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Structure–reactivity relationships: the oxidation of aliphatic diols on a gold electrode

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The electrooxidation of a series of vicinal and terminal aliphatic diols ranging from ethanediol to hexanediol including an unsaturated diol at a polycrystalline gold electrode in contact with an alkaline electrolyte solution has been studied. Significant differences found in the oxidation activity are rationalized based on the molecular structure and the different electrosorption behaviour as deduced from additional adsorption measurements.

1. Introduction

Gold has been identified as an electrocatalyst with considerable activity for the oxidation of alcohols and related compounds in alkaline and neutral solutions [1]. The mechanism of the reaction includes, as a rate determining step, the abstraction of a hydrogen atom from the α-carbon atom [2, 3]. This has led to numerous studies of the kinetics and mechanism of the oxidation of a broad variety of organic molecules [4, 5]. More recently the oxidation of propanol-1 at a gold electrode in 1 M KOH has been studied by Ocon *et al.* [6]. Their results provide further suggestions for an understanding of the mechanism. Adsorption data for the hydroxyl ion coverage indicated that, at electrode potentials where the oxidation starts, a considerable coverage is present. Subsequently, the reaction takes place on an Au–OH surface.

Because initial adsorption of the reacting molecule always precedes the electrochemical reaction step, the electrosorption of some of these compounds has been studied [4, 7–9]. Naturally the strong adsorption of the hydroxyl ion prevents direct measurements with alkaline electrolyte solutions; accordingly most studies were performed with solutions containing NaF, $KClO_4$ or $NaClO_4$ as supporting electrolyte. Nevertheless it was demonstrated that, with dilute alkaline solutions, at least qualitative adsorption data are available [9]. Consequently, it was suggested that results on the adsorption of alcohols from solutions with specifically adsorbing ions can be used for the interpretation of kinetic data obtained with alkaline solutions. From comparative studies of primary and secondary alcohols [4, 5, 10] and butanediols with various substitution patterns [4], an influence of the molecular structure resulting in inductive and resonance effects stabilizing the radical formed in the rate determining step was deduced.

The present study deals with the electrooxidation of a series of vicinal and terminal aliphatic diols (from ethanediol to hexanediol); in order to study the influence of C=C double bond an unsaturated butanediol was included. A detailed discussion of the adsorption measurements has been presented elsewhere [11].

2. Experimental details

Cyclic voltammetry (CV) was performed with a polycrystalline gold sheet working electrode (99.99%). A gold sheet counter electrode and a hydrogen reference electrode [12] were used in a conventional H-cell with three compartments separated by glass frits. The electrochemical cell and the evaluation procedure employed in the voltammetric measurements of the differential double layer capacitance have been described previously [4, 7, 9].

Electrolyte solutions were prepared from triple distilled water, KOH (p.A., POCH) or $NaClO_4$ (recrystallized from water, POCH) and the following alcohols (p.A. grade, distilled under nitrogen, checked for purity with NMR spectroscopy): ethanediol (POCH); 1,2-propanediol (Fluka); 1,3-propanediol (Fluka); 1,2-butanediol (Merck); 2-butene-1,4-diol (Roth); 1,2-pentanediol (Aldrich); 1,5-pentanediol (Aldrich); 1,2-hexanediol (Aldrich) and 1,6-hexanediol (Merck).

All experiments were performed at room temperature (25° C) with solutions purged with argon.

3. Results and discussion

A set of cyclic voltammograms in Fig. 1 illustrates the different electrooxidation activities of the vicinal diols (from ethanediol to 1,2-hexanediol). For comparison a CV for 2-hexanol is included. The oxidation of alcohols like eg 1,2-cyclohexandiol [13] or 2,3-butanediol [4] with two secondary HCOH groups yields currents significantly higher, in particular in the lower

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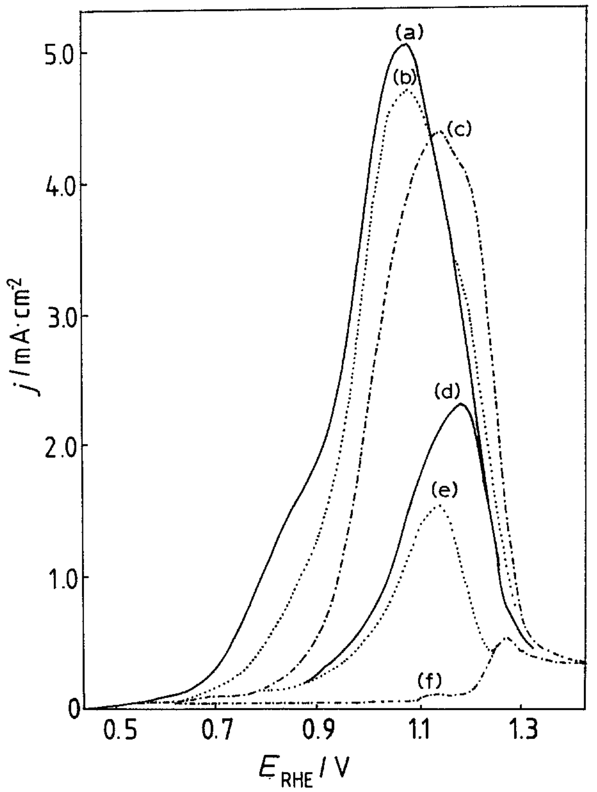

Fig. 1. Cyclic voltammograms of a polycrystalline gold electrode in a solution of 0.1 M KOH with 0.005 M alcohol added: (a) 1,2-hexanediol, (b) 1,2-butanediol, (c) 1,2-propanediol, (d) ethanediol, (e) 2-hexanol, (f) supporting electrolyte; $dE/dt = 100\,mV\,s^{-1}$.

electrode potential range between $E_{RHE} = 600$ and 1000 mV. The striking difference between 2-hexanol and 1,2-hexanediol, caused by the presence of the second hydroxyl group, is obvious. In passing from C_2 to C_6 (1,2-pentanediol is omitted from the figure for clarity; the curve coincides almost completely with that for 1,2-hexanediol) the oxidation current increases. Various factors influencing the overall reaction rate must be considered: adsorptive interaction of the alcohol with the surface, inductive and resonance effects of molecular groups affecting the strength of the α-C–H bond and resonance effects stabilizing the radical formed in the initial reaction step. Since for the corresponding secondary monohydric alcohols [7, 9] the values of ΔG^0_{ad} are the same, the inductive effect of the vicinal OH-group [14] on the α-C-H group is the main reason for the high activity. Considering the increased stability of secondary radicals in the first reaction step the secondary α-C–H group is probably participating. In the case of the 1,2-diols there is always a primary and a secondary hydroxyl group; accordingly structural effects are limited to an increase in the chain length, slightly increasing the accelerating inductive effect. Thus the influence of the adsorption has to be taken into account (see below).

In Fig. 2 CVs depicting the much smaller reactivities of the terminal diols are shown. The behaviour of the unsaturated 2-butene-1, 4-diol is only quantitatively different; the oxidation current is higher than those of the other diols in this figure. The structural effects of the second hydroxyl group are comparably smaller. All alcohols contain only primary CH_2OH groups; thus a resonance effect of a vicinal group will be effective only in the case of ethanediol (see above). As can be seen by comparing curve 1 in Fig. 1 (ethanediol) and curve 1 in Fig. 2 (1,3-propanediol) the additional CH_2 group between the terminal H_2COH groups significantly reduces this effect. The accelerating inductive effect of the additional methylene group seems to be much smaller as compared to the resonance effect of a vicinal hydroxyl group; however the two effects cannot be separated. Again an increase in chain length is accompanied by an increase in electrochemical activity. A slightly enhanced inductive effect of the $(CH_2)_x$ may be, in part, the reason. Again, adsorptive interaction probably contributes considerably. In the case of the unsaturated 2-butene-1,4-diol the double bond in the middle of the molecule again makes the resonance effect of the OH-groups effective; causing the high activity.

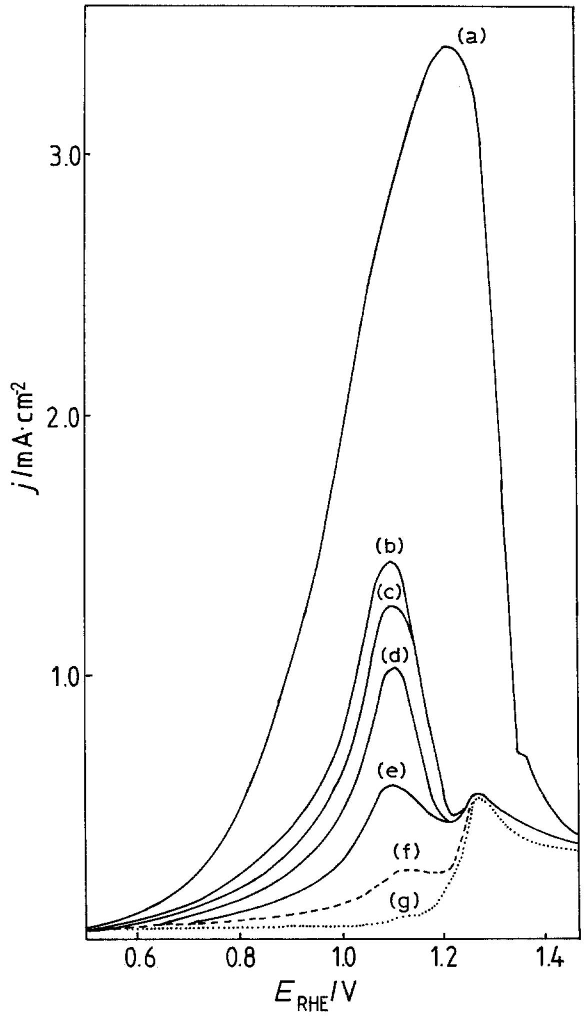

Fig. 2. Cyclic voltammograms of a polycrystalline gold electrode in a solution of 0.1 M KOH with 0.005 M alcohol added: (a) 2-butene-1,4-diol, (b) 1,6-hexanediol, (c) 1,5-pentanediol, (d) 1,4-butanediol, (e) 1,3-propanediol, (f) 1-butanol, (g) supporting electrolyte; $dE/dt = 100\,mV\,s^{-1}$

An analysis of the CVs in the kinetic region yields Tafel slopes ranging from $120\,mV\,dec^{-1}$ for 1,2-hexanediol to $160\,mV\,dec^{-1}$ for ethanediol (Fig. 3). Values of αn range from 0.5 to 0.3 (with α = transfer coefficient, n = number of electrons transferred).

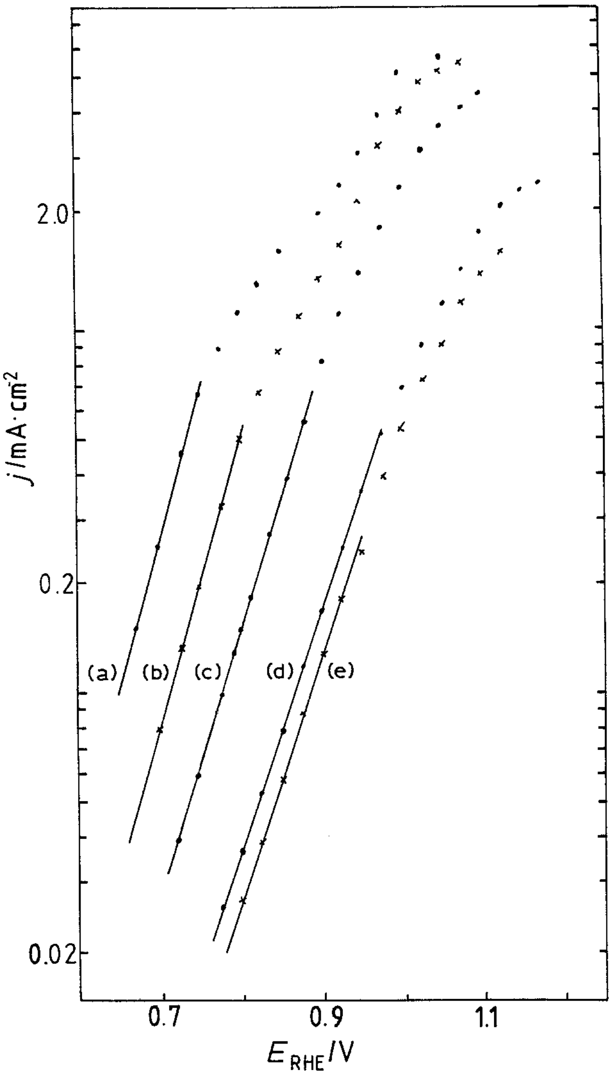

Fig. 3. Tafel plot of the kinetic current for vicinal diols (Fig. 1), 0.1 M KOH + 0.005 M alcohol: (1) 1,2-hexanediol, (2) 1,2-butanediol, (3) 1,2-propanediol, (d) ethanediol, (e) 2-hexanol; dE/dt = 100 mV s^{-1}.

These results support the reaction sequence with the first electron transfer connected to the oxidation of the hydrogen atom abstracted from the α-C atom as the rate determining step.

The asymmetric shape of the current peaks observed with the most active diols as a shoulder in the peak suggests that oxidation may proceed in two different ways. In the lower electrode potential range the coverage of the electrode surface with OH$^-$-ions is far from complete [6]. In this region the reaction order is one with respect to c_{OH^-} up to $c_{OH^-} = 0.02$ M. The order with respect to the alcohol concentration is always 1 (Fig. 4). Accordingly, coadsorption of both alcohol molecules and hydroxyl ions occurs. Oxidation of the adsorbed alcohol occurs only when both particles are close to each other. If the ratio of adsorbed species shifts from a 1:1 relationship, as effected eg by changing the concentration ratios, the oxidation current will decrease (see Fig. 5). With the much less electroactive 1-butanol a reaction order of zero, indicating no further increase of current with c_{OH^-}, is observed at $c_{OH^-} = 0.0005$ M [3]. This points to the weaker adsorption and lower reactivity of 1-butanol [9]. In the more anodic electrode potential range the oxidation proceeds on top of a rather complete hydroxide coverage as proposed by Ocon [6]. The reaction order with respect to c_{OH^-} is 0, with respect to c_{alc} the order is one in all cases.

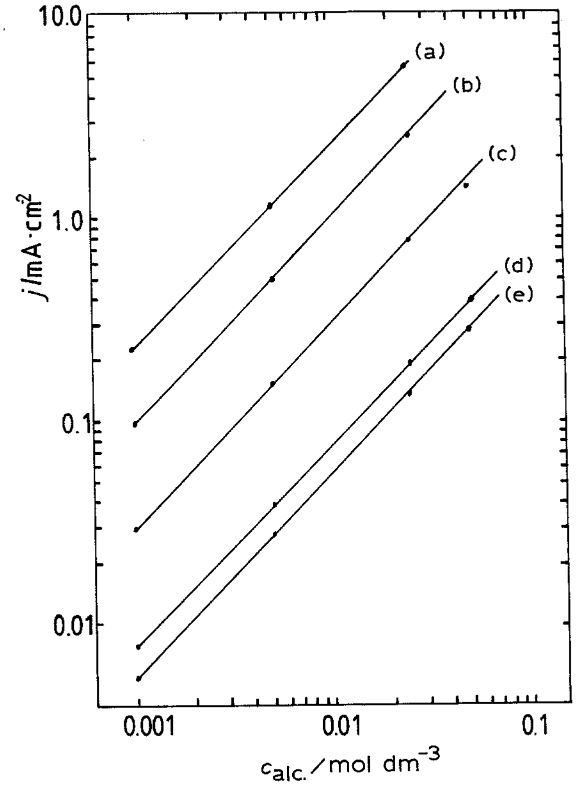

Fig. 4. Plot of log j against log c_{alc} for various alcohols at $E_{RHE} = 800$ mV, 0.1 M KOH, (a) 1,2-hexanediol, (b) 1,2-butanediol, (c) 1,2-propanediol (d) ethanediol, (e) 2-hexanol; dE/dt = 100 mV s^{-1}.

The influence of the adsorption of the alcohol preceding its oxidation, as discussed elsewhere in more detail [11], can be ascertained by voltammetric measurements. Differential capacitance against electrode potential curves, recorded in the solutions where electrooxidation was studied, showed a pronounced decrease of capacitance attributed to the adsorption of alcohol in a potential range where electrooxidation commences. As discussed previously [9] a quantitative evaluation of these curves is not possible because of the competing adsorption of alcohol and OH$^-$-ions. Thus C-E curves with a supporting electrolyte of 0.02 M NaClO$_4$ have been measured. A straightforward transfer of the results to the alkaline systems discussed here is not possible because of differences in pH-values and solution composition. In addition the obtained thermodynamic data are relevant, at first glance, only for adsorbate molecules directly interacting with the metal surface. Nevertheless, the free enthalpy of adsorption includes not only the strength of the electrode-adsorbate interaction, but also the alcohol-solvent and alcohol-alcohol interaction. Thus the contribution of ΔG^0_{ad} to the rate of oxidation for alcohols with an increased chain length in the more anodic potential range is presumably caused, in part, by a systematic change of alcohol-solvent interactions, enforcing their adsorption at a phase boundary. Therefore the adsorption data

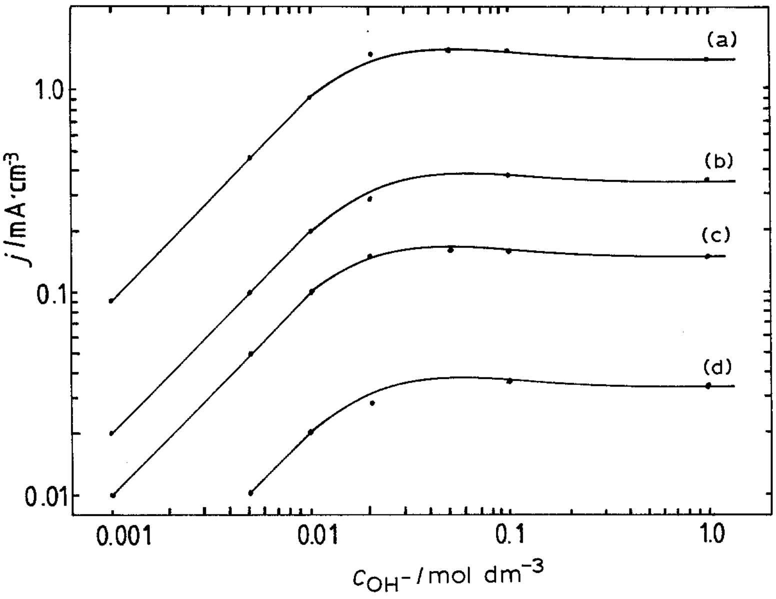

Fig. 5. Plot of log j against log c_{OH^-} for various alcohols at $E_{\mathrm{RHE}} = 800\,\mathrm{mV}$, (a) 0.05 M 1,2-propanediol, (b) 0.05 M ethanediol, (c) 0.005 M 1,2-propanediol, (d) 0.005 M ethanediol; $\mathrm{d}E/\mathrm{d}t = 100\,\mathrm{mV\,s^{-1}}$.

also give at least qualitative information for interactions of diols with a hydroxyl ion covered gold electrode.

A representative set of C–E curves illustrating the adsorption behaviour of 1,2-butanediol is shown in Fig. 6. At the negative electrode potential limit the curves merge; this indicates complete desorption, even at the highest alcohol concentration employed. The capacity minimum observed with the supporting electrolyte gives the electrode potential of zero charge ($E_{\mathrm{pzc}} = -10\,\mathrm{mV}$ vs SCE) within the range of results reported in the literature [15, 16]. Upon addition of increasing concentrations of alcohol the capacitance is significantly diminished at electrode potentials around the E_{pzc}; the capacitance peak negative to the E_{pzc} is smaller and shifted. The minimum of the curve is shifted to negative electrode potentials; at

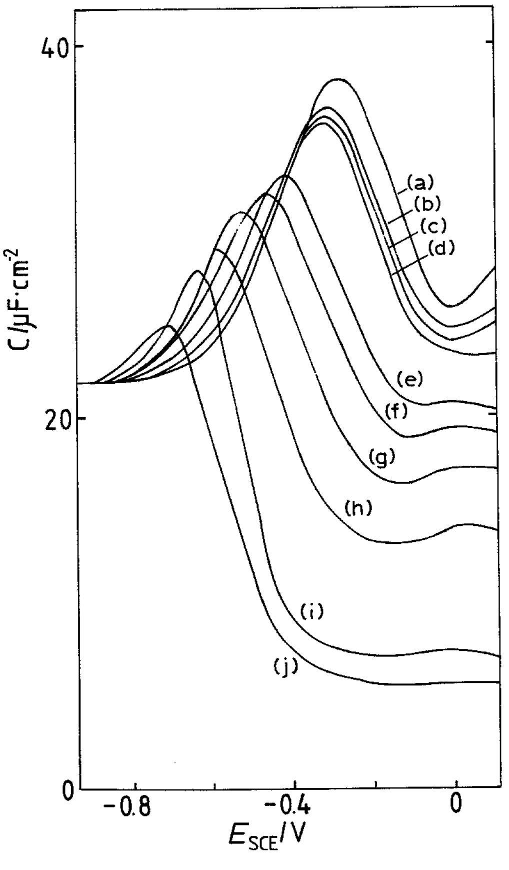

Fig. 6. C–E curve of a polycrystalline gold electrode in a solution of 0.02 M $\mathrm{NaClO_4}$ with varying concentrations of 1,2-butanediol: (a) 0.0 M (b) 0.095 M, (c) 0.1 M, (d) 0.14 M, (e) 0.3 M, (f) 0.4 M, (g) 0.525 M, (h) 0.8 M, (i) 2.0 M, (j) 3.025 M, $\mathrm{d}E/\mathrm{d}t = 5\,\mathrm{mV\,s^{-1}}$, argon purged.

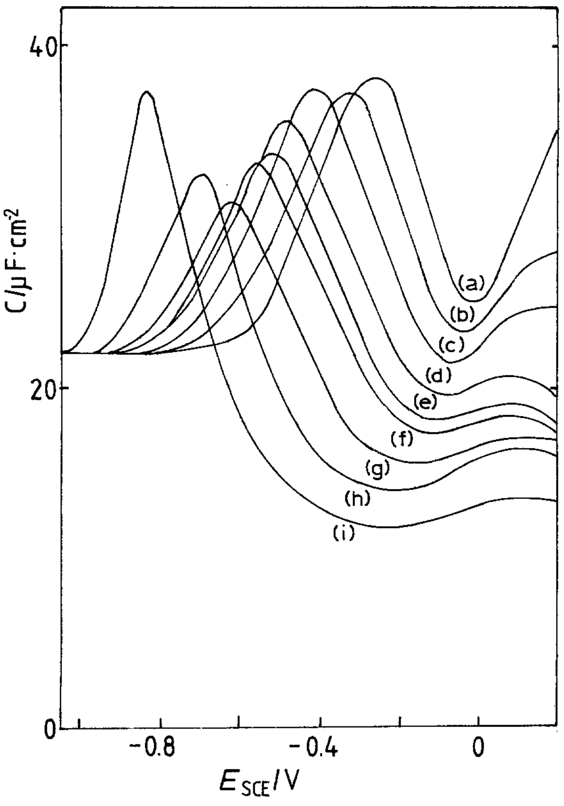

Fig. 7. C–E curve of a polycrystalline gold electrode in a solution of 0.02 M $\mathrm{NaClO_4}$ with varying concentrations of 2-butenediol-1,4: (a) 0.0 M, (2) 0.00025 M, (c) 0.0005 M, (d) 0.0008 M, (e) 0.00125 M, (f) 0.0015 M, (g) 0.0024 M, (h) 0.0045 M, (i) 0.005 M; $\mathrm{d}E/\mathrm{d}t = 5\,\mathrm{mV\,s^{-1}}$, argon purged.

Table 1. Adsorption data for aliphatic diols

Diol	$\Delta G^0_{ad}/kJ\ mol^{-1}$	*a*	$C_{min}/\mu F\,cm^{-2}$	$c_{(\theta=0.5)}/M$
Ethanediol	−6.93	0.8	14.6	1.5†
1,2-propanediol	−8.64	0.7	14.6	0.85†
1,3-propanediol	−11.0	0.6	14.9	0.36†
1,2-butanediol	−11.0	0.5	5.4	0.4†
1,4-butanediol	−13.1	0.3	12.3	0.2*
1,2-pentanediol	−13.6	0.4	8.5	0.15†
1,5-pentanediol	−15.9	0.3	5.2	0.07†
1,2-hexanediol	−16.0	0.3	6.8	0.06†
1,6-hexanediol	−17.9	0.2	4.4	0.03†
2-butene-1,4-diol	−27.7	0.2	11.7	0.0006

Standard state: unit mole fraction in the bulk phase and unit coverage in the adsorbed layer
* data taken from [4]
† data taken from [11]

higher alcohol concentrations the pronounced minimum is flattened. This cathodic shift of the minimum indicates that the adsorbed dipolar alcohol molecules are oriented with the positive end of the dipole towards the electrode. The capacitance at the minimum recorded with saturation coverage of 1,2-butanediol is significantly smaller than the value found with 1,4-butanediol (see Table 1). The behaviour of 2-butene-1,4-diol as visible in a set of C–E curves in Fig. 7 is essentially very similar; the shift of the capacitance minimum is much stronger. The capacitance minimum shows a value very similar to that found with 1,4-butanediol (Table 1). By comparison it can be seen that the negative capacitance hump attributed to the desorption of the alcohol is shifted to more negative electrode potentials; accordingly the alcohol is adsorbed more strongly. Evaluation of the capacitance values at an electrode potential of $E_{SCE} = -125\,mV$ (this value has been identified previously as the potential of maximum adsorption [17] resulting in the thermodynamic data of adsorption followed a procedure described elsewhere [7, 9]. All relevant data taken from the C–E curves and calculated assuming a Frumkin isotherm are collected in Table 1. The particularly large absolute value for G^0_{ad} indicates that the double bond interacts especially effectively with the gold electrode. The high electrooxidation activity observed with this alcohol indicated the strong alcohol-electrode interaction, this supports the interpretation of the adsorption data. This is completely different for 2-butyne-1,4-diol adsorbed at a mercury/water interface [18]. In the latter system the results for the unsaturated compound and the corresponding 1,4-butanediol are exactly the same, indicating complete absence of any specific interaction between the triple bond and the electrode. Although the exact data for the dielectric constant ϵ of 2-butene-1,4-diol are not known it seems reasonable to conclude, from a comparison of related data*, that the value is close to that reported for 1,2-butanediol [19]. Accordingly the double layer thickness in the case of $\Theta = 1$ is the same for both alcohols; 2-butene-1,4-diol is also adsorbed in the entirely flat orientation proposed for 1,4-butanediol [9].

For both series of homologous alcohols the increase in chain length corresponds to an increase in ΔG^0_{ad}. The increments for an additional CH_2 group are somewhat larger with the terminal diols [11]. Although a quantitative evaluation of the changes of the oxidation current as a function of ΔG^0_{ad} is not possible the data strongly suggest that the enhanced diol-surface interaction is the main reason for the increased activity.

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