ADSORPTION EFFECTS OF THIOUREA AT THE Hg ELECTRODE IN WATER–DIMETHYL SULFOXIDE MIXTURES ON Zn(II) REDUCTION

Barbara MARCZEWSKA

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

Received November 21, 1996
Accepted January 29, 1997

The adsorption of thiourea (TU) and the kinetics of Zn(II) reduction at mercury electrode from the solutions of $NaClO_4$ in 10 and 70 vol.% dimethyl sulfoxide (DMSO) at various concentrations of TU have been studied. The obtained results indicate that in the process of Zn(II) electroreduction the dominant role is played by the structure of the primary solvation shell of Zn(II).
Key words: Mixed solvent; Electroreduction; Mercury electrode; Solvation shell.

It has been known for almost twenty years that thiourea accelerates the process of zinc(II) electroreduction in aqueous solutions[1]. More recently such a phenomenon has also been shown to occur in mixed water–organic solutions[2–5]. It has been observed for constant degree of coverage of the electrode surface with thiourea (where zinc ion is selectively hydrated) that similar values of standard rate constants of zinc(II) electroreduction are obtained in mixed and aqueous solutions. The observation has been confirmed for a broad range of concentration of the organic component in such mixed solvents as water–methanol[4], water–ethanol and water–acetone[5]. It was not found in solvents where zinc ion is selectively solvated, such as DMF (ref.[3]) and 98% ethanol[6]. Therefore, it seemed interesting to analyse this phenomenon in DMSO solutions where zinc ion is selectively solvated at high DMSO concentrations, whereas at low DMSO concentrations is hydrated[7].

EXPERIMENTAL

Apparatus and Measurements

Measurements were carried out with a PA-4 polarograph from Laboratorni pristroje (Prague) employing a static mercury drop electrode (SMDE) manufactured by Laboratorni pristroje; Ag/AgCl with saturated NaCl was used as a reference electrode. A platinum wire was the counter electrode. All potentials in Table I employing data published in ref.[8] were referred to the internal ferrocene/ferricenium reference system (Fc).

The double-layer capacity was measured using ac impedance technique at the frequency of 800 Hz with a frequency analyser type 9121 and a generator type 9131 (by Atlas–Sollich). Capacitance was

measured with a precision of ±0.2%. For the whole polarization range, capacity dispersion was tested at five different frequencies between 400 and 25 000 Hz. In the studied potential range no dispersion of the capacitance was observed.

A dropping Hg electrode constructed according to Randles[9] was used. The drop time was 12 s and the flow rate 0.957 mg s^{-1} for the mercury column height of 50 cm. An aqueous saturated NaCl calomel electrode was used in measurements.

The potential of zero charge E_Z was measured using a streaming mercury electrode[10,11]. Interfacial tension at E_Z was measured by the maximum bubble pressure method according to Schiffrin[12].

The kinetic parameters for the reduction of Zn(II) were determined using the cyclic voltammetric technique over a wide range of sweep rates (0.005–20 V s^{-1}) with a precision of ±7% employing a Model 270 Electrochemical Analysis System (EG&G PAR) and SMDE. The hanging mercury electrode had a surface area of 0.0109 cm^2.

Reagents

Chemicals of analytical grade from Merck were used. Water and mercury were distilled twice. DMSO, $Zn(NO_3)_2 . 6 H_2O$ were used without further purification. The concentration of $NaClO_4$ in the investigated mixtures was 1 mol l^{-1}. DMSO concentrations in the solutions were 10 and 70 vol.%. Measurements were carried out at 298 ± 0.1 K. Solutions were deaerated using nitrogen presaturated with the investigated solution. Nitrogen passed over the solution during the measurements.

RESULTS

Figure 1 presents the potential of zero charge E_Z as a function of concentration of thiourea in 0, 10, 70 vol.% of DMSO. With increasing concentration of the active substance, the value of E_Z shifted towards negative potentials as a linear function of concentration. The values of $\partial E/\partial(\log c_{TU})$ coefficients in 10 and 70 vol.% DMSO are in agreement with equivalent value for thiourea in aqueous solutions[13]. This agreement may indicate that in all the examined cases a decisive influence on E_Z potential change is exerted by the specific adsorption of TU on the mercury surface.

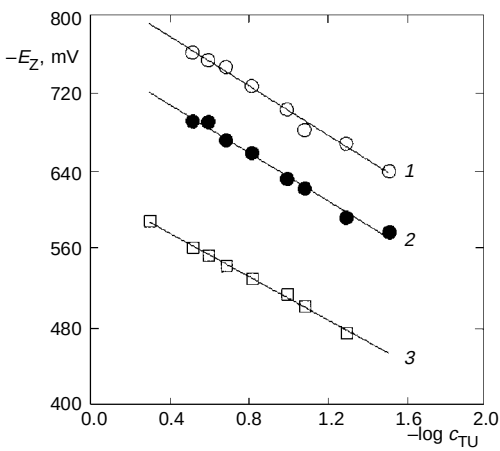

FIG. 1
Dependence of E_Z on the concentration of TU in the solutions: *1* 0, *2* 10, *3* 70 vol.% DMSO

The adsorption of TU on mercury from 10 and 70 vol.% DMSO mixtures containing 1 mol l^{-1} $NaClO_4$ and 0.03–0.8 mol l^{-1} TU was investigated on the basis of measurements of differential capacity. The capacity values for all the examined potentials in solutions containing TU were higher than those for the base solution. Their behaviour was the same as that of thiourea in other solutions.

The relative surface excess was calculated from surface pressure data obtained by a double integration of *C–E* plots, leading to γ–*E* curves, and then from the Parsons' relation[14]

$$\Delta\Phi = \xi^{b} - \xi = \gamma^{b} - \gamma + \sigma_{M}(E^{b} - E) \quad , \qquad (1)$$

where the superscript b denotes the values for the base solution.

The adsorption of TU was estimated according to the Gibbs adsorption equation by the differentiation of Φ *vs* ln *c* curves. The estimated error of the graphical differentiation technique was the same as in ref.[15].

The relative surface excess of the investigated substances was calculated from Eq. (*2*) (ref.[16]):

$$\Gamma' = -\frac{1}{RT}\left(\frac{\partial\Phi}{\partial \ln c}\right)_{c_{NaClO_4},\, c_{DMSO},\, c_{aq},\, \sigma_M} \quad . \qquad (2)$$

Figure 2 shows the values of Γ′ obtained for 0.25 mol l^{-1} TU in 10 vol.% DMSO and 0.25, 0.5, 0.8 mol l^{-1} TU in 70 vol.% DMSO as a function of potential. The plots indicate that at the potential of zinc reduction the surface excess of TU was $0.88 \cdot 10^{-6}$ mol m^{-2} in 10 vol.% DMSO, while in solutions containing 70 vol.% DMSO and TU concentrations of 0.25, 0.5, 0.8 mol l^{-1} they were $0.28 \cdot 10^{-6}$, $0.68 \cdot 10^{-6}$ and $1.04 \cdot 10^{-6}$ mol m^{-2}, respectively. The saturation value Γ_s was estimated by extrapolation of $1/c_{org} = 0$ in $1/\Gamma_{org}$ *vs* $1/c_{org}$ plot. The value $\Gamma_s = 5.55 \cdot 10^{-6}$ mol m^{-2} corresponds to the area $A_s \approx$

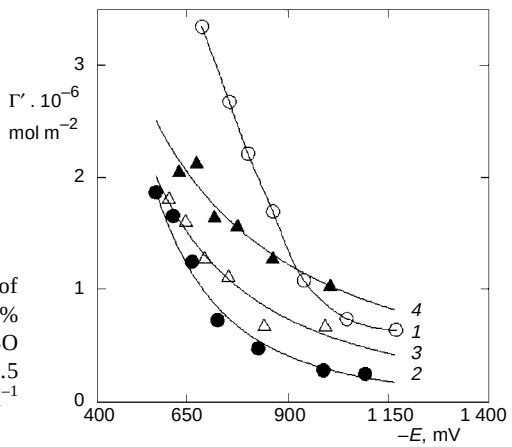

FIG. 2
Dependence of the relative surface excess of TU on potential in the solutions: *1* 10 vol.% DMSO + 0.25 mol l^{-1} TU, *2* 70 vol.% DMSO + 0.25 mol l^{-1} TU, *3* 70 vol.% DMSO + 0.5 mol l^{-1} TU, *4* 70 vol.% DMSO + 0.8 mol l^{-1} TU

$1/\Gamma_s = 0.33$ nm^2 for 10 and 70 vol.% DMSO. The values Γ_s and A_s do not differ significantly from those obtained in aqueous solution.

The kinetic parameters of the Zn(II)/Zn(Hg) system in DMSO–H_2O mixtures in the presence of 0.25, 0.5 and 0.8 mol l^{-1} TU are collected in Table I. They have been taken from data in ref.[2] or calculated from cyclic voltammetric measurements. The procedure of the measurement has been described in ref.[17]. As the results given in Table I indicate, addition of TU to 10 vol.% DMSO caused an increase of 14.4 times the value of apparent rate constant k_s^{app}. In a solution of 70 vol.% DMSO, however, the value of the standard rate constant gradually increased with the increase of thiourea concentration. For successive applied concentrations of TU the increase was by 1.3, 2.7, 4.1 times.

In an aqueous solution and in a 10 vol.% DMSO (Table II), with the same degree of electrode coverage by TU (0.16), the values of the standard rate constants of the electrode process were almost identical and they were 72.4 . 10^{-3} cm s^{-1} and 73.6 . 10^{-3} cm s^{-1}.

TABLE I
Kinetic parameters of Zn(II)/Zn(Hg) system in H_2O–DMSO + 1 mol l^{-1} $NaClO_4$ and in H_2O–DMSO + 1 mol l^{-1} $NaClO_4$ + TU mixtures

c_{DMSO} vol.%	c_{TU} mol l^{-1}	D_{ox} . 10^6 cm$_2$ s^{-1}	$-E_f^0$ V(*v*sFc)	k_s^{app} . 10^3 cm s^{-1}	α^{app}
10	0.00	5.1[a]	1.079	5.1[a]	0.34
10	0.25	5.0[a]	1.078	73.6[a]	0.48
70	0.00	0.9[a]	1.224	0.7[b]	0.36[b]
70	0.25	0.9	1.209	0.9[a]	0.30
70	0.50	0.9	1.206	1.9	0.31
70	0.80	0.9	1.207	2.9	0.29

[a] Ref.[2]; [b] ref.[7].

TABLE II
Standard rate constants of the electrode reaction of the Zn(II)/Zn(Hg) system in H_2O and H_2O–DMSO solutions at the same values of degree of TU surface coverage at the Hg electrode

θ	$k_s^{app}(H_2O)$. 10^3 cm s^{-1}	c_{DMSO} vol.%	k_s^{app}(DMSO) . 10^3 cm s^{-1}
0.16	72.4	10	73.6
0.05	17.5	70	0.9
0.12	48.0	70	1.9
0.19	100.0	70	2.9

In an aqueous solution and in 70 vol.% DMSO the standard rate constants of the zinc reduction process were significantly different for the electrode coverage by TU equal to 0.05, 0.12 and 0.19 (Table II).

The values of formal potential E_f^0 (Table I) determined using cyclic voltammetry[17] did not change after a TU addition in 10 vol.% DMSO solution similarly to an aqueous solution. In a 70 vol.% DMSO, regardless of TU concentration, E_f^0 was shifted towards positive potentials by about 20 mV.

The approximate diffusion coefficients calculated from limiting currents[17] using the Ilkovic equation did not change after addition of TU to the examined solutions.

DISCUSSION

In aqueous solutions with thiourea concentration of 0.25 mol l^{-1} and 0 vol.%, 10 vol.% and 70 vol.% DMSO, the adsorption of thiourea observed at the zinc reduction potential was $1.32 \cdot 10^{-6}$, $0.88 \cdot 10^{-6}$ and $0.28 \cdot 10^{-6}$ mol m^{-2}, respectively. The difference is most probably connected with the changing of the double layer composition. In an aqueous solution the surface of the electrode is covered by water molecules, while in mixed solutions by molecules of water and DMSO. The degree of coverage of the mercury molecule with DMSO in its 10 vol.% solution is 0.45. In a 70 vol.% DMSO the surface is fully covered by DMSO molecules[7].

With a rising DMSO concentration (0, 10, 70 vol.%), standard rate constants of Zn(II) electroreduction attain the values of $109.0 \cdot 10^{-3}$, $72.4 \cdot 10^{-3}$, and $0.9 \cdot 10^{-3}$ cm s^{-1}, respectively. It indicates a strong dependence of the standard rate constant (Table I) on the amount of adsorbed thiourea on the electrode surface. Thus, the 1.5 fold decrease of TU adsorption in 10 vol.% DMSO, in comparison with the aqueous solution[2], entails a 1.5 fold decrease of the standard rate constant. In 70 vol.% DMSO solution the TU adsorption decreases about 5 times in comparison with the aqueous solution, while the value of the standard rate constant decreases about 120 times.

It seems therefore that some other factor must play an important role here. In aqueous solution and in 10 vol.% DMSO, with the same degree of electrode coverage with thiourea (Table II), the values of standard rate constants of Zn(II) electroreduction are almost identical. It is most probably connected with the fact that in both, the aqueous solution and the 10 vol.% DMSO solution, the zinc ion is in the form of an aquo complex[7].

Similar values of the standard rate constants to those of the aqueous solution, with the same degree of electrode coverage with thiourea, was also observed in other mixed solutions, where zinc ion is selectively hydrated in a broad range of concentrations of the organic component[4].

The values of standard rate constants obtained (at the same degree of electrode coverage) in aqueous solution and in 70 vol.% DMSO, where zinc is solvated by DMSO molecules[7] differ significantly (Table II). It should be noted, that in DMSO

solutions, according to the calculations in ref.[18], the number of solvent molecules for Zn(II) in the first solvation sphere was found to be 7.

The obtained dependences indicate that the composition of coordination sphere of reduced zinc ion plays the decisive role in the value of the rate constant. The observed increase in the rate of the electroreduction of zinc ions in presence of thiourea is connected with the formation of a thiourea complex adsorbed on the electrode. The composition of the complex varies, depending on the composition of the first coordination sphere of the ion being reduced. It should be added that the acceleration of the process takes place when thiourea is adsorbed on the electrode surface at the reduction potential of zinc(II) (ref.[1]). The adsorbed molecules of thiourea push molecules of water or other solvent out from the zinc(II) coordination sphere, taking their place. Simultaneously they play the role of a bridge which facilitates the electron transfer. The aquo complex with zinc ion is very labile and the presence of thiourea causes no changes in the value of the formal potential. The DMSO solvates cations much better than water. In 70 vol.% DMSO in presence of TU positive shift of the formal potential by about 20 mV takes place, regardless of the thiourea concentration (Table I). This fact undoubtedly indicates the formation of complex Zn–TU–DMSO which composition does not depend on TU concentration.

In the light of such data it seems that the process of zinc(II) electroreduction is strictly connected with the composition of the first coordination sphere of the complex reduced on the electrode surface. There seems to be no doubt that the solvent present in the solvation sphere of the reactant ion plays very important role in the process of electroreduction of Zn(II).

REFERENCES

1. Sykut K., Dalmata G., Nowicka B., Saba J.: J. Electroanal. Chem. *90*, 299 (1978).
2. Marczewska B.: Polish J. Chem. *67*, 2205 (1993).
3. Marczewska B.: Gazz. Chim. Ital. *125*, 259 (1996).
4. Marczewska B.: Monatsh. Chem. *127*, 859 (1996).
5. Marczewska B.: Unpublished results.
6. Marczewska B.: Croat. Chem. Acta. *69*, 11 (1996).
7. Taraszewska J., Walega A.: J. Electroanal. Chem. *171*, 243 (1984).
8. Malyszko J., Scendo M.: J. Electroanal. Chem. *250*, 61 (1988).
9. Randles J. E. B.: *Transactions of the Symposium on Electrode Processes* (E. Yeager, Ed.) p. 209. Wiley, New York 1961.
10. Grahame D. C., Larsen R. P., Poth M. A.: J. Am. Chem. Soc. *71*, 2978 (1949).
11. Grahame D. C., Coffin E. M., Commings J. J., Poth M. A.: J. Am. Chem. Soc. *74*, 1207 (1952).
12. Shiffrin D. J.: J. Electroanal. Chem. *23*, 168 (1969).
13. Ivanova R. W., Ivanova O. G.: Elektrokhimiya *15*, 1474 (1979).
14. Parsons R.: Proc. R. Soc. London, A *261*, 79 (1961).
15. Minc S., Jastrzebska J., Jurkiewicz-Herbich M.: J. Electroanal. Chem. *152*, 223 (1983).
16. Jurkiewicz-Herbich M., Jastrzebska J.: J. Electroanal. Chem. *58*, 58 (1984).
17. Marczewska B.: J. Electroanal. Chem. *374*, 251 (1994).
18. Maksymiuk K., Stroka J., Galus Z.: J. Electroanal. Chem. *279*, 1 (1990).