

# COMPARATIVE STUDY OF ADSORPTION AND KINETIC BEHAVIOUR OF $\omega$ -AMINOPROPANOL, $\omega$ -CHLOROPROPANOL AND $n$ -PROPANOL ON A Pt ANODE

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A comparison was made of the adsorption and kinetic behaviour of  $n$ -propanol,  $\omega$ -chloropropanol and  $\omega$ -aminopropanol. The differences observed are interpreted by considering a sorbate more oxidized at  $E=0.4$  V than the one sorbed in  $n$ -propanol solution.

Although the anodic oxidation of various alcohols has been investigated rather extensively, much less attention has been paid to the electrochemical behaviour of their substitution derivatives, *i.e.* halo- and aminoalcohols. The substitution considerably affects the polarization of the parent molecule and thus it might be expected that the electrochemical behaviour will be altered as well. In the case of aminoalcohols the change in the properties is important, because this type of compound might be a source of the electrochemical preparation of aminoacids [1, 2]. So far only few works have been published regarding the investigation of these processes.

In the present paper a comparison is made of the sorption and reaction properties of  $n$ -propanol,  $\omega$ -chloropropanol and  $\omega$ -aminopropanol.

## *Experimental*

The experimental set-up was essentially the same as in [3]. The chemicals used were of reagent purity and were redistilled in a reduced nitrogen atmosphere. Their purities were checked by gas-chromatography. The base solution was prepared from  $\text{HClO}_4$  of Suprapur grade and triply distilled water, combined with pyro-distillation [4]. As reference, a hydrogen electrode was used in the same solution. The working electrode was a bright Pt disc with  $3.4 \text{ cm}^2$  real surface area, rotated at 1000 rpm. The coverage by the strongly bound organic species was determined *via* cathodic potential impulses at  $20 \text{ V s}^{-1}$ .

## *Results and discussion*

The current observable in the solution of  $\omega$ -aminopropanol changes with time similarly as in the case of  $n$ -propanol and  $\omega$ -chloropropanol [5], as a result of the inhibiting effect of the accumulation of strongly bound species (Fig. 1). The change

in coverage at  $E=0.4$  V is shown in Fig. 2. The rate of sorption can be seen to decrease in the sequence *n*-propanol,  $\omega$ -chloropropanol,  $\omega$ -aminopropanol. The rate of oxidation of  $\omega$ -aminopropanol proved to be slightly dependent on the potential between 0.4 and 0.75 V (Fig. 3), if the rates are compared at the same coverage. The extent of sorption decreases with the potential (Fig. 4.).

The charge required to oxidize the sorbed species (determined by means of anodic potential impulses at  $20 \text{ V s}^{-1}$ ) reveals that the composition of the sorbed species does not change with the extent of adsorption at  $E=0.4$  V (Fig. 5).

The substitution affects not only the rate of sorption but also the rate of reaction. As may be seen on Fig. 6, at  $E=0.4$  V the oxidation of *n*-propanol takes place with a much higher rate than those of  $\omega$ -aminopropanol and  $\omega$ -chloropropanol, there being practically no difference between the rates for these latter compounds. The features observed might suggest the possibility that with the substitution the reactivity of the alcohol is altered. On the other hand, it might be assumed that, due to the presence of the substituent, it becomes more difficult for the molecule to reach the surface. The latter assumption seems to be in contradiction with the observation that the difference in currents for the substances studied appears even at the small coverage values.

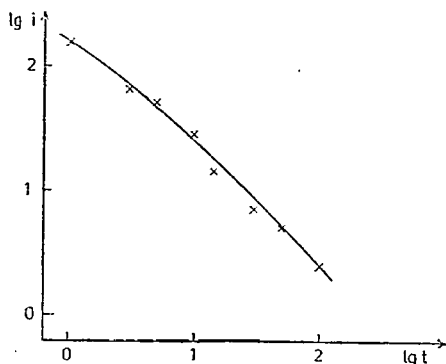


Fig. 1. Current vs. time of adsorption curve taken in  $0.03 \text{ mol dm}^{-3}$   $\omega$ -aminopropanol solution in  $1 \text{ mol dm}^{-3}$   $\text{HClO}_4$  at  $E = 0.4$  V

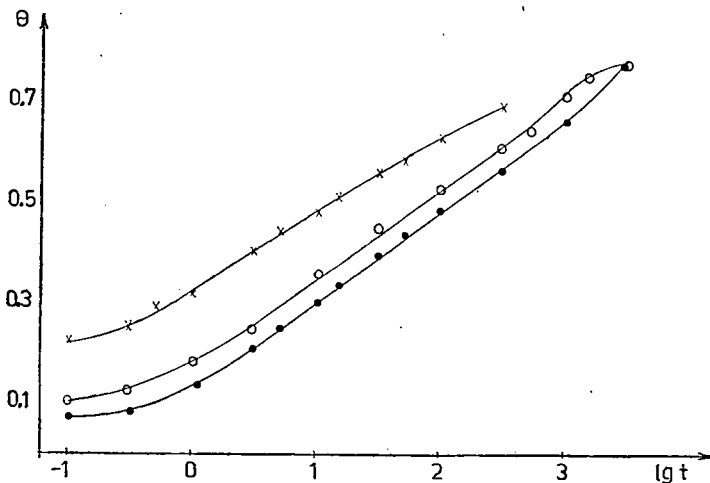


Fig. 2. The increase of sorption in time in a  $0.03 \text{ mol dm}^{-3}$  solution of x — *n*-propanol; o —  $\omega$ -chloropropanol; • —  $\omega$ -aminopropanol

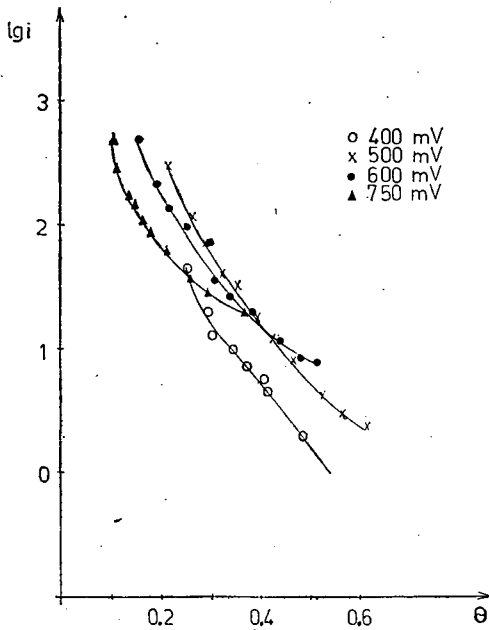


Fig. 3. Current vs. coverage relationships in  $0.1 \text{ mol dm}^{-3}$   $\omega$ -aminopropanol solution at different potentials: o — 0.4 V; x — 0.5 V; ● — 0.6 V; ▲ — 0.75 V

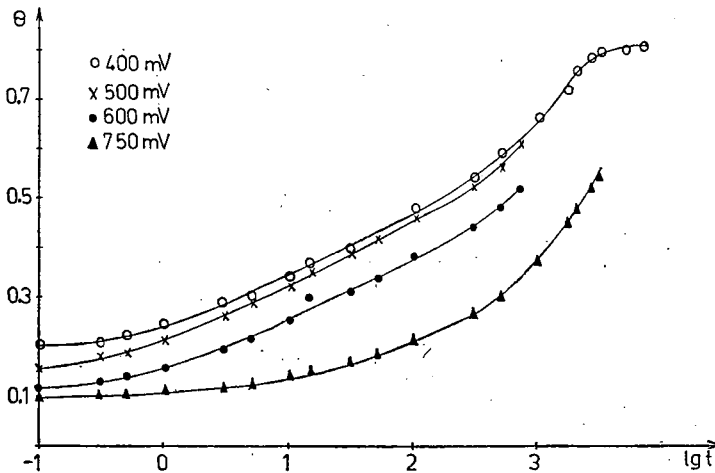


Fig. 4. Coverage values as a function of the time of adsorption in  $0.1 \text{ mol dm}^{-3}$   $\omega$ -aminopropanol solution at different potentials: o — 0.4 V; x — 0.5 V; ● — 0.6 V; ▲ — 0.75 V

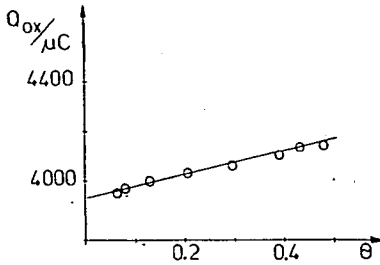


Fig. 5. The charge required to oxidize the sorbate at  $E= 0.4$  V as a function of the coverage

As further possibility, it may be taken into account that the composition of the sorbed species seems to be different. This can be concluded from the charge necessary to oxidize the species sorbed at  $E=0.4$  V, which is 1 electron/adsorption centre for *n*-propanol [6] and 0.5 electron/adsorption centre for  $\omega$ -aminopropanol (Fig. 5). Therefore it may be concluded that the sorbed species are in a state of higher oxidation in the latter case, resulting in a more profound inhibiting effect, similarly to the case of  $\omega$ -chloropropanol as well [5]. This conclusion appears to be supported by the observation obtained in the following experiment. If the species adsorbed at 0.4 V are oxidized by switching the potential to 0.75 V, the change in coverage and the current observed may be characterized according to Fig. 7. Thus, in the case of *n*-propanol an oxidative-desorption occurs in the first period of time following the change in potential, without considerable change in the current, whereas with  $\omega$ -aminopropanol there is no decrease in the amount of the sorbed species, only the current dropping.

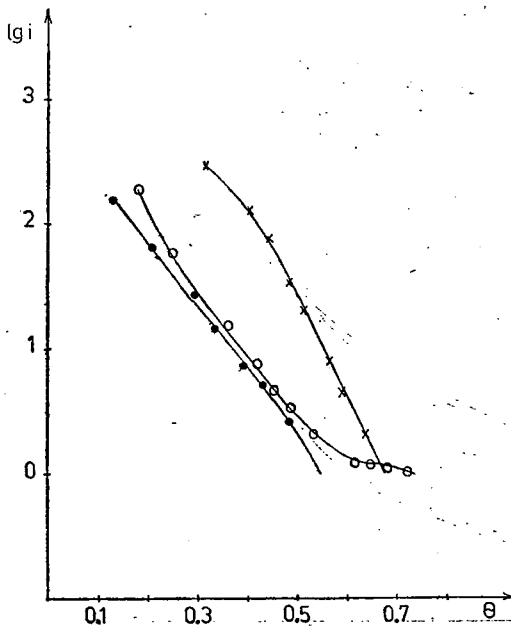


Fig. 6. Current vs. coverage relationships in a  $0.03 \text{ mol dm}^{-3}$  solution of x — *n*-propanol: o —  $\omega$ -chloropropanol; ● —  $\omega$ -aminopropanol

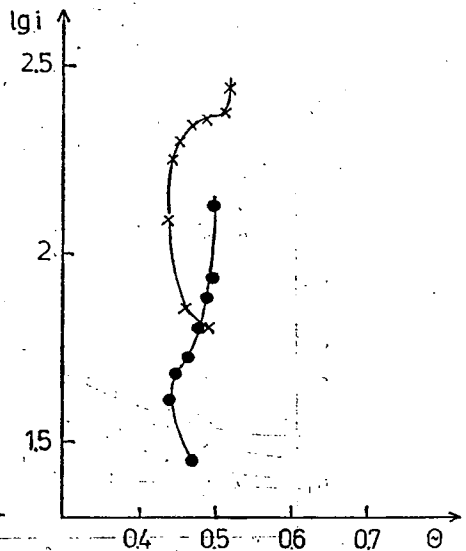


Fig. 7. Changes in current and coverage following switching of the potential from 0.4 to 0.75 V. x — *n*-propanol,  $\theta_{0.4} = 0.54$ ; ● —  $\omega$ -aminopropanol,  $\theta_{0.4} = 0.59$

On the basis of these observations it might be concluded that the substitution increases the inhibiting effect by promoting the formation of a more oxidized state of the strongly sorbed species.

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#### СРАВНИТЕЛЬНОЕ ИЗУЧЕНИЕ АДсорбЦИОННЫХ И КИНЕТИЧЕСКИХ СВОЙСТВ $\omega$ -АМИНО-, $\omega$ -ХЛОРО-, И Н-ПРОПАНОЛА

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Проведено сравнение адсорбционных и кинетических свойств н-пропанола,  $\omega$ -хлоропропанола и  $\omega$ -аминопропанола. Различия объяснены при предположении более окисленного сорбата чем при  $E=0,4$  V окисленной в среде н-пропанола.