

ist somit einerseits für Industriebetriebe von Bedeutung, die auf die Wirkung der Amylasen angewiesen sind, und es kann andererseits prophylaktisch genutzt werden, um Schädigungen biologischer Systeme zu verhindern.

Literatur

1. Englard, S., Sorof, S., Singer, T. P.: J. Biol. Chem. **189**, 217 (1951).
2. Geike, F.: J. Chromatog. **44**, 95 (1969).

Dr. F. Geike
Biologische Bundesanstalt für Land- und Forstwirtschaft
Institut für Pflanzenschutzmittelforschung
D-1000 Berlin-Dahlem
Königin Luise-Straße 15–19
Deutschland

Effect of Chloride, Nitrate, Sulphate, and Acetate in the Polarography of Nickel(II)

Über den Einfluß von Chlorid, Nitrat, Sulfat und Acetat bei der Polarographie von Nickel(II)

P. S. JAIN

J. K. Synthetic Works, Kota, Rajasthan, India

S. LAL

Chemistry Department, University of Kentucky,
Lexington, Ky. 40506, U.S.A.

Received July 10, 1971

Polarographic behaviour of nickel(II) has been amply studied in complexing and non-complexing media. However, no comparative study has been made in ascertaining the role of the anions of the depolarizer in governing the magnitudes of diffusion current (i_d), half-wave potentials ($E_{1/2}$) and diffusion coefficients (D) of different nickel salts in 0.2 M KNO_3 as the base electrolyte.

Experimental. Depolarizers $NiCl_2 \cdot 6 H_2O$, $NiSO_4 \cdot 7 H_2O$, $Ni(NO_3)_2 \cdot 6 H_2O$, $Ni(CH_3COO)_2 \cdot 4 H_2O$ were of E. Merck (G.R.) and their solutions were prepared in conductivity water. These solutions were standardized with EDTA titrations. Potassium nitrate was a B.D.H. AnalaR product. The polarization curves were recorded on a Sargent Polarographic Model XXI using a d.m.e. with the capillary characteristics $mt^{2/3+1/6} = 2.63 \text{ mg}^{2/3} \text{ sec}^{-1/2}$. Deaeration was done by purging Linde's prepurified nitrogen. Pure triple distilled mercury was used for the d.m.e. The diffusion coefficients were determined by the method of McBain and Dawson [2].

Results and Discussion. Nickel(II) in 0.2 M KNO_3 is irreversibly reduced with $E_{1/2} = -1.01 \text{ V}$ vs. SCE in case of each depolarizer salt. The reduction appeared to be the most irreversible for nickel

Table

Polarography of $5 \times 10^{-4} \text{ M Ni(II) Salts}$ in 0.2 M KNO_3

Salt	$i_d, \mu A$	$D \times 10^6 \text{ cm}^2/\text{sec}$	GK cal
$NiCl_2 \cdot 6 H_2O$	6.1	8.88	182.0
$NiSO_4 \cdot 7 H_2O$	5.9	6.68	176.4
$Ni(NO_3)_2 \cdot 6 H_2O$	5.6	5.58	153.4
$Ni(CH_3COO)_2 \cdot 4 H_2O$	4.9	5.46	148.1

chloride and the least for nickel acetate which is evidenced by ΔG values (calculated by Delahay's treatment and Eyring's equation) [1]. The results are given in the Table.

It is apparent from the Table that diffusion current is the greatest for nickel chloride and the least for nickel acetate. The magnitude of the diffusion current is governed by effective diffusion coefficient (D) of the depolarizer ion, any specific adsorption of anions or cations, capillary characteristics and viscosity of the medium. Measurements were made each time in the same medium with identical capillary parameters. Hence, the latter two factors seem to be inoperative in this case. The electrocapillary studies yield the gradation of interfacial tension in the manner

$$\gamma_{NO_3^-} > \gamma_{SO_4^{2-}} > \gamma_{Ac^-} > \gamma_{Cl^-}$$

which implies Cl^- is the most adsorbed species (interfacial tension least). However, at far negative potentials $\sim -1.2 \text{ V}$, the cathodic parts of the electrocapillary curve in all the nickel salts are almost coincident with one another. This shows that specific adsorption may not contribute significantly in controlling i_d values at the nickel plateau. Thus, the diffusion currents seem to be controlled by effective diffusion coefficients of nickel ions in the various salts employed. The diffusion coefficients are possibly subject to variance due to the relative competition of other anions with aquo-nickel complexes resulting in the replacement of water molecules from the hydration shell which can alter the ionic radius and consequently D of the depolarizer ion. The diffusion coefficient for nickel chloride is the maximum and the least for nickel acetate which corresponds to their behaviour in diffusion currents.

References

1. Delahay, P.: J. Am. Chem. Soc. **73**, 4944 (1951).
2. McBain, J. W., Dawson, C. R.: Proc. Roy. Soc. London **A 152**, 32 (1935).

Dr. S. LAL
Department of Chemistry
University of Kentucky
Lexington, Ky. 40506, U.S.A.