$, and $(BL)_{ads}$
$\gamma_{B,max}$, $\gamma_{m,L}$, $\gamma_{BML,max}$, $\gamma_{m,ML}$	maximum surface concentrations of the ligands B and L and of the adsorbed complexes $(BML)_{ads}$ and $(ML)_{ads}$
γ_{max}	maximum surface concentration, common for several adsorbed species
λ_1	stability constant of the adsorbed complex $(ML)_{ads}$

REFERENCES

1. O'Dom G. W., Murray R. W.: Anal. Chem. *39*, 51 (1967); J. Electroanal. Chem. *16*, 327 (1968).
2. Caselli M., Papoff P.: J. Electroanal. Chem. *23*, 41 (1969).
3. Barclay D. J., Anson F. C.: J. Electrochem. Soc. *116*, 438 (1969); J. Electroanal. Chem. *28*, 71 (1970).

4. Kalvoda R., Anstine W., Heyrovský M.: Anal. Chim. Acta *50*, 93 (1970).
5. Berge H., Ringstorff H.: Anal Chim. Acta *55*, 201 (1971).
6. Ramley L., Dalziel J. A., Tan W. T.: Can. J. Chem. *59*, 3334 (1981).
7. Kalvoda R.: Anal. Chim. Acta *138*, 11 (1982).
8. Van Leeuwen H. P.: J. Electroanal. Chem. *133*, 201 (1982); *162*, 67 (1984).
9. Lubert K. H., Schnurrbusch M., Thomas A.: Anal. Chim. Acta *144*, 123 (1982).
10. Lam N. K., Kalvoda R., Kopanica M.: Anal. Chim. Acta *150*, 79 (1983).
11. Buffle J., Mota A. M., Simoes-Goncalves M. L. S.: J. Electroanal. Chem. *223*, 235 (1987).
12. Capodaglio G., Van den Berg C. M. G., Scarponi G.: J. Electroanal. Chem. *235*, 275 (1987).
13. Van den Berg C. M. G., Nimmo M.: Anal. Chem. *59*, 924 (1987).
14. Mlakar M., Branica M.: J. Electroanal. Chem. *257*, 269 (1988).
15. Mlakar M., Branica M.: Anal. Chim. Acta *221*, 279 (1989).
16. Irving H. M. N. H. in: *Solvent Extraction Chemistry*, p. 91. North Holland, Amsterdam 1967.
17. Subramanian M. S., Khopkar P. K., Shukla J. P., Pai S. A.: J. Inorg. Nucl. Chem. *36*, 3862 (1974).
18. Sato T.: J. Inorg. Nucl. Chem. *25*, 109 (1963); *26*, 311 (1964).
19. Marcus Y., Kolarik Z.: J. Inorg. Nucl. Chem. *38*, 1969 (1976).
20. Kalina D. G., Mason G. W., Horwitz E. P.: J. Inorg. Nucl. Chem. *43*, 159 (1981).
21. Irving H. M. N. H., Edgington D. N.: J. Inorg. Nucl. Chem. *15*, 158 (1960); *20*, 314 (1961); *21*, 169 (1961).
22. Rane A. T.: J. Inorg. Nucl. Chem. *42*, 1520 (1980).
23. Singh J. M., Tandon S. N.: J. Inorg. Nucl. Chem. *41*, 1205 (1979).
24. Akaiwa H., Kawamoto H.: J. Inorg. Nucl. Chem. *29*, 1345 (1967).
25. Akiba K.: J. Inorg. Nucl. Chem. *35*, 3323 (1973).
26. Lovrić M.: Anal. Chim. Acta, in press.
27. Aggett J., Grossley P.: J. Inorg. Nucl. Chem. *29*, 1113 (1967).
28. Lovrić M.: J. Electroanal. Chem. *170*, 143 (1984); *181*, 35 (1984); *197*, 49 (1986); *223*, 271 (1987).
29. Galus Z. in: *Fundamentals of Electrochemistry*, p. 116. Polish Scientific Publishers, Warsaw 1976.
30. Wopschall R. H., Shain I.: Anal. Chem. *39*, 1515 (1967).
31. Timmer B., Sluyters-Rehbach M., Sluyters J. H.: J. Electroanal. Chem. *18*, 93 (1968).
32. Wijnhorst C. A., Sluyters-Rehbach M., Sluyters J. H.: J. Electroanal. Chem. *87*, 17 (1978).
33. Lovrić M., Komorsky-Lovrić Š., Murray R. W.: Electrochim. Acta *33*, 739 (1988).
34. Lovrić M., Komorsky-Lovrić Š.: J. Electroanal. Chem. *248*, 239 (1988).
35. Flanagan J. B., Takahashi K., Anson F. C.: J. Electroanal. Chem. *85*, 257 (1977).
36. Komorsky-Lovrić Š., Lovrić M.: J. Electroanal. Chem. *190*, 1 (1985).
37. Flanagan J. B., Takahashi K., Anson F. C.: J. Electroanal. Chem. *81*, 261 (1977).
38. Lovrić M.: J. Electroanal. Chem. *218*, 77 (1987).
39. Angerstein-Kozlowska H., Klinger J., Conway B. E.: J. Electroanal. Chem. *75*, 45 (1977).
40. Laviron E. in: *Electroanalytical Chemistry* (A. J. Bard, Ed.), Vol. 12, p. 54. Marcel Dekker, New York 1982.
41. Mlakar M., Branica M.: Croat. Chem. Acta *60*, 325 (1987).
42. Krznarić D., Ćosović B., Branica M.: J. Electroanal. Chem. *33*, 61 (1971).