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Mechanism of the catalyzed by cysteine electroreduction of the insoluble in water cobalt(II) salt as a component of carbon paste electrode

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Abstract The mechanism of the Co(II) catalytic electroreduction of water insoluble CoR_2 salt in the presence of cysteine $\left(H_2L^{\pm}\right)$ was developed. CoR_2=cobalt(II) cyclohexylbutyrate is the component of a carbon paste electrode. Electrode surface consecutive reactions are: (a) fast (equilibrium) reaction of the $CoR_2\left(H_2L^{\pm}\right)_{ads}$ complex formation, (b) rate-determining reversible reaction of the promoting process of $CoR(Ac^+)$ complex formation, (c) rate-determining irreversible reaction of the electroactive $CoR(Ac)\left(H_2L^{\pm}\right)_{ads}$ complex formation with ligand-induced adsorption, and (d) fast irreversible reaction of the $CoR(Ac)\left(H_2L^{\pm}\right)_{ads}$ electroreduction. Reactions (a,b) connected with CoR_2 dissolution and reactions (c,d) connected with CoR_2 electroreduction are catalyzed by $\left(H_2L^{\pm}\right)_{ads}$. Regeneration of $\left(H_2L^{\pm}\right)_{ads}$ (reactions "b,d") and accumulation of atomic Co(0) (reaction "d") take place. Experimental data [Sugawara et al., Bioelectrochem Bioenergetics 26:469, 1991]: i_a vs E (i_a is anodic peak, E is cathodic accumulation potential), i_a vs c_{H_2L}, and i_a vs pH have been quantitatively explained.

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Introduction

Sugawara et al. [1–4] have studied electroreduction of metal ions from insoluble in water metal salts that were contained in a carbon paste electrode in contact with different ligands in a solution. After cathodic metal accumulation, the rate of which depended on the ligand concentration, the anodic peak (anodic stripping voltammetry) for high sensitive ligand determination was measured. However, the mechanism of the process, especially its quantitative analysis, was developed insufficiently.

The task of this work is to develop the mechanism and corresponding kinetic equations of both cathodic and anodic stages of this process using the theory of the catalytic metal ion electroreduction under the catalysis by a ligand [5–9]. As the model for theoretical analysis, we have chosen the experimental data obtained by Sugawara et al. [2] for CoR_2—a cysteine system where CoR_2 is a water insoluble cobalt(II) cyclohexylbutyrate, which is a component of a carbon paste electrode.

Acid-base and complexing characterizations of the CoR_2—cysteine—supporting electrolyte system in bulk solution

The supporting electrolyte is an aqueous acetate buffer at pH=3.2–6.2 and under the condition [2]:

$$[HAc] + [Ac^-] = C_{buff} = 0.1\,M \tag{1}$$

Using Eq. 1 and the acetic acid dissociation constant [10]:

$$K_{HAc} = \frac{[H^+][Ac^-]}{[HAc]} = 1.74 \times 10^{-5} \qquad (2)$$

we obtain the equation for ionic strength (I) and [Ac$^-$] calculation:

$$I = [Ac^-] = \frac{K_{HAc}C_{buff}}{[H^+] + K_{HAc}} \qquad (3)$$

Taking into account K_{HAc} and $C_{buff} = 0.1$ M for pH$=3.2$–6.2, we find that $I = 3.10^{-3}$ to 0.1 that allows to accept in further calculations the activity coefficients close to one. Because [Ac$^-$]$\gg$[CoR$_2$], the calculation of the equilibrium Ac$^-$ concentration from Eq. 3 gives a correct value without discount for its complexing with Co^{2+}.

For cyclohexylbutyric acid (HR), we have accepted the acid dissociation constant K_{HR} close to K_{HAc}:

$$K_{HR} = \frac{[H^+][R^-]}{[HR]} \cong K_{HAc} = \frac{[H^+][Ac^-]}{[HAc]}$$
$$= 1.74 \times 10^{-5} \qquad (4)$$

taking into account the closeness of the acid dissociation constants for butyric and acetic acids [10].

Acid-base characterizations of the cysteine are the following:

$$K_{H_3L^+} = \frac{[H^+][H_2L^\pm]}{[H_3L^+]} = (1.0 - 1.1) \times 10^{-2} \qquad (5)$$

[11–13]

$$K_{H_2L^\pm} = \frac{[H^+][HL^{\pm-}]}{[H_2L^\pm]} = (3.3 - 7.4) \times 10^{-9} \qquad (6)$$

[12, 13]

$$K_{HL^-} = \frac{[H^+][L^{2-}]}{[HL^{\pm-}]} = 7.8 \times 10^{-11} \qquad (7)$$

[12]

where H_3L^+ is the cysteine ion protonated on nitrogen, $H_2L^\pm$ is the cysteine zwitterion (dissociation at the carboxylic group and protonation of nitrogen), $HL^{\pm-}$ is the cysteine ion (dissociation of carboxylic and thiol groups and protonation of nitrogen), and L^{2-} is the cysteine ion with dissociated carboxylic and thiol groups.

On the basis of Eqs. 5, 6, and 7, the conclusion can be made that, in the investigated pH range (pH$=3.2$–6.2) among the cysteine forms, the zwitterions $H_2L^\pm$ are dominating.

The complexing of the Co^{2+} with L^{2-} system is characterized by the stability constant:

$$\beta_{CoL} = \frac{[CoL]}{[Co^{2+}][L^2]} = 2.0 \times 10^9 \qquad (8)$$

[14]

Taking into account Eqs. 5, 6, 7, and 8, the complex CoL at pH 3.2–6.2 can be neglected.

For the evaluation of $\beta\{Co(H_2L^\pm)\}^{2+}$, we have used the stability constant for In^{3+} complex:

$$\beta_{\{In(H_2L_S^\pm)\}^{3+}} = \frac{[\{In(H_2L_S^\pm)\}^{3+}]}{[In^{3+}][H_2L_S^\pm]} = 2.4 \times 10^2 \qquad (9)$$

[15]

where $H_2L_S^\pm$ is the isomeric form of the cysteine zwitterion with thiol group dissociated and nitrogen protonated. However, because $[H_2L^\pm] \gg [H_2L_S^\pm]$, and the obtained β (Eq. 9) is relatively small for $H_2L_S^\pm$, it is more correct to accept that this constant, $\beta\{In(H_2L^\pm)\}^{3+}$, is without some changes in the method and the procedure used in [15]. If now, to discount that for the same ligands in complexes $\beta(Co^{2+}) < \beta(In^{3+})$, we find:

$$\beta_{\{Co(H_2L^\pm)\}^{2+}} = \frac{[\{Co(H_2L^\pm)\}^{2+}]}{[Co^{2+}][H_2L^\pm]} < 2.4 \times 10^2 \qquad (10)$$

Using the maximum value of $C_{H_2L} = 6.0 \times 10^{-7}$ [2], we obtain from Eq. 10:

$$\frac{[\{Co(H_2L^\pm)\}^{2+}]}{[Co^{2+}]} < 1.4 \times 10^{-4} \qquad (11)$$

i.e., the influence of $[\{Co(H_2L^\pm)\}^{2+}]$ on [Co^{2+}] can be practically neglected. On the other hand, if to accept for very low solubility of CoR$_2$, the [Co^{2+}] value $\leq 10^{-5}$ M, we find from the correlation 10:

$$[\{Co(H_2L^\pm)\}^{2+}] < 2.4 \times 10^{-3}[H_2L^\pm] \qquad (12)$$

Hence, $\{Co(H_2L^\pm)\}^{2+}$ complex practically does not reduce $H_2L^\pm$ in the solution, and taking into account the analysis of Eq. 5, 6, and 7 carried out above, we obtain:

$$[H_2L^\pm] \cong C_{H_2L} \qquad (13)$$

At the same time, the complexing between Co^{2+} and Ac$^-$ at [Ac]$=3 \times 10^{-3}$–0.1 M from Eq. 3, and using the stability constants:

$$\beta_{\{Co(Ac)\}^+} = \frac{[\{Co(Ac)\}^+]}{[Co^{2+}][Ac^-]} = 31.6 \qquad (14)$$

[16]

$$\beta_{Co(Ac)_2} = \frac{[Co(Ac)_2]}{[Co^{2+}][Ac^-]^2} = 79.4 \qquad (15)$$

[16]

at the first stage of the complexing (Eq. 14) should be taken into account. However, only $[Co^{2+}]$ value is reduced, but $[Ac^-]$ is kept practically constant because of $[Ac^-] \gg [Co^{2+}]$. Considering the closeness of $\beta_{\{CoR\}^+}$, β_{CoAc^+} and β_{CoR_2}, $\beta_{\{Co(Ac)_2\}}$, and taking into account the very low $[R^-]$ due to the very low solubility of CoR_2, the $[\{CoR\}^+]$ and $[CoR_2]$ concentrations in the bulk solution as compared to $[Co^{2+}]$ can be neglected. Thus, the general concentration of cobalt(II) in the bulk solution, $C_{Co(II)}$, can be described by the equation:

$$C_{Co(II)} = [Co^{2+}] + [\{Co(Ac)\}^+] \qquad (16)$$

Saturation of bulk supporting electrolyte by CoR_2

This saturation is carried out from carbon paste electrode before the cathodic electrocatalytic process. Dissolution is

accelerated due to the combination of stirring and chemical effect of the solution components $H_2L^\pm$, H^+, and Ac^-. At the saturation, the equilibrium

$$(CoR_2)_{paste} \rightleftharpoons Co^{2+} + 2R^- \qquad (17)$$

is established. This equilibrium is described by the solubility product

$$Sp = [Co^{2+}][R^-]^2 \qquad (18)$$

Equation 18 allows to obtain the equation for determination of [HR] in the bulk solution that will be necessary below. With this objective, discounting Eq. 16, the equation:

$$2([Co^{2+}] + [\{Co(Ac)\}^+]) = [HR] + [R^-] \qquad (19)$$
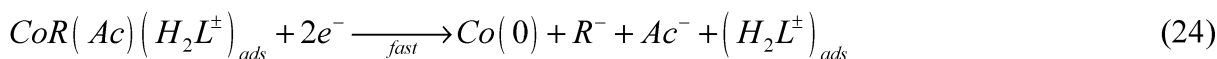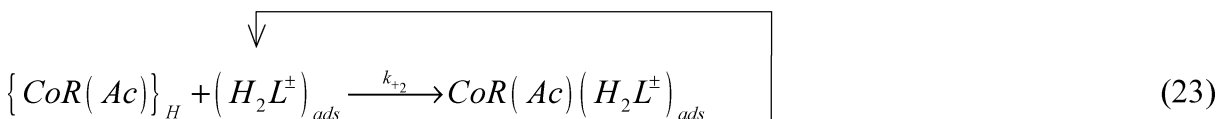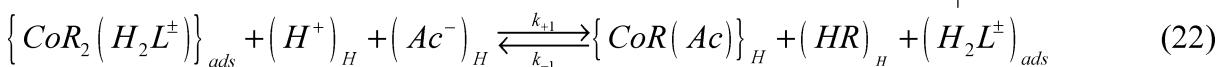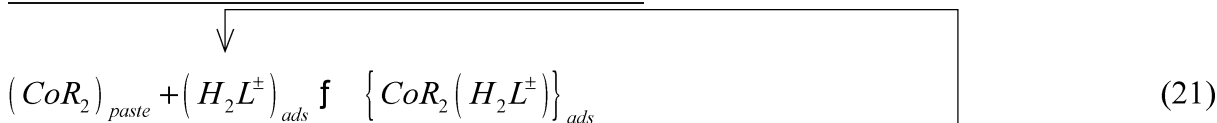
was used. On the basis of Eqs. 3, 4, 14, 18, and 19, we find:

$$[HR] = \frac{[H^+]}{K_{HAc}} \left\{ \frac{2S_p K_{HAc}([H^+] + K_{HAc} + \beta_{\{CoAc\}^+} + K_{HAc}C_{buff})}{([H^+] + K_{HAc})^2} \right\}^{1/3} \qquad (20)$$

Cathodic CoR_2 dissolution and electroreduction reactions

The peculiarity of the considered process is the passing of the cathodic consecutive surface reactions of the CoR_2

dissolution and its electroreduction. Both these reactions are catalyzed by $(H_2L^\pm)_{ads}$, and potentials of the CoR_2 catalytic electroreduction are more positive than potentials without $H_2L^\pm$. Schemes 21, 22, 23, and 24 are accepted for description of this process:

$$(CoR_2)_{paste} + (H_2L^\pm)_{ads} \ \rotatebox[origin=c]{180}{f} \ \{CoR_2(H_2L^\pm)\}_{ads} \qquad (21)$$

$$\{CoR_2(H_2L^\pm)\}_{ads} + (H^+)_H + (Ac^-)_H \underset{k_{-1}}{\overset{k_{+1}}{\rightleftharpoons}} \{CoR(Ac)\}_H + (HR)_H + (H_2L^\pm)_{ads} \qquad (22)$$

$$\{CoR(Ac)\}_H + (H_2L^\pm)_{ads} \xrightarrow{k_{+2}} CoR(Ac)(H_2L^\pm)_{ads} \qquad (23)$$

$$CoR(Ac)(H_2L^\pm)_{ads} + 2e^- \xrightarrow{fast} Co(0) + R^- + Ac^- + (H_2L^\pm)_{ads} \qquad (24)$$

where index "H" denotes the outer Helmholtz plane; k_{-+1}, k_{-1}, and k_{+2} are heterogeneous rate constants. Stage 21 is the fast (reversible) reaction proceeding in the adsorbed layer. Complex $\{CoR_2(H_2L^\pm)\}_{ads}$ is not catalytically electroactive because it is not a ligand-induced adsorption [6, 7]. Besides, the slow dissociation of hydrophobic

ligands (R^-) takes place. Stage 22 is the rate-determining reversible reaction of the promoting complex $CoR(Ac)$ formation and the catalyst $(H_2L^\pm)_{ads}$ regeneration. Promoting the effect of Ac^- ligand in surface electrocatalytic reactions was considered in detail in the work [9]. Stage 23 is the rate-determining irreversible reaction of the catalyt-

ically electroactive complex $CoR(Ac)(H_2L^\pm)_{ads}$ formation. This complex is differed by the ligand-induced adsorption [6, 7]. Analogical surface catalytic reaction was observed for cysteine during In^{3+} electroreduction [15]. Irreversibility of reaction 23 is caused by fast reaction 24. Stage 24 is the fast reaction of the irreversible electroreduction $CoR(Ac)(H_2L^\pm)_{ads}$ complex to the atomic Co(0) accompanied with the catalyst $(H_2L^\pm)_{ads}$ regeneration. From reaction 24, it follows that atomic Co(0), but not cysteine, is accumulated, as was supposed in the work [2]. The accumulation of cysteine cannot explain the catalytic nature of the process.

Kinetic equations

Using conditions of the fresh paste for each new measurement [2] and the stationary state nature of the process caused by the rate-determining reactions 22 and 23, we find for the cathodic-limiting catalytic current (i_c):

$$i_c = k'_{+1}[CoR_2(H_2L^\pm)]_{ads}[H^+]_H[Ac^-]_H - k'_{-1}[CoR(Ac)]_H[HR]_H[H_2L^\pm]_{ads} \tag{25}$$

$$i_c = k'_{+2}[CoR(Ac)]_H[H_2L^\pm]_{ads} \tag{26}$$

where k'_{+1}, k'_{-1}, and k'_{+2} are constants directly proportional to the heterogeneous rate constants k_{+1}, k_{-1}, and k_{+2} of reactions 22 and 23, respectively. The absence of the diffusion limitations in the surface processes 21, 22, 23, and

24 makes the rate-determining stages 22 and 23 considerably faster than the analogous stages with diffusion of particles from the bulk solution. Therefore, in Eqs. 25 and 26, this influence is not assumed. We also neglected the increase in [HR] and [R$^-$] during the accumulation (Eqs. 22 and 24), taking into account the relatively larger solution volume (20 ml) and stirring of the solution.

The following equation describes equilibrium 21:

$$\beta_a = \frac{[CoR_2(H_2L^\pm)]_{ads}}{[H_2L^\pm]_{ads}} \tag{27}$$

The adsorption equilibrium for cysteine corresponds to the Henry isotherm ($C_{H_2L} \leq 6.0 \times 10^{-7}$ M), which, considering Eq. 13, has the form:

$$K_H = \frac{[H_2L^\pm]_{ads}}{10^{-3}C_{H_2L}} \tag{28}$$

Concentrations of charged particles in the Helmholtz plane (index "H") in Eq. 25 depend from potential in this plane (Φ_0 potential). However, in Eq. 25, this effect is intercompensated, and for uncharged particles, this effect equals to zero. Therefore, in the further text, the index "H" will be omitted and bulk concentrations will be used.

On the basis of Eqs. 3, 4, 20, 25, 26, 27, and 28, the kinetic equation for cathodic-limiting catalytic current has the form:

$$i_c = \frac{k''_{+1}C_{H_2L}}{\frac{[H^+]+K_{HAc}}{[H^+]} + k''_{-1}\left\{([H^+]+K_{HAc})\left([H^+]+K_{HAc}+\beta_{(CoAc)^+}K_{HAc}C_{buff}\right)\right\}^{1/3}} \tag{29}$$

where k''_{+1} and k''_{-1} are the constants:

$$k''_{+1} = k'_{+1}10^{-3}K_H\beta_a K_{HAc}C_{buff} \tag{30}$$

$$k''_{-1} = \frac{k'_{-1}}{k'_{+2}10^{-3}K_H}\left(\frac{2S_p}{K_{HAc}^2}\right)^{1/3} \tag{31}$$

Taking into account that limiting (independent from accumulation potential) the anodic peak (i_a) is directly proportional to limiting the cathodic accumulation current:

$$i_a = ki_c \tag{32}$$

we find:

$$i_a = \frac{k'''_{+1}C_{H_2L}}{\frac{[H^+]+K_{HAc}}{[H^+]} + k''_{-1}\left\{([H^+]+K_{HAc})\left([H^+]+K_{HAc}+\beta_{(CoAc)^+}K_{HAc}C_{buff}\right)\right\}^{1/3}} \tag{33}$$

where

$$k'''_{+1} = k k''_{+1} \tag{34}$$

Thus, we have obtained the kinetic equations for both cathodic-limiting catalytic current (Eq. 29) and anodic-limiting current (Eq. 33).

Results and discussion

Kinetic Eqs. 29 and 33 correspond to fast reaction 24 that is achieved by the increase in the negative potential (exponential potential dependence). Hence, the limiting current i_a was observed [2].

From Eq. 33, direct proportional dependence i_a vs C_{H_2L} follows at pH=const that is confirmed by data in [2] for the wide C_{H_2L} range (5×10^{-9}–6×10^{-7} M).

Equation 33 also explains maximum on curve i_a vs pH at $C_{H_2L} = $ const (Fig. 2 in [2]). This maximum is caused by reaction 22; the rate of which passes through the maximum with a pH increase. At low pH (pH 3–4), the rate is increased with pH rising due to the dominating effect of the

Table 1 Comparison of $(i_a)_{exp}$ with $(i_a)_{calc}$ and parameters X_1 and X_2 in Eq. 36

pH	$(i_a)_{exp}$ (μA)	$(i_a)_{calc}$ (μA)	X_1	X_2
3.25	5.5	5.6	1.03	6.79
3.50	7.4	7.5	1.06	4.80
3.75	10.1	9.6	1.10	3.47
4.00	12.1	11.7	1.17	2.58
4.25	13.6	13.3	1.31	2.00
4.50	13.6	13.8	1.55	1.63
4.75	11.4	13.0	1.98	1.40
5.00	9.6	11.1	2.74	1.24
5.25	8.2	8.4	4.10	1.15
5.50	6.8	5.8	6.51	1.10
5.75	5.1	3.7	10.78	1.06
6.00	3.8	2.3	18.40	1.00

[H$_2$R] decrease. At higher pH (pH 5–6), the rate is decreased with pH increase due to the dominating effect of the [H$^+$] decrease. The point of the considered maximum $(di_a/d[\text{H}^+])=0$ obtained from Eq. 33 allows to determine the constant k''_{-1}:

$$k''_{-1} = \frac{3K_{HAc}\left\{\left([\text{H}^+]_{max} + K_{HAc}\right)\left([\text{H}^+]_{max} + K_{HAc} + \beta_{(CoAc)^+}K_{HAc}C_{buff}\right)\right\}^{2/3}}{[\text{H}^+]_{max}^2\left(2[\text{H}^+]_{max} + 2K_{HAc} + \beta_{(CoAc)^+}K_{HAc}C_{buff}\right)} \tag{35}$$

where $[\text{H}^+]_{max}$ corresponds to pH$_{max}$=4.2–4.5 [2]. For k''_{-1} determination (Eq. 35), we have used pH$_{max}$=4.5, which gives best agreement between $(i_a)_{exp}$ and $(i_a)_{calc}$ for all the curves i_a vs pH (see Table 1). Using the values pH$_{max}$=4.5, K_{HAc}=1.74×10^{-5}, $\beta_{(CoAc)^+} = 31.6$, and C_{buff}=0.1 M, we obtained $k''_{-1} = 9.5 \times 10^2 (1/\text{mol})^{2/3}$. The obtained values of k''_{-1} and i_a=13.6 μA [2] at pH$_{max}$=4.5 and $C_{H_2L} = 4.0\times 10^{-7}$ M allowed us to obtain $k''_{+1} = 1.1 \times 10^8$ μA 1 mol^{-1}.

On the basis of the found k''_{-1} and k''_{+1} values by means of Eq. 33, the values of $(i_a)_{calc}$ have been calculated for the whole i_a vs pH curve at $C_{H_2L} = 4.0 \times 10^{-7}$ M. The comparison of $(i_a)_{exp}$ with $(i_a)_{calc}$ is shown in Table 1.

In the pH range 3.2–5.5, the differences between $(i_a)_{exp}$ and $(i_a)_{calc}$ do not exceed 16% (Table 1). At pH>5.5, the $(i_a)_{exp}>(i_a)_{calc}$, probably due to influence of the parallel catalytic reaction with the participation of $\left(\text{HL}^{\pm-}\right)_{ads}$ [15].

Sugawara et al. [2] supposed that the maximum on i_a vs pH curve is connected with isoelectric point of cysteine. However, as indicated above, the H$_2$L$^\pm$ concentration change in pH 3.2–6.2 range, including isoelectric point, is insignificant for the explanation of the maximum.

Equation 33 allows to evaluate the contribution of the rate-determining reactions 22 and 23 in general kinetics. For this objective, we give the Eq. 33 the form:

$$i_a = \frac{k'''_{+1} C_{H_2L}}{X_1 + X_2} \tag{36}$$

where

$$X_1 = \frac{[\text{H}^+] + K_{HAc}}{[\text{H}^+]} \tag{37}$$

$$X_2 = k''_{-1}\left\{\left([\text{H}^+] + K_{HAc}\right)\left([\text{H}^+] + K_{HAc} + \beta_{\{Co(Ac)\}^+}K_{HAc}C_{buff}\right)\right\}^{1/3} \tag{38}$$

At low pH, when $X_2 \gg X_1$, and, taking into account in this condition, achievement of the equilibrium on stage 22, we obtain from Eqs. 27, 30, 31, 34, 36, and 38:

$$i_c = k''_{+2}[CoR(Ac)]\left[H_2L^{\pm}\right]_{ads} \tag{39}$$

i.e., reaction 23 has dominating influence on the general kinetics. As it can be seen from Table 1, this condition is fulfilled close to pH≤3.2. On the other hand, at increased pH, the correlation $X_1 \gg X_2$ takes place. From Eq. 3, 27, 30, 34, 36, and 37, we find:

$$i_c = k'_{+1}\left[CoR_2\left(H_2L^{\pm}\right)\right]_{ads}[H^+][Ac^-] \tag{40}$$

i.e., the influence of reaction 22 on the kinetics will be dominating. As it can be seen from Table 1, the considered condition is valid close to pH≥5.5.

The mechanism of the catalytic process proposed by us allows to note two important advantages of Sugawara et al.'s [1–4] method, which were not considered earlier. First, the absence of diffusion limitations increases the sensitivity of the analysis. Secondly, the low metal ions' concentration increases the difference between the potentials belonging to the catalytic and uncatalyzed processes of the metal ions' discharge, and this makes analysis more accurate.

Conclusions

1. The mechanism of the Co(II) catalytic electroreduction in CoR_2 water insoluble salt in the presence of cysteine $(H_2L^{\pm})$ has been developed. CoR_2—cobalt(II) cyclohexylbutyrate is the component of a carbon paste electrode.
2. $H_2L^{\pm}$ is the zwitterion of the cysteine dominating at pH 3.2–6.2 (acetate buffer).
3. Electrode reactions are: (a) fast (equilibrium) reaction of the $\left\{CoR_2\left(H_2L^{\pm}\right)\right\}_{ads}$ complex formation, (b) rate-determining reversible reaction of the promoting process of CoR(Ac) complex formation, (c) rate-determining irreversible reaction of the electroactive $CoR(Ac)\left(H_2L^{\pm}\right)_{ads}$ complex formation with ligand-induced adsorption, and (d) fast irreversible electro-reduction of the $CoR(Ac)\left(H_2L^{\pm}\right)_{ads}$.

4. Reactions (a,b) connected with $(CoR_2)_{paste}$ dissolution and reactions (c,d) connected with the CoR_2 electro-reduction are catalyzed by $\left(H_2L^{\pm}\right)_{ads}$. The regeneration of $\left(H_2L^{\pm}\right)_{ads}$ (reactions "b,d") and the accumulation of the atomic Co(0) (reaction "d") take place.
5. The following experimental data [2] were quantitatively explained: (1) limiting anodic peak (i_a) in i_a vs E (E is cathodic accumulation potential); (2) direct proportionality for i_a vs C_{H_2L} (pH=const); (3) curve i_a vs pH (C_{H_2L} = const) with the maximum; and (4) at pH≤3.2, the dominating effect of the reaction (c), at pH≥5.5, the dominating effect of reaction (b).

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