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The memory effect in solution

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Abstract Cyclic voltammetric measurements of N,N-dimethyl-p-toluidine (**1**) and other organic π -systems in acetonitrile reveal that under special experimental conditions the first voltammetric cycle differs markedly in shape and peak position from subsequent ones. This phenomenon is only observed when the electrode is polarized at negative potentials of -1.5 V for a waiting time of several minutes, scan rates of at least 5 V/s and an excess of a base. A similar phenomenon is known from conducting polymers, where the so-called memory effect is ascribed to a conformational relaxation. A detailed explanation for the corresponding phenomenon of small molecules which remain in solution cannot be given yet, but a conformational relaxation requiring longer chains can be ruled out.

Keywords Conducting polymers · Memory effect · Cyclic voltammetry · Electron transfer kinetics · Passivating layers

Introduction

The electrochemistry of organic conducting polymers has introduced quite a large number of phenomena not observed in conventional electrochemical experiments. In voltammetric experiments these involve, among other things, strong hysteresis between charging and discharging, a steep anodic wave followed by a broad current plateau and the so-called memory effect (Fig. 1). The characteristic of the memory effect is that after a waiting time in the discharged state of a polymer the first

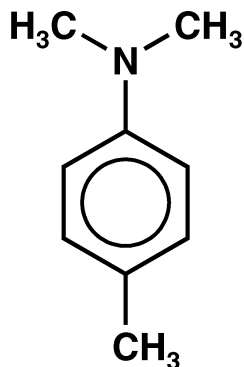
voltammetric cycle differs markedly in shape and peak position from subsequent cycles. While, the anodic wave of the very first cycle appears at relatively positive potentials and is normally both steep and small, all subsequent anodic scans show broadened waves which are significantly shifted towards the negative potential. Very often two overlapping waves can be seen [1–4]. The reasons for this effect are not completely clear yet, but in general a conformational relaxation effect upon oxidation is supposed to be responsible for this phenomenon [5–8]. In fact, up to now the memory effect has been observed only with polymer films. In the case of small molecules in solution, it was unknown.

However, in recent studies we came across the following phenomenon: the voltammetric response of N,N-dimethyl-p-toluidine (**1**) is characteristically changed by polarizing a Pt working electrode in an acetonitrile solution in the presence of base at a potential of -1.5 V versus Ag/AgCl for a few minutes before starting the voltammetric experiment. In contrast to voltammetric experiments without any waiting time, in which the response is that of a reversible or quasireversible process, the anodic wave of the oxidation of **1** is shifted to higher potentials in the very first cycle, and in the reverse sweep a trace crossing is observed. Multisweep experiments reveal that this shift and the crossover only occur in the first cycle, whereas, the current–voltage curves of the following sweeps are almost identical to each other and correspond in shape and current to cyclic voltammograms obtained without waiting time. This finding is interesting in so far as it resembles the well-known memory effect investigated for conducting polymers, as mentioned above [5, 7]. In both cases, a waiting time at a potential beyond the oxidation potential results in a voltammetric response in which the first sweep significantly differs from the following ones.

To observe the aforementioned phenomena requires a high substrate concentration ($c \approx 10^{-2}$ M), the presence of a base and relatively high scan rates (≥ 5 V/s). Moreover, the effect is favoured by an excess of base and high temperatures. As we observed it for the first time in

Dedicated to Professor M.A. Vorotyntsev on the occasion of his 60th birthday.

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N,N-dimethyl-p-toluidine (**1**)

solutions of **1** in acetonitrile, we were interested in the question of whether it is limited to this system. A combination of various substances and solvents were tried and to some extent similar effects were observed. In the following, we provide a descriptive summary of the various experiments and try to give possible theoretical explanations for these results.

Materials and methods

Instruments

Cyclic voltammetric measurements were carried out with a transistorized three-electrode potentiostat-galvanostat (Jaisle IMP 88) connected to a function generator (EG

Fig. 1 Cyclic voltammogram of a potentiodynamically generated polyethylenedioxythiophene film in acetonitrile (CH_3CN)/0.1 M TBAPF₆, $\nu=0.1$ V/s, $T=253$ K: typical example of the memory effect observed with polymers. (first cycle = full line, subsequent cycles = dotted line)

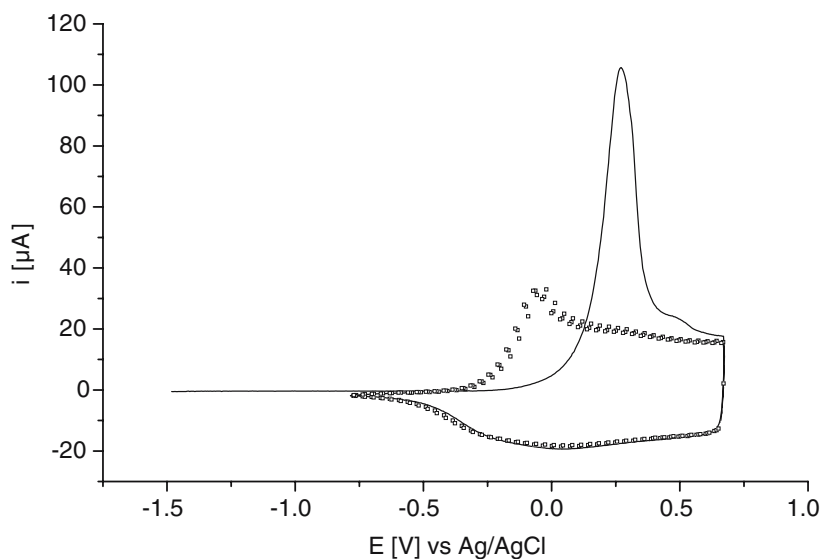


Fig. 2 Cyclic voltammogram of the oxidation of **1** ($c = 1.5 \times 10^{-2}$ M) in acetonitrile (CH_3CN)/0.1 M TBAPF₆, $\nu = 10$ V/s, $T = 303$ K, $c(\text{Base}) = 1.5 \times 10^{-2}$ M, showing the typical memory effect (first cycle, full line; second cycle, dotted line)

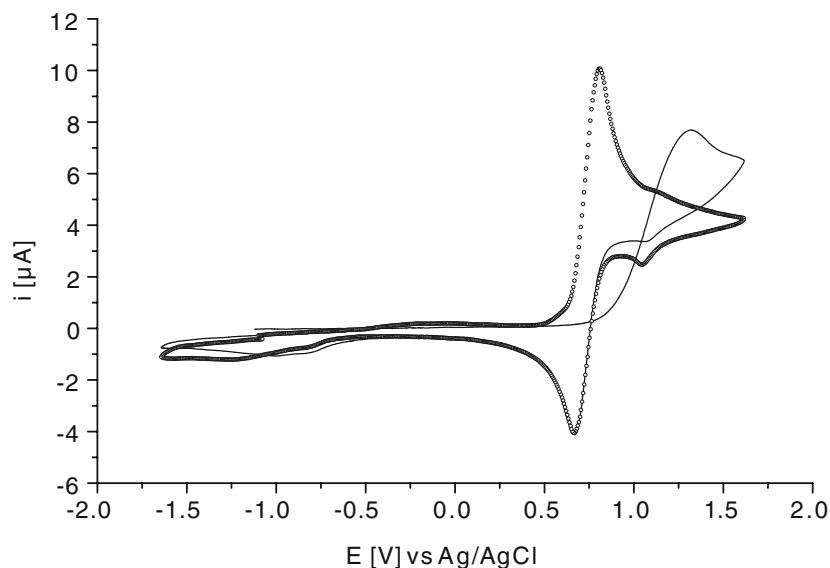
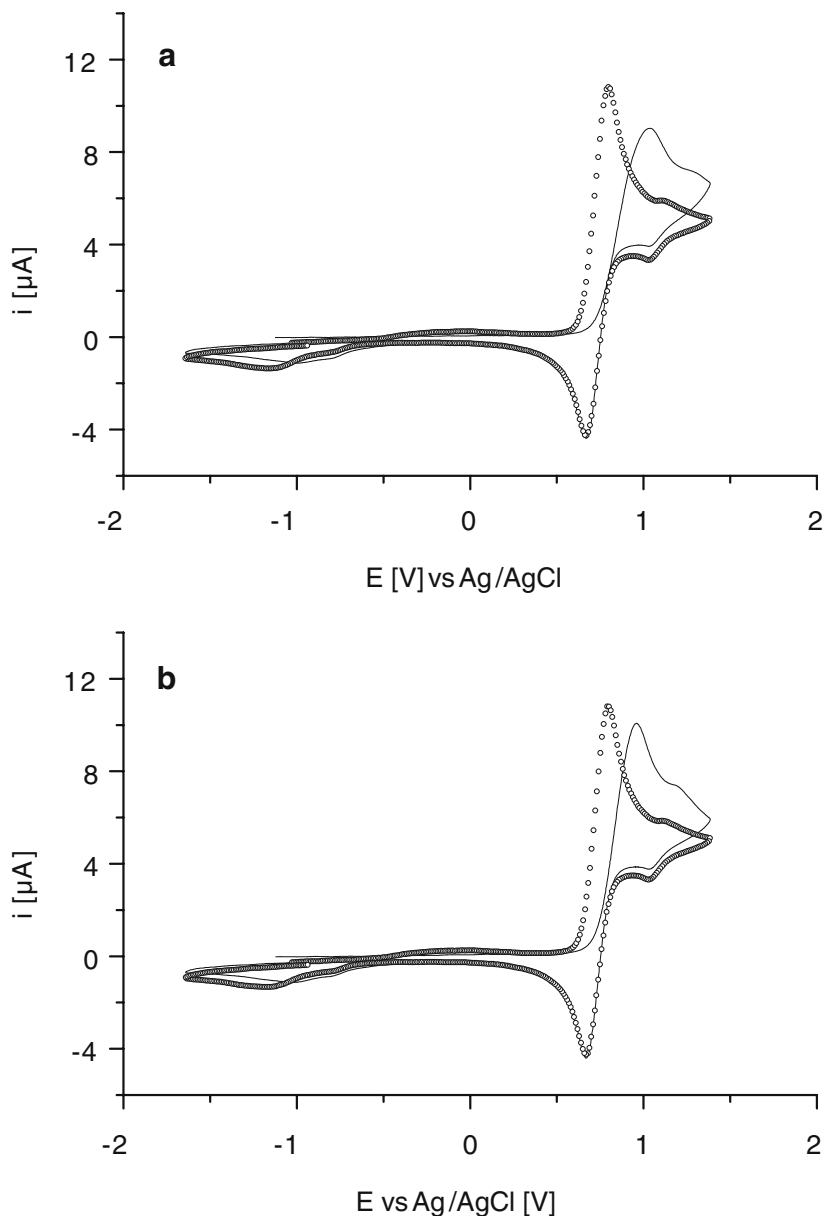


Fig. 3 Cyclic voltammograms of the oxidation of **1** ($c = 1.5 \times 10^{-2}$ M) in acetonitrile (CH_3CN)/0.1 M TBAPF_6 , $v = 10$ V/s, $T = 303$ K, $c(\text{Base}) = 1.5 \times 10^{-2}$ M: in spite of exactly the same experimental conditions they are not perfectly identical (first cycle, *full line*; second cycle, *dotted line*)



& G PARC 175). The resulting pairs of current/potential data were read with a computerized transient recording system developed by our working group that monitors the cyclic voltammograms in a roll-on mode. All obtained data were digitally stored using a function call driver (Keithley DAS-1700 Series).

Chemicals

N,N-dimethyl-*para*-toluidine (99%) was bought from Acros Organics and used as received. Thianthrene and 9,10-dimethylantracene were purchased from Aldrich. Commercially available 2,6-di-*tert*butyl-4-methylpyridine chosen as basic additive was used as received from Lancaster.

Tetrabutylammoniumhexafluorophosphate (TBAPF_6), used as supporting electrolyte (Fluka purity > 98%)

was recrystallized from ethanol and dried at 120°C under vacuum. Basic alumina (Super I) was purchased from ICN Biomedicals.

Cell and electrodes

All cyclic voltammetric measurements were performed in a cell developed by Kiesele [9] containing an internal drying column with highly activated alumina.

The measurements were carried out with a typical three-electrode arrangement. A 1 mm platinum wire embedded in soft glass, served as the working electrode. A Pt wire wrapped around the working electrode was used as the counter electrode. The pseudo reference electrode consisted of a silver wire. Potentials were calibrated with cobaltociniumperchlorate against the standard potential of a saturated Ag/AgCl electrode

(−0.960 V). Cyclic voltammetric measurements of **1** were performed in acetonitrile and dichloromethane at different scan rates, temperatures and concentrations.

Results and discussion

N,N'-dimethyl-*p*-toluidine (**1**) in acetonitrile and dichloromethane

The curious effect that the voltammetric response of an electroactive species drastically changes between the first and the second cycle was accidentally detected during

electrochemical studies of **1**. Applying scan rates higher than 1 V, the first anodic wave of **1** in a multisweep experiment appeared at potentials which were far more positive than normally observed at a scan rate of 100 mV/s. After passing the switching potential in the first cycle, all the succeeding waves seemed to be quite normal (Fig. 2).

As can be seen from Fig. 3 showing two different voltammetric experiments performed under the same conditions, the results are qualitatively reproducible, although there is no complete quantitative identity related to the peak shift and shapes of the waves. This is a first hint that the shift and the crossover,

Fig. 4 Cyclic voltammograms of the oxidation of **1** ($c = 1.5 \times 10^{-2}$ M) in acetonitrile (CH_3CN)/0.1 M TBAPF_6^- , $T = 313$ K, $c(\text{Base}) = 1.5 \times 10^{-2}$ M at different scan rates: **a** 10 V/s, **b** 20 V/s, **c** 50 V/s, $T = 313$ K (first cycle, *full line*; second cycle, *dotted line*)

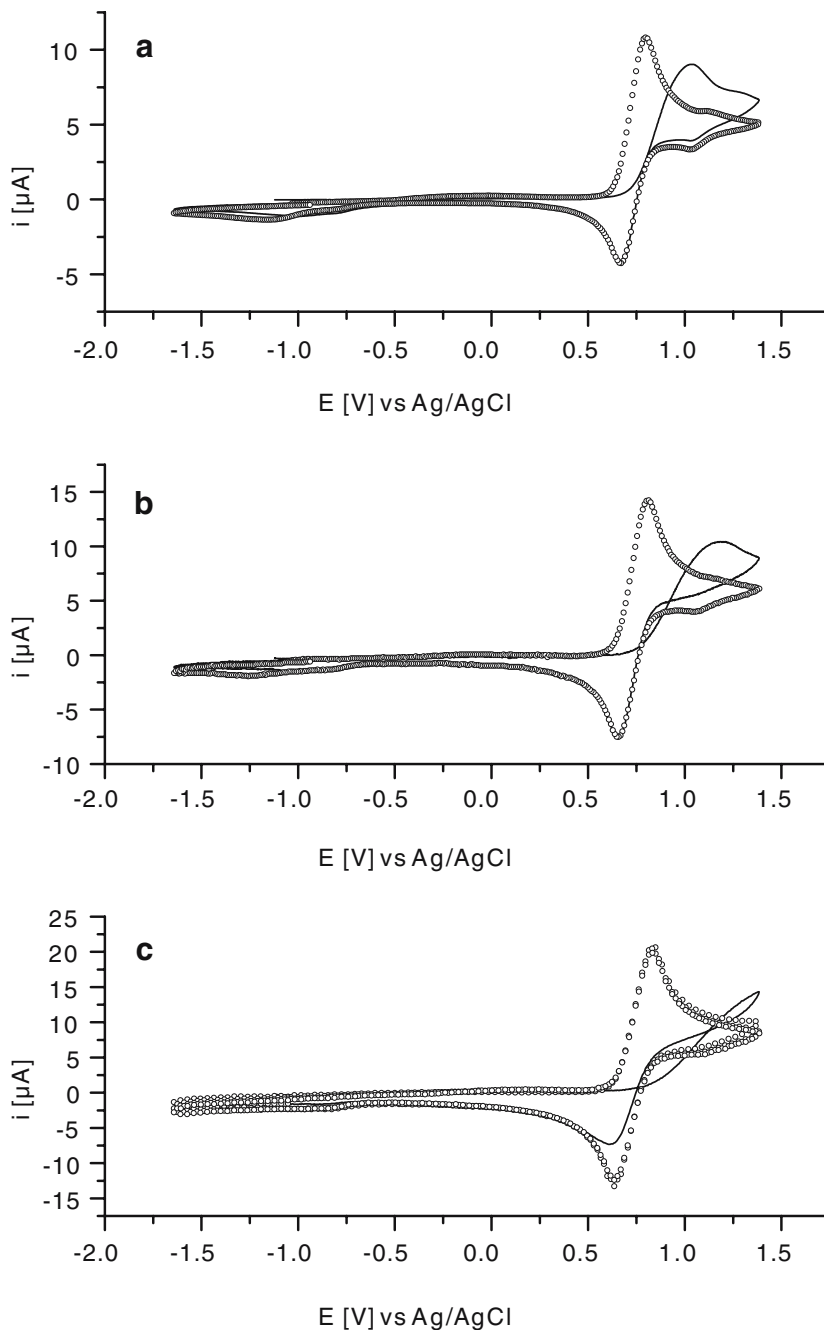
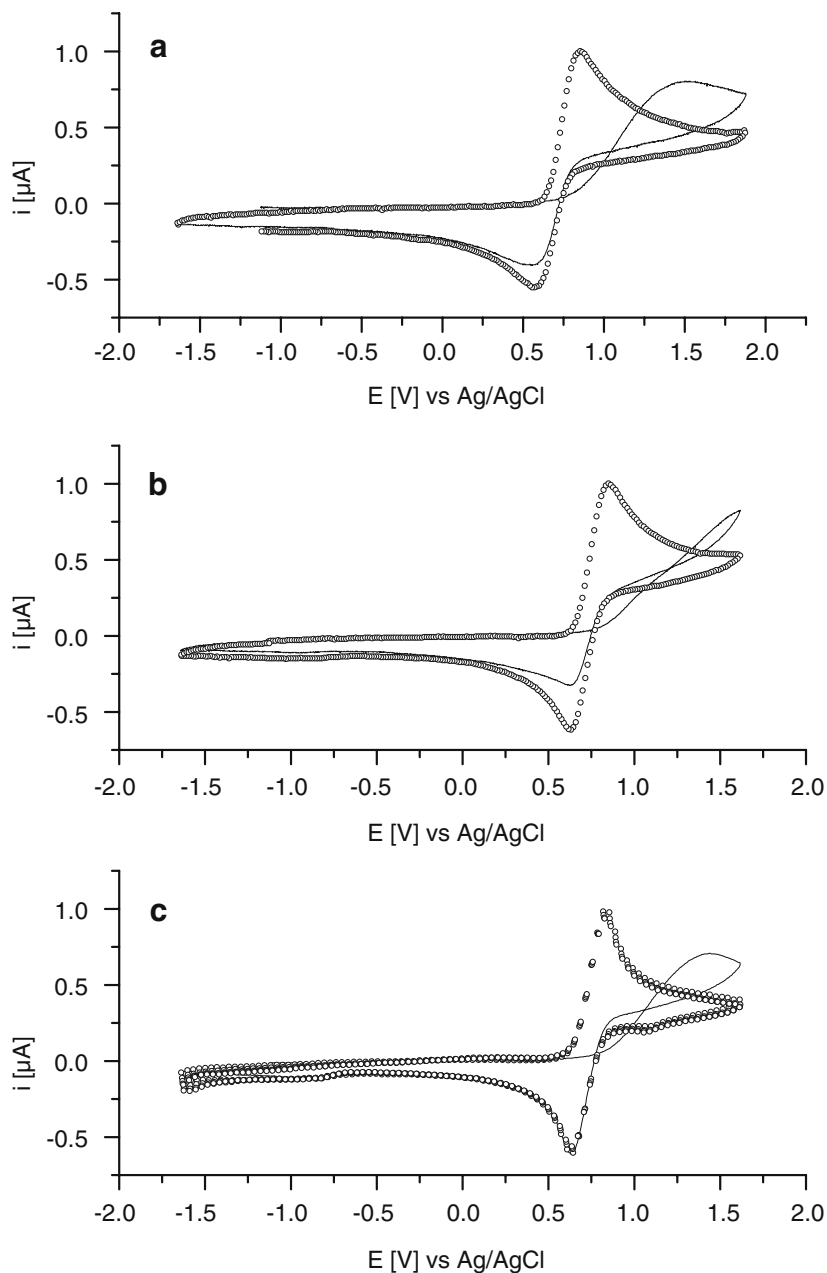


Fig. 5 Cyclic voltammograms of the oxidation of **2** ($c = 1.5 \times 10^{-2}$ M) in acetonitrile (CH_3CN)/0.1 M TBAPF_6 , $v = 50$ V/s, $c(\text{Base}) = 1.5 \times 10^{-2}$ M at different temperatures: **a** 273 K, **b** 293 K, **c** 313 K (current normalized) (first cycle, *full line*; subsequent cycle(s), *dotted line*)



respectively, are rather complex, most likely heterogeneous phenomena, which cannot be described by simple homogeneous reaction kinetics or thermodynamics.

Figure 4 shows cyclic voltammograms recorded at different scan rates after identical waiting times. One can see that the higher the scan rate, the stronger the wave shift and trace crossing. Again, crossing and shift effects disappear in subsequent cycles. These observations lead to the conclusion that the heterogeneous charge transfer kinetics change during voltammetric cycling. Obviously, waiting at a potential of -1.5 V changes the properties of the electrode–solution interface in such a way that the electron transfer becomes

sluggish, an effect which disappears after the oxidation of the redoxactive species. Additional experiments confirm this assumption. If the cause of the potential shift really is kinetic, temperature changes should influence the shift, too. In fact, temperatures above 273 K induce a stronger shift in the first anodic half cycle to positive potentials, while the response in the reverse sweep remains almost unaffected. Representative voltammograms are shown in Fig. 5. One possible explanation for this behaviour is that electrode surface changes occur more efficiently at high temperatures than at 273 K.

When dichloromethane is used as solvent no differences between the first and subsequent scans can be

observed. Only one experiment carried out under the exceptional condition of a boiling solvent showed a crossing but, in contrast to measurements in acetonitrile, this crossing still exists in multisweep experiments, and the shift remains (Fig. 6).

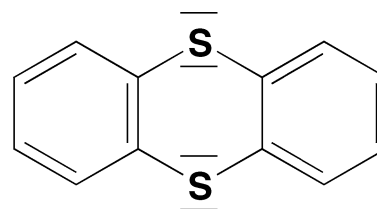
Comparing the measurements of *N,N'*-dimethyl-*p*-toluidine in acetonitrile and dichloromethane, one can state that the characteristic changes between the first and the successive sweeps only occur with acetonitrile as solvent. To this extent, there seems to be a solvent dependence of this sort of “memory effect”.

Thianthrene (2) in various solvents

To verify the solvent dependence and to see if the wave shift might be limited to **1**, a series of measurements with thianthrene (**2**) were performed. Different concentrations of **2** and base were used and different temperatures were applied. The experiments were carried out under three different general conditions: (a) rather low substrate concentration (1.5 mM), no base added, (b) high substrate concentration, no base added, (c) high substrate concentration (6 mM), excess of base added (ratio base: thianthrene 2 : 1).

Unfortunately, there was quite a strong adsorption at approximately +0.25 V, no matter which of the two solvents were used. Adsorption waves could be seen at scan rates above 5 V/s, independent of the concentration of **2** and base (Figs. 7, 8). Nevertheless, the strong shift of the first voltammetric oxidation wave of **2** reappeared after a waiting time at negative potentials, provided an excess of base was present and the experiments were carried out in acetonitrile. The experimental curves are shown in Fig. 7.

Again, the experiments revealed that the “memory effect” was favoured by high temperatures (Fig. 7).



Thianthrene (**2**)

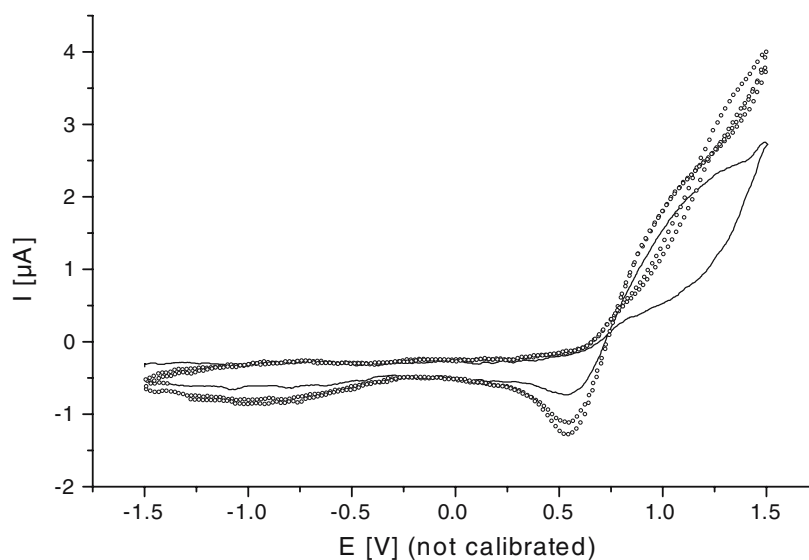
Whereas, at room temperature (296 K) only a drastic shift of the peak potential took place, increasing the temperature up to 313 K led to a crossing. It is interesting to note that in the case of **2** a waiting potential of -1.0 V is sufficient to cause the “memory effect” (Fig. 8).

Surprisingly, experiments in which dichloromethane was used instead of acetonitrile also produced the memory effect in solution. Thianthrene concentrations of 5 mM and higher and an excess of sterically hindered pyridine base resulted in the characteristic shift of the first voltammetric cycle (Fig. 9).

9,10-dimethylantracene (3) in acetonitrile

As final example we studied the oxidation of 9,10-dimethylantracene (**3**) in acetonitrile. In contrast to the other experiments, no memory effect could be observed at room temperatures, even at high concentrations and with an excess of base. Our experiments were successful at elevated temperatures of 328 K and scan rates of ≥ 50 V/s (Fig. 10). Nevertheless, the shift and crossing effects were significantly weaker than in the case of **1** and **2**.

Fig. 6 Cyclic voltammogram of the oxidation of **1** at a Pt-electrode of 0.2 mm-diameter ($c = 2 \times 10^{-2}$ M) in dichloromethane (CH_2Cl_2)/0.1 M TBAPF₆, $T = 333$ K, $v = 100$ V/s, (first cycle, *full line*; subsequent cycles, *dotted line*)



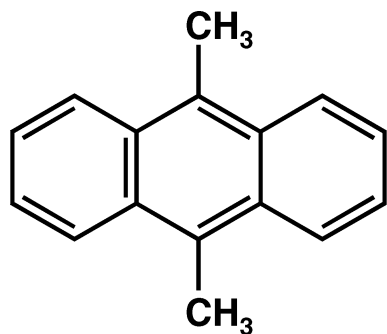
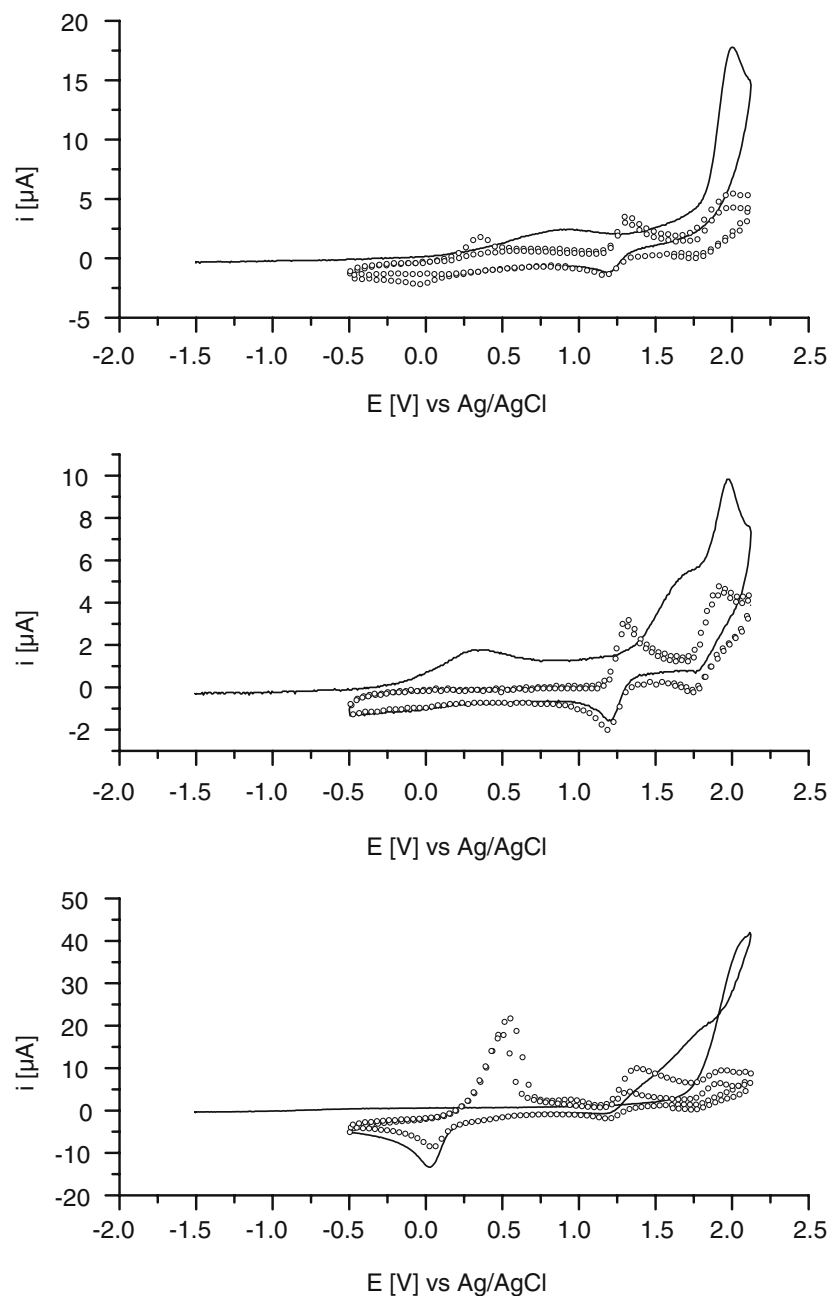
9,10-dimethylanthracene (**3**)

Fig. 7 Temperature dependence of the voltammetric responses of **2**: cyclic voltammogram of the oxidation of **2** ($c = 5 \times 10^{-3}$ M) in acetonitrile (CH_3CN)/0.1 M TBAPF_6 , $v = 100$ V/s, $c(\text{Base}) = 1 \times 10^{-2}$ M, $T = 296$ K (*top*), $T = 303$ K (*middle*), $T = 313$ K (*bottom*) (first cycle, *full line*; subsequent cycles, *dotted line*)



Mechanistic considerations

Based on the described results, what could be the reason for this “memory effect in solution”? As already mentioned, the absence of perfect reproducibility leads us to conclude that heterogeneous rather than homogeneous interactions are the reason for the peak shift in the first scan of cyclic voltammetric experiments. Such heterogeneous interactions take place between the electrode surface on the one hand and the solution on the other hand. The strong scan rate dependence indicates that the charge transfer at the electrode interface is hindered, an effect probably initiated by a passivating layer produced during the waiting time at

Fig. 8 Cyclic voltammogram of the oxidation of **2** ($c = 5 \times 10^{-3}$ M) in acetonitrile (CH_3CN)/0.1 M TBAPF_6 , $v = 100$ V/s, $c(\text{Base}) = 10^{-2}$ M, after a waiting time of 10 min at -1.0 V, $T = 313$ K (first cycle, *full line*; subsequent cycles, *dotted line*)

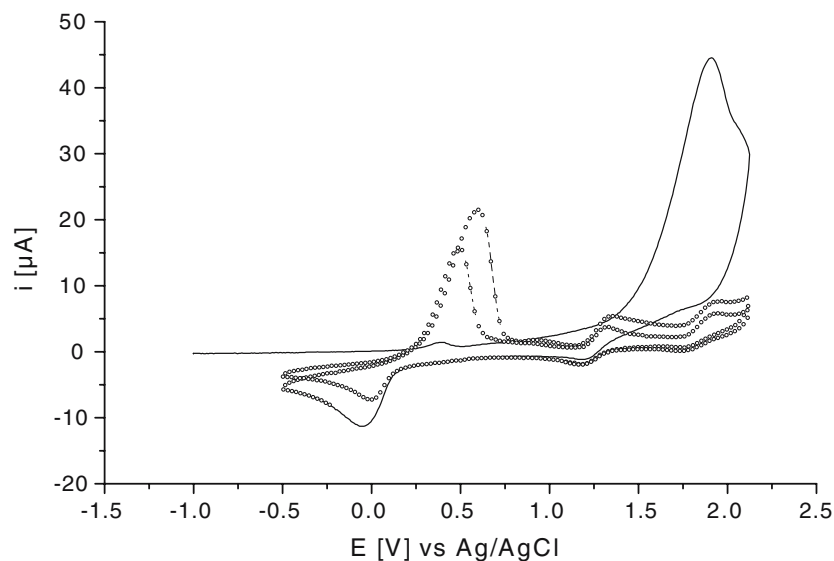
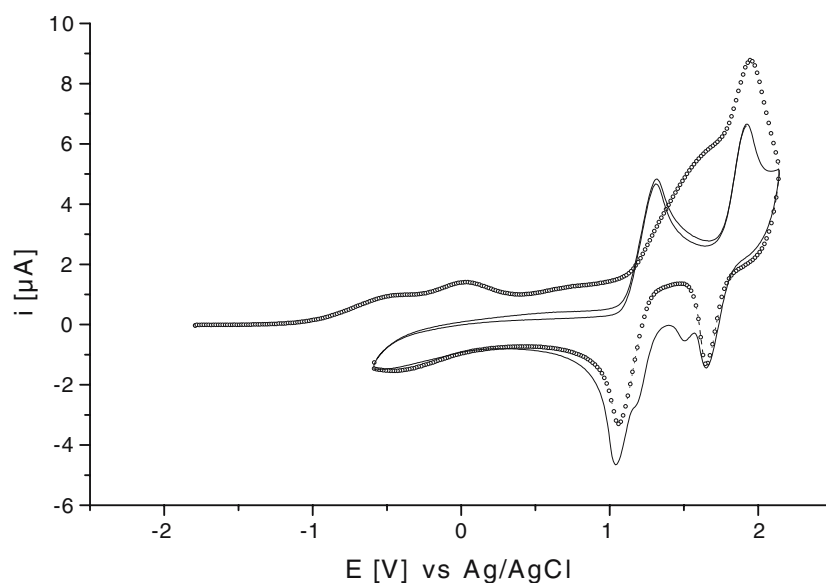


Fig. 9 Cyclic voltammogram of the oxidation of **2** ($c = 1 \times 10^{-2}$ M) in dichloromethane (CH_2Cl_2)/0.1 M TBAPF_6 , $v = 100$ V/s, $T = 303$ K after a waiting time of 10 min (first cycle, *full line*; subsequent cycles, *dotted line*)



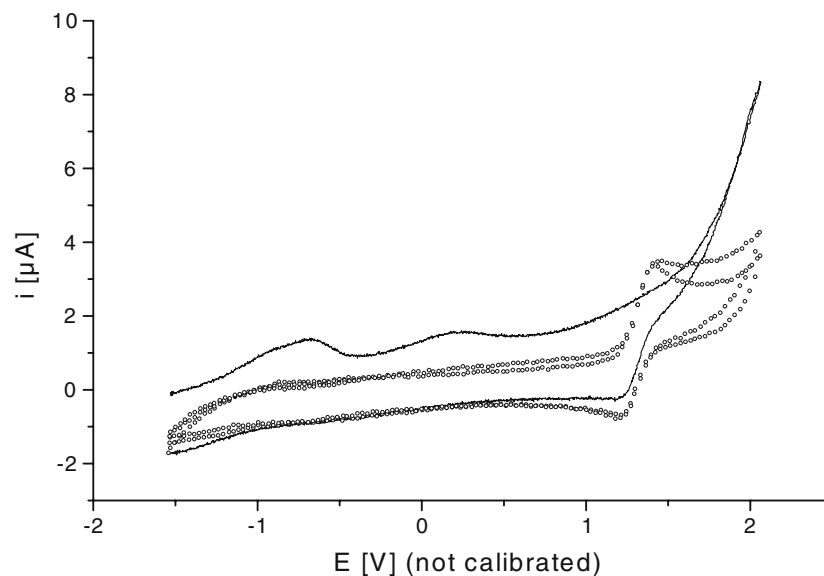
the electrode surface. During oxidation of the electroactive species this passivating layer is rapidly destroyed so that the electron transfer accelerates up to a normal rate. Under these assumptions, the peak shift in the first scan compared to the following ones seems to be due to kinetic hindrance of the electron transfer, which disappears after it has happened once (“autocatalysis”). Obviously, waiting at a sufficiently negative potential changes the electrode surface in such a way that the electron transfer is kinetically hindered. A hint about what happens at highly anodic potentials might be provided by a chronoamperometric measurement at the characteristic polarization potential of -1.5 V. However, the measured current was extremely small and did not give any findings about surface modification at that potential.

So what is the species forming the passivating layer? Principally, one might consider that a slow adsorption of

the pristine organic species takes place, which leads to a higher oxidation potential than that of the redox-species in solution. However, the shape of the first voltammetric cycle is typical for the case of a slow electron transfer of a species in solution.

At least in the case of acetonitrile, a more concrete explanation is possible. It has long been known and described in the literature, that the polymerization of nitriles, as highly unsaturated π -systems, can resemble that of acetylene-compounds [10, 11]. Compared to acetylene or even vinylene compounds, acetonitrile, indeed nitriles in general, need stronger activation. Thus, a polyacetonitrile could be formed using a base as catalyst. This polymer might be adsorbed onto the electrode surface, forming a passivating layer and thus hindering the heterogeneous electron transfer between electrode and substrate. It should be mentioned that, according to the literature, metal chlorides as electrophilic Lewis

Fig. 10 Cyclic voltammogram of the oxidation of **3** ($c = 2 \times 10^{-2}$ M) in acetonitrile (CH_3CN)/0.1 M TBAPF_6 , $v = 50$ V/s, $T = 328$ K $c(\text{Base}) = 3 \times 10^{-1}$ M (first cycle, *full line*; subsequent cycles, *dotted line*)



acids are necessary. The exact reaction pathway is described by Oikawa et al. [12, 13]. After removal of a proton, a carbanion is formed, which is stabilized by forming a complex with the metal chloride. Another acetonitrile molecule is protonated, and the resulting carbocation couples with the carbanion. In our case, no metal chloride was present. Nevertheless, a similar mechanism is possible thanks to the amphoteric character of acetonitrile: the base could deprotonate an acetonitrile molecule and give its proton to another acetonitrile molecule. Although, the thermodynamic equilibrium will lie on the side of the neutral acetonitrile in both reactions, the small amounts of carbocations and carbanions might suffice to form polyacetonitrile, which blocks the electrode.

Conclusion

A phenomenon corresponding to the so-called memory effect, known up to now only from the potentiodynamic charging/discharging of polymer films, has been observed for small molecules in solution, too. The difference in form and shape between the first and subsequent sweeps has been observed for a number of organic π -systems and requires special experimental

conditions, e.g. polarizing the electrode for several minutes at negative potentials and using relatively high scan rates. Moreover, it is favoured in polarization at high temperatures. These findings lead to the conclusion that this sort of memory effect in solution has its origin in surface effects and their kinetics. A more detailed explanation requires further experiments and analysis.

References

1. Villeret B, Nechtschein M (1989) *Phys Rev Lett* 63:1285
2. Odin C, Nechtschein M (1991) *Synth Met* 44:177
3. Tourillon G, Garnier F (1984) *J Electroanal Chem* 161:51
4. Andrieux CP, Audebert P, Hapiot P, Nechtschein M, Odin C (1991) *J Electroanal Chem* 305:153
5. Heinze J, Störz bach M, Mortensen J (1987) *Ber Bunsenges Phys Chem* 91:960
6. Heinze J, Bilger R, Meerholz K (1988) *Ber Bunsenges Phys Chem* 92:1266
7. Otero TF, Grande H, Rodriguez J (1997) *J Phys Chem B* 101:8525
8. Grande H, Otero TF (1998) *J Phys Chem B* 102:7535
9. Kiesele H (1981) *Anal Chem* 53:1952
10. Kargin VA, Kabanov VA, Zubov VB, (1961) *AP Dokl Akad Nauk SSSR* 139:605
11. Wöhrl D (1972) *Adv Polym Sci* 10:35
12. Oikawa E, Kambara S (1964) *Bull Chem Soc Japan* 37:1849
13. Oikawa E, Mori K, Saito G (1966) *Bull Chem Soc Japan* 39:1182