

INFLUENCE OF SPECIFIC ADSORPTION OF REACTANT
AND PRODUCT UPON CHARGE-TRANSFER PROCESSES
IN VOLTAMMETRY: THE I_2/I^- COUPLE IN ACETIC ACID
AND ACETIC ANHYDRIDE ON PLATINUM

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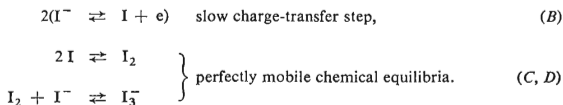
Received June 23rd, 1970

With increasing the bulk concentration of the depolarizer both the voltammetric anodic waves of iodide to iodine and the cathodic waves of iodine to iodide on smooth platinum in acetic acid as well as in acetic anhydride progressively deviate from reversibility. This behaviour has been interpreted on the basis of the specific adsorption of iodide ions and iodine atoms on the electrode surface. In this connection it has been assumed that the elementary charge-transfer step $I^- \rightarrow I + e$ occurs between adsorbed species obeying Langmuirian isotherms.

The mechanism of the overall electrode process



on platinum in aqueous media has been the subject of several researches¹⁻⁴. Vetter², upon determining the orders of the electrochemical reaction (A) with respect to the species I^- and I_3^- has proposed the following mechanism:



It should be noted that Vetter does not specify whether reaction (C) takes place among iodine atoms adsorbed at the electrode surface or occurs homogeneously. Subsequently Newson and Riddiford⁴ have confirmed mechanism (B)–(D) by making use of a disk platinum electrode. In the theoretical treatment formulated by the above authors the atomic iodine, I, is clearly considered to be adsorbed at the electrode surface. A different position is adopted on the other hand, regarding the iodine ion, whose eventual adsorption is not taken into account. According to Newson and Riddiford⁴ the surface coverage by iodine atoms is much less than unity at any potential. The above conclusion contrasts with radiotracer experiments with ¹³¹I (ref.^{5,6}), which show that the maximum surface concentration of I^- ($\sim 1 \cdot 10^{-9}$ mol cm⁻²) is achieved at a bulk

concentration of iodide of about 10^{-4} mol/l, whereas the maximum surface concentration of iodine ($\sim 1.3 \cdot 10^{-9}$ mol cm^{-2}) is achieved at a still lower bulk concentration than the iodide ion. Osteryoung and Anson⁶, on the basis of certain electrochemical experiments with the I_2/I^- couple carried out with the use of several transient methods, concluded that adsorbed iodide is electroinactive and consequently criticize the mechanism proposed by Newson and Riddiford⁴ as well as other mechanisms^{1,3} based on the assumption that the charge-transfer takes place between specifically adsorbed species. As a matter of fact the interpretation of transients given by Osteryoung and Anson⁶ is far from being reliable, since it does not take into due account that charge separation and recombination may take place at an interphase without flow of external current^{7,8}. On the other hand the difficulties which are encountered in accounting for the influence exerted by the adsorption of electroactive species upon the double layer structure⁹ render particularly difficult the correct analysis of the results of step-function measurements.

In this respect the investigation of those cases in which the specific adsorption of the depolarizer and of the electrode product hinders the charge-transfer is particularly profitable. In fact the influence of such an adsorption upon the electron-transfer may be detected with conventional polarographic instrumentation at electrolysis times sufficiently long to allow the surface excesses both of electroactive and electroinactive species to reach steady-state values. In this time scale the charging of the double layer may be legitimately neglected, whereas the influence of the specific adsorption of electroactive species upon the rate of the electron-transfer step may offer useful indications about the extent of such an adsorption¹⁰. Unfortunately the rate of the overall charge-transfer process $2\text{I}^- \rightleftharpoons \text{I}_2 + 2\text{e}$ on platinum in aqueous media is too high to be measured by the polarographic method. A somewhat different situation is encountered in acetic acid and in acetic anhydride where the exchange current density for the above electrode process is likely to be less than in water. Both in CH_3COOH and $(\text{CH}_3\text{CO})_2\text{O}$ the voltammetric curve of I^- to I_2 as recorded on a hemispherical smooth platinum electrode with periodical renewal of the diffusion layer consists of two successive anodic steps, respectively from I^- to I_3^- and from I_3^- to I_2 (ref.¹¹). These steps, which are polarographically reversible for bulk concentrations of I^- , C_1^* , less than $2 \cdot 10^{-3}$ mol/l tend to become more drawn out the more C_1^* is increased beyond this value. Analogously the overall reduction curves of I_2 to I^- in CH_3COOH and $(\text{CH}_3\text{CO})_2\text{O}$ are polarographically reversible for bulk concentrations of iodine, C_2^* , less than 10^{-4} mol/l but deviate progressively from the reversible behaviour as C_2^* is increased beyond this value.

The aim of the present work is to justify the above behaviour on the basis of the effect of the adsorption of iodine and iodide upon the charge-transfer process.

EXPERIMENTAL

Voltammograms were recorded using a three-electrode system consisting of a Metrohm Polarecord E 261 polarograph (sweep rate = 0.47 mV/s) coupled with a Metrohm iR-Compensator E 446. The indicator electrode was a hemispherical platinum microelectrode with periodical renewal of the diffusion layer described by Cozzi and coworkers¹². This electrode was polished with finely powdered Cr_2O_3 before each recording. The potential of the indicator electrode was

controlled *versus* a Ag/AgCl, 0.3M-LiCl (CH₃COOH) reference electrode in the measurements done in acetic acid and *versus* a Ag/AgCl, saturated LiCl ((CH₃CO)₂O) reference electrode in the measurements done in acetic anhydride. All potentials reported in the present paper are referred to the preceding reference electrodes. All chemicals employed were reagent grade. CH₃COOH was dried by the method using triacetyl borate¹³ prepared according to Pictet and Galeznoff¹⁴. (CH₃CO)₂O (Merck, unaffected by chromic acid) was purified by fractional distillation. Particular care was placed in deaerating the I⁻ solutions in CH₃COOH and (CH₃CO)₂O, as they are easily oxidized by air. The potentiometric measurements were made by adding increasing aliquots of a 0.126M-I⁻ solution in acetic acid to a 0.012M-I₂ solution in the same solvent in a perfectly deaerated reaction environment and measuring the potential of a platinum indicator electrode with a Métrohm E 353 potentiometer.

THEORETICAL

We shall assume that the mechanism by which the electro-oxidation of I⁻ on platinum takes place in CH₃COOH and (CH₃CO)₂O is identical to that proposed by Vetter² and by Newson and Riddiford⁴ in aqueous media. In agreement with Newson and Riddiford⁴ we shall postulate that the charge-transfer step (*B*) involves adsorbed iodine atoms, I. Furthermore we shall assume that the electro-oxidation of iodide is necessarily preceded by its specific adsorption. In order to relate the surface concentrations Γ_1 and Γ_2 of I⁻ and I to the volume concentrations \bar{C}_1 and \bar{C}_2 of I⁻ and I₂ at the electrode surface, we shall postulate that the adsorption steps:



are in equilibrium and that the propositions on which Langmuirian adsorption is based are satisfied. In Eq. (E) * denotes a single adsorption site, whereas in Eq. (F)** denotes a pair of adjacent adsorption sites. Upon assuming that the maximum value, Γ_m , attained by Γ_1 is equal to that attained by Γ_2 , the concentration of the free single adsorption sites is proportional to $1 - \theta \cong 1 - [(\Gamma_1 + \Gamma_2)/\Gamma_m]$, where θ is the degree of coverage of the electrode. Analogously the concentration of dual adsorption sites is proportional to $(1 - \theta)^2$. If we equate the rates of adsorption and of desorption both for iodide ions (see Eq. E) and for iodine atoms (see Eq. F), we immediately obtain:

$$\frac{\Gamma_1}{\Gamma_m} = K_1 \bar{C}_1 \left(1 - \frac{\Gamma_1 + \Gamma_2}{\Gamma_m} \right), \quad (1)$$

$$\frac{\Gamma_2}{\Gamma_m} = K_2 \bar{C}_2^{1/2} \left(1 - \frac{\Gamma_1 + \Gamma_2}{\Gamma_m} \right), \quad (2)$$

where K_1 and K_2 are proportionality constants expressing the adsorption coefficients of I^- and I respectively. A simple rearrangement of Eq. (1) and (2) leads to the two Langmuirian isotherms:

$$\Gamma_1 = \Gamma_m K_1 \bar{C}_1 / (1 + K_1 \bar{C}_1 + K_2 \bar{C}_2^{1/2}), \quad (3)$$

$$\Gamma_2 = \Gamma_m K_2 \bar{C}_2^{1/2} / (1 + K_1 \bar{C}_1 + K_2 \bar{C}_2^{1/2}). \quad (4)$$

The expression for the instantaneous current i as a function of the surface concentrations Γ_1 and Γ_2 is of the usual type:

$$i/FA = k_f^0 \Gamma_2 \Theta^{-\alpha} - k_b^0 \Gamma_1 \Theta^{1-\alpha}, \quad (5)$$

where F and A retain their customary significance and Θ is defined by the equation:

$$\Theta = \exp [(F/RT)(E - E^0)].$$

In Eq. (5) k_f^0 and k_b^0 are the rate constants for the forward and backward electrode processes at a given reference potential E^0 and α is the electron transfer coefficient. If we substitute Γ_1 and Γ_2 from Eq. (3) and (4) into Eq. (5) and we choose E^0 in such a way that at this particular potential the equality $\Gamma_m K_2 k_f^0 = \Gamma_m K_1 k_b^0 \equiv k_s$ holds, then we obtain:

$$\frac{i}{FA} = \frac{k_s}{1 + K_1 \bar{C}_1 + K_2 \bar{C}_2^{1/2}} (\bar{C}_2^{1/2} \Theta^{-\alpha} - \bar{C}_1 \Theta^{1-\alpha}). \quad (6)$$

The previously chosen potential E^0 coincides with the standard potential of the I_2/I^- couple, as appears from the fact that under equilibrium conditions (*i.e.* for $i = 0$) Eq. (6) reduces to the Nernst equation. The current-potential relationship employed by Newson and Riddiford (Eq. (26) and (27) of ref.⁴) is a particular case of Eq. (6) to which this latter equation reduces when the specific adsorption of I^- and I is negligible ($K_1 \bar{C}_1 + K_2 \bar{C}_2^{1/2} \ll 1$):

$$i/FA = k_s (\bar{C}_2^{1/2} \Theta^{-\alpha} - \bar{C}_1 \Theta^{1-\alpha}). \quad (7)$$

From Eq. (7) it clearly appears that the parameter k_s expresses the rate constant for the electrode process (B) at the standard potential E^0 in the absence of adsorption phenomena. Eq. (6) differs from Eq. (7) in that the standard rate constant k_s is replaced by an "apparent" standard rate constant, $k_s/(1 + K_1 \bar{C}_1 + K_2 \bar{C}_2^{1/2})$. Such an "apparent" rate constant is always less than the "actual" rate constant k_s , which shows that the specific adsorption of I^- and I increases the overpotential

with which the charge-transfer process (*B*) takes place. It should be noted that, while k_s is a parameter independent of the potential E applied to the electrode, the apparent rate constant depends on E mostly through the concentrations \bar{C}_1 and \bar{C}_2 at the electrode surface, but also through K_1 and K_2 .

Taking into account that for a given bulk concentration of the depolarizer, the current i may reach at most the value of the corresponding diffusion limiting current, if the apparent rate constant is sufficiently high along the whole rising portion of the voltammetric curve, then the term within the round brackets in Eq. (6) may be approximately equated to zero. By doing so we immediately obtain the Nernst equation applied to the volume concentrations \bar{C}_1 and \bar{C}_2 at the electrode surface:

$$E = E^0 + (RT/F) \ln (\bar{C}_2^{1/2}/\bar{C}_1). \quad (8)$$

Under these conditions the voltammetric curve is reversible and does not permit the detection of adsorption phenomena. In case the value of k_s is not exceedingly high, it is possible that with increasing the bulk concentration of the depolarizer the values assumed by the apparent rate constant, $k_s/(1 + K_1\bar{C}_1 + K_2\bar{C}_2^{1/2})$ along the rising portion of the voltammetric curve become too low to justify the validity of Eq. (8). Under these circumstances the gradual deviation of the voltammetric curve from reversible behaviour allows useful conclusions to be drawn as to the adsorption of iodine and iodide.

In order to eliminate \bar{C}_1 and \bar{C}_2 from Eq. (6) we shall note that the current i is bounded to the fluxes of the diffusing species I^- , I_3^- , and I_2 at the electrode surface through the equations:

$$i = 2FAD[(\partial C_3/\partial r)_{r,0} + (\partial C_2/\partial r)_{r,0}] = -FAD[(\partial C_1/\partial r)_{r,0} + (\partial C_3/\partial r)_{r,0}]. \quad (9)$$

Here r^0 is the radius of the hemispherical platinum microelectrode, C_3 is the volume concentration of triiodide, and D is the diffusion coefficient which for simplicity has been considered equal for I^- , I_2 , and I_3^- .

As a matter of fact the expression for the faradaic current should contain a further additive term $-Fd(A\Gamma_2)/dt$ in the second member of Eq. (9) and a term $+Fd(A\Gamma_1)/dt$ in the third member of the same equation. Since, however, the experimental measurements were carried out using an electrode of constant area A , and furthermore since the constancy of Γ_1 and Γ_2 with electrolysis time may be assumed with good approximation in the time scale of polarographic measurements, the use of Eq. (9) appears to be satisfactory.

Upon resorting to the approximate diffusion layer concept, we shall assume that at any given potential the volume concentrations \bar{C}_1 , \bar{C}_2 , and \bar{C}_3 at the electrode surface do not vary with electrolysis time and that the concentration gradients of I^- , I_2 , and I_3^- at the electrode surface are given by the equations:

$$(\partial C_1/\partial r)_{r^0} = (C_1^* - \bar{C}_1)/\delta; \quad (\partial C_2/\partial r)_{r^0} = (C_2^* - \bar{C}_2)/\delta; \quad (\partial C_3/\partial r)_{r^0} = (C_3^* - \bar{C}_3)/\delta, \quad (10)$$

where the diffusion layer thickness δ is given by $1/(l\sqrt{(\pi Dt)} + 1/r^0)$ for the case of diffusion towards a spherical electrode of radius r^0 . If we substitute the various concentration gradients from Eq. (10) into Eq. (9) and we integrate this latter equation over the period of electrolysis, t_1 , then we obtain:

$$\bar{i} = (1/t_1) \int_0^{t_1} i \, dt = 2Al(C_3^* + C_2^* - \bar{C}_3 - \bar{C}_2) = Al(\bar{C}_1 + \bar{C}_3 - C_1^* - C_2^*), \quad (11)$$

where $l \equiv F(2D^{1/2}/\sqrt{(\pi t_1)} + D/r^0)$. When the average cathodic limiting current \bar{i}_c is attained, the concentrations \bar{C}_2 and \bar{C}_3 approach zero. From Eq. (11) it immediately follows that:

$$\bar{i}_c = 2Al(C_3^* + C_2^*).$$

Analogously, when the anodic limiting current \bar{i}_a is reached, we have $\bar{C}_1 = \bar{C}_3 = 0$ so that Eq. (11) becomes:

$$\bar{i}_a = -Al(C_1^* + C_3^*).$$

For convenience \bar{i}_a instead of \bar{i} will be chosen as the potential axis on the $\bar{i} - E$ plane. Upon designating by \mathcal{I} the mean current referred to this new orthogonal coordinate system, one has:

$$\mathcal{I} = \bar{i} - \bar{i}_a$$

$$\mathcal{I}_d = \bar{i}_c - \bar{i}_a = Al(C_1^* + 3C_3^* + 2C_2^*) = AlC, \quad (12)$$

where C denotes the overall bulk concentration of the various species containing iodine in g -atoms of iodine per unit volume. The application of the law of mass action to the homogeneous equilibrium (D) leads to the equation:

$$K = C_3/(C_1 C_2) \quad (13)$$

valid at any distance from the electrode and for any value of the electrolysis time. Upon combining Eqs (11), (12) and (13) we readily obtain the expressions of \bar{C}_1 and \bar{C}_2 as functions of the stability constant K for triiodide, of C , as well as of the ratio $R = \mathcal{I}/\mathcal{I}_d$ between the mean current \mathcal{I} at a given potential along the rising portion of the voltammetric curve and the corresponding mean diffusion limiting current \mathcal{I}_d :

$$\bar{C}_2 = \{ -b + \sqrt{[b^2 + 2CK(1 - R)]} \} / (2K), \quad (14)$$

$$\bar{C}_1 = CR / (1 + K\bar{C}_2), \quad (15)$$

where $b = 1 + (KC/2)(3R - 1)$.

If we integrate Eq. (6) over t_1 under the usual assumption that \bar{C}_1 and \bar{C}_2 do not vary during the period of electrolysis, taking into account the definitions of \mathcal{F} and \mathcal{F}_d given in Eq. (12) we obtain:

$$R = \frac{C_1^* + C_3^*}{C} + \frac{F}{IC} \frac{k_s}{1 + K_1\bar{C}_1 + K_2\bar{C}_2^{1/2}} (\bar{C}_2^{1/2}\Theta^{-\alpha} - \bar{C}_1\Theta^{1-\alpha}).$$

Upon giving α the value 0.5, for simplicity, Θ may be expressed in the following explicit form:

$$\Theta^{\pm} = \{ -a + \sqrt{(a^2 + 4\bar{C}_1\bar{C}_2^{\pm})} \} / (2\bar{C}_1), \quad (16)$$

where

$$a = \frac{IC}{F} \left(R - \frac{C_1^* + C_3^*}{C} \right) \left(\frac{1 + K_1\bar{C}_1 + K_2\bar{C}_2^{1/2}}{k_s} \right). \quad (17)$$

Equations (14)–(16) allow the theoretical current–potential characteristic to be derived, once the parameters K , k_s , K_1 , K_2 and E^0 are known. In this connection it is sufficient to give R a series of values ranging from 0 to 1, determining for each of these values initially the value of \bar{C}_2 from Eq. (14), subsequently the value of \bar{C}_1 from Eq. (15) and lastly the value of Θ from Eq. (16).

RESULTS AND DISCUSSION

It has already been mentioned that for sufficiently low bulk concentrations of the depolarizer both the voltammetric anodic curves of I^- to I_2 and the cathodic curves of I_2 to I^- in CH_3COOH as well as in $(\text{CH}_3\text{CO})_2\text{O}$ are polarographically reversible. The investigation of these curves, which obey equations derived in ref.¹⁵, does not allow us to draw conclusions either about the mechanism of the overall electrode process $2I^- \rightleftharpoons I_2 + 2e$ or about the influence of the adsorption of the electroactive species upon the charge-transfer, but nevertheless it permits the derivation of the parameters K and E^0 . The determination of the stability constant of I_3^- in CH_3COOH and in $(\text{CH}_3\text{CO})_2\text{O}$ from the voltammetric curves given by solutions of I^- of concentrations less than $2 \cdot 10^{-3}$ mol/l has been carried out in a preceding paper¹¹.

In the case of the I_2/I^- system in CH_3COOH it has been found convenient to determine the values of E^0 and K also from potentiometric measurements. On the

contrary the potentiometric method did not prove satisfactory in $(\text{CH}_3\text{CO})_2\text{O}$, where iodine tends to disproportionate at an appreciable rate into I^- and CH_3COOI (ref.¹⁶). The potentiometric measurements carried out in acetic acid have been interpreted as follows. If we designate by C_{1-} and C_{1_2} the analytical concentrations of I^- and I_2 , then from Eq. (13) it immediately follows that:

$$C_{1-} = C_1^* + C_3^* = C_1^*(1 + KC_2^*),$$

$$C_{1_2} = C_2^* + C_3^* = C_2^*(1 + KC_1^*).$$

If $C_{1_2} \gg C_{1-}$, then, in view of the high stability of I_3^- in acetic acid, we can write to a good degree of approximation that:

$$C_{1-} \cong C_3^* = KC_1^*C_2^*; \quad C_2^* \cong C_{1_2} - C_{1-}. \quad (18)$$

Taking into account Eq. (18), the Nernst equation as applied to the I_2/I^- couple assumes the form:

$$E = E^0 + (RT/2F) \ln (C_2^*/C_1^{*2}) \cong E^0 + (RT/2F) \ln [K^2(C_{1_2} - C_{1-})^3/C_1^{*2}]. \quad (19)$$

The experimental plot of E versus $\log [(C_{1_2} - C_{1-})^3/C_1^{*2}]$ for $C_{1_2} > 2.46C_{1-}$ is actually linear with a slope of 0.030 V at 25°C. The potential corresponding to the intercept of this straight line with the ordinate axis equals 0.555 V. From Eq. (19) it immediately follows that:

$$0.555 \text{ V} = E^0 + 0.060 \log K. \quad (20)$$

In the case in which $C_{1-} \gg C_{1_2}$, the following relations hold with good approximation:

$$C_{1_2} \cong C_3^* = KC_1^*C_2^*; \quad C_1^* \cong C_{1-} - C_{1_2}.$$

Hence the Nernst equation assumes the form:

$$E \cong E^0 + (RT/2F) \ln [C_{1_2}/K(C_{1-} - C_{1_2})^3]. \quad (21)$$

The experimental plot of E versus $\log [C_{1_2}/(C_{1-} - C_{1_2})^3]$ for $C_{1-} > 2.44C_{1_2}$ is linear with a slope of 0.030 V and intersects the ordinate axis at a potential of 0.132 V. From Eq. (21) it follows that:

$$0.132 \text{ V} = E^0 - 0.030 \log K. \quad (22)$$

Upon combining Eq. (20) and (22) one has that in acetic acid $E^\circ = 0.273$ V and $K = 10^{4.7}$ l/mol. The above values of E° and K are in satisfactory agreement with those derivable from the voltammetric curves given by solutions of I^- of concentrations less than $2 \cdot 10^{-3}$ mol/l (ref.¹¹).

Both in acetic acid and in acetic anhydride the comparison between the experimental voltammograms obtained from solutions of I^- , I_2 , or I_3^- of bulk concentrations sufficiently high to produce a deviation from reversibility and the theoretical characteristics derivable from Eq. (14)–(16) reveal that in all cases the inequality $K_1\bar{C}_1 + K_2\bar{C}_2^{1/2} \gg 1$ holds along the whole rising portion of these voltammograms. From Eq. (14)–(17) it immediately follows that, besides E° and K , the unknown parameters contained in the theoretical expression for the current–potential characteristic are two in number, namely K_1/k_s and K_2/k_s . This circumstance, while allowing an easier comparison between experimental behaviour and theoretical expectations, does not however permit the separation of the kinetic parameter k_s from the parameters K_1 and K_2 , expressing the extent of the adsorption of iodide and iodine.

The solid curves 1a, 1b, 1c and 2a, 2b, 2c in Fig. 1 represent respectively the experimental oxidation curves of $3 \cdot 10^{-3}$ M, $5 \cdot 10^{-3}$ M and $6 \cdot 10^{-3}$ M iodide to iodine and the reduction curves of $1.5 \cdot 10^{-3}$ M, $2.5 \cdot 10^{-3}$ M, and $3 \cdot 10^{-3}$ M iodine to iodide. The vertical lines relative to the three pairs of curves 1a–2a, 1b–2b, and 1c–2c refer to the standard potential $E^\circ = 0.273$ V of the I_2/I^- couple in CH_3COOH . The dashed curves superimposed on the corresponding solid curves express the theoretical current–potential characteristics derived from Eq. (14)–(16) using the following data: $E^\circ = 0.273$ V, $K = 10^{4.7}$ l/mol, $K_1/k_s = 10^{10}$ cm^{11/4} s mol^{-5/4} and $K_2/k_s =$

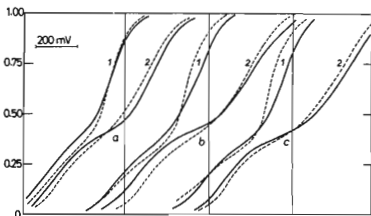


FIG. 1

Voltammograms of I^- and I_2 in Acetic Acid

The solid curves 1a, 1b, 1c and 2a, 2b, 2c represent respectively the I/I_d versus E plots relative to the experimental oxidation curves of $3 \cdot 10^{-3}$ M, $5 \cdot 10^{-3}$ M and $6 \cdot 10^{-3}$ M iodide and to the reduction curves of $1.5 \cdot 10^{-3}$ M, $2.5 \cdot 10^{-3}$ M, and $3 \cdot 10^{-3}$ M iodine. The dashed curves superimposed on the corresponding solid curves express the theoretical behaviour.

$= 10^6 \text{ cm}^{5/4} \text{ s mol}^{-3/4}$. Since the experimental values of r^0 and t_1 are respectively 0.1 cm and 4 s and the diffusion coefficient of I^- in CH_3COOH at 25°C amounts to $3.5 \cdot 10^{-6} \text{ cm}^2/\text{s}$, the parameter l/F has been given a value of $1.09 \cdot 10^{-3} \text{ cm/s}$. The agreement between the experimental and theoretical curves may be considered relatively satisfactory if we consider that the method followed in the solution of the present diffusional problem is only approximate. Furthermore we must consider that α has been arbitrarily given a value of 0.5. Moreover we have assumed just as arbitrarily that the isotherms for I^- and I are of the Langmuirian type and that K_1 and K_2 remain constant with a change in the applied potential. It should be noted however that in the present case these latter two assumptions do not affect the agreement between experimental data and theoretical expectations in a critical way, since, under the experimental conditions employed, $K_1\bar{C}_1 + K_2\bar{C}_2^{1/2}$ is much greater than 1 along the whole rising portion of the voltammetric curves. This implies that the coverage of the electrode by I^- and I is practically total at all potentials explored, so that a variation in the applied potential does not cause an appreciable change in the total amount of I^- and I adsorbed at the electrode surface but simply a change in the ratio between Γ_1 and Γ_2 .

The adsorption of iodine and iodide on platinum in acetic anhydride has been studied on the basis of an examination of the voltammograms given by solutions of I^- and I_3^- , owing to the already mentioned instability of I_2 . The solid curves 1a, 1b, 1c and 3a, 3b, 3c in Fig. 2 represent respectively the oxidation curves of $4 \cdot 10^{-3}\text{M}$, $7 \cdot 10^{-3}\text{M}$, $1 \cdot 10^{-2}\text{M}$ iodide to iodine and the cathodic curves of $1.33 \cdot 10^{-3}\text{M}$, $2.33 \cdot 10^{-3}\text{M}$, and $3.33 \cdot 10^{-3}\text{M}$ triiodide. The vertical lines relative to the three pairs

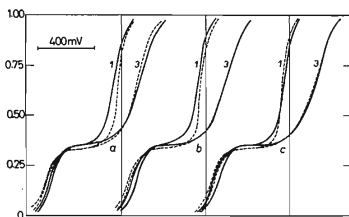


FIG. 2

Voltammograms of I^- and I_3^- in Acetic Anhydride

The solid curves 1a, 1b, 1c and 3a, 3b, 3c represent respectively the j/j_d versus E plots relative to the experimental oxidation curves of $4 \cdot 10^{-3}\text{M}$, $7 \cdot 10^{-3}\text{M}$, $1 \cdot 10^{-2}\text{M}$ iodide and to the cathodic curves of $1.33 \cdot 10^{-3}\text{M}$, $2.33 \cdot 10^{-3}\text{M}$, and $3.33 \cdot 10^{-3}\text{M}$ triiodide. The dashed curves superimposed on the corresponding solid curves express the theoretical behaviour.

of curves $1a-3a$, $1b-3b$, and $1c-3c$ refer to the standard potential E° of the I_2/I^- couple in acetic anhydride. The dashed curves superimposed on the corresponding solid curves express the theoretical behaviour derived from Eq. (14)–(16) using the following data: $E^\circ = 0.100$ V, $K = 10^9$ l/mol, $K_1/k_s = 10^9$ cm^{11/4} s mol^{-5/4} and $K_2/k_s = 10^3$ cm^{5/4} s mol^{-3/4}. Noting that the diffusion coefficient of I^- in $(CH_3CO)_2O$ at 25°C is about $6 \cdot 10^{-6}$ cm²/s and that the experimental values for r° and t_1 are respectively 0.1 cm and 4 s, we attributed to l/F the value of $1.44 \cdot 10^{-3}$ cm/s.

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