

KINETICS AND MECHANISMS OF ELECTRO-CHEMICAL REACTIONS ON PLATINUM WITH SOLUTIONS OF IODINE-SODIUM-IODIDE IN DIMETHYLSULPHOXIDE*

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Abstract—The kinetics and mechanisms of the iodine and tri-iodide ion reduction and iodide and tri-iodide ion oxidation on platinum have been determined, from a study of the electrochemical kinetic behaviour of DMSO solutions containing an iodine/sodium-iodide ratio greater than one.

The likely mechanisms are the same as those recently discussed for the iodine-sodium-iodide solutions in acetonitrile, and all comprise consecutive reaction schemes involving, for the processes in the anodic direction, an ion-plus-atom reaction as rate-determining step, and the reverse reaction for the cathodic processes.

Résumé—On a déterminé après une étude du comportement cinétique électrochimique de solutions de DMSO contenant une proportion d'iode/iodure de sodium au dessus de l'unité, la cinétique et les mécanismes de la réduction de l'iode et de l'ion tri-iodure, ainsi que l'oxydation des ions iodure et tri-iodure sur le platine.

Les mécanismes de réaction probables sont les mêmes que ceux déterminés récemment pour les solutions d'iode-iodure-de-sodium dans l'acétonitrile. Tous comprennent des schémas de réaction consécutifs qui comportent, pour les processus anodiques, une réaction d'un ion plus un atome comme étape régulatrice, et la réaction inverse pour les processus cathodiques.

Zusammenfassung—Die Kinetik und Mechanismus der Reduktion von Jod und Trijodidion und der Oxydation von Jodid und Trijodidionen auf Platinelektroden in DMSO wurden bestimmt, nachdem das elektrochemische kinetische Verhalten von DMSO-Lösungen mit einem Jod/Natriumjodid Verhältnis von mehr als eins studiert worden war.

Die wahrscheinlichen Reaktionsmechanismen sind dieselben wie die neulich for Jod-Natriumjodid in Acetonitril bestimmten. Alle zeigen aufeinanderfolgende Reaktionsschemen welche für die anodische Prozesse eine Ion-plus-Atomreaktion als Geschwindigkeitsbestimmende Stufe und die umgekehrte Reaktion für die kathodischen Prozesse umfasst.

INTRODUCTION

THE ELECTROCHEMISTRY of solutions of sodium iodide and iodine in dimethylsulphoxide (DMSO), on platinum electrodes involving a molecular sodium-iodide/iodine ratio greater than one, have been studied recently.¹⁻³ The anodic reaction was characterized by a current/voltage curve comprising two waves, while the cathodic reaction presented only one. The kinetics of the reaction indicated that the electrode process, at currents lower than the limiting current, was under simultaneous activation and convective-diffusion control. The contribution of each polarization term was evaluated by means of a platinum rotating disk electrode.

These results, together with those obtained for the same system in acetonitrile,⁴ indicate that for DMSO solutions containing a molecular sodium-iodide/iodine ratio smaller than one, the current/voltage curves should exhibit two waves in the cathodic region and only one in the anodic region, for the amount of iodide ion present in

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those solutions should be negligible as deduced from the equilibrium constant related to tri-iodide ion formation in DMSO.⁵ Hence the kinetic study of DMSO solutions containing a sodium-iodide/iodine ratio smaller than one, and a supporting electrolyte, has been attempted on a platinum rotating disk electrode. This information supplements that formerly published² in an attempt to elucidate the reaction mechanism of the iodine-tri-iodide-iodide electrode in DMSO on platinum and it assists in determining the validity of reaction mechanisms which are common for that electrode in most aprotic solvents, where the tri-iodide ion formation equilibrium constant is various orders of magnitude larger than in aqueous solutions.

EXPERIMENTAL TECHNIQUE

The rotating disk electrode technique was employed as already described in previous publications.^{2,4} Platinum disks of 0.3 cm diameter embedded in glass rods were used. In the present case the current/voltage curves were recorded either galvanostatically or potentiostatically. Further details of the experimental technique are published elsewhere.^{2,4} Two kinds of solutions were employed, either containing pure iodine or mixtures of iodine and sodium iodide with an excess of the former. Iodine and sodium iodide concentrations are shown in Table 1. All solutions contained 0.8 M sodium perchlorate as supporting electrolyte. Experiments were performed at $25.0 \pm 0.05^\circ\text{C}$. The rotation speed of the working electrode covered a range from 200 up to 3000 rpm or thereabouts.

RESULTS

Current/voltage curves were obtained for each solution at various rotation speeds. As experiments started from an electrically symmetrical system the initial pd was nil. Then the pd reading, ΔE , at each current, I , corresponding to the working-electrode/reference-electrode couple was the total overvoltage related either to the anodic or cathodic processes. As ΔE is defined as the difference between the working electrode potential at current I and the equilibrium potential a positive sign for ΔE corresponds to anodic processes and a negative sign to cathodic processes. Typical current/voltage curves are shown in Figs. 1-4, covering the whole range of experimental conditions. To correct current/voltage curves for any residual current interfering with the electrode processes due either to solvent or to supporting-electrolyte decomposition, blank runs were performed. Over a potential range of about 3 V no correction was necessary if very pure solvent and supporting electrolyte were used.⁶ But at high cathodic overvoltage, when the purest commercial chemicals were employed, the residual current partially distorted the current/voltage curves, and then a correction was required to avoid a misleading interpretation of results. This is clearly shown in Fig. 1. The cathodic current/voltage curves exhibit two well-defined waves whereas the anodic curves comprise only one.

The second cathodic wave shows a remarkable sort of hysteresis. Thus, when the current/voltage curve is first traced up reaching the limiting current region and afterwards traced back, no full coincidence is observed, as shown in Figs. 3 and 4. At a fixed overvoltage the current related to it is larger for the returning curve, suggesting that there is a depolarizing effect due to the large cathodic polarization reached in the first trace. No appreciable hysteresis effect appears either in the first cathodic wave or in the anodic wave.

FIG. 1. Anodic and cathodic current/voltage curves.

25°C. $C_{I_2} = 0.00834$ M, $C_{NaI} = 0.00693$ M, $C_{NaClO_4} = 0.8$ M. Residual currents of 0.8 M $NaClO_4$ solutions in DMSO are indicated.

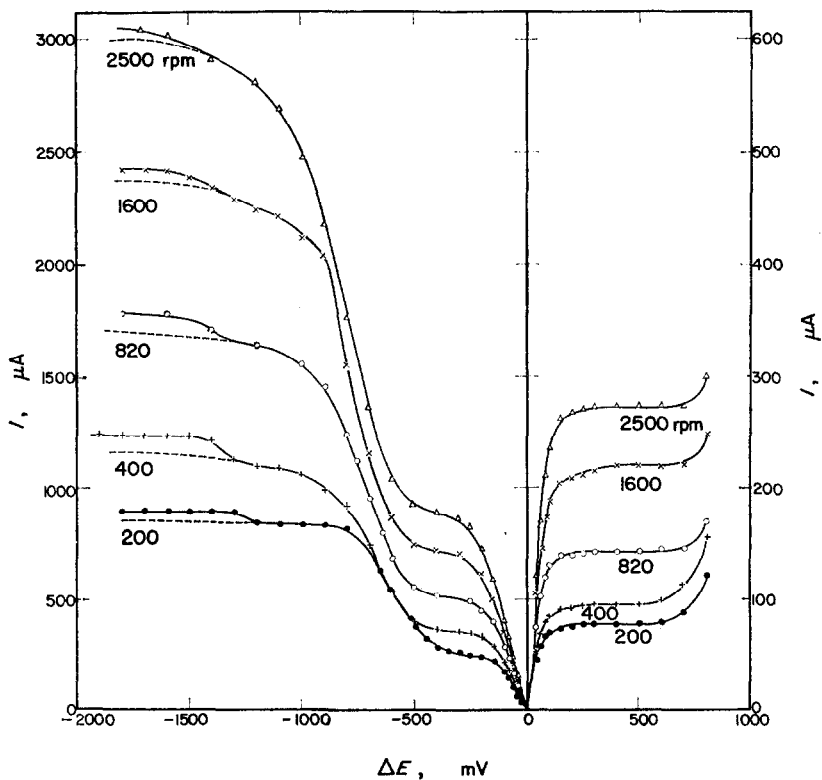
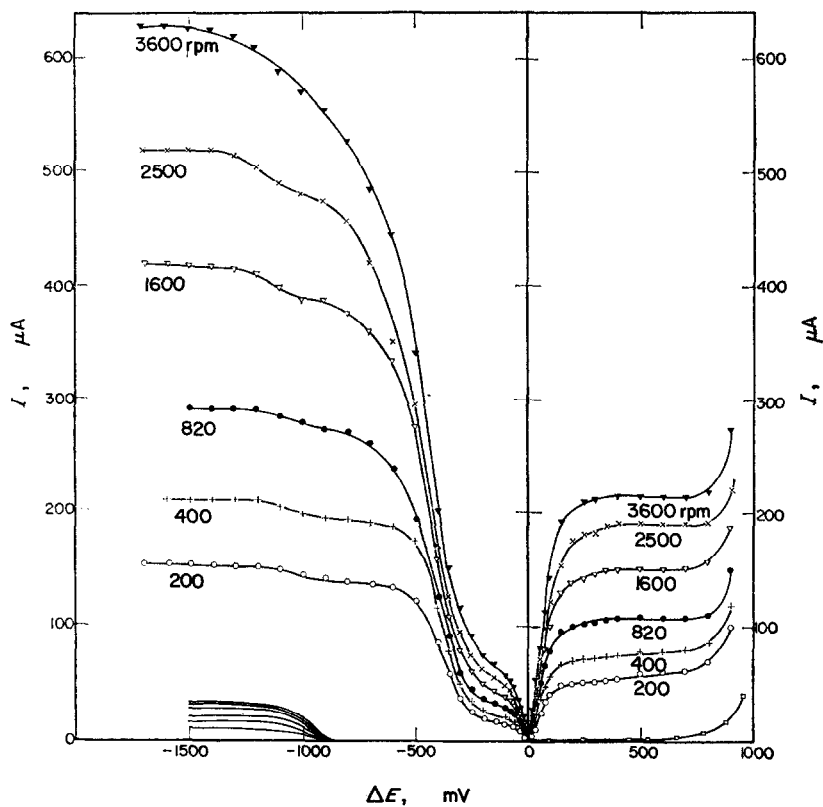


FIG. 2. Anodic and cathodic current/voltage curves.

25°C. $C_{I_2} = 0.05560$ M, $C_{NaI} = 0.01108$ M, $C_{NaClO_4} = 0.8$ M. Dotted lines correspond to the second cathodic wave after correction for residual currents.

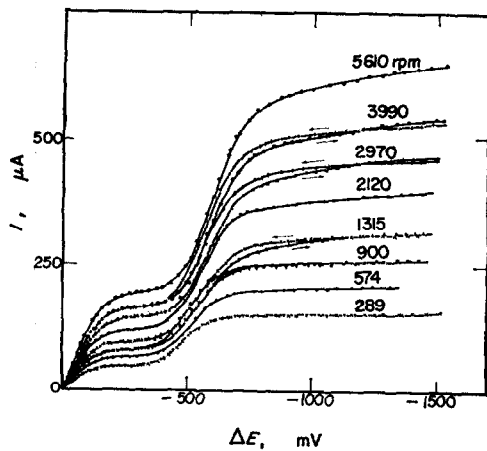


FIG. 3. Cathodic current/voltage curves obtained by changing the cathodic overpotential in both directions.

25°C. $C_{I_2} = 0.01077$ M, $C_{NaClO_4} = 0.8$ M.

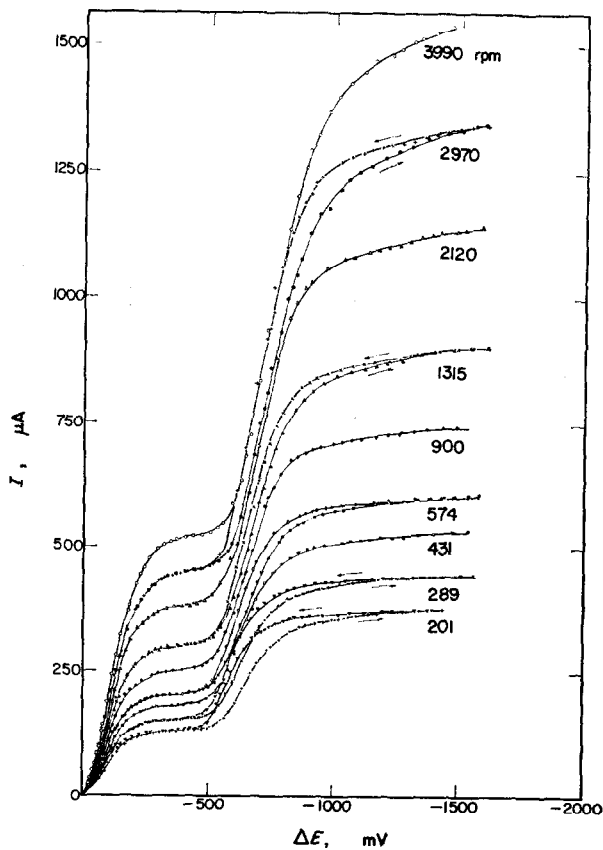


FIG. 4. Cathodic current/voltage curves.
25°C. $C_{I_2} = 0.02164$ M, $C_{NaClO_4} = 0.8$ M.

The limiting cd, referred to the apparent disk area, whatsoever the process, increases at a constant composition and temperature linearly with the square root of the rotation speed, ω (rad/s), of the working electrode. At a constant rotation speed it is also linearly dependent on the concentration of the reacting species, which are, in the present circumstances, the tri-iodide ion in the anodic reaction and iodine and tri-iodide ion, for the first and second waves, respectively, in the cathodic reaction. Both dependences are shown in Figs. 5-8.

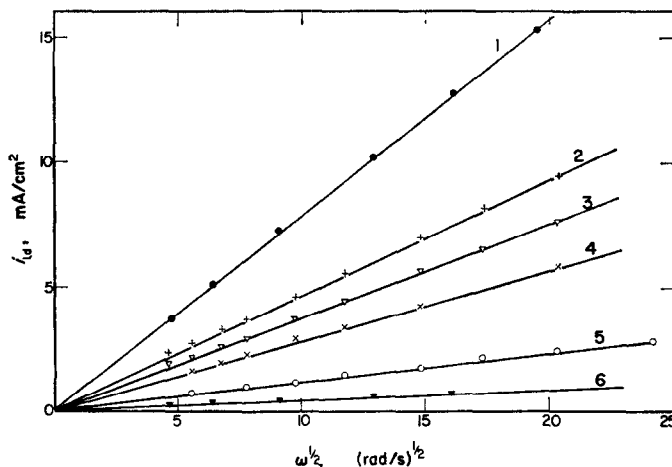


FIG. 5. Plot of i_{ld} vs $\omega^{1/2}$, reduction of iodine.
25°C $C_{NaClO_4} = 0.8$ M.

	C_{I_2} M	C_{NaI} M
1,	0.05560	0.01108
2,	0.02903	—
3,	0.02164	—
4,	0.01820	—
5,	0.00713	—
6,	0.00834	0.00693

INTERPRETATION AND DISCUSSION

The apparent equilibrium constant of tri-iodide ion in DMSO

In recent years the apparent dissociation constants of tri-iodide ion in dimethylformamide (DMF), acetonitrile (ACN) and acetic anhydride have been reported.⁷⁻⁹ They were determined by emf measurements of galvanic cells comprising the I_2/I^- and the I^-/I_3^- redox couples, respectively. The values obtained are within the range 10^{-7} to 10^{-8} at 25°C. This apparent equilibrium constant of tri-iodide ion in DMSO can be estimated from the half-wave potentials, $(E)_{1/2}$, related to the different waves.

As already known, the total reactions occurring during the electrolysis of DMSO solutions of iodine plus iodide on platinum are



and



Reaction (1) is related to the first cathodic wave and the reverse reaction to the second anodic wave. Reaction (2) corresponds to the second cathodic wave and the

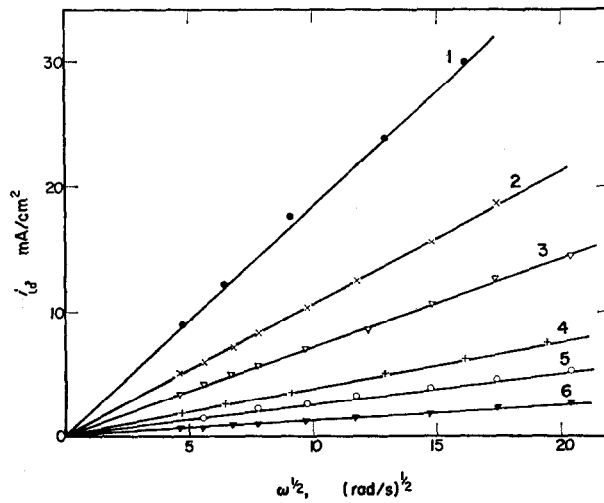


FIG. 6. Plot of i_{ld} vs $\omega^{1/2}$, reduction of tri-iodide ion.
25°C. $C_{\text{NaClO}_4} = 0.8 \text{ M}$.

	C_{I_2} M	C_{NaI} M
1,	0.05560	0.01108
2,	0.02903	—
3,	0.02164	—
4,	0.00834	0.00693
5,	0.01077	—
6,	0.00295	—

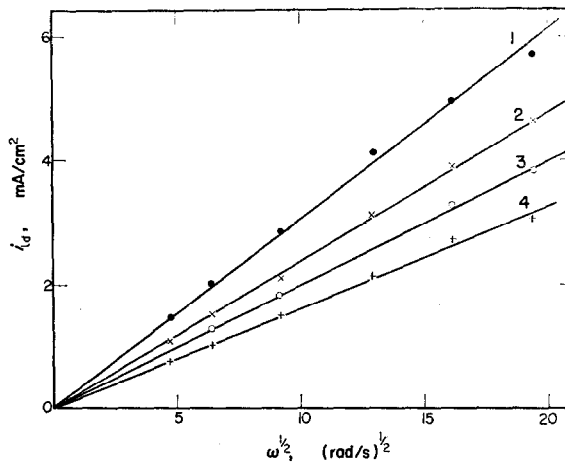


FIG. 7. Plot of i_{ld} vs $\omega^{1/2}$, oxidation of tri-iodide ion.
25°C. $C_{\text{NaClO}_4} = 0.8 \text{ M}$.

	C_{I_2} M	C_{NaI} M
1,	0.05608	0.01600
2,	0.05560	0.01108
3,	0.04939	0.00985
4,	0.00834	0.00693

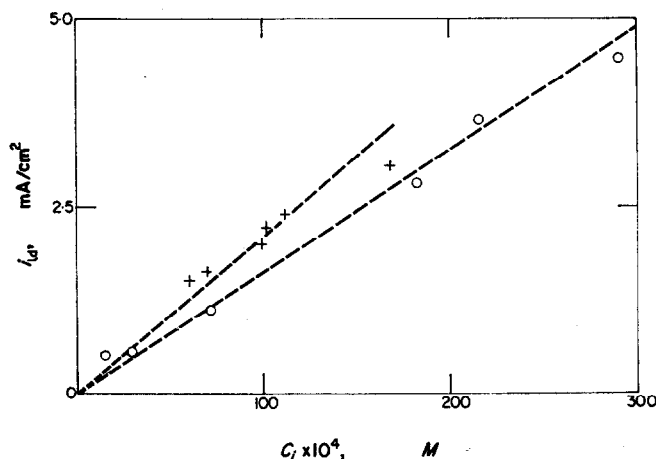


FIG. 8. Concentration dependence of limiting current densities.
25°C. $C_{\text{NaClO}_4} = 0.8$ M.

○, i_{ld} (reduction of iodine) vs concentration of free iodine.
+, i_{ld} (oxidation of tri-iodide ion) vs initial iodide ion concentration.

reverse reaction to the first anodic wave. Considering that equilibria (1) and (2) occur in the presence of a large excess of supporting electrolyte, the corresponding Nernst equations may be written in terms of concentrations instead of activities,

$$E_1 = E_1^{\circ*} + \frac{RT}{2F} \ln \frac{C_{I_2}}{C_{I^-}^2}, \quad (3)$$

and

$$E_2 = E_2^{\circ*} + \frac{RT}{2F} \ln \frac{C_{I_3^-}}{C_{I^-}^3}. \quad (4)$$

In (3) and (4) the C 's refer to the molar concentration of the different species; $E_1^{\circ*}$ and $E_2^{\circ*}$ are the apparent standard potentials of the redox couples (1) and (2), respectively, at constant ionic strength.

In experiments done with the iodine-iodide and tri-iodide-iodide couples, the following approximations are respectively introduced:

$$C_{I_2} \approx C_{I_3^-} = C_a \quad (5)$$

and

$$C_{I^-} \approx C_{I_3^-} = C_b. \quad (6)$$

From (3), (4), (5) and (6) we have

$$E_1 = E_1^{\circ*} + \frac{RT}{2F} \ln C_a \quad (7)$$

and

$$E_2 = E_2^{\circ*} - \frac{RT}{F} \ln C_b. \quad (8)$$

If the dependences of E_1 and E_2 on C_a and C_b are respectively obtained and they

fit (7) and (8), it is possible to get reliable values of $E_1^{\circ*}$ and $E_2^{\circ*}$. If the dissociation of tri-iodide ion takes place according to



its apparent stability constant, K^* , is given by

$$K^* = \frac{C_{I_2} \times C_{I^-}}{C_{I_3^-}}. \quad (10)$$

From (7), (8) and (9), its value, expressed in terms of pK^* , at 25°C, is

$$pK^* = \frac{E_2^{\circ*} - E_1^{\circ*}}{0.087}. \quad (11)$$

At least at the lower rotation speed, we assume

$$E_2^{\circ} - E_1^{\circ} = E_2^{\circ*} - E_1^{\circ*} = (E_2)_{1/2} - (E_1)_{1/2}, \quad (12)$$

where $(E_2)_{1/2}$ and $(E_1)_{1/2}$ are respectively the half-wave potentials, measured against the same reference electrode, of the second cathodic and anodic waves. Equations (11) and (12) yield an approximate value of the apparent stability constant given by (10). The values of pK^* resulting from the experiments lie between 10^{-7} to 10^{-8} , as for the case of the aprotic solvents already mentioned.

Diffusion coefficients of the reacting species

From the linear dependence of the limiting currents on the square root of the rotation speed, the evaluation of the diffusion coefficients, D_i (cm²/s), of the reacting species, i , is obtained from

$$i_{ld} = 0.62nFC_1D_i^{2/3}\nu^{-1/6}\omega^{1/2}; \quad (13)$$

i_{ld} (A/cm²) is the limiting cd related to the convective-diffusion process, ν (cm²/s) the kinematic viscosity of the solution, C_1 (mole/cm³) the bulk concentration of species i and n the number of electrons per mol of reacting species. The diffusion coefficients of iodine and tri-iodide ion are evaluated according to reactions (1) and (2), taking into account the solutions containing an excess of iodine. The former is obtained either from the first cathodic step, for solutions containing only iodine and the supporting electrolyte, or from the total cathodic limiting cd, when solutions containing iodine plus sodium iodide are employed, since the total reaction in such case is



the sum of reactions (1) and (2). Hence, when the first cathodic wave is considered, $n = \frac{2}{3}$ and C_1 is taken as the initial iodine concentration. When the total cathodic current is employed, $n = 2$ and C_1 is the initial iodine concentration. Further details about this calculation are given in a recent paper.⁴

The diffusion coefficient of tri-iodide ion is evaluated from the single anodic wave taking $n = 1$ and the tri-iodide ion concentration equal to the initial iodide ion concentration. These procedures are justified because of the magnitude of the equilibrium constant related to (9) in this solvent.

Results are assembled in Tables 1 and 2. The diffusion coefficients of iodine calculated either from the first cathodic wave or from the total cathodic limiting

TABLE 1. DIFFUSION COEFFICIENTS OF IODINE AND IODIDE AND TRI-IODIDE IONS IN 0.8 M NaClO₄ DMSO SOLUTIONS

C_{I_3} M	C_{NaI} M	$\left(\frac{\Delta i_{i,1}}{\Delta \omega^{1/2}}\right) \times 10^4$ A. cm ⁻² rad ^{-1/2} s ^{1/2}	$D_{I_3} \times 10^6$ cm ² /s	$\left(\frac{\Delta i_{i,01}}{\Delta \omega^{1/2}}\right) \times 10^4$ A. cm ⁻² rad ^{-1/2} s ^{1/2}	$D_{I^-} \times 10^6$ cm ² /s	$\left(\frac{\Delta i_{i,02}}{\Delta \omega^{1/2}}\right) \times 10^4$ A. cm ⁻² rad ^{-1/2} s ^{1/2}	$D_{I_3^-} \times 10^6$ cm ² /s
0.02164	—	3.80	3.95	—	—	—	—
0.00713	—	1.20	3.61	—	—	—	—
0.02903	—	4.80	3.61	—	—	—	—
0.00295	—	0.50	3.64	—	—	—	—
0.01820	—	3.00	3.58	—	—	—	—
0.00834	—	4.30	3.89	—	—	—	—
0.00693	0.00693	27.0	3.50	—	—	1.61	3.31
0.05560	0.01108	28.3	3.64	—	—	2.40	2.96
0.05608	0.01600	27.2	3.64	—	—	3.25	2.94
0.05170	0.00750	—	3.95	—	—	1.53	2.70
0.02166	0.01007	—	—	—	—	2.24	2.80
0.04939	0.00985	—	—	—	—	2.00	2.68
0.01300	0.05100	—	—	8.33	3.55	—	—
—	0.03610	—	—	6.15	3.79	—	—
0.00090	0.03530	—	—	5.77	3.55	—	—
—	0.02580	—	—	4.41	3.79	—	—
—	0.00630	—	—	1.08	3.68	—	—
—	0.00432	—	—	0.718	3.79	—	—

TABLE 2. AVERAGE DIFFUSION COEFFICIENTS

D_{I_2}	$= (3.71 \pm 0.21) \times 10^{-6} \text{ cm}^2/\text{s}$
\bar{D}_{I^-}	$= (3.68 \pm 0.13) \times 10^{-6} \text{ cm}^2/\text{s}$
$D_{I_3^-}$	$= (2.90 \pm 0.41) \times 10^{-6} \text{ cm}^2/\text{s}$
$\left(\frac{D\eta}{T}\right)_{I_2}$	$= 4.56 \times 10^{-10} \text{ g. cm/s}^2\text{K}$
$\left(\frac{D\eta}{T}\right)_{I^-}$	$= 4.53 \times 10^{-10} \text{ g. cm/s}^2\text{K}$
$\left(\frac{D\eta}{T}\right)_{I_3^-}$	$= 3.57 \times 10^{-10} \text{ g. cm/s}^2\text{K}$
ν	$= 3.18 \times 10^{-2} \text{ cm}^2/\text{s}; \delta = 1.15 \text{ g/cm}^3$

current are satisfactorily coincident. Diffusion coefficients of iodide ion were recalculated using data previously published² and are also compiled in Table 2. The average diffusion coefficients of the three species as well as the corresponding Einstein-Stokes ratios ($D\eta/T$), (η being the dynamic viscosity (g/cm s) and T the absolute temperature) are assembled in Table 2. The Einstein-Stokes ratios for the three species in DMSO are larger than the values reported in ACN solutions.⁴

Kinetic parameters of the iodine-tri-iodide-iodide electrode in DMSO

As earlier observed in ACN solutions,⁴ the limiting cds indicate that there is a potential range in the current/voltage curves where the electrode reactions are under convective-diffusion control. At lower overvoltages in the current region preceding the limiting current, a region obeying intermediate kinetics exists, as denoted by a departure of current/voltage curves from the expectation assuming pure concentration polarization. Thus, as the speed of the working electrode increases, the limiting cd region decreases. Analogous departures are observed when the plot i vs $\omega^{1/2}$ is attempted at low overvoltages. The existence of intermediate kinetics appears also in the change of the half-wave potentials with rotation speed.

To evaluate the activation polarization contribution in the electrode process, current/voltage curves were processed according to the Frumkin-Tedoradse method,¹⁰ applied as described in previous publications,^{2,4} including the pseudo-ohmic drop evaluation. Results obtained assuming first-order kinetics are shown in Figs. 9-10. When $1/i$ is plotted against $1/\omega^{1/2}$ a set of straight lines is obtained having a constant slope at high overvoltages, equal to $\omega^{1/2}/i_{id}$, each line corresponding to a fixed overvoltage. In Figs. 9-10 data from the first cathodic and second anodic wave are included. The results from other waves are coincident with those already published.² The extrapolation of the straight to $1/\omega^{1/2} = 0$, yields the cd, i_L , at the activation overvoltage, η_k . Plots of η_k vs $\log i_L$ are shown in Fig. 11. From these Tafel lines, the Tafel slope b_T , the apparent exchange current density i_0 and the experimental transfer coefficient α related to iodine reduction are evaluated. The kinetic parameters for the four processes are assembled in Table 3. Furthermore, considering the dependence of cd on $\omega^{1/2}$, the reaction order of one for iodine reduction has also been checked. The apparent exchange cds related to the four reactions under the same experimental conditions are nearly equal.

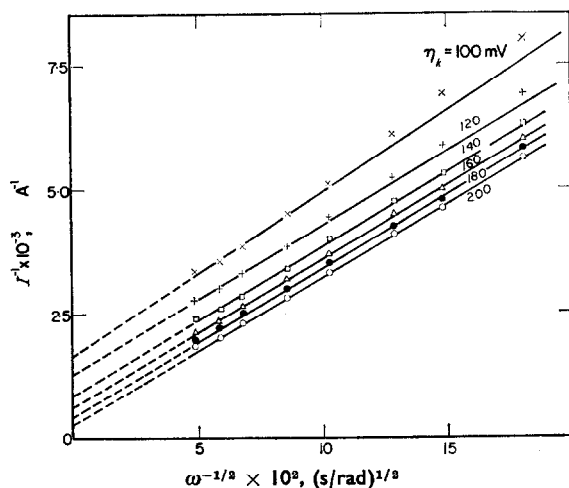


FIG. 9. Plot of $1/I$ vs $1/\omega^{1/2}$, reduction of iodine. 25°C. $C_{I_2} = 0.02903$ M, $C_{NaClO_4} = 0.8$ M.

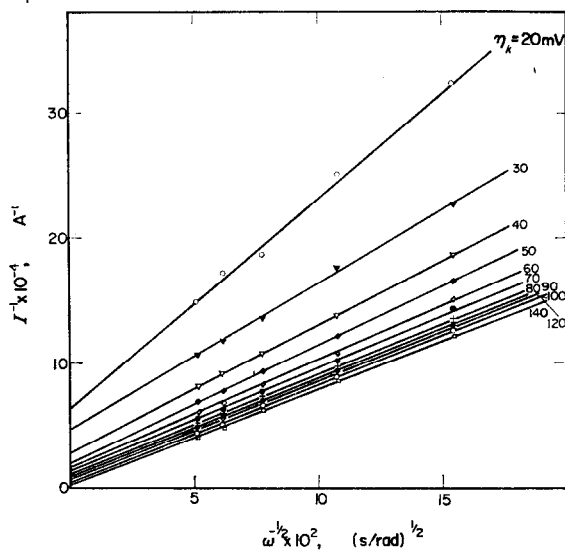


FIG. 10. Plot of $1/I$ vs $1/\omega^{1/2}$, oxidation of tri-iodide ion. 25°C. $C_{I_3} = 0.05608$, $C_{NaI} = 0.0160$ M, $C_{NaClO_4} = 0.8$ M.

Reaction mechanisms

To establish the more likely reaction mechanisms of the iodine-tri-iodide-iodide electrode in DMSO, the discussion is based in the first place upon the recent discussion of reaction mechanisms for the same processes occurring in ACN, which are very similar. Nevertheless, the molecular complex formation between DMSO and I_2 should be kept in mind when iodine reduction is considered. As far as the electrode kinetics is concerned, it appears that molecular iodine is the main cathodic reacting species in the first cathodic wave region.

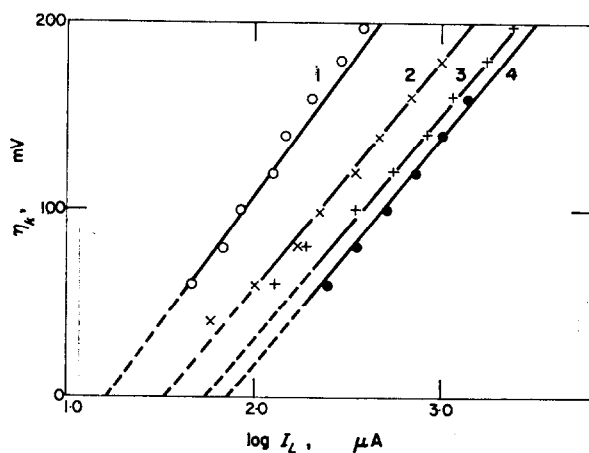


FIG. 11. Tafel plots, reduction of iodine.
25°C. $C_{\text{NaClO}_4} = 0.8 \text{ M}$.

	C_{I_2} M
1,	0.00295
2,	0.00713
3,	0.01820
4,	0.02903

TABLE 3. KINETIC PARAMETERS*

C_i M	b_T V	$(i_0) \times 10^3$ A/cm ²	Order	α	Temp °C
Reduction of iodine					
0.00295	0.136 ± 0.010	0.22 ± 0.03	0.95 ± 0.15	0.44 ± 0.03	25.0 ± 0.05
0.00713	0.122	0.45	1.10	0.49	25.0
0.01820	0.120	0.76	0.95	0.50	25.0
0.02903	0.120	0.98	0.98	0.50	25.0
Reduction of tri-iodide ion†					
0.0003	0.230	0.09	0.95	0.26	25.0
0.0022	0.220	0.28	0.98	0.27	24.9
0.0105	0.250	1.17	0.82	0.24	27.0
0.0116	0.230	1.23	1.01	0.26	26.8
Oxidation of iodide ion†					
0.0074	0.200	0.38	1.00	0.30	27.2
0.0340	0.200	1.43	1.00	0.30	25.1
0.0504	0.215	1.30	1.01	0.27	29.5
0.0510	0.220	1.36	0.92	0.27	26.7
Oxidation of tri-iodide ion†					
0.0025	0.120	0.16	1.00	0.50	25.2
0.0120	0.120	1.29	1.00	0.50	27.3
0.0192	0.120	1.43	1.05	0.50	27.2
0.0310	0.130	0.80	0.98	0.46	27.0

* Determined from i vs $\omega^{1/2}$ plots as described in the literature.¹⁰

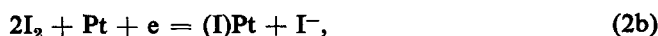
† Data taken from literature.³

Kinetic parameters obtained for iodine and tri-iodide ion reduction and iodide and tri-iodide ion oxidation² are interpreted with the reaction schemes postulated for the same processes in ACN, namely

(a) Iodine reduction



(b) Tri-iodide ion reduction,



(c) Iodide oxidation,



(d) Tri-iodide oxidation,



Taking as a diagnostic criterion the Tafel slope and the first-order kinetics involved in the first cathodic reaction, it is concluded that iodine reduction under Langmuir conditions for the adsorption of intermediates occurs preferentially through mechanism (a) involving (1a) as the rate-determining step. The rate equation derived from mechanism (a) at sufficiently high negative overpotentials is

$$i_L = 2Fk_{1a}\bar{C}_{I_2} \exp[-\Delta\phi F/2RT]; \quad (15)$$

k_{1a}' is the specific rate constant of the rds, \bar{C}_{I_2} the concentration of iodine at the interface, the symmetry factor is taken equal to 0.5, and $\Delta\phi$ the potential drop at the reaction interface. The same reaction scheme in the anodic direction interprets the tri-iodide ion oxidation: mechanism (d) involving (3d) as rds. Thus, at high positive overpotentials, the rate equation for the tri-iodide ion oxidation is

$$i_L = 2FK_{1d} \frac{\bar{C}_{I_3^-}}{\bar{C}_{I_2}} \exp[\Delta\phi F/2RT], \quad (16)$$

involving a first order kinetics with respect to tri-iodide ion concentration and a Tafel slope of $2RT/F$, assuming the symmetry factor equal to 0.5.

This interpretation makes the general reaction picture of the iodine-tri-iodide-iodide electrode sounder, the first cathodic wave being complementary with the second anodic wave. Therefore, with the information gathered at present, we are able to give a more complete reaction scheme than that previously postulated for the electrode reactions occurring in the second anodic wave.

Let us consider now the tri-iodide ion reduction and iodide ion oxidation through mechanisms (b) and (c) respectively, postulated for these processes in ACN solutions. Evidently, the Tafel slope found for tri-iodide reduction on platinum² is much larger than the value $2RT/F$ as derived from mechanism (b) involving step (2b) as rate-determining. This value, however, is independent of the adsorption model prevailing on the electrode. Notwithstanding additional facts such as the reaction order with respect to tri-iodide ion in the rate equation, which is one, and that the cathodic reaction involved in the second wave is complementary to the anodic reaction related to the first anodic wave, for the Tafel slope alone is not sufficient as a mechanistic criterion.

From this standpoint, mechanisms (b) and (c) involving respectively (2b) and (2c) as rate-determining steps are the only ones that explain the known experimental facts correctly. Accordingly, at high overpotentials the rate equations for the tri-iodide ion reduction and iodide ion oxidation are respectively

$$i_L = 2FK_{1b}k_{2b} \frac{\bar{C}_{I_3^-}}{\bar{C}_{I^-}} \exp [-\Delta\phi F/2RT] \quad (17)$$

and

$$i_L = 2Fk_{2c}\bar{C}_{I^-} \exp [\Delta\phi F/2RT], \quad (18)$$

where the meaning of symbols is the same as in (15).

The high Tafel slope obtained from the cathodic current/voltage curves in the forward direction is certainly related to the hysteresis effect. If the activated process is calculated from returning current/voltage curves, a lower Tafel slope results, involving a transfer coefficient between 0.25 and 0.50. The hysteresis effect observed in the present circumstances is reverse of that described for the same process in ACN solutions. No film formation occurs on platinum electrodes at negative potentials in iodine-sodium-iodide solutions in DMSO, as is the case for ACN solutions. Then the surface of the working electrode becomes more active after reaching the high cathodic overvoltage region.

As far as iodide-ion oxidation is concerned, (18) assumes a large electrode surface coverage by iodine atoms and the transfer coefficient of 0.5 is nearly twice the experimental value. A Tafel slope higher than $2RT/F$ for iodide ion oxidation indicates probable changes on the electrode surface during the course of the reaction which are not included in the simple reaction mechanisms already presented. This matter, however, deserves further work under different conditions to allow a more detailed interpretation.

We finally conclude that the iodine-tri-iodide-iodide electrode in DMSO on platinum behaves in a formally similar manner to that in ACN solutions. The kinetics of the processes related to it are interpreted basically with the same reaction mechanisms, once data for the four processes are known. These processes comprise essentially the same rate-determining step, namely the atom + ion reaction for the anodic processes and the corresponding reverse reaction for the cathodic processes. The conclusion is, as far as ACN and DMSO are concerned, that the existence of two waves in current/voltage curves is conditioned by the magnitude of the equilibrium constant of reaction (9). It is likely that the same reaction schemes also apply to the processes occurring in other electron-donor solvents.

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