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FULL PAPER

The Theoretical Description for Magnesium Chlorate Electrochemical Determination on a Magnezone-XC Modified Electrode

Volodymyr V. Tkach*[a], Marta V. Kushnir[a], Sílvio C. de Oliveira[b], Dilfuza M. Musayeva[c], Hanifa Zh. Salomova[c], Yana G. Ivanushko[a,d], Oleksandra V. Ahafonova[d], Petro I. Yagodynets´[a], Zholt O. Kormosh[e], Olga V. Luganska[f], Zoya O. Gagolkina[g]

[a]Chernivtsi National University, 58012, Kotsyubyns'ky Str., 2, Chernivtsi, Ukraine.
[b]Universidade Federal de Mato Grosso do Sul, Av. Sen. Felinto. Müller, 1555, C/P. 549, 79074-460, Campo Grande, MS, Brazil.
[c]Abu Ali Ibn Sino Bukhara State Medical Institute, 705018, Navoi Str. 1, Bukhara, Uzbekistan.
[d]Bukovinian State Medical University, 58001, Teatralna Sq., 9, Chernivtsi Ukraine.
[e]East Ukrainian National University, 43000, Voli Ave., 13, Lutsk, Ukraine.
[f]Zaporizhzhia National University, 69600, Zhukovsky Str. 66, Zaporizhzhia, Ukraine.
[g]Institute of Macromolecules, NAS of Ukraine, 02160, Kharkiv Highway, 50, Kyiv, Ukraine.

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Abstract:

An interesting electroanalytical process for magnesium chlorate electrochemical determination has been described theoretically. The process involves the complex formation of magnesium cation with the azo dye Magnezone XC and the electropolymerization of the resulting complex compound in the presence of the chlorate-ion by two parallel mechanisms. The correspondent mathematical model has been developed and analyzed by means of linear stability theory and bifurcation analysis. It has been shown that from both electroanalytical and electrosynthetical points of view the system is efficient. The linear dependence between the electrochemical parameter and salt concentration is obtained easily, and the material formed during the electroanalytical process is highly conductive and catalytic. On the other hand, the oscillatory behavior in this system will be caused by double electric layer influences on both complexation and electropolymerization stages.

Keywords: intoxication prevention; pesticide; magnesium chlorate; magnezone XC; complexation; electropolymerization

1. Introduction

Magnesium chlorate [1-4] is one of the widely used inorganic pesticides. It is used as secant and defoliant agents in beans, cotton and sunflower. Its structure is described on the Fig. 1.

Its mechanism of action is based on its hydroscopic properties. As it forms crystallohydrates with the water molecules, it literally "dries" the leaves of the undesirable plant, leading to its degeneration [3-4]. Nevertheless, while taken in excess, it is may influence not only the weed, but also the cultural plants. Also, it is highly toxic to animals and humans, as the chlorate-ion is a strong oxidant [5-8]. Therefore, the development of the method for determination of magnesium chlorate is really actual [7-8], and the electroanalytical methods, which have already been used for both magnesium and chlorate ions [7-10], could give an interesting service.

The classical method for the magnesium cation determination consists in its complexation with magnezone azo dye group [11-12]. One of these dyes is Magnezone XC, one of Sudan dyes (Fig. 2).

It may be adapted for the electrochemical

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[*] Corresponding author. E-mail: nightwatcher2401@gmail.com

determination of magnesium cations. Furtherly, the magnezone XC complex may electropolymerize, as in [13 – 15], leading to the appearance of a novel material, also capable to assist the electroanalytical processes.

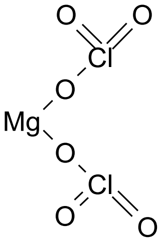

Figure 1. Magnesium chlorate.

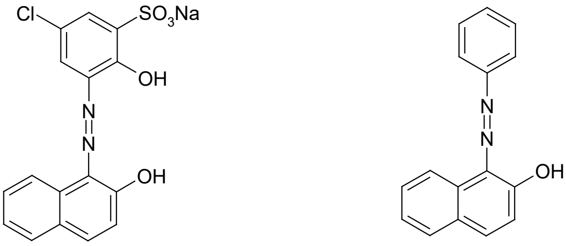

Figure 2. Magnezone XC (left) and sudan I (right).

Nevertheless, the development of novel electroanalytical systems with the new analytes may be impeded by:

- the indecision concerning the exact mechanism of chemical and electrochemical reactions;

- necessity of determination of the parameter region, correspondent to the most efficient active substance and mediating action;

- the presence of electrochemical instabilities, yet described for the electropolymerization processes [16-18].

The mentioned problems may only be solved by means of an analysis of a mathematical model, capable to describe adequately the neotame electrochemical determination Moreover, it is also capable compare the behavior of this system with that for the similar ones without any experimental essay.

So, the goal of this work is the mechanistic theoretic analysis of the magnesium chlorate electrochemical determination, assisted by Magnezone XC-modified electrode. In order to achieve it, we realize the specific goals:

- suggestion of the mechanism of the reaction consequence, leading to the appearance of analytical signal;

- development of the balance equation mathematical model, correspondent to the electroanalytical system;

- analysis and interpretation of the model in terms of the electroanalytical use of the system;

- the seek for the possibility of electrochemical instabilities and for the factor, causing them;

- the comparison of the mentioned system´s behavior with the similar ones [19-21].

2. Material and Methods

2.1 System and its Modeling

In this system, the magnezone XC firstly reacts with magnesium cation, yielding a complex, which is furtherly polymerized. The complex compound is more electrochemically active than the original dye for three reasons:

- the donor effect of magnesium reduces its polymerization potential;

- the ionic interaction within the complex compound makes it more conducting;

- the overvoltage is much lower in a complex compound than in a dye-covered surface.

Therefore, the electroanalytical process will be depicted as on the Fig. 3.

In order to describe the behavior of this electroanalytical process, we introduce three variables:

m – magnesium cations concentration in the pre-surface layer;

c – chlorate anions concentration in the pre-surface layer;

b – complex compound surface coverage degree.

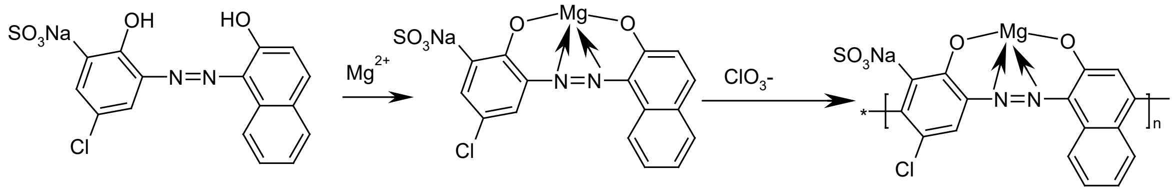

Figure 3. The scheme of the electroanalytical process.

To simplify the modeling, we suppose that the reactor is intensively stirred, so we can neglect the convection flow. Also we assume that the background electrolyte, containing neither magnesium nor perchlorate nor other interfering ions (e.g., sodium sulfate), is in excess, so we can neglect the migration flow. The diffusion layer is supposed to be of a constant thickness, equal to δ, and the concentration profile in it is supposed to be linear.

It is possible to show that the behavior of the electrochemical system may be described by the trivariant equation-set, exposed as:

$$\begin{cases} \frac{dm}{dt} = \frac{2}{\delta}\left(\frac{M}{\delta}(m_0 - m) - r_c\right) \\ \frac{dc}{dt} = \frac{2}{\delta}\left(\frac{C}{\delta}(c_0 - c) - r_{p1} - r_{p2}\right) \\ \frac{db}{dt} = \frac{1}{B}\left(r_c - r_{p1} - r_{p2}\right) \end{cases} \tag{1}$$

Herein, M and C are cation and anion diffusion coefficients, m_0 and c_0 are their bulk concentrations, B is the complex compound maximal surface concentrations and the parameters r are complexation and polymerization rates, described as:

$$r_c = k_c m(1-b)\exp(\alpha b) \tag{2}$$

$$r_{p1} = k_{p1} b^x c^y \exp\left(\frac{(2x-2)F\varphi_0}{RT}\right) \tag{3}$$

$$r_{p2} = k_{p2} b^z c^w \exp(-\alpha b) \tag{4}$$

in which the parameters k are rate constants of the reactions, x, y, z and w are reaction orders, α is the derivative, describing the double electric layer (DEL) structural changes during the chemical and electrochemical stages, F is the Faraday number, φ_0 is the potential slope in DEL, relative to the zero-charge potential, R is the universal gas constant, and T is the absolute temperature.

Compared to the similar system [19 – 21], this will be somehow more interesting, as it is combining the electroanalysis with electrosynthesis. Its behavior will be somehow similar to that observed during the isoproturon and sudan dyes electrochemical determination simultaneously [19 - 20], but somehow less dynamic and more efficient, as shown below.

3. Results and Discussion

In order to investigate the magnesium chlorate Magnezone XC-assisted electrochemical determination, we analyze the equation-set (1) by means of linear stability theory. The steady-state Jacobian matrix members will be exposed as:

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{23} & a_{33} \end{pmatrix} \tag{5}$$

Herein,

$$a_{11} = \frac{2}{\delta}\left(-\frac{M}{\delta} - k_c(1-b)\exp(\alpha b)\right) \tag{6}$$

$$a_{12} = 0 \tag{7}$$

$$a_{13} = \frac{2}{\delta}\left(k_c m \exp(\alpha b) - \alpha k_c m(1-b)\exp(\alpha b)\right) \quad (8)$$

$$a_{21} = 0 \quad (9)$$

$$a_{22} = \frac{2}{\delta}\left(-\frac{C}{\delta} - y k_{p1} b^x c^{y-1} \exp\left(\frac{(2x-2)F\varphi_0}{RT}\right) - w k_{p2} b^z c^{w-1} \exp(-\alpha b)\right) \quad (10)$$

$$a_{23} = \frac{2}{\delta}\left(-x k_{p1} b^{x-1} c^y \exp\left(\frac{(2x-2)F\varphi_0}{RT}\right) + j k_{p1} b^x c^y \exp\left(\frac{(2x-2)F\varphi_0}{RT}\right) - z k_{p2} b^{z-1} c^w \exp(-\alpha b) + \alpha\, k_{p2} b^z c^w \exp(-\alpha b)\right) \quad (11)$$

$$a_{31} = \frac{1}{B}\left(k_c(1-b)\exp(\alpha b)\right) \quad (12)$$

$$a_{32} = \frac{1}{B}\left(-y k_{p1} b^x c^{y-1} \exp\left(\frac{(2x-2)F\varphi_0}{RT}\right) - w k_{p2} b^z c^{w-1} \exp(-\alpha b)\right) \quad (13)$$

$$a_{33} = \frac{1}{B}\left(-k_c m \exp(\alpha b) + \alpha k_c m(1-b)\exp(\alpha b) - x k_{p1} b^{x-1} c^y \exp\left(\frac{(2x-2)F\varphi_0}{RT}\right) + j k_{p1} b^x c^y \exp\left(\frac{(2x-2)F\varphi_0}{RT}\right) - z k_{p2} b^{z-1} c^w \exp(-\alpha b) + \alpha\, k_{p2} b^z c^w \exp(-\alpha b)\right) \quad (14)$$

As in the similar systems [19-21], the *oscillatory behavior* in this system, relatively probable. It is explained by the DEL influences of electrochemical and both of the chemical stages stages.

The formation of the complex compound and its chemical and electrochemical polymerization in the presence of an anion present in the solution leads to the cyclic changes of DEL ionic forces and, consequently, of its conductivity. Therefore, the oscillatory behavior will be realized due to them. Mathematically, it will be described by the positivity of the elements $\alpha k_c m(1-b)\exp(\alpha b) > 0$ and $\alpha\, k_{p2} b^z c^w \exp(-\alpha b) > 0$, if $\alpha > 0$, like also of $j k_{p1} b^x c^y \exp\left(\frac{(2x-2)F\varphi_0}{RT}\right) > 0$ if j>0, which is necessary for the Hopf bifurcation to realize. The oscillations are expected to be frequent and of small amplitude, realizing far beyond the detection limit.

Yet if the mentioned element is negative, the *steady-state stability* is warranted. Really, applying the Routh-Hurwitz criterion to the Jacobian matrix and introducing new variables, having it rewritten as (15):

$$\frac{4}{\delta^2 B}\begin{vmatrix} -\kappa_1 - \Xi & 0 & \Sigma \\ 0 & -\kappa_2 - \Omega & -P - T \\ \Xi & -\Omega & -\Sigma - P - T \end{vmatrix} \quad (15)$$

Opening the straight brackets and applying the Det J<0 requirement, salient from the criterion, we obtain the steady-state stability condition, exposed as:

$$-\kappa_1(\kappa_2\Sigma + \kappa_2 P + \kappa_2 T + \Omega\Sigma) - \Xi(\kappa_2 P + \kappa_2 T) < 0 \quad (16)$$

Really, if the parameters α and j are negative, the left side of the inequity (16) will be shifted to the more negative values, stabilizing the steady-state. Taking into account the high presence of the diffusion related elements κ_1 and κ_2, their positive values, like also the rapidity of chemical and electrochemical reactions, the electrochemical process will be diffusion-controlled.

As there are no side reactions, capable to compromise the electroanalytical process, the steady-state stability will be correspondent to the linear dependence between the concentration of the inorganic salt. Therefore, it will be electroanalytically efficient. Moreover, as the resulting polymer is highly conductive and with a well-developed catalytic surface, this process is also efficient from the electrosynthetic point of view.

The detection limit is defined by the *monotonic instability*, depicting the margin between the stable steady-states and unstable states. Its condition is Det J = 0, and, for this system:

$$-\kappa_1(\kappa_2\Sigma + \kappa_2 P + \kappa_2 T + \Omega\Sigma) - \Xi(\kappa_2 P + \kappa_2 T) = 0 \quad (17)$$

The resulting material is highly catalytic as an electrode modifier for fuel cells, electroorganic synthesis and electroanalytical reactions. Also, it may be used as a supercapacitor. Therefore, this system may be effectively used not only for electroanalytical but also for electrosynthetical process. Moreover, this process may be used for $Ca(ClO_3)_2$ removal from the environment. The electroanalytical aspects of the poly (magnesium magnezonate XC) will be exposed in our next works.

4. Conclusions

From the system with the electrochemical determination of magnesium chlorate on magnezone XC-modified electrode it was possible to conclude that:

- The system's behavior is relatively dynamic, due to the intense influence of all of the three chemical and electrochemical transformations to the double electric layer conductivity, capacitance and ionic force;
- The electroanalytical process is diffusion controlled with the easy realization of linear dependence between the concentration and the current;
- The resulting polymer material tends to be highly conductive with well-developed catalytic area and capacitance properties;
- The oscillatory behavior tends to be relatively probable, due to DEL influences, promoting the cyclical ionic force, capacitance and conductivity changes in DEL and on the surface.

References and Notes

[1] Jahnen-Dechent, W.; Ketteler, M. *Kidn. J.* **2012**, *5,* 3, [Crossref]

[2] Kossev, K.; Tsvetanova, L.; Dimowa, L.; *et al. Bulg. Chem. Commun.* **2013,** *45*, 543. [Link]

[3] Elliott, F. C. Cotton Defoliation Guide for Texas, in Texas Agricultural Extension Service, 1957, pp. 5-57.

[4] Ismail, M. S. *Assiut J. Agric.* **1990,** *21*, 23, [Link]

[5] Borges, R.; Miguel, E. C.; Dias, J.R. *et al. Plant Sci,* **2004,** *166,* 1057. [Crossref]

[6] Wolterink, A. Characterization of (per)chlorate-reducing bacteria. [Ph.D. Thesis]. Wageningen Universiteit, The Netherlands, **2004**

[7] Shriver-Lake, L. C.; Zabetakis, D.; Dressick, W.J. *et al. Sensors* ***2018,*** *18,* 328. [Crossref]

[8] Trammell, S. A.; Shriver-Lake, L. C.; Dressick, W. J. *Sens. Act. B. Chem.* **2017,** *239,* 951. [Crossref]

[9] Salleh, S. H.; Birbilis, N.; Musameh, K. *et al. J. Electrochem. Soc.*, **2018,** *165,* 771. [Crossref]

[10] Das, A.; Majumder, S. B.; Chaudhuri, A. R. *J. Pow. Sources,* **2020**, *461,* 228149. [Crossref]

[11] Magomedov, A. G. *Izv. Dagest. Gos. Ped. Univ.* **2016,** *10,* 9. [Link] (in Russian).

[12] Tataeva, S. J.; Magomedov, K. E.; Oibolatova, S. I. *Innov. Nauk,* **2013,** *16,* 1. [Link] (in Russian).

[13] Ranathunge, T. A.; Ngo, D. T.; Karunarathilaka, D. *et al. J. Mat. Chem.* **2020,** *8*, 5934. [Crossref]

[14] González, D. M.; Cruz, N. B.; Hernández, L. A. *et al. J. Polym. Sci.* **2020,** *58,* 557. [Crossref]

[15] Martin, C. S.; Machini, W. B. S.; Teixeira, M. F. S. *RSC Adv.* **2015,** *5*, 39908. [Crossref]

[16] Das, I.; Goel, N.; Agrawal, N. R.; Gupta, *J. Phys. Chem. B* **2010**, *114*, 12888. [Crossref]

[17] Bazzaoui, M.; Bazzaoui, E. A.; Martins, L.; Martins, J. I. *Synth. Met.* **2002**, *130*, 73. [Crossref]

[18] Das, I.; Goel, N.; Gupta, S. K.; Agrawal, N. R. *J. Electroanal. Chem.* **2012**, *670*, 1. [Crossref]

[19] Tkach, V. V.; Kushnir, M. V.; Dubenska, L. O. *et al. Biointerface Res. Appl. Chem.* **2021,** *11*, 11519, [Crossref]

[20] Tkach, V. V.; Kushnir, M. V.; de Oliveira, S. C. *et al. Lett. Appl. NanoBioSci,* **2020,** *9,* 1451. [Crossref]

[21] Tkach, V. V.; Kushnir, M. V.; de Oliveira, S. C. *et al. Ukr. Bioorg. Acta,* **2020,** *15,* 47. [Crossref]