

CATALYTIC PRE-WAVE OF NICKEL(II) IN PRESENCE OF COCARBOXYLASE (DISULFIDE FORM) IN BORATE MEDIUM

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Abstract - A brief study is made of the nickel(II) polarography in borate medium. The nickel(II) in borate medium gives one or two waves depending on its concentration as well as the medium composition.

In a borate medium, cocarboxylase in its disulfide form gives a nickel(II) pre-wave. The effects of the cocarboxylase (disulfide form) concentration, nickel(II) concentration and mercury column height on the pre-wave are described.

The effect of neutral salts on the pre-wave is studied and it is seen that an increase in the ionic strength is accompanied by a decrease in pre-wave current, being of decreasing effect in the order $K^+ < Na^+ < Li^+$. The electrocapillary curves are present, and it is shown that the presence of cocarboxylase (disulfide form) in the solution causes a decrease in the interfacial tension.

The results are discussed and a mechanism for the electrode process of the pre-wave is proposed. Using the approximate method for the catalytic currents, nickel(II) and cocarboxylase-thiol are shown to form the catalytic complex in the relationship 1:1.

INTRODUCTION

In the presence of some substances, catalytic pre-waves of Co(II)[1-3] and Ni(II)[4-6] have been described. Their mechanism has been explained by postulating the formation of complexes which are discharged to the pre-wave potential, freeing the ligand which takes part in the reaction sequence several times.

This paper investigates the catalytic pre-wave of nickel(II) in presence of disulfide of cocarboxylase.

EXPERIMENTAL TECHNIQUE

Polarograms were obtained by means of Radiometer PO4 polarograph using a thermostatted polarographic cell at 20°C and a saturated calomel electrode (*sce*) as reference electrode. The dropping mercury electrode (*dme*) used in these experiments, at a height of 39 cm Hg had the following characteristics: $m = 2.64 \text{ mg s}^{-1}$ and $t = 2.93 \text{ s}$ at -1.50 V (*vs sce*) in 0.06 M borax 0.05 M HCl.

The pH values were measured with a Radiometer pH-meter, Model 26.

The cocarboxylase employed was from Fluka purum grade and all other chemicals were of Merck reagent grade and their solutions were prepared in doubly-distilled water. The mercury used in the *dme* was first purified chemically and subsequently twice distilled.

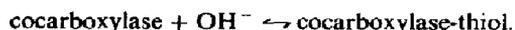
The standard 10^{-3} M cocarboxylase (disulfide form) solution was obtained in the following way[1]: to 5 ml 10^{-2} M cocarboxylase solution was added 0.1 M sodium hydroxide solution until the pH of the solution reached 12.5; it was left for about 10 min to ensure that the cocarboxylase was converted into its thiolic form, then to it was added 25 ml 0.1 M borax (pH = 9.3) and (quickly) 2 ml $5 \times 10^{-2} \text{ M}$ iodine solution. The solution was diluted to 50 ml with water.

Every solution of cocarboxylase (disulfide form)

contains iodine and sodium hydroxide as is explained above.

RESULTS AND DISCUSSION

In nickel(II)-borate medium the thiol form of cocarboxylase gives a pre-wave of nickel. The thiazolic ring of cocarboxylase opens at pH 9.6 being the following equilibrium:



At pH > 11 - in which the cocarboxylase is completely like cocarboxylase-thiol - the nickel(II) has a small solubility. Decreasing the pH, the equilibrium is displaced to the left and at pH < 9.6 the cocarboxylase is not in the thiolic form.

Thus we have proceeded to the formation of the cocarboxylase disulfide (see experimental technique), which is reduced in the *dme* giving the corresponding thiol form. So, in nickel(II)-borate medium the disulfide form of cocarboxylase gives a pre-wave of nickel.

The nickel(II) - in borate medium - gives one or two waves depending about its concentration as well as the medium composition. Thus, we need to study briefly the waves of nickel(II) in borate medium before the study and interpretation of nickel pre-waves in presence of cocarboxylase disulfide.

In 0.06 M borax medium (pH 9.3), the 0.5 M nickel(II) gives two waves (Fig. 1, polarogram B1), the first at $E_{1/2} = -1.10 \text{ V}$ and the second at $E_{1/2} \approx -1.6 \text{ V}$. Adding hydrochloric acid at the medium (pH 8.4), an increase in the first wave intensity and an almost disappearance of the second was observed, changing the half-wave potential of the first wave at a more positive potential ($E_{1/2} = -1.07 \text{ V}$). This fact cannot be explained only by the pH decrease, because when boric acid is added (pH 7.8) the half-wave potential corresponding to the first wave is not

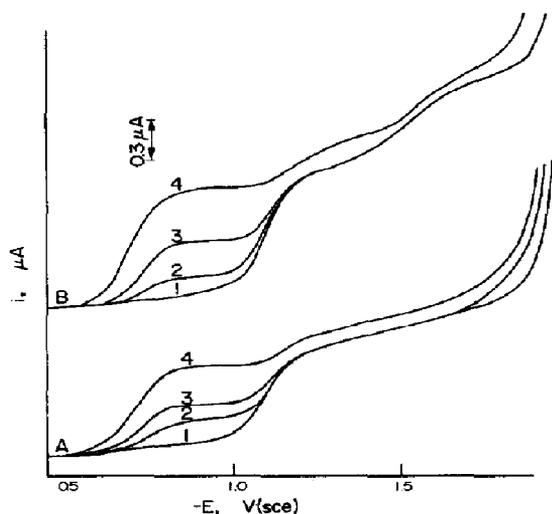


Fig. 1. Pre-waves of Ni(II) in presence of cocarboxylase disulfide in 0.06 M borax medium (pH 9.3). Polarograms (A) 0.2 mM Ni(II), cocarboxylase (disulfide form) concentration: (1) 0; (2) 5×10^{-6} ; (3) 1.5×10^{-5} ; (4) 7.5×10^{-5} M. Polarograms (B) 0.5 mM Ni(II), cocarboxylase (disulfide form) concentration: (1) 0; (2) 2.5×10^{-6} ; (3) 1.5×10^{-5} ; (4) 10×10^{-5} M.

changed. But similarly, on addition of hydrochloric acid, the first wave intensity increased, and the second one disappeared.

Adding sodium perchlorate until 0.5 M to the (a) nickel(II)-borax; (b) nickel(II)-borax-HCl; (c) nickel(II)-borax- BO_3H_3 solutions, the half-wave potential of the first wave is shifted - in any case - 40 mV to more negative potentials. The limiting current was ill-defined and increased slightly with negative potential. However, even at potentials just before the sodium ion discharge the current in 0.5 M perchlorate was in solution (a) some 17% less than in the absence of perchlorate as well as 4% and 7% less in the (b) and (c) solutions, respectively. A similar observation has been made in the reduction of divalent cobalt in borate medium[7].

The second wave is not well-defined, and therefore its intensity and half-wave potential cannot be measured exactly, both parameters kept approximately constant by addition of sodium perchlorate to the nickel(II)-borate solutions.

When nickel(II) is 0.2 mM, the polarograms present only the first wave in borax (Fig. 1, polarogram A1) as well as borax-HCl medium.

The nickel(II) in borate medium is present as metaborate, tetraborate and another polyborates complexes[8] (with negative charge or without charge) in equilibrium with aquo-nickel ion (with two positive charges).

The reduction occurs at potentials at which the mercury carries a considerable negative charge. Addition of perchlorate ion results in a change of the ψ potential in the double layer to less negative potentials and so it would shift the reduction of divalent aquo-nickel positive ion to more negative potentials[7,9]. Since this change is observed in the first wave of nickel reduction it may be concluded that the aquo-nickel ion

is the species which is reduced. This conclusion is substantiated by the observation that at high ionic strength the apparent limiting current is markedly suppressed and increases with the negative potential. A similar observation has been made in the reduction of divalent nickel ion in non-complexing medium[10].

Since the first wave of nickel has been ascribed to the aquo-nickel ion reduction, it is possible that the second wave is due to the reduction of nickel(II) borate complexes.

But for our paper we do not need a greater study of the above named second wave, since it is not affected by the cocarboxylase (disulfide form) presence.

In 0.5 mM nickel(II)-0.06 M borax medium (pH 9.3) the cocarboxylase (disulfide form) gives a pre-wave of nickel (Fig. 1, polarograms B). The pre-wave intensity does not vary linearly with the disulfide concentration, but tends toward the same limiting current as that of the first wave of nickel(II) (i_{d1}) (Fig. 2). The second wave of nickel(II) was not changed by the disulfide presence. When the nickel(II) concentration is 0.2 mM (in this case, the polarograms present only one wave), the intensity of its pre-wave increases also with disulfide concentration, tending toward the same limiting value as that of the nickel(II) diffusion current (\bar{i}_d) (Fig. 2).

The half-wave potential of nickel pre-wave becomes less negative with increasing the concentration of cocarboxylase (disulfide form) being -0.75 V at 2.5×10^{-6} M and -0.70 V at 7.5×10^{-5} M.

As the solubility of nickel(II) in borax-HCl medium is higher than in borax medium, the study of the influence of nickel(II) concentration has been made in the former one. The variation of pre-wave current with nickel(II) concentration is linear (Fig. 3) until 0.4 mM, separating of this linearity at higher con-

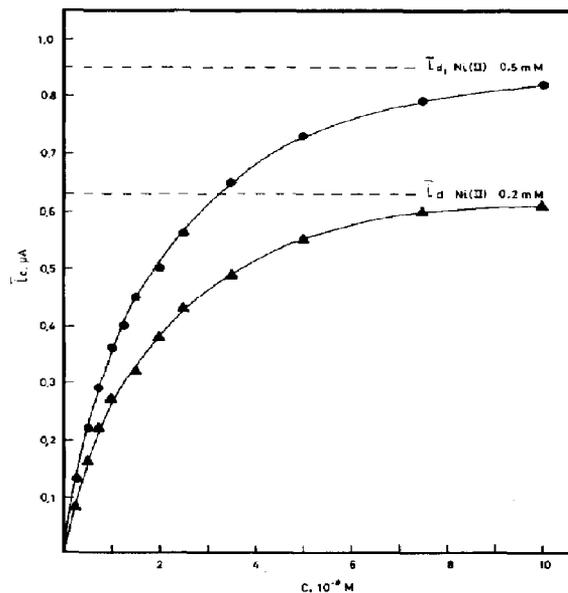


Fig. 2. Dependence of pre-wave catalytic current on the cocarboxylase (disulfide form) concentration in 0.06 M borax medium (pH 9.3); Ni(II) concentration: \blacktriangle 0.2 mM; \bullet 0.5 mM.

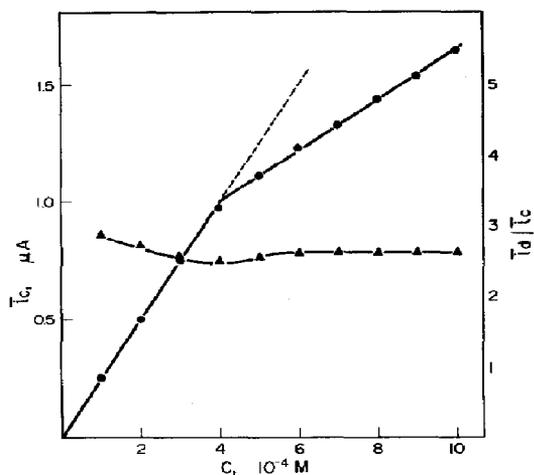


Fig. 3. Dependence of pre-wave catalytic current (●) and of I_d/I_c ratio (▲) on the Ni(II) concentration. 5×10^{-6} M cocarboxylase (disulfide form); 0.06 M borax–0.05 M HCl (pH 8.4).

concentrations. The ratio I_d/I_c decreases with increasing of nickel(II) concentration, reaching a minimum at 0.4 mM.

In any case, low concentrations of cocarboxylase (disulfide form) gives a pre-wave whose current is several times larger than the diffusion current to be expected by the nickel(II)–cocarboxylase-thiol complex. This is indicative that in the electrodic process the ligand is regenerated and defines the catalytic nature of this wave.

The pre-wave current, when it is lower than 20% of the nickel(II) diffusion current, is independent of the mercury height, characteristic behavior of an electrodic reaction controlled by the rate of a previous chemical reaction. Otherwise, the pre-wave current, when comes near the value of the nickel(II) diffusion current, tends to change with the square root of the

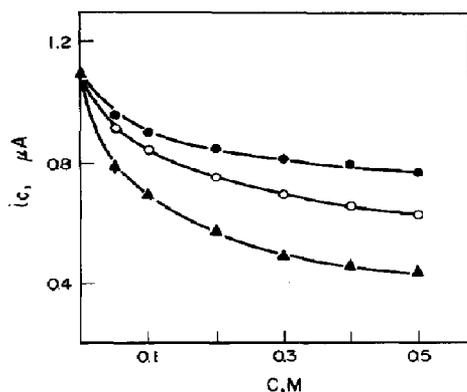


Fig. 4. Dependence of pre-wave catalytic current on concentration of neutral salts. 5×10^{-6} M cocarboxylase (disulfide form); 0.5 mM Ni(II); 0.06 M borax–0.05 M HCl (pH 8.4). ● KCl; ○ NaCl; ▲ LiCl.

height of mercury, which proves that in this condition, it depends on the nickel(II) diffusion rate.

The effect of neutral salts on the pre-wave has been studied by adding various amounts of different alkali metal chlorides to a 0.5 mM nickel(II)–0.06 M borax–0.05 M HCl– 5×10^{-6} M cocarboxylase (disulfide form) system. An increase in the ionic strength due to the addition of a salt is accompanied by a decrease in pre-wave current (Fig. 4). The decreasing effect is in the order $K^+ < Na^+ < Li^+$, that means, when the cation radius is decreasing and therefore in the order that causes less decrease in the absolute value of the ψ potential. This effect is the opposite of those met for other nickel pre-waves[5, 11].

This fact can be explained by taking into account the great negative charge of the cocarboxylase-thiol in basic medium due to its pyrophosphate group. Although a decrease of the negative value of ψ potential tends to decrease the aquo-nickel ion concentration in the electrodic surface, on the other hand the orientation of cocarboxylase-thiol toward the electrode is being favored, and therefore the formation of the complex of cocarboxylase-thiol with nickel ion.

The electrocapillary curves were obtained in 0.06 M borax–0.05 M HCl in the absence and presence of cocarboxylase (disulfide form) and nickel(II). Curve 1 in Fig. 5 corresponds to the borax–HCl system that was also 5×10^{-4} M with respect to iodine and 5×10^{-3} M with respect to sodium hydroxide, that is, the concentrations of these reagents originating from the standard solution of cocarboxylase (disulfide form) employed. These substances are also present in the same concentrations in the solution with which curves 2 and 3 are obtained. As can be seen, the presence of

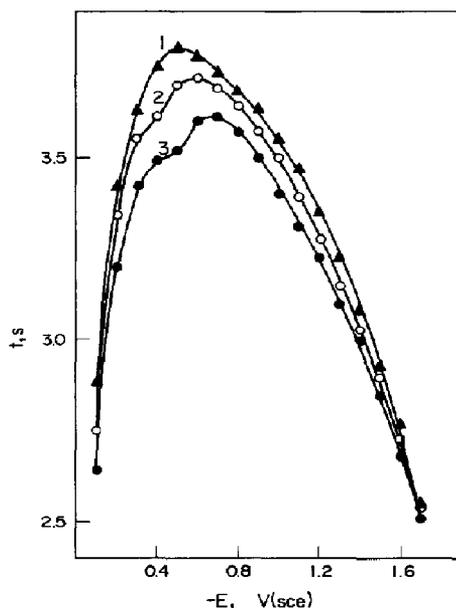


Fig. 5. Electrocapillary curves: (1) 0.06 M borax–0.05 M HCl containing 5 mM NaOH–0.5 mM I_2 ; (2) 0.06 M borax–0.05 M HCl with 0.1 mM cocarboxylase (disulfide form); (3) 0.06 M borax–0.05 M HCl with 0.1 mM cocarboxylase (disulfide form)–0.5 mM Ni(II).

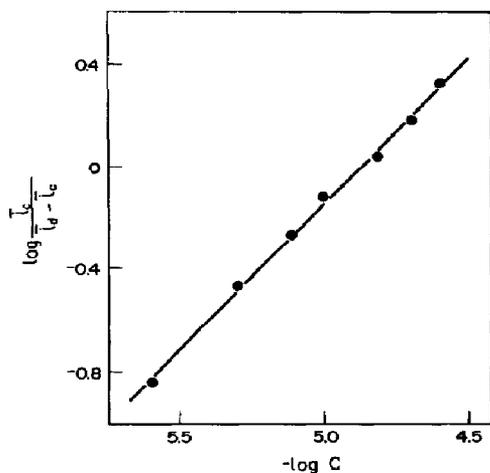


Fig. 6. Plot of $\log \frac{\bar{i}_c}{\bar{i}_d - \bar{i}_c}$ vs $\log C$, where C is the cocarboxylase (disulfide form) concentration. 0.2 mM Ni(II); 0.06 M borax (pH 9.3).

cocarboxylase (disulfide form) in the solution causes a decrease in the interfacial tension. This decrease is more marked between -0.3 and -0.5 V, potential in which the disulfide group is reduced to the thiol one. In nickel presence – and therefore there is formed nickel complex – the decrease of the interfacial tension is greater. It is therefore reasonable to suggest that this process involves the participation of the thiolic form of cocarboxylase adsorbed on the electrode surface.

The pointed out results suggest that the mechanism of these pre-waves is similar to that attributed to others already described[1–6]. The aquo-nickel ion – in equilibrium with the nickel poliborate complexes – is reacting with the thiolic form of cocarboxylase, which is produced by reduction of the disulfide form of cocarboxylase in the *dme*. The complex formed between nickel(II) and the thiolic form of cocarboxylase is discharged to the pre-wave potential, freeing the ligand, which takes part several times in the reaction sequence.

Considering that the Henry adsorption isotherm is obeyed – in the low cocarboxylase concentration range studied by us – and using the approximate method for the catalytic current, can be calculated the cocarboxylase-thiol:nickel(II) relationship in the catalytic complex. Examples of this calculation and deduction of the equation used can be seen in[1] and[5].

The equation for our process acquires the following form:

$$\log \frac{\bar{i}_c}{\bar{i}_d - \bar{i}_c} = \text{constant} + z \log C, \quad (1)$$

where \bar{i}_c is the average limiting catalytic current of the prewave, \bar{i}_d the average limiting current of nickel(II), C the cocarboxylase (disulfide form) concentration and z the complex stoichiometric coefficient.

It can be seen from Fig. 6 that (1) holds true, the slope being close to the unity. Then the catalytic complex is formed between cocarboxylase-thiol and nickel(II) in the relationship 1:1.

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