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Short-lived Inorganic Species: Physico-chemical Properties and Kinetics of Transient Inorganic Anions

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The redox properties of inorganic unstable anions, produced by pulse irradiation of aqueous solutions, have been studied by a fast quasi-coulostatic technique, and the results compared to those obtained by a quasi-galvanostatic technique.

Attention is focussed on the experimental problems connected to the detection and measurement of electrical signal produced by faradaic processes at a dropping mercury electrode of a polarographic cell. The discrepancies on the results obtained using the two electrochemical techniques are discussed.

Introduction

High energy radiation interacts with diluted aqueous solutions by energy transfer to water molecules. The chemical change, induced by the interaction, can be schematically represented by:

$$H_2O \rightsquigarrow H_3O^+, e_{aq}^-, H, OH, H_2, H_2O_2 \qquad (1)$$

The yields, G, expressed as the number of molecules produced per 100 eV of energy absorbed by the system, are $G_{(e_{aq}^-)} = 2.7$; $G_{(H)} = 0.6$; $G_{(OH)} = 2.7$; $G_{(H_2)} = 0.45$, $G_{(H_2O_2)} = 0.7$.

The primary radicals can react with solutes and produce transient species which undergo secondary reactions, and eventually form stable products.

The pulse radiolysis technique employs a short and intense pulse of high energy electrons, to produce μmolar concentrations of primary products in a time short compared to their life-time. The decay of the transient species is followed by fast physico-chemical monitoring techniques.

Among the primary radicals produced in the radiolysis of water, e_{aq}^- and H are powerful reducing agents and OH is an oxidizing agent. Using N_2O saturated solution the hydrated electron is converted to an OH radical;

$$N_2O + e_{aq}^- \xrightarrow{H_2O} N_2 + OH^- + OH \qquad (2)$$

so that the initial intermediate is almost entirely an oxidizing agent.

In a nitrous oxide saturated solution of halide ions, X^-, the hydroxyl radical can oxidize the solute [1–4].

The reaction mechanism, for measurements at values of elapsed time in the μs range, is schematically represented by:

$$X^- + OH \xrightarrow{X^-} X_2^- + OH^- \qquad (3)$$

$$X_2^- + X_2^- \longrightarrow X_2 + 2X^- \qquad (4)$$

Previous work [5] on the electrochemical properties of the radicals X_2^- ($X^- = I^-, Cl^-, Br^-, CNS^-$) obtained by a fast quasi-galvanostatic* technique suggests conclusions which are in serious discrepancy [6] with the results obtained by a quasi-coulostatic method in the present work and with information obtained by conventional polarography.

We have studied N_2O saturated solutions 0.5 *M* Na_2SO_4 in the presence of 10^{-3} *M* KCNS or KI

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*The term 'galvanostatic' here implies current measurement at supposedly constant potential. 'Coulostatic' implies no flow of charge from the external circuit(s), *i.e.* a virtually open circuited cell.

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and acidified solution, pH = 1, of KCl. The values of the potential applied to the cell are referred to the saturated calomel electrode, SCE.

Experimental

Experimental Requirements for Short-time-polarography Studies

In the detection and measurement of faradaic current due to the reduction or oxidation of short-lived species at the working electrode of a polarographic cell [7], the major problem is to obtain an adequate signal:noise ratio in the presence of low concentrations of the active species, in order to avoid complications in the analysis of experimental data caused by second order decay processes of the intermediates.

Another problem is the elimination of massive electrical interference coming from the electron or X-ray source. This may, in addition to making the minimum value of elapsed time large, introduce unsuspected errors due to long term effects following massive overloading of the electronic amplifying circuits needed to raise the electrochemical signal to a level sufficiently large for oscilloscopic display.

In general, the time constant for the combination of monitor electrode double layer capacity and effective solution resistance will be of the order of at least 25 μs. Consequently a current measurement at supposedly constant potential may be in error if the elapsed time is not larger than *ca.* 100 μs. This is a difficulty that cannot usually be avoided by sophisticated potentiostatic means (involving current feedback), because of the concomitant deterioration in signal:noise ratio, already a problem in the context of making the radiation dose sufficiently small to avoid complications at the measurement time in the analysis of results caused by intermediate reactions in pairs. These problems can be solved by studying, instead of the faradaic current, the transient potential change at the double layer capacity induced by the faradaic processes in a virtually open circuited cell [6].

The coulostatic change is given by:

$$\Delta E = \frac{1}{C_{dl}} \cdot \int_0^t \Sigma_{X=A,B,C...}\, i_X \, dt \tag{5}$$

where t is the time after radiation pulse, i_X is the contribution of the species X to the total faradaic current density at the electrode surface, and C_{dl} is the specific differential capacity. In the presence of a single, diffusion-controlled process, and no loss of the active intermediate by reaction in pairs or by reaction with any other intermediate, the change in interfacial potential is proportional to $\sqrt{t}$ and is given by:

$$\Delta E = \frac{1}{C_{dl}} \cdot \frac{2nF}{\pi^{1/2}} \cdot D_x{}^{1/2} \cdot C_x \cdot t^{1/2} \tag{6}$$

where n is the number of electrons involved in the faradaic reaction of the electroactive species and D_x and C_x are its diffusion coefficient and concentration respectively, and F is the Faraday.

Employing this experimental approach the double layer capacity of the test electrode in effect becomes a current integrating capacity and, from the viewpoint of good signal:noise ratio (hence low dose), it is important to match as far as possible without serious distortion of the studied signal the cell (2-electrode as regards the studied signal) to the input circuit of the electronic amplifier. The studied signal at the cell terminals is normally quite small (typically 0.1–0.5 mV).

One disadvantage of this coulostatic and indirect approach to current measurement is that ultimately, using the supposedly known double layer capacity, potential change must be transformed into faradaic charge density change (ΔQ). Capacity measurements thus may have to be made in separate experiments so that due allowance can be made for the dependence of capacity both on potential and solution composition. The use of the coulostatic method in conjunction with a stationary electrode (*e.g.* a hanging mercury drop) is not desirable, except perhaps in the special and quite exceptional case where the aim is the study of reactions involving heterogeneous photolysis of species that are present virtually only on the electrode surface. The double layer capacity of a stationary electrode, such as one of a noble metal or of glassy carbon, is never sufficiently polarizable for use in *quantitative* studies of current produced by homogeneously-formed reaction products. Even a hanging mercury drop will normally slowly become contaminated in solution and yield results impossible to interpret quantitatively. If surface contamination cannot be avoided (*e.g.* for solutions containing surface-active solutes) the simpler galvanostatic method must be employed.

The Hardware System

The radiation source is a 2 MeV Febetron electron accelerator, and a thin tantalum target at the exit of the cathode provides a 30 ns duration X-ray pulse, Fig. 1. The pulse originates close to a slowly dropping (*ca.* 10 s drop-life) mercury electrode, DME, of a 3-electrode polarographic cell situated inside a thick-wall aluminium screening box containing the lead-screened preamplifier system. The box wall thickness is reduced considerably in the vicinity of the DME so as to bring the DME as close as possible to the target outside the box, largely to

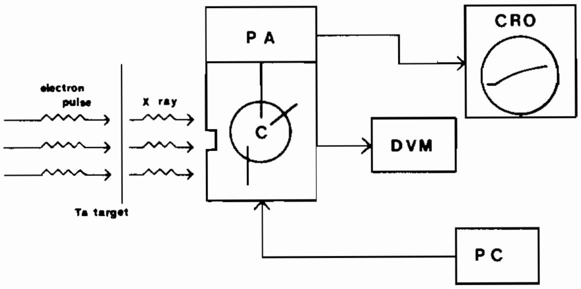

Fig. 1. Schematic layout of the quasi-coulostatic system; P.A.: preamplifier; C: 3-electrode polarographic cell; P.C.: potential control; DVM: digital voltmeter; C.R.O.: oscilloscope.

minimise the dose received by the large mercury pool counter-electrode, CE. Electrical contact between the accelerator and X-ray target and the aluminium box is avoided and none of the Febetron electrons fall on the screening box. As far as possible the latter is made conducting in all directions. All leads entering and leaving the box are subject to filtering at high frequencies to prevent the permeation of electrical interference into the box.

Despite these precautions, and the amplification of the studied signal (normally X 300) prior to transmission via metal ducts for oscilloscopic study in the screened Febetron control room, electrical interference still prevents the making of measurements at elapsed times below *ca.* 4 μs. This is an improvement on what can be achieved by a simple galvanostatic approach but is not as good as was hoped for. Currently it is believed that a residual problem is interference resulting from the diffusion to the outer walls of the cells of radiation-produced ions in the gas surrounding the cell, and the use of a cell metallized on the outside is planned.

The preamplifier employed is switchable to permit operation in the simpler galvanostatic mode, but – as normally used – the input signal, the coulostatic voltage change appearing between the test electrode and the mercury pool counter-electrode, is applied simultaneously to the bases of 10 n-p-n low noise transistors (2N2484) connected in parallel. Feedback from a later point in the amplifier circuit is used to enhance the input impedance of the amplifier (to *ca.* 1 Kohm). The first stage of amplification is followed by a second stage of variable gain and normally the preamplifier enhances the cell signal by a factor of *ca.* 300 and the output signal is studied and recorded photographically, using a storage oscilloscope. The studied coulostatic signal is only slightly dependent on mercury drop size and hence manual triggering can be used to ensure irradiation at a sufficiently constant time in the drop-life. Experimental data were processed using a Hewlett-Packard desk calculator.

Dosimetry

The dose absorbed by the irradiated system was measured from the coulostatic signal obtained from 10^{-3} *M* $K_4Fe(CN)_6$ solution saturated with nitrous oxide. The OH radical react with ferrocyanide:

$$\mathrm{Fe(CN)_6{}^{4-} + OH \longrightarrow Fe(CN)_6{}^{3-} + OH^-} \qquad (7)$$

and the ferricyanide ion formed induces a reduction current at the working electrode. By means of eqn. 6, the relevant parameter $G_{(OH)}$ and the diffusion coefficient of the active species being known, a dose of 1 Krad per pulse was calculated.

The doses calculated, for the same pulse, from the change in interfacial potential due to the reduction of ferricyanide ions and from the optical absorption change (same cell geometry) due to the formation of ferricyanide, differ by a factor of nearly 2. The explanation for this discrepancy may in part be that the interaction of the X-ray pulse with the mercury electrode produces low and high energy photoelectrons which ultimately undergo hydration in the proximity of the electrode surface and contribute significantly to the production of intermediates at the double layer. The dose measurements obtained by both the coulostatic and galvanostatic techniques refer to processes which occur very close to the electrode and are not averaged over the solution volume as much as in the case of the optical measurements. Therefore differences in the concentration of intermediates between the bulk solution and the region close to the electrode, if not considered, may result in serious misinterpretation of the results obtained*.

The ferricyanide system has been used to test the techniques by comparison of the results obtained with conventional polarography measurements. Figure 2 shows the dependence on potential of the double layer charge for an elapsed time of 50 μs obtained by the coulostatic method, the conventional polarogram and the dependence on potential of the current for 10 μs of elapsed time, obtained by the galvanostatic method, as reported in ref. 8. The coulostatic method gives results** which, after normalization, agree with literature polarographic data for ferricyanide reduction. The galvanostatic method at potentials at which the capacity at the mercury electrode double layer is large and at low

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*It should be noted that, although the average dose close to the electrode may be enhanced, there is little evidence for marked non-uniformity of dose in this region.

**For an elapsed time of 10 μs the coulostatic results deteriorate in reliability but are still in fair agreement with the literature data.

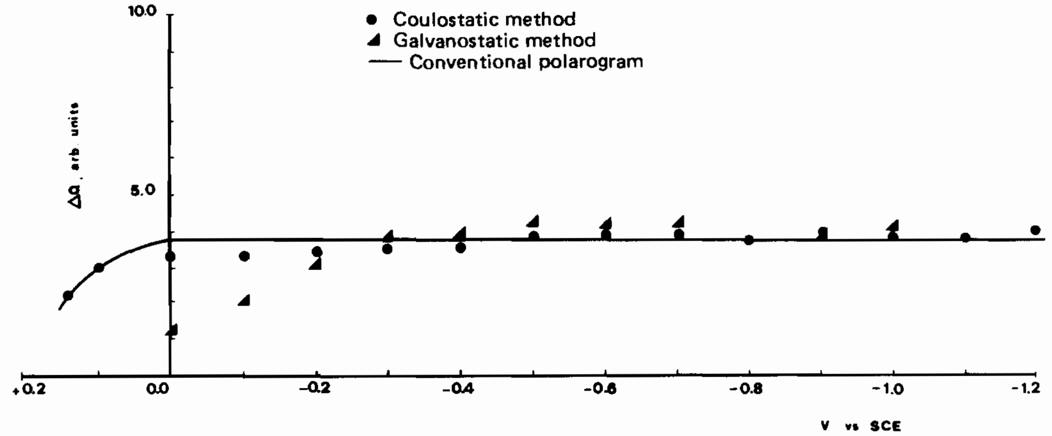

Fig. 2. Coulostatic charge density change *vs.* potential for 0.5 *M* Na_2SO_4, saturated with N_2O in presence of 10^{-3} *M* $K_4(Fe(CN)_6)$.

values of elapsed time tends to give misleading results which can be in error due to the relatively high values of the time constant for potential control.

The time resolution and the high dose necessary in the galvanostatic method, with the consequent low value of radical life-time (typically 20 μs for OH, [8]), limit the precision, reliability and applicability of the galvanostatic technique. To some extent, at least, the coulostatic approach seems to enhance the status of polarographic methods for the study of the electrochemistry of intermediates arising in pulse radiolysis with some increase in complexity.

Results and Discussion

Oxidation of Cl^-

Adding KCl to 0.5 *M* sodium sulphate solution saturated with N_2O, and studying the effect of the additions on the temporal variation of the coulostatic signal, information about intermediates formed by the following homogeneous reactions can be obtained.

$$OH + Cl^- \longrightarrow OH^- + Cl\cdot \quad (8)$$

$$Cl\cdot + Cl^- \longrightarrow Cl_2^- \quad (9)$$

$$2Cl_2^- \longrightarrow 2Cl^- + Cl_2 \text{ (or } Cl_3^-\text{)} \quad (10)$$

The addition of chloride ion, 10^{-3} *M*, to acid solutions (pH = 1 to 3), appreciably changes the electrode response at all potentials in the range 0.0 to −1.2 V. The species which contribute to the change in charge density are the radicals H and Cl_2^- (and possibly Cl_2 or Cl_3^-). Knowing the electrochemical behaviour and parameters of the H radical [9], it was possible to correct the composite charge density changes for the radical contribution and obtain data connected with reactions 8–10.

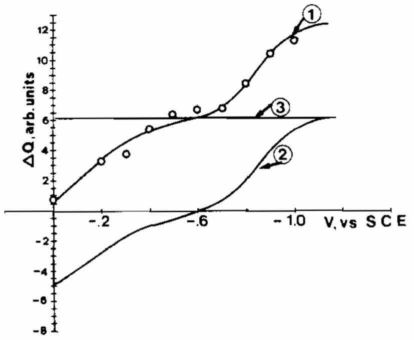

Fig. 3. Coulostatic charge density changes *vs.* potential for 0.5 *M* Na_2SO_4 solutions containing 5 × 10^{-3} *M* KCl: processed coulostatic data, ①; theoretical contribution of H radicals, ②; approximate calculated contribution of Cl_2^- radicals, ③. The data refer to 50 μs elapsed time.

Figure 3 displays the processed coulostatic data at different electrode potentials (curve 1), the calculated contribution of H radicals (curve 2), and the approximate calculated contribution of Cl_2^- (curve 3, obtained by subtraction of curve 2 from curve 1), which takes no account of effects due to the possible reduction by the electrode of Cl_2 or Cl_3^-.

The best fit to experimental points (curve 1) was obtained using $D_{Cl_2^-} = 1.2 \pm 0.15 \times 10^{-5}$ cm² s⁻¹ and $2\ k_{10} \cong 0$. However pulse radiolysis and flash photolysis experiments give for reaction 10 the apparent value $2\ k_{10} = 1.5 \times 10^{10}$ [10].

The anomalous value $2\ k_{10} \cong 0$ ($2\ K_{10} < 10^3\ M^{-1}\ s^{-1}$) necessary to fit the experimental points is explained by the reduction at the electrode not only of Cl_2^- but also of the product of reaction 10, *i.e.* Cl_2 or Cl_3^-. Either two Cl_2^- radicals are reduced at

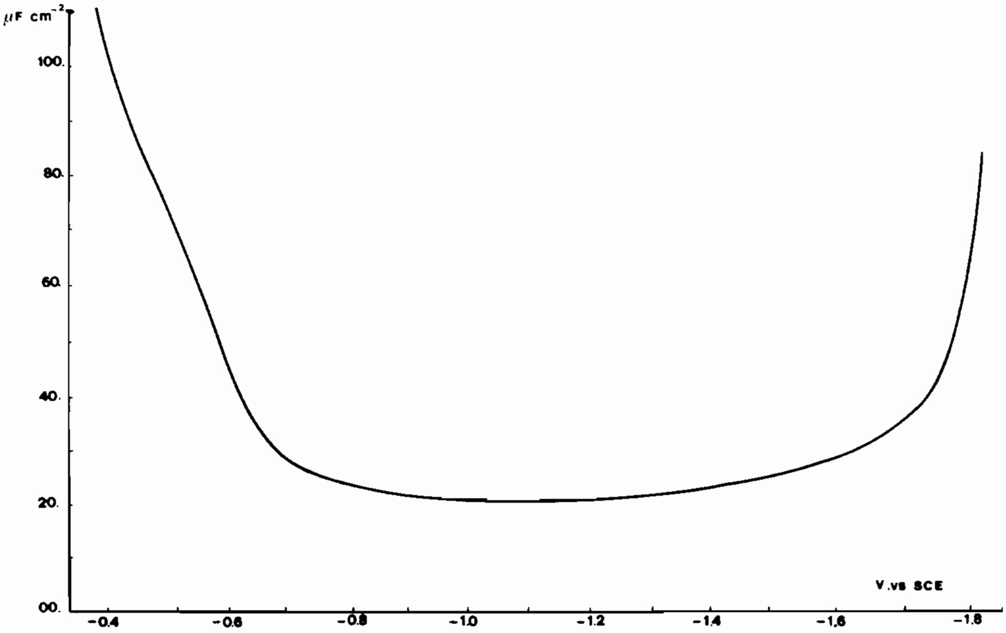

Fig. 4. Specific double layer capacity for 10^{-3} *M* KI in 0.5 *M* Na_2SO_4, deaerated solution.

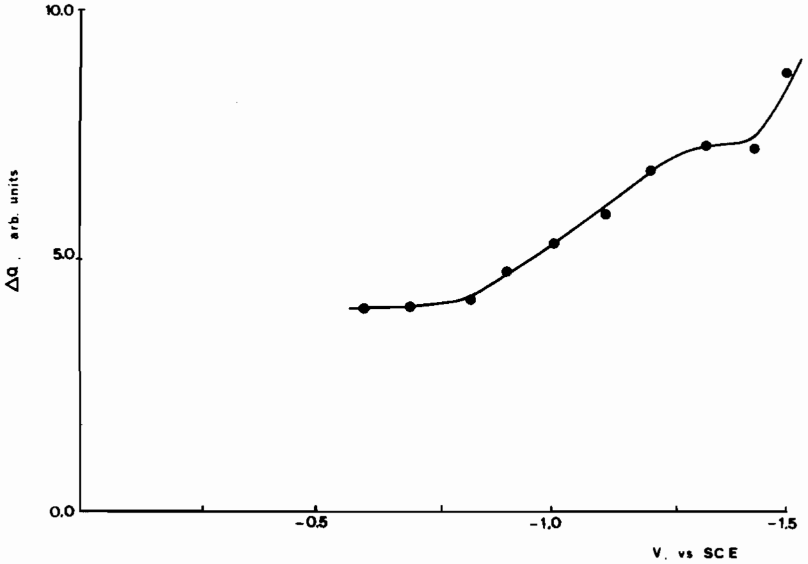

Fig. 5. Coulostatic charge density changes *vs.* potential for 0.5 *M* Na_2SO_4, N_2O saturated solution containing 10^{-3} *M* KI. The data refer to 20 μs elapsed time.

the electrode by a one electron faradaic process or one Cl_2 (or Cl_3^-) undergoes a two electron faradaic process. Therefore, with respect to reaction 10 the net change in faradaic current is small (the only possible difference depends on $1 - (\sqrt{D_{Cl_2^-}/D_{Cl_3^-}})$, which one expects to be much smaller than unity.

Figure 3 shows that for Cl_2^- reduction the process is diffusion-controlled (as is also the reduction of the products of reaction 10) throughout the studied potential range, in disagreement with results of earlier work. It would seem that the apparent value of the half-wave potential reported for the reduction of Cl_2^- at pH = 2, namely $E_{1/2}$ = –0.64 V, was calculated without taking into account the appreciable contribution of H radicals to the faradaic current. At pH = 5.3 the formation of Cl_2^- could only be detected at KCl concentrations > 0.1 *M*. The present results appear to agree with data reported by Anbar and Thomas [11].

Oxidation of I^- and CNS^-

Adding 10^{-3} *M* KI to 0.5 *M* Na_2SO_4 saturated with nitrous oxide, the electrochemical behaviour of the products of reactions 11–13:

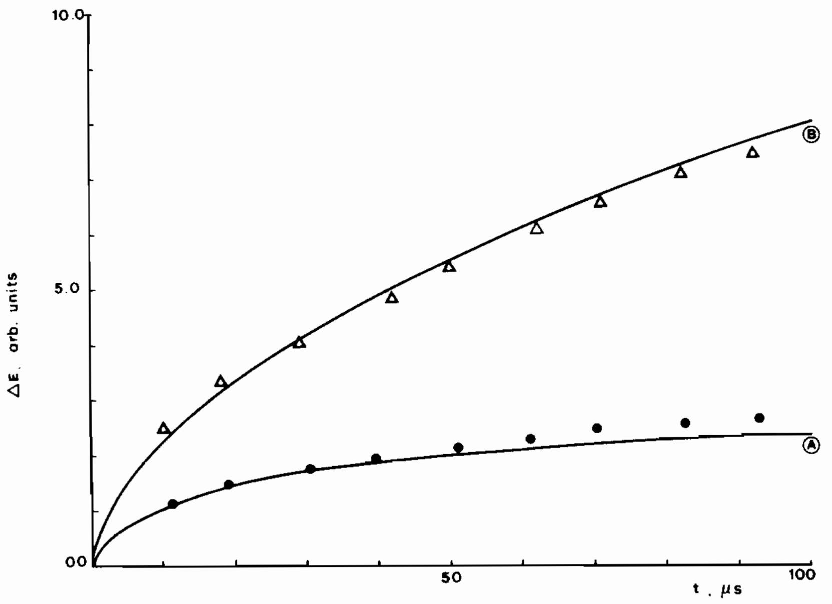

Fig. 6. Coulostatic changes in electrode potential with elapsed time for 0.5 M Na_2SO_4, N_2O saturated solution containing 10^{-3} M KI; Ⓐ, −0.7V; Ⓑ, −1.3 V.

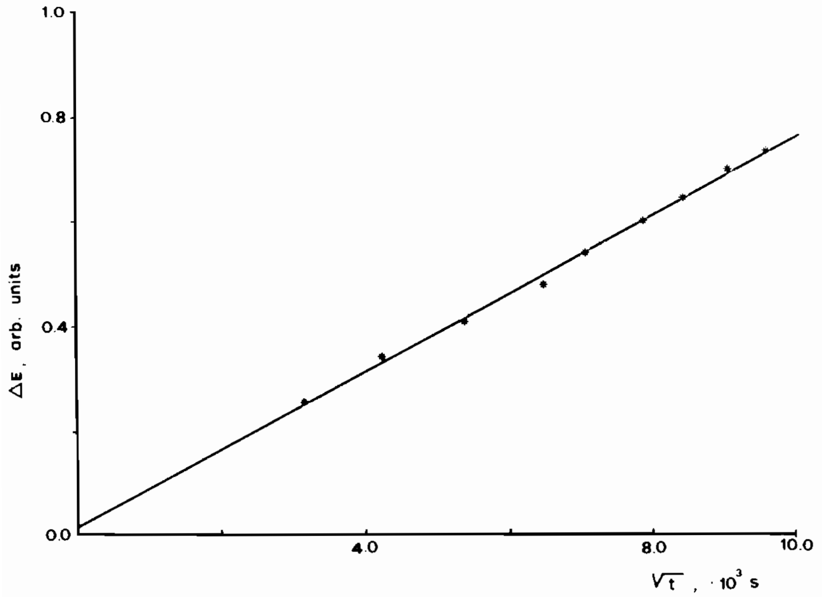

Fig. 7. Plot of the coulostatic signal *vs.* the square root of the elapsed time at −1.3 V, for 0.5 M Na_2SO_4, N_2O saturated solution containing 10^{-3} M KI.

$$I^- + OH \longrightarrow OH^- + I\cdot \quad (11)$$

$$I\cdot + I^- \longrightarrow I_2^- \quad (12)$$

$$I_2^- + I_2^- \longrightarrow 2I^- + I_2 \text{ (or } I_3^-) \quad (13)$$

was investigated. The study at potentials more positive than −0.5 V was prevented by the high values of the double layer capacity, Fig. 4.

The change in interfacial potential shows an increase in the charge density as the potential is made more negative than −0.8 V, Fig. 5.

The more positive reduction wave has to be attributed to the discharge at the electrode surface of I_2^-. The change of the charge density with the elapsed time at −0.7 V, Fig. 6, is consistent with a species which decays by a second order process and a rate constant $2\,k = 1.2 \times 10^{10}$ M^{-1} s^{-1}, in

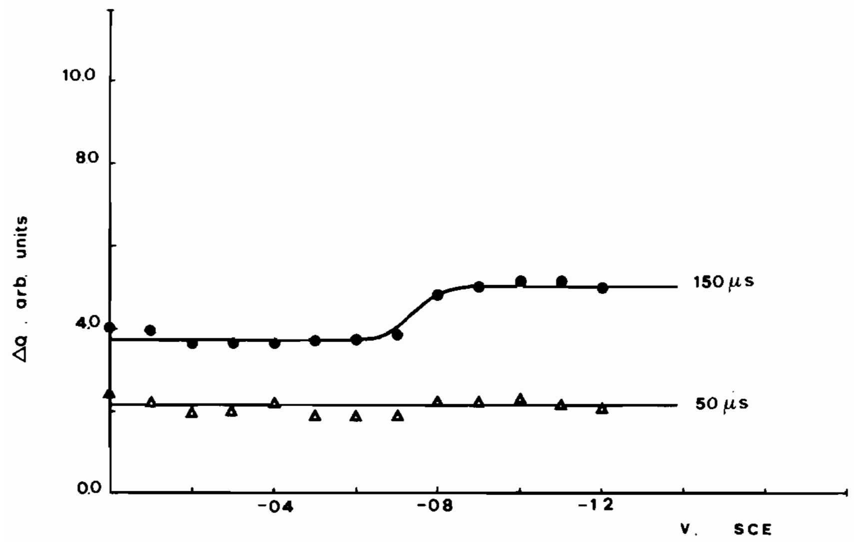

Fig. 8. Coulostatic charge density change *vs.* potential for 0.5 *M* Na_2SO_4, N_2O saturated solution containing 10^{-3} *M* KCNS.

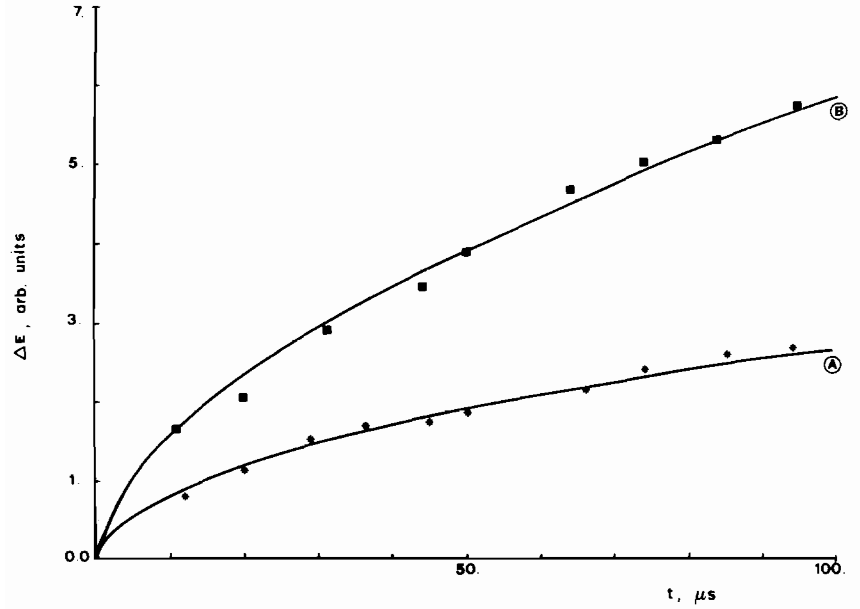

Fig. 9. Coulostatic change in electrode potential with elapsed time for 0.5 *M* Na_2SO_4, N_2O saturated solution containing 10^{-3} *M* KCNS; Ⓐ: −0.5 V, Ⓑ: −1.2 V.

good agreement with the value reported for reaction 13, at pH = 6 [10]. The calculated value of the diffusion coefficient was $D_{I_2^-} = 1.1 \pm 0.15 \times 10^{-5}$ $cm^2\ s^{-1}$. The coulostatic signal at −1.3 V is proportional to $\sqrt{t}$, Figs. 6 and 7. This dependence is expected when the active species do not undergo homogeneous reactions, eqn. 6. However the unstable radical I_2^- contributes to the faradaic process at this potential. The results, therefore, indicate that the more negative cathodic wave is due to the reduction of products of the I_2^- decay, I_2 or I_3^- (?). The best fit to experimental data was obtained assuming that the number of electrons per molecule involved in the faradaic reaction is equal to the number of I_2^- radicals which disappear per molecule of product formed.

A value equal to $D_{I_2^-}$ was assumed for all the species which contribute to the signal at −1.3 V and no allowance was made for the contribution of H_2O_2. Previous work [5] has attributed the cathodic wave at more negative potential to the reduction of I_2^-, but the present results clearly indicate that the radical I_2^- is reduced at a DME by a diffusion-controlled process in the whole potential range available.

In irradiated 0.5 *M* Na_2SO_4 solution, saturated with N_2O in the presence of 10^{-3} *M* KCNS, the CNS^- ion behaves as the halide ions:

$$CNS^- + OH \longrightarrow CNS\cdot + OH^- \qquad (14)$$

$$CNS\cdot + CNS^- \longrightarrow (CNS)_2^- \qquad (15)$$

$$(CNS)_2^- + (CNS)_2^- \longrightarrow 2\ CNS^- + (CNS)_2 \qquad (16)$$

The coulostatic signal shows two reduction processes, Fig. 8, one of which is diffusion-controlled throughout the potential range available, and one which occurs at potentials more negative than –0.7 V, with $E_{1/2} = -0.75$ V.

The time dependence of the coulostatic signal at –0.5 V and –1.2 V, Fig. 9, indicates that the first reduction process is induced by a transient species, $(CNS)_2^-$, which disappears by homogeneous second order reaction and a rate constant $2k = 2.0 \times 10^9$ M^{-1} s^{-1}, as calculated by the best fit to experimental data and in agreement with a previous reported value [12].

The second reduction process is consistent with a calculated time-dependence of the coulostatic signal induced by a species which is forming, $(CNS)_2$ (?), according to second order reaction, with $2k = 1.5 \times 10^9$ M^{-1} s^{-1}, and which is reduced by a 2-electron process.

The calculated value of the diffusion coefficient was $D_{(CNS)_2^-} = 1.1 \pm 0.15 \times 10^{-5}$ cm^2 s^{-1}. In the calculation $D_{(CNS)_2^-} = D_{(CNS)_2}$ was assumed.

The electrochemical behaviour of the system is therefore similar to that of KI solution.

The anodic signal reported at 0.0 V [5] is most likely to be due to the oxidation of the mercury salt [13].

The anodic process in 0.1 *M* KNO_3 and 10^{-3} *M* KCNS, obtained by conventional polarography, with $E_{1/2} = +0.18$ V, is attributed to $Hg(CNS)_2$. Besides, the reported current *vs.* time curve at –0.4 V shows an initial increase with a maximum at 200 μs, and has been attributed to a slowly forming product, *i.e.* $(CNS)_2$. We believe that the rise observed is an experimental artifact caused by the high value of the response time, *ca.* 100 μs, due to the actual value of the double layer capacity which, at this potential, is 32 $\mu F\ cm^{-2}$.

The contribution of H atoms to the coulostatic signals, obtained in the presence of 10^{-3} *M* KI and 10^{-3} *M* KCNS, has been ignored. In these systems the atomic hydrogen produced undergoes secondary reactions such as:

$$H + I^- \longrightarrow HI^- \qquad (17)$$

$$H + I_2^- \longrightarrow H^+ + 2I^- \qquad (18)$$

$$H + I_3^- \longrightarrow H^+ + I_2^- + I^- \qquad (19)$$

$$H + CNS^- \longrightarrow HCN + S^{\cdot}\quad (?) \qquad (20)$$

The yields of reactions 17 and 20 are low, G(H) = 0.6, and the diffusion coefficients of the formed products should be comparable to $D_{I_2^-}$ and $D_{(CNS)_2^-}$. Their contributions are likely to be lower than 10% and therefore cannot fully account for the results obtained.

It cannot be said that the electrochemical reactions connected with the oxidation of Cl^-, I^- and CNS^- are adequately understood; however the results of the coulostatic studies have clarified that the radicals Cl_2^-, I_2^- and $(CNS)_2^-$ are reduced at all potentials available using a mercury electrode and that the conclusions reported on the reduction power of these radicals derived from quasi-galvanostatic measurements have to be reviewed.

Acknowledgements

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