

POTENTIAL DEPENDENCE OF THE RATE OF ANODIC OXIDATION OF PRIMARY ALCOHOLS

By

M. NOVÁK, J. LANTOS and F. MÁRTA

Institute of General and Physical Chemistry, Attila József University, Szeged

(Received July 4, 1972)

Taking into account the inhibiting effect of the adsorbed material and the change of its amount with the potential, the current value proves to be independent of the potential at constant coverage in the anodic oxidation of primary alcohols. The process is controlled by a non-electrochemical step.

Introduction

In the investigation of anodic oxidation of alcohols one of the basic problems is the change of the reaction rate with the potential. The data available in literature do not give definite answer in this respect. According to RIGHTMIRE *et al.* [1], the process of ethanol oxidation is controlled by charge transfer in the 0.55—0.75 V region, and acetaldehyde was found to be the primary and main product. BAGOTZKY'S results [2] show that a non-electrochemical step controls the oxidation. Taking into account that the adsorbed material inhibits the process of oxidation and its amount is changing with the potential, it is not clear how the rate of the alcohol oxidation is affected by the change of potential.

In order to study these processes, experiments have been carried out with primary alcohols in acidic solutions.

Experimental

The experimental equipment and the method were the same as described before [3]. The base solution was 1 N H₂SO₄, the concentration of alcohol was 0.1 M/l and the electrode of 1.6 cm² real surface area was rotated with 1000 r.p.m. The potential values are given for the hydrogen electrode in the same solution and the current for the whole electrode surface.

Results

As it can be seen from Fig. 1, the current values measured in ethanol solution at the same time of electrolysis at different potential values increase with the potential, showing an apparent potential effect. Ethanol, propanol and butanol show similar behaviour.

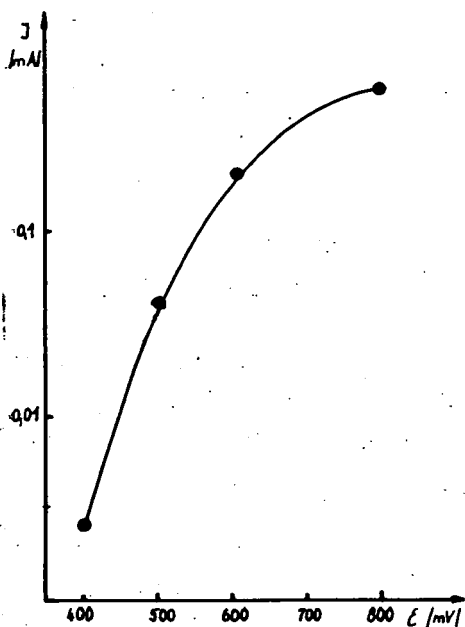


Fig. 1. Current-potential relationship in 0.1 M/l ethanol solution. Base solution is 1 N H_2SO_4 .

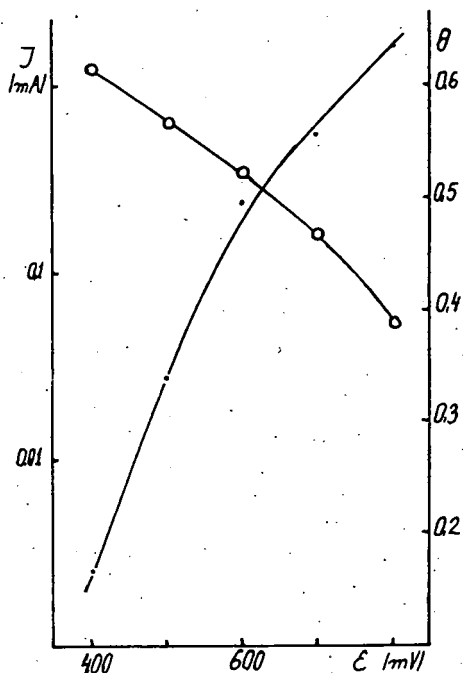


Fig. 2. Change in current and in coverage with the potential in 0.1 M/l *n*-butanol solution at $t=500$ s.

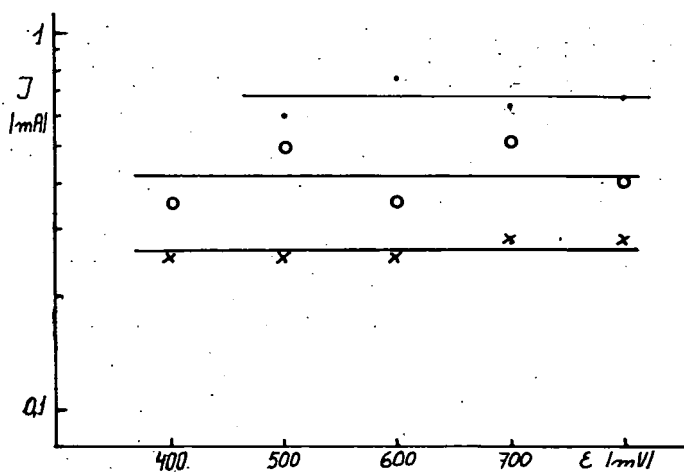


Fig. 3. Current-potential relationship at $\theta=0.2$ for ethanol (●) *n*-propanol (o) and *n*-butanol (x).

As shown in Fig. 2, the surface coverage of the electrode changes with the potential, therefore, in determining the relationship between the current and electrode potential this has to be taken into account. Considering that the adsorbate inhibits the reaction [4], the change in coverage causes changes in the inhibition, therefore the dependence of the reaction rate on the potential should be considered at constant inhibition effect.

Accordingly, in Fig. 3 the current values are plotted against the electrode potential at $\Theta=0.2$ coverage for ethanol, propanol and butanol. It turns out, that the reaction rate does not change with the electrode potential, thus the assumption based on the overall character of the reaction in [1] becomes questionable. This independence can be found not only at the value $\Theta=0.2$ but also at different coverages, too, as it is shown in the case of ethanol in Fig. 4. On the basis of these experimental results it is to be accepted that the alcohol oxidation *i.e.* aldehyde formation [4] is controlled by a chemical step and the increase in current with the potential is due to the decrease in the inhibition.

In order to specify this rate limiting chemical step, one might assume that if the desorption of the product would be the slow step, the coverage should increase with the potential and the rate would be proportional to the coverage. This is not proved by experimental results. In the case of a rate-controlling process taking place between the charge transfer steps, the character would be similar to the previous one. The change of the current with the potential would result from the increase of the coverage by the intermediate, thus this assumption has to be rejected, too.

The adsorption of the reacting molecule as a rate determining step makes it possible to interpret the negligible amount of the reaction intermediate on the surface and the inhibiting nature of the adsorbate, since the fast steps, following the rate-determining step, produce the aldehyde, which leaves the surface. This product might be adsorbed again.

Further examination of the reaction is in progress.

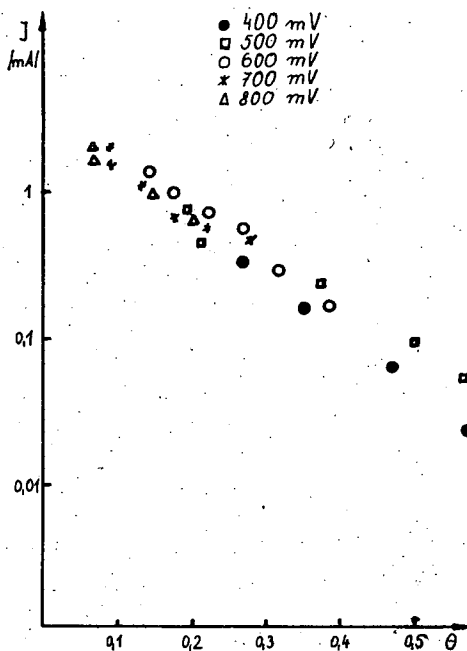


Fig. 4. Current-coverage relationship for ethanol at different potential values.

References

- [1] *Rightmire, R. A., R. L. Rowland, D. L. Boos, D. L. Beals*: J. Electrochem. Soc. **111**, 242 (1964).
- [2] *Bagotzky, V. S., Yu. B. Vassilyev, I. I. Pyshnograeva*: Electrochim. Acta, **16**, 2141 (1971).
- [3] *Novák, M., J. Lantos, F. Márta*: Acta Phys. et Chem. Szeged **18**, 147 (1972).
- [4] *Novák, M., J. Lantos, F. Márta*: Acta Phys. et Chem. Szeged **18**, 151 (1972).

СКОРОСТЬ АНОДНОГО ОКИСЛЕНИЯ ПЕРВИЧНЫХ СПИРТОВ
В ЗАВИСИМОСТИ ОТ ПОТЕНЦИАЛА

М. Новак, Й. Лантош и Ф. Марта

При анодном окислении сила тока не зависит от величины потенциала при постоянных значениях θ . Определяющим фактором процесса являются не электрохимические изменения.