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The Influence of Aminobenzoic Acid on Zn(II) Electroreduction on a Mercury Electrode in Water-Methanol

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Summary. The influence of the isomers of aminobenzoic acid on the reaction Zn(II)/Zn(Hg) was studied in water-methanol mixtures. The *o*- and *m*-isomers accelerate this reaction in all investigated solutions. The standard rate constants are similar at the same degree of electrode coverage with these isomers in water and mixed solutions. *p*-Aminobenzoic acid inhibits the process of Zn(II)/Zn(Hg) electroreduction. The results suggest that the decisive role in the acceleration is played by the formation of the active complex inside the adsorption layer.

Keywords. Electroreduction of Zn (II); Mixed solvent; Isomers of aminobenzoic acid; Acceleration.

Der Einfluß von Aminobenzoesäure auf die Elektroreduktion von Zn(II) an einer Quecksilberelektrode in Methanol-Wasser

Zusammenfassung. Der Einfluß der verschiedenen Isomeren von Aminobenzoesäure auf die Reduktion von Zn(II) an einer Quecksilberelektrode wurde in Methanol-Wasser-Mischungen untersucht. Die *o*- und *m*-Isomeren beschleunigen die Reaktion, und die Reaktionsgeschwindigkeiten sind in Wasser und in Methanol-Wasser gleich. Die Beschleunigung wird wahrscheinlich durch Bildung des aktivierten Komplexes innerhalb der Adsorptionsschicht verursacht. *p*-Aminobenzoesäure hemmt die Elektroreduktion.

Introduction

One of the main reasons of applying nonaqueous or mixed aqueous-organic solutions in chemical studies is the insolubility or low solubility of many substances in water. Enhancing their solubility or making them soluble creates a possibility of studying such substances in a solution and enables a better insight into the mechanism of many processes.

o-Aminobenzoic acid (**1**) belongs to a class of compounds which accelerate the process of zinc ion electroreduction on a mercury electrode according to the cap-pair principle [1], but in aqueous solutions this effect is only weak [2]. A probable cause of this is the low solubility of the compound in water. In order to verify this hypothesis, it seemed to be interesting to examine the effect of the enhanced solubility of the compound in mixed water-methanol solutions. Examinations also covered two other isomers of this acid, *m*-aminobenzoic acid (**2**) and *p*-aminobenzoic acid (**3**) which are poorly soluble in water; their solubility also increases in the presence of alcohol.

The aim of the present investigations was an examination of the accelerative effect of enhanced solubility of aminobenzoic acid isomers on the precess of zinc ion electroreduction in water-methanol as well as an attempt to answer the questions whether the substitution position is of importance for the acceleration of the process and whether the acceleration is related to the amount of the compound adsorbed on the electrode surface.

Results and Discussion

Adsorption of aminobenzoic acid isomers

The adsorption of the isomers of aminobenzoic acid on the mercury electrode from the examined mixtures was investigated on the basis of measurements of differential capacity. In all cases examined, an addition of aminobenzoic acid to the investigated solutions caused an increase in the differential capacity of the double layer at zinc reduction potential. Figures 1–3 present *C-E* curves for the base solution and solutions containing the isomers at various concentrations. In the presence of **1**–**3**, the curves reveal humps which shift towards more negative potentials with growing concentration. In water, the curves for both **1** and **3** are almost identical. The convergence of the *C-E* curves with that of the supporting electrolyte at the potential $E = -1.5\,\mathrm{V}$ suggests total desorption of aminobenzoic acid from the electrode surface in that region. This permits to use the back-integration method in quantitative adsorption studies of aminobenzoic acid at mercury.

The relative surface excess was calculated from the surface pressure Φ obtained by double integration of the *C-E* plots, leading to γ–E curves, and subsequent application of *Parsons*' relation [4]

$$\Delta\Phi = \xi^{\mathrm{b}} - \xi = \gamma^{\mathrm{b}} - \gamma + \sigma_{\mathrm{M}}(E^{\mathrm{b}} - E) \tag{1}$$

where superscript b denotes the values for the base solution.

The adsorption of the isomers of aminobenzoic acid was estimated according to the *Gibbs* adsorption equation by differentiation of the Φ *vs.* $\ln c$ curves. The estimated error in the graphical differentiation technique is the same as in Ref. [5].

The relative surface excess of the investigated substances was calculated from Eq. (2) [6]

$$\Gamma' = -\frac{1}{\mathrm{R}T}\left(\frac{\partial\Phi}{\partial \ln c}\right)_{c_{\mathrm{NaClO_4}},c_{\mathrm{MeOH}},c_{\mathrm{aq}},\sigma_{\mathrm{M}}} \tag{2}$$

or at constant potential according to

$$\Gamma' = -\frac{1}{\mathrm{R}T}\left(\frac{\partial\gamma}{\partial \ln c}\right)_{c_{\mathrm{NaClO4}},c_{\mathrm{MeOH}},c_{\mathrm{aq}},E} \tag{3}$$

The results obtained from Eqs. (2) and (3) are similar. Figures 4–6 show the values of the relative surface excess obtained for variable concentrations of the isomers of

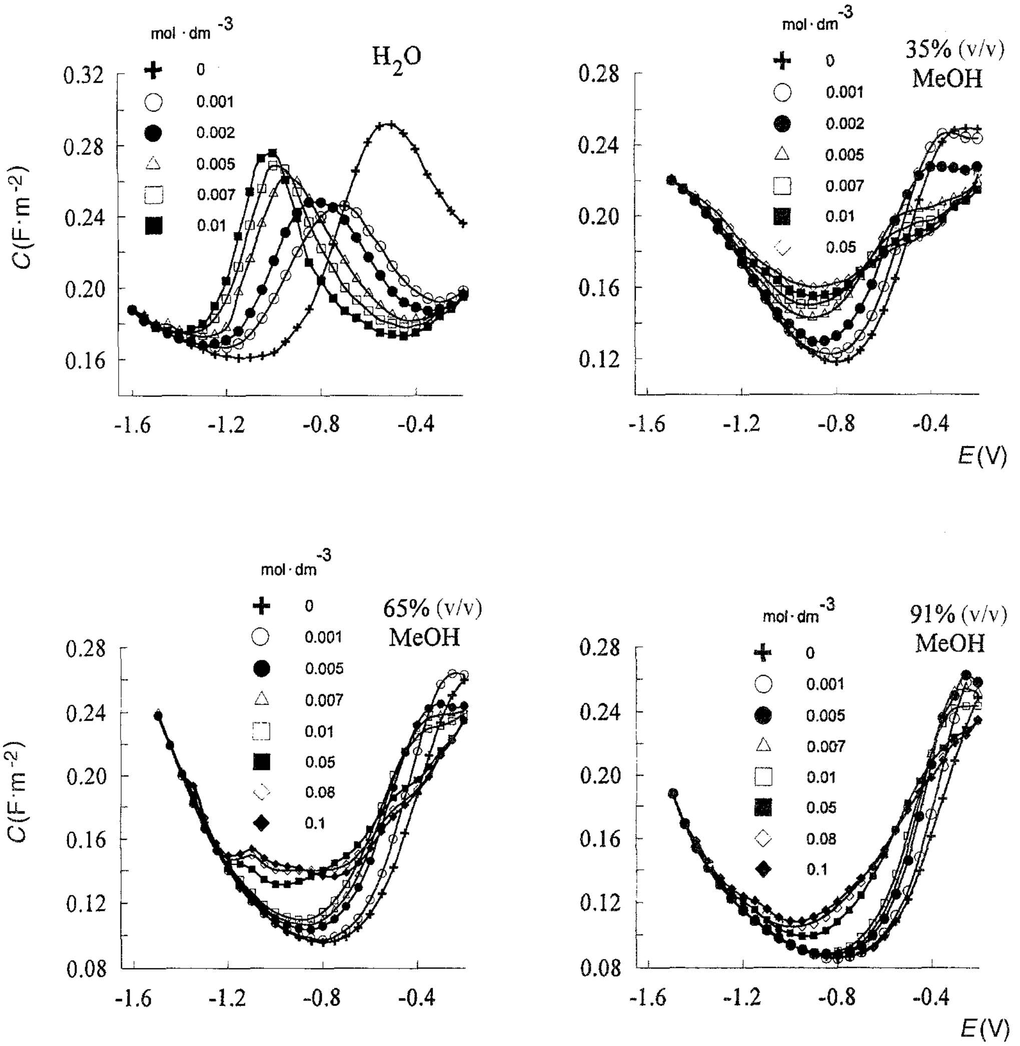

Fig. 1. Differential capacity curves of Hg/1 *M* $NaClO_4$ in H_2O and in 35, 65, and 91% (v/v) MeOH for different contents of **1**

aminobenzoic acid in 0, 35, 65, and 91% (v/v) MeOH as a function of potential (*E*). The saturation values Γ_s was estimated by extrapolation of the linear plot of $1/\Gamma_{org.}$ *vs.* $1/c_{org.}$ to $1/c_{org} = 0$. The obtained values of Γ_s for **1**, **2**, and **3** in 0, 35, 65, and 91% (v/v) MeOH are 2.6×10^{-6}, 1.3×10^{-6}, and $2.6 \times 10^{-6}\,mol \cdot m^{-2}$, respectively.

Diffusion coefficient

The approximate diffusion coefficients of Zn(II) in the examined solutions were calculated from limiting currents using the *Ilkovič* equation. The polarographic wave of Zn(II) in 0.1 *M* KNO_3 with a Zn(II) diffusion coefficient of $D = 6.9 \times 10^{-6}\,cm^2 \cdot s^{-1}$ was used as a standard [7]. The reproducibility of the results obtained was ±10%. The value of the diffusion coefficient of zinc in mercury which are required for further calculations were taken from the literature as equal

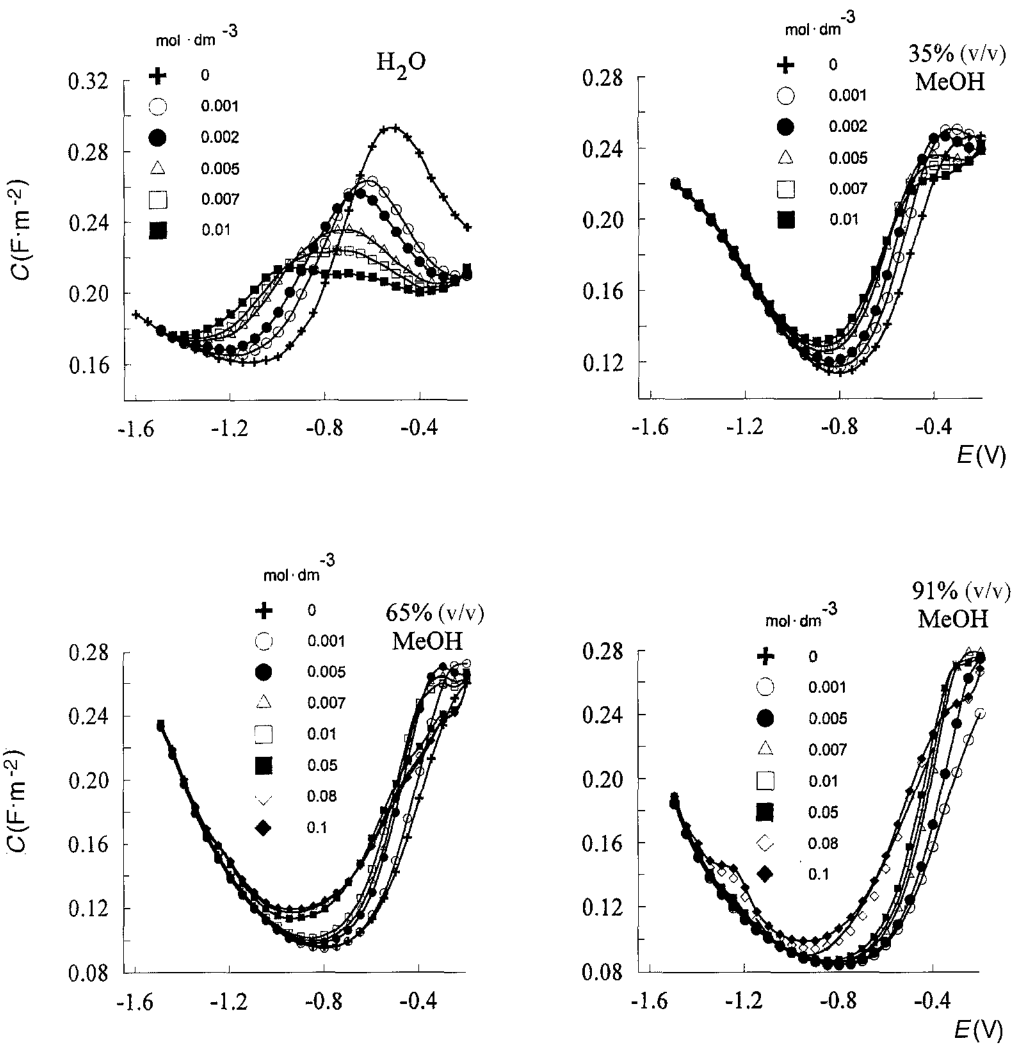

Fig. 2. Differential capacity curves of Hg/1 M $NaClO_4$ in H_2O and 35, 65, and 91% (v/v) MeOH for different contents of **2**

to $1.67\times10^{-5}\,\mathrm{cm}^2\cdot\mathrm{s}^{-1}$ [8]. The obtained values of the diffusion coefficients in the examined solutions in the presence of the accelerating substances changed slightly compared to solutions without additives.

Formal potential of the Zn(II)/Zn(Hg) system

The formal potentials of the reduction of Zn(II) were calculated on the basis of $E^{\mathrm{r}}_{1/2}$ values determined by cyclic voltammetry. The procedure for the measurements is described in Ref. [9]. The formal potentials for irreversible processes were calculated using the modification of *Randles'* method for cyclic voltammetry [9, 10]. They were determined with an accuracy of ±3 mV and are given as a function of MeOH and isomers concentration in Tables 1–3.

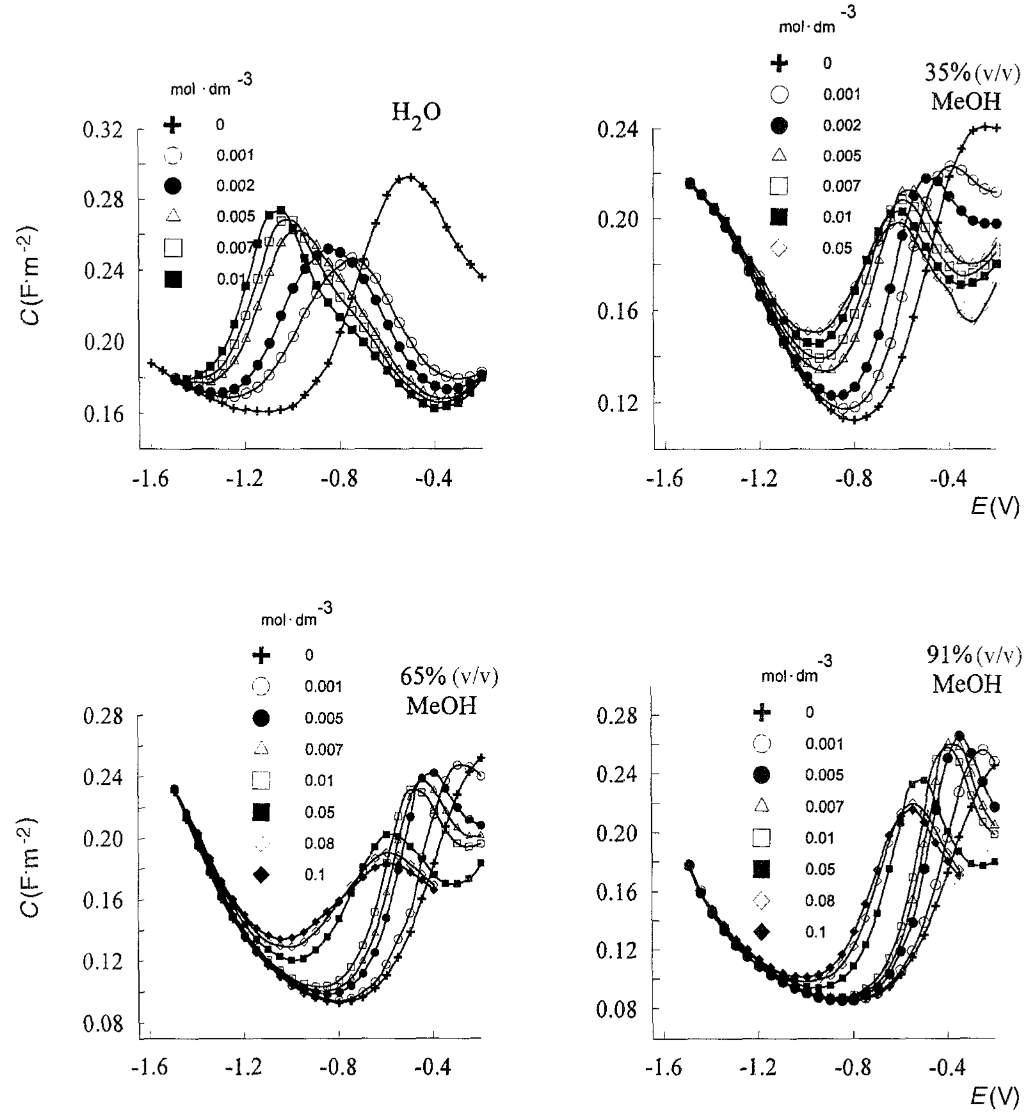

Fig. 3. Differential capacity curves of Hg/1 *M* NaClO$_4$ in H$_2$O and in 35, 65, and 91% (v/v) MeOH for different contents of **3**

Kinetic parameters of the Zn(II)/Zn(Hg) system

The apparent rate constants for the investigated systems were calculated from impedance (FI) measurements. The ohmic resistance of the electrode solution and the mercury capillary was obtained as the real impedance component at a frequency of 10 kHz and at a potential outside the faradaic region. The activation polarization resistances were calculated from $Z' = f(\omega Z'')$ and $Z'' = f(Z')$ [11, 12,] where Z' is the real and Z'' the imaginary part of the cell impedance. The reaction rate constants k_s were calculated according to Eq. (4) where c is the concentration of the depolarizer and R_A is the activation polarization resistance.

$$k_s = RT/n^2F^2cR_A \qquad (4)$$

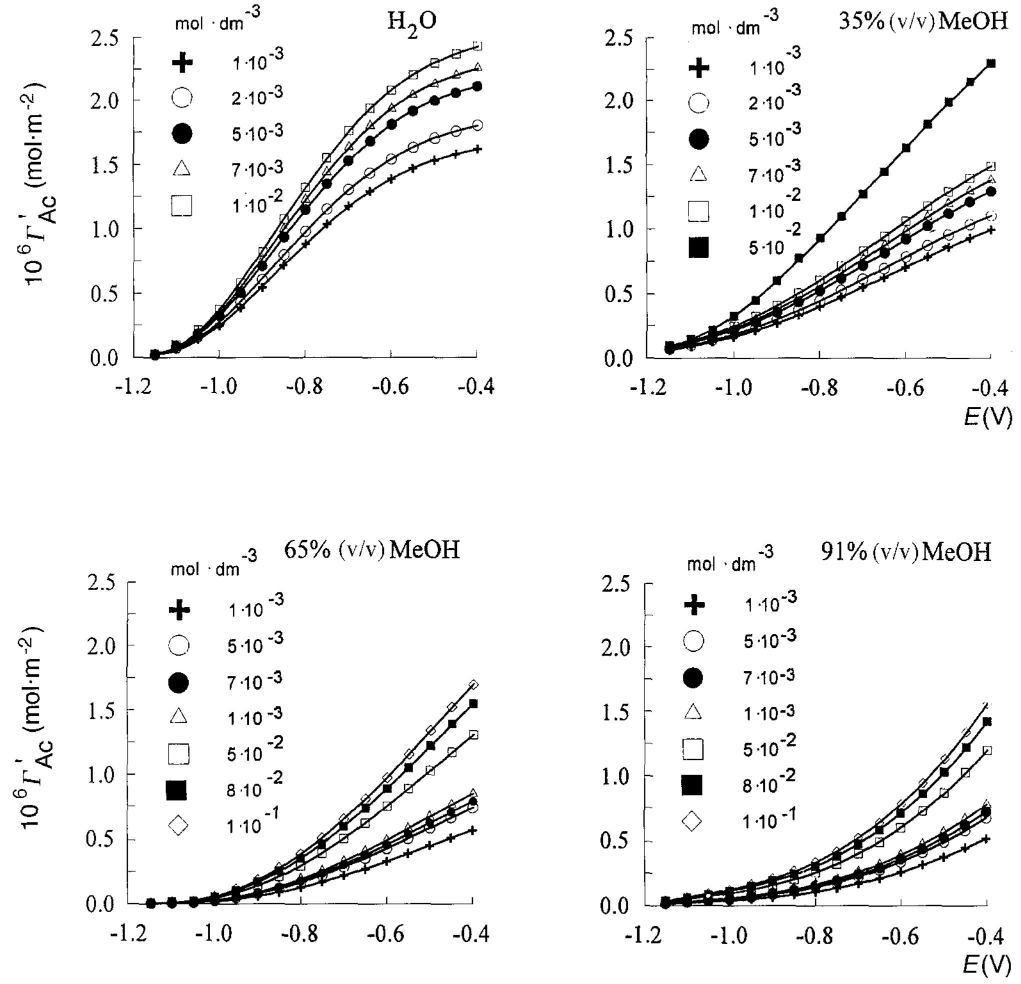

Fig. 4. Relative surface excess of **1** as a function of potential for different contents of **1** in 1 *M* $NaClO_4$ + H_2O, + 35, + 65, and + 91% (v/v) MeOH

The kinetic parameters of the investigated system were also calculated from cyclic voltammetry (CV) measurements by the method described by *Nicholson* and *Shain* [13] using the equations for an irreversible process or by *Nicholson*'s method [14] for quasi-reversible processes. The results obtained by both methods show satisfactory agreement.

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 $1/v$ (v = sweep rate).

The results of the kinetic calculations for the Zn(II)/Zn(Hg) system in the investigated solutions are compiled in Tables 1–3. The apparent standard rates k_s^{app} of the zinc electroreduction process for the investigated mixtures in the presence of **1**, **2** were higher than those in the MeOH solutions.

The *C-E* curves obtained at $pH = 5.3$ exhibit a pronounced hump, usually characteristic of the adsorption of anions. It has been observed for many large

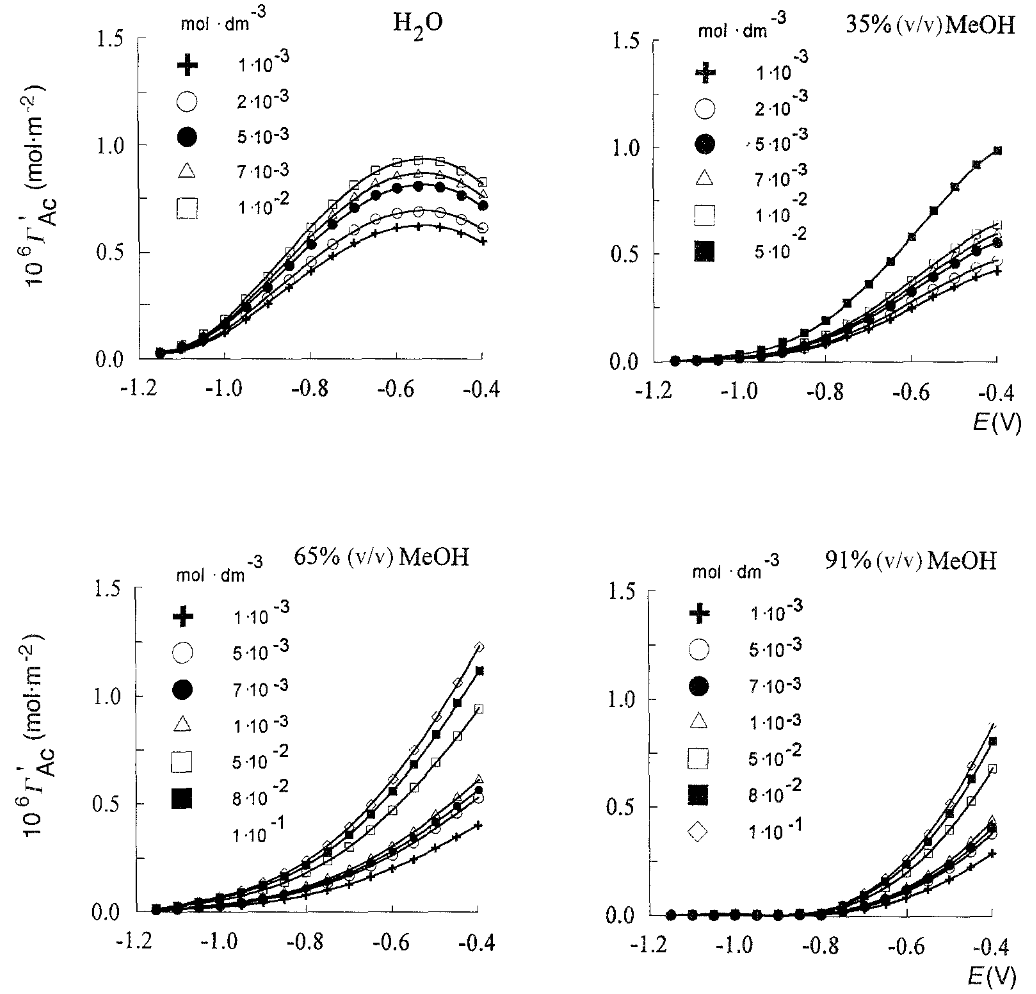

Fig. 5. Relative surface excess of **2** as a function of potential for different contents of **2** in 1 *M* $NaClO_4 + H_2O$, + 35, + 65, and + 91% (v/v) MeOH

organic ions [15]. It seems, therefore, that this hump is connected with the adsorption of the anionic form of dissociated acids. Adsorption of the neutral form of aminobenzoic acid is probably similar to that of nicotinic acid [16] and must be very weak. Knowing pK_1 and pK_2 of aminobenzoic acids in aqueous solution [17, 18], the concentrations of the anionic form of the acids were calculated. It follows that the concentration of **1** in the anionic forms 72%, that of **2** 84%, and that of **3** 73%. It seems therefore that adsorption will involve the anionic form rather than neutral molecules.

An increase in concentration of **1** and **3** causes a shift of E^0 (Fig. 7) towards more negative values as is usual for the adsorption of anions. $dE^0/d(\log c_{Ac^-})$ is about 0.062 V and resembles very nearly that for alkali-metal salts with specifically adsorbed anions (which is approximately $2.3 \cdot RT/F$) [19]. However, it is interesting to note that an increase in concentrations of **2** causes also a shift of E^0 towards more negative values, $dE^0/d(\log c_{Ac^-})$ beeing about 0.033 V which is lower than

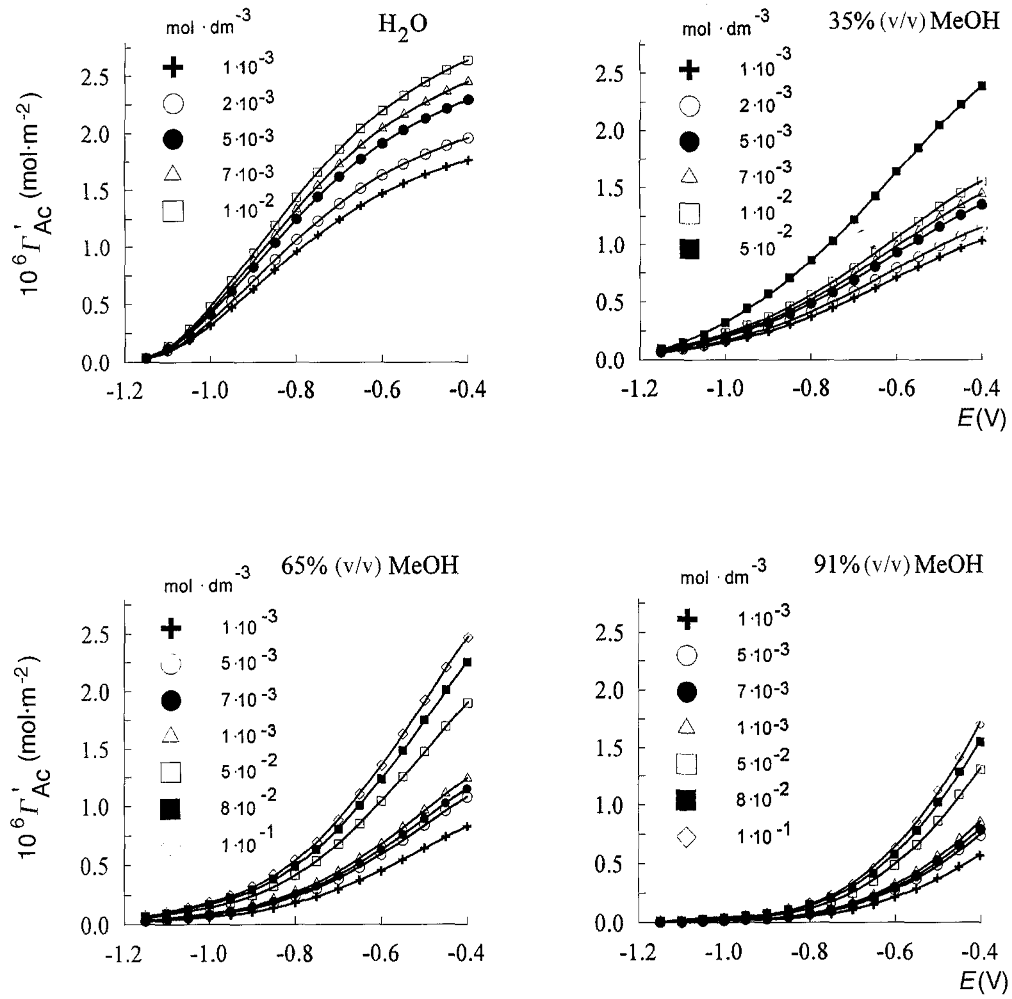

Fig. 6. Relative surface excess of **3** as a function of potential for different contents of **3** in 1*M* $NaClO_4$ + H_2O, + 35, + 65, and + 91% (v/v) MeOH

that for alkali-metal salts with specifically adsorbed anions. It is probable that the contribution of the $\mathbf{2}^-$ dipole potential to the potential drop across the inner layer is small, which is in agreement with the suggestion about the flat orientation of **2**. Increasing concentration of **2** causes a change in the sign of $dE^0/d(\log c_{Ac^-})$. This behaviour may be connected with the formation of well-organized structures on the surface. The saturation value Γ_s for **1** and **3** is 2.6×10^{-6} mol · m^{-2} and corresponds to the value of the co-area, *i.e.* 0.66 nm^2 · $molecule^{-1}$ for a flat orientation. A molecular model of **3** constructed from crystallographic data gives a value of 0.65 nm^2 [20]. Γ_s for **2** is 1.3×10^{-6} mol · m^{-2} which is equivalent to a molecular area of 1.25 nm^2. This value is twice as large than that for **1** and **3**. A similar effect has been observed by *Baugh et al.* [21] in neutral solutions for glycine where the maximum values observed corresponded to 1 molecule per 1.6 nm^2 and the project area of the model was found to be 0.25 nm^2. This may be explained by the fact that

Table 1. Kinetic parameters of the Zn(II)/Zn(Hg) system in H_2O + MeOH + 1 *M* $NaClO_4$ in the absence and presence of **1**

c_{MeOH} (% v/v)	c_1 (mol · dm^{-3})	$-E_f$(V) (*vs.* Fc)	$10^3 \cdot k_s^{app}$ (cm · s^{-1})	α^{app}
0	0.000	1.064	3.3	0.3
0	0.005	1.063	4.7	0.5
0	0.010	1.062	8.3	0.4
35	0.000	1.137	2.2	0.3
35	0.005	1.138	3.0	0.3
35	0.050	1.150	4.1	0.5
65	0.000	1.150	0.5	0.3
65	0.005	1.154	1.5	0.3
65	0.010	1.171	3.1	0.3
91	0.000	1.166	0.6	0.3
91	0.005	1.185	1.2	0.4
91	0.010	1.201	2.9	0.3

Table 2. Kinetic parameters of the Zn(II)/Zn(Hg) system in H_2O + MeOH + 1 *M* $NaClO_4$ in the absence and presence of **2**

c_{MeOH} (% v/v)	c_2 (mol · dm^{-3})	$-E_f$(V) (*vs.* Fc)	$10^3 \cdot k_s^{app}$ (cm · s^{-1})	α^{app}
0	0.000	1.064	3.3	0.3
0	0.005	1.058	16.6	0.4
0	0.010	1.054	17.2	0.4
35	0.000	1.137	2.2	0.3
35	0.005	1.136	1.4	0.3
35	0.050	1.136	3.1	0.4
65	0.000	1.150	0.5	0.3
65	0.005	1.149	1.4	0.4
65	0.100	1.148	3.7	0.4
91	0.000	1.166	0.6	0.3
91	0.005	1.199	0.5	0.3
91	0.100	1.193	1.5	0.4

electrostatic repulsion must be the reason for these large values. However, it is difficult to explain this fact for **2**.

A quantitative presentation of the phenomenon of acceleration of electrode processes is a determination of their standard rate constants. In the presence of **1** and **2** the standard rate constants of the zinc electroreduction process constantly show higher values than in solutions without the addition of the acid. However, the presence of **3** has no such effect on the electroreduction precess; in fact, it even slightly inhibits it. The inhibiting action of **3** in living organisms where it may totally suppress the bactericidal action of sulfanilamid is well known. It is presumably connected with the structure of the acid molecule which, in the form of

Table 3. Kinetic parameters of the Zn(II)/Zn(Hg) system in H_2O + MeOH + 1M $NaClO_4$ in the absence and presence of **3**

c_{MeOH} (% v/v)	c_3 ($\mathrm{mol \cdot dm^{-3}}$)	$-E_f$(V) (*vs.* Fc)	$10^3 \cdot k_s^{\mathrm{app}}$ ($\mathrm{cm \cdot s^{-1}}$)	α^{app}
0	0.000	1.064	3.3	0.3
0	0.005	1.057	2.2	0.3
0	0.010	1.059	2.5	0.3
35	0.000	1.137	2.2	0.3
35	0.005	1.134	1.3	0.3
35	0.050	1.130	1.4	0.3
65	0.000	1.150	0.5	0.3
65	0.005	1.151	0.5	0.3
65	0.100	1.142	0.6	0.3
91	0.000	1.166	0.6	0.3
91	0.005	1.187	0.5	0.3
91	0.100	1.184	0.5	0.3

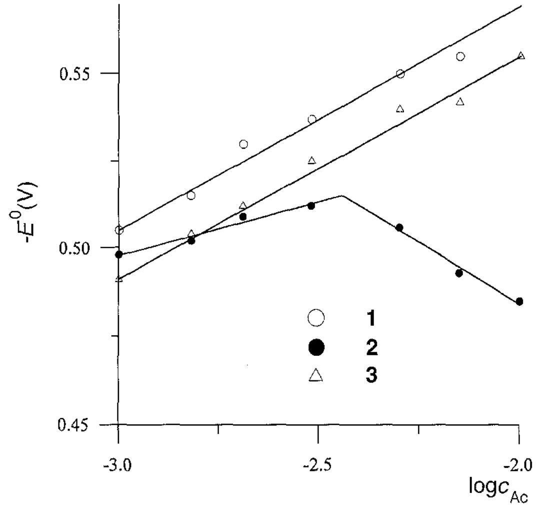

Fig. 7. Dependence of E^0 on the concentration of **1**, **2**, and **3**

3 cannot form an active complex on the electrode surface in view of the blocked $-NH_2$ groups as suggested by *Hills et al.* [22] and in view of the orientation of the $-CH_2-COO^-$ group. The orientation of **1** and **2** should involve a disposition of the $-CH_2-COO^-$ moiety towards the solution.

All examined isomers are better soluble in the presence of methanol. Their solubility increases along with rising methanol concentration. And thus, in comparison with an aqueous solution, the solubility of **1** and **2**, beginning with a methanol concentration of 65% (v/v), rises about ten times, that of **3**, however, twenty times. The examined acids undergo adsorption on the surface of the mercury electrode which is one of the conditions of the cap-pair effect [1].

Table 4. Standard rate constants of electrode reduction of the Zn(II)/Zn(Hg) system in H_2O and H_2O + MeOH and aminobenzoic acid coverage of the Hg electrode

c_{MeOH} (% v/v)	**1**		**2**		**3**	
	θ	$10^3 \cdot k_s^{\mathrm{app}}$ $(\mathrm{cm}^2 \cdot \mathrm{s}^{-1})$	θ	$10^3 \cdot k_s^{\mathrm{app}}$ $(\mathrm{cm}^2 \cdot \mathrm{s}^{-1})$	θ	$10^3 \cdot k_s^{\mathrm{app}}$ $(\mathrm{cm}^2 \cdot \mathrm{s}^{-1})$
0	0.14	4.7	0.15	16.6	0.14	2.2
	0.18	8.3	0.21	17.2	0.17	2.5
35	0.08	3.0	0.02	1.4	0.07	1.3
	0.14	4.1	0.04	3.1	0.14	1.4
65	0.02	1.5	0.02	1.4	0.03	0.5
	0.07	3.1	0.06	3.7	0.07	0.5

However, their higher solubility in methanol is not accompanied by a greater adsorption on the electrode surface. The highest adsorption capability is displayed in aqueous solution. The decrease of acid adsorption along with rising methanol concentration is connected with competitive methanol adsorption. Nevertheless, it should be noted that at a given methanol concentration, acid adsorption increases with its rising concentration, which involves an increase of reversibility in the case of the first two isomers.

Thus, comparing the standard rate constant of the process of zinc ion electroreduction, it seems that it is not the amount of dissolved substance that should be taken into consideration but rather its adsorption on the electrode surface. The obtained results (Table 4) seem to indicate the following dependence: with a similar degree of electrode coverage, the obtained values of rate constants are similar for **1**, regardless of methanol content. The same dependence holds true in the presence of **2**. These dependencies imply that the structure of the active complex in both aqueous and methanoic solution is the same. It is probably connected with the fact that, even at high methanol concentration, zinc is selectively hydratated [23]. Similar effects have also been observed in methanolic solution in the presence of thiourea [24].

One should also note that similar values of electrode coverage at zinc reduction potential yield higher rate constants in the presence of **2** than in the presence of **1** which suggests that the structure of the complex plays a decisive role in the acceleration phenomenon.

The relative accelerating effect for **1** and **2** at a concentration of $1 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$ in aqueous solution is 2.5 and 5.2, respectively, and in a solution of 65% (v/v) MeOH at a concentration of $1 \times 10^{-1}\,\mathrm{mol\,dm^{-3}}$ the relative acceleration for both isomers is $\approx$6.2 and 7.4, respectively. These values indicate that an increase in the solubility of the examined acids in methanol causes an increase of the relative effect of acceleration of the process of zinc ion electroreduction, although this effect is slight.

The values of the cathodic transfer coefficient α in solutions with and without an addition of acids are almost the same, indicating that the mechanism of the process in both solutions is probably the same.

Thus, contrary to expectations, the presented studies have revealed only a slight effect of the solubility of an examined compound on the process of zinc ion electroreduction, indicating a considerable dependence of this process on the kind of the applied isomer.

Conclusions

The results can be summarized as follows:

1. The structure of the aminobenzoic acid molecule has an influence on the acceleration process which is probably connected with the structure of the active complex on the electrode surface.
2. The acceleration of the electrode process is related to the degree of electrode coverage with the accelerating compound.
3. With a similar degree of electrode coverage with the accelerating substance in a given solution, one obtains similar values of standard rate constants.
4. The increased solubility of a compound exerts only a slight influence with respect to acceleration of the process of zinc ion electroreduction.

Experimental

Apparatus and measurements

The measurements were carried out with a polarograph PA-4 from Laboratorni Pristroje, Prague, Model 270 Electrochemical Analysis System, Model 388 Electrochemical Impedance System (EG&G PAR), and an IBM 486 PC equipped with a data translation interface and employing a static mercury drop electrode (SMDE) manufactured by Laboratorni Pristroje, Prague, with a surface area of 0.0133 cm^2. As the reference electrode, Ag/AgCl with saturated NaCl was used. The reference electrode was connected to the electrolytic cell *via* an intermediate vessel filled with the solution to be investigated. The counter electrode was a platinum wire.

The kinetic parameters for the reduction of Zn(II) were determined using the cyclic voltammetry technique (sweep rates from 0.005 to 20 V $\cdot$ s^{-1}) with a precision of ±7% and by impedance measurements with a precision of ±5%. The complex cell impedance was obtained at 20 frequencies in the range from 100 to 25000 Hz at formal potential.

Additionally, the voltammetric curves of the ferrocene-ferricinium system (Fc) were recorded and all potentials in Tables 1–3 are referred to this internal reference system.

The double layer capacity was measured using the ac impedance technique at a frequency of 800 Hz with an impedance meter EJM-2 (made at Łódź University). The capacitance was measured with a precision of ±0.2%. For these measurements, a dropping Hg electrode constructed according to *Randles* was used [3]. The balance of the bridge was achieved after 6 s of drop growth. The drop time was 8 s, and the flow rate was 0.957 mg $\cdot$ s^{-1} at a mercury column height of 50 cm. In measurements of differential capacitance, a saturated NaCl aqueous calomel electrode (SSCE) was used as the reference electrode.

For the whole polarisation range, capacitance dispersion was tested at five different frequencies between 400 and 2000 Hz. In the potential range studied no dispersion of the capacitance was observed.

Reagents

Chemicals of analytical grade from Merck were used. Water and mercury were distilled twice. Methanol and $Zn(NO_3)_2 \cdot 6H_2O$ were used without further purification. The specific conductivity of methanol was 8×10^{-1} $S \cdot m^{-1}$. The Zn(II) concentration in the solutions was 10^{-3} $mol \cdot dm^{-3}$. The concentrations of MeOH were 0, 36, 65, and 91% (v/v). The concentration of $NaClO_4$ in the investigated mixtures was $1\,mol \cdot dm^{-3}$. Measurements were carried out at 298±0.1 K. Solutions were deaereated using nitrogen which was also passed over the solution during the measurements.

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