тонов, что, в свою очередь, также приводит к увеличению концентрации аниона $[AuCl_4^-]$.

Следует отметить, что с увеличением концентрации кислоты наблюдается незначительное уменьшение количества сорбированного золота (III). По всей видимости, при высоких концентрациях кислоты становится возможным конкурентное связывание иммобилизованным катионом $[КДБ18К6^+]$ хлорид-, нитрат- и перхлорат-анионов.

Сравнение констант хемосорбции золота (III) из водных растворов ПДБ18К6 (см. таблицу) с константами хемосорбции палладия (II) и платины (II), равными 121 ± 21 и 476 ± 92 моль$^{-1}$·л соответственно [2], свидетельствует о более прочном связывании иммобилизованным на поверхности катионом $[КДБ18К6^+]$ золотосодержащих анионов по сравнению с палладий- и платинусодержащими анионами.

Таким образом, хемосорбция иммобилизованным на поверхности краун-эфиром ДБ18К6 анионов $[PdCl_4^{2-}]$, $[PtCl_4^{2-}]$ и $[AuCl_4^-]$ может быть представлена как многостадийное субстрат-рецепторное взаимодействие. В данном случае одной из важнейших является стадия образования рецептора, которая включает в себя внедрение иона калия в полость краун-эфира. В результате последующего ионного взаимодействия между образовавшимся рецептором — катионом $[КДБ18К6^+]$ и субстратом — анионами $[PdCl_4^{2-}]$, $[PtCl_4^{2-}]$ и $[AuCl_4^-]$ образуется сложное соединение состава полимер — краун-эфир—ион калия—комплексный палладий (II), платину (II) и золото (III) содержащий анион.

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РЕЗЮМЕ. Вивчено сорбцію золота (III) з водних розчинів краун-ефіром ДБ18К6, іммобілізованим на поверхні полімерної матриці. Досліджено вплив кислотності розчинів та природи кислоти, що додається (HCl, HNO_3 та $HClO_4$), на термодинамічні параметри сорбції золота (III). Показано, що константа сорбції золота (III) полімернозв'язаним ДБ18К6 зменьшується в ряду $Cl^- > NO_3^- > ClO_4^-$. На підставі порівняння результатів сорбції $[AuCl_4^-]$ та ізоелектронних $[PdCl_4^-]$ та $[PtCl_4^-]$ полімернозв'язаним краун-ефіром ДБ18К6 встановлено, що ступінь зв'язування металу збільшується в ряду Pd (II)<Pt (II)<Au (III).

SUMMARY. Gold (III) chemisorption into polymer-supported crown-ester DB18C6 from aqueous solution has been investigated. Influence of solution acidity as well as nature of added acid (HCl, HNO_3 or $HClO_4$) upon thermodynamic parameters of gold (III) chemisorption have been studied. It has been shown that the constant of gold (III) chemisorption with polymer-supported DB18C6 decreases in the row $Cl^- > NO_3^- > ClO_4^-$. On the grounds of comparison of chemisorption results of $[AuCl_4^-]$ and isoelectronic $[PdCl_4^{2-}]$ and $[PtCl_4^{2-}]$ by polymer-supported DB18C6 it may be concluded, that metal sorption level increases in the row Pd (II)<Pt (II)<Au (III).

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NATURE OF BISTABLE STATES IN THE CASE OF ANODIC DISSOLUTION OF METALS IN MULTICOMPONENT ELECTROLYTES

A theoretical model is proposed, which describes the mechanism of the anodic dissolution of metals in multicomponent electrolytes. The relation between chemical reaction and transport processes may give rise to two stable states in the electrochemical system. It has been shown that in the case of controlling the rate of the mass transfer process

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in electrochemical systems with a number of components of ≥ 3, the outer Helmholtz plane potential may take on two values at the same electrode potential value. The question of the appearance of anodic dissolution limiting currents has been studied for electrolytes containing four sorts of ions with arbitrary charges and diffusion coefficients. The existence and magnitude of limiting current are also dependent on the charge of the complex formed.

The composition and concentration of electrolyte constituents, electrode potential, and the structure of double electrical layer affect [1] the rate of anodic dissolution of metals. Anodic dissolution and corrosion of metals give rise to concentration changes in the near-electrode layer [2], which may result in electrochemical-wave propagation [3—6]. The concentration changes may play [4] a determining role in the appearance of spatially distributed potential patterns at the interface. During the anodic dissolution of a metal, solution anions may form [1] with it intermediate complexes, which withdraw from the anode surface to the bulk electrolyte through a diffusion boundary layer. The diffusion control of electrodissolution is either by delivery of anions to the electrode or by the withdrawal of the complex formed from the electrode [7, 8].

Moreover it is known [9] that in the case of complex formation in the near-electrode layer of a multicomponent electrolyte, two different values of ligand concentration may correspond to the same electrode potential value at the same electrolysis conditions. It may be assumed that this effect is due to the fact that outer Helmholtz plane potential takes on two different values at the same electrode potential. In its turn, outer Helmholtz plane potential is determined by diffusion-migration processes in the near-electrode layer. Mass-transfer-controlled anodic dissolution of metals is important in some types of local corrosion, in electropolishing, and in electrochemical treatment [9]. Theoretical aspects of the diffusion kinetics of anodic metal dissolution involving complex formation are discussed in Ref [2] for solutions containing three sorts of ions.

In this paper, we present a mathematical model of stationary diffusion-migration transport in anodic metal dissolution involving formation of a complex with anion of solution containing four sorts of ions with arbitrary charges and diffusion coefficients and examine the reasons of the appearance of bistability.

Consider a stationary process of anodic dissolution of metal M in an electrolyte solution consisting of cations $K_1^{z_1}$, $K_2^{z_2}$ and anions A^{z_3}, which involves formation of ionic complex B^{z_4} as a result of the following electrode reaction:

$$M + aA^{z_3} \rightarrow bB^{z_4} + ne\,, \qquad (1)$$

where $n = bz_4 - az_3$.

In terms of the Nernst diffusion model, the set of equations of ionic mass transfer in anodic dissolution is of the form:

$$j_k = -D_k \frac{dc_k}{dx} - D_k z_k c_k \frac{F}{RT}\frac{dE}{dx}\,; \qquad (2)$$

$$\sum_{k=1}^{4} z_k c_k = 0\,, \qquad (3)$$

here j_k is diffusion flows of ions $K_1^{z_1}$, $K_2^{z_2}$, A^{z_3}, B^{z_4} and c_k, D_k are the local concentrations and diffusion coefficients of these ions, and E is the electric potential which is reckoned from bulk solution. F, R, and T have their usual meaning.

If we denote anode current density by i and assume that cations $K_1^{z_1}$ and $K_2^{z_2}$ are not involved in the electrode reaction, then the following expressions will be valid for flows j_k:

$$j_1 = 0;\ j_2 = 0;\ j_3 = -\frac{ai}{nF};\ j_4 = \frac{bi}{nF}\,. \qquad (4)$$

We shall assume that the current density i is related to the electrode potential E by the Folmer equation:

$$i = Knc_{3\,s}^{a}\cdot\exp\left[\frac{\alpha\, nF}{RT}(E_0 - E_s)\right], \qquad (5)$$

here K and α are constants, and the subscript s implies that the corresponding quantity must be taken at $x=0$.

The boundary conditions for the set of equations (3), (4) are of the form:

$$c_1 = c_{1\infty};\ c_2 = c_{2\infty};\ c_3 = c_{3\infty};\ c_4 = 0;\ E = 0, \qquad (6)$$

at $x=\delta$. Here δ is the Nernst diffusion layer thickness.

Let us introduce dimensionless variables:

$$y = \frac{x}{\delta};\quad C_k = \frac{c_k}{c_{3\,\infty}};\quad \Psi = \frac{FE}{RT};\quad J_k = \frac{j_k\delta}{D_k c_{3\,\infty}};\quad I = \frac{i\delta}{nFD_3 c_{3\,\infty}}\,. \qquad (7)$$

With dimensionless variables, the set of equations (2)—(3) and the boundary conditions (7) are written as:

$$\frac{dC_k}{dy} + z_k C_k \frac{d\Psi}{dy} + J_k = 0\,; \qquad (8)$$

$$\sum_{k=1}^{4} z_k C_k = 0\,; \qquad (9)$$

$$C_1^0 = \frac{c_{1\infty}}{c_{3\infty}};\quad C_2^0 = \frac{c_{2\infty}}{c_{3\infty}};\quad C_3^0 = 1;\quad C_4^0 = 0 \qquad (10)$$

at $y = 1$.

By multiplying all terms of eq (8) by z_k and summing with respect to k we obtain:

$$\frac{d\Psi}{dy} = -\frac{a(z_4 - \chi z_3)}{\chi} I \left(\sum_{k=1}^{4} z_k^2 C_k \right)^{-1}; \quad (11)$$

$$\chi = \frac{aD_4}{bD_3}. \quad (12)$$

The characteristic parameter χ of the set of equations depends on the ratio of the diffusion coefficients of the complex formed and electrolyte anion and stoichiometric coefficients of eq (1).

Following [2], we use the dimensionless potential as a new independent variable. From eqs (8)—(11) we obtain the set of equations:

$$\frac{dC_k}{d\Psi} + z_k C_k + \frac{J_k \chi}{a(z_4 - \chi z_3) I} \sum_{k=1}^{4} z_k^2 C_k = 0. \quad (13)$$

With the boundary conditions at $\Psi=0$

$$C_1^0 = \frac{c_{1\infty}}{c_{3\infty}}; \; C_2^0 = -\frac{z_3 + z_1 C_1^0}{z_2}; \; C_3^0 = 1; \; C_4^0 = 0. \quad (14)$$

The solution of the set of equations (13) with the boundary conditions (14) is of the form:

$$C_1 = C_1^0 \exp(-z_1 \Psi); \quad (15)$$

$$C_2 = C_2^0 \exp(-z_2 \Psi); \quad (16)$$

$$C_3 = a_{31}\exp(-z_1\Psi) + a_{32}\exp(-z_2\Psi) + a_{33}\exp\left[\frac{(\chi - 1) z_3 z_4}{z_4 - \chi z_3} \Psi\right]; \quad (17)$$

$$C_4 = a_{41}\exp(-z_1\Psi) + a_{42}\exp(-z_2\Psi) + a_{43}\exp\left[\frac{(\chi - 1) z_3 z_4}{z_4 - \chi z_3} \Psi\right]; \quad (18)$$

where:

$$a_{31} = C_1^0 \frac{z_1}{z_3} \frac{\chi z^*}{1 - \chi z^*}; \quad a_{32} = C_2^0 \frac{z_2}{z_3} \frac{\chi z^{**}}{1 - \chi z^{**}};$$

$$a_{33} = 1 - a_{31} - a_{32}; \quad a_{41} = -C_1^0 \frac{z_1}{z_4} \frac{1}{1 - \chi z^*};$$

$$a_{42} = -C_2^0 \frac{z_2}{z_4} \frac{1}{1 - \chi z^{**}}; \quad a_{43} = -a_{41} - a_{42};$$

$$z^* = \frac{z_3}{z_4} \frac{z_1 - z_4}{z_1 - z_3}; \quad z^{**} = \frac{z_3}{z_4} \frac{z_2 - z_4}{z_2 - z_3}.$$

Substituting the concentration distribution (15—(18) into eq (11), we find the potential distribution in the diffusion layer:

$$\frac{I a(1-y)}{\chi} z_4(1 - \chi z^*) = C_1^0(z_1 - z_4)(1 - e^{-z_1\Psi}) + C_2^0(z_2 - z_4)(1 - e^{-z_2\Psi}) + \frac{1}{(\chi - 1) z_3} \left\{ z_2 C_2^0 \left[(z_3 z^{**} \chi - z_4) \frac{1 - \chi z^*}{1 - \chi z^{**}} - \chi z_3 z^* \right] - z_3^2 - z_1 z_4 C_1^0 \right\} \left\{ 1 - \exp\left[\frac{(\chi - 1) z_3 z_4}{z_4 - \chi z_3} \Psi \right] \right\}. \quad (19)$$

Knowing the ion concentration distribution and potential distribution we can determine the current-voltage characteristic of the anodic dissolution process. The kinetic equation (5) may be rewritten with the dimensionless variables (7):

$$I = I_0 C_{3s}^a \exp[\alpha n(\Psi_0 - \Psi_s)], \quad (20)$$

where

$$I_0 = \frac{K\delta c_{3\infty}^{(a-1)}}{FD_3}.$$

Substituting expression (17) for C_{3s} into eq. (20) yields:

$$I = I_0 e^{\alpha n \Psi_0} \left\{ (1 - a_{31} - a_{32}) \exp\left\{ \left[\frac{(\chi - 1) z_3 z_4}{z_4 - \chi z_3} - \frac{\alpha n}{a} \right] \Psi_s \right\} + a_{31} \exp\left[-(z_1 + \frac{\alpha n}{a}) \Psi_s \right] + a_{32} \exp\left[-(z_2 + \frac{\alpha n}{a}) \Psi_s \right] \right\}^a. \quad (21)$$

The outer Helmholtz plane potential can be found by making use of eq (19) for potential distribution setting $y=0$:

$$I = \frac{1}{az_4} \frac{\chi}{(1 - \chi z^*)} \left\{ (z_1 - z_4) C_1^0 (1 - e^{-z_1\Psi}) + (z_2 - z_4) C_2^0 \frac{1 - \chi z^*}{1 - \chi z^{**}} (1 - e^{-z_2\Psi}) + \frac{1}{z_3(\chi - 1)} \left\{ z_2 C_2^0 \left[(\chi z_3 z^{**} - z_4) \frac{1 - \chi z^*}{1 - \chi z^{**}} - \chi z_3 z^* \right] - z_3^2 - z_1 z_4 C_1^0 \right\} \cdot \left\{ 1 - \exp\left[\frac{(\chi - 1) z_3 z_4}{z_4 - \chi z_3} \Psi_s \right] \right\} \right. \quad (22)$$

From eqs (21), (22) we derive functional dependence of outer Helmholze plane potential on electrode potential:

$$I_0 \exp[(\Psi_0 - \Psi_s)\alpha n] \left\{ a_{31} e^{-z_1\Psi_s} + a_{32} e^{-z_2\Psi_s} + (1 - a_{31} - a_{32}) \exp\left[\frac{(\chi - 1) z_3 z_4}{z_4 - \chi z_3} \Psi_s \right] \right\}^a = \frac{1}{az_1 z_4} \frac{\chi}{(1 - \chi z^*)} \left\{ (z_1 - z_4) C_1^0 (1 - e^{-z_1\Psi_s}) + (z_2 - z_4) C_2^0 \frac{1 - \chi z^*}{1 - \chi z^{**}} (1 - e^{-z_2\Psi_s}) + \frac{1}{z_3(\chi - 1)} \left\{ z_2 C_2^0 \left[(\chi z_3 z^{**} - z_4) \frac{1 - \chi z^*}{1 - \chi z^{**}} - \right. \right. \right. \quad (23)$$

$$-\chi z_3 z^*\Big] - z_3^2 - z_1 z_4 C_1^0\Big\}\cdot\Big\{1-\exp\Big[\frac{(\chi-1)z_3 z_4}{z_4-\chi z_3}\Psi_s\Big]\Big\}\Big\}.$$

Equations (22), (23) describes in parametric form the current-voltage characteristic of anodic metal dissolution involving complex formation. Relations (22), (23) obtained make it possible to investigate limiting current magnitudes in the case of anodic metal dissolution involving complex formation.

A condition for the appearance of limiting current is decrease to zero of the near-electrode concentration of anions directly involved in the metal dissolution reaction. Consider several cases.

1. *Formation of an anionic complex ($z_4<0$, $z_1=z_2=z$)*. This case is realized when the anion concentration at the anode surface is zero. The entire process is controlled by diffusion, i.e. by delivery of anions to the anode surface. From eq (17) we derive an expression for the potential at which limiting current appears:

$$\Psi_s^l = \frac{(z_4-\chi z_3)\ln\chi z^*}{z_4(z-z_3)(1-\chi z^*)}.$$

In this case, limiting current is:

$$I_{\lim} = \frac{(z-z_3)}{az(\chi-1)}[\chi-(\chi z^*)^n], \qquad (24)$$

where η is defined by the expression:

$$\eta = \frac{z_3(\chi-1)}{(z-z_3)(1-\chi z^*)}.$$

For $\chi\to 1$ and $z<0$, limiting current is:

$$I_{\lim} = \frac{z-z_3}{az}\Big[1+\frac{z_3 z_4}{z(z_4-z_3)}\ln\frac{z_4(z-z_3)}{z_3(z-z_4)}\Big]. \qquad (25)$$

Consider the case where $\chi z^*=1$. Limiting current will be:

$$I_{\lim} = \frac{\chi-(\chi z^*)^n}{\chi-1}\left(\frac{z-z_3}{az}\right). \qquad (26)$$

It should be noted that this limiting current is observed always when $z_4<0$ for any values of the χ parameter.

If the diffusion coefficient of the complex is much higher than that of anion ($\chi\to\infty$), the limiting current magnitude is determined by the charges of cations and anion:

$$I_{\lim} = \frac{z-z_3}{az}. \qquad (27)$$

2. *Formation of a cationic complex ($z_4>0$, $\chi>1$)*. In this case, the limiting current magnitude depends on the parameter χ and the charge values of cations and anion:

$$I_{\lim} = \frac{\chi}{\chi-1}\frac{z-z_3}{az}. \qquad (28)$$

As is evident from the above expressions in terms of the present mathematical model, addition of one more cation in the case of $z_1=z_2=z$ does not change the dependence of limiting current on the characteristic parameters of an electrochemical system in comparison with three-component solution [2].

3. *Formation of a neutral complex ($z_4=0$)*.

$$I_{\lim} = \frac{1}{az_3}\{C_1^0(z_3-z_1)+C_2^0(z_3-z_2)\}.$$

The outer Helmholz plane potential is the main variable for the description of dynamic instability and self-organization phenomena in an electrochemical system with nonlinear current-potential characteristics. Fig. 1 shows the theoretical dependence, calculated from eqs (21), (22), of outer Helmholtz plane potential on electrode potential for the case of anionic complex formation at the parameter values: $z_1=z_2=1$; $z_3=-1$; $z_4=-2$; $\alpha=1/2$; $n=-1$; $\chi=1/2$.

As is seen from fig. 1, a region exists in which the relation between electrode potential and outer Helmholtz plane potential is ambiguous. In this electrode potential range, a bistability may arise in an electrochemical system. Bistability is of frequent occurrence and corresponds to the situation in which a system can exist in two stable steady states at the same conditions. The presence of several stationary states in the case of anodic dissolution is associated with a complexation reaction at the interface and with mass transfer processes, which determine the potential value on the outer Helmholtz plane. The

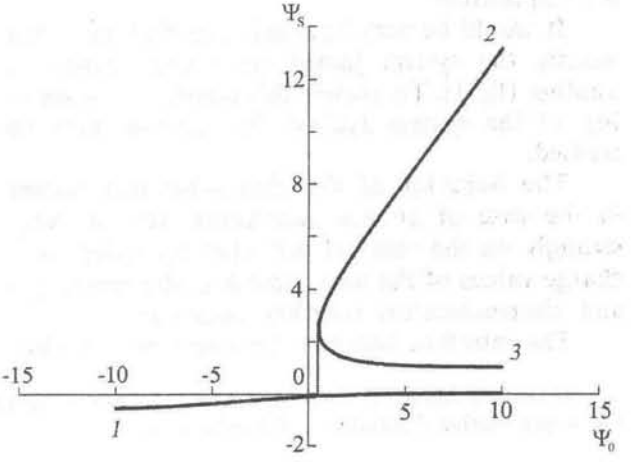

Fig. 1. The theoretical dimensionless dependence of outer Helmholtz plane potential Ψ_s on electrode potential Ψ_0 for the case of anionic complex formation.

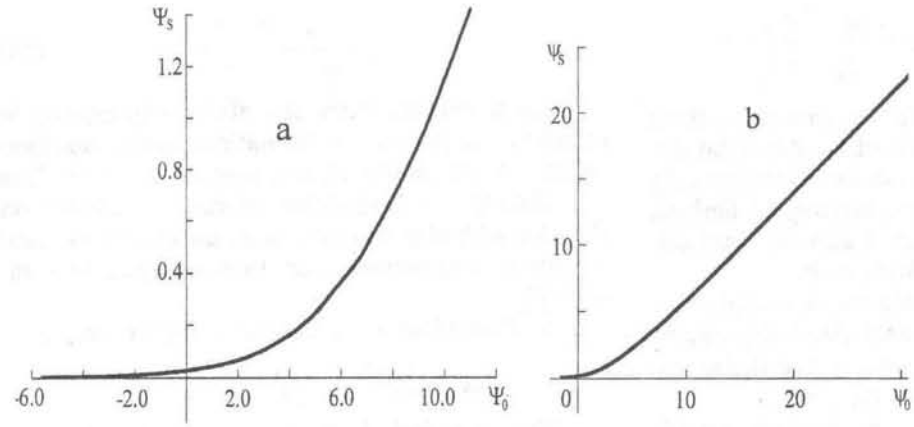

Fig. 2. The theoretical dimensionless dependence of outer Helmholtz plane potential Ψ_s on electrode potential Ψ_0 for the case of neutral (*a*) and cationic (*b*) complexes formation at the parameter values: *a* — $z_1=z_2=1$; $z_3=-1$; $z_4=0$; $\alpha=1/2$; $\chi=1/2$; *b* — $z_1=z_2=1$; $z_3=-1$; $z_4=1$; $\alpha=1/2$; $\chi=1/2$.

variation of outer Helmholtz plane potential through migration may affect greatly the concentration profile in the diffusion layer, which in turn may lead to variation of outer Helmholtz plane potential.

It should be noted that in the case of anionic complex formation, bistability is observed not always but only at certain values of the parameters that characterize the electrochemical system.

In the case of formation of a positive and a neutral complex, the relation between electrode potential and outer Helmholtz plane potential is unambiguous.

Fig. 2, *a* and *b* shows plots of outer Helmholtz plane potential against electrode potential for the case of formation of a neutral and a positive complex respectively.

It would be very interesting to find out when exactly the system jumps from one branch to another (fig 1). To answer this question, the stability of the system against fluctuations must be studied.

The behavior of the electrochemical system in the case of anodic dissolution depends very strongly on the ratio of diffusion coefficient and charge values of the ions present in the electrolyte and electrochemical reaction constants.

The interface between the electrode and electrolyte is decisive for the kinetics of any electrochemical reaction. Pattern formation in electrochemical systems occurs at the electrode / electrolyte interface and results from the interplay between interfacial kinetics and transport processes near the electrode surface.

РЕЗЮМЕ. Предложена математическая модель, описывающая механизм анодного растворения металлов в многокомпонентных электролитах. Связь между химической реакцией комплексообразования растворяющихся ионов металла с анионом раствора и транспортными процессами может обусловливать появление двух стабильных состояний в электрохимической системе. Показано, что в случае, когда скорость процесса контролируется массопереносом, в электрохимической системе с числом компонентов ≥3 потенциал внешней плоскости Гельмгольца может принимать два значения при одном и том же значении потенциала электрода. Исследованы условия появления предельного тока в зависимости от величины заряда образующегося комплекса в растворе, содержащем четыре сорта ионов.

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