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REMOVAL OF SODIUM LINEAR ALKYLBENZENE SULPHONATE BY ELECTROCOAGULATION-ELECTROFLOTATION

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ABSTRACT. This paper took into consideration the behaviour of an aluminium electrode in the presence and in the absence of sodium linear alkylbenzene sulphonate. It acted as the organic component of a simulated wastewater. In addition, the effect of the organic load (surfactant concentration) on the separation of the surfactant from water was studied. The characterisation of the electrode material was carried out by polarisation measurements under potentiostatic and galvanostatic conditions with scan rates of 0.02 V/s and 0.0001 A/s, respectively. The electrode processes could be stimulated or inhibited depending on the history of the electrode and the composition of the simulated wastewater. The change of the anodic inhibition or activation was interpreted by the character of the superficial oxide film and partially de-filming process. The simulated wastewater treatment was carried out in an electrocoagulation-electroflotation cell in galvanostatic conditions. The efficiencies of treatment ranged between 70-80% as Chemical Oxygen Demand (COD) removal. The increase of surfactant concentration over 0.75 g/L caused a sharp fall of the treatment efficiency.

INTRODUCTION

The removal of synthetic surfactants from aqueous solution (industrial and rinsing wastewaters) is not so easy to accomplish. The diphilic feature of surfactant molecules and hydrophilic interactions of their micelles determine a rather difficult separation from water.

Electrocoagulation alone or together with electroflotation provides effective separation and can offer a better treatment than the conventional ne with reagents. This method implies wastewater electrolysis using soluble metal anodes, coagulant generation and pollutant separation by combined effects [1-10].

Various aspects of aluminium behaviour have been reported extensively by many authors [7-20]. However, case studies concerning the behaviour of aluminium in wastewater containing surfactant have been reported less frequently [4-10].

This paper investigated the interactions between sodium linear alkylbenzene sulphonate (LABS) and aluminium anode with consequences regarding the effective separation of surfactant from water. The working conditions referred to low concentration of sodium chloride (Cl^- as activator), sodium sulphate as supporting electrolyte and the absence or the presence of surfactant. The pH of 4.0 was in agreement with the initial pH in an operating electrocoagulation-electroflotation cell. Other objectives of this paper were to study the effect of the organic load on the separation of the surfactant and to find out a limiting surfactant concentration.

RESULTS AND DISCUSSION

The first series of voltammetric measurements aimed to reveal the behavioural pattern of the aluminium electrode in selected conditions of sulphate content and low chloride concentration. Fig. 1 gives the plots of current (logarithmic scale) against potential at 0.02 V/s scan rate. The passivation sector was substantially wider for sulphate (curve 1) than the equivalent one for chloride (curve 2). This was in good agreement with previously reported data for higher concentrations of anions [12-16].

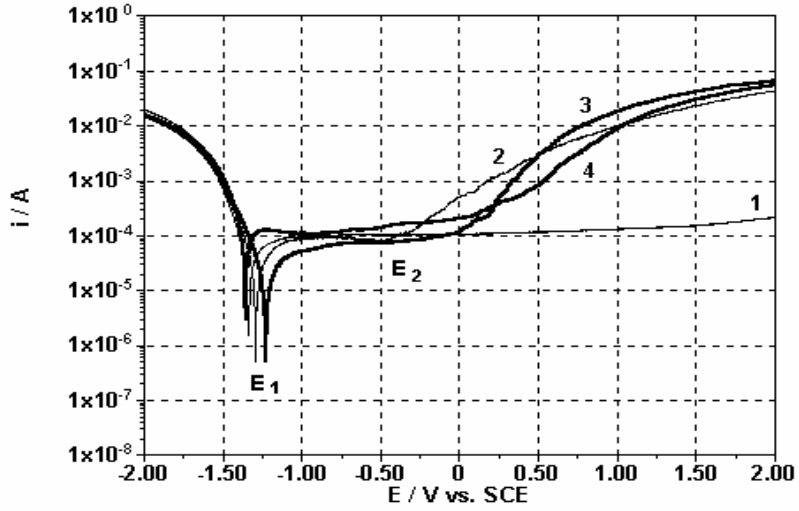

Fig. 1. Potentiostatic polarisation data for aluminium electrode at 0.02 V/s in Na_2SO_4 0.1 M (***1***); Na_2SO_4 0.1 M + NaCl 0.01 M (***2***); Sodium Linear Alkylbenzene Sulphonate (LABS) 0.5 g/L + Na_2SO_4 0.1 M + NaCl 0.01 M (***3***) and LABS 1.5 g/L + Na_2SO_4 0.1 M + NaCl 0.01 M (***4***); pH 4.0

The lower limit of the passivation potential range could be set up for potential E_1, which corresponded to zero current passage. E_1 can be considered conventionally as a "corrosion potential". The upper limit, E_2, is the breakdown potential, pointing out the beginning of the active dissolution that occurred mostly in presence of chloride (almost two orders of magnitude vs. sulphate). The cathodic prepolarisation generated OH^- ions, which then were involved in the formation of a superficial "film" (hydrated oxide) with the anodically generated aluminium ions. Two effects were overlaid on the anodic branch: diffusion limitations and the formation of the superficial layer. The latter aspect implied the permeability of that layer, which could be also a limiting factor.

The shape of polarisation curves was not changed essentially in the presence of sodium linear alkylbenzene sulphonate. The higher the concentration of the surfactant the longer the passivation sector corresponding to E_1-E_2.

The cyclic voltammograms in Fig. 2, in the presence and in the absence of the surfactant, pointed out again the activating effect of chloride ion. The aluminium electrode was practically passivated over an extended range of potential (curve 1) in the presence of sulphate as the only component of the solution. Curves 2, 3 and 4 pointed out a supplementary and remanant activation on the backward branch due to enough induction time for the film breakdown, increased roughness of the active surface and diffusion of anodically generated species. The increase of LABS concentration determined lower currents both on the forward and backward branches of the curves. Even in the presence of the surfactant (curves 3 and 4), the behavioural pattern of the electrode was predominant. However, the involvement of surfactant in electrode processes might be discussed as a wetting effect at controlled potential and pH change on the very surface of the electrode.

Galvanostatic polarisation data were required for a better approach to the common galvanostatic conditions in electrochemical wastewater treatment (electrocoagulation-electroflotation). Comparable and reproducible data could be obtained by cathodic prepolarisation followed by galvanostatic scan from –0.020 A to +0.020 A. Those values corresponded to the upper limits of current density in an electrocoagulation-electroflotation cell.

The cathodic prepolarisation also generated OH^- ions, which interacted with anodically generated aluminium ionic species. Duration of diffusion, formation of the superficial layer and defilming by chloride activation were correlated with the scan rate. The scan rate of 0.1 mA/s was chosen for all measurements to provide enough time for activation and diffusion of the anodic products. Without cathodically controlled prepolarisation, the formation of the superficial layer occurred randomly.

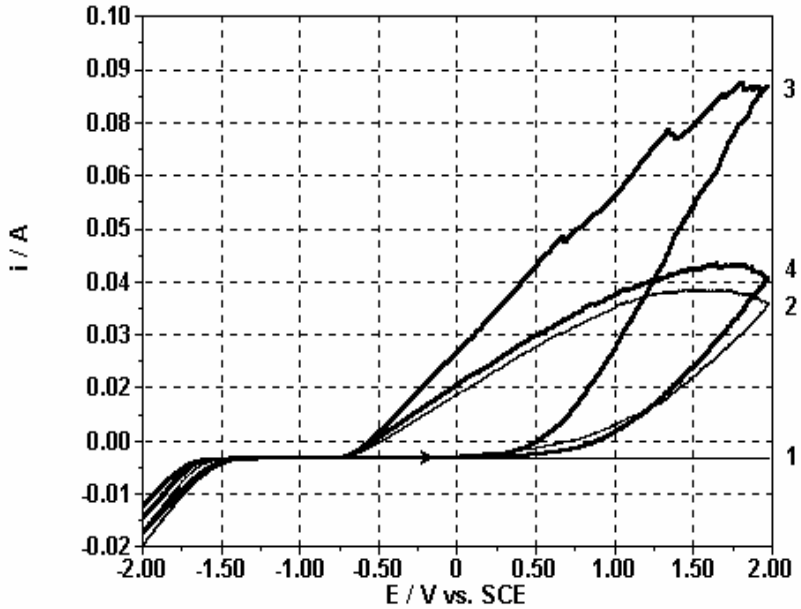

Fig. 2. Potentiostatic cyclic voltammograms for aluminium electrode at 0.02 V/s in Na_2SO_4 0.1 M (***1***); Na_2SO_4 0.1 M + NaCl 0.01 M (***2***); Sodium Linear Alkylbenzene Sulphonate (LABS) 0.5 g/L + Na_2SO_4 0.1 M + NaCl 0.01 M (***3***) and LABS 1.5 g/L + Na_2SO_4 0.1 M + NaCl 0.01 M (***4***); pH 4.0

Figure 3 shows the effect of the surfactant and the inorganic components at pH 4.0. The formation of the superficial layer determined the increase of polarisation. The most pronounced increase was given by sulphate. The anodic peaks were smaller in the presence of LABS, but at higher current densities, the curve 4 corresponded to an increase of polarisation. This aspect could be interpreted as an increase of thickness and permeability of the layer.

The experiments for the separation of the anionic surfactant were carried out in an electrocoagulation-electroflotation cell taking into account the galvanostatic polarisation data and the fact that LABS is widely used in various compositions of detergents. The current density ranged between 50-200 A/m^2. In all separation experiments, the initial pH was 3.1. The initial concentration of LABS ranged between 0.1-2.5 g/L to simulate various compositions of wastewater.

Tables 1 to 4 show the influence of the current density on the treatment efficiency and power consumption. At 200 A/m^2 the process developed very intensively, but the improvement of the treatment efficiency was not significant in comparison with the lower current densities. The effect of surfactant concentration on the evolution of treatment by electrocoagulation-

electroflotation was studied for a current density of 50 A/m^2. Two situations of 0.15 and 0.30 Ah quantity of electricity are shown in Fig. 4. In comparable conditions of quantity of electricity, the treatment efficiencies decreased with the increase of surfactant load. It would have been necessary higher quantities of electricity to get higher removal of chemical oxygen demand.

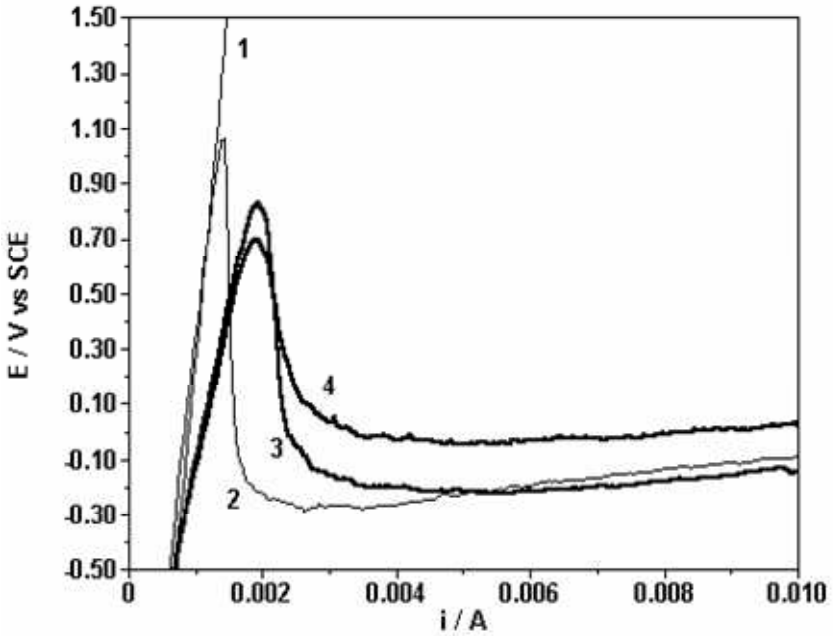

Fig. 3. Galvanostatic polarisation data for aluminium electrode at 0.0001 A/s in Na_2SO_4 0.1 M (***1***); Na_2SO_4 0.1 M + NaCl 0.01 M (***2***); Sodium Linear Alkylbenzene Sulphonate (LABS) 0.5 g/L + Na_2SO_4 0.1 M + NaCl 0.01 M (***3***) and LABS 1.5 g/L + Na_2SO_4 0.1 M + NaCl 0.01 M (***4***); pH 4.0

Table 1.

The evolution of treatment by electrocoagulation-electroflotation for the separation of sodium linear alkylbenzene sulphonate (i_A 50 A/m^2; C_i 0.5 g/L; COD_i 915 mg O_2/L; pH_i 3.1; NaCl 1 g/L; at 22 ℃)

Q (Ah)	U (V)	pH_f	COD (mg O_2/L)	COD removal (%)	W_{sp} (kWh/m^3)
0.05	1.30	3.4	352	61.5	0.1
0.10	1.35	4.4	337	63.2	0.2
0.15	1.35	4.7	222	75.7	0.3
0.20	1.35	4.8	177	80.7	0.4
0.30	1.35	5.0	162	85.7	0.6

Q-Quantity of electricity; U-Cell voltage; i_A- Current density; C_i-Initial surfactant concentration; COD-Chemical Oxygen Demand; pH_i, pH_f-Initial and final pH; W_{sp}-Specific electric energy consumption

Table 2.
The evolution of treatment by electrocoagulation-electroflotation for the separation of sodium linear alkylbenzene sulphonate (i_A 100 A/m^2; C_i 0.5 g/L; COD_i 915 mg O_2/L; pH_i 3.1; NaCl 1 g/L; 22 ℃)

Q (Ah)	U (V)	pH_f	COD (mg O_2/L)	COD removal (%)	W_{sp} (kWh/m^3)
0.05	2.0	4.6	402	56.1	0.1
0.10	2.0	4.9	254	72.2	0.3
0.15	2.0	5.2	178	80.5	0.4
0.20	2.0	6.0	178	80.5	0.6
0.30	2.0	7.0	147	83.9	0.9

Table 3.
The evolution of treatment by electrocoagulation-electroflotation for the separation of sodium linear alkylbenzene sulphonate (i_A 150 A/m^2; C_i 0.5 g/L; COD_i 915 mg O_2/L; pH_i 3.1; NaCl 1 g/L; 22 ℃)

Q (Ah)	U (V)	pH_f	COD (mg O_2/L)	COD removal (%)	W_{sp} (kWh/m^3)
0.05	2.8	4.6	406	55.6	0.2
0.10	2.7	4.8	266	70.9	0.4
0.15	2.7	5.3	239	73.9	0.6
0.20	2.7	6.2	217	76.3	0.8
0.30	2.6	7.1	180	80.3	1.1

Table 4.
The evolution of treatment by electrocoagulation-electroflotation for the separation of sodium linear alkylbenzene sulphonate (i_A 200 A/m^2; C_i 0.5 g/L; COD_i 915 mg O_2/L; pH_i 3.1; NaCl 1 g/L; 22 ℃)

Q (Ah)	U (V)	pH_f	COD (mg O_2/L)	COD removal (%)	W_{sp} (kWh/m^3)
0.05	3.2	4.6	516	43.6	0.2
0.10	3.3	4.8	262	71.4	0.5
0.15	3.1	5.3	213	76.8	0.7
0.20	3.2	5.9	174	81.0	0.9
0.30	3.2	7.0	150	83.6	1.2

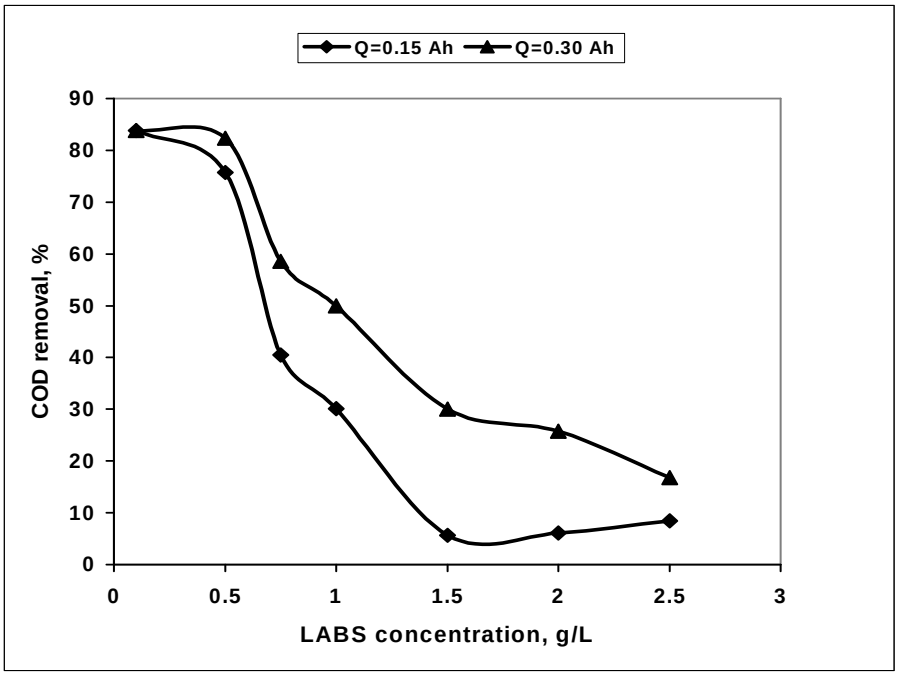

Fig. 4. The influence of sodium linear alkylbenzene sulphonate concentration on treatment efficiency.

The separation of the surfactant was badly affected over concentration of 0.75 g/L when the destabilisation of surfactant micelles was more difficult to accomplish. The effect of the organic load could be associated with hydrophilic interactions within the bulk of solution. The colloidal system consisting of aluminium hydroxocomplexes was stabilised by the presence of the surfactant.

At surfactant concentration below 0.7 g/L, the treatment was conducted in conditions of satisfactory power consumption (0.2-0.3 kWh/m^3) and chemical oxygen demand removal (60-80%). The voltage of the cell did not reflect any limitations of aluminium dissolution, the only limiting interactions resulting from the increase of the organic load were in the bulk of solution. The effect of the organic load was more significant in the experiments of water treatment than in those ones concerning polarisation curves.

EXPERIMENTAL

The behaviour of aluminium electrode (Al 99.3%, an ALRO Company product) was investigated in potentiostatic and galvanostatic conditions. The working electrode in voltammetric measurements was cleaned with two-grade emery paper, filter paper, degreased with acetone and washed

carefully. The aluminium cylindrical working electrode (2.8 mm diameter) was mounted vertically and had an exposed surface area of 1 cm^2. Thus, current (A) was equivalent to current density (A/cm^2). The counter electrode was made of aluminium and had a large surface area. A saturated calomel electrode (SCE) was used as a reference electrode. The cell used for the voltammetric measurements had no separated anodic and cathodic compartments.

The device used was the system Autolab-Ecochemie PGstat 20. The overall anodic and cathodic processes were studied by voltammetric techniques: cyclic voltammetry (linear scan), linear sweep voltammetry (current integration) and linear sweep voltammetry (galvanostatic). The potential ranged from -2 to +2, V vs. SCE in potentiostatic measurements and the current ranged from –0.020 A cathodic current to +0.020 A. The scan rates were 0.02 V/s and 0.0001 A/s, respectively. The static working electrode was pre-polarised cathodically (3 minutes) to provide conventionally reproducible conditions.

The electrocoagulation-electroflotation cell used in the wastewater treatment experiments is shown in Fig. 5.

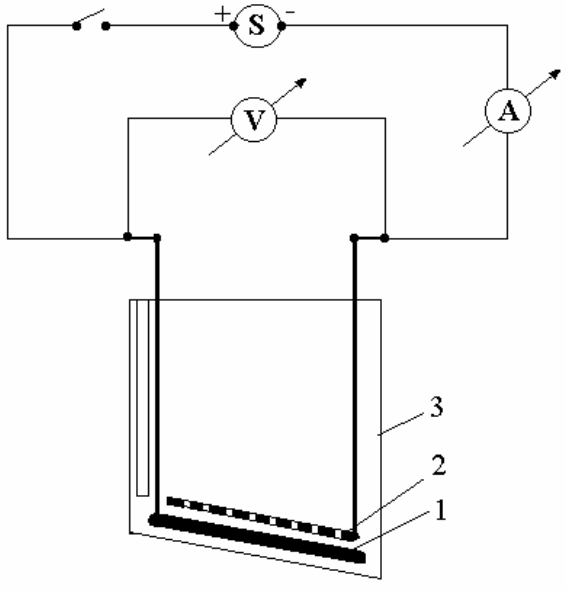

Fig. 5. Schematic diagram for experimental set-up of surfactant separation in an electrocoagulation-electroflotation cell: 1-Anode: aluminium plate, surface area, 60 cm^2; 2-Cathode: grid of stainless steel wires, Φ 3 mm; Surface area ratio, S_A/S_C 1.44; 3-cell, made of plexiglass; Surfactant concentration: 0.1-2.5 g/L; Batches of 0.7 L were run into the cell;

The reagents were NaCl and Na_2SO_4 p.a. (Rompar), technical grade sodium linear alkylbenzene sulphonate: CH_3-$(CH_2)_{11}$-C_6H_4-SO_3Na supplied by Romtensid Romania and doubly distilled water. The supporting electrolyte used for voltammetric measurements contained Na_2SO_4 0.1M and NaCl 0.01 M as activator. The temperature was 22±1℃.

CONCLUSION

The behaviour of aluminium as electrode material was studied in various solutions (low sodium chloride concentration, sodium sulphate and sodium linear alkylbenzene sulphonate anionic) and at pH 4.0. The overall anodic and cathodic processes were studied by voltammetric techniques: cyclic voltammetry and linear sweep voltammetry in potentiostatic and galvanostatic variants.

The potentiostatic polarisation curves were analysed as resultant curves. Even in the presence of the surfactant, the behavioural pattern of the electrode was predominant. However, the involvement of the surfactant in electrode processes might be discussed as a wetting effect at controlled potential and pH change on the very surface of the electrode.

The change of the anodic inhibition or activation was developed more clearly in conditions of galvanostatic polarisation of the electrode and interpreted by the character of superficial film and partially defilming process. The formation of the superficial layer determined the increase of polarisation. The effect of LABS correlated partially with the increase of the surfactant concentration, when polarisation was higher towards higher current densities. This aspect could be interpreted as an increase of thickness and permeability of the layer.

The simulated water treatment was carried out in an electrocoagulation-electroflotation cell in galvanostatic conditions. In addition to the electrode processes, reactions in the bulk of solution influenced the processes that occurred at the adsorption surface of the electrochemically-generated coagulant.

The wastewater treatment by electrocoagulation-electroflotation at 50 A/m^2 current density yielded higher separation efficiency (70-80%) even at 0.15 Ah and low specific energy consumption (0.2-0.3 kWh/m^3) for surfactant concentrations of 0.1-0.5 g/L. The increase of surfactant concentration over 0.75 g/L caused a sharp fall of the treatment efficiency and the method was no longer feasible. The limiting surfactant concentration of 0.75 g/L was associated with the hydrophilic interactions and the stabilisation of the colloidal system.

Usually, high concentrations of surfactants are not common in rinsing and industrial wastewater. Some of our experiments with real wastewater pointed up the same high treatment efficiencies as those for the treatment simulations.

REFERENCES

1. S.V. Yakovlev, I.G. Krasnoborod'ko and V.M. Rogov, *Technologhiya elektrokhimicheskoi ochistki vody*, Stroizdat, L., 1987.
2. L. A. Kulskyi, P.P. Stokach, V.A. Slipenko and E.I. Saigak, *Ochistka Vody Electrokoagulyatsei*, Budivelnik, Kiev, 1978.
3. K. Scott, *Electrochemical Processes for Clean Technology*, The Royal Society of Chemistry, London (1995).
4. C. Berset, H. Jaskiewicz, C. Tran Manh Sung and F. Sandret, *Trib. CEBEDEAU* 1979, **427**, 79.
5. S. P. Novikova, T. L. Skorbatova and E. Ya. Sokol, *Khim. Tekh. Vody*, 1982,**4**, 352.
6. V. Cocheci, C. Radovan, A. Bugarski and L. Andres, *Rev. Chim.*, 1989, **40**, 446.
7. C. Radovan, I. Vlaicu, G.A. Ciorba and M. Adam-Stoia, in *Proceedings of the Symposium "Energy and Electrochemical Processing for a Cleanner Environment"*, (Edited by C.W. Walton and E.J. Rudd), **27-28**, p. 427, ECS, Pennington, N.J. 1998.
8. C. Radovan, I. Vlaicu, G.A. Ciorba and M. Adam-Stoia, *Annals of West University of Timisoara, Ser. Chem.*, 1997, **6**, 259.
9. C. Radovan, G.A. Ciorba and I. Vlaicu, *Annals of West University of Timisoara, ser. chem.*, 1997, **6**, 267.
10. G. Ciorba, C. Radovan, I. Vlaicu, L. Pitulice, submitted to *Electrochimica Acta*
11. M. Pourbaix, *Atlas of Electrochemical Equilibria in Aqueous Solutions*, Pergamon Press, London 1966.
12. A.D. Davydov and A.N. Kamkin, *Eletrokhimiya*, 1978, **14**, 979.
13. M. Kliskic, J. Radosevic, S. Gudic and M. Smith, *Electrochim. Acta*, 1998, **43**, 3241.
14. D.M. Drazic, S.K. Zecevic, R.T. Atanasoski and A.R. Despic, *Electrochim. Acta*, 1983, **28**, 751.
15. R.M. Stevanovic, A.R. Despic and D.M. Drazic, *Electrochim. Acta*, 1988, **33**, 397.
16. L. Tomcsany, C. Varga, I. Bartik, G. Horanyi and E. Maleczky, *Electrochim. Acta*, 1989, **34**, 855.
17. L. Chen, N. Myung, P.T.A. Sumodjo and K. Nobe, *Electrochim. Acta*, 1999, **44**, 2751.
18. E. Brillas, P.L. Cabot, F. Centelas, J.A. Garido, E. Perez and R.M. Rodriguez, *Electrochim. Acta*, 1998, **43**, 799.
19. S.M. Moon and S. Pyun, *Corros. Sci*, 1997, **39**, 399.
20. S. Real, M. Urquidi-Macdonald and D.D. Macdonald, *J. Electrochem.Soc.*, 1988, **135**, 1633.