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EFFECTS OF WATER AND SODIUM DODECYL SULFATE ADDITIVES ON Cr(III) IONS ELECTROREDUCTION IN A DEEP EUTECTIC SOLVENT

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Kinetics of Cr(III) ions electroreduction in a deep eutectic solvent (ethaline) was studied by using electrochemical impedance spectroscopy. The influence of water and sodium dodecyl sulfate on the kinetic parameters was established. The developed equivalent circuit included polarization resistance of the electrochemical reaction, constant phase element and finite Warburg impedance. The respective parameters of the accepted equivalent circuit were calculated and discussed. The obtained results indicated that the charge transfer is a rate-determining step of an electrochemical reaction occurring on a heterogeneous electrode surface. An increase in content of water in electrolytes resulted in an increase in polarization resistance, indicating the deceleration of Cr(III) ions electroreduction due to the changes in Cr(III) speciation. In addition, the introduction of extra water caused an increase in the value of a capacitive component of electrochemical impedance because of a rearrangement of the double electrical layer. The polarization resistance of Cr(III) ion discharge was increased in the presence of sodium dodecylsulfate in electrolyte due to adsorption of dodecylsulfate anion on the electrode surface. A Warburg impedance component disappeared in electrolytes containing relatively high water content, which was associated with corresponding reduction of solution viscosity and acceleration of diffusion mass transfer.

Keywords: electroreduction, Cr(III) ion, electrochemical impedance, deep eutectic solvent, sodium dodecylsulfate, water.

Introduction

Deep eutectic solvents (DESs) is an emerging type of ionic liquids which is characterized by availability, low prices, ecological compatibility and a unique complex of physicochemical properties that are superior to those typical of both common organic solvents and water-based systems [1,2]. Kinetics and mechanism of electrochemical reduction of different metal ions in DES-based electrolytes were under consideration in a number of recent publications [3,4]. A special attention was paid to the electrochemical reduction of Cr(III) ions [5−9], since this reaction is an integral part of the total process of electrodeposition of chromium from trivalent chromium plating bath that is of paramount importance in the light of development of novel high-performance and eco-friendly metal finishing processes [10−13].

Earlier, the features of electroreduction of Cr(III) ions in a DES, ethaline (an eutectic mixture of choline chloride and ethylene glycol), and water− ethaline mixtures were studied on a glassy carbon electrode [14]. Some kinetics characteristics were determined based on the registered voltammetry responses. It was established that the addition of extra water to the DES-based electrolyte appreciably affects the kinetics of charge transfer in electrochemical couple Cr(III)/Cr(II) as well as the transport characteristics of the ionic liquid under consideration. Thus, water can be considered a special additive to DES-containing plating electrolytes [3,6,7,10,11,14]. In addition, the application of traditional organic surfactants is of great interest, because they could strongly and favorably influence separate stages of an electrochemical process of metal deposition [12]. Unfortunately, there are no data on the effects of surfactants on the kinetics of Cr(III) ion electroreduction in DES-based electrochemical systems.

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The investigation of Cr(III) ions discharge was performed in a number of previous studies [6−10,14] by means of cyclic and linear voltammetry technique. However, the capabilities of this method are restricted; for instance, it cannot give detailed information about the state of the electrode surface. In this context, electrochemical impedance spectroscopy attracts close attention, since it allows determining exhaustive parameters of the electrochemical process and the state of the electrode surface even in cases of exclusively complicated reactions mechanisms.

Therefore, the aim of this work was to investigate the kinetics of Cr(III) ion electroreduction in DES-based electrochemical systems by means of electrochemical impedance spectroscopy technique. We established the effect of extra water on kinetic parameters of electrochemical reaction. In addition, we studied the influence of sodium dodecylsulfate (SD) on the rate of Cr(III) reduction. The choice of SD for our investigation was due to the fact that it is a typical surfactant used in trivalent chromium plating electrolytes [12]. The effects of various surfactants on the kinetic of electrochemical processes occurring in DES-based systems have been studied insufficiently.

Experimental

A eutectic mixture of choline chloride and 1,2-ethanediol (in the molar ratio of 1:2, respectively) was used in this study. This DES is also known as ethaline [1−3]. The preparation of ethaline and Cr(III)-containing electrolyte based on ethaline was described elsewhere [14]. The content of residual moisture in ethaline was determined by Karl Fischer method and did not exceed 1%. Sodium dodecylsulfate and water were dissolved directly in DES-based electrolytes.

Electrochemical measurements were conducted in a thermostated glass three-electrode cell at the temperature of 298 K. An end face of a glassy carbon disk electrode (∅ 5 mm) was used as a working electrode, the electrode being embedded into Teflon cylinder. The surface of glassy carbon disk electrode was mechanically polished with alumina slurry, treated in hydrochloric acid solution for several minutes, washed with bidistilled water and dried. Then the electrode was inserted into an electrochemical cell. Pt gauze served as a counter electrode. The electrode potentials were registered against a silver wire pseudo-reference electrode [14].

Potentiostat Reference 3000 (Gamry) with automatic compensation of ohmic potential drop was applied to carry out electrochemical investigations. The electrochemical impedance spectra were recorded at open circuit potential at the AC voltage amplitude of 5 mV in the frequency range of 0.01 Hz to 100 kHz. The obtained results were treated by Gamry Elchem Analyst software.

Results and discussion

Effect of water additive

Figure 1 demonstrates Nyquist plots recorded in Cr(III)-containing ethaline at different content of water. As can be seen, Nyquist plots are flattened semicircles, which indicates that the charge transfer is a rate-determining step of an electrochemical reaction occurring on a heterogeneous electrode surface. Only for electrolyte without extra water (Fig. 1, curve 1), electrochemical impedance spectrum exhibits diffusion behavior at low frequencies revealing the presence of Warburg impedance.

To fit the obtained data, an equivalent circuit was used (inset in Fig. 1) which contains ohmic resistance of solution (R_s), polarization resistance of the electrochemical process (R_{ct}), constant phase element (CPE) and finite Warburg impedance (W_D). The calculated parameters of the adopted equivalent circuit are summarized in Table 1 as a function of water content in electrolyte.

An increase in water content in DES-based electrolyte results in an increase in polarization resistance, R_{ct}, caused by deceleration of Cr(III) ions electroreduction. This observation is in good
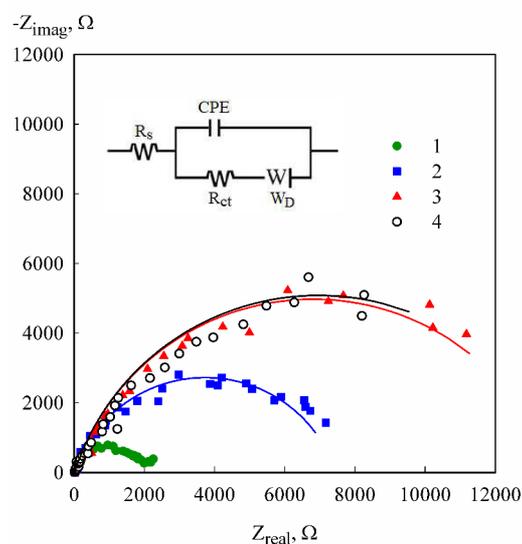

Figure 1. Nyquist plots recorded in solutions containing 0.05 M CrCl₃·6H₂O in ethaline at different content of extra water: 1 − without extra water, 2 − 10%, 3 − 15%, 4 − 20%. Inset presents equivalent circuit used for simulating the electrochemical impedance of a solid electrode/solution interface

Table 1

Calculated parameters of electrochemical impedance for the systems containing 0.05 M CrCl$_3$·6H$_2$O in ethaline at different content of water

Water content, %	R_s, Ω	R_{ct}, kΩ cm^2	$Q \cdot 10^6$, Ω^{-1} s^n cm^{-2}	n	$Y_W \cdot 10^3$, Ω^{-1} s$^{1/2}$	B, s$^{1/2}$
–	9.40	1.95	70	0.805	7.36	55.6
10	7.20	7.45	230	0.804	–	–
15	5.15	13.60	240	0.804	–	–
20	3.70	13.90	400	0.804	–	–

agreement with the findings reported earlier[1] [14], according to those a decrease in the rate of charge transfer is associated with the changes in Cr(III) ions speciation. The introduction of water causes a gradual substitution of Cl$^-$ anions with water molecules in the first coordination sphere of chromium-containing complex ions [7]. The formation of chloride complexes promotes the charge transfer in the electrochemical reaction Cr(III)+e$^-$→Cr(II), whereas aqua complexes of Cr(III) are discharged relatively slowly.

Considering the effect of water on the parameters characterizing the constant phase element, it should be noted that the electrochemical impedance of the CPE is expressed by the following equation:

$$Z_{CPE} = \left[Q(j\omega)^n \right]^{-1},$$

where Q is a constant reflecting the capacitive component of electrochemical impedance, $j = \sqrt{-1}$ is the imaginary unit, $\omega = 2\pi f$ is the angular frequency, and n is the dimensionless empirical parameters denoting a phase deviation.

Commonly, the value of n is attributed to the energy and geometric heterogeneity of the electrode surface. As expected, the change in water content has no effect on this parameter, since the state of the glassy carbon electrode cannot be altered by the introduction of water. The calculated value of n is about 0.8, which is appreciably less than unity, indicating that the surface of a glassy carbon electrode used in this work deviates from the state of a completely homogeneous electrode.

It should be observed that the value of Q, which is usually ascribed to the capacitive component of electrochemical impedance, is increased with increasing water concentration (Table 1). The value of Q obtained for the systems without extra water is close to that reported earlier for differential capacity of solid electrodes in some deep eutectic solvents [15]. However, parameter Q grows when the content of water in electrolytes increases. It might be supposed that a gradual substitution of ions and/or molecules of organic constituents in a double electrical layer by water molecules, having higher dielectric constant, causes an observed increase in the capacitive component Q. Thus, the changes in Q parameter can be associated with a rearrangement of the double electrical layer.

As far as a finite Warburg impedance is concerned, it can be given as follows:

$$Z_W = \frac{1}{Y_W} \tanh\left[B\sqrt{j\omega} \right],$$

where Y_W is a constant, and $B = \frac{\delta}{\sqrt{D}}$, where δ is the thickness of the diffusion layer and D is the diffusion coefficient.

Our calculations show the presence of a Warburg impedance component for the solutions without any extra water. This may be due to a decelerated diffusion of Cr(III) ions to the electrode surface. However, all these diffusion limitations disappear in electrolytes containing additional water, which is resulted from a corresponding reduction of solution viscosity and acceleration of diffusion mass transfer [6,14]; accordingly, a Warburg impedance component vanishes.

Effect of sodium dodecylsulfate additive

Electrochemical impedance spectra obtained in DES-based electrolytes containing sodium dodecylsulfate at various water contents are shown in Fig. 2. Their shape is similar to that presented in Fig. 1, implying that the above equivalent circuit is also valid in this case. The calculated parameters of electrochemical impedance are given in Table 2.

As would be expected, the variation in SD content in electrolytes had no effect on the value of dimensionless empirical parameter n. At the same time, an increase in the SD concentration caused a decrease in the values of capacitive component Q,

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[1] The corresponding polarization curves showing the effect of water on the kinetics of Cr(III) electroreduction can be seen in ref. [14].
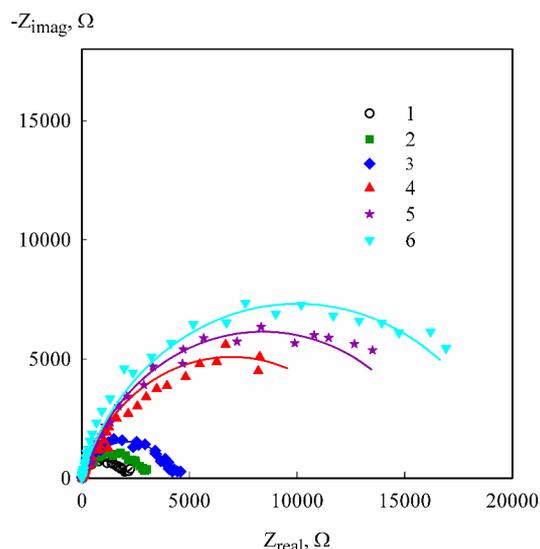
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Figure 2. Nyquist plots recorded in solutions containing 0.05 M $CrCl_3 \cdot 6H_2O$ in ethaline at different content of sodium dodecylsulfate (mol m^{-3}): 1 and 4 − without SD; 2 and 5 − 0.001; 3 and 6 − 0.05. The content of water: 1, 2 and 3 − without extra water; 4, 5 and 6 − 20%

which can be caused by the adsorption of dodecylsulfate anion on the electrode surface. Other conditions being equal, the introduction of additional water led to an increase in the value of parameter Q (Table 2).

It should be observed that the introduction of sodium dodecylsulfate into the DES-based electrolyte results in an increase in the polarization resistance of electrochemical reaction $Cr(III)+e^-\rightarrow Cr(II)$. The polarization curves registered in the same electrolytes confirm this conclusion (Fig. 3). Indeed, their ascending (exponential) cathodic segments corresponding to slow charge transfer shift towards negative potentials, indicating deceleration of electrochemical process, both in electrolytes without any extra water and in those containing some extra water. We think that the obtained results can be interpreted in terms of adsorption of dodecylsulfate anion on the electrode surface leading to inhibition of cathodic reaction.

Let us note that the adsorption of an anionic surfactant in the course of electroreduction of cations

Table 2

Calculated parameters of electrochemical impedance for the systems containing 0.05 M $CrCl_3 \cdot 6H_2O$ in ethaline at different contents of water and sodium dodecylsulfate

Content of water, %	Content of sodium dodecyl sulfate, mol dm^{-3}	R_s, Ω	R_{ct}, $k\Omega$ cm^2	$Q \cdot 10^6$, Ω^{-1} s^n cm^{-2}	n	$Y_W \cdot 10^3$, Ω^{-1} s$^{1/2}$	B, s$^{1/2}$
−	−	9.40	1.95	70	0.805	7.36	55.6
−	0.001	9.35	2.78	40	0.804	7.07	40.6
−	0.05	9.30	4.15	25	0.804	6.71	37.6
20	−	3.70	13.90	400	0.804	−	−
20	0.001	3.60	16.80	220	0.804	−	−
20	0.05	3.60	20.00	160	0.804	−	−

a

b
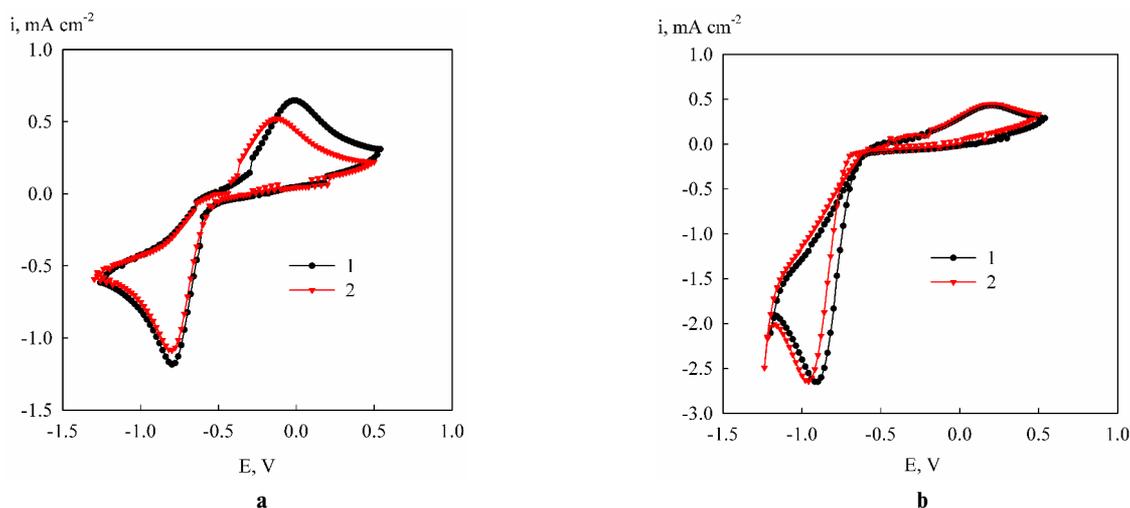
Figure 3. Polarization curves recorded on glassy carbon electrode in solutions containing 0.05 M $CrCl_3 \cdot 6H_2O$ in ethaline at different content of sodium dodecylsulfate: 1− without SD; 2 − 0.001 mol m^{-3}. The content of water: a − without extra water; b − 20%. Scan rate 50 mV s^{-1}

implies several different effects [16]: inhibiting steric factor, change in the potential in the localization plane of the activated complex, and the electrostatic and chemical interactions of the activated complex with the adsorption layer. In our opinion, the inhibition steric factor prevails in the case under study.

The presence of Warburg impedance component was observed for the systems without extra water. At higher water content, Warburg impedance disappeared completely due to elimination of mass transfer limitations (see above).

Conclusions

The effect of water and a typical surfactant, sodium dodecylsulfate, on the kinetics of the electroreduction of Cr(III) ions in a deep eutectic solvent, ethaline, was studied by electrochemical impedance spectroscopy using a glassy carbon electrode. Ii was shown that the rate of electrochemical reaction is controlled by the charge transfer and occurs on heterogeneous electrode surface. The introduction of extra water into the DES-based system causes an increase in polarization resistance of the charge transfer, indicating the deceleration of Cr(III) ions electroreduction. This effect is associated with changes in Cr(III) speciation.

DES-based system without any additional water demonstrated the presence of a Warburg impedance component implying some diffusion limitations. Due to a decrease in electrolyte viscosity, a Warburg impedance component vanished in electrolytes containing extra water.

The introduction of sodium dodecylsulfate resulted in a deceleration of Cr(III) electroreduction because of adsorption of dodecylsulfate anion on the electrode surface. The inhibitory action of sodium dodecylsulfate was observed both in electrolytes without extra water and in solution containing some additional water.

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ВПЛИВ ДОБАВОК ВОДИ І НАТРІЙ ДОДЕЦИЛСУЛЬФАТУ НА ЕЛЕКТРОВІДНОВЛЕННЯ ІОНІВ Cr(III) В НИЗЬКОТЕМПЕРАТУРНОМУ ЕВТЕКТИЧНОМУ РОЗЧИННИКУ

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Кінетика електровідновлення іонів Cr(III) в низькотемпературному евтектичному розчиннику (ethaline) була досліджена методом спектроскопії електродного імпедансу. Встановлено закономірності впливу води і натрій додецилсульфату на кінетичні параметри. Запропонована еквівалентна електрична схема, що включає поляризаційний опір електрохімічної реакції, елемент сталої фази і кінцевий імпеданс Варбурга. Обчислені і обговорені відповідні параметри прийнятої еквівалентної схеми. Одержані результати вказують на те, що уповільненою стадією електрохімічної реакції є перенесення заряду, що відбувається на гетерогенній електродній поверхні. Збільшення вмісту води в електролітах приводить до зростання поляризаційного опору, вказуючи на гальмування електровідновлення іонів Cr(III) унаслідок змін у складі комплексів Cr(III). Окрім того, введення додаткової води викликає збільшення значення ємнісного компонента електродного імпедансу у зв'язку із перебудовою подвійного електричного шару. Поляризаційний опір розряду іонів Cr(III) підвищувався за присутності натрій додецилсульфату в електроліті унаслідок адсорбції додецилсульфат-аніоном на електродній поверхні. Імпеданс Варбурга зникає у електролітах, що містять відносно велику кількість води, що пов'язане із відповідним зниженням в'язкості розчину і прискоренням дифузійного масоперенесення.

Ключові слова: електровідновлення; іони Cr(III); електродний імпеданс; низькотемпературний евтектичний розчинник; натрій додецилсульфат; вода.

EFFECTS OF WATER AND SODIUM DODECYL SULFATE ADDITIVES ON Cr(III) IONS ELECTROREDUCTION IN A DEEP EUTECTIC SOLVENT

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Kinetics of Cr(III) ions electroreduction in a deep eutectic solvent (ethaline) was studied by using electrochemical impedance spectroscopy. The influence of water and sodium dodecyl sulfate on the kinetic parameters was established. The developed equivalent circuit included polarization resistance of the electrochemical reaction, constant phase element and finite Warburg impedance. The respective parameters of the accepted equivalent circuit were calculated and discussed. The obtained results indicated that the charge transfer is a rate-determining step of an electrochemical reaction occurring on a heterogeneous electrode surface. An increase in content of water in electrolytes resulted in an increase in polarization resistance, indicating the deceleration of Cr(III) ions electroreduction due to the changes in Cr(III) speciation. In addition, the introduction of extra water caused an increase in the value of a capacitive component of electrochemical impedance because of a rearrangement of the double electrical layer. The polarization resistance of Cr(III) ion discharge was increased in the presence of sodium dodecylsulfate in electrolyte due to adsorption of dodecylsulfate anion on the electrode surface. A Warburg impedance component disappeared in electrolytes containing relatively high water content, which was associated with corresponding reduction of solution viscosity and acceleration of diffusion mass transfer.

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