ACTA UNIVERSITATIS LODZIENSIS
FOLIA CHIMICA 7, 1987

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STUDY OF CHLORINE EVOLUTION ON THE Pt ELECTRODE IN NITROMETHANE SOLUTION

Electrochemical chlorination of non-saturated organic compounds in the aqueous and non-aqueous solvents depends on the mechanism of halogen formation. The mechanism of chloride ion discharge has been investigated in nitromethane on the rotating Pt disc electrode using $Ag/AgClO_4$ system in the galvanostatic measurement as the reference electrode.

For the quasi-equilibrium process the constant k_1 and the constant of electron K_2 transmission have been determined for the recombination process occuring at 0.1 V.

INTRODUCTION

The electrochemical halogenation of unsaturated organic substances, either in aqueous or in anhydrous media, has proved a good method for the formation of bifunctional substances. In these halogenations the halogen evolution plays a fundamental role, but nevertheless its mechanism is not yet clear in every respect. This fact is well illustrated by the disagreement which received publicity in [1]. Yokoyama and Enyo, who earlier [2] described a charge transfer-controlled mechanism, argued [1] that the limiting current character found by Conway et al. [3] is probably due to "an artefact involving interferences by surface oxidation and/or Cl^- ion adsorption". In reply, Conway gave further evidence [4] in support of the recombination-controlled mechanism in aqueous trifluoracetic acidic solutions. The adsorption of Cl^- and its effects on oxide film formation have also been discussed [5, 6]. General surveys concerning chlorine evolution are given in [7, 8]. As chloride ion discharge is the elementary step of chlorination processes in nitromethane (NM) solution [9-12], the aim of the present work was to obtain data on the reaction of chlorine evolution on a Pt electrode in this solvent.

EXPERIMENTAL

The experimental set-up and the methods of preparation of solution were the same as previously described [9]. As anode, a Pt disc of 0.66 cm^2 geometric area was used. The electrode was rotated at 580 rpm. An $Ag/AgClO_4$, Et_4NClO_4 electrode in the same solution was applied as reference. The current vs. potential curves were recorded with a multichannel digital memory scope (EMG 1500) and the data were transferred to a VDT-52 computer.

RESULTS AND DISCUSSION

Voltammetric curves for a rotating disc electrode above 600 mV in NM solution show a limiting current, which increases linearly with the square root of the rotation speed (Fig. 1), indicating that in this potential region mass transfer becomes rate-determining.

Data obtained by galvanostatic polarization reveal a similar limiting current behaviour (Fig. 2), indicating that in NM solution, at large overpotentials, mass transfer controls the overall reaction. In the range of small overpotentials, the experimental data were treated as in [3]. Chlorine evolution takes place in two steps:

$$Cl^- + Pt \rightleftharpoons Pt\text{-}Cl^{\cdot} + e^-$$

$$2\ Pt\text{-}Cl^{\cdot} \xrightarrow{k_2} 2\ Pt + Cl_2$$

The current can be related to recombination control:

$$i = 2\ F k_2\ \theta^2_{Cl^{\cdot}} \qquad (1)$$

while $\theta_{Cl^{\cdot}}$ is in quasi-equilibrium. Assuming Langmuir-type kinetics:

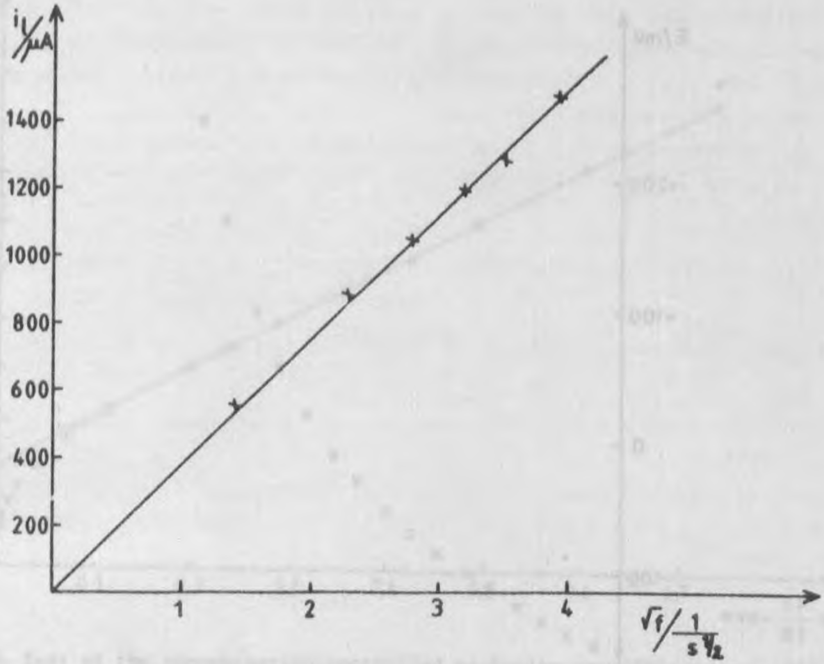

Fig. 1. Limiting currents of the voltammetric curves vs. square root of the rotation speed in 0.1 mol dm^{-3} Et_4NClO_4 and Et_4NCl solution of NM

$$\Theta_{Cl^\cdot} = \frac{K_1[Cl^-]\exp(\eta F/RT)}{1 + K_1[Cl^-]\exp(\eta F/RT)} \tag{2}$$

After substitution and transfromation:

$$i^{-1/2} = \frac{1}{(2Fk_2)^{1/2}} + \frac{\exp - (\eta F/RT)}{K_1[Cl^-](2Fk_2)^{1/2}} \tag{3}$$

As Fig. 3 shows, in the range $\eta \leqslant 0.1$ V the recombination-controlled mechanism is confirmed.

From the slope and intercept, the equilibrium constant for the charge transfer (K_1) and the rate constant of the recombination reaction (k_2) can be determined.

These measurements were carried out in the temperature range 25-65°C and the recombination-controlled mechanism proved to be

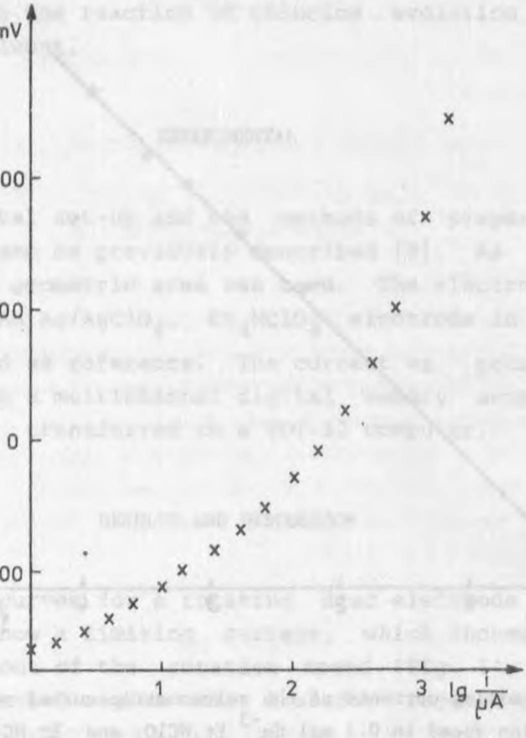

Fig. 2. Tafel plot of potential-current data measured galvanostatically in NM solution at concentration of 0.1 mol dm^{-3} for Et_4NCl

valid up to 45°C. Starting from 50°C, the shape of the curves is modified, due presumably to a change in the mechanism. K_1 and k_2 data are listed in Tab. 1.

Table 1

Quasi-equilibrium constants for the charge transfer and rate constants of the recombination step determined according to eqn. (3) at different temperatures

T/K	K_1/mol^{-1}dm^3	$k_2 \cdot 10^{10}$/mol s^{-1}cm^{-2}
298	2.2	1.67
303	1.5	2.88
308	1.4	4.85
313	1.2	7.27
318	1.2	9.24

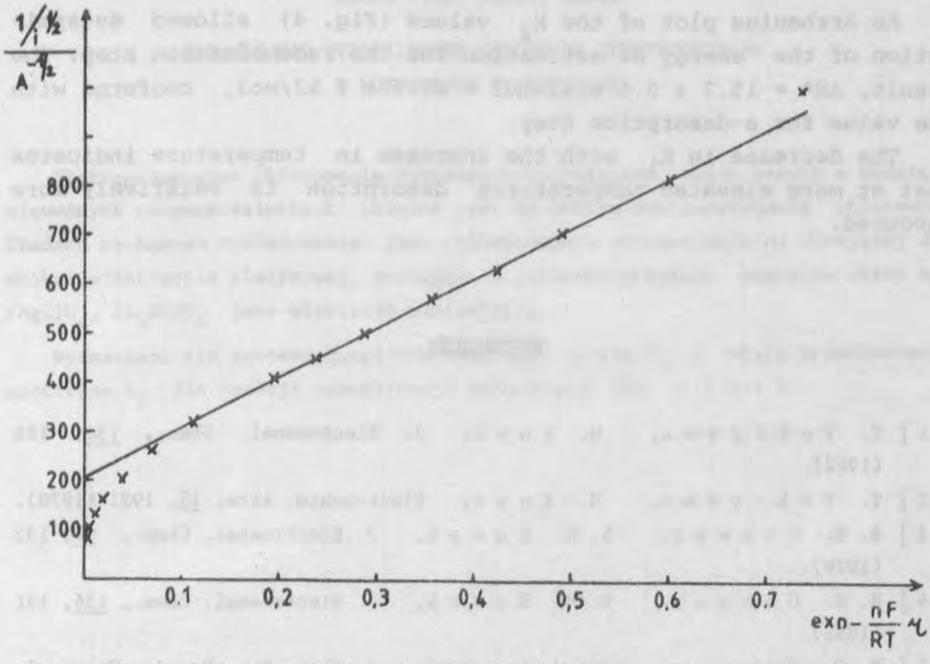

Fig. 3. Test of the recombination-controlled mechanism according to eqn. (3) from the galvanostatic measurements

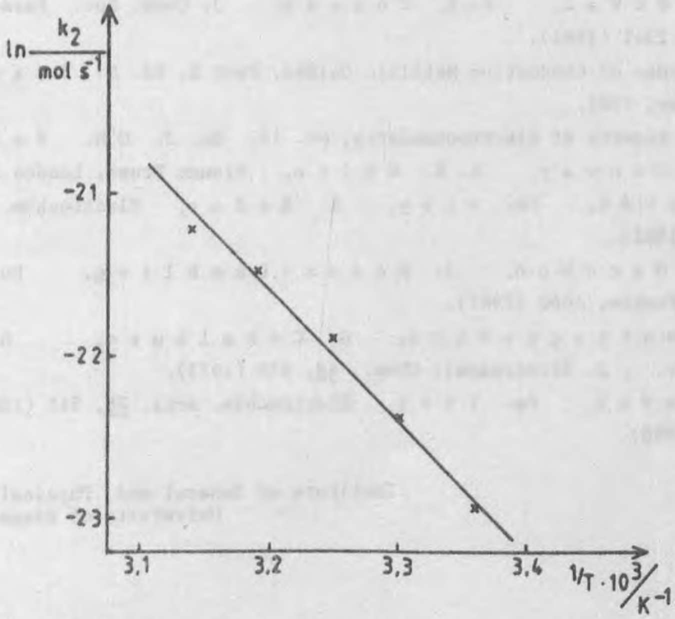

Fig. 4. Arrhenius plot of the rate constant of the recombination step

An Arrhenius plot of the k_2 values (Fig. 4) allowed determination of the energy of activation for the recombination step. The result, $\Delta H^* = 15.7 \pm 0.5$ kcal/mol = 65.8 ± 2 kJ/mol, conforms with the value for a desorption step.

The decrease in K_1 with the increase in temperature indicates that at more elevated temperatures desorption is relatively more favoured.

REFERENCES

[1] T. Yokoyama, M. Enyo, J. Electroanal. Chem., 136, 185 (1982).

[2] T. Yokoyama, M. Enyo, Electrochim. Acta, 15, 1921 (1970).

[3] B. E. Conway, D. M. Novak, J. Electroanal. Chem., 99, 133 (1979).

[4] B. E. Conway, D. M. Novak, J. Electroanal. Chem., 136, 191 (1982).

[5] B. E. Conway, J. Mozota, J. Chem. Soc. Faraday Trans. I, 78, 1717 (1982).

[6] D. M. Novak, B. E. Conway, J. Chem. Soc. Faraday Trans. I, 77, 2341 (1981).

[7] Electrodes of Conductive Metallic Oxides, Part B, Ed. S. Trasatti, Elsevier, 1981.

[8] Modern Aspects of Electrochemistry, No. 14, Ed. J. O'M. Bockris, B. E. Conway, R. E. White, Plenum Press, London 1982.

[9] M. Novák, Cs. Visy, K. Bodor, Electrochim. Acta, 27, 1293 (1982).

[10] J. C. Marchon, J. Badoz-Lambling, Bull. Soc. Chim. France, 4660 (1967).

[11] M. Mastragostino, G. Casalbore, S. Valcher, J. Electroanal. Chem., 48, 419 (1973).

[12] M. Novák, Cs. Visy, Electrochim. Acta, 28, 511 (1983); 28, 507 (1983).

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BADANIA NAD WYDZIELANIEM CHLORU NA ELEKTRODZIE Pt W ROZTWORACH NITROMETANU

Elektrochemiczne chlorowanie nienasyconych połączeń organicznych w wodzie i niewodnych rozpuszczalnikach zależne jest od mechanizmu powstawania chlorowca. Zbadano mechanizm rozładowania jonu chlorkowego w nitrometanie na wirującej dyskowej elektrodzie platynowej, stosując w galwanostatycznym pomiarze układ Ag/ /$AgClO_4$, Et_4NClO_4 jako elektrodę odniesienia.

Wyznaczano dla procesu quasi-równowagowego stałą K_1 i stałą przeniesienia elektronu k_2 dla reakcji rekombinacji zachodzącej dla $\eta \leqslant 0.1$ V.