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MECHANISM OF THE REDUCTION OF Ni(II)-ALCOHOLAMINE COMPLEXES ON THE DROPPING MERCURY ELECTRODE

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ABSTRACT

The polarographic characteristics of the Ni(II) ion in presence of the four aminoalcohols monoethanolamine, N-methylethanolamine, N-ethylethanolamine and N,N-dimethylethanolamine are reported. In general, half-wave potentials for the complexes are more positive than for the aquo-ion, and shift towards more negative values as the concentration of ligand increases. Transfer coefficients, α , electrode reactions rates and activation energies were determined for the reduction of the complexes. Differences between the reduction mechanism of the various Ni(II)- aminoalcohol complexes are pointed out.

INTRODUCTION

The unusual electrochemical behaviour exhibited at the dropping mercury electrode by complexes of Ni(II) with nitrogen bearing ligands, which has long been known, has recently been the subject of a number of articles (1-4). As far as we know, however, there has been only one study (5) of the electrochemical behaviour of Ni(II)-alcoholamine complexes, and only a qualitative description was given. The present article reports quantitative electrochemical

data for complexes of Ni(II) with monoethanolamine (MEA), N-methylethanolamine (NMEA), N-ethylethanolamine (EMEA) and N,N-dimethylethanolamine (NNMEA).

EXPERIMENTAL

All reagents were Merck p.a. products. Alcoholamines were purified by standard procedures before use and their concentrations checked by titration against acid. Ni(II) solutions were prepared from $\text{Ni}(\text{NO}_3)_2$ and their concentrations determined by titration against EDTA.

All polarographic studies were carried out using $1,33 \cdot 10^{-4} \text{ M}$ Ni(II) solutions. The concentrations of alcoholamine were varied over the ranges listed in Table 1. Ionic strengths were held at 0,1M by addition of suitable quantities of KNO_3 .

Polarograms were obtained using a Methrom E506 polarograph with an E505 stand. A three-electrode cell was used, and the drop time was controlled automatically ($t = 3\text{s}$) except when investigating the step controlling limiting current. All experiments were performed in d.c. mode. Solutions were thermostatted at 298,0, 303,0 and 308,0 \pm 0,1K, and pure nitrogen was bubbled through them for at least ten minutes before the experiments commenced. In no case was maximum suppressor necessary.

Potentiometric measurements were performed in a 250 ml cell thermostatted at 298,0 \pm 0,1K by a Haake D3 thermostat. Emf was measured using a CRISON Digilab 517 pH-meter accurate $\pm 0,1\text{mV}$ equipped with an Ingold electrode and calibrated as according Williams method (6).

The coefficients and rate constants of the electrode reactions (the later obtained at formal potential of the pair $\text{Ni}(\text{H}_2\text{O})_x^{2+}/\text{Ni}(\text{Hg})$ (7)) were calculated by the methods of Gellings (8), Hale and Parsons (9), Bridcka (10) and Oldham and Parry (11), using an Epson HX-20 microcomputer.

RESULTS AND DISCUSSION

The reduction of Ni(II)-alcoholamine complexes studied produced a single, irreversible two-electron wave, whose half-wave potentials depended on the identity of the alcoholamine and its concentration (Table 1). Except in the case of the NNMEA, the electrochemical reduction of Ni(II) under the influence of the alcoholamine took place at smaller overpotential than the aquo-ion. The observed relationship $\lg i \propto h^{1/2}$, and the temperature coefficients of limiting currents of the four complexes (all about 2% $^\circ\text{C}^{-1}$) show that the limiting currents of the polarograms obtained were diffusion controlled.

Table 1. — Electrochemical characteristics of Ni(II)-alcoholamine systems^a.

ligand	[conc] (M)	$E_{1/2}$ (V)	α	$k (10^{-9} \text{ cm}^2 \text{ s}^{-1})^{b,c}$	$E_a (\text{KJmol}^{-1})$
MEA	0.022 – 1.11	-0.81 – -0.99	0.76	0.17	78
NMEA	0.048 – 1.72	-0.91 – -1.06	0.62	0.36	99
EMEA	0.098 – 1.91	-0.88 – -1.05	0.50	7.34	111
NNMEA	0.310 – 1.87	-1.18 – -1.22	0.40	0.12	107

a) For the reduction of the $\text{Ni}(\text{H}_2\text{O})_x$: $E_{1/2} = -1.16\text{V}$; $\alpha = 0.40$; $E_a = 200$

b) [MEA] = 0.19; [NMEA] = 0.23; [EMEA] = 0.25; [NNMEA] = 0.30

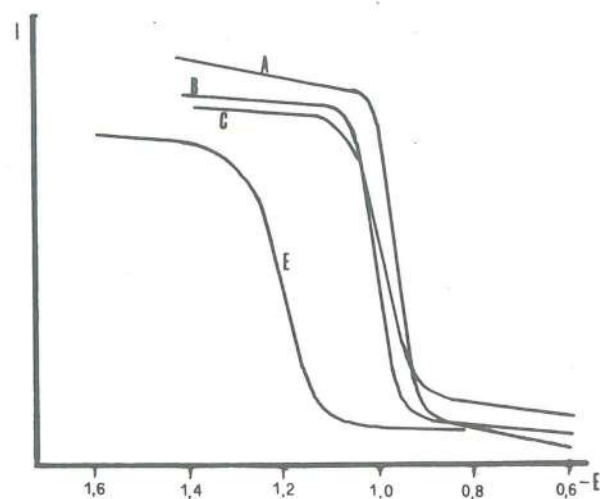
c) Determined at $E' = -0.62\text{V}$, the formal potential of $\text{Ni}(\text{H}_2\text{O})_x/\text{Ni}(\text{Hg})$ (7)

The diffusion coefficients of the complexes, calculated from the observed limiting currents using Ilkovic's equation, were only slightly affected by the concentration of the ligand. The mean

diffusion coefficient increased slightly with ligand concentration at low values, reached a maximum at about 0,5M, and fell gradually at higher concentrations of ligand. This finding agrees with the observed behaviour of Ni(II) complexes with other ligands of similar nature (2,4).

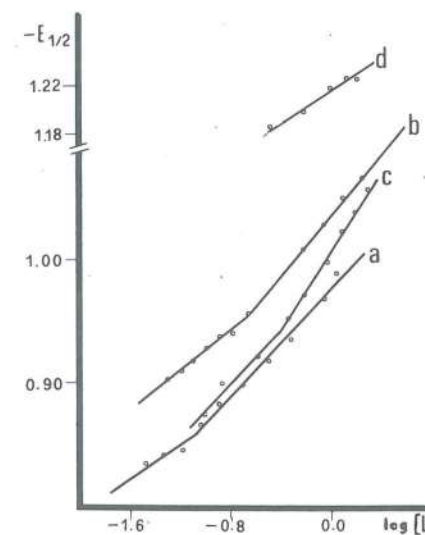
In all cases, logarithmic analysis of the polarograms (Fig 1), yielded straight lines whose slopes depended on the identity of the alcoholamine but not on its concentration or temperature. For each of the alcoholamines studied, the value of α , and hence the electrochemical step of the electrode reaction, is therefore the same throughout the ranges of concentration and temperature investigated. The mean values of α , calculated as described in Experimental Section, are listed in Table 1.

Fig. 1- Polarographic curves for the reduction of nickel-alcoholamine complexes: a) MEA; b) NMEA; c) EMEA; d) NNMEA



For a given concentration of alcoholamine, the rate constants of the electrode reactions of the complexes studied follow the order NNMEA < MEA < NMEA < EMEA (Table 1). In general, the rate constant increases with decreasing concentration of alcoholamine and with rising temperature, a phenomenon related to the effect of these two variables on the half-wave potential.

Fig. 2- Plot of $E_{1/2}$ vs $\log [L]$ of complexing agents: a) MEA; b) NMEA; c) EMEA; d) NNMEA.



The variation of half-wave potentials with temperature allows the activation energies, E_a , to be calculated using the equation:

$$\alpha n f (E_{1/2} - E') / 2,303RT = \log A^* - (E_a - 1/2 Q_d) / 2,303RT$$

where Q_d is the activation energy of diffusion (which is obtained from the temperature dependence of the limiting currents), E' is the potential for which activation energies are calculated and A^* comprises all terms that are independent of temperature. The mean activation energies, calculated at the same potentials as the rate constants, are listed in Table 1. They show that the influence of the temperature on the rate of the electro-reduction increases as stability of the complexes decrease (13), a phenomenon which has already been reported for similar systems (3).

For all the systems studied, increasing the concentration of alcoholamine caused the half-wave potential to shift to more negative values, showing that in the range of the concentrations investigated the increase in concentration of reducible complexes was outweighed by the greater degree of complexation in the solution. This dependence of the half-wave potential on concentration may be used to determine which species are directly involved in the electrode reaction. The relationship between half-wave potential, the concentration of ligand, the transfer coefficient and the stoichiometric indexes of the predominant species in solution (N) and the species actually reduced at the electrode (k) is given by the equation (14,15)

$$d(E_{1/2}/d(\log[L])) = -(N-k) \frac{2,303RT}{nF}$$

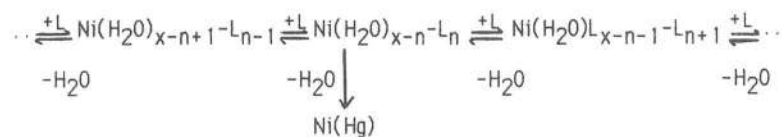
Plotting $E_{1/2}$ against $\log[L]$ for the Ni(II)-alcoholamine systems studied yields a graph consisting of a single straight line in the

case of NNMEA and two straight segments in the cases of MEA, NMEA and EMEA (Fig 2). The values of the slopes of these lines, together with the stoichiometric indexes of the predominant complexes in solution (determined by potentiometric titrations in the same conditions of the polarographic experiences using Bjerrum and Refn method (12)), imply that the directly reducible species is $Ni(H_2O)_{x-2}L_2$ in the case of MEA, $Ni(H_2O)_{x-1}L$ for NMEA and EMEA and $Ni(H_2O)_x$ for NNMEA (Table 2). The latter conclusion fully agrees with that suggested by comparison of the half-wave potentials and the values of α obtained for $Ni(H_2O)_{x-1}NMEA$ and those obtained for Ni(II) in media containing no complexing agent (7).

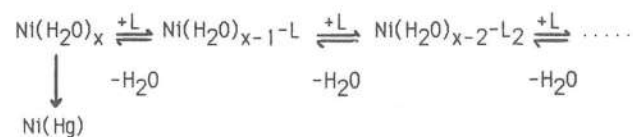
Table 2 - Dependence of N and k values on concentration of complexing agents.

Ligand	Conc (M)	N-k	N	k
MEA	1.11 - 0.089	2.7	4.9	2
	0.067 - 0.022	1.8	3.7	2
NMEA	1.72 - 0.16	2.6	3.9	1
	0.13 - 0.048	1.7	2.8	1
EMEA	1.91 - 0.64	2.6	3.6	1
	0.45 - 0.098	1.9	3.0	1
NNMEA	1.87 - 0.31	1.0	1.0	0

The above results suggest that the mechanism of the polarographic reduction of Ni(II) in aqueous alcoholamine solution is



for L = MEA (n=2) and L = NMEA or EMEA (n=1), and



for L = NNMEA

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