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**REDUCTION OF THE Ni(II) ION AT THE DROPPING MERCURY ELECTRODE FROM AMOXICILLIN WATER SOLUTION**Milenko R. ERCEG<sup>a</sup>, Vera P. KAPETANOVIĆ<sup>b</sup> and Desanka Ž. SUŽNJEVIĆ<sup>c</sup><sup>a</sup> *Institute of Physical Chemistry, Faculty of Science,  
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The nature of polarographic precursors of Ni(II) ion in the presence of amoxicillin as well as the behaviour of amoxicillin in the electrical double layer has been investigated. It has been established the formation of the mono complex of Ni(II) ion with amoxicillin adsorbed at the mercury. The reduction mechanism of the complex has been proposed. Taking into account the effect of the double layer on the kinetics, the rate constant of the heterogeneous reaction of the complex formation has been found to be  $5.8 \cdot 10^3 \text{ l mol}^{-1} \text{ s}^{-1}$ .

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Recent studies of the polarographic prewave which arises at more anodic potential ( $\sim 300 \text{ mV}$ ) to the main Ni(II)-aquo wave in the presence of ampicillin ( $\alpha$ -amino-benzyl penicillin) have shown its kinetic-catalytic nature<sup>1-4</sup>. Amoxicillin ( $\alpha$ -amino-*p*-hydroxybenzyl penicillin) also belongs to the group of semisynthetic  $\beta$ -lactam antibiotics and is structurally related to ampicillin. Many properties of amoxicillin are similar to those of ampicillin. Our previous papers<sup>5-8</sup> have shown the complex properties of ampicillin as well as of amoxicillin. Especially attention was initiated to the polarographic behaviour of Ni(II) ion in the presence of these compounds. The polarographic reduction of Ni(II) ion in the presence of amoxicillin has been shown to be determined by the kinetics of the formation of mono Ni(II)-amoxicillin complex<sup>9</sup>. The stoichiometric ratio and stability constant of this complex have been evaluated by polarographic method. In this paper, quantitative aspects of the effects of electrical double layer structure and amoxicillin adsorbed on the dropping mercury electrode on the limiting currents of the catalytic prewave of Ni(II) ions, are studied.

## EXPERIMENTAL

### Apparatus

Dp polarograms were recorded on a PAR-174 polarograph connected with three electrode cell (dropping mercury, DME, saturated calomel, SCE and Pt-auxiliary). The following conditions were used in dp polarography: 2 s drop time, 25 mV pulse amplitude and  $2 \text{ m Vs}^{-1}$  scan rate.

A PAR-370 was used for ac polarography, and the potentials are referred to a silver/silver chloride electrode. The following conditions were used: the amplitude of alternating sinusoidal voltage of 5 mV peak to peak frequency of 400 Hz and  $t$  2 s.

### Reagents

$\text{Ni}(\text{NO}_3)_2$ ,  $\text{KNO}_3$  and  $\text{NaClO}_4$ , all of analytical grade were used.  $\text{Ni}(\text{NO}_3)_2$ , was standardized by complexometric method. Standard amoxicillin-anhydrous "Sigma" was used. The solutions were prepared just before use, and renewed each day.

When experiments were performed in unbuffered media, pH value of solutions was adjusted by using nitric or perchloric acid and sodium hydroxide, respectively. In other case, experiments were performed in Britton-Robinson buffer.

## RESULTS AND DISCUSSION

The extensive study of the effects of the amoxicillin on the differential capacity of mercury in the wide range of potential, in the presence of supporting electrolyte ( $0.2 \text{ M-NaNO}_3$ ), at pH 5.6, shows the existence of a strong adsorption in the system.

In Fig. 1 the capacity line depression of the supporting electrolyte in the presence

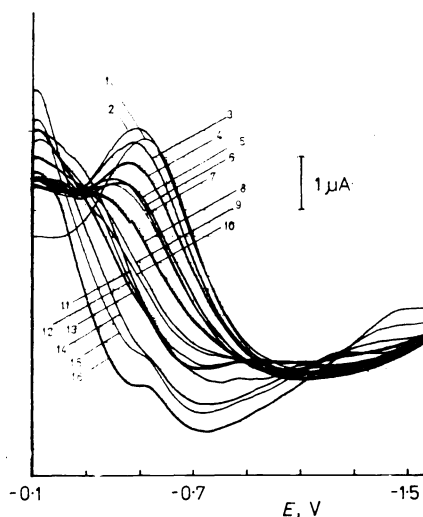


FIG. 1

$i$ - $E$  curves of:  $0.2 \text{ M-NaNO}_3$  (pH 5.6) (1); in the presence of amoxicillin ( $\text{mol l}^{-1}$ )  $1 \cdot 10^{-5}$  (2);  $2 \cdot 10^{-5}$  (3);  $4 \cdot 10^{-5}$  (4);  $6 \cdot 10^{-5}$  (5);  $8 \cdot 10^{-5}$  (6);  $1 \cdot 10^{-4}$  (7);  $2 \cdot 10^{-4}$  (8);  $4 \cdot 10^{-4}$  (11);  $8 \cdot 10^{-4}$  (12);  $1 \cdot 10^{-3}$  (13);  $2 \cdot 10^{-3}$  (14);  $3 \cdot 10^{-3}$  (15);  $5 \cdot 10^{-3}$  (16)

of different concentrations of amoxicillin can be observed. The current–potential curves that were obtained, display a marked decrease of the capacitance around the electrocapillary maximum, as well as adsorption–desorption peaks on its negative side. The strong adsorption around the p.z.c. indicates the behaviour very similar to the adsorption of a neutral organic molecule. However, at pH 5.6, the predominating ionic form<sup>10</sup> of amoxicillin is a zwitter ion ( $pK_1$  2.4,  $pK_2$  7.4).

From the analysis of the  $C$ – $E$  curves obtained for different amoxicillin concentrations, at pH 5.6,  $\mu$  0.2, the adsorption isotherm was constructed at the prewave limiting current potential ( $-0.75$  V), from which the surface excess of the adsorbed species was calculated  $\Gamma_{\max} = 1.24 \cdot 10^{-10}$  mol  $\text{cm}^{-2}$ . The prewave characteristics were studied in relation to the following parameters: the concentration of Ni(II) ion, the concentration of the complexing ligand, the mercury column height, temperature and the nature of the anion and concentration of the supporting electrolyte.

At a constant amoxicillin concentration ( $2.4 \cdot 10^{-3}$  mol  $\text{l}^{-1}$ ) the prewave limiting current was found to be linear within the concentrations of Ni(II) ion from  $3.5 \cdot 10^{-5}$  mol  $\text{l}^{-1}$  to  $3.6 \cdot 10^{-4}$  mol  $\text{l}^{-1}$ . When increasing the amoxicillin concentration, at a constant Ni(II) ion concentration ( $1 \cdot 10^{-4}$  mol  $\text{l}^{-1}$ ), constant ionic strength and pH, the limiting current reaches saturation. It has been also established that the mercury column height has practically no effect on the prewave characteristics. However, the cations investigated (Li, K, Cs) show a significant decrease of the prewave limiting current, following the order  $\text{Li} > \text{K} > \text{Cs}$ . Keeping the concentration of Ni(II) and amoxicillin constant, variation of the supporting electrolyte concentration leads to considerable changes of the prewave height. The limiting prewave current was decreased when increasing the  $\text{KNO}_3$  concentration, as seen in Fig. 2.

These results suggest that the prewave is due to a slow chemical reaction, kinetically controlled. The proposed mechanism of the prewave appearance in the Ni(II)–amoxicillin system includes the chemical reaction of the complex formation between Ni(II) and amoxicillin adsorbed at the electrode surface, according to the following

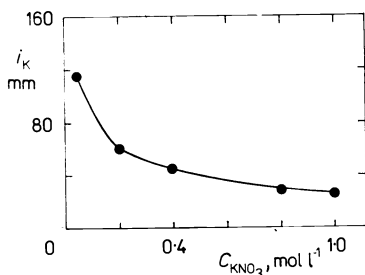
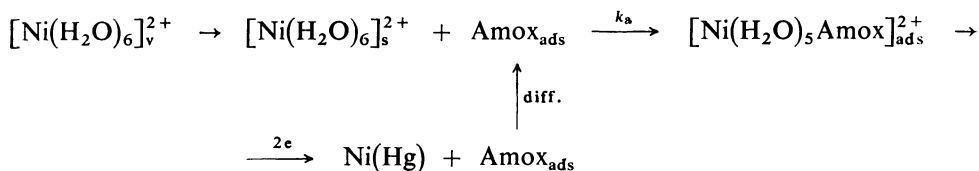


FIG. 2  
Dependence of the prewave height,  $i_k$ , on the concentration of the supporting electrolyte.  $1 \cdot 10^{-3}$  M-Ni(II),  $5 \cdot 10^{-4}$  M amoxicillin

scheme<sup>11</sup>:



Species in the bulk of the solution and at the electrode surface are denoted by the symbols "v" and "s", respectively. If it is assumed that the adsorption equilibrium is established sufficiently quickly, the rate constants obtained for the reactions of the complex formation are approximately the same, irrespective of whether the process is considered to be a "volume" or a "surface" one.

It can be supposed that adsorbed amoxicillin reacts slowly with Ni(II)-aquo ions diffusing from the bulk of the solution, forming a complex prior to the charge transfer. In that case, as a first approximation, the reaction is a "volume" one and Koutecký's theory<sup>12</sup> can be applied. The more accurate consideration of these processes presumes the simultaneous occurrence of homogeneous and heterogeneous complexing reactions. Since the limiting current is believed to be determined by two parallel processes of the complex formation (surface and bulk), it was necessary to consider the effect of the double layer<sup>13</sup> on the kinetics. Taking into consideration the bulk process, the following relation<sup>11</sup> is valid for the overall process:

$$Z_{\Sigma i_k} = \frac{\sum \bar{i}_k}{\bar{i}_d - \sum \bar{i}_k} = \frac{nF\bar{q}}{\bar{x}} \cdot k_a \Gamma_{\text{amox}} \exp\left(-\psi_1 \frac{zF}{RT}\right) + \frac{10^{-3}nF\bar{q}}{\bar{x}} \mu k_r C_{\text{amox}} \quad (1)$$

where  $\sum \bar{i}_k$  is the mean value of the limiting current of the total prewave,  $\bar{i}_d$  is the mean value of the limiting diffusion current of Ni(II),  $\bar{q}$  is the mean area of the electrode,  $k_a$  and  $k_r$  are the rate constants of the mono Ni(II)-amoxicillin formation in the adsorption layer and in the bulk of the solution, respectively,  $\mu$  is the thickness of reaction layer:

$$\mu = \left( \frac{D_{\text{Ni-amox}}}{k_r K_1} \right)^{1/2},$$

$K_1$  is the instability constant of Ni(II)-amoxicillin complex<sup>9</sup>,  $\psi_1$  is the potential on outer Helmholtz plane (V), and  $z$  is the charge of the electroactive species in the electric double layer. If the associative mechanism<sup>14,15</sup> is assumed to be true for the formation of Ni(II)-amoxicillin complex as for other Ni(II)-complexes, then  $k_r$  may be assumed to be equal to  $1 \cdot 10^3 - 1 \cdot 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$ . As in this case the value of  $K_1$  is appreciably greater than unity, the second term in Eq. (1) may be

neglected if the ionic strengths are  $\leq 0.2$ . Hence, it follows:

$$Z_{\Sigma ik} = \frac{nF\bar{q}}{\bar{z}} k_a \Gamma_{\text{amax}} \exp\left(-\psi_1 \frac{zF}{RT}\right). \quad (2)$$

Plotting  $\log Z_{\Sigma ik}$  vs  $\psi_1$  (the values of the  $\psi_1$ -potentials calculated according to the Gouy–Chapman theory for NaF solutions<sup>16</sup>), a straight line with a slope of 28 mV is obtained, whence it follows that the charge of the species in the double layer is +2. The extrapolation of the straight line to  $\psi_1 = 0$  gave the average value of  $k_a$  of  $5.8 \cdot 10^3 \text{ l mol}^{-1} \text{ s}^{-1}$ , at  $-0.75 \text{ V}$ . The value of  $\Gamma_{\text{max}}$  obtained earlier was used in calculation.

#### REFERENCES

1. Veselinović D., Kapetanović V.: *Journées d'Electrochimie 85. Résumés et index des auteurs*, p. 8. Firenze 1985.
2. Sužnjević D., Kapetanović V.: *Journées d'Electrochimie 87. Résumés et index des auteurs*, p. 5. Dijon 1987.
3. Kapetanović V., Erceg M., Sužnjević D.: *Proceedings of the X. Yugoslav. Symposium of Electrochemistry, Bečići 1987*; p. 60.
4. Sužnjević D., Kapetanović V.: *Electroanalysis 1*, 457 (1989).
5. Veselinović D., Kapetanović V.: *J. Serb. Soc.* 50, 401 (1985).
6. Veselinović D., Kapetanović V.: *Vestn. Slov. Druš. Supl.* 33, 203 (1986); *Chem. Abstr.* 106, 188415y (1987).
7. Veselinović D., Kapetanović V.: *J. Pharm. Belg.* 43, 163 (1988).
8. Veselinović D., Kapetanović V.: *Microchim. Acta 1*, 191 (1989).
9. Kapetanović V., Veselinović D.: *Arch. Pharm.* 321, 559 (1988).
10. Albert A., Serjeant E. P.: *The Determination of Ionization Constants*, 3rd ed. Chapman and Hall, New York 1984.
11. Turiyan Ya. I., Ruvinskii O. E.: *J. Electroanal. Chem.* 23, 61 (1969).
12. Koutecký J.: *Collect. Czech. Chem. Commun.* 19, 857 (1954).
13. Frumkin A. N., Bagotskii V. S., Iofa Z. A., Kabanov B. N.: *Kinetika elektrodnykh processov*, p. 175. MGU, Moscow 1952.
14. Eigen M.: *Z. Elektrochem.* 64, 115 (1960).
15. Eigen M., Tamm K.: *Z. Elektrochem.* 66, 107 (1962).
16. Russel C. D.: *J. Electroanal. Chem.* 6, 486 (1963).