THE EFFECT OF *p*-TOLUIDINE ON THE TWO-STEP ELECTROREDUCTION OF Zn(II) IN WATER–METHANOL AND WATER–DIMETHYLFORMAMIDE

Barbara MARCZEWSKA

Faculty of Chemistry, Maria Curie-Skłodowska University, PL 20-031 Lublin, Poland;
e-mail: bmarc@hermes.umcs.lublin.pl

The acceleration effect of *p*-toluidine on the electroreduction of Zn(II) on the mercury electrode surface in binary mixtures water–methanol and water–dimethylformamide is discussed. The obtained apparent and true forward rate constants of Zn(II) reduction indicate that the rate constant of the first electron transfer increases in the presence of *p*-toluidine. The acceleration effect may probably be accounted for by the concept of the formation on the mercury electrode an activated complex, presumably composed of *p*-toluidine and solvent molecules.
Key words: Acceleration of rate constant; Zinc; Electrochemistry; Electroreduction; Polarography; Coulometry.

The electroreduction of Zn(II) ion has been frequently studied on a mercury electrode and used as a model system in electrode kinetics[1,2]. In aqueous solutions, a simple two-electron reduction mechanism was proposed[2,4]. Other studies indicated the occurrence of two one-electron transfer steps[5–7]. Andreu *et al.*[8] suggested a multi-step reduction of Zn(II) preceded by a partial desolvation of the reagents.

The electroreduction of Zn(II) ion has also been studied in several nonaqueous and mixed solvents, such as DMF (refs[9–12]) and MeOH (refs[13,14]). Like in aqueous solutions, single[9,13,14] and two-step processes have been considered[12,15].

It is well known that the Zn(II) electroreduction can be accelerated in presence of adsorbed nonelectroactive species on mercury electrode in aqueous[16,17] and in mixed water–organic solvents[18–21]. The catalyzing organic substance always contain sulfur or nitrogen atoms with electron pairs capable of forming coordinate bonds[22].

Among some organic compounds which accelerate the electroreduction processes of cations on mercury electrode, *p*-toluidine exerts relatively

strong influence on the electroreduction of Zn(II) in aqueous solutions[23]. It should also be noted that it is a compound utilized in pharmaceutical industry and in medical diagnostics[24,25].

The purpose of this study is to determine the mechanism of the acceleration effect of *p*-toluidine on Zn(II) electroreduction on the mercury electrode surface in binary mixtures water–MeOH and water–DMF with a defined form of solvated Zn(II) ion, in the expectation of understanding better the nature of the catalytic effect.

EXPERIMENTAL

Apparatus and Measurements

Measurements were carried out using a three-electrode cell containing a dropping mercury electrode constructed according to Randles[26], a saturated sodium chloride–calomel electrode (SSCE), and a platinum spiral as a counter electrode. The ferricinium–ferrocene (Fc) redox system was used as a solvent-independent reference electrode.

Impedance measurements were carried out with a 9121 FR Analyzer and 9131 Electrochemical Interface (Atlas Sollich, Gdańsk, Poland). The potential of zero charge (E_z) was measured using the streaming mercury electrode[27,28]. Interfacial tension at E_z was measured by the maximum bubble pressure following Schiffrin's method[29].

Polarographic measurements were carried out using a polarograph PA-4 (Laboratorní přístroje, Prague, Czech Republic). Cyclic voltammetric and chronocoulometric experiments were carried out employing a Model 270 Electrochemical Analysis system (EG&G PAR, Princeton, NJ) with a static mercury drop electrode (Laboratorní přístroje, Prague, Czech Republic).

Absorption spectra were taken with a Zeiss Specord M 42 spectrophotometer using 1 cm quartz cells to obtain records in the 200–700 nm region at 294 ± 1 K. The spectra were stored on disk in the format of the Zeiss Specord M 500.

Reagents

Chemicals of analytical grade from Merck were used. Water and mercury were distilled twice. The electrolyte concentrations were always 10^{-3} M $Zn(ClO_4)_2 \cdot 6\ H_2O$, 1 M $NaClO_4$ and 10^{-5} M $HClO_4$. The concentration of MeOH was 91 vol.%, DMF 90 vol.% and *p*-toluidine 0.03–0.1 mol l^{-1}. Measurements were carried out at temperature 298 ± 0.1 K. The solutions used were deaerated by nitrogen which was passed over the solutions during the measurements.

RESULTS

Double Layer Analysis

The double layer capacity in the investigated solutions was measured at the frequency of 800 Hz. The capacitance was measured with an accuracy of

±0.2%. In the whole polarisation range, capacitance dispersion was tested at five different frequencies between 400 and 2 000 Hz. In the potential range studied, no dispersion of capacitance was observed.

Figures 1 and 2 present *C–E* curves for the base solution and the solutions containing *p*-toluidine at various concentrations. An addition of *p*-toluidine (0.03–0.1 mol l⁻¹) to MeOH and DMF solutions, in spite of its better solubility in these solutions than in water, results in a very slight increase in the differential capacity of the double layer at the zinc reduction potential. In all the cases, however, an addition of *p*-toluidine to investigated solutions caused its adsorption at the zinc reduction potential.

Figure 3 presents the potential of zero charge, E_z, as a function of logarithm of *p*-toluidine concentration in 91 vol.% MeOH and in 90 vol.% DMF solutions. An increase in the active substance concentration shifts the value of E_z in MeOH and DMF solutions towards negative potentials which is a regularly observed phenomenon for aromatic compounds. This dependence is linear.

Polarographic Measurements

The diffusion coefficients of Zn(II) in examined solutions were calculated from limiting currents using the Ilkovič equation. The polarographic wave
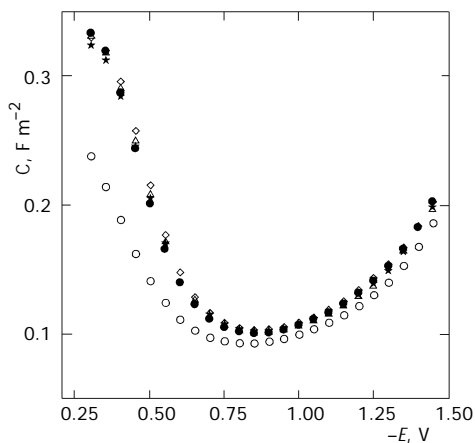

FIG. 1
Differential capacitance C_d of Hg for 1 M NaClO₄ in 91 vol.% MeOH in the presence of: ○ 0.00, ● 0.03, △ 0.07, * 0.09, ◇ 0.10 M *p*-toluidine
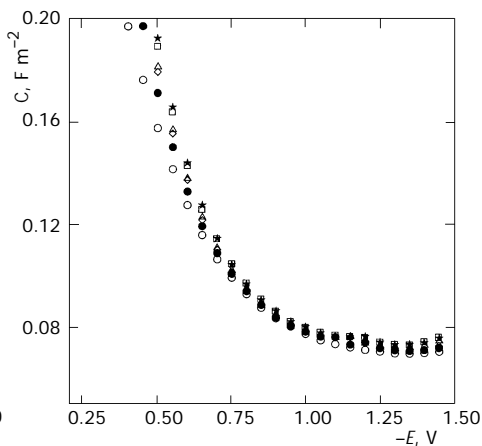
FIG. 2
Differential capacitance C_d of Hg for 1 M NaClO₄ in 90 vol.% DMF in the presence of: ○ 0.00, ● 0.03, ◇ 0.05, △ 0.07, * 0.09, ❑ 0.1 M *p*-toluidine

of Zn(II) in 0.1 M KNO$_3$ with the value of the Zn(II) diffusion coefficient D = 6.9 · 10^{-6} cm^2 s^{-1} was used as a standard[30]. The reproducibility of results obtained was ±5%. The values of the diffusion coefficients of zinc in mercury, which are required for further calculations, were taken from the literature[31] as equal to 1.67 · 10^{-5} cm^2 s^{-1}. The presence of *p*-toluidine had no effect on the values of diffusion coefficients of Zn(II) in MeOH and DMF solutions.

Formal Potential of the Zn(II)/Zn(Hg) System

The formal potentials of the reduction of Zn(II) were calculated on the basis of $E^r_{1/2}$ values determined by cyclic voltammetry (sweep rates from 0.005 to 0.02 V s^{-1}). The procedure of measurements was described in ref.[32]. Formal potentials for irreversible processes were calculated using the modification of Randles' method for cyclic voltammetry[32,33] with an accuracy of ±3 mV and their values are given in Table I as a function of *p*-toluidine concentration in MeOH and DMF solutions.

Chronocoulometric Search for Zn(II) Ion Coadsorption

To find out whether or not Zn(II) can be accumulated in the surface layer by the interaction with adsorbed *p*-toluidine molecules, chronocoulometric measurements were carried out in the presence of its 0.1 mol l^{-1}. The plot of the maximum charge of Zn(II) electroreduction at potential –1.1 V *versus* the square root of the integration time was linear and crossed the coordinate origin after subtraction of the double layer charge recorded for blank
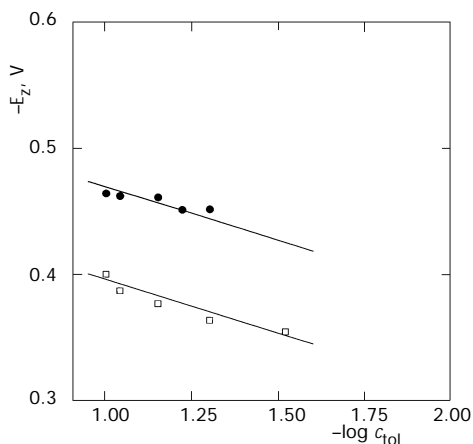

Fig. 3

Dependence of E_z on the concentration of *p*-toluidine in: ● 91 vol.% MeOH, ❑ 90 vol.% DMF

solution. This points out that under such conditions, cathodic reduction of Zn(II) is limited by diffusion and that induced adsorption of Zn(II) cannot be detected within the limits of experimental error.

Spectrophotometric Measurements

To find evidence of complex formation by Zn(II) on addition of an accelerating substance to the investigated solutions, spectrophotometric measurements were carried out. The presence of *p*-toluidine caused no changes in the UV spectrum.

The Double Layer Correction

The potentials ϕ_2 at the outer Helmholtz plane at a particular electrode potential E were derived in the usual manner assuming the validity of the Gouy–Chapman–Stern theory[34]. Table II lists the charge densities σ^M and potentials of the outer Helmholtz plane ϕ_2 as a function of potential E for 91 vol.% MeOH, 90 vol.% DMF solutions in the presence of 0.1 M *p*-toluidine.

The Rate of Electroreduction

The complex cell impedance was obtained at 20 different frequencies in the range from 100 to 30 000 Hz within the faradaic potential region in 10 mV intervals. The impedance data were analysed by fitting to the expressions valid in the case of Randles' equivalent circuit[35,36]. The results rely mainly

TABLE I
Formal potentials of Zn(II)/Zn(Hg) system in 91 vol.% MeOH or 90 vol.% DMF, in the absence and presence of *p*-toluidine

c_{tol}, mol l^{-1}	MeOH	DMF
	$-E_f^0$, V	$-E_f^0$, V
0.00	1.206	1.388
0.07	1.255	1.356
0.10	1.264	1.358

on the analysis of the R_{ct} (charge transfer resistance) values as a function of dc potential. The values k_f^a (apparent rate constants) were computed from R_{ct} according to ref.[8].

As in the case of pure perchlorate supporting electrolyte[8] at negative potentials the rate constant of the first electron transfer in two-step process is determined as $k_f = k_{lim} = k_1$. At more positive potentials the overall rate is determined simultaneously by both steps according to the equation:

$$1/k_f = 1/k_1 + K_1/k_2 ,\qquad\qquad (1)$$

where k_2 is the rate constant of the second electron transfer and K_1 is the equilibrium constant of the first electron transfer reaction (at standard formal potential, E_f^0, $K_1 = 1$).

In MeOH solutions, at p-toluidine concentration of 0.07–0.1 mol l^{-1}, the values of rate constants remain unchanged, as it was also observed in DMF. The effective potential difference acting on the activation energy barrier of charge transfer shoud be $E-\phi_2$ rather than E. Using the Frumkin[37] correction, true rate constants can be obtained. The accelerating influence of

TABLE II
Charge and potential 2 values at various potentials for 0.1 mol l^{-1} p-toluidine in 91 vol.% MeOH or 90 vol.% DMF

Solvent					
91 vol.% MeOH			90 vol.% DMF		
$-E$, mV	$-\sigma^M$, µC cm^{-2}	$-\phi_2$, mV	$-E$, mV	$-\sigma^M$, µC cm^{-2}	$-\phi_2$, mV
932	6.2	51	1 000	7.9	52
942	6.3	51	1 003	8.0	52
953	6.4	51	1 014	8.1	52
963	6.5	52	1 024	8.2	52
972	6.6	52	1 033	8.2	52
983	6.7	52	1 042	8.2	53
993	6.8	52	1 053	8.3	53
1 004	6.9	52	1 063	8.4	53
1 013	7.0	52	1 072	8.5	53

p-toluidine (0.1 mol l^{-1}) on apparent k_f^a and true k_f^t rate constants at potential E_f^0 is presented in Table III.

DISCUSSION

The examination of the effect of *p*-toluidine on Zn(II) ion electroreduction in 91 vol.% MeOH and 90 vol.% DMF solutions required a determination of both *p*-toluidine adsorption on the Hg electrode in relevant solutions and the kinetic parameters of the electroreduction process. The choice of the organic solvent was determined by different abilities to solvate Zn(II) ions. Whereas in 91 vol.% MeOH solution zinc ion is selectively hydrated[14], in 90 vol.% DMF solution it is strongly solvated in the first coordination sphere[10].

The compound *p*-toluidine accelerates the process of Zn(II) ion electroreduction in an aqueous solution[23]. Preliminary examinations carried out by the cyclic voltammetry qualitatively demonstrated the acceleration in MeOH and DMF solutions as well as the fact that the highest acceleration takes place at concentration [H$^+$] = 10^{-5} mol l^{-1}.

The presence of *p*-toluidine slightly increases the differential capacity of the double layer in solutions such as 91 vol.% MeOH and 90 vol.% DMF (Figs 1 and 2). Meanwhile, the attempt to determine *p*-toluidine surface excesses in above-mentioned solutions failed, in spite of its higher solubility. An increase in adsorption can be expected if organic solvent significantly increases solubility of the examined substance considerably lowering its activity coefficient. This condition can be met only for substances with low solubility in water and with relatively high activity coefficients. Low ad-

TABLE III
Apparent and true rate constants of the first and second electron transfer in Zn(II) reduction on Hg electrode in 91 vol.% MeOH or 90 vol.% DMF solutions, in the absence and presence of *p*-toluidine

Solution	c_{tol} mol l^{-1}	$k_1^a \cdot 10^3$ cm s^{-1}	$k_2^a \cdot 10^3$ cm s^{-1}	$k_1^t \cdot 10^3$ cm s^{-1}	$k_1^t \cdot 10^3$ cm s^{-1}
MeOH	0.00	0.5	3.1	0.11	0.05
91 vol.%	0.10	4.3	71.0	0.40	1.16
DMF	0.00	1.4	4.4	0.18	0.10
90 vol.%	0.10	4.3	4.6	1.29	0.14

sorption may be associated with the plot position of adsorbed *p*-toluidine molecule to the electrode surface in MeOH and DMF facilitating thus interactions between π electrons of evenly arranged rings and the mercury surface. Evidences can be found in the shift of E_z towards more negative potentials with rising *p*-toluidine concentration (Fig. 3). The orientation of *p*-toluidine molecules on mercury surface may result in small differences in differential capacity curves for MeOH or DMF in absence and presence of *p*-toluidine (Figs 1 and 2). It should also be noted that no adsorption–desorption peaks can be found in MeOH and DMF although such peaks appear in aqueous solution[23]. The curves with *p*-toluidine added resemble those obtained in the presence of thiourea, characteristic for anions. The orientation of *p*-toluidine molecules on mercury surface does not allow to compare the accelerating effect of amine on its adsorption.

In MeOH solutions, the values of E_f^0 shift towards negative potentials in presence of *p*-toluidine, while in DMF solutions, E_f^0 moves towards positive values. However, in the bulk of solution no change in UV-VIS spectrum of Zn(II) was observed by the addition of amine hence Zn(II)/*p*-toluidine complex formation is unlikely.

The absence of changes in the diffusion coefficients after *p*-toluidine addition shows that the form of cation both in the absence and presence of *p*-toluidine remains the same.

Thus, even if quantitative determination of *p*-toluidine adsorption in MeOH and DMF appears to be impossible, its effects on the Zn(II) electroreduction rate constants can be observed. Relative acceleration calculated from ratio of rate constants in the presence and in the absence of *p*-toluidine (k_{Stol}^a/k_s^a) was about 13 in MeOH and about 2 for DMF. The increase of *p*-toluidine solubility in MeOH and DMF however, is not accompanied by an increase in rate constants. They remain unchanged in MeOH for *p*-toluidine concentration from 0.07 to 0.1 mol l^{-1}, which is also observed in DMF. This effect is probably associated with the similar extent of *p*-toluidine adsorption.

From the literature it can be stated that Zn(II) undergoes a stepwise reduction in aqueous solution, as well as in 91 vol.% MeOH and 90 vol.% DMF solutions[38]. The experiments performed also indicate a stepwise course of Zn(II) ion electroreduction in the presence of *p*-toluidine in all the examined solutions but the apparent and true rate constants of the first electron transfer are higher. Similarly, the rate of the second electron transfer increased in MeOH solution. At higher *p*-toluidine concentrations apparent and true rate constants reached the value obtained in aqueous solution[8,39]. Toluidine had no effect on the rate of the second electron

transfer in DMF solution. It can be suggested that in aqueous and methanolic solutions the mechanism of the process is the same. In DMF solution the rate constant of the second electron transfer in the presence of *p*-toluidine is different form that in water, giving an independent proof that the zinc ion exists in different forms in MeOH and DMF solutions.

The studies reported in this paper indicate that the most significant role in the acceleration process is played by the activated complex formed on the electrode. In MeOH it may consist of molecules of water and *p*-toluidine, while in DMF solution of molecules of water and DMF. Due to stronger solvation in DMF the Zn(II) reduction is more difficult than in MeOH, where formation of activation complex is more feassible.

The binding of the first electron is the slow step in Zn(II) electroreduction because it is associated with significant change in solvation energy. The latter results from the fact that the rearrangement of the solvation sphere during electroreduction requires much higher energy expenditure than the complete removal of dipoles from the neighbourhood of Zn(I) ion.

Summing up, it can be concluded:

The presence of *p*-toluidine accelerates the zinc electroreduction in all the examined systems.

The acceleration follows the rule of the cap-pair effect.

The Zn(II) ion electroreduction consists of two steps. The stage limiting the overall rate of the electrode process is the rate of the transfer of the first electron. This step is accelerated in the presence of *p*-toluidine.

REFERENCES

1. Brodd R. J., Leger V. E. in: *Encyclopedia of Electrochemistry of the Elements* (J. Bard, Ed.), Vol. 5, Chap. 1. Dekker, New York 1976.
2. Tamamushi R.: *Kinetic Parameters of Electrode Reactions of Metallic Compounds*. Butterworths, London 1975.
3. Kang S., Madsuda K., Tamamushi R.: *Collect. Czech. Chem. Commun.* **1982**, *47*, 1433.
4. Go W. S., Osteryoung J.: *J. Electroanal. Chem.* **1987**, *233*, 275.
5. Hush N. S., Blackledge J.: *J. Electroanal. Chem.* **1963**, *5*, 420.
6. Salié G.: *Z. Phys. Chem.* **1970**, *244*, 1.
7. Van der Pol F., Sluyters-Rehbach M., Sluyters J. H.: *J. Electroanal. Chem.* **1975**, *58*, 177.
8. Andreu R., Sluyters-Rehbach M., Remijnse A. G., Sluyters J. H.: *J. Electroanal. Chem.* **1982**, *134*, 101.
9. Dunnett J. S., Gearey D.: *Electrochim. Acta* **1974**, *19*, 907.
10. Taraszewska J., Walega A.: *J. Electroanal. Chem.* **1986**, *200*, 261.
11. Fawcett W. R.: *J. Phys. Chem.* **1989**, *93*, 2675.
12. Fawcett W. R., Lasia A.: *J. Electroanal. Chem.* **1990**, *279*, 243.

13. Behr B., Taraszewska J., Stroka J.: *J. Electroanal. Chem.* **1975**, *58*, 71.

14. Taraszewska J., Broda A.: *J. Electroanal. Chem.* **1983**, *153*, 243.

15. Rawdel B. A., Jefimov A. G., Karbasov B. G., Tichonov K. J.: *Elektrokhimiya* **1980**, *16*, 1061.

16. Sykut K., Saba J., Marczewska B., Dalmata G.: *J. Electroanal. Chem.* **1984**, *178*, 295.

17. Ikeda G., Watanabe K., Taniguhi Y., Tamura H.: *Bull. Chem. Soc. Jpn.* **1984**, *57*, 3363.

18. Marczewska B.: *Monatsh. Chem.* **1996**, *127*, 859.

19. Marczewska B.: *Indian J. Chem.* **1997**, *36A* , 440.

20. Marczewska B.: *Collect. Czech. Chem. Commun.* **1997**, *62*, 843.

21. Marczewska B.: *Gazz. Chim. Ital.* **1996**, *126*, 259.

22. Sykut K., Dalmata G., Nowicka B., Saba J.: *J. Electroanal. Chem.* **1978**, *90*, 299.

23. Dalmata G., Nieszporek J.: *Pol. J. Chem.* **1994**, *68*, 2009.

24. Johnson R. A., Gorman R. R., Wnuk R. J., Crittenden N. J., Aiken J. W.: *J. Med. Chem.* **1993**, *36*, 3202.

25. Bryant M. S., Vineis P., Skipper P. L., Tennenbaum S. R.: *Proc. Natl. Acad. Sci. U.S.A.* **1995**, *85*, 9788.

26. Randles J. E. B. in: *Transactions of Symposium on Electrode Processes* (E. Yeager, Ed.), p. 209. Wiley, New York 1969.

27. Grahame D. C., Larsen R. P., Poth M. A.: *J. Am. Chem. Soc.* **1949**, *71*, 2978.

28. Grahame D. C., Coffin E. M., Comminges J. J., Poth M. A.: *J. Am. Chem. Soc.* **1952**, *74*, 1207.

29. Schiffrin D. J.: *J. Electroanal. Chem.* **1969**, *23*, 168.

30. Turnham D. S.: *J. Electroanal. Chem.* **1965**, *10*, 19.

31. Furman N. H., Cooper W. C.: *J. Am. Chem. Soc.* **1950**, *72*, 5667.

32. Baranski A., Dojlido J., Galus Z., Guminski C., Krygowski., Lasia A., Lipkowski J., Malyszko J., Stroka J., Wrona P. K. in: *Elektrochemiczne wyznaczania stalych fizykochemicznych* (Z. Galus, Ed.), p. 251. PWN, Warszawa 1979.

33. Randles J. E. B. in: *Progress in Polarography* (P. Zuman and I. M. Kolthoff, Eds), Vol. 1, p. 123. Interscience, New York 1962.

34. Mohilner D. M. in: *Electroanalytical Chemistry* (J. Bard, Ed.), Vol. 1, p. 241. Dekker, New York 1966.

35. Sluyters-Rehbach M., Sluyters J. H. in: *Electroanalytical Chemistry* (J. Bard, Ed.), Vol. 4, p. 1. Dekker, New York 1970.

36. Sluyters-Rehbach M., Sluyters J. H. in: *Comprehensive Treatise of Electrochemistry* (E. Yeager, J. O. M. Bockris, B. E. Convay and S. Sarangapani, Eds), Vol. 9, p. 177. Plenum, New York 1984.

37. Frumkin A. N.: *Z. Phys. Chem., A* **1933**, *164*, 121.

38. Marczewska B.: *Electroanalisis* **1997**, *10*, 50.

39. Koene L., Sluyters-Rehbach M., Sluyters J. H.: *J. Electroanal. Chem.* **1996**, *402*, 57.