2676 © *1989 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, **62**, 2676—2683 (1989) [Vol. 62, No. 8

Solvent and Electrode Kinetic Effects on Cathodic Reduction of $I_3^- + 2e \rightarrow 3I^-$ in Some Pure and Mixed Dipolar Aprotic Solvents†

Swapan BHATTACHARYA and Kiron K. KUNDU*
Physical Chemistry Laboratories, Jadavpur University, Calcutta 700032, India

(Received September 14, 1988)

Exchange current densities (i_0) of the redox reaction $I_3^- + 2e^- = 3I^-$ have been determined at 25 °C on platinum (Pt) and graphite (C) electrodes in acetonitrile (ACN), propylene carbonate (PC), *N,N*-dimethylformamide (DMF), and their binary mixtures by potentiostatic polarization studies under near equilibrium conditions. The studies in pure solvents have also been extended to 15 and 35 °C and also on platinized graphite (C)Pt electrode. The kinetic solvent effect data at 25 °C have been analyzed in the light of relative solvation of I_2 and transition state (TS) as reflected from the previously reported transfer free energies (ΔG_t°) of I_2 and that of TS derived therein for the respective solvent systems. The electrocatalytic activities of (C)Pt electrode in different solvent systems are found to be of the same order as that of Pt electrode possibly because of its large roughness factor. But the observed energies of activation (E_a) being of the order $C \gg C(Pt) \approx Pt$ suggest that graphite is intrinsically a weaker electrocatalyst than both the (C)Pt and Pt electrodes, which are however equivalent to each other so far as electrocatalytic activity is concerned. Moreover, while the electrocatalytic activity of Pt and (C)Pt electrodes is found to be in the order ACN > PC > DMF, that of C is ACN > DMF > PC, which have been ascribed to result from the differential adsorption propensities of the solvent molecules with respect to Pt and C surfaces respectively.

The electrode kinetics of I_3^--I^- redox couple had received wide interests[1-12] long since. It is chiefly because of its fairly reversible character in both aqueous[7-9] and various nonaqueous[1-6,10-12] solvents especially on Pt surface. This makes it a suitable reference electrode for the use of different electrochemical studies and also as a galvanic element in some potential primary and secondary batteries.[12-19] In fact its fairly high exchange current densities (i_0) on Pt-surface in some nonaqueous solvents led Coetzee and Gardner[20] to recommend it as a useful reference electrode in those solvents.

Although it is well-known that the degree of reversibility of an electrode depends on the nature of the solvent, electrode surface, temperature etc., relatively few work[20,21] have yet been reported on these aspects of this redox couple. This should have been useful particularly to understand the relative electrode kinetic behavior of this galvanic element to be used either as cathodes in some high energy rechargeable nonaqueous batteries or as the redox couple in some potential nonaqueous photoelectrochemical (PEC) cells.

True, exchange current densities of the I_3^-/I^- redox couple on Pt, steel and glassy carbon electrodes in some pure nonaqueous solvents are available in the literature.[20,21] But they are referred to the different conditions and concentrations, and measured by different techniques. Consequently, these are not amenable to the direct comparison is respect of solvent kinetic effect and of the electrocatalytic activity of the different electrodes, which in fact are vital for the search of the proper solvent and electrode to be used as the potential galvanic elements with increased efficiency either in the nonaqueous batteries[22-24] or in nonaqueous PEC cells.[8,23]

In a recent study[24] from this laboratory it has been observed that the efficiency of charging-discharging behavior of a potential rechargeable cell comprising I_3^-/I^- as a galvanic element, in dipolar aprotic solvents like ACN, PC, and DMF and their binary mixtures is better in some of these mixtures than in pure solvents. So, it was considered highly interesting and useful to make systematic studies on the thermodynamic and kinetic aspects of the involved galvanic reactions not only on the widely used Pt electrode but also on some cheaper electrode substrates. With this end in view in a recent paper[25a] we have reported the solvent effect on the relative E° values of I_3^-/I^-, I_2/I_3^-, and I_2/I^- redox couples and the formation constant (K_f) of I_3^- as per $I_2 + I^- \rightleftarrows I_3^-$ equilibrium, in terms of the solvation behavior of I_2, I^-, and I_3^- species. In another paper[25b] we have also reported the rate constant (k_s) values of the galvanic reaction:

$$3I^- \rightleftarrows I_3^- + 2e\,;\, 2I_3^- \rightleftarrows 3I_2 + 2e$$

on Pt electrode as determined by use of cyclic voltammetric technique. Both these reactions however exhibited quasi-equilibrium type cyclic voltammograms (CVG) in each of these solvent systems, and as a result the evolution of k_s values posed to be an involved problem.

In the present paper we are therefore reporting the exchange current densities (i_0) of the galvanic reaction: $I_3^- + 2e \rightleftarrows I_3^-$ as determined by potentiostatic polarization technique under near equilibrium conditions using both the costly Pt and the cheaper graphite carbon (C) electrodes in each of the solvent systems. Moreover, the studies in pure solvents have also been extended to two other temperatures viz. 15 and 35 °C and also with platinized graphite (C)Pt

---

† Presented in the National Seminar on Electrodics held in Central Electrochemical Research Institute, Karaikundi, Tamilnadu, India during July, 23—25, 1988.

electrode. It is hoped that the activation energies (E_a) of the reaction on different electrode substrates and in different pure solvents will help reflect the intrinsic electrocatalytic activities of the three electrode substrates viz. Pt, C, and (C)Pt and also their relative electrocatalytic behavior in the three dipolar aprotic solvents. Moreover, with a view to have a preliminary reflection about the solvent effect on the reaction mechanism attempts have also been made to take CV's of the reaction in those pure solvents.

Experimental

The solvents ACN (AR, BDH), DMF (E. Merck), and PC (Koch Light) were purified by the methods described earlier.[26,27] KI (GR, E. Merck) was dried by keeping it in vacuum desiccator for a week. I_2 (E. Merck) was purified by sublimation twice under vacuo.

Solvent mixtures were prepared by weight. Solutions of I^- and I_3^- of known strengths in a given solvent were prepared by mixing the appropriate amounts of the standard stock solutions of KI and I_2 in that solvent, the concentrations of which being checked by potentiometric titration with standard $AgNO_3$ solution and volumetric titration with standard thiosulfate solution respectvely.

The cell used in the polarization studies under near equilibrium conditions consists of a three electrode assembly of which the counter electrode is a Pt-foil electrode of 4 cm^2. The test and reference electrodes are either two identical Pt-foils [geometric area A=0.5 cm^2] or of two graphite/platinized graphite electrodes [A=0.1 cm^2]. The advantage of taking the two identical electrodes is that the potential difference between them in any given solution is zero in absence of any external source.[20] The reference electrode immersed in the test solutions is separated from the remainder by a glass cage ending with a fibre-tip similar to that described earlier.[20] In the case of cyclic voltammetric measurements, however, instead of using Pt or C, aqueous saturated calomel electrode SCE(W) was used as the reference electrode. Potentiostatic polarization and linear sweep cyclic voltammetric measurements were carried out with a standard Wenking ST 72 potentiostat along with a Wenking model VSG 72 voltage scan generator. A Houston Omnigraphic X-Y(t) recorder (model 2000) recorded the current and potential which have also been checked by a Kiethley digital electrometer (model 616).

The Pt-foils were pretreated with aqua regia and activated by burning in ethanol flame. Graphite electrodes taken from Nippo dry battery were boiled alternatively in concentrated HCl and hot water, and then dried. They were then covered with a plastic sheet inert to the test solution and the open portion was then polished by rubbing it with a fine file. Some of the graphite electrodes were platinized from 2% hexachloroplatinic acid solution (prepared with 2 M HCl solution; 1 M=1 mol dm^{-3}) using a current of 5 mA from a DB 300 constant current source (Galvanostat) for 30 minutes. The roughness factors of these electrodes were being known from a similar study[28] from this laboratory. The solutions were static at the time of measurements but shaken with a magnetic stirrer at the end of a single measurement, when the drifted voltage of the test electrode reverts back to its original equilibrium value within a time period of maximum five minutes. The initial equilibrium values however reached by about 0.5 hour. The steady state current at a given overpotential η has however reached within 10 minutes. No significant transient effect was observed except immediately after the onset of the over potential, when the rate of rise of current was relatively high. IR-drop was also found to be negligibly small as verified by altering the distance between the test and the reference electrodes even at the relatively high current drain condition. All the solutions were deoxygenated by passing O_2-free pure N_2 for about 15—20 minutes.

Cyclic voltammograms (CVG's) of 0.001 M I_2 solution in presence of 0.1 M $NaClO_4$ supporting electrolyte in water, DMF, ACN, and PC were taken on Pt electrodes with a scan rate of 50 mV s^{-1}. In polarization studies the solution consisted of I_3^- and I^- with a concentration $C_{I_3^-}=C_{I^-}=0.05$ M in those pure organic solvents as well as 25, 50, 75 wt% of their binary mixtures.

Results

A set of typical current (i)-overpotential (η) plots for the I_3^-/I^- redox couples in these solvent systems are shown in Fig. 1. The linear portions in near equilibrium regions are shown, beyond which they are curved. The plots for both Pt and C electrodes in different solvent systems are exactly similar in nature but different only in the extent of linear portions which usually increased with increased exchange current densities for different electrode-solvent pairs, indicating greater reversibility. Since very much low current (ca. 10^{-6} A) passed in the experimental near equilibrium condition (10 mV>η>−10 mV), the mass transfer polarization has been taken to be negligibly small. Moreover, the fact that a few measurements

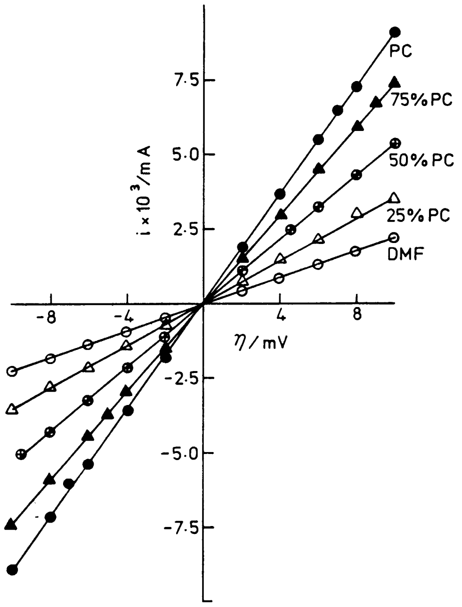

Fig. 1. Plots of i×10^3/mA vs. η/mV for the cathodic solution of $I_3^-+2e^-\rightarrow 3I^-$ on carbon electrodes in PC (●), 75% PC +25% DMF (▲), 50% PC +50% DMF (⊕), 25% PC +75% DMF (△), and DMF (○) solvents.

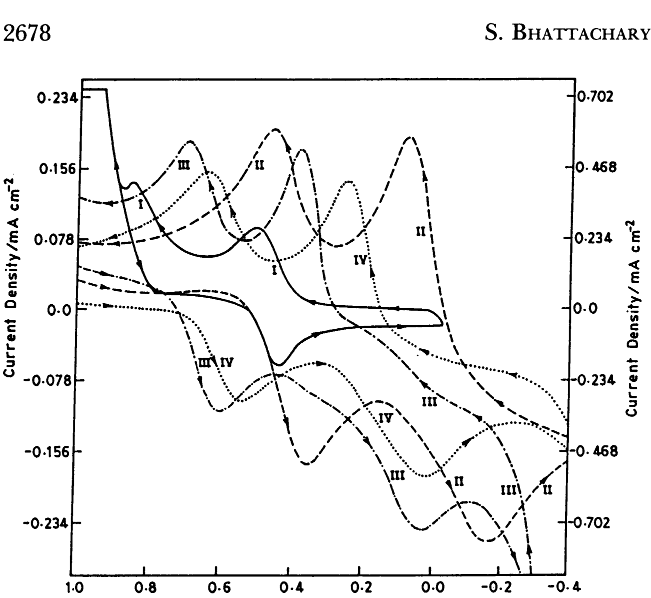

Fig. 2. Cyclic voltammograms of I_2 (10^{-3}M) solutions on platinum electrode. Reference electrode: saturated aqueous calomel. Solvents: H_2O (I) (current scale right hand side) (———), ACN (II) (---------), DMF (III) (—·—·—), PC (IV) (·········).

both at the static and stirring conditions of the solutions show no difference in the readings except some little fluctuations within tolerance limits, also appears to substantiate the above assumption.

The exchange current density (i_0) values for the reaction in different solvents have been determined by use of the Ohmic relation[29]

$$i_0 = \frac{RT\nu}{nF}(i/\eta)_{\eta\to 0} \tag{1}$$

where i is the current, η is the overpotential, n is the number of electrons involved in the overall reaction, and ν is that in the rate-determining step (rds), which are taken to be 2 and 1 respectively.

In fact, although several mechanisms[20,21,29–33] have been proposed for the I_3^-/I^- system, none is without controversy. We therefore assumed, as Coetzee et al. did,[20] the widely accepted mechanism of Dane et al.[31]

$$I_3^- \rightleftarrows I_2 + I^-$$

$$I_2 + e^- \xrightarrow{\text{rds}} I_{ads} + I^-$$

$$I_{ads} + e^- \rightleftarrows I^-$$

Scheme 1.

for which n=2 and ν=1. This is likely to be true in these solvent systems as well, as is evident from the similar behavior of CVG's in the solvents. As could be seen from Fig. 2, the observed CVG's exhibit two peaks in all the cosolvents including water, where the first peak is somewhat subdued. This kind of behavior has also been reported earlier in some of these cosolvents.[9,23] Thus the two peaks indicate that the reduction of I_2 takes place in two overall reactions

$$3\,I_2 + 2e = 2\,I_3^-$$

$$I_3^- + 2e = 3\,I^-$$

Scheme 2.

in all the cosolvent systems though at different potential regions because of the solvent effect on $E°$ value.[26a] Notably, the peak currents (i_p) for both the reactions vary in the increasing order PC<DMF<ACN<H_2O whereas the peak potentials (E_p) vary in the order H_2O<DMF<PC<ACN. While the former order reflects relative kinetic solvent effect, the latter reveals the relative thermodynamic solvent effect of the reaction in the solvents concerned. Evidently, in H_2O the reactions are both thermodynamically and kinetically favorable, whereas in ACN although the reactions are not so much favorable thermodynamically, they are fairly so kinetically as compared to other cosolvents. Since the nature of CVG's for I_2–I_3^- and I_3^-–I^-systems are nearly similar at least in all these organic solvents, their mechanisms are likely to be same in all the solvents concerned. This led us to believe, as Coetzee et al. did, that the widely accepted Dane et al.'s mechanism: Scheme 1 is also likely to be true in all these solvents.

Discussion

The values of the exchange current densities (i_0) in different solvent mixtures are presented in Table 1 and the variation of RT ln ($_si_0$ /$_ri_0$) with cosolvent compo-

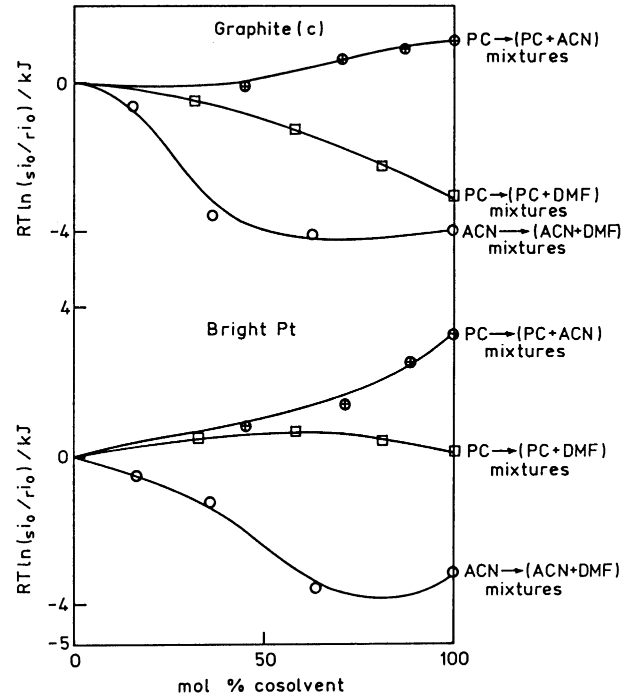

Fig. 3. Variation of $RT\ln(_si_0/_ri_0)$ against mol% cosolvent for the cathodic reduction of $I_3^-+2e\to 3I^-$ on bright Pt and carbon C electrodes in PC→PC+ACN, PC→PC+DMF, and ACN→ACN+DMF mixtures at 25 °C.

Table 1. Values of i_0 in A cm^{-2}, $RT\ln({}_si_0/{}_ri_0)$, $RT\ln({}_sk_s/{}_rk_s)$, $\Delta G_t^\circ(I_2)$, and $\Delta G_t^\circ(TS)$ in kJ mol^{-1} for the Cathodic Reduction of $I_3^- + 2e \rightarrow 3I^-$ on Pretreated Bright Platinum (Pt) Electrode in Some Dipolar Aprotic Solvent Systems

Wt % cosolvent	Mole fraction cosolvent	$i_0\times10^5$	$RT\ln({}_si_0/{}_ri_0)$	$\Delta G_t^\circ(I_2)$	$-\delta(\Delta G^{\neq}) = RT\ln\frac{{}_sK_s}{{}_rK_s}$	$\Delta G_t^\circ(TS)$
PC → (PC+DMF) mixtures						
0	0	7.6	0	0	0	0
25	0.32	9.2	0.5	−6.8	−4.4	−2.5
50	0.58	10.1	0.7	−8.7	−4.6	−4.1
75	0.80	8.7	0.3	−9.3	−5.4	−3.9
100	1.00	8.1	0.2	(−9.5)	−5.6	−3.9
PC → (PC+ACN) mixtures						
0	0	7.6	0	0	0	0
25	0.45	10.6	0.8	−0.4	−2.6	2.2
50	0.71	13.1	1.4	−0.2	−4.0	3.8
75	0.88	21.2	2.5	0.0	−3.7	3.7
100	1.00	28.0	3.2	0.0	−4.7	4.7
ACN → (ACN+DMF) mixtures						
0	0	28.0	0	0	0	0
25	0.16	22.5	−0.5	−4.6	−3.1	−1.5
50	0.36	17.0	−1.2	−6.8	−2.4	−4.4
75	0.63	6.5	−3.6	−8.5	−2.8	−5.7
100	1.00	8.1	−3.1	(−9.5)	−1.2	−8.3

sition in Fig. 3, where subscripts s and r refer to the solvent and the assumed reference solvent respectively. In the cases of PC+ACN and ACN+DMF solvent systems, PC is the reference solvent and ACN and DMF are the cosolvents whereas in the case of ACN+DMF solvent system ACN is the reference solvent and DMF is the cosolvent. The results show a strong solvent dependence of i_0 values obtained for both types of electrodes: bright platinum (Pt) and graphite carbon (C), the highest value being almost 10 times greater than the lowest value. The order of the i_0 values of Pt electrode in different solvents follows the sequence: ACN≫DMF≈PC whereas that on C electrode is ACN>PC>DMF.

Moreover, from the data in Table 1 and in Fig. 3 it can be seen that in the case of Pt electrode while the i_0 values in PC-DMF solvent system remain more or less same with a slight maximum around 50 mol% DMF, those in PC-ACN solvent system increase almost monotonically with increase of cosolvent ACN and those in ACN-DMF system decrease monotonically upto 70 mol% of the cosolvent DMF beyond which there is an upward trend.

In the case of graphite electrode, although the behavior of $RT\ln({}_si_0/{}_ri_0)$-composition profiles in PC+ACN or ACN+DMF mixtures is nearly similar to those on Pt surface in the respective solvent systems, that for PC+DMF system takes a sharp downward trend right from zero percent DMF, instead of 50 mol% DMF observed in the case of Pt. Moreover, while the i_0 value in PC on C electrode remains nearly same as that on Pt electrode, this however gets increased with the addition of ACN and decreased with DMF. Evidently, rates of the electrode reaction are not only a function of the solvent properties but also on the electrode materials to some extent, as expected.

As the electrode reactions are multistep reactions, understanding of the solvent effect on electrode reactions, such as this, is an involved problem. This is because the reactions are not only guided by the solvated species involved in the different steps in Scheme 1 but also dependent on the coverage of the electrode by solvent molecules (θ_s). Besides, the solvent effect on the equilibrium potential $\Delta\phi_e$ involved in the expression for exchange current density (i_0):

$$i_0 = nF\vec{k}_s C_{I_2}\exp(-\beta\Delta\phi_e F/RT) \qquad (2)$$

where $\vec{k}_s$ is the specific rate constant depending upon the solvent and the electrode surface, β the symmetry factor and other terms having usual significance, is also equally important. So, in order to see the true solvent effect let us examine the relative rates and solvation effect on the reactant I_2 in the rds and that of the transition state (TS) as obtained by use of the relation (3)

$$\begin{aligned} RT\ln({}_s\vec{k}_s/{}_r\vec{k}_s) &= -\delta(\Delta G^{\neq}) = (-{}_s\Delta G^{\neq}) - (-{}_r\Delta G^{\neq}) \\ &= \Delta G_t^\circ(I_2) - \Delta G_t^\circ(TS) \qquad (3) \end{aligned}$$

which follows from the assumed rds as $I_2 + e(M) \rightarrow TS \rightarrow$ products and $RT\ln({}_s\vec{k}_s/{}_r\vec{k}_s)$ is related to $RT\ln({}_si_0/{}_ri_0)$ by Eq. A7 [vide appendix]. Here $\Delta G_t^\circ(i)$ stands for the transfer free energy of any species i from the standard state in the assumed reference solvent (r) to the standard state in the solvent (s) i.e. for the transfer process: i(r)→i(s). In Table 2 we present the values of transfer free energies of I_2 as obtained from a

Table 2. Values of i_0 in A cm^{-2}, $RT\ln({}_si_0/{}_ri_0)$, $RT\ln({}_sk_s/{}_rk_s)$, $\Delta G_t^\circ(I_2)$, and ΔG_t°(TS) in kJ mol^{-1} for the Cathodic Reduction of $I_3^-+2e\rightarrow3I^-$ on Pretreated Graphite (C) Electrode in Some Dipolar Aprotic Solvent Systems

Wt % cosolvent	Mole fraction cosolvent	$i_0\times10^5$	$RT\ln({}_si_0/{}_ri_0)$	$\Delta G_t^\circ(I_2)$	$-\delta(\Delta G^{\neq}) = RT\ln\frac{{}_sK_s}{{}_rK_s}$	ΔG_t°(TS)
		PC → (PC+DMF) mixtures				
0	0	9.0	0	0	0	0
25	0.32	7.3	−0.5	−6.8	−5.3	−1.5
50	0.58	5.1	−1.4	−8.7	−6.7	−2.0
75	0.80	3.5	−2.3	−9.3	−8.1	−1.2
100	1.00	2.6	−3.1	(−9.5)	−8.8	−0.7
		PC → (PC+ACN) mixtures				
0	0	9.0	0	0	0	0
25	0.45	8.3	−0.2	−0.4	−3.6	3.2
50	0.71	11.5	0.6	−0.2	−4.7	4.5
75	0.88	12.5	0.8	0.0	−5.4	5.4
100	1.00	13.6	1.0	0.0	−6.9	6.9
		ACN→ (ACN+DMF) mixtures				
0	0	13.6	0	0	0	0
25	0.16	10.9	−0.6	−4.6	−3.2	−1.5
50	0.36	3.1	−3.7	−6.8	−4.8	−2.0
75	0.63	2.6	−4.1	−8.5	−3.3	−5.2
100	1.00	2.6	−4.1	(−9.5)	−2.1	−7.6

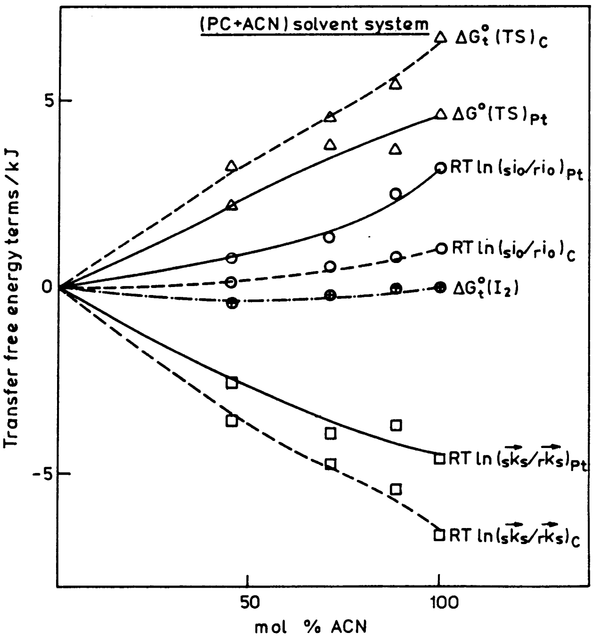

Fig. 4. Variation of $RT\ln({}_si_0/{}_ri_0)$ (○), $RT\ln({}_s\vec{k}_s/{}_r\vec{k}_s)$ (□), ΔG_t° (I_3) (—·—·—), and ΔG_t° (TS) (Δ) for the cathodic reduction of $I_3^-+2e^-\rightarrow3I^-$ on Pt (solid lines) and graphite (C) (dotted lines) electrodes with mol% ACN in PC→PC+ACN solvent system.

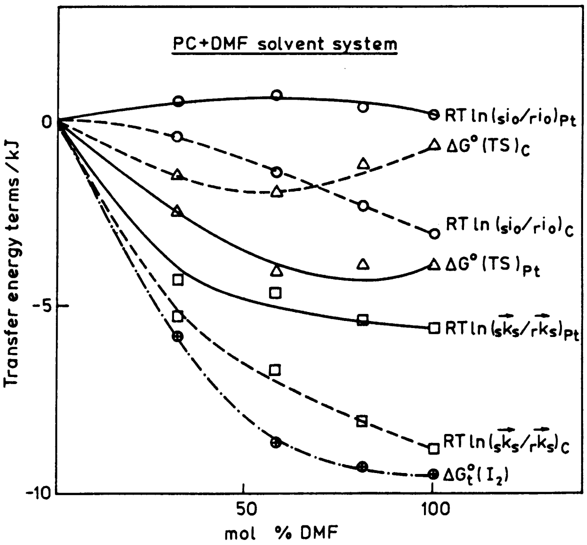

Fig. 5. Variation of $RT\ln({}_si_0/{}_ri_0)$ (○), $RT\ln({}_s\vec{k}_s/{}_r\vec{k}_s)$ (□), ΔG_t° (I_2) (—·—·—), and ΔG_t° (TS) (Δ) for the cathodic reduction of $I_3^-+2e^-\rightarrow3I^-$ on Pt (solid lines) and graphite (C) (dotted lines) electrodes with mol% DMF in PC+DMF solvent system.

previous paper[25a] and those of $-\delta(\Delta G^{\neq})$ as well as ΔG_t°(TS) as computed by use of Eq. 3 for both Pt and C electrodes and for all the three solvent systems, taking PC as the reference solvent in the PC+DMF and PC+ACN solvent systems and ACN in the ACN+DMF solvent system. Figures 4—6 depict the plots of $\Delta G_t^\circ(I_2)$, $[-\delta(\Delta G^{\neq})=RT\ln({}_s\vec{k}_s/{}_r\vec{k}_s)]$, ΔG_t°(TS), and $RT\ln({}_si_0/{}_ri_0)$ values as a function of the composition of the added cosolvent for both Pt and C electrodes.

From the plots of $RT\ln({}_s\vec{k}_s/{}_r\vec{k}_s)$ it may be noted that the values of the rate constant $\vec{k}_s$ of the reaction decrease as DMF or ACN is added to PC in PC+DMF and PC+ACN solvent systems respectively, but the values pass through a distinct minima when DMF is added to ACN in ACN+DMF solvent system. Notably, the actual values on Pt and C electrodes though

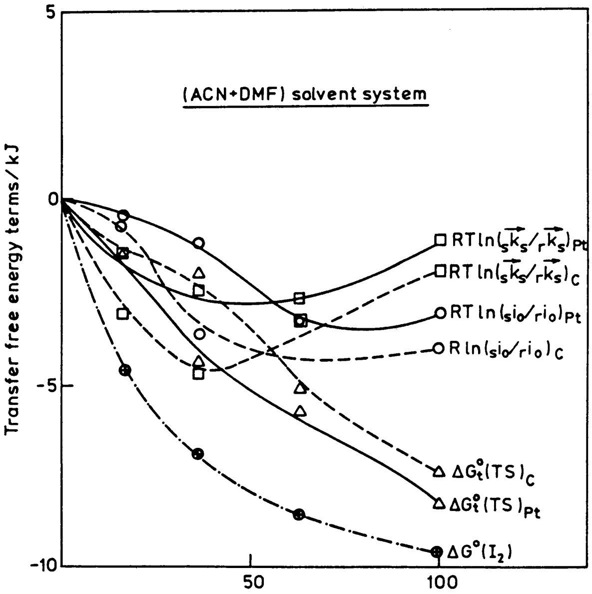

Fig. 6. Variation of $RT\ln({}_si_0/{}_ri_0)$ (○), $RT\ln({}_s\vec{k}_s/{}_r\vec{k}_s)$ (□), $\Delta G_t^\circ(I_2)$ (—·—·—), and ΔG_t° (TS) (△) for the cathodic reduction of $I_3^-+2e^-\rightarrow 3I^-$ on Pt (solid lines) and graphite (C) (dotted lines) electrodes with mol% DMF in ACN→ACN+DMF solvent system.

differ appreciably, their overall behavior is more or less similar in nature in the respective solvents. Moreover, the relative behavior of $\vec{k}_s$ values is also fairly different from that of i_0 values in the respective solvents. Evidently, either the increasing solvation of the reactant I_2 in the rds or decreasing solvation of the transition state (TS) is responsible for the observed solvent effect on $\vec{k}_s$ values in these solvent systems.

Thus in PC+ACN solvent system as the cosolvent ACN is added to PC the solvation of I_2 hardly alters for $\Delta G_t^\circ(I_2)_{PC\rightarrow PC+ACN}$ remains nearly invariant, whereas the solvation of TS decreases to a large extent (see Fig. 4). And hence the decreased solvation of TS is responsible for the decreased rate constant values in the solvent system. The reason for decreased solvation of TS with increased ACN content may be attributed partly to the larger dipolar and dispersion interactions of TS with PC molecules compared to ACN molecules [$\mu_{PC}=4.98$D, $\mu_{ACN}=3.92$D; $\alpha_{PC}=8.56\times10^{-24}$ cm^3, $\alpha_{ACN}=4.41\times10^{-24}$ cm^3][25a] and partly to the smaller coverage θ_s and hence larger free surface $(1-\theta_s)$ in the case of PC molecules compared to the respective cases in the increased proportion of ACN molecules. This is because of the intrinsic structural and electronic configuration of the organic molecules. The decreased reaction rates on C surface compared to Pt surface seemingly result from the fact that a carbon atom with sp^2 electrons can usually be expected to undergo interaction with π-electron clouds of the donor -C≡N or >C=O groups of the solvent molecules. Moreover, as CH_3CN is smaller in size and bears greater thickness of the π-electron cloud than those of PC or DMF, it is expected to get adsorbed more on porous C electrode than bright Pt electrode.[34-36]

In PC+DMF solvent system, as DMF is added to PC the relative reaction rates get reduced on both the electrodes because of the pronounced solvation of I_2 molecules rather than the solvation of TS molecules which in fact get less solvated in the cases of both C and Pt electrodes at DMF rich compositions. Evidently, the effect of possible increased solvation of the TS by DMF molecules due to dispersion interactions[25a] is overcome by the superimposed effect of $(1-\theta_s)$ factors which seem to increase with DMF content and on C surface compared to Pt surface.

In ACN+DMF mixtures however, as DMF is added to ACN, the relative reaction rates, i.e. $RT\ln({}_s\vec{k}_s/{}_r\vec{k}_s)$, are found to pass through a minimum in both the cases of Pt and C electrode surfaces. The observed variation of this is seemingly guided by the effect of pronounced solvation of I_2 molecules as opposed by the pronounced solvation of TS molecules which being larger in the case of Pt than on C surface, the relative profile for Pt lies above that for C. Since θ_{ACN} is likely to be greater than θ_{DMF}, solvation of TS through $(1-\theta_{org})$ is more in ACN-DMF mixtures than in ACN and this is again less on C surface than on Pt, thus resulting in the observed relative nature and positions of the profiles of relative rate constants on Pt and C surface in this solvent mixture. As the effect of temperature and the related energy of activation is expected to impart better reflection on the effect of electrode surfaces on the reaction rate, we may com-

Table 3. Logarithms of Exchange Current Densities at Different Temperatures and the Activation Energies (E_a)/kJ in the Different Solvents

$T^{-1}\times10^3$	$-\log i_0$								
	ACN			PC			DMF		
	PT	C/Pt	C	Pt	C/Pt	C	Pt	C/Pt	C
3.470	3.67	3.55	4.10	4.29	4.18	5.64	4.41	4.08	4.75
3.354	3.62	3.48	3.87	4.20	4.00	5.02	4.24	3.90	4.49
3.245	3.55	3.44	3.71	4.10	3.97	4.11	4.09	3.83	4.25
Activation energy (E_a)/kJ mol^{-1}	8.5	8.4	32.0	16.2	16.2	13.5	26.6	26.2	44.4

pare the i_0 values at different temperatures at least for three pure solvents as presented in Table 3. A plot of log i_0 vs. T^{-1} for the reaction at a particular concentration of the reacting species yielded straight lines. The slopes of the lines yielded the E_a values as

$$E_a = -[\delta \ln {}_s i/\delta(T)^{-1}]_{c=\text{const.}} \tag{4}$$

The E_a values so obtained are presented in Table 3. From the perusal of E_a values it may be noted that E_a values for both bright Pt and C(Pt) electrodes are nearly equal to each other in the respective solvents whereas that on bare C electrode is fairly larger than those of both bright Pt and (C)Pt electrodes. This implies that (C)Pt electrode is as good as bright Pt electrode as the electrocatalyst for this reaction, whereas the bare C electrode is a much weaker electrocatalyst than either of the other two types of electrodes. The catalytic effect of Pt surface compared to C surface may be attributed$^{20)}$ to the fact that sp^2 hybridized electrons of graphite C atom interacts more strongly with the nonbonding and π electrons of the O and N centers of the solvent molecules rather than with 5s electrons of I atom. This again seemingly indicates that the relative values of θ_s play an important role in dictating the relative catalytic activity of the electrode surfaces.

It may also be noted that E_a values on Pt and (C)Pt electrodes in the three solvents lie in the order ACN< PC<DMF, while that on C electrode is ACN< DMF<PC. In fact while the E_a values on Pt and (C)Pt electrodes and in the ratio ACN:PC: DMF=1:2:3, that on bare C electrode is 1:4:1.5. The strikingly larger E_a values on C surface in PC compared to other solvents apparently indicates that the differential propensities for adsorption of cosolvent molecules (θ_s) on C compared to Pt surface is possibly the dictating factor. But as is clear from our earlier discussion, just as for i_0 values, the solvent effect on E_a values as well should be an involved problem, as the latter is afterall computed from the temperature coefficient of i_0 values rather than that of $\vec{k}_s$ values, which should give a better reflection of the solvent effect on the involved kinetics of the reaction. But the limited knowledge on the temperature coefficients of $\Delta G_t^\circ(i)$ terms and hence the $\vec{k}_s$ values does not permit us to further examine the solvent effect on E_a values at this stage.

Thanks are due to the CSIR, Govt. of India for the financial assistance.

Appendix I

Consider the reaction scheme (Scheme A) for the overall reaction $I_3^- + 2e^- \rightleftarrows 3I^-$:

$$\begin{array}{ll} I_3^- \rightleftarrows I_2 + I^- & \\ I_2 + e^- \xrightarrow{\text{rds}} I^- + I & \text{Scheme A.} \\ I + e^- \rightleftarrows I^- & \end{array}$$

The exchange current i_0 is given by

$$i_0 = nF\vec{k}_s C_{I_2} \exp(-\beta \Delta\phi_e F/RT) \tag{A1}$$

where the terms have usual significance. Replacing C_{I_2} by $K_f C_{I_3^-}/C_{I^-}$ where K_f stands for the formation constant of I_3^- : $I_2 + I^- \rightleftarrows I_3^-$, we have

$$i_0 = nF\vec{k}_s \frac{I}{K_f} \frac{C_{I_3^-}}{C_{I^-}} \exp(-\beta \Delta\phi_e F/RT) \tag{A2}$$

If we consider the equantities of $\ln i_0$ in the solvent (s) relative to the reference solvent (r) and multiply both sides by RT we have

$$\begin{aligned} RT\ln({}_s i_0/{}_r i_0) &= RT\ln\frac{{}_s\vec{k}_s}{{}_r\vec{k}_s} + RT\ln\frac{{}_rK_f}{{}_sK_f} \\ &+ RT[\Delta\ln\frac{C_{I_3^-}}{C_{I^-}}] - \beta F[{}_s\Delta\phi_e^\circ - {}_r\Delta\phi_e^\circ] \\ &+ \beta F\frac{RT}{2F}[\Delta\ln\frac{C^3_{I^-}}{C_{I_3^-}}] \end{aligned} \tag{A3}$$

where Δ's stand for the differences of the respective quantities in the solvent(s) and the reference solvent (r).

Since K_f values are fairly large and comparable,$^{25a)}$ from the experimental condition we have $C_{I_3^-} = C_{I^-} = 0.05$ M for all the solvents.

and hence, $\Delta\ln(C_{I_3^-}/C_{I^-}) = 0$, and $\Delta\ln(C^3_{I^-}/C_{I_3^-}) = 0$

Thus we have

$$\begin{aligned} RT\ln({}_s i_0/{}_r i_0) &= RT\ln({}_s\vec{k}_s/{}_r\vec{k}_s) \\ &+ RT\ln({}_rK_f/{}_sK_f) - \beta F({}_s\Delta\phi_e^\circ - {}_r\Delta\phi_e^\circ). \end{aligned} \tag{A4}$$

If we express the second and third terms of Eq. A4 in terms of the involved transfer free energies, ΔG_t° of the species involved

$$\begin{aligned} RT\ln({}_rK_f/{}_sK_f) &= \Delta G_t^\circ(I_3^-) - \Delta G_t^\circ(I_2) \\ &- \Delta G_t^\circ(I^-) \end{aligned} \tag{A5}$$

and

$$\begin{aligned} -\beta F({}_s\Delta\phi_e^\circ - {}_r\Delta\phi_e^\circ) &= \frac{3}{4}\Delta G_t^\circ(I^-) \\ &- \frac{1}{4}\Delta G_t^\circ(I_3^-) \end{aligned} \tag{A6}$$

if β is taken equal to 1/2.
Replacing these terms by transfer free energy terms Eq. A4 can be written as

$$\begin{aligned} RT\ln({}_s i_0/{}_r i_0) &= RT\ln({}_s\vec{k}_s/{}_r\vec{k}_s) + \frac{3}{}\Delta G_t^\circ(I_3^-) \\ &- \Delta G_t^\circ(I_2) - \frac{1}{4}\Delta G_t^\circ(I^-) \end{aligned} \tag{A7}$$

As the transfer free energies of I_2, I_3^-, and I^- are already known for the concerned solvent systems,$^{25a)}$ $RT\ln({}_sk_s/{}_rk_s)$ values for the systems can be computed by using Eq. A7.

References

1) M. C. Giordano, J. C. Bazan, and J. Arvia, *Electrochim. Acta,* **11**, 1553 (1966).

2) A. T. Hubbard, R. A. Osteryoung, and F. C. Anson, *Anal. Chem.,* **38**, 692 (1966).

3) I. E. Barbasheva, UYu M. Povarov, and D. D. Ludovlsev, *Elektrokhimiya,* **3**, 9, 1149 (1967)

4) I. M. Kolthoff and J. F. Coetzee, *J. Am. Chem. Soc.*, **75**, 1571 (1953).

5) Yu. M. Povarov, I. E. Barbasheva, and D. D. Lukovlsev, *Elektrokhimiya*, **3**, 10, 1202 (1967); *Soviet Electochem.*, **3**, 1071 (1967).

6) A. I. Popov and D. H. Geske, *J. Am. Chem. Soc.*, **80**, 1340 (1958).

7) a) S. Mine, J. Sobkowski, and K. Kisowska, *Roezniki Chem.*, **40**, 9, 1575 (1966); b) G. Dryhurst and P. J. Elving, *Anal. Chem.*, **39**, 606 (1967).

8) a) H. Gerischer, *Advan. Electrochem., Electrochem. Eng.*, **1**, 1978 (1961); b) W. Kautek and F. Willing, *Electrochim. Acta*, **26**, 1702 (1981); c) O. Peraldo and L. Bicelli, *Trans SAEST*, **19**, 243 (1984).

9) R. Nakata, and S. Okazaki, and T. Fujinaga, *J. Electroanal. Chem.*, **125**, 413 (1981).

10) I. V. Nelson and R. T. Iwamoto, *J. Electroanal. Chem.*, **7**, 218 (1964).

11) M. C. Giordano, J. C. Bazan, and A. J. Arvia, *Electrochim. Acta*, **12**, 723 (1967)

12) G. Raspi, F. Pergola, and R. Guidelli, *Anal. Chem.*, **344**, 472 (1972).

13) V. A. Tyagai and G. Yu. Kolbasov, *Electrokhimiya*, **7**, 11, 1722 (1971).

14) H. S. Swofford and J. H. Propp, *Anal. Chem.*, **37**, 974 (1965).

15) a) S. Schuldiner and T. B. Warner, *Anal. Chem.*, **36**, 2510 (1964); b) F. C. Anson and R. A. Osteryoung, *Anal. Chem.*, **36**, 2511 (1964).

16) V. S. Bagotzky, Yu. B. Vassitiev, and I. I. Pyshnogracra, *Electrochim. Acta*, **16**, 12, 2141 (1971).

17) R. B. Fulton and H. S. Sworford, Jr., *Anal. Chem.*, **40**, 1373 (1968).

18) G. Piccardi and R. Guidelli, *J. Phys. Chem.*, **72**, 2782 (1968).

19) J. Jorne and P. G. Pai, *J. Electrochem. Soc.*, **132**, 1612 (1985).

20) J. F. Coetzee and C. W. Gardner, Jr., *Anal. Chem.*, **54**, 2530 (1982).

21) R. T. Iwamoto, *Anal. Chem.*, **31**, 955 (1959).

22) Y. Matsuda and H. Stake, *J. Electrochem. Soc.*, **127**, (1980).

23) S. Bhattacharya, U. Mondol, J. Dutta, K. Das, and K. K. Kundu, "Advances in Electrochemical Science and Technology," Oxford & IBH Publishing Co. Ltd., New Delhi (1988).

24) "Semiconductor Electrodes," ed by H. O. Finklaa, Elsevier (1988).

25) J. Dutta, A. Bhattacharya, and K. K. Kundu a) *Bull. Chem. Soc. Jpn.*, **61**, 1735 (1988); b) *Bull. Chem. Soc. Jpn.*, Communicated.

26) a) K. Das, A. K. Das, and K. K. Kundu, *Electrochim. Acta*, **26**, 471 (1981); b) K. Das, K. Bose, and K. K. Kundu, *Electrochim. Acta*, **26**, 479 (1981).

27) J. L. Murray and Y. L. Howard, *J. Phys. Chem.*, **77**, 26 (1973).

28) P. K. Guha, Ph. D. Thesis, Jadavpur University, Calcutta, India (1987).

29) J. O'M. Bockris, A. K. N. Reddy, "Modern Electrochemistry," Plenum Press, New York (1977), Vol. 2.

30) L. M. Dane, L. J. J. Janspen, and J. G. Hoogland, *Electrochim. Acta*, **13**, 507 (1968)

31) E. Gileadi, E. Kirowa-Eisner, J. Penciner, "Interfacial Electrochemistry," Addison, Wesley Publishing Company Inc, Massachusetts, U. S. A. (1975).

32) K. J. Velter, "Electrochemical Kinetics," Academic Press, New York (1967).

33) P. G. Desideri, L. Lepri, and D. Helmler, "Encyclopedia of Electrochemistry of the Elements," ed by A. Bard, Marcel Dekku, New York (1973), Vol. 1.

34) A. Wieedowski, *Electrochim. Acta*, **26**, 1121 (1981).

35) M. sSzklarezyk and J. Sobkowski, *Electrochim. Acta*, a) **26**, 345 (1981); b) **25**, 1597 (1980).

36) H. Yoshida and K. Kamegaua, Ext Abstr Program Bienn Conf Carbon 15th, 252 (1981).