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THE INVESTIGATION OF ELECTROCHEMICAL BEHAVIOUR OF GOLD ELECTRODE IN ORGANIC ACIDS THE EFFECT OF THE NUMBER OF COOH GROUPS

SEMRA BİLGİÇ and MELİKE KABASAKALOĞLU

Department of Chemistry, Faculty of Science University of Ankara, Turkey

SUMMARY

In this study the electrochemical behaviour of gold electrode in 0,5 M acetic, succinic and citric acid solutions was investigated by the help of current-potential curves. It was observed that the potentials where the anodic current starts to flow shifted towards more positive values and the average thickness of the oxide layer (L) grew as a number of COOH group in the acid was increased. The oxide coverage ratio θ_{ox} increased and the organic coverage ratio θ_{org} decreased as the medium was changed from 0,5 M acetic acid to 0,5 M citric acid.

INTRODUCTION

Gold possesses the widest double layer region among the noble metals. This region covers 0,4–0,8 V in Pt, 0,3–0,5 V in Rh and 0,2–0,8 V in gold. That is why gold is the most suitable metal to investigate most of organic reactions and synthesis organic compounds.

The main purpose of this study was to investigate the number of COOH groups upon the current-potential curves of gold electrode by using mono, di and tri carboxylic acids.

EXPERIMENTAL

All the current-potential curves were recorded by using Tacussel PRT 10–05 potentiostat and Tacussel EPL–2 recorder at a constant potential scanning rate of 50 mV s^{-1}. Measurements were carried out in a three armed pyrex cell. The counter (Pt), the working and the reference electrodes were dipped into the first, second and third arms respectively.

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The stopcock between the counter and the working electrode compartment was kept close during the experiments. The reference and the working electrode compartments were separated from each other by a luggin capillary and a stopcock.

The working electrode was a gold wire (dia 0,5 mm approximate length 3 cm., purity 99,999 %) obtained from Johnson Matthey Ltd. Before each measurement it was potentiostatted for seven minutes at 1650 mV in 0,5 M H_2SO_4. Then it was reduced for seven minutes at 300 mV under a flow of purified nitrogen. As a reference electrode saturated calomel electrode was used and all the potentials given in this work are reported relative to the hydrogen electrode. Solutions were prepared by double distilled water and all the chemicals were chemically pure. Nitrogen was bubbled through the solution for 20 minutes before and throughout the experiment.

RESULTS AND DISCUSSION

1. The i–E curves of gold in various acids

The current-potential curves of gold obtained in 0,5 M acetic, succinic and citric acids were plotted in Fig 1. As it is clearly seen in the figure the potentials where the anodic current begins to flow shifted towards more positive values as a number of COOH groups in the acid increased (i.e. as the medium was changed from acetic to citric acid). Figure 2 shows the characteristic curve of gold in 0,5 M H_2SO_4. The potential at which the anodic current starts to flow in this medium is 1390 mV. The oxygen evolution takes place above 1900 mV (Bilgiç and Kabasakaloğlu, 1981). The oxide film starts to form from 1390 mV in 0,5 M acetic acid while this value is 1410 mV in 0,5 M succinic acid. The difference in these potentials corresponds the difference in pH. The pH's measured in 0,5 M acetic and 0,5 M succinic acids are 2,20 (Bilgiç, 1983) and 1,85 respectively. (The potentials shift 59–60 mV per unit pH). But the situation in citric acid is different. Figure 3 shows the i–E curves obtained for 0,5 M H_2SO_4 and 0,5 M citric acid. According to the difference in their pH values the current in citric acid expected to pass 80–90 mV more negative than that of H_2SO_4. But the oxide formation in citric acid medium starts at 1470 mV. This shows that there is something which retards the formation of film (Bilgiç and Kabasakaloğlu, 1981). This is thought to be the adsorption of citric acid or citrate anion. The pH of 0,5 M citric acid is 1,45. The acidity

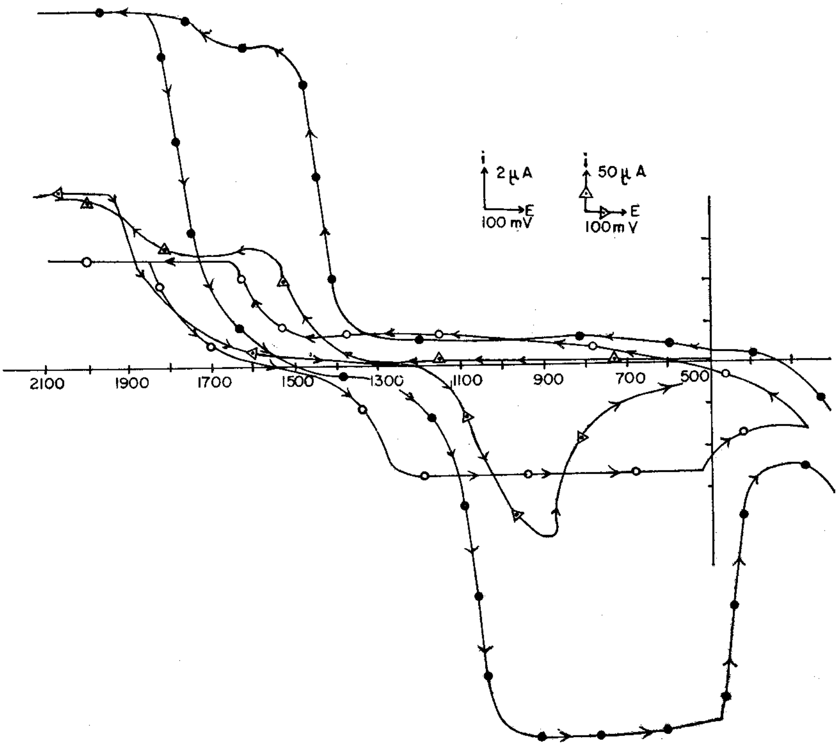


Figure 1. The i–E curves of gold obtained in 0,5 M acetic, succinic and citric acide.
(O) Acetic acid; (●) Succinic acid; (△) Citric acid

constant shows that there can only be $[H_2Cit]^-$ anions present at this pH (Barradas, Donaldson and Shoesmith, 1973).

The potentials where reduction currents flow in the cathodic region corresponds the differences in pH values. The adsorption of citric acid does not vary the reduction potential, but the shapes of the curves are different. For instance, the sharp cathodic peak obtained in 0,5 M H_2SO_4 becomes flattened to form a plateau whose height increases as the E_λ potential is raised in acetic, succinic and citric acids Fig 1.

2. The change of $\frac{Q_a}{Q_c}$ of gold with E_λ

The change of $\frac{Q_a}{Q_c}$ found from the i–E curves obtained in 0,5 M acetic, succinic and citric acids with reversal potential E_λ is shown

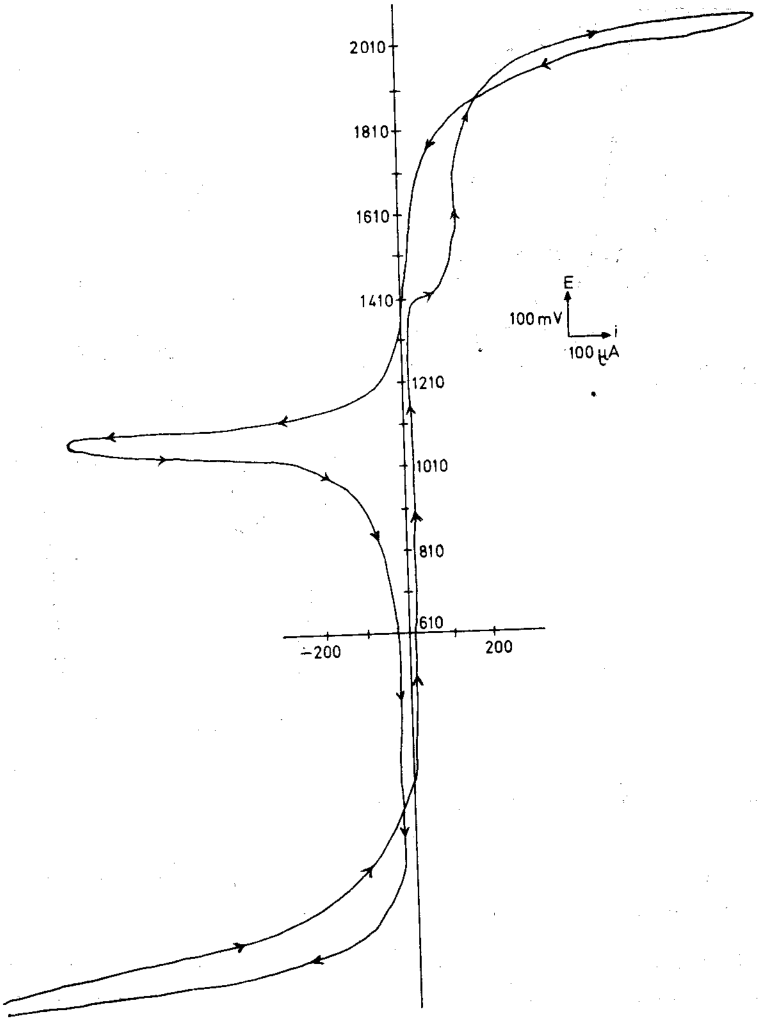


Figure 2. The characteristics i–E curve of gold in 0,5 M H_2SO_4.

in Fig 4. The value obtained in 0,5 M H_2SO_4 is also given on the same plot for the comparative purposes. The value of $\frac{Q_a}{Q_c} \cong 1$ in 0,5 M H_2SO_4 while it is greater than unity in other acids. The fact that the charge in anodic region is higher than the charge in cathodic region can be explained in two ways. Either the metal dissolves or there occurs a partial charge transfer during the adsorption of organic acid.

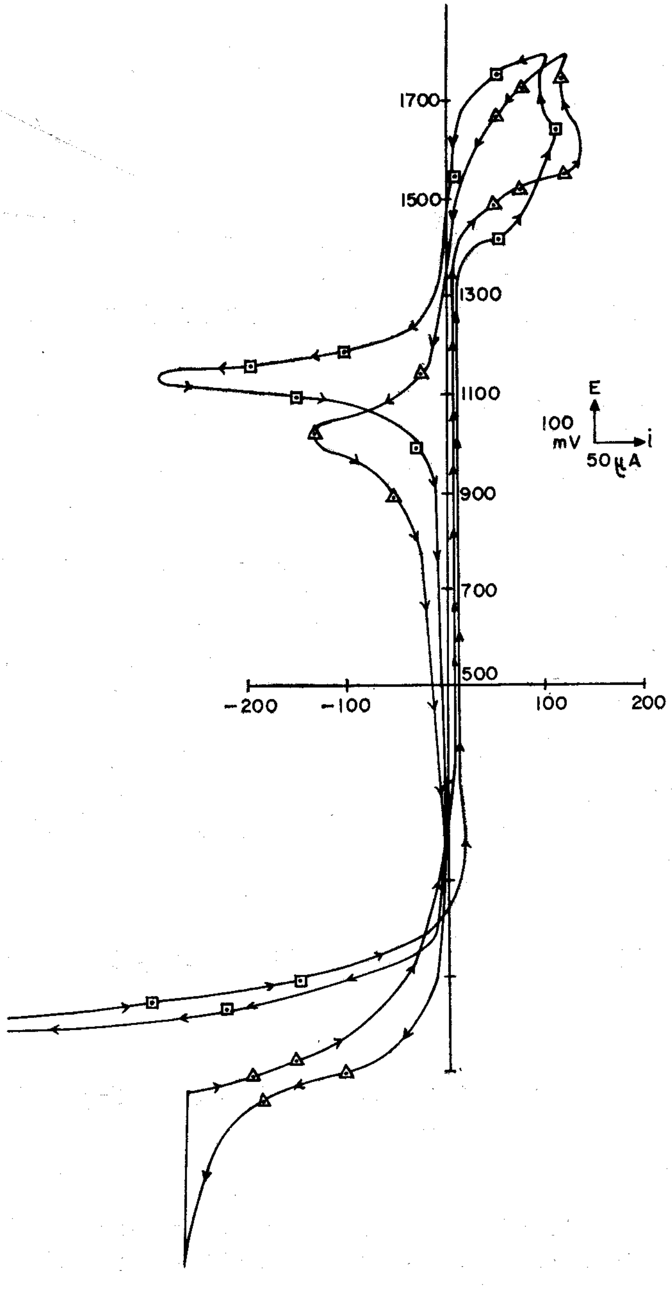


Figure 3. The i–E curves of gold obtained for 0,5 M H_2SO_4 and 0,5 M citric acid (⊡) H_2SO_4; (△) Citric acid

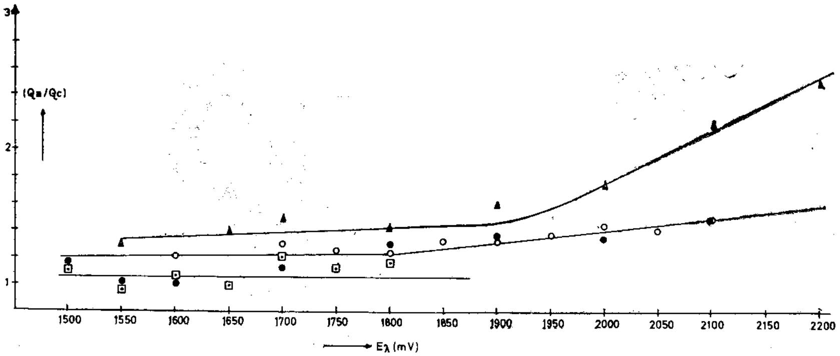
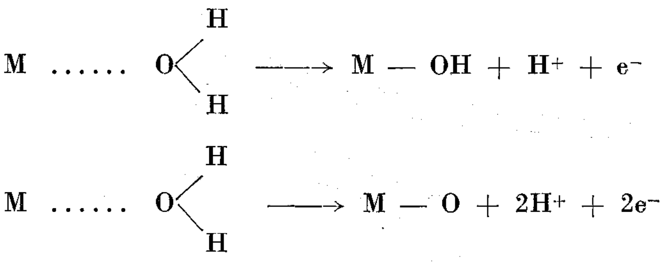


Figure 4. The change of $\frac{Q_a}{Q_c}$ in 0,5 M acetic, succinic and citric acids with reversal potential Eλ.
(□) H_2SO_4; (○) Acetic acid; (●) Succinic acid; (△) Citric acid.

There is no dissolution in H_2SO_4 since $Q_a = Q_c$. Therefore one that $\frac{Q_a}{Q_c} > 1$ in acetic and succinic acids can be attributed to partial electron transfer as mention in Kolbe synthesis (Vijh and Conway, 1967).

There is a competition between the organic and water molecules to be adsorbed on the electrode surface. The adsorption of organic molecules displaces the water molecules from the surface. This situation prevents the



$$M \ldots\ldots O{<}^{H}_{H} \longrightarrow M - OH + H^+ + e^-$$

$$M \ldots\ldots O{<}^{H}_{H} \longrightarrow M - O + 2H^+ + 2e^-$$

reactions.

The potential where the anodic current increases in citric acid (1470 mV) is very close to the potential at which gold dissolves as three valent ions (Pourbaix, 1966).

$$Au \longrightarrow Au^{3+} + 3e^- \qquad Eo = 1{,}498$$

Although there was no citrate complex of gold encountered in the literature the fact that $\frac{Q_a}{Q_c}$ value increases with E_λ much faster in citric acid compared with other acids makes one think that gold might be dissolving as citrate complexes.

3. The thickness of oxide films

The monomolecular oxide layers are characterised either with coverage ratio of oxygen ions θ or the average thickness of oxide layer L. The average thickness of oxide layer is calculated from

$$L = \frac{Q_c}{nF} \cdot \frac{M}{r\rho}$$

where Q_c the amount of charge necessary to completely reduce the oxide, F = Faraday constant, r = roughness factor and n = Faraday number. The surface oxide is the most probably stable Au_2O_3. If the molar volume of Au_2O_3 is taken to be 40 cm^3mol^{-1} (Dickertmann, Schultze and Vetter, 1974) n and r are assumed to be 6 and 1 respectively. The average thickness of oxide layer is calculated as

$$L = \frac{Q_c \cdot 40}{6F} = 6{,}9.10^{-3}\ Q_c$$

If Q_c is taken as $\mu C/cm^2$ the value of L is found in A°.

The thickness of oxide layers in 0,5 M H_2SO_4, acetic, succinic and citric acids were calculated by the help of this equation plotted against E_λ (Fig 5).

The plot of oxide layer thickness against the potential shows that the plots have two different slopes in 0,5 M H_2SO_4. According to this electric field is smaller up to 1600 mV (5.10^6 V/cm) and gets bigger after 1600 mV (10^7 V/cm) (Bilgiç and Kabasakaloğlu, 1981). The higher electric field the less conductive the oxide layer is (Gileadi, 1967). The thickness of the coverage of electrode surface with monomolecular oxide is 3–4 A°. Thus at 1600 mV the surface is completely covered with oxide layer. This breakage in the oxide layer thickness against potential graph occurs at 1800 mV in citric acid solution. In other words the potential needed to cover the surface with a monomolecular layer of oxide film is 1800 mV in this medium. The value of L increases with E_λ increases and after the thickness of monomolecular coverage is reached, the oxygen evolution takes place. The value of $\frac{dE_\lambda}{dL}$ is $1{,}1.10^7$ V/cm in citric

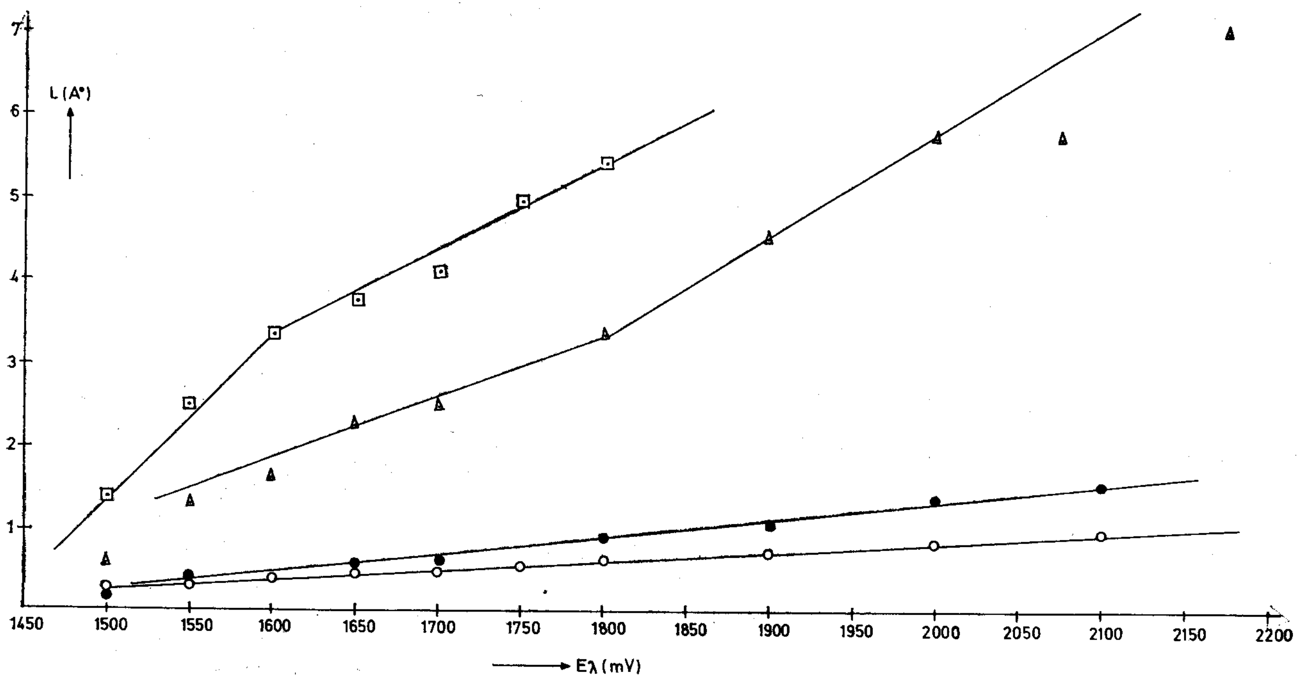


Figure 5. The change of thickness of oxide layers L with reversal potential Eλ in 0,5 M H_2SO_4, acetic, succinic and citric acids. (⊡) H_2SO_4; (O) Acetic acid; (●) Succinic acid; (△) Citric acid.

acid (in the region up to 1800 mV) and this value is very close to that found in the second region in 0,5 M H_2SO_4 (Bilgiç and Kabasakaloğlu, 1981). The L values in 0,5 M acetic and succinic acids also increase with E_λ, but it is not possible to reach the thickness of monomolecular oxide coverage thickness in these mediums. Therefore there is no oxygen evolution in both of these mediums.

The variation of L values with E_λ is given in Table I.

As it is clearly seen from the table that the L values in all acids increase with E_λ. The L value increases with increasing the number of COOH for the same E_λ value. However, although the results obtained in monocarboxylic acetic and dicarboxylic succinic acids are very close to each other, the result obtained in citric acid is significantly different. Citric acid is a tricarboxylic acid and contains an additional OH group in its structure. According to these results the oxide layer forms in acetic acid is the thinnest the oxide layer occurs in succinic acid is a bit thicker and the oxide layer forms in citric acid is the thickest.

Table I. The variation of oxide layer in 0,5 M H_2SO_4 and organic acids.

E_λ (mV)	0,5 MH_2SO_4	0,5 M Acetic acid	0,5 M Succinic acid	0,5 M Citric acid
1500	1.410	0.280	0.248	0.600
1550	2.490	0.351	0.386	1.340
1600	3.360	0.410	0.420	1.680
1650	3.760	0.499	0.552	2.300
1700	4.170	0.511	0.900	2.550
1750	4.960	0.587	—	—
1800	5.450	0.650	0.890	3.380
1900	—	0.750	1.080	4.520
2000	—	0.860	1.390	5.760
2100	—	1.010	1.540	5.750
2200	—	—	—	7.100

The oxide coverage ratios θ_{ox} for all these acids were calculated by dividing the L values found for with 3,36 A°, the value which corresponds the film thickness at 1600 mV in 0,5 M H_2SO_4 and the change of θ_{ox} with E_λ potential is tabulated in Table II

As it is clearly seen from the table that the oxide coverage ratio of the surface in acetic, succinic and citric acids increases with increasing E_λ.

The θ_{ox} values at the same potential also show an increase with increasing number of COOH groups in the acid.

Table II. The change of oxide coverage ratio θ_{ox} with E_λ in organic acids.

E_λ (mV)	0,5 M Acetic acid	0,5 M Succinic acid	0,5 M Citric acid
1500	0.083	0.074	0.179
1550	0.104	0.115	0.399
1600	0.122	0.125	0.500
1650	0.149	0.164	0.685
1700	0.152	0.205	0.759
1750	0.175	—	—
1800	0.193	0.265	1.006
1900	0.223	0.321	1.345
2000	0.256	0.414	1.714
2100	0.299	0.458	1.711

The θ_{org} values can be calculated from the θ_{ox} values listed in Table III. ($\theta_{org} = 1-\theta_{ox}$). In Table III these θ_{org} values are listed against E_λ potential.

Table III. The change of organic compound coverage ratio θ_{org} with E_λ in organic acids.

E_λ (mV)	0,5 M Acetic acid	0,5 M Succinic acid	0,5 M Citric acid
1500	0.917	0.926	0.821
1550	0.896	0.885	0.601
1600	0.878	0.875	0.500
1650	0.851	0.836	0.315
1700	0.848	0.795	0.241
1750	0.825	—	—
1800	0.807	0.735	—
1900	0.777	0.679	—
2000	0.744	0.589	—
2100	0.701	0.542	—

As it is seen here that the value of θ_{org} changes with E_λ and number of COOH group in the acid. The θ_{org} values decrease with increasing E_λ in acetic, succinic and citric acids. The θ_{org} values at the same potential also show a decrease with increasing E_λ. This value is the highest in mono carboxylic acetic acid. It is a bit lower in succinic and the lowest in citric acids. The fact that the oxide and organic coverage ratios in both acetic and succinic acids are very close makes one think that they both adsorb on the surface in the same way. Their adsorptions take place though COOH groups. However the adsorption in citric acid may take place though OH group.

Let's consider the adsorbed water molecules on the electrode surface. There are two limiting case for the orientation of water molecules according to the change of the molecule (Bockris and Reddy, 1977).

The first case is that the charge on the electrode is highly positive. Under these conditions the electrical field vector is directed from metal to solution. The dipoles are oriented in order to make their dipole vector parallel to the field (Fig 6a). Thus the oxygen atoms contact with the electrode. This situation is known as "flip-up state".

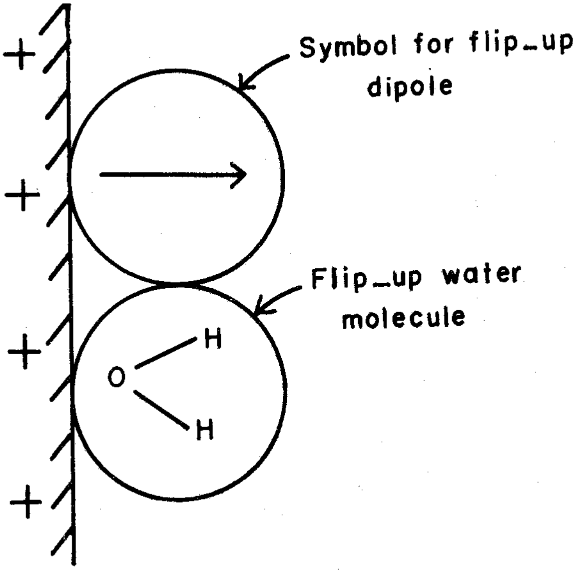


Figure 6a. The flip-up orientation of a water molecule on an electrode.

The other limiting case is to make the electrode negative by pumping electrons to it. If we think in electrostatic point of view, it is obvious that all the "flip-up" molecules will turn round to assume a "flop-down" state. In this situation hydrogens make contact with the electrode (Fig 6b).

If we assume that the electrode metal is positively charged two water molecules will have to be displaced from the surface for the adsorption of one COOH group since COOH contains two oxygens. Therefore two and four water molecules desorbed for the adsorption of one acetic acid and one succinic acid molecules respectively. However θ_{org} values are nearly the same, so we can say that both acids adsorb on the same functional group COOH. The water adsorption on metal at positive potentials is shown in (Fig 6c).

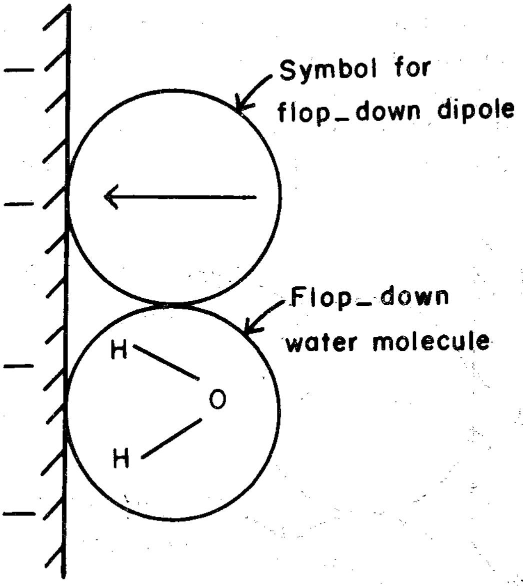


Figure 6b. The flop-down orientation of a water molecule on an electrode.

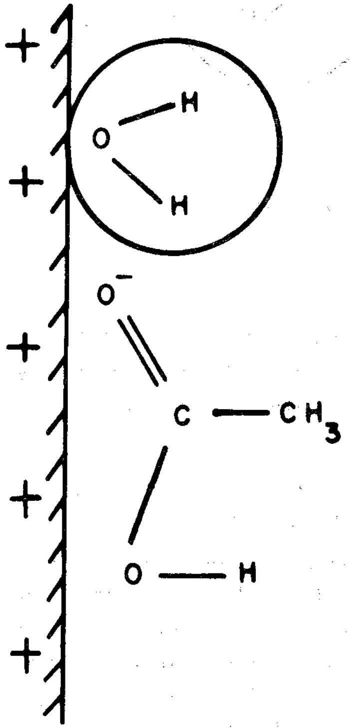


Figure 6c. The water adsorption on metal at positive potentials.

As the number of functional group which carries θ in citric acid is high, the desorption of a great number of water molecules is necessary. However, this is hard to achieve therefore $\theta_{\text{citric acid}}$ has to be found low. The values is Table III indicates this fact.

The adsorption of citric acid passivates the surface until complex citrate formation starts.

The results of this experiments are speculative. In fact there is no experimental technique developed to see and investigate reactions in molecular level. A characteristic study about this subject is as follows (Bockris and Reddy, 1977).

REFERENCES

BARRADAS R.G., DONALDSON G.J. and SHOESMITH D.W.1973. J. Electroanal. Chem. 41, 243.

BİLGİÇ S. and KABASAKALOĞLU M. 1981. Commun. Fac. Sci. Univ. D'Ankara 27, Serie B.

BİLGİÇ S. 1983. Ph. D. Thesis. 60.

BOCKRIS J.O' M. and REDDY A.K.N. 1977. Modern Electrochemistry 2, 779.

DICKERTMANN D., SCHULTZE J.W. and VETTER K.J. 1974. J. Electroanal. Chem. 55, 429.

GILEADI E. 1967. Electrosorption. Plenum Press. New York 73.

POURBAIX M. 1966. Atlas of Electrochemical Equilibria in Aqueous Solutions. Pergamon, New York.

VIJH A.K. and CONWAY B.E. 1967. Chem. Rev. 67, 623.