

KINETICS OF ZINC(II) REDUCTION AT THE Hg ELECTRODE IN WATER-ETHANOL MIXTURES

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The kinetics of the Zn(II)-Zn(Hg) electrode process was studied in water-ethanol-NaClO₄ mixtures. Diffusion coefficients, formal potential and charge transfer rate constants were determined. The results are interpreted taking into account the change of the activation energy of the process.

A growing interest in the research in the kinetics of electrode processes in mixed solvents has begun after the analysis of the Zn(II)-Zn(Hg) reaction by Jaenicke and Schweitzer¹. Jaenicke's experiments provoked much interest but also controversies concerning the interpretation of the obtained results.

Since then many papers have appeared, devoted to electrode reactions in non-aqueous and mixed solvents. Some of them concerned the systems examined in study¹ (acetone-water, methanol-water) but they were more detailed and they specified such data as diffusion coefficients and formal potentials²⁻⁶.

Tanaka et al.⁷ examined the process of zinc electroreduction in the EtOH-water system with ethanol concentrations of 10, 20 and 50 vol.%. However, there are no data for intermediate concentrations and those above 50 vol.%. Such data would provide more information about the occurrence and the possible nature of this process.

The purpose of the present paper was to study the Zn(II) reduction from H₂O-EtOH mixtures 0 - 90 vol%. EtOH in 1 M NaClO₄. EtOH is interesting because it is aprotic solvent more basic than water. The choice of NaClO₄ was determined by earlier studies in aqueous solution⁸.

EXPERIMENTAL

Apparatus and Measurements

Measurements were carried out with polarograph PA-4 by Laboratorni pristroje, Prague and PEG&G Parc Instrument model 384 B, employing a static mercury drop electrode (SMDE) manufactured by Laboratorni pristroje, Prague and by PAR (EG&G Parc model 303). Ag/AgCl with saturated NaCl solution was used as a reference electrode. The counter electrode was a platinum wire. Additionally,

voltammetric curves of the ferrocene–ferricinium system (F_c) were recorded and all potentials in Table I were referred to this internal system. The kinetic parameters for the reduction of Zn(II) were determined using the cyclic voltammetry technique in a wide range of sweep rates ν (0.005 to 20 V s⁻¹) employing Model 270 Electrochemical Analysis System EG&G PAR and SMDE.

A hanging mercury drop electrode with a surface area of 0.01827 cm² was used as a working electrode.

The viscosities of the solutions were determined using the Hoppler viscometer (Haake Mess technik, Karlsruhe).

Reagents

Chemicals of analytical grade from Merck were used. Water and mercury were distilled twice. Zn(NO₃)₂ · 6 H₂O was used without further purification. The Zn(II) concentration in the solutions was always 4 · 10⁻⁴ mol l⁻¹. Concentration of NaClO₄ in the investigated mixtures was 1 mol l⁻¹. The specific conductivity of the ethanol was 1.36 · 10⁻⁶ Q⁻¹ cm⁻¹. Measurements were carried out at 298 ± 0.1 K.

Solutions were deoxygenated using nitrogen which was passed through a vanadous sulfate solution and presaturated with the investigated solution. This gas passed over the solution during the measurements.

RESULTS

The Formal Potential E_f^0 of the Zn(II)–Zn(Hg) System

The formal potential for quasi-reversible processes was calculated on the basis of reversible half-wave potential $E_{1/2}^r$ determined using cyclic voltammetry. The procedure of the measurements has been described in study⁹. The formal potential for irreversible processes was calculated using the modification of Randles method for cyclic voltammetry^{9,10}. They were determined with the accuracy of ±3 mV. These potentials as a function of EtOH concentration are collected in Table I. The increase of EtOH content shifted the formal potential towards more negative values.

Diffusion Coefficients

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

The polarographic wave of Zn(II) in 0.1 mol l⁻¹ KNO₃ with the value of the Zn(II) diffusion coefficient $D = 6.9 \cdot 10^{-6}$ cm² s⁻¹ (ref.¹¹) was used as a standard. The reproducibility of the results obtained was ±10%. The value of the diffusion coefficients of zinc in mercury, which are required for further calculations, were taken from the literature as equal to 1.67 · 10⁻⁵ cm² s⁻¹ (ref.¹²).

The influence of the EtOH content in the mixture on the diffusion coefficients of Zn(II) is shown in Table I.

Plots of the relative Walden products and viscosities of H₂O–EtOH in the presence of 1 mol l⁻¹ NaClO₄ are shown in Fig. 1.

Kinetic Parameters of the Zn(II)–Zn(Hg) System

The kinetic parameters of the Zn(II)–Zn(Hg) system in 1 mol l⁻¹ NaClO₄ in H₂O–EtOH were calculated from cyclic voltammetry measurements by Nicholson's method for the quasi-reversible process¹³ and for the irreversible process by the method described by Nicholson and Shain¹⁴. The cathodic transfer coefficient α for the quasi-reversible process was determined on the basis of the dependence of the formal values αn_α on $1/\nu$. The results of kinetic calculations for the Zn(II)–Zn(Hg) system in the investigated solutions are compiled in Table I.

In mixtures containing 1 mol l⁻¹ NaClO₄, the values of apparent rate constants k_s^{app} of Zn(II) reduction pass through a shallow minimum at about 50 vol.% of EtOH. In mixtures, the observed transfer coefficient has values between 0.38 and 0.29.

TABLE I
Kinetic parameters of the Zn(II)–Zn(Hg) system in H₂O–EtOH mixtures with 1 mol l⁻¹ NaClO₄

EtOH, vol.%	1 mol l ⁻¹ NaClO ₄			
	$D_{\text{ox}} \cdot 10^6, \text{cm}^2 \text{s}^{-1}$	$-E_f^0, \text{V (vs } F_c)$	$k_s^{\text{app}} \cdot 10^3, \text{cm s}^{-1}$	α^{app}
0	6.6	1.064	3.26	0.29
10	5.7	–	1.23 1.4 ^a	0.33 0.33 ^a
20	4.6	1.076	0.55 0.54 ^a	0.32
30	4.3	1.095	0.37	0.28
40	3.9	1.103	0.30	0.29
50	3.7	1.115	0.27 0.22 ^a	0.38 0.38 ^a
60	3.6	1.124	0.33	0.38
70	3.7	1.129	0.46	0.34
80	3.9	1.131	0.67	0.31
90	4.4	1.130	1.15	0.30

^a Values published in ref.⁷.

DISCUSSION

The kinetic parameters of the electrode reactions in H₂O–organic solvent mixtures depend on the adsorption of the organic solvent which modifies the structure of the double layer at the electrode surface and on the properties of the bulk of the solution. The adsorption of EtOH on the Hg electrode from mixture with H₂O has been studied previously^{15,16}. The most important property is the solvation of the reactant in the bulk of the solution and in the surface phase. Studies of Zn(II) reduction showed that the rate constants of reduction from H₂O–EtOH solutions in 1 mol l⁻¹ NaClO₄ (Table I) pass through a minimum at about 50 vol.% of EtOH. This is qualitatively similar to the value reported by Jaenicke et al.¹. A minimum of the rate constant as a function of the solvent composition could be expected if the reactant is preferentially hydrated and the organic solvent is adsorbed at the electrode. This has been confirmed for Zn(II) reduction from H₂O–acetone mixtures³, where strong preferential hydration of Zn(II) was found⁴.

The formal potentials of the Zn(II)–Zn(Hg) system expressed with respect to the ferrocene electrode scale undergo a shift towards negative values with an increase of the EtOH content in solution. This value is comparable with that of the liquid junction potential between H₂O and CH₃OH (ref.⁶) estimated from the data of Duschek and Gutman¹⁷ for the F_c reference system.

It seems that zinc is preferentially hydrated in ethanol similarly to methanol where preferential hydration was postulated in up to 95 vol.% of CH₃OH (ref.⁶).

This conclusion seems indicated by the values of the relative Walden product of H₂O–EtOH mixtures vs EtOH content (Fig. 1) and small changes of the values of the Gibbs energy transfer calculated on the basis of the F_c system as a function of solvent

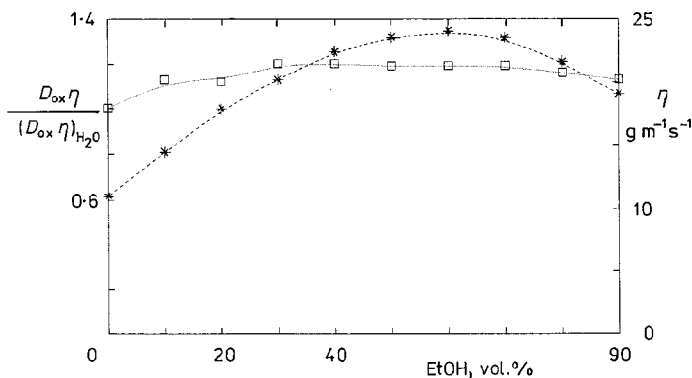


FIG. 1

Relative Walden product (1) and viscosity (2) of H₂O–EtOH mixtures vs EtOH content in the presence of 1 M NaClO₄

composition (Fig. 2). The Gibbs energy transfer reaches an approximate constant value of 12.5 kJ mol^{-1} at the concentration of about 90 vol.% of EtOH; above that concentration, it seems that Zn(II) ions are totally solvated by EtOH molecules.

The explanation of the course of Zn(II) reduction from H_2O -EtOH mixtures may be as follows. It seems possible that the presence of EtOH with water in the solvation shell of Zn(II) ions causes the water molecules to be more strongly bound than in the case of a pure aquo complex. Therefore, a higher activation energy is needed to free the Zn(II) ion from its solvation shell and the rate constant decreases. As the number of ethanol molecules in the solvation shell of Zn(II) increases, the bonding of both water and ethanol may be weaker and the rate constant increases up to the value characteristic for pure ethanol.

The change in the rate constant is probably also affected by the viscosity which changes along with EtOH concentration and reaches a maximum at about 60 vol.% EtOH (Fig. 1).

The variation of the diffusion coefficient (Table I) of Zn(II) with a changing composition of the H_2O -EtOH mixture is undoubtedly a complex function of the viscosity and the radius of the ion which depends on preferential solvation. The latter can also change the local viscosity around the ion.

From the kinetic parameters for Zn(II) electroreduction collected in Table I follows that the cathodic transfer coefficient practically does not change in the entire composition range of the mixture. This suggests that the mechanism of the electrode process in H_2O -EtOH mixture is similar to that in pure aqueous solution.

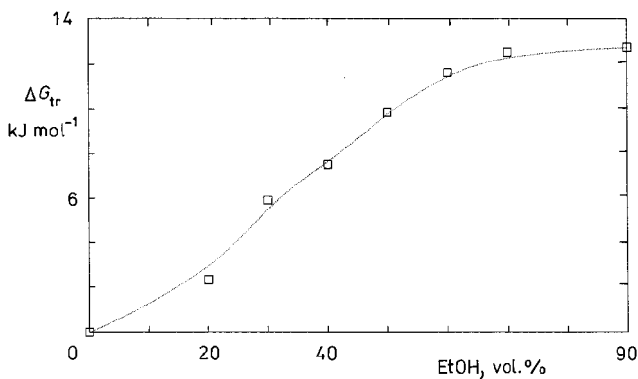


FIG. 2

Changes in the transfer energies of Zn(II) ion from aqueous solution of $1 \text{ mol l}^{-1} \text{ NaClO}_4$ to $1 \text{ mol l}^{-1} \text{ NaClO}_4$ in H_2O -EtOH mixtures referred to the F_c potential scale

REFERENCES

1. Jaenicke W., Schweitzer P. H.: *Z. Phys. Chem.*, N. F. 52, 104 (1967).
2. Behr B., Taraszewska J.: *J. Electroanal. Chem.* 58, 71 (1975).
3. Behr B., Taraszewska J., Stroka J.: *J. Electroanal. Chem.* 58, 71 (1975).
4. Behr B., Gutknecht J., Schneider H., Stroka J.: *J. Electroanal. Chem.* 86, 289 (1978).
5. Taraszewska J., Behr B.: *J. Electroanal. Chem.* 91, 11 (1978).
6. Taraszewska J., Broda A.: *J. Electroanal. Chem.* 153, 243 (1983).
7. Tanaka N., Aaki Y., Yamada A.: *Extended Abstracts of U.S.-Japan Cooperative Sciences Seminar on Electrochemistry in Non-Aqueous Solvents*, p. 117. Taniguchi, Tokyo 1973.
8. Andreu R., Sluyters-Rehbach M., Remijnse A. G., Sluyters J. H.: *J. Electroanal. Chem.* 134, 101 (1982).
9. Galus Z. (Ed.): *Elektrochemiczne wyznaczenia stałych fizykochemicznych*. PWN, Warszawa 1979.
10. Randles J. E. B.: *Progress in Polarography*, p. 123. Interscience, New York 1962.
11. Turnham D. S.: *J. Electroanal. Chem.* 10, 19 (1965).
12. Furman N. S., Cooper W. Ch.: *J. Am. Chem. Soc.* 72, 5667 (1950).
13. Nicholson R. S.: *Anal. Chem.* 37, 1351 (1965).
14. Nicholson R. S., Shain J.: *Anal. Chem.* 36, 706 (1964).
15. Majzlisz P. C., Teordowskij J. P., Frumkin A. H.: *Zh. Fiz. Khim.* 28, 87 (1954).
16. Randles J. E. B., Behr B.: *J. Electroanal. Chem.* 35, 389 (1972).
17. Duschek O., Gutmann V.: *Monatsh. Chem.* 104, 990 (1973).