CROATICA CHEMICA ACTA CCACAA **64** (4) 625–635 (1991)

ISSN-0011-1643
UDC 541.1
CCA-2029

Original Scientific Paper

Solvent Polarity and Supporting Electrolyte Concentration Influences on Faradaic Conductivity of Quinhydrone Solutions

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Received April 19, 1991

Using micrometer twin-electrode thin-layer cell, the heterogeneous redox reaction of quinhydrone is explored in water and in mixed solvents with the ratios of toluene : acetonitrile = 9:1 and 4:6. The concentration of the supporting electrolyte is varied from zero to 0.5 mol/L. Supporting electrolyte decreases the kinetic polarization of electrodes and increases the faradaic current until concentration polarization occurs. In dilute electrolytes, the migration of redox species influences the limiting current significantly. The mechanism of reduction and oxidation of quinhydrone and the conditions required for permanent faradaic conduction are determined empirically.

INTRODUCTION

There is considerable interest in the investigation of electrochemical reactions in the absence of any deliberately added electrolyte, or in the presence of very low electrolyte concentrations.[1-7] Besides, faradaic charge transfers were analyzed in dry electroactive polymers without either electrolyte or solvent[8] added. The experiments were performed with microelectrodes[1-6] and sandwich electrodes.[7,8]

The purpose of this communication is to report on the influence of solvent polarity and concentration of a supporting electrolyte on heterogeneous redox reactions at an electrode surface, and to discuss the experimental conditions required for permanent faradaic conductivity. The redox reaction of quinhydrone in water and toluene/acetonitrile mixed solvents with different electrolytes was investigated. The experiments were performed with a micrometer twin-electrode thin-layer cell,[9,10] which is convenient for conductometric measurements because of the small distance between the electrodes mitigating ohmic resistance. Micrometer cells are very sensitive and enable the measurement of ultra-low conductivities.

Quinhydrone is a well known redox couple.[11-28] In a buffered water solution , its polarographic response is a single, reversible, two-electrons wave:[11-14] $Q + 2e^- + 2H_3O^+ \rightleftharpoons H_2Q + 2H_2O$. Electroactive species[12,13] are Q and Q^{2-}, but the anion Q^{2-} is in dissociation equilibrium[15] with HQ^- and H_2Q. In organic, aprotic solvents, quinhydrone is a mixture of two redox couples.[16-18] Quinone reduces in two steps.[16,19-21] The first step is reversible and the product is a semiquinone anion radical $Q^{\cdot -}$. The second step is irreversible and the product is quinone dianion Q^{2-}. Weak acids, like phenol,[22] neutralize Q^{2-} to hydroquinone H_2Q. Strong acids neutralize $Q^{\cdot -}$ to semiquinone radical $HQ^{\cdot}$, which undergoes fast reduction to HQ^- and the protonation to H_2Q. In the presence of strong acids, the two steps of quinone reduction emerge in a single, two-electron, irreversible wave.[22] Oxidation of hydroquinone occurs at about 1.10 V *vs.* SCE and involves simultaneous transfer of two electrons:[16,23-27]

$$H_2Q \longrightarrow HQ^+ + 2e^- + H^+.$$

The formation of dimer HQ–QH and its subsequent disproportionation were proposed,[16,23] but seriously questioned by several investigators.[25-27] The re-reduction of HQ^+ occurs at + 0.13 V *vs.* SCE.[23]

EXPERIMENTAL

Toluene (Fisher) and acetonitrile (Burdick & Jackson) were distilled and stored over 4-Å molecular sieves. Water was treated by »Bantam« and »Sybron-Barnstead« (both Fisher) demineralizers and then twice distilled in a »Corning« distillation apparatus. Quinhydrone (H_2Q/Q, Eastman Kodak), hydroquinone (H_2Q, purified, Fisher), tetrahexylammonium chloride (THA-Cl, Fisher), $LiClO_4$ (anhydrous, G. Frederic Smith) and $NaClO_4 \cdot H_2O$ (purified, Fisher) were used as received.

The two-platinum-electrode thin-layer cell[9] was constructed by attaching Pt disk (0.2 cm^2) to the spindle of a Starrett-2A micrometer and to a Starrett-212 adapter which was insulated from the main body by a slip of Scotch tape.[10] The upper (spindle) electrode was shrouded with a 1 cm Teflon cylinder; the lower electrode was also shrouded with Teflon which had a concentric groved well and wall to provide a cavity for reactant solution. The electrodes were polished to mirror finish with 1 μm alumina.

The two-electrodes experiments were performed without any reference electrode. For three-electrodes measurements, the reference electrode was a silver wire thickly covered with electrolytically-produced silver chloride and directly immersed into the investigated solution, without a salt bridge. All experiments were performed with a PAR-174/A polarographic analyzer (Princeton Applied Research, maximum sensitivity 0.02 μA/10 V). The current responses were recorded by the use of x-y recorders (Hewlett-Packard 7046/A, 7004/B or 7015/B). The sensitivity of the set-up was 2×10^{-11} A/mm.

RESULTS AND DISCUSSION

Water

Most of experiments were performed with a two-electrode micrometer cell, which was linearly charged between 0 and 1.5 V, and the current responses were recorded.

The solution of quinhydrone (quinone + hydroquinone; H_2Q/Q at a ratio of 1:1) in pure distilled water, without any deliberately added supporting electrolyte, exhibits

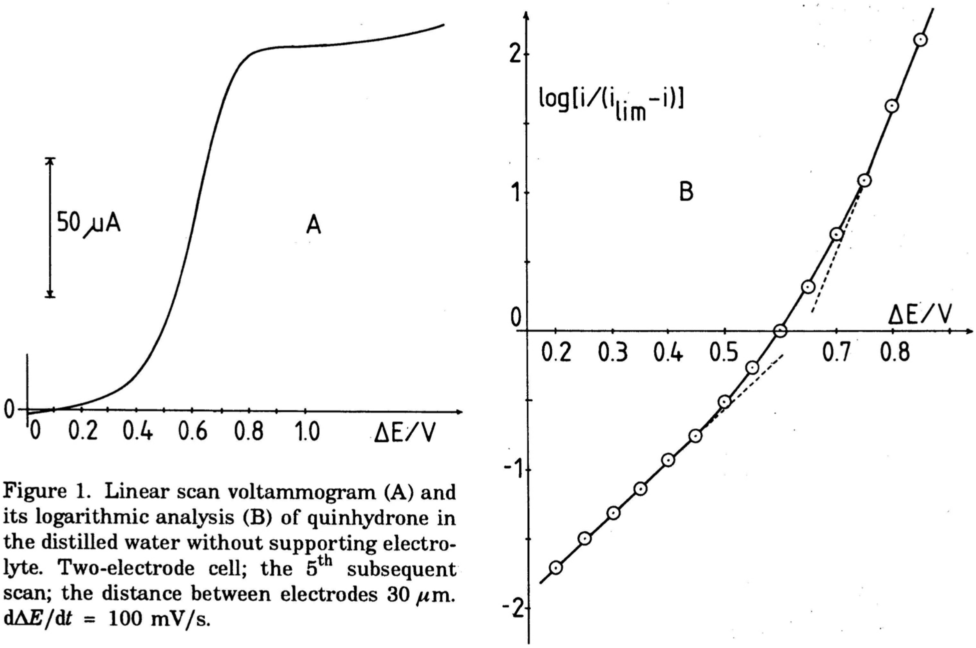

Figure 1. Linear scan voltammogram (A) and its logarithmic analysis (B) of quinhydrone in the distilled water without supporting electrolyte. Two-electrode cell; the 5th subsequent scan; the distance between electrodes 30 μm. $d\Delta E/dt$ = 100 mV/s.

a well-defined polarographic wave with the half-wave potential $\Delta E_{1/2}$ = 0.60 V, as shown in Figure 1. Logarithmic analysis of the wave yields a curve with two asymptotes. The lower one has a slope of 265 mV, while the upper has a slope of 95 mV. The distance between the electrodes was 30 μm. Steady-state responses (the regular waves without voltammetric maxima prior to the limiting currents) were observed for $d\Delta E/dt$ = 50 mV/s. Under the influence of supporting electrolyte (1 mol/L $NaClO_4$), the half-wave potential shifts to $\Delta E_{1/2}$ = 0.58 V and the limiting current decreases to about 90% of the value recorded in the pure distilled water. That decrease indicates the influence of the migration current on the total limiting current in pure distilled water. The observed shift of the half-wave potential to 0.60 V appears because of the local changes of the pH in the vicinity of the electrodes:[13]

$$\text{Cathode: } Q + 2e^- + 2H_2O \longrightarrow H_2Q + 2OH^- \qquad (1)$$

$$\text{Anode: } H_2Q + 2H_2O \longrightarrow Q + 2e^- + 2H_3O^+ \qquad (2)$$

In a well buffered solution, the half-wave potential appears at 0 V.[12,13]

Toluene/acetonitrile/LiClO₄

Experiments were performed with 0.001 mol/L hydroquinone and quinhydrone solutions in the mixed solvent toluene : acetonitrile = 4:6, using a three-electrode cell. The supporting electrolyte was 0.5 mol/L $LiClO_4$.

Cyclic voltammetric response of H_2Q is shown in Figure 2, peaks I and II. The H_2Q oxidation peak appears at +0.89 V *vs.* Ag/AgCl (peak I, dE/dt = 50 mV/s). The peak current is a linear function of the square root of scan rate, ranging from 24 μA (for 10 mV/s) to 90 μA (for 200 mV/s). The peak potential changes from +0.86 V (for 10 mV/s) to +0.93 V *vs.* Ag/AgCl, for 200 mV/s. The peak of re-reduction appears at +0.17 V *vs.* Ag/AgCl (peak II). It appears only if preceded by the oxidation of H_2Q. The hydroquinone from the solution of quinhydrone reacts in the same way as the pure solution of hydroquinone. Eggins and Chambers[23] have ascribed the oxidation peak to the reaction: $H_2Q \longrightarrow HQ^+ + H^+ + 2e^-$, and the peak of the re-reduction to the same reaction in inverse direction. The proton was assumed to be loosely bound to the solvent molecules and supported by anions of the electrolyte. In the quinhydrone solution, partial protonation of quinone may be assumed: $H_2Q^{\cdot +} + Q \longrightarrow HQ^{\cdot} + HQ^+$. The radical $HQ^{\cdot}$, formed by the dissociation of $H_2Q^{\cdot +}$, is very reactive and reacts immediately to form HQ^+. The single, two-electrons oxidation wave of H_2Q has been observed by several investigators.[24-27]

The reduction of quinone from the solution of 0.001 mol/L quinhydrone in 0.5 mol/L $LiClO_4$ appears at –0.28 V *vs.* Ag/AgCl, as shown in Figure 2, peak III. The reoxidation peak appears at –0.16 V *vs.* Ag/AgCl (peak IV). According to Peover and Davies,[28] the reduction of quinone in the presence of lithium ions in DMF includes the formation of a lithium-semiquinone complex radical in the first reduction step, as well as a lithium complex with the quinone dianion in the second step. The formation of $LiQ^{\cdot}$ shifts the half-wave potential of the first, reversible wave in the positive direction. The $E_{1/2}$ of the second, irreversible wave is shifted in the positive direction for two reasons: because of the formation of Li_3Q^+ complex species and because the complex radical $LiQ^{\cdot}$ is reduced much faster than the anion radical $Q^{\cdot -}$. The shift of the second wave may lead to the formation of the single, two-electron wave. Instead of the formation of Li_3Q^+, in the solution of quinhydrone the protonation is more probable: $LiQ^- + H_2Q \longrightarrow 2HQ^- + Li^+$. The hydroquinone is a weak acid. Its first dissociation constant is almost equal to the dissociation constant of phenol:[15] 10^{-10} Phenol readily

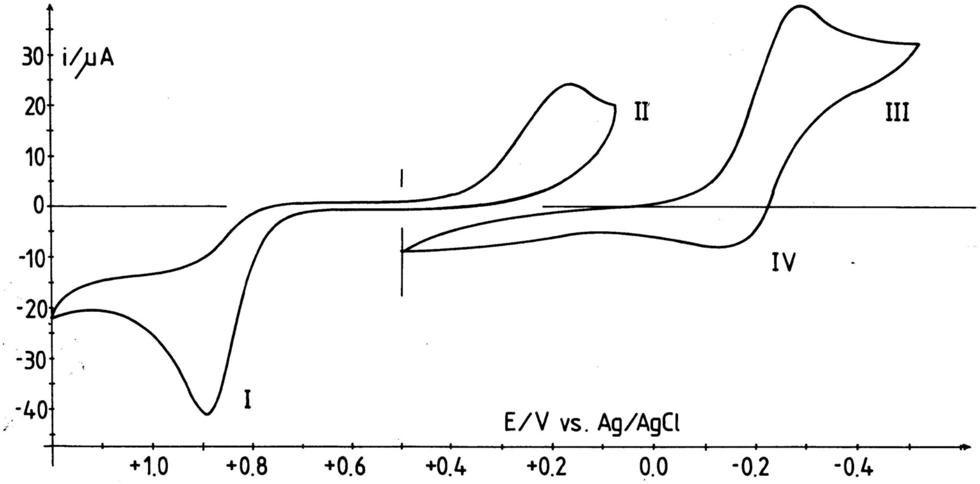

Figure 2. Cyclic voltammetry of hydroquinone and quinone in the mixed solvent toluene : acetonitrile 4:6. Two separate experiments. The supporting electrolyte 0.50 mol/L $LiClO_4$. The three-electrodes cell; dE/dt = 50 mV/s.

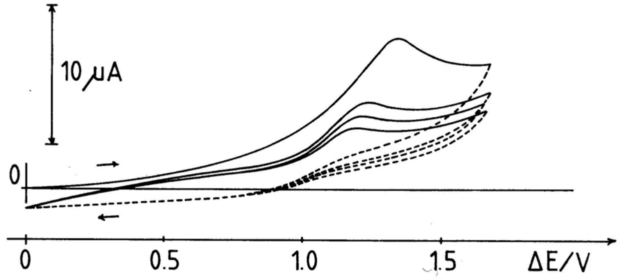

Figure 3. Multiple cyclic voltammetry of 0.001 mol/L quinhydrone in 0.50 mol/L $LiClO_4$. Mixed solvent, toluene : acetonitrile 4:6; two-electrodes cell; the distance between electrodes 20 μm; $d\Delta E/dt$ = 200 mV/s.

protonates quinone dianion, but not the anion radical. Hydroquinone has been used as a proton donor in the DMF.[29]

Experiments with a two-electrode micrometer cell (d = 20 μm) have shown that cyclic voltammograms of 0.001 mol/L quinhydrone in 0.5 mol/L $LiClO_4$ exhibit maxima at ΔE_{max} = 1.20 V, which are followed by limiting currents, as shown in Figure 3. The observed ΔE_{max} is very close to the difference between the potentials of the maximum oxidation current of hydroquinone and the maximum reduction current of quinone. Experiments at constant potential (ΔE = 1.30 V) have shown that a 20 μm layer of this solution can maintain a constant current of 20 μA for more than 20 minutes. This indicates that two redox couples must exist (R_1 being reduced to P_1 at the first electrode and R_2 being oxidized to P_2 at the second one). The $E_{1/2}$ of the wave is the difference between the half-wave potentials of these processes. If only one redox couple exists (R_1 is reduced to P_1 at the first, and P_1 is oxidized to R_1 at the second electrode), the observed $\Delta E_{1/2}$ should be close to 0 V. Besides, a certain mechanism of regeneration of both reactants R_1 and R_2 must exist. Otherwise, the thin layer of solution between the electrodes would not be able to maintain the constant current during 20 minutes of electrolysis at constant potential. The simplest possible mechanism includes a reaction between the products: $P_1 + P_2 \longrightarrow R_1 + R_2$.

Considering the reactions of H_2Q and Q, the following mechanism may be proposed:

$$\text{Cathode: } Q + Li^+ + 2e^- \longrightarrow LiQ^- \tag{3}$$

$$LiQ^- + H_2Q \longrightarrow 2HQ^- + Li^+ \tag{4}$$

$$\text{Anode: } H_2Q + Q \longrightarrow 2HQ^+ + 2e^- \tag{5}$$

This includes recombination in the middle of the thin layer of solution:

$$HQ^+ + HQ^- \longrightarrow H_2Q + Q \tag{6}$$

The proposed mechanism is very simple, but satisfies the requirements for maintaining the steady-state faradaic conductivity.

Toluene/acetonitrile/THA-Cl

Toluene is a non-polar and aprotic solvent. Between 0 and 1.5 V, its specific conductivity for direct current is $\kappa^o = 3 \cdot 10^{-12}$ S/cm, if measured by using a two-electrode micrometer cell. The mixture of toluene and acetonitrile exhibits only capacitive current if $\Delta E < 1.5$ V. The apparent capacitance, defined as: $C^* = (i/A)/(\mathrm{d}\Delta E/\mathrm{d}t) = [C + \Delta E(\mathrm{d}C\ \mathrm{d}\Delta E)]/A$, is 15 μF/cm^2 (where A is the electrode surface area). The capacitance does not change if the ratio between toluene and acetonitrile is changed from 9:1 to 4:6. Quinhydrone is poorly soluble in toluene. Its saturated solution increases the d.c. conductivity to $\kappa^o = 10^{-11}$ S/cm, at $\Delta E = 1.5$ V. Tetrahexylammonium chloride (THA-Cl) is well soluble in toluene (more than 1 mol/L) and its potential window in the two-electrodes cell is 1.7 V.[16] The addition of THA-Cl to a saturated solution of H_2Q/Q in toluene changes the d.c. conductivity. If [THA-Cl] < 10^{-3} mol/L, it gradually increases to $\kappa^o = 6 \cdot 10^{-11}$ S/cm. With $5 \cdot 10^{-3}$ mol/L THA-Cl, the first capacitive current appears and increases proportionally to the THA-Cl concentration. It indicates that THA-Cl in toluene dissociates to a certain degree. However, no sign of the faradaic current corresponding to the redox reaction of H_2Q/Q can be observed below [THA-Cl] = 0.05 mol/L.

The concentration of quinhydrone in toluene could be increased if toluene were mixed with a certain amount of acetonitrile. Such mixed solvent possesses a higher degree of polarity and better supports the ionic species that appear as intermediates in the redox reactions of quinhydrone. If the ratio between toluene and acetonitrile is 7:3 and the concentration of H_2Q/Q is 0.01 mol/L, the faradaic response of the quinhydrone could be recorded even if no supporting electrolyte is added. As shown in Figure 4, the response is a wave with a marked prewave and half-wave potential near 1.17 V. It is interesting that the limiting current increases with repetition of voltammetric cy-

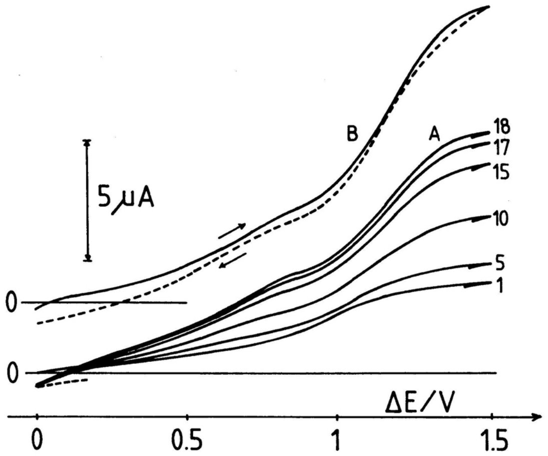

Figure 4. Multiple cyclic voltammetry of 0.01 mol/L quinhydrone in the mixed solvent toluene : acetonitrile 7:3 without supporting electrolyte. Two-electrode cell; the distance between electrodes 30 μm; $\mathrm{d}\Delta E/\mathrm{d}t$ = 100 mV/s. A: only cathodic scan; the numbers of scans indicated beside the curves. B: the 20th scan; both cathodic and anodic scans.

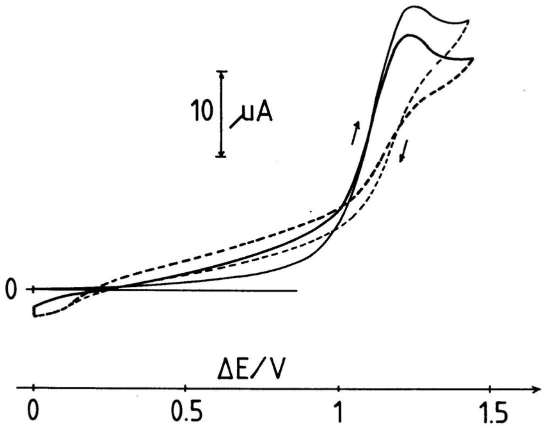

Figure 5. Multiple cyclic voltammetry of 0.001 mol/L quinhydrone in 0.5 mol/L THA-Cl. Mixed solvent, toluene : acetonitrile 9:1; two-electrode cell; the distance between electrodes 30 μm; $d\Delta E/dt$ = 50 mV/s; thin line: the 1st cycle; thick line: the 5th and subsequent cycles.

cling. In the first cycle only one wave appears, and then gradually the prewave develops while the limiting current increases. It cannot be said for certain what causes this phenomenon. The polarographic wave of the redox reaction of H_2Q/Q can be recorded also in a solvent with a ratio toluene : acetonitrile = 8:2 but it is not as nicely developed. However, when the ratio was 9:1, no faradaic response of H_2Q/Q could be registered in the absence of the supporting electrolyte. In the range $\Delta E < 1.5$ V, the solution exhibits only the capacitive current, which is similar to that of the pure solvent mixture. The experiments show that, as in the pure distilled water, the redox reaction of the H_2Q/Q can occur in the absence of the supporting electrolyte, if the solvent possesses a sufficient degree of polarity. Moreover, if the polarity is not sufficient, the redox reaction does not occur even in the presence of a considerable amount of supporting electrolyte.

To investigate the influence of supporting electrolyte on redox reaction in media of low dielectric constant, we have chosen the 1.00×10^{-3} mol/L solution if quinhydrone in a mixed solvent with a ratio toluene : acetonitrile 9:1. This system exhibits very low conductivity in the absence of supporting electrolyte, but in the presence of 0.50 mol/L THA-Cl, the faradaic response of H_2Q/Q is fully developed. The result of the multiple cycling linear scan voltammetric experiment is shown in Figure 5. The peak current decreases in the second and the subsequent cycles, until it reaches a certain value. For $d\Delta E/dt$ = 50 mV/s, the peak potential is ΔE_{max} = 1.25 V. If the potential scan rate is smaller than 15 mV/s, the response is a polarographic wave without voltammetric maximum. Its half-wave potential is $\Delta E_{1/2}$ = 1.06 V. Its logarithmic analysis is a curve with two asymptotes. The lower one has a slope of 220 mV, while the upper one has a slope of 100 mV. The limiting current is a linear function of quinhydrone concentration. At higher scan rates, the peak currents are linear functions of the square root of the scan rate and $[H_2Q/Q]$. To investigate the current response under steady-state conditions, the electrodes were charged to a certain constant potential and the current was monitored during 25 minutes (»*i-t*« curves). Before the potential was

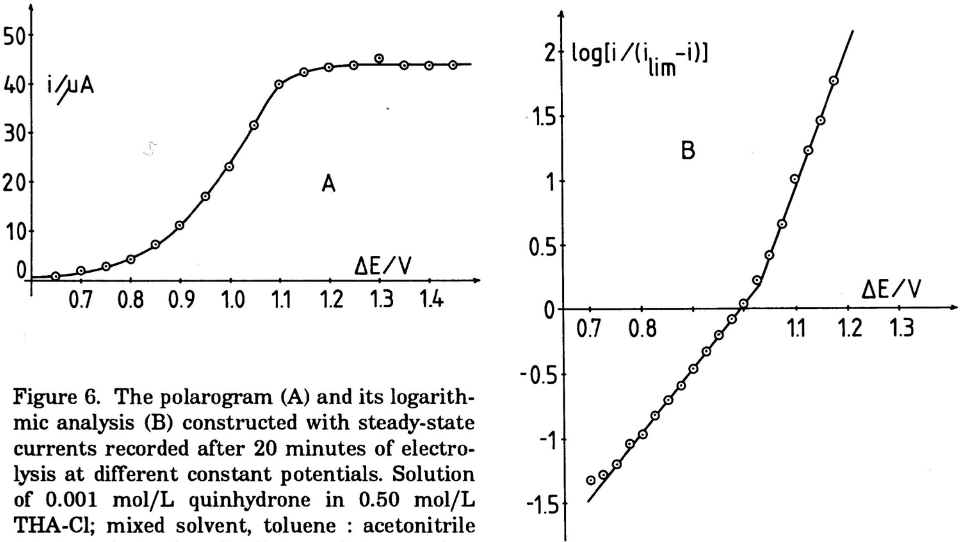

Figure 6. The polarogram (A) and its logarithmic analysis (B) constructed with steady-state currents recorded after 20 minutes of electrolysis at different constant potentials. Solution of 0.001 mol/L quinhydrone in 0.50 mol/L THA-Cl; mixed solvent, toluene : acetonitrile 9:1; two-electrode cell; distance between electrodes 20 μm.

changed to some other values and the measurement was repeated, the electrodes were disconnected and the micrometer was unscrewed to increase the distance between the electrodes. After the solution was well mixed, the electrodes were again brought close together to the controlled distance. This procedure was always used for renewing the thin layer of the solution between the electrodes. The observed »*i-t*« curves were constant in the range between 1 minute and 25 minutes. The dependence of these steady-state currents (recorded after 20 minutes of electrolysis) on the applied potentials is shown in Figure 6A. The half-wave potential of this wave is $\Delta E_{1/2} = 0.99$ V. Its logarithmic graph (Figure 6B) is a curve with a lower asymptotic slope of 200 mV and the upper slope of 95 mV. These slopes are similar to those of the polarographic wave recorded with very slow scan rate, as well as to those of the wave recorded in pure distilled water. From the similarity of slopes we may assume that the number of electrons transferred in the single act of reduction, or oxidation, could be the same in both water and toluene. Utilizing the equation for the steady-state current: $i = nFADc_{ox}/\delta$, where δ is a half-distance between two Pt micrometer electrodes, the effective diffusion coefficient of quinhydrone was estimated as $D = 1.20 \times 10^{-6}$ cm^2/s, if $n = 2$. Redox responses of quinone and hydroquinone, measured in this medium by a three-electrode cell, are very similar to those of Figure 3. It seems that the reduction step (III) is not crucial for maintaining the steady-state faradaic conductivity in the toluene/acetonitrile mixed solvents. The mechanism is probably influenced by traces of water present in solvents and the supporting electrolyte.

The influence of THA-Cl concentration on the LSV responses of H_2Q/Q is shown in Figure 7. The main characteristic of these results is the absence of concentration-polarization when the concentration of the supporting electrolyte is less than or equal

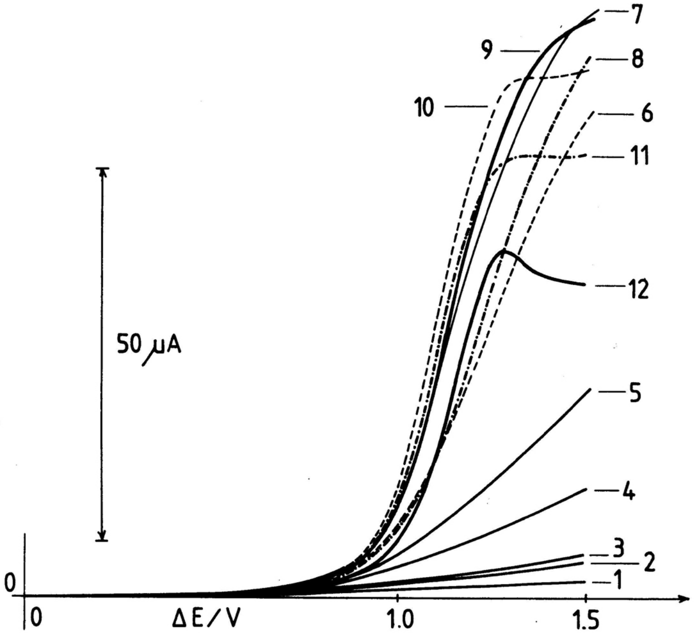

Figure 7. The dependence of voltammetric response (the first scan) of 0.001 mol/L quinhydrone solution in the mixed solvent (toluene : acetonitrile 9:1) on the concentration of the THA-Cl. Two-electrode cell; distance between electrodes 30 μm; $d\Delta E/dt$ = 50 mV/s; [THA-CL]/(mol/L) = 0.0001 (1), 0.0005 (2), 0.001 (3), 0.005 (4), 0.01 (5), 0.03 (6), 0.05 (7), 0.07 (8), 0.1 (9), 0.2 (10), 0.3 (11) and 0.5 (12).

to 0.01 mol/L. In this range of THA-Cl concentration, the current increases monotonically over the entire potential range from 0 to 1.5 V. Such a current-potential curve appears when the rate of a certain redox reaction at an electrode surface is much smaller than the mass transfer rate of the reactant. If the concentration of THA-Cl is smaller than 0.10 mol/L, the LSV peaks of H_2Q/Q appear in the form of a shoulder. The current at 1.50 V increases proportionally to the increase of THA-Cl concentration. In the range of the highest THA-Cl concentrations, the faradaic response of H_2Q/Q involves more pronounced limiting currents, which decreases as the THA-Cl concentration increases. The relationship between the maximal LSV current response of H_2Q/Q and the logarithm of THA-Cl concentration is shown in Figure 8. The current recorded at ΔE = 1.50 V was used when the response of H_2Q/Q did not exhibit either limiting or maximal current. The results obtained with various scan rates follow the same path, which is marked by a maximal response at 0.07 mol/L THA-Cl. The maximum is probably caused by the migration of electroactive species. The increase of the concentration of the supporting electrolyte simultaneously accelerates the charge transfer of H_2Q/Q and decreases its migration.

This measurement indicates that the polarity of the solvent strongly influences faradaic conductivity. If a non-ionic redox couple is dissolved in non-polar, aprotic sol-

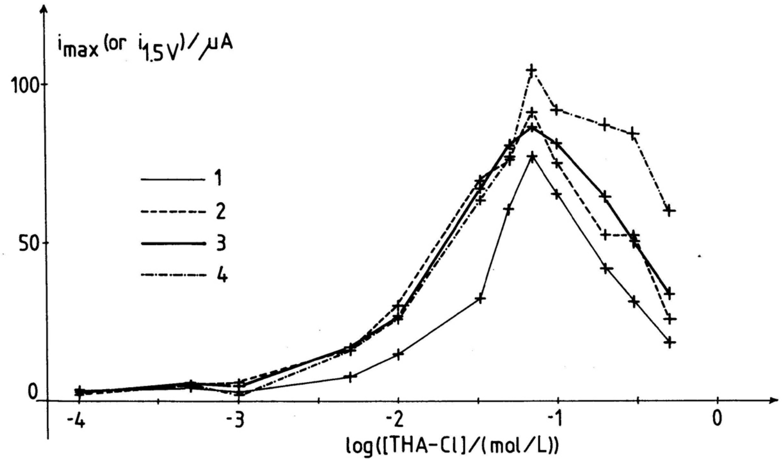

Figure 8. The relationship between the maximal current responses of quinhydrone and the logarithm of the THA-Cl concentration. If the response of H_2Q/Q does not exhibit either limiting, or maximal current, the current recorded at ΔE = 1.50 V is used instead. Solution of 0.001 mol/L quinhydrone in the mixed solvent (toluene : acetonitrile 9:1); two-electrode cell; distance between electrodes 30 μm; the scan rate in mV/s = 5 (1), 20 (2), 50 (3) and 200 (4).

vent and no supporting electrolyte is added, the faradaic reaction does not occur because the ionic species which would result from the charge transfer cannot be solvated and supported by the solvent. The faradaic conductivity can be most significantly enhanced if the polarity of the solvent is increased by addition of polar solvent to the non-polar solvent. In a mixed solvent with a ratio toluene : acetonitrile 7:3, the faradaic response of quinhydrone is observed in the absence of supporting electrolyte. In pure distilled water, this response is as well developed as it was in a 1.00 mol/L solution of $NaClO_4$ in water. It is less important if ionic impurities are present in the polar solvent because the faradaic reaction is not primarily promoted by ions but rather by polarity. In a solvent of low polarity, the presence of ions of the supporting electrolyte strongly influences the charge transfer rate at the electrode surface. If the concentration of THA-Cl is low, the faradaic current increases proportionally to the potential difference; concentration polarization occurs only if the THA-Cl concentration is rather high. The solvent is polar enough to produce a capacitive current and to support the dissociation of the THA-Cl. Consequently, it is probably able to solvate the ionic products of quinhydrone electrolysis and to allow their migration. If THA-Cl influenced the mass transfer, the concentration polarization would appear at the lowest THA-Cl concentration and the limiting current would increase proportionally to the concentration of THA-Cl. If there is no concentration polarization, then the charge transfer at the electrode surface should be the rate determining step. The ions THA^+ and Cl^- can influence the charge transfer if they change the conditions in the double layer at the electrode surface. It seems that the charge transfer rate increases proportionally to the concentrations of the ions of the supporting electrolyte in the double layer.

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SAŽETAK

Utjecaj polarnosti otapala i koncentracije osnovnog elektrolita na faradaysku vodljivost otopina kinhidrona

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Mikrometarska tankoslojna ćelija s dvije platinske elektrode korištena je za mjerenje permanentne faradayske vodljivosti otopina kinhidrona u vodi i u miješanim otapalima s omjerom toluena prema acetonitrilu 9:1 i 4:6.

Koncentracija osnovnog elektrolita mijenjana je od 0 do 0.5 mol/L. Osnovni elektrolit smanjuje elektrokinetičku polarizaciju i povećava faradaysku struju, sve dok ne dođe do koncentracijske polarizacije elektroda. Kod niskih koncentracija elektrolita, migracija elektroaktivnih vrsta bitno povećava graničnu struju. Empirijski su određeni uvjeti koje treba zadovoljiti da bi se ostvarila permanentna faradayska vodljivost. Pretpostavljen je mehanizam redoks-reakcije kinhidrona pod odabranim uvjetima.