Radicals Occurring During the Electroreduction of Acrylic Acid at Mercury Cathodes Detected by Electrochemical in situ EPR Spectroscopy

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We performed electrochemical reduction investigations of acrylic acid and methylacrylate in aqueous solutions at a mercury cathode. Tetraalkylammoniumhalides were used as supporting electrolytes and the pH was adjusted in the range of pH = 3 – 12. Electrolyses in 1 M solutions of acrylic acid have yielded oligomers with a degree of polymerization depending on the pH value. At $pH > pK_s + 1$ the acrylate anion is reduced and forms oligomers, if alkali ions are absent. Polarographic techniques are used to characterize the electrochemical behaviour of the acid and the ester, especially the coupling of two monomeric units, that was found as a radical-substrate coupling reaction for the acrylate anion and an ion-substrate coupling for the ester. The radical species were detected and characterized by electrochemical in situ EPR spectroscopy. The EPR spectrum is attributed to a propagating chain radical of the acrylate anion. In the case of methylacrylate no EPR spectrum could be recorded during the electroreduction. Finally, a reaction scheme for the electrochemical reduction of acrylate anions in aqueous media containing tetraalkylammonium cations is presented.

1. Introduction

The polymerization of acrylic acid by a free radical mechanism has been known for a long time [1]. The aim of this work was to investigate the mechanism of the electroreduction of acrylic acid at mercury cathodes with respect to the polymerization of the monomer under these conditions. Aqueous solutions in the range of $5.5 < pH < 12$ were used as the reaction medium containing tetraalkylammonium salts as supporting electrolyte. Such conditions are known to favour the hydrodimerization of acrylic acid derivatives, e.g. the esters and the nitrile [2 – 4] at the mercury cathode, instead of their hydration. The reason is the hydrophobic behavior of the cation, that causes a lower activity of water in the specific adsorption layer of the cathode. In contrast, the use of alkali salts as supporting electrolyte leads to the hydration of the vinyl group, forming the corresponding propionic acid derivative [2]. The addition of a polymerization initiator, for example peroxide compounds, was avoided in this work to estimate the ability of the acrylate anion itself to start a polymerization reaction in the given electrolyte solution. The minimization of the salt concentration in electrolytes for polymer coating formation is important. Thus, the coating does not contain large amounts of salt, which increase the probability of swelling and the breakdown of adhesion of the film.

Dineen, Schwan and Wilson [5] stated that a neutralized solution of acrylic acid gave no polymer by electrolysis at a mercury cathode and a platinum anode but without any hint to the neutralization base. Thus we tried to form a polymer in aqueous tetraalkylammonium salt electrolytes, which provide a low water activity at the electrode. There were many contributions concerning the electropolymerization of acrylic esters and the nitrile [6 – 9], but acrylic acid itself is less investigated especially in neutralized and basic aqueous solutions.

Furthermore, no experimental data are known for the radical intermediates that occur during electrochemical polymerization of acrylic acid derivatives. Beck [10] stated that EPR spectroscopic measurements in the polymerization of acrylonitrile provided only small signals.

2. Experimental

Acrylic acid (Merck) was distilled under vacuum over a 20 cm vigreux-column. The middle fraction was used. Tetramethylammoniumhydroxide (20% solution in water, Merck) was used as received. The mercury as cathode material was of analytical grade (Merck).

The polarographic measurements (direct current polarography, differential pulse polarography) were carried out with a VA Processor 693/VA Stand 694 from Metrohm (Switzerland) in 0.1 M aqueous solutions of tetramethylammoniumiodide that were purged with nitrogen.

The EPR spectra were recorded with a X-band spectrometer ESP 300 E (Bruker, Karlsruhe, Germany). We used a rectangular cavity resonant in the TE_{102} mode. The amplitude of the 100 kHz modulation was 1 – 4 Gauss. The electrochemical flat cell, located in the resonator, was made from quartz glass with an inner width of 0.5 mm (Fig. 1). The meniscus of the mercury cathode stands in the centre of the resonator. The area of the mercury cathode was 4 mm^2. As anode we used a platinum mesh, the reference electrode was a Ag wire coated with AgI. The electrochemical cell in the resonator for electrochemical studies at mercury electrodes and the mercury handling are presented in Fig. 1. The electrolyte solution was deaerated by bubbling with pure nitrogen. For the electrical polarization we used a HEKA potentiostat (PG285, HEKA, Lambrecht, Germany).

3. Results and Discussion

DC- and DP-polarographic measurements in aqueous solutions of tetramethylammoniumiodide with addition of acrylic acid derivatives show differences in the polarographic behaviour of acrylic esters and the acid (Figs. 2, 3)

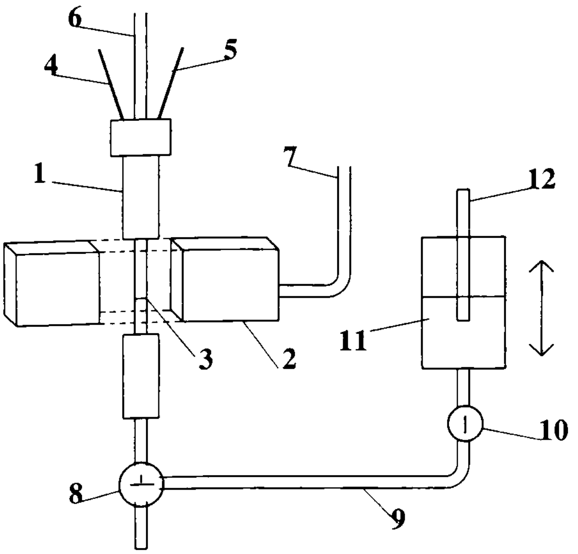

Fig. 1
Scheme of in situ electrochemical EPR measurements: (1) electrochemical flat cell, (2) resonator of the spectrometer, (3) mercury meniscus (working electrode), (4) counter electrode, (5) reference electrode (Ag/AgI), (6) gas entrance for N_2 (99.999%), (7) X-band wave guide, (8) three way stop cock, (9) flexible tube, (10) stopcock, (11) mercury reservoir, (12) electrical contact for the mercury

[11]. In the case of methylacrylate (Fig. 2), two DP-polarographic peaks can be observed in the pH range lower than pH = 5. The peak marked as H-ions appears at a potential of − 1615 mV (Ag/AgCl, 3 M Cl^-) and is independent of the acrylic ester investigated [11]. The peak height only depends on the total amount of hydrogen ions in the solution and has the same value as in the supporting electrolyte of the same pH. The potential of the second peak, marked as MA, is different for several acrylic esters but can be observed in the whole pH range investigated here. The reduction peak corresponds to the formation of the hydrodimer of the ester [2, 3], e.g. the electrochemical reaction of the vinyl group.

When acrylic acid was added to the electrolyte, only one reduction step at low pH values was found depending only on the total hydrogen concentration (Fig. 3, pH < 5.5). It is related to the reduction of hydrogen ions, too. If the acidic form of acrylic acid itself was reduced, a current plateau should be seen in the i_{Peak}/pH dependence at pH values lower than pK_s (pK_s = 4.25). The higher current compared to that of the esters at the same pH values is due to the hydrogen ions from the carboxyl group of the acid molecule. In contradiction to the results with the ester no reduction of the vinyl group of acrylic acid appears in acidic solutions. Only in the pH range of about pK_s two DP polarographic peaks can be seen in the polarogram (Figs. 3, 4).

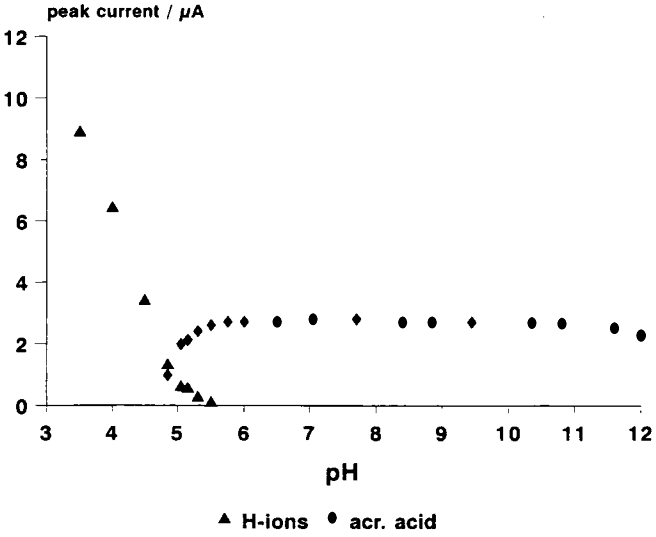

Fig. 3
Dependence of the DP polarographic peak current of acrylic acid on the pH in 0.1 M tetramethylammoniumiodide solution

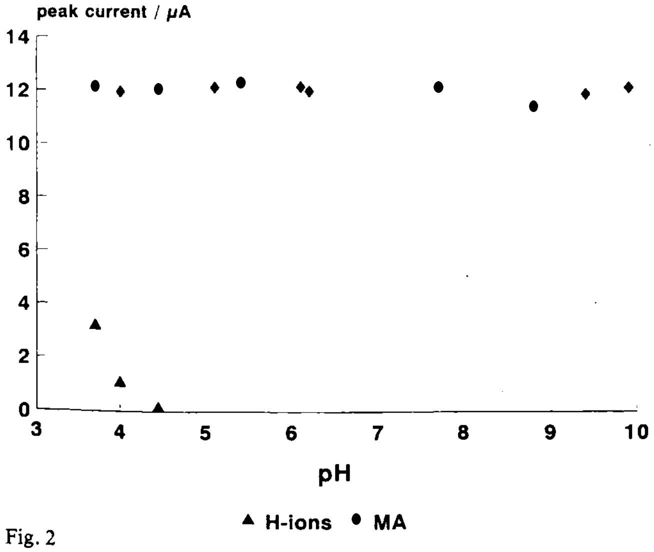

Fig. 2
Dependence of the DP polarographic peak current of methylacrylate on the pH in 0.1 M tetramethylammoniumiodide solution

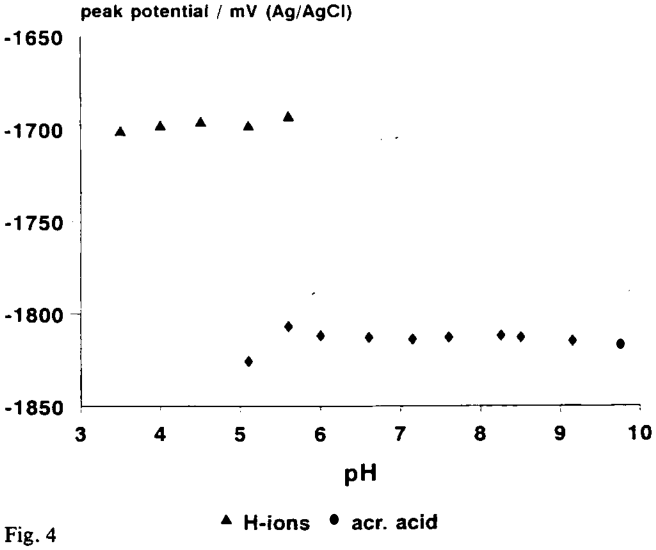

Fig. 4
Dependence of the DP polarographic peak potential of acrylic acid on the pH in 0.1 M tetramethylammoniumiodide solution

The second peak at − 1815 mV (Ag/AgCl, 3 M KCl) corresponds to the reduction of the acrylate anion. Both the peak height as well as the peak potential are constant for pH values up to 12. The peak height linearly depends on the concentration of the acrylate ion.

Based on these results potentiostatic electrolysis of 1 M acrylic acid in aqueous solutions of various pH values was done at potentials derived from polarographic measurements for the reduction of the vinyl group (in acidic solutions at the cathodic decomposition potential). The anode in the divided cell was a platinum mesh, while the cathode was a bottom mercury electrode. Table 1 shows the results of batches with various pH values and the neutralizing base employed [11]. The organic reaction products were separated by extraction with ether and characterized by GC/MS.

Table 1
Products of electrolysis of 1 M acrylic acid in various electrolytes

Electrolyte solution	Reaction products/remarks
Acrylic acid + H_2SO_4, pH = 1	Polymer precipitable with acetone; yield 15 – 25 µg/As
Acrylic acid without supporting electrolyte, pH = 2.25	Polymer precipitable, yield 10 – 25 µg/As; hydrodimer- and -trimer (from GC/MS)
Acrylic acid, pH = 5 (adjusted with NH_3)	hydrodimer- and -trimer; low degree of conversion
Acrylic acid, pH = 9.4 (adjusted with NH_3)	Polymer precipitable; yield 30 – 90 µg/As; adipic acid as low molecular main product; low molecular reaction products with no endstanding methyl groups (GC/MS)
Acrylic acid, pH = 9.4 (adjusted with tetramethylammoniumhydroxide)	dto., additionally formation of a thin polymer film on the electrode surface

The electropolymerization of acrylic acid in acidic solutions was already investigated in the literature [5, 12, 13]. We focused on investigations in weak basic electrolytes, especially tetraalkylammonium salts. The oligomer (last line in Table 1) with a current yield of 30 – 90 µg/As has a degree of polymerization of about 10 – 15, which was found by means of potentiostatic coulometry. The oligomers can be precipitated from the aqueous medium with acetone and form furthermore a thin colourless gel film at the mercury/solution interface. The film and the precipitable oligomer are insoluble in organic media, such as DMF, DMSO, THF, methanol and dioxane.

In polarographic measurements at $pH > pK_s + 1$ the acrylate anion itself is reduced and during the electrolysis at the mercury pool electrode in the concentration range of polarography ($10^{-4} - 10^{-2}$ M) only the hydrodimer adipic acid was formed [11]. Therefore one electron per monomer molecule is consumed. So, in polarography the dimerization mechanism can be investigated. The mathematical analysis of the DC-polarographic current potential curve according to Nadjo and Saveant [14 – 16] resulted in a special dimerization sequence. The coupling of two monomeric units was identified as a radical-substrate coupling for the acrylate anion, because the DC polarographic curve could only be linearized with the set of constants in the I-U curve [14 – 16], that are characteristic for this kind of coupling. In contrast, acrylic esters and amides undergo an ion-substrate coupling [4] like acrylonitrile [3]. Because the product of a radical-substrate coupling will be a radical too, the acrylate anion can undergo a radical polymerization mechanism with direct electrochemical initiation. This is the case at higher monomer concentrations, e.g. at 1 mol/l (Table 1).

For in situ EPR experiments at room temperature we used an aqueous solution of acrylic acid, being adjusted to pH = 8 by the addition of tetramethylammoniumhydroxide. In Fig. 5 the coincidence of the EPR signal with the electrochemical reduction current of acrylate anions is demonstrated. The EPR intensity is expressed as the height of the central band of the spectrum. It is evident that the EPR signal corresponds with the reduction of the anion of acrylic acid.

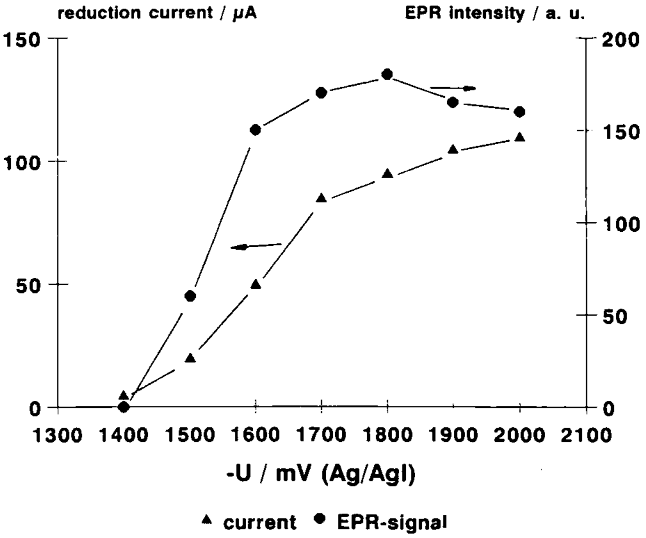

Fig. 5
EPR signal and reduction current of acrylate anions in dependence on the electrode potential (1 M acrylic acid; pH = 8, adjusted with tetramethylammoniumhydroxide)

The EPR spectrum recorded of radicals produced in the potential range between − 1600 and − 2000 mV vs. Ag/AgI is shown in Fig. 6. The spectrum has the shape of a triplett but with clear characteristics of a powder pattern. Fig. 6 also shows a spectrum simulated for one isotropic coupling of 26 Gauss and one anisotropic hyperfine coupling with principal values of the coupling tensor of 8, 24 and 30 Gauss. This interpretation agrees with that given in [17]. It was found there that in the most probable conformation of the radical (structure discussion below) only one β-coupling is observed and the α-proton shows strong anisotropic coupling with principal values of 11, 21 and 33 Gauss. The absence of the second β-coupling is due to the strong angular dependence of the coupling constant. The occurrence of a powder pattern for a radical produced in aqueous

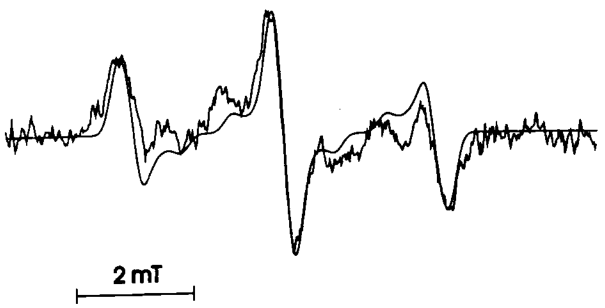

Fig. 6
EPR spectrum recorded during the electroreduction of acrylic acid in aqueous solution with tetramethylammoniumhydroxide, pH = 8, at 25 °C; simulated spectrum with coupling constants in the text

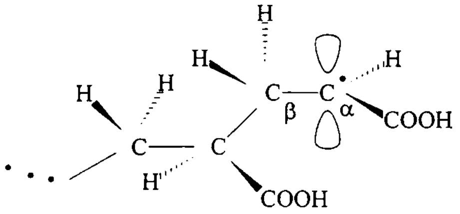

Fig. 7
Proposed structure of the propagating chain radical of acrylate anions at the mercury electrode

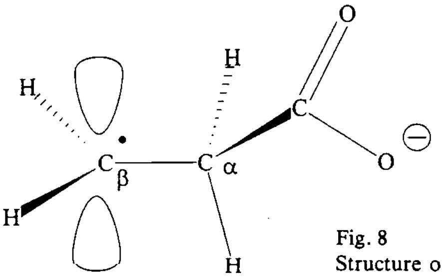

Fig. 8
Structure of the monomer radical

solution at room temperature indicates a lower mobility of the radicals due to the formation of a polymer layer [17, 18] at the surface of the electrode. A part of this polymer layer is found at the glass wall of the flat cell after removing the mercury. In this layer the radicals are immobilized even at room temperature but their mobility is higher than at 77 K [17], so that the anisotropy of the coupling tensor partially can be averaged out. This might be the reason for the small difference between the anisotropic coupling reported in [17] and that from our experiment.

If the meniscus of the mercury cathode is lowered under the resonator, the EPR signal immediately disappears. On the other hand, if the current is switched off with the cathode surface remaining in the resonator the radical species can be furthermore detected with decreasing intensity with time. This is an additional hint for the radical as a propagating chain radical of the acrylic acid anion. The spectrum found agrees with the findings of several authors [19 – 25] investigating the polymerization of acrylic acid. Nitta et al. [23] point out in the investigation of single crystals of acrylic acid at low temperatures, that by warming up to a critical temperature a triplett spectrum can be detected, which the authors attribute to the starting polymerization of the monomer in the solid state. In [26] it is concluded from quantum mechanical calculations, that such a triplett must be correlated to a propagating chain radical of the acrylate anion. Fischer and Giacometti [19] pointed out that polymer radicals of acrylic compounds with a length of more than two monomeric units cannot be distinguished by means of their coupling constants. The radical structure suggested is presented in Fig. 7.

The unpaired electron is located at an α-carbon atom of the polymeric acid molecule. The main triplett shape must be explained by the restricted mobility of rotation in the C_α-C_β axis [17, 21, 27] (Fig. 7). So, only the α- and one of the β-hydrogen atoms can couple with the unpaired electron at the carbon atom. Because the mean values of the coupling tensor of the α- and β-hydrogen atoms are similar, the polymer radical provides a spectrum like a triplett [22].

The analysis of the low molecular water-soluble products (dimer and trimer) [11] has shown that these low oligomers do no contain endstanding methyl groups. If the observed radical is a product of the radical-substrate coupling mechanism, which was concluded from the analysis of the polarographic curves, the monomer radical should have the structure as described in Fig. 8.

From thermodynamical reasons this structure is not the expected one [21, 28]. The single electron should be located at the α-carbon atom of the monomer radical, but the steric situation at the electrode interface can give an explanation for the genesis of the intermediate according to Fig. 8. In Fig. 9 a mechanism is given. The cathode surface is covered with tetramethylammonium cations. Because of the electrostatic repulsion of the carboxyl group the acrylate anion should be perpendicular to the surface. The inductive effect (-I) of the carboxyl group causes a positive partial charge at the β-C atom of the vinyl group. The electron is transferred from the electrode onto this atom. This step is immediately followed by a protonation at the α-C atom from a water molecule. This idea agrees with similar proposals in the literature [4, 10, 29]. The so formed monomer radical undergoes a radical-substrate coupling reaction with a further monomer molecule. This dimer radical either reacts

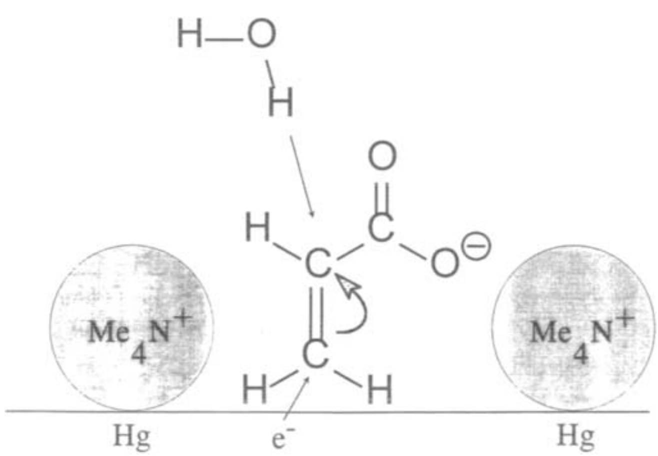

Fig. 9
Mechanism for the formation of the monomer radical structure given in Fig. 8

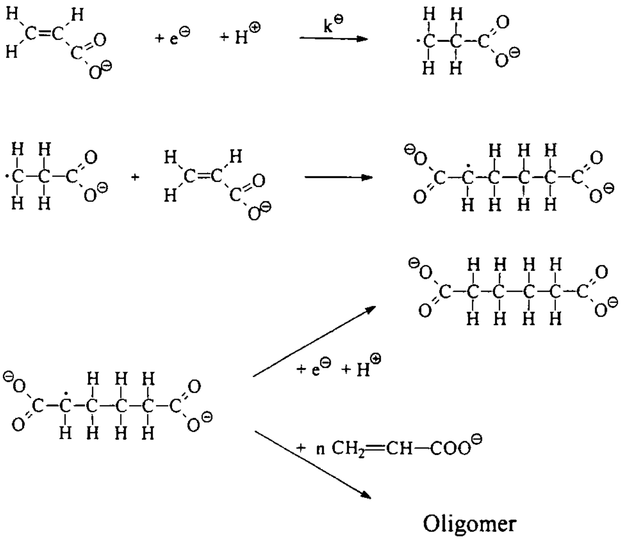

Fig. 10
Complete reaction scheme of the electroreduction of the acrylate anion

with monomers to form a propagating chain of an oligomer or accepts a second electron with the hydrodimer as the reaction product. The first case is favoured at high monomer concentrations. The complete reaction scheme is given in Fig. 10.

In EPR measurements with methylacrylate in the same electrolyte solution no EPR signal could be found, although the reduction current was in the same range as in the case of acrylic acid. The reason of this behavior is the different coupling mechanism of two monomeric units for acrylate anions and acrylic esters. The product of an ion-substrate coupling can only form a radical in a disproportionation reaction, while the product of a radical-substrate coupling is a radical itself. Such a radical producing disproportionation does not seem to occur in the case of acrylic esters.

4. Conclusions

It has been shown that radical species occur during the electroreduction of acrylic acid anions at mercury cathodes in aqueous solutions with tetraalkylammonium salts as supporting electrolyte. They were detected by in situ EPR spectroscopy. The EPR spectrum has a powder pattern, which is correlated to the formation of a polymer film on the electrode surface, where the radical species are immobilized. The radical detected is a propagating chain of acrylic acid anions.

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