Int. J. Electrochem. Sci., 9 **(2014)** 371 - 379

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Effect of Triton-×-100 on the Rate of Hydrogen Evolution at a Cathode

A. M. Ahmed[1,*], *Mona Darweesh*[2]

[1]Department of Chemistry, Faculty of Science, Alexandria University, Ibrahimia, and P.O. Box 426, Alexandria 21321, Egypt.
[2] Department of Chemistry, Faculty of engineering, Tanta University, Egypt.
[*]E-mail: profabdelmonem@gmail.com

Received: 23 July 2013 / *Accepted:* 28 September 2013 / *Published:* 15 November 2013

The effect of H_2 evolution on the mass-transfer coefficient of cathode reduction of potassium ferricyanide at a mercury cathode was studied with the aim of (i) comparing the mass transfer behavior at a Hg cathode with that at solid electrodes under gas-evolving conditions and (ii) testing the effect of non-ionic surface-active agent on the mass transfer behavior of an H_2-evolving Hg cathode. It is found that the mass transfer coefficient at the Hg cathode was much higher than the value at a solid cathode. The mass transfer coefficient at H_2 evolving Hg was found to decrease in the presence of Triton-×-100 surfactant by an amount ranging from 62 to 82%, depending on the H_2 discharge rate and the Triton-×-100 concentrations.

Keywords: Triton-×-100 - Mass transfer – Rate of H_2-evolving.

1. INTRODUCTION

Industrial electrolytic processes such as electrosynthesis and metal deposition often involve diffusion-controlled reactions, which take place with a current efficiency below 100%, owing to the simultaneous evolution of H_2 or O_2 at the working electrode.

The effect of gas evolution on the performance characteristics of electrochemical reactors, such as current distribution, ohmic drop, and mass transfer, has recently received considerable attention. [1,2]

Previous studies on the effect of gas evolution on the rate of mass transfer have been limited to solid electrodes despite the importance of Hg pool cathodes in electro-organic synthesis. [3]

The Hg cathode is used widely in electro-organic synthesis in view of (i) its high H_2, over potential, (ii) its catalytic effect, which determines the reaction product, and (iii) its clean and reproducible surface. The aim of the present work is to study (i) the mass transfer behavior of the H_2-evolving Hg pool cathode in comparison with that of a solid electrode. Since (ii) electro-organic synthesis, the major user of Hg cathodes, often involves surface-active reactants or products, it would be of interest to study also the effect of surfactants on the rate of mass transfer at the evolving Hg pool cathodes. Previous mass transfer studies at Hg pool cathodes have dealt with the effect of external gas sparging on the mass transfer coefficient. Clinton and Perona [4] studied the effect of bubbling N_2 through a horizontal Hg pool cathode on the rate of mass transfer, while Savall and Lacoste [5] studied the effect of a two-phase flow (N_2 and electrolyte) injected through a mercury pool cathode. Theoretical studies have shown that gas evolution at the electrode can accelerate mass transfer by four means:

1. According to Stephan and Vogt, liquid in the vicinity of the adhering bubble is pushed away by the growth of the bubble diameter, resulting in a periodic disturbance of the diffusion layer with an increase of mass transfer (micro convection model). [2]
2. According to Ibl and Venczel, when a bubble separates from the interface it leaves a void into which fresh solution flows, thus supplying the electro-active species to the electrode (penetration model). [6]
3. According to Janssen and Hoogland, the ascending bubble swarm causes an axial flow of the solution past the electrode surface with a consequent reduction of the diffusion layer thickness (hydrodynamic model). [7]
4. According to Sedahmed, the detached bubbles induce radial momentum transfer, which brings a fresh supply of the electro-active species to the electrode surface (surface renewal model). [8]

Surface active agents have been mainly used as corrosion inhibitors from iron [9,10], copper [10-12] alminium [13,14] and steel. [15-22]

Many attempts have been made to study the corrosion of various types of steels and their inhibition by different types of organic inhibitors in acid solution. [15-24]

Ionic and non-ionic surfactants have been reported to be corrosion inhibitors for metals like copper, aliminum and mild steel. [25-27]

In paricular non-ionic surfactants (where the polar head group is without charge) are known to have many applictions in industry, including cosmetics, detergents and also as corrosion inhibitors. In addition to these valuble properties, they are not expensive to produce.

The aime of the work is study of non-ionic surfactants (Triton-×-100) on the rate of hydrogen evolution at cathode.

2. EXPERIMENTAL

The apparatus (Fig. 1) consisted of a cell and an electrical circuit. The cell was a 1-l glass container of diameter 14 cm divided into two compartments by a porous porcelain diaphragm of diameter 7 cm.

The cell cathode was made up of an Hg pool of depth 1 cm placed in the inner compartment. A cylindrical stainless steel screen of diameter 14 cm placed in the outer compartment was used as anode. The electrical circuit consisted of a 6V d.c. power supply with a voltage regulator and a multirange ammeter connected in series with the cell.

The procedure for determining the mass transfer coefficient under gas-evolving conditions was similar to that used in previous studies. [7,8]

Electrolysis of a solution containing 0.1 mol/l K_3 $Fe(CN)_6$, 0.1 mol/l $K_4Fe(CM)_6$, and 2 mol/l NaOH with simultaneous H_2 evolution and cathodic reduction of K_3 $Fe(CN)_6$ was conducted galvanostatically for a time ranging from 5 to 8 min. At the end of electrolysis, the inner solution (catholyte) was analyzed for ferricyanide using iodometry. [28]

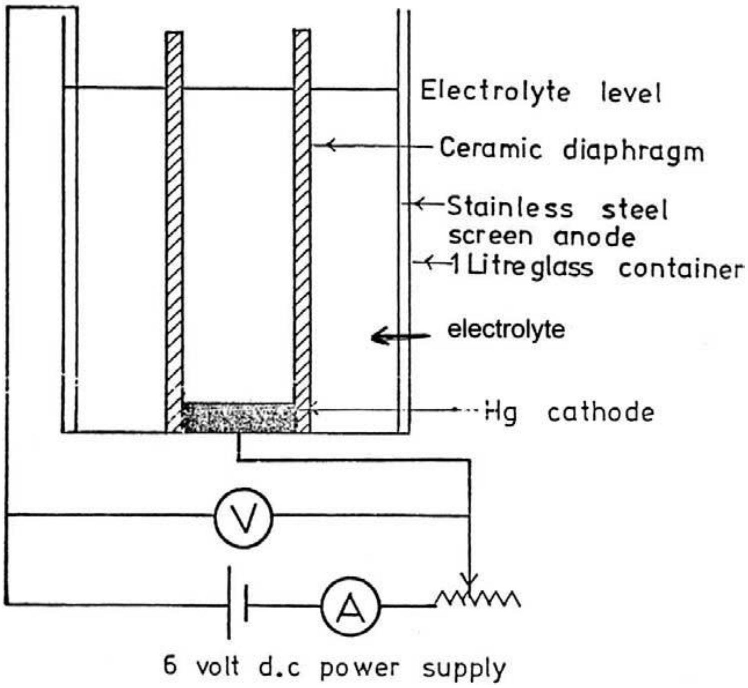

Figure 1. Cell and electrical circuit

The change in ferricyanide concentration under different H_2 discharge rates at the cathode ranged from 4 to 7%. The mass transfer coefficient of the cathodic reduction of K_3 $Fe(CN)_6$ was calculated from the equation:

$$K = I/(ZFCA) \quad (1)$$

where:

K : mass transfer coefficient
I : limiting current
Z : valency = 1
F : Faraday constant = 96,500 C
C : concentration of K_3 $Fe(CN)_6$
A : area of cathode

The current I consumed in reducing K_3 $Fe(CN)_6$ at the Hg cathode was calculated from the analytically determined amount reacted according to Faraday's law. The H_2 discharge rate (V) was calculated from the current consumed in H_2 evolution using Faraday's law and the gas law, namely,

$$V_g = RT/(PZFA) \times I\ H_2 \tag{2}$$

where:

V_g : H_2 discharge velocity
R : gas constant
T : absolute temperature
P : pressure = 1 atm
Z : valency = 1
F : Faraday constant
A : area of cathode

The current consumed in H_2 evolution at the Hg pool cathode is the difference between the total current passing during electrolysis and the current consumed in reducing K_3 $Fe(CN)_6$. To compare the mass transfer coefficient at the Hg cathode with that at a solid electrode, the Hg pool cathode was replaced by a horizontal nickel disc cathode of diameter 7 cm in the cell shown in Figure 1. To test the effect of surface-active agents on the mass transfer coefficient at gas evolving Hg pool cathode, Triton-×-100, non-ionic surfactant of molecular weight 648 was used. Surfactant concentration ranged from 6×10^{-5} to 24×10^{-5} mol/l. In all cases the blank solution was 0.1 mol/l K_3 $Fe(CN)_6$, 0.1 mol/l K_4 $Fe(CN)_6$, and 2 mol/l NaOH. All solutions were prepared from distilled water and A.R. grade chemicals. Surface tension was measured by the torsion balance method. [29]

Temperature was 23 ± 1°C during electrolysis. Current density ranged from 0.0026 to 0.077 A/cm^2. The effective diffusivity of ferricyanide ion in blank and surfactant solution was measured by the rotating disc technique as described elsewhere. [30]

The limiting current of the cathodic reduction of ferricyanide ion at the

Hg cathode under natural convection conditions was measured for solution containing different Triton concentrations by the traditional method. [31]

3. RESULTS AND DISCUSSION

Figure 2 shows the effect of H_2 discharge velocity on the mass transfer coefficient of the cathodic reduction of K_3 $Fe(CN)_6$ at a mercury pool cathode and a horizontal nickel cathode. It is found that, the mass transfer coefficient is much higher at the mercury cathode of the same H_2 discharge velocity. Ibl et al. showed that solid electrode material has a negligible effect on the mass transfer coefficient. [32]

This lends support to the fact that the mobile nature of mercury is responsible for the high mass transfer coefficient. O_2 is present in a very small amount soluble in water. The mass transfer data at the mercury cathode fit the equation:

$$K = \alpha_1 V_g^{0.28} \tag{3}$$

while the data at the nickel cathode fit the equation:

$$K = \alpha_2 V_g^{0.35} \tag{4}$$

where:

V_g : H_2 discharge velocity

K : mass transfer coefficient

α_1 : constants

α_2 : constants

The exponent 0.35 obtained in case of the nickel cathode agree well with the values obtained by different authors, who studied mass transfer at H_2-evolving horizontal solid electrodes using alkaline solution. [2,33]

The exponents agree also with the prediction of hydrodynamic and surface renewal model.

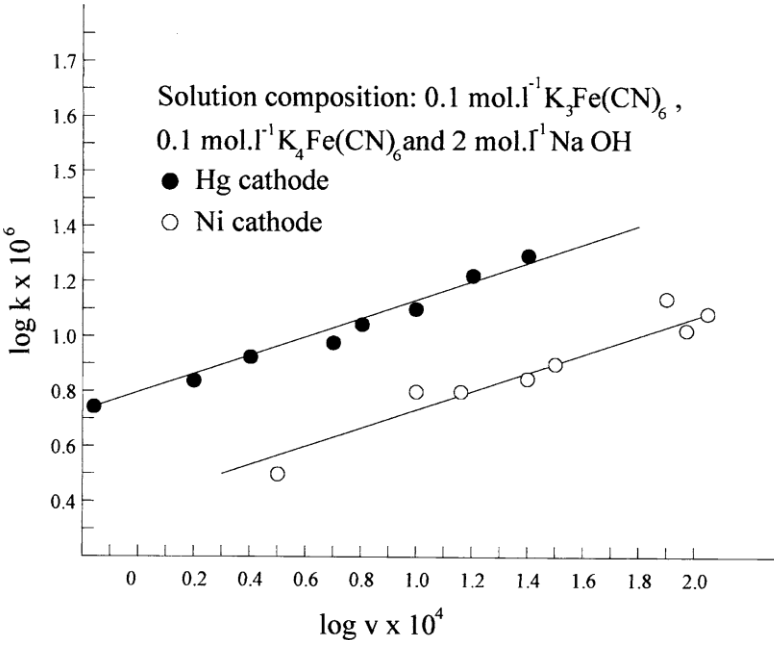

Figure 2. Effect of H_2 discharge velocity on the mass transfer coefficient at Hg and Ni cathodes.

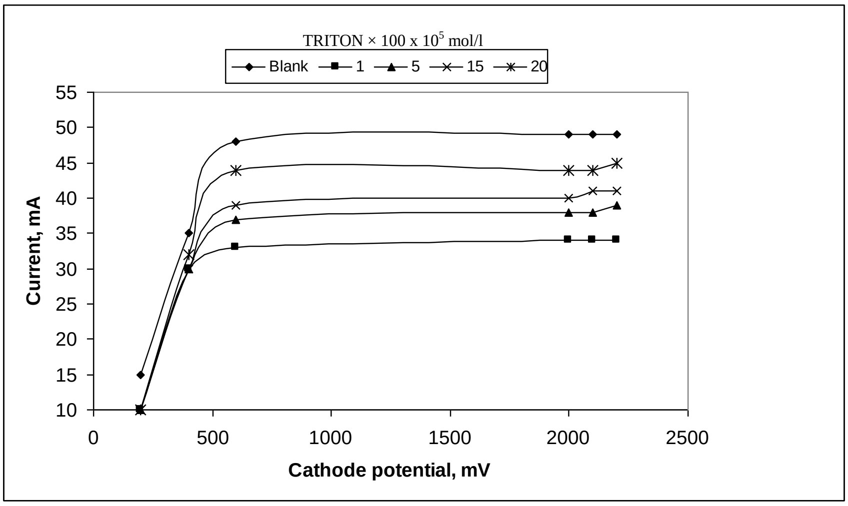

Figure 3. Polarization date in solution containing different Triton-×-100.

Effect of Triton-×-100 on the rate of H_2 evolution at cathode

Before testing the effect of Triton-×-100 on the rate of mass transfer at the mercury pool cathode under H_2 -evolving conditions, care was taken to make sure that the presence of Triton-×-100 in solution did not alter the diffusion-controlled nature of cathodic reduction of ferricyanide. Figure 3 shows that polarization curves with a good limiting current plateau are obtained in Triton-×-100solution; i.e., the presence of Triton-×-100 does not affect the diffusion-controlled nature of the cathodic reaction of ferricyanide ion. Figure 3 shows that Triton-×-100 decreases the limiting current and accordingly the rate of mass transfer by an amount ranging from 10.3 to 33.3% depending on the Triton-×-100 concentration. This decrease in natural convection mass transfer may be attributed to an increase in interfacial viscosity as a result of surfactant adsorption on the cathode. [34] The increase in the interfacial viscosity leads to a decrease in the effective diffusivity of the ferricyanide ion.

Measurement of the effective diffusivities of ferricyanide ion in solutions containing different Triton-×-100 concentrations by the rotating disc method has shown that Triton-×-100 decreases the effective diffusivity [35] by an amount ranging from 5.18 to 18.5%, depending on Triton-×-100 concentration. Triton-×-100 is adsorbed at the cathode with its polar end attached to the solution and its non-polar end attached to Hg.

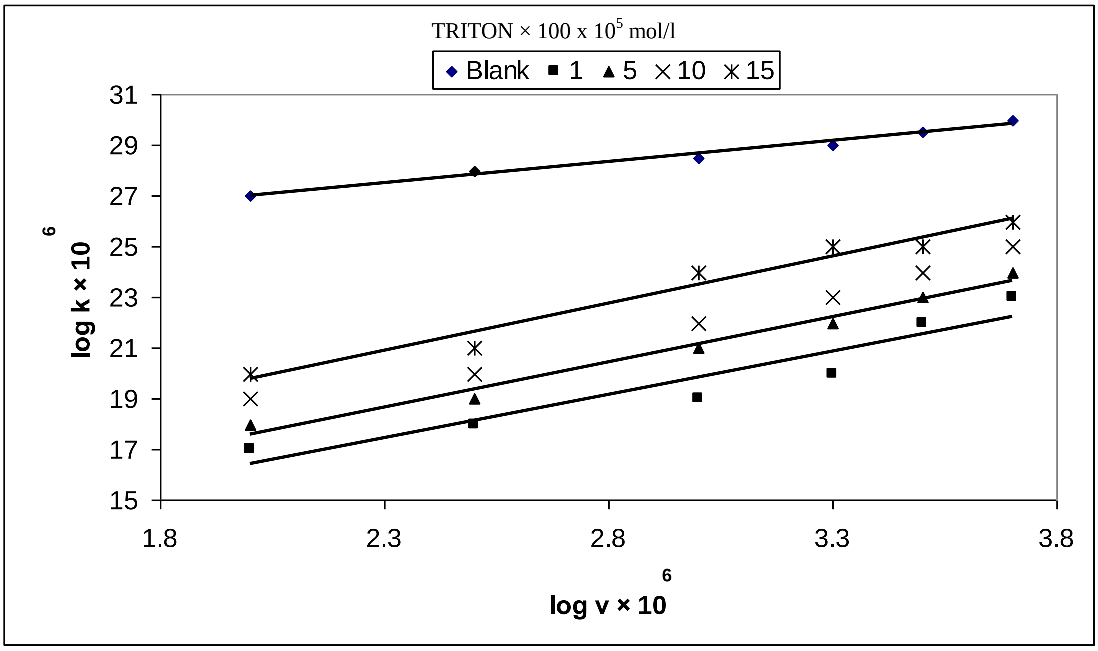

Figure 4. Effect of H_2 evolution rate on the mass transfer coefficient of different Triton-×-100 concentrations.

This linkage of the solution to the cathode may resist the natural convection flow of the solution past a mercury surface. Figure 4 shows the effect of Triton-×-100 on the mass transfer coefficient at different H_2 discharge rates.

The mass transfer coefficient decreases with increasing surfactant concentration by an amount ranging from 58.8 to 76% depends on Triton-×-100 concentration and H_2 discharge rate. The decrease in the mass transfer coefficient of Triton-×-100 may ascribed to the three following effects. First, the decrease in the solution surface tension caused by Triton-×-100. Figure 5 gives rise to early detachment of small H_2 bubbles from the cathode surface. Besides the adsorption of surfactant at the bubble surface makes the bubbled surface rigid with a consequent decreases in the bubble rise velocity. [36,37]

The gas evolution of small rigid H_2 bubbles of low-rise velocity reduces the rate of mass transfer. Second, adsorption of Triton-×-100 on the mercury cathode interferes with the beneficial radial flow of the Hg cathode because in the presence of Triton-×-100, Hg surface tension remains practically constant over a wide range of potential. [38,39]

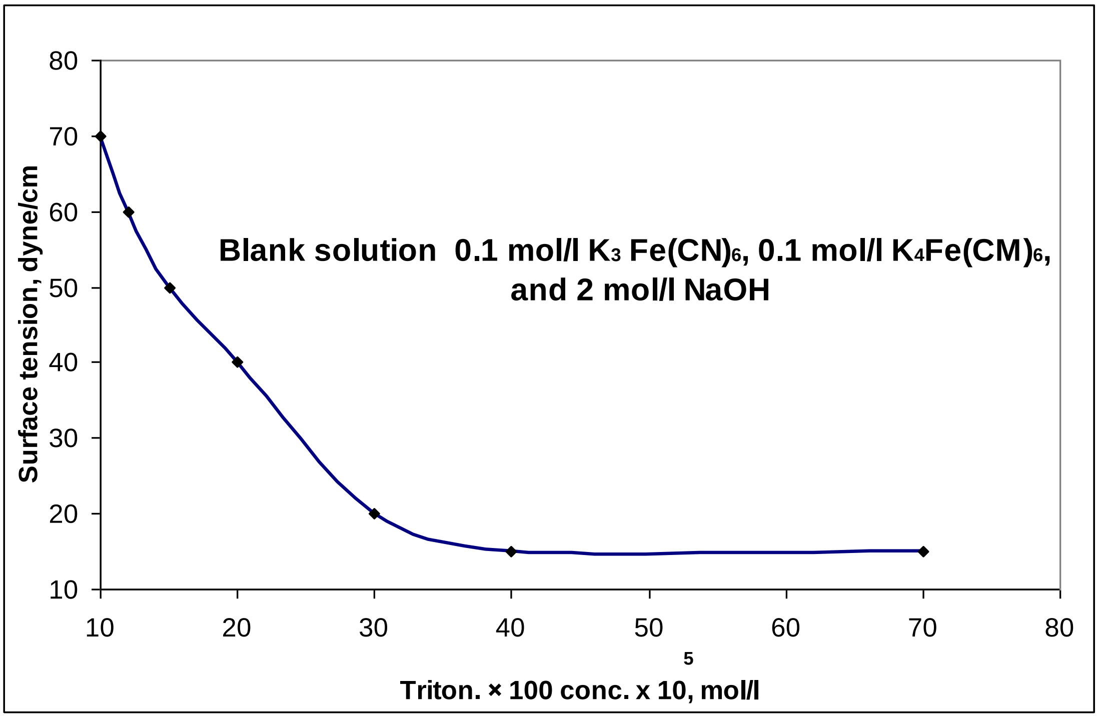

Figure 5. Effect of Triton-×-100 concentration on solution surface tension.

Third, as mentioned before, Triton-×-100 adsorption on the cathode increases with the interfacial viscosity and decreases with the effective diffusivity of the ferricyanide ion. [35,39]

The decrease in limiting current in the presence of Triton-×-100 is due to the surface blockage as a result of Triton-×-100 adsorption than due to the increase in interface viscosity.

A possible explanation for this effect could be as follows. The "n" value for Triton-×-100 is between 9 and 10. It has also been reported [40] that non-ionic surfactants with shorter polar chains form flat "disks", a structure of which approaches the structure of a more uniform bilayer, the smaller the number of groups "n".

The presence of 'oligomers' with a larger number of polar groups induces the formation of smaller cylindrical structures of a more fragmental nature because of the repulsive dipolar interaction between these aggregates. [40,41]

In other words, the coalescence of surface aggregates that is favoured by molecules with short polar chains, seems to be hampered by the presence of longer polar chains. [42]

4. CONCLUSION

The measurement of the mass transfer coefficient of H_2 evolution in cathode reduction at a Hg cathode leads to the following results:

[a] The mass transfer at a Hg cathode is higher than that at a solid electrode.

[b] Addition of non-ionic Triton-×-100 leads to decreases in the rate of mass transfer by an amount ranging from 62 to 82% depending on Triton-×-100 concentration and H_2 discharge rate.

References

1. D.J. Pickett, *Electrochemical Reactor Design*, Elsevier, Amsterdam, 1977.
2. H. Vogt, in: E.B. Yeager, J.O'M. Bockris, B.E. Conway, S. Sarangapani (Eds.), Comprehensive Treatise of Electrochemistry, Vol. 6, Plenum, New York, 1983, pp. 445–489; C.R. Wilke, M. Eisenberg, C.W. Tobias, *J. Electrochem. Soc*. 100 (1953) 513–523.
3. B.V. Tilak, S. Sarangapari, N.L. Weinberg, in: A. Weissberger (Ed.), Technique of Electroorganic Synthesis, Wiley, New York, 1982, pp. 195–249.
4. S.D. Clinton, J.J. Perona, *Ind. Eng. Chem. Fund*. 21 (1982) 269–271.
5. A. Savall, G. Lacoste, *Chem. Eng. Sci*. 35 (1980) 389–395.
6. N. Ibl, J. Venczel, *Metalloberflache* 24 (1970) 365–374.
7. L.J.J. Janssen, J.D. Hoogland, *Electrochim. Acta* 15 (1970) 1013-1023.
8. G.H. Sedahmed, *J. Appl. Electrochem*. 17 (1987) 746–752.
9. K.F. Khaled, *Appl. Surf. Sci.* 230 (2004) 307.
10. S.A. Abd El-Maksoud, *J. Electroanal. Chem.* 565 (2004) 321.
11. A. Lalitha, S. Ramesh, S. Rajeswari, *Electrochim. Acta* 51 (2005) 47.
12. R. Subramanian, V. Lakshminarayanan, *Corros. Sci.* 44 (2002) 535.
13. A.K. Maayla, N.A.F. Al-Rawashdeh, *Corros. Sci.* 46 (2004) 1129.
14. P.J. Martin, G.T. Cheek, W.E.O. Grady, P.M. Natishan, *Corros. Sci.* 47 (2005) 3187.
15. M.A. Migahed, *Mater. Chem. Phys. 93 (2005) 48.*
16. F. Bentiss, M. Traisnel, M. Lagrenée, *Corros. Sci.* 42 (2000) 127.
17. M. Lagrenée, B. Mernaru, N. Chaibi, M. Traisnel, H. Vezin, F. Bentiss, *Corros. Sci.* 43 (2001) 951.
18. A. Popova, M. Christov, S. Raicheva, E. Sokolova, *Corros. Sci.* 46 (2004) 1333.
19. M. Hosseini, F.L. Mertens, M.R. Arshadi, *Corros. Sci.* 45 (2003) 1473.
20. L. Xueming, T. Libia, L. Lin, M. Guannan, L. Guangheng, *Corros. Sci.* 48 (2006) 308.
21. F. Bentiss, M. Lebrini, M. Lagrenée, *Corros. Sci.* 47 (2005) 2915.
22. R. Fuchs-Godec, *Colloids Surf. A* 280 (2006) 130.
23. M. El Azhar, B. Mernari, M. Traisnel, F. Bentiss, M. Lagrenée, *Corros. Sci.* 43 (2001) 2227.
24. T.Y. Soror, M.A. El-Ziady, *Mater. Chem. Phys. 77 (2002) 697.*
25. R. Fuchs-Godec, V. Doleček, *Colloids Surf. A* 244 (2004) 73.
26. V. Branzoi, F. Golgovici, F. Branzoi, *Mater. Chem. Phys. 78 (2002) 122.*

27. S.T. Keera, M.A. Deyab, *Colloids Surf. A* 266 (2005) 129.
28. A.I. Vogel, A Text Book of Quantitative Analysis, Longmans, Green, London, 1960.
29. A. Findly, Practical Physical Chemistry, Longmans, Green, London, 1935.
30. E. Heitz, J. Kreysa, VCH, Weinheim/New York, 1986.
31. C.R. Wilke, M. Eisenberg, C.W. Tobias, *J. Electrochem. Soc*. 100 (1953) 513–523.
32. N. Ibl, Adam, J. Venczel, E. Schalch, *Chem. Ing. Tech*. 43 (1971) 202–215.
33. G.H. Sedahmed, A.M. Ahmed, *J. Chem. Eng*. 7 (1989) 2511.
34. V.G. Levich, Physicochemical Hydrodynamics, Prentice–Hall, Englewood Cliffs, NJ, 1962.
35. A.A. Taha, A.M. Ahmed, D.A. Ebrahim, *Egypt. J. Chem*. 43 (2000) 435.
36. Y.T. Shah, B.G. Kelkar, S.P. Godbole, *AIChE J*. 28 (1982) 353–379.
37. K.V. Dapkus, P.J. Sides, *Int. J. Multiphase Flow* 13 (1987) 403–413.
38. J.K. Brimacombe, A.D. Graves, D. Inman, *Chem. Eng. Sci*. 25 (1970) 1718–1817.
39. J.O'M. Bockris, D.M. Drazic, *Electrochemical Science*, Taylor & Francis, London, 1972.
40. F. Portet, P.L. Desbéne, C. Treiner, *J. Colloid Interface Sci.* 194 (1997) 379.
41. S. Paria, K.C. Khilar, *Adv. Colloid Interface Sci.* 110 (2004) 75.
42. R. Fuchs-Godec, *Electrochim. Acta* 52 (2007) 4947.