THE INFLUENCE
OF SURFACE COVERAGE
ON THE ELECTRON TRANSFER REACTION Co en$_3^{2+}$/Co en$_3^{3+}$
AT PLATINUM ELECTRODES

H.BARTELT, R.LANDSBERG and M.PRÜGEL

Sektion Chemie,
*Humboldt-Universität zu Berlin, DDR*

Dedicated to the 65th anniversary of the late Academician R. Brdička.

Products of hydrolysis in the redox system Co en$_3^{2+}$/Co en$_3^{3+}$ cause an irregular dependence of exchange current on concentration which allows the degree of coverage due to these products of hydrolysis to be determined. It could be shown that hydrolysis as well as the complexing agent lead to a surface covering, which is in accordance with non-electrochemical observation reported in the literature. The total degree of surface coverage is equal to the sum of partial degrees of coverage due to complexing agent, Co(III) and Co(II). The non-linear diffusion method is less sensitive, *i.e.* the exchange current density method has a higher power of resolution for detecting effects.

Previous investigations of the electrochemical parameters of the transfer reaction

$$\text{Co en}_3^{2+} \quad \rightleftharpoons \quad \text{Co en}_3^{3+} + \text{e} \qquad (A)$$
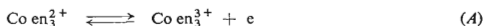
(en = ethylenediamine) using platinum electrodes showed[1,2] that this redox system does not behave ideally, because of side reactions leading to surface coverage. The apparent electrochemical reaction order determined by varying the Co en$_3^{3+}$ ion concentration is less than one. This is due to hydrolysis of the Co en$_3^{3+}$ ion in the alkaline medium of the complexing agent (pH 11·8) causing a coverage of the platinum electrode.

It was Bjerrum[3] who observed the hydrolysis of the otherwise stable Co en$_3^{3+}$ ion in alkaline solutions. Bjerrum and Rasmussen[4] described in great detail the following equilibration:

$$\text{Co en}_3^{3+} + 2\,\text{OH}^- \quad \rightleftharpoons \quad \text{Co en}_2(\text{OH})_2 + \text{en}\,. \qquad (B)$$
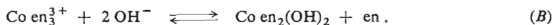
The active carbon catalyst added is quickly poisoned and caused a partial decomposition to Co(OH)$_3$. For this reason the authors added only a small portion of the catalyst at a time. In this paper[4] there are also data on the adsorption of ethylenediamine on active carbon thus 13% of the en added to a 0·1M-en solution are adsorbed, the corresponding figure for a 0·01M solution is about 20%.

Douglas[5] showed that at 100°C active carbon causes a fast racemisation of optically active

Co en$_3^{3+}$ ions (within a few minutes). During the course of reaction the carbon activity diminishes. Sen and Fernelius[6] examined the exchange reaction on active carbon and platinum black. They showed that Co en$_3^{3+}$ ions hydrolyse within the investigated temperature range which extended to 100°C. Desactivation of the catalyst was observed showing that platinum promotes hydrolysis of the Co en$_3^{3+}$ ions in the same way as active carbon does. This desactivation, observed whenever hydrolysis takes place, can only be explained by surface coverage.

The adsorption of Co en$_3^{3+}$ ions on mercury in 0·1M-en solution and various conducting electrolytes was investigated by Laitinen and Chambers[7]. They found that the amount of Co en$_3^{3+}$ ions adsorbed at the electrode decreases on adding Co en$_2^{2+}$ ions. According to our observations too, the quantity of Co en$_3^{3+}$ ions adsorbed is largest in the absence of Co en$_2^{2+}$ ions.

Anson[8] examined the adsorption of Co en$_3^{3+}$ ions under almost identical conditions and could not find any adsorption by means of a chronocoulometric method. In a reply to Anson, Laitinen[8] and Chambers pointed[9] out that the displacement of the maximum of the electrocapillarity curve indicates the adsorption of Co en$_3^{3+}$ ions. The adsorption of the Co en$_2^{2+}$ ion could not be examined because unidentified kinetic processes interfere with the anodic part of the current density–potential curve[10]. We would like to stress that chronocoulometric evidence for adsorption or presence of surface coverage presumes that these are electrochemically active.

Our experimental results, however, lead us to the conclusion that the products of the above hydrolysis formed on the surface are electrochemically inactive in contrast to Co en$_3^{3+}$ itself.

THEORETICAL

The non-linear diffusion method developed by us to characterise a surface coverage is particularly applicable if this is electrochemically inactive[11–13]. Our basic model was confirmed by experiment and showed that for stationary as well as non stationary conditions the thickness of the diffusion layer, δ, in the appropriate equations must be corrected by an additive term for a partially covered electrode:

$$S = \sum A_n \, \text{tgh} \left(X_n \delta / r_2 \right), \qquad (1)$$

where $\sum A_n$ is a coefficient for which Smythe[14] has derived an equation, and which has been tabulated by us[11], x_n are zero points of the first order Bessel function, r_2 is the radius of the diffusion cylinder containing the circular active area of radius r_1 at its centre. The experimental test of the model proved the validity of the relation

$$N \, \pi r_2^2 = q \, ,$$

where N denotes the total number of active areas i.e. diffusion cylinders and q is the geometric electrode surface.

a) For small rates of rotation the dependence of the limiting diffusion current (I_{gr}) to a rotating disk electrode on rate of rotation is given by

$$\frac{1}{I\text{gr}} = \frac{1·61 \, v^{1/6} U^{-1/2}}{n F D^{2/3} \, c_L \, q (2\pi)^{1/2}} + \frac{|\sum A_n| \, \delta}{n F D c_L \, q} \qquad (2)$$

where v is the kinematic viscosity, n number of electrons exchanged, F Faraday's constant, D diffusion coefficient, c_L concentration of depolariser in the solution, U number of rotation per second. On plotting I_{gr}^{-1} *versus* $U^{-1/2}$ a straight line is thus obtained which is parallel to the one representing the Levich relationship (first term on the right hand side of (2)).

b) For high rates of rotation the experimental results may be represented by a straight line in the same plot going through the origin[12]. It is steeper than the straight line corresponding to the Levich-relationship. The basic model, leading to the equations derived by us, does not apply in this case (in contrast to analogous non-stationary experiments[13]), because it neglects centrifugal convection.

Our experiments[15] showed on the other hand that deviations from the linear relationship observed for low rates of rotation begin to occur for $\delta \simeq r_1$. The points of beginning deviation and of intersection between the extrapolated straight line and the ordinate supply the data needed for a determination of r_1, r_2 and Θ, the degree of coverage of the electrode.

Near equilibrium a similar situation prevails, the overpotential is determined by terms representing the charge-transfer process, linear and non-linear diffusion respectively[16]. The dependence of polarisation resistance of partially covered electrodes on rate of rotation is analogous to the dependence of the limiting diffusion current on rate of rotation at the same electrode. At high rates of rotation the polarisation resistance is linearly dependent on $U^{-1/2}$ despite the neglected centrifugal convection.

The exchange current density may be directly determined from this plot by extra-
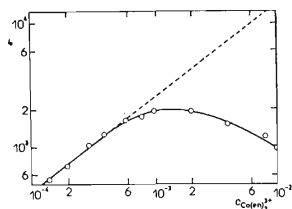

FIG. 1

Dependence of Exchange Current Density i_0 ($\mu A \cdot cm^{-2}$) on Co(III) Concentration (varied between $1 . 10^{-4}$ and $1 . 10^{-2}M$) at Constant Co(II) Concentration ($1 . 10^{-3}M$) in 1M-KCl and 0·1M en ($\alpha = 0·77 \pm 0·02$)
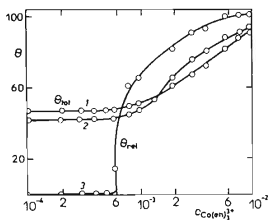

FIG. 2

Dependence of Relative and Total Degree of Coverage Θ (%) on Co(III) Concentration (mol/l) at Constant Co(II) Concentration ($1 . 10^{-3}M$) in 1M-KCl and 0·1M en on *1*. Near Equilibrium and *2*. Limiting Current

polating to infinite rates of rotation. $\sum A_n$ is found by extrapolating the straight line obtained for low rates of rotation in the same way.

EXPERIMENTAL

The cell, the circuit, the pretreatment of the electrode and the preparation of the solutions have been previously described[1,2]. The rotating disk electrode was driven by a synchronous motor which in turn was driven by a frequency generator with an amplifier. The rate of rotation could be continuously varied from $U^{1/2} = 0.8 \text{ s}^{-1/2}$ to $U^{1/2} = 8 \text{ s}^{-1/2}$. The experiments were carried out at 25 ± 0.2 °C.

RESULTS

Coverage due to Co(III) Compounds

Dependence of exchange current density on Co en$_3^{3+}$-concentration (between $1 \cdot 10^{-4}$M and $1 \cdot 10^{-2}$M while the Co en$_3^{2+}$ concentration was kept constant at 1 mM) is shown in Fig. 1.

Hydrolysis causes a deviation from the expected relationship between exchange current density and concentration beginning at $c_{\text{Co(III)}} = 5 \cdot 10^{-4}$M. Beyond this point towards higher concentrations the exchange current density goes through a maximum. This is the direction of increasing electrode coverage. We could show in our preceding communication[2] that for certain experimental conditions the logarithm of exchange current density depends linearly on the logarithm of Co en$_3^{3+}$ concentration and the electrochemical reaction order is one. With the beginning of hydrolysis a part of the surface of the electrode becomes covered and is no longer available for the process of electron transfer.
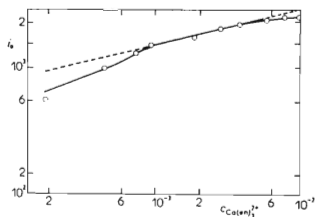
FIG. 3

Dependence of Exchange Current Density i_0 (μA . cm^{-2}) on Co(II) Concentration (mol/l) at Constant Co(III) Concentration ($1 \cdot 10^{-3}$M) in 1M-KCl, 0·1M en
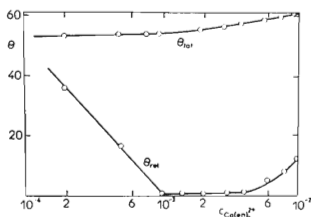
FIG. 4

Dependence of Relative and Total Degree Θ (%) of Coverage on Co(II) Concentration (mol/l) at Constant Co(III) Concentration ($1 \cdot 10^{-3}$M) in 1M-KCl, 0·1M en

The degree of coverage, Θ, may be found by means of the deviation from normal behaviour according to the relation:

$$i_0 = nFk_{el}C_{ox}^{\alpha}C_{red}^{1-\alpha}\left(1 - \Theta\right), \qquad (3)$$

where i_0 is the exchange current density, k_{el} electrochemical rate constant, C_{ox}, C_{red} concentration of Co en$_3^{3+}$ and Co en$_3^{2+}$-ions respectively, α, $1 - \alpha$ anodic and cathodic transfer coefficient respectively. Fig. 2 shows the results. The experiments were carried out at an en concentration $c_{en} = 0.1$M.

The degree of coverage determined in this manner from the deviating kinetics will be called relative degree of coverage, it contains no information on the degree of coverage present before the polarisation experiment begins. The non-linear-diffusion method[11,12] described above may, however, be used to determine the total degree of coverage, Θ_{tot}, including the one present before the current starts flowing (initial coverage).

The limitation of this method is due to the fact that only those inactive areas produce an effect the dimensions of which are not much less than the diffusion boundary layer thickness (not more than one order of magnitude). On the other hand inactive sites of much smaller dimension are capable of lowering the exchange current density. The "power of resolution" of exchange current density method (also dependent on experimental condition) is potentially much higher. In our experiments we varied the Co(III) concentration between $1 . 10^{-4}$M and $1 . 10^{-2}$M and found an initial coverage using the non-linear-diffusion method. Fig. 2 shows that the degree of coverage remains constant up to $5 . 10^{-4}$M Co en$_3^{3+}$. This observation shows that our formely employed method[1] of determining the electrochemical reaction order using experimental points within this concentration range is correct. Fig. 2 also shows that Θ_{tot} rises from $\Theta_{tot} = 0.47$ in 0.01M en to $\Theta_{tot} = 0.92$ in 0.1M en. This is due to hydrolysis.

Covering Effect due to Co(II) *Ions*

We have previously pointed out[1,2] that the exchange current density found for system (A) very much depends on the order in which the redox components are added to the electrolyte. In our experiments the concentration of the Co(II) ions normally remained higher than that of the Co(III) ions; only in this case is it possible to determine the parameters of the electron transfer reaction readily. The experiments depicted in Fig. 3 were begun at the concentrations $2 . 10^{-4}$M Co en$_3^{2+}$/$1 . 10^{-3}$M Co en$_3^{3+}$, the Co en$_3^{3+}$ concentration was then raised to $1 . 10^{-2}$M.

Kinetic measurements revealed: *1.* At low concentrations of Co(II) the kinetic behaviour is irregular, the deviation is caused by hydrolysis of the Co(III) component leading to a covering of the surface. *2.* This deviation diminishes with increasing Co(II) concentration, when both redox components are equally concentrated the

normal linear relationship between the logarithms of exchange current density and Co(II) concentration is found in this case, leading to $1 - \alpha = 0.23 \pm 0.02$. 3. On further increasing the Co(II) concentration there is again a deviation from the regular linearity, the apparent reaction order is less than one.

There is a discrepancy when relative and total degree of coverage as a function of Co(II) concentration are compared at low Co(II) concentration. This is very probably due to small inactive sites influencing the exchange current density, however, because they are considerably smaller than the thickness of the diffusion boundary layer, they cannot be detected by the non-linear-diffusion method[11,12] (Fig. 4).

The Coverage Caused by the Complexing Agent

The dependence of the degree of coverage on the concentration of the complexing agent is itself dependent on electrode pretreatment and the way in which the solution has been prepared *i.e.* the order in which reagents are added to the solution.

For the first series of measurements in Fig. 5 for instance, only 2mM en was added to a solution containing 1mM of Co^{2+} and 1 mM of $Co\ en_3^{3+}$. For the complete coordination of the Co^{2+} ions this quantity of en is insufficient. The following reaction can take place:

$$Co^{2+} + 2\ en + 2\ OH^- \rightarrow Co\ (en)_2\ (OH)_2\ . \qquad (C)$$
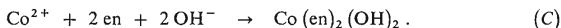
It must be assumed that the reaction product covers the electrode leading to a high degree of coverage ($\Theta = 0.8$). Further addition of en does not lower the degree of coverage, so that dissolution by en can be ruled out.

The second series was carried out at the same concentrations of Co^{2+} and $Co\ en_3^{3+}$, the en concentration, however, was raised to $1 . 10^{-2}M$, *i.e.* a threefold excess of en was present so that the formation of the complex was practically complete.
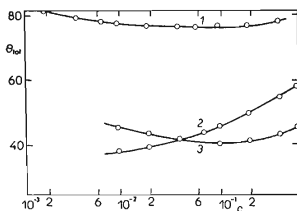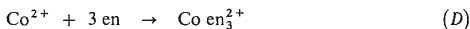
$$Co^{2+} + 3\ en \rightarrow Co\ en_3^{2+} \qquad (D)$$

Fig. 5

Dependence of Total Degree of Coverage $\Theta_{tot}(\%)$ on Concentration of Complexing Agent c (mol/l)

Co(II) concentration $1 . 10^{-3}M$, 1M-KCl, Co(III) concentration: $1\ 4 . 10^{-4}$, $2\ 1 . 10^{-3}$ $3\ 4 . 10^{-4}M$; *1* from limiting current, *2* and *3* determined near equilibrium.

The degree of coverage is accordingly much less. It reached about 0·45 when working at the usual concentrations of 1 mM Co en$_3^{2+}$/1 mM Co en$_3^{3+}$ in 0·1M-en and represents the equilibrium value of our former investigations[1,2]. It did not alter on varying the Co en$_3^{3+}$ (Fig. 2) or the Co en$_3^{2+}$ concentrations (Fig. 3). Even so the third series of measurements, carried out at a lower concentration of Co en$_3^{3+}$ (4 . 10^{-4}M), shows that occasionally the product of hydrolysis is redissolved.

DISCUSSION

The results show that the degree of coverage determined by diffusion resistance measurements near equilibrium ($\eta \approx 5$ mV) and the coverage found by means of the limiting diffusion currents agree well (Fig. 2, curve *1* and *2* respectively).

Furthermore the dependence of exchange current density on concentration is evidence for a process of hydrolysis involving the Co(III) ions which causes an additional covering of the electrode surface; this may be calculated using equation (*3*). The total degree of coverage may be found utilising the method of non-linear-diffusion[11,12].

It consists of the following additive terms

$$\Theta_{tot} = \Theta_{en} + \Theta_{Co(III)} + \Theta_{Co(II)} \qquad (4)$$

which depend on experimental conditions.

$\Theta_{Co(III)}$ and $\Theta_{Co(II)}$ may be determined by means of the abnormal dependence of exchange current density on concentration (Fig. 1 and 3 respectively). The remaining term Θ_{en} is due to a substance which is not directly involved in the electron exchange reaction and Θ_{en} can only be found indirectly.

Fig. 2 shows that up to a Co(III) concentration of 6 . 10^{-4}M the degree of coverage remains constant. The kinetic parameters which we determined for the transfer reaction in the system Co en$_3^{3+}$/Co en$_3^{2+}$ therefore refer to a constant area. The exact size of this area is a problem, however, because apart from the degree of coverage the surface roughness must be considered when calculating exchange current densities.

Our findings confirmed the observation of Bjerrum and Rasmussen[4] that the complexing agent is strongly adsorbed. We could also confirm Laitinen and Chambers[9] conclusion that both redox partners are adsorbed in equimolar solutions. In the absence of Co(II) ions it is not, however, the Co en$_3^{3+}$ ions which are adsorbed, as Chambers and Laitinen believed, but the product of their hydrolysis as Bjerrum and Rasmussen[4] already recognised. This fact resolves the dispute between Laitinen and Chambers[9] on the one hand and Anson[8] on the other. Anson could not reduce the adsorbed film, because it did not consist of the original complex but contained Co en$_2$(OH)$_2^+$ ions which are electrochemically inactive. If the diffusion coefficient is derived from the slope of a Levich plot at speeds of rotation between 9 and 16

revolutions per second a value of $D_{Coen_3}^{3+} = 4\cdot6 \cdot 10^{-6}$ cm^2 s^{-1} is obtained which agrees with the results of Laitinen and Chambers[7]. The surface is, however, partially covered and the diffusion coefficient should be determined from a plot according to (2) i.e. I_{gr}^{-1} vs. $U^{-1/2}$. From the slope of the straight line so obtained for lower speeds of rotation we calculated $D_{Coen_3}^{3+} = 7\cdot5 \cdot 10^{-6}$ cm^2 s^{-1}.

REFERENCES

1. Bartelt H., Skilandat H.: J. Electroanal. Chem. 23, 407 (1969).
2. Bartelt H., Skilandat H.: J. Electroanal. Chem. 24, 207 (1970).
3. Bjerrum J.: Metal Amine Formation in Aqueous Solution, p. 220. Haase, Copenhagen 1941.
4. Bjerrum J., Rasmussen S.: Acta Chem. Scand. 6, 1265 (1952).
5. Douglas B. E.: J. Am. Chem. Soc. 76, 1020 (1954).
6. Sen D., Fernelius W. C.: J. Inorg. Nucl. Chem. 10, 269 (1959).
7. Laitinen H. A., Chambers L. M.: Anal. Chem. 36, 5 (1964).
8. Anson F. C.: Anal. Chem. 36, 932 (1964).
9. Laitinen H. A., Chambers L. M.: Anal. Chem. 36, 1881 (1964).
10. Laitinen H. A., Randles J. E. B.: Trans. Faraday Soc. 51, 54 (1955).
11. Scheller F., Müller S., Landsberg R., Spitzer J.: J. Electroanal. Chem. 19, 187 (1968).
12. Scheller F., Landsberg R., Müller S.: J. Electroanal. Chem. 20, 375 (1969).
13. Lindemann H. J., Landsberg R.: J. Elektroanal. Chem. 25 (App. 20) 29, 261 (1970); 30, 79 (1971).
14. Smythe W. R.: J. Appl. Phys. 24, 70 (1953).
15. Scheller F., Landsberg R., Wolf H.: Electrochim. Acta 15, 525 (1970).
16. Scheller F., Landsberg R.: Z. Physik. Chem. Leipzig 244, 273 (1970).