The Influence of Fluoride Media and CH_3CN on the Voltammetric Behavior of Ferrocene, Quinhydrone, and Methyl Phenyl Sulfide on Pt and Carbon Electrodes

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Received: November 29, 1999
Final version: February 4, 2000

Abstract

Cyclic voltammetric behavior of ferrocene, quinhydrone, and methyl phenyl sulfide on Pt, glassy carbon (GC) and polypropylene composite graphite (CPP) electrodes are compared in TBAP/CH_3CN, triethylamine (TEA).3HF/CH_3CN and TEA.3HF media. In medium containing CH_3CN, the voltammetric behavior of title compounds are quite similar in the absence and presence of fluoride ions. The voltammetric features vary only slightly, due to some adsorption effects and catalytic hydrogen evolution on Pt. In TEA.3HF medium, all three electrodes show significantly higher background currents in the middle potential region itself. The peak potential and the charge transfer rate constant of these compounds are also found to be significantly different in TEA.3HF room temperature melt. The analytical implications of these medium effects are also discussed.

Keywords: Triethylamine tris-hydrogen fluoride, Acetonitrile, Ferrocene, Quinhydrone, Methyl phenyl sulfide, Electrooxidation, Cyclic voltammetry

1. Introduction

Pt and carbon electrodes have been generally employed as voltammetric sensors in fluoride media of widely different activities. In liquid HF medium, Pt and glassy carbon electrodes (GCE) gave distinct voltammetric peaks for hydroquinone [1] and a number of other organic compounds [2]. Potentiometric [3] as well as voltammetric [4] methods were employed in this medium. Even in strong super acid HF solutions containing SbF_5, Pt served as a reproducible inert electrode without exhibiting any surface effects [5]. In aprotic DMF medium, the presence of BF_4^- ions led to a fluoride film formation effect on GCE, leading to a slight decrease in the electron transfer rate of simple electron transfer reactions [6]. However, voltammograms in aprotic fluoride medium are routinely carried out [7–9] to determine the potential for constant potential electrolysis in selective electrochemical fluorination. In high temperature cryolite melt [10] as well as low temperature KF-2HF melts [11], although the formation of surface C–F bond has been established [12], the electron-transfer properties were not significantly affected by these films [11, 12]. In the inorganic analysis involving mixture of cationic species in aqueous solutions, fluoride ions are commonly employed to reduce interference and improve selectivity. This is despite the observation that the carbon electrodes can undergo significant surface transformations in fluoride medium [13] especially under strong polarization conditions [14].

Anhydrous HF containing bases like pyridine and trialkylamine are nonviscous liquids showing reasonable electrical conductivity and room temperature stability. These may essentially be treated as room temperature fluoride melts [15, 16]. In pyridinium- HF medium, substantially higher oxidation of electrode surface as well as direct oxidation of pyridine were noticed when pyridine content exceeded 5 % [17]. In triethylamine-3HF [18], triethylamine-5HF [19], and tetraalkylammonium fluoride media, considerably higher background currents are noticed. However, distinct voltammetric responses could be obtained for organic compounds when higher reactant concentrations are employed [18–21].

Despite the use of various fluoride media as indicated above, no direct comparison of different types of fluoride media to evaluate the effect of fluoride content and presence of solvent have been reported. What is the influence on fluoride ion concentration on the voltammetric responses of electroactive species? Do the electroanalytical parameters like peak current and peak potential depend on fluoride ion concentration, electrode materials and solvents such as commonly employed CH_3CN? What is the electrode of choice for different fluoride media? What are the causes of elctrode effects if any? The objective of the present investigation is to find answers to some of the above issues. Ferrocene, quinhydrone and methyl phenyl sulfide were taken as typical compounds which show reversible, quasi-reversible, and irreversible charge transfer responses in aprotic medium. In addtion to Pt and GCE, a polypropylene composite graphite electrode (CPP) containing 80 % polypropylene was also chosen for the evaluation of surface effects. Acetonitrile containing tetrabutylammonium perchlorate (TBAP/CH_3CN) and triethylamine-trishydrogen fluoride (TEA.3HF/CH_3CN) were compared to identify the influence of fluoride ion. The latter was then compared with the voltammetric behavior in TEA.3HF liquid to evaluate the effect of absence of CH_3CN and higher fluoride content.

2. Experimental

Ferrocene, quinhydrone, and methyl phenyl sulfide have been obtained from Sisco Research Laboratory (SRL), India. CH_3CN (HPLC) was used as the solvent. TEA.3HF was prepared by mixing TEA with freshly distilled anhydrous HF (AHF) (TANFAC, India) at low temperature, evaluating the HF content by titration and adjusting TEA.3HF ratio accordingly. TBAP was dried in vaccum dessicator and used. Pt wire, fused through a glass tube (exposed area 0.088 cm^2) was employed as the working electrode. GCE and CPP rods tight fitting into Teflon also served as working electrodes (area 0.07 cm^2). A Pt foil served as the counter electrode. Though TEA.3HF and other

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fluoride media employed in the present work are not aggressive towards glass, a polypropylene undivided cell was used throughout. The choice of reference electrode posed some serious problems. The palladium Pd/H_2 electrode showed instability especially in TEA.3HF medium in which Pd dissolution was noticed. Hence, a Pt wire was used in TEA.3HF as a quasi-reference. The reference potential, however, was compared from time to time externally against saturated calomel electrode (SCE). The potential drift was generally found to be within in $\pm$ 5 mV. In the other two media, SCE was used as the reference electrode. All the potential data reported here are against SCE. In general, $\pm$ 3 % variation in peak current values and $\pm$ 5 mV variation in peak potential values were considered to be satisfactory levels of reproducibility. All the voltammetric measurements were carried out at 303 $\pm$ 1 K.

A Wenking Potentiostat (Model LB 75L) and voltage scan generator (Model VSG 72) were used for potential control and programming and Rikandenki (Model NP-0363) was used to record the results. SEM was performed with a JEOL (Model 30CF) scanning electron microscope.

3. Results and Discussion

3.1. Voltammetric Behavior in 0.05 M TBAP/CH_3CN and 0.1 M TEA.3HF/CH_3CN Medium

Typical cyclic voltammograms of 2 mM ferrocene in acetonitrile containing 0.05 M TBAP on Pt, GCE and CPP electrodes under otherwise identical experimental conditions are presented in Figure 1 A,B,C, respectively. Distinct, highly reversible cyclic voltammograms are observed on all three electrodes. However, slight differences are noticed among the voltammetric responses. The background current in the double layer region is very low on Pt electrode, but increases on GCE and CPP electrodes, in this order. The anodic peak potential (E_{pa}) increases slightly from Pt electrode to CPP electrode in the same order (Table 1). The anodic peak current density per unit concentration (i_{pa}/C) decreases slightly in the same order (Table 2). The peak separation value ($\Delta E_p = E_{pa} - E_{pc}$) on these electrodes varies only slightly with sweep rate as well as electrode material. Assuming the diffusion coefficient D to be 2.4×10^{-5} [22] in all the three media and using the Nicholsons method for calculation of heterogeneous charge transfer rate constants ($k_h^{\cdot}$) from ΔE_p values [23, 24], these $k_h^{\cdot}$ values were calculated for ferrocene/ferricinium ion redox couple on all the three electrodes. In the present TBAP/CH_3CN medium, the $k_h^{\cdot}$ values on Pt, GCE and CPP electrodes do not vary substantially (Table 3). The $k_h^{\cdot}$ values calculated at different sweep rates are also consistent, thus validating the method of calculation (Table 3).

The anodic as well as cathodic peak currents (i_{pa}, i_{pc}) for ferrocene on all three electrodes increase with square root of sweep rate ($v^{1/2}$) and concentration (C). However the i_{pa} vs. $v^{1/2}$ as well as i_{pa} vs. C plots do not pass through the origin. It appears that ferrocene as well as ferricinium species exhibit weak adsorption on the electrode surface. The total i_{pa} value thus constitutes a concentration independent adsorption current and a concentration dependent diffusion current [25, 26]. This is probably the cause for the i_{pa} vs. C plots not passing through the origin.

Qualitatively the voltammetric responses of ferrocene in TEA.3HF/CH_3CN medium are quite similar to those in TBAP/CH_3CN. On Pt electrode in TEA.3HF medium with or without CH_3CN (Section 3.2) the hydrogen evolution reaction starts around 0.2 V (vs. SCE). This is probably associated with the catalytic hydrogen evolution through triethyl ammonium cations [27, 28].

$$2(C_2H_5)_3NH^+ + 2e \longrightarrow 2(C_2H_5)_3N + H_2 \qquad (1)$$

$$(C_2H_5)_3N + 2HF \longrightarrow (C_2H_5)_3NH^+ + HF_2^- \qquad (2)$$

This type of processes may probably be responsible for the difference in the properties of tetraethylammonium fluorides [20, 21] and triethylammonium fluorides [18, 19].

The anodic peak potential for ferrocene in TEA.3HF/CH_3CN medium is shifted in the negative direction by around 60 mV on all the three electrodes (Table 1). This trend was observed at other concentrations and sweep raates as well. The anodic peak current was slightly higher on Pt electrodes when compared to the other two electrodes (Table 2). This may be due to higher activity of the Pt electrode. The ΔE_p values and hence the charge transfer rate constants are once again quite similar on all the three electrodes. The average charge transfer rate constant values ($k_{have}^{\cdot}$) are not very different from that in TBAP/CH_3CN medium (Table 3).

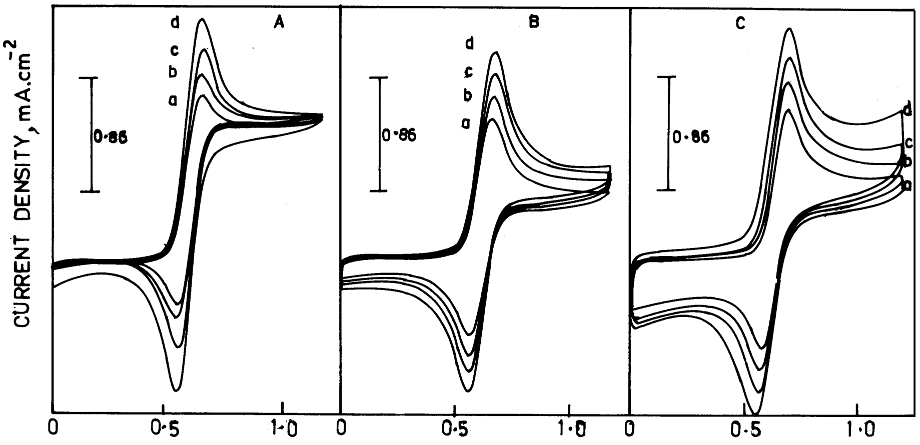


Fig. 1. Effect of sweep rate on the voltammetric behavior of 2 mM ferrocene on A) platinum, B) GC, and C) CPP electrodes in 0.05 M TBAP/CH_3CN medium. v (mV s^{-1}) a) 40, b) 60, c) 80, and d) 100.

Table 1. Comparison of E_{pa} values of ferrocene, quinhydrone and methyl phenyl sulfide in 0.05 M TBAP/CH_3CN, 0.1 M TEA.3HF/CH_3CN and TEA.3HF on Pt, GC, and CPP electrodes at 40 mV s^{-1}.

				Anodic peak potentials, E_{pa} (V)			
No.	*Compounds*	*Concentration (mM)*	*Electrode*	*TBAP/CH_3CN*	*TEA.3HF/CH_3CN*	*Concentration (mM)*	*TEA.3HF*
			Pt	0.64	0.58		0.42
		2	GC	0.67	0.60	25	0.44
			CPP	0.67	0.61		0.48
1	Ferrocene		Pt	0.69	0.62	50	0.48
		8	GC	0.76	0.68		0.50
			CPP	0.76	0.70		0.52
			Pt	1.50	1.14		0.72
		2	GC	1.46	1.14	25	0.72
			CPP	1.50	1.14		0.74
2	Quinhydrone		Pt	1.56	1.20		0.74
		8	GC	1.56	1.20	50	0.76
			CPP	1.56	1.20		0.77
			Pt	1.88	1.62		1.09
		2	GC	1.80	1.72	25	1.03
			CPP	1.80	1.74		1.07
3	Methyl phenyl sulfide		Pt	1.96	1.70		1.12
		8	GC	1.86	1.82	50	1.06
			CPP	1.88	1.82		1.10

Even a relatively slow redox process, namely quinhydrone redox reaction, does not show significant electrode effect in the TBAP/CH_3CN medium. Typical cyclic voltammograms of 2 mM quinhydrone on Pt, GCE, and CPP electrodes are shown in Figure 2 A,B,C, respectively. Voltammetric responses are qualitatively similar on all the three electrodes. The anodic peak potential shows small variation from Pt to CPP electrodes (Table 1). The anodic peak current values decrease in the same direction (Table 2). The ΔE_{p} value also does not vary significantly on all three electrodes (Table 4). The peak current ratio ($i_{\mathrm{pa}}/i_{\mathrm{pc}}$) is substantially lower on all the three electrodes for quinhydrone. On Pt electrode, the cathodic peak could be seen only at higher sensitivity and higher sweep rates. Apart from these differences, the voltammetric responses of quinhydrone on all three electrodes are quite similar.

In TEA.3HF/CH_3CN medium, the anodic peak current of quinhydrone is slightly higher on all three electrodes (Table 2). The anodic peak potentials decrease between 200 mV to 300 mV in this medium when compared to TBAP/CH_3CN medium (Table 1). The E_{pc} values decrease by only 120 to 160 mV in this

Table 2. Comparison of i_{pa}/C values of ferrocene, quinhydrone and methyl phenyl sulfide in 0.05 M TBAP/CH_3CN, 0.1 M TEA.3HF/CH_3CN and TEA.3HF on Pt, GC, and CPP electrodes at 40 mV s^{-1}.

				Anodic peak currents, i_{pa}/C (mAcm^{-2} mM^{-1})			
No.	*Compounds*	*Concentration (mM)*	*Electrode*	*TBAP/CH_3CN*	*TEA.3HF/CH_3CN*	*Concentration (mM)*	*TEA.3HF*
			Pt	0.53	0.64		0.68
		2	GC	0.47	0.43	25	0.47
			CPP	0.47	0.43		0.47
1	Ferrocene		Pt	0.49	0.61		0.68
		8	GC	0.42	0.43	50	0.44
			CPP	0.41	0.43		0.44
			Pt	0.82	0.90		1.02
		2	GC	0.66	0.72	25	0.89
			CPP	0.61	0.70		0.78
2	Quinhydrone		Pt	0.79	0.88		1.06
		8	GC	0.63	0.70	50	0.90
			CPP	0.60	0.69		0.80
			Pt	1.00	1.20		1.02
		2	GC	0.85	0.98	25	0.78
			CPP	0.80	0.96		0.69
3	Methyl phenyl sulfide		Pt	0.91	1.16		0.99
		8	GC	0.79	0.96	50	0.71
			CPP	0.72	0.90		0.71

Table 3. Calculation of rate constants of 8 mM ferrocene in 0.05 M TBAP/CH_3CN, 0.1 M TEA.3HF/CH_3CN and TEA.3HF on Pt, GC, and CPP electrodes at different sweep rates.

			ΔE_p (mV)			$k_h \times 10^3$ cm s^{-1}		
No.	*Medium*	*Sweep rate (mV s^{-1})*	*Pt*	*GC*	*CPP*	*Pt*	*GC*	*CPP*
		40	100	120	120	5.8	3.5	3.5
1	TBAP/CH_3CN	60	120	120	140	4.3	4.3	3.1
		80	120	120	140	4.9	4.9	3.5
		100	120	120	160	5.4	5.4	3.1
					Average	5.1	4.5	3.3
		40	100	100	100	5.8	5.8	5.8
2	TEA.3HF/CH_3CN	60	100	100	100	7.1	7.1	7.1
		80	100	110	100	8.1	6.4	8.1
		100	120	120	100	5.4	5.4	8.9
					Average	6.6	6.2	7.5
		40	160	140	180	2.0	2.5	1.5
3	TEA.3HF	60	160	140	180	2.4	3.1	1.8
		80	160	140	180	2.8	4.9	2.1
	(Conc., = 25 mM)	100	160	160	200	3.1	3.1	1.9
					Average	2.6	3.4	1.8

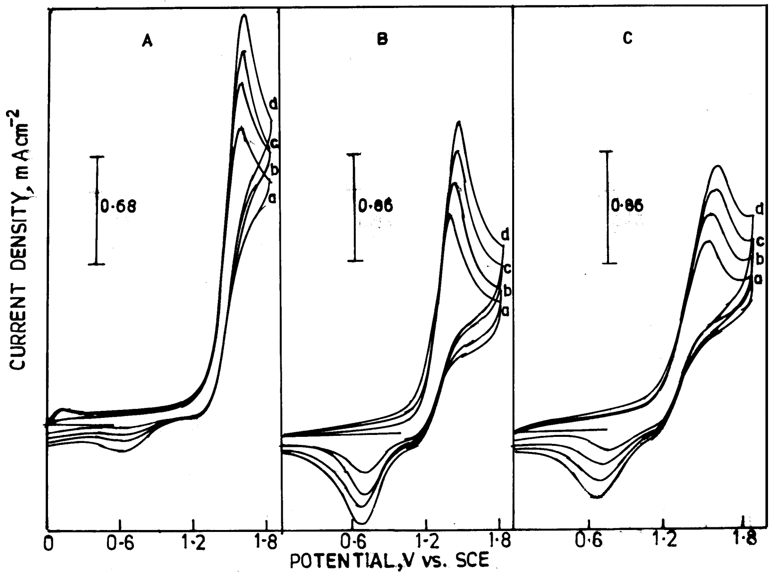


Fig. 2. Effect of sweep rate on the voltammetric behavior of 2 mM quinhydrone in A) platinum, B) GC, and C) CPP electrodes in 0.05 M TBAP/CH_3CN medium. v (mV s^{-1}) a) 40, b) 60, c) 80, and d) 100.

Table 4. Comparison of E_{pa}, E_{pc} and ΔE_p values of 8 mM quinhydrone in 0.05 M TBAP/CH_3CN, 0.1 M TEA.3HF/CH_3CN and TEA.3HF on Pt, GC, and CPP electrodes at 40 mV s^{-1}.

		Electrode potential	*Electrodes*		
No.	*Medium*	*(V)*	*Pt*	*GCE*	*CPP*
		E_{pa}	1.56	1.56	1.56
1	TBAP/CH3CN	E_{pc}	0.56	0.56	0.56
		ΔE_p	1.00	1.00	1.00
		E_{pa}	1.14	1.20	1.20
2	TEA.3HF/CH3CN	E_{pc}	0.30	0.36	0.38
		ΔE_p	0.84	0.84	0.82
		E_{pa}	0.74	0.76	0.77
3	TEA.3HF	E_{pc}	0.38	0.44	0.44
		ΔE_p	0.36	0.32	0.33

medium on all three electrodes (Table 4). The overall ΔE_p value thus decreases from around 1.0 V in TBAP/CH_3CN medium to above 0.81 V in TEA.3HF/CH_3CN medium (Table 4).

Methyl phenyl sulfide was taken as a typical irreversible chemical system for comparative purposes. Typical cyclic voltammograms are presented in Figure 3. The main oxidation process occurs in the same potential region of around 1.8 V. The anodic peak potential (Table 1) and peak current values (Table 2) show small variations, quite similar to the other two compounds discussed above. On Pt electrode, a small prepeak is noticed at around 1.6 V in this medium. Pt probably shows stronger adsorption towards methyl phenyl sulfide when compared to the other two electrodes.

Methyl phenyl sulfide gave a single well-defined peak on all the three electrodes in TEA.3HF/CH_3CN medium. No prepeak was noted on Pt electrode and slightly lower (100–120 mV) E_{pa} values (Table 1) and higher i_{pa} values (Table 2) were noticed.

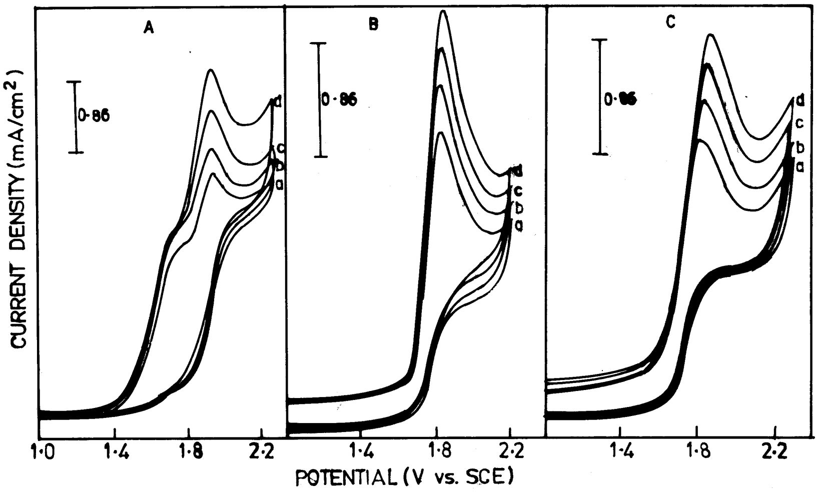


Fig. 3. Effect of sweep rate on the voltammetric behavior of 2 mM methyl phenyl sulfide on A) platinum, B) GC, and C) CPP electrodes in 0.05 M TBAP/CH_3CN medium. v (mV s^{-1}) a) 40, b) 60, c) 80, and d) 100.

3.2. Voltammetry in TEA.3HF Medium

TEA.3HF can conveniently be used as a room temperature melt [15, 16]. However, this medium shows at least 8–10 times higher background currents when compared to the other two solvent-supporting electrolyte systems discussed above, on all three electrodes including Pt. This necessitated the use of relatively higher reactant concentrations (more than 20 mM) when compared to CH_3CN based systems (even less than 2 mM) discussed above. Hence in all the voltammetric measurements in this medium, 25 mM to 50 mM concentration range was employed. For comparative data in Table 1 to Table 4. 25 mM and 50 mM reactant concentrations were employed. The peak current values in Table 2 are compared per unit concentration (i_{pa}/C) to take care of this concentration effect.

Typical CV responses of 25 mM ferrocene TEA.3HF medium on all three electrodes are presented in Figure 4. Higher background levels and a lower sensitivity can be seen for all three electrodes (compare Fig. 1 and Fig. 4). The E_{pa} values are once again found to decrease by about 180 mV in this medium when compared to TEA.3HF/CH_3CN (Table 1). The i_{pa}/C values, however, do not vary significantly between TEA.3HF/CH_3CN and TEA.3HF medium. The ΔE_p values for ferrocene in TEA.3HF medium are consistently higher on all the three electrodes at different sweep rates and concentrations (Table 3). The average rate constant values ($k_h^\cdot$) also decrease by 50 % on all three electrodes.

Typical CV responses for quinhydrone in this medium are presented in Figure 5 on all three electrodes. Despite higher concentraions of 25 mM, the i_{pa}/C values do not vary significantly in this medium (Table 2), once again suggesting predominantly diffusion controlled nature of the electrode process in all these media. TEA.3HF medium, however, significantly influences the E_{pa}, and ΔE_p values. E_{pa} values decrease by about 500 mV in the absence of CH_3CN (Table 1) while the E_{pc} value remains around 0.4 V (vs. SCE) on the three electrodes (Table 4). Hence, the ΔE_p value for quinhydrone redox system decreases from around 0.8 V in presence of acetonitrile to around 0.3 V in TEA.3HF medium (Table 4).

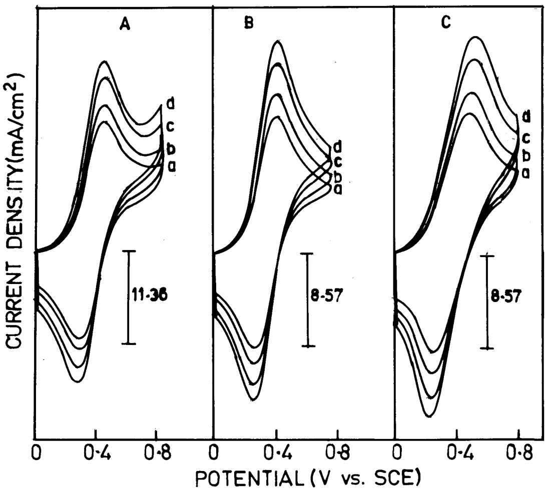


Fig. 4. Effect of sweep rate on the voltammetric behavior of 25 mM ferrocene on A) platinum, B) GC, and C) CPP electrodes in TEA.3HF medium. v (mV s^{-1}) a) 40, b) 60, c) 80, and d) 100.

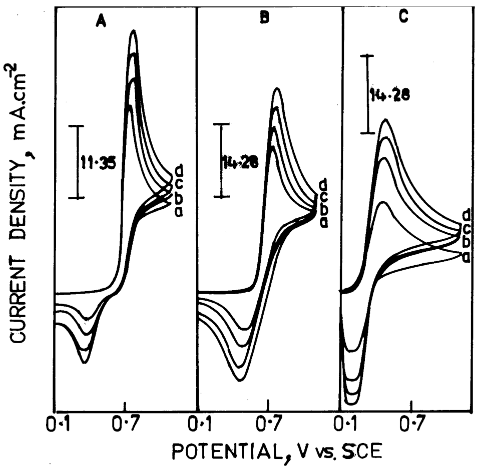


Fig. 5. Effect of sweep rate on the voltammetric behavior of 25 mM quinhydrone on A) platinum, B) GC, and C) CPP electrodes in TEA.3HF medium. v (mV s^{-1}) a) 40, b) 60, c) 80, and d) 100.

Methyl phenyl sulfide once again gave an irreversible voltammetric response in this medium on all three electrodes. For this compound also, the E_{pa} values decrease by 700 mV in this medium when compared to TEA.3HF/CH_3CN (Table 1). The anodic peak currents showed only slight variation (Table 2).

Since all three electrodes gave higher background currents in this medium, a few more experiments were carried out to study stability of the electrodes. In one such experiment, the voltammetric responses of 25 mM methyl phenyl sulfide were recorded at 40 mV s^{-1} on the same electrode in solution at 10 minutes regular intervals. The voltammetric response of Pt electrode was stable and exactly reproducible. The voltammograms recorded on GCE showed small but systamatic increase in peak current at least during the first hour (Fig. 6A). On CPP electrode there was a much higher increase in peak currents during the first two recordings. Subsequently, however, the increase in peak currents became marginal (Fig. 6B).

The carbon electrodes were also subjected to polarization at constant potential of 2.0 V for half an hour in TEA.3HF medium and the electrode surface was subjected to SEM analysis. Figure 7A shows that CPP electrode undergoes surface roughening under this condition. GCE was relatively stable and occasionally, some surface pits were noticed (Figure 7B). The density of the pits on the electrode surface also were not significantly high. Similar polarization followed by SEM measurements under identical conditions in presence of CH_3CN did not exhibit any surface transformation.

In simple, outer sphere electron transfer reactions, significant surface effects have been noticed in aqueous solutions. In the case of ferricyanide/ferrocyanide redox system for example $k_h^{\cdot}$ values on Pt were generally found to be higher than that of GCE [29]. In aprotic medium, Pt, highly oriented pyrographite (HOPG) and GC electrodes are interchangebly used and surface effects are generally marginal. In the present investigations also, only small increase in oxidation peak potentials and slight decrease in anodic peak currents are noticed on GC and CPP electrodes when compared to Pt electrodes (Table 1 to 4) in CH_3CN medium.

The background currents in TBAP/CH_3CN and TEA.3HF/CH_3CN media are almost equal. Hence, in the presence of solvents and low concentration of fluoride ions, the oxidation processes in middle potential region is relatively small on all three electrodes. Pt electrode, however, does not undergo any surface roughening in TEA.3HF medium of high fluoride ion concentration. On GCE, only a few pits are formed occasionally. Significantly, higher surface roughening occurs on graphite electrodes.

The anodic peak currents are also quite similar in all the three media investigated. Some adsorption effects especially for methyl phenyl sulfide were noticed in TBAP/CH_3CN. In general, the anodic peak current values were found to be slightly lower on carbon electrodes when compared to Pt electrodes (Table 2). Some weak adsorption of reactants on the electrode surface is also likely. This is confirmed by the i_p vs. C and i_p vs. $v^{1/2}$ plots which do not pass through the origin (Table 2).

There is a general decrease in E_{pa} values for all the three compounds while going from TBAP/CH_3CN through

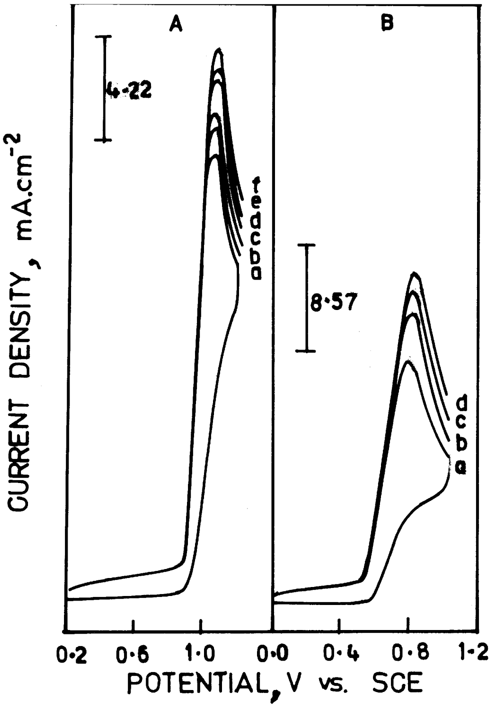
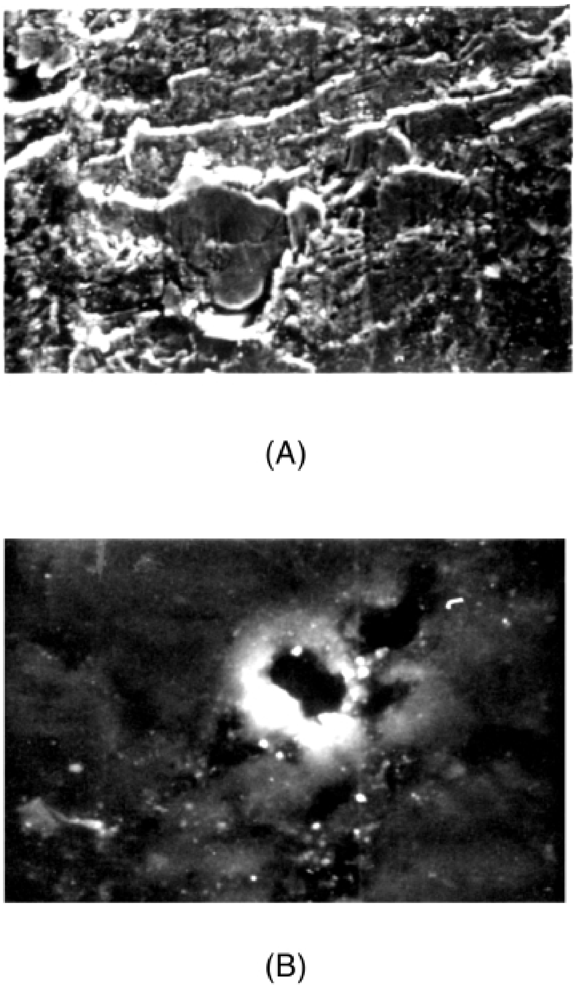


Fig. 6. Effect of time on the voltammetric behavior of 25 mM of methyl phenyl sulfide on A) GC and B) CPP electrodes in TEA.3HF medium. $v = 40$ mV s^{-1}; time interval (minutes) a) 10, b) 20, c) 30, d) 40, e) 50, and f) 60.


(A)

(B)

Fig. 7. SEM of A) CPP and B) GC electrodes after constant potential polarization at 2.0 V in TEA.3HF medium for 30 minutes (A,B × 240).

TEA.3HF/CH_3CN to TEA.3HF. In the case of reversible electron transfer reaction, involving ferrocene/ferricinium redox system, the E_{pa} shifts by around 60 to 160 mV for each medium. In the case of quinhydrone the shifts in the E_{pa} values are much higher when moving from TEA.3HF/CH_3CN to TEA.3HF (Table 1). The value is still higher for methyl phenyl sulfide oxidation. The shifts in E_{pa} values on all the three electrodes are consistent. In earlier work also, consideribly lower oxidation potential for organic compounds have been noticed in Py-HF [17], TEA.3HF [18, 19] and tetraethylammonium fluoride-HF [20, 21]. The exaxct cause, however, has not yet been discussed.

The heterogeneous rate constant $k_{\mathrm{h}}^{\cdot}$ of ferrocene in TEA.3HF/CH_3CN is found to be slightly higher than that of TBAP/CH_3CN. However, it is quite surprising to note that in TEA.3HF, the charge transfer rate constants show noticeable decrease on all three electrodes (Table 3). This may be due to surface fluoride-film formation on Pt, GC, CPP electrodes in this highly concentrated fluoride medium. Formation of fluoride films on carbon electrodes in molten KF-2HF medium [11, 12] as well as $TBABF_4$/DMF medium [6] has already been established. The exact nature of films formed on Pt and Carbon electrodes in TEA.3HF and TEA.3HF/CH_3CN media, however, require further investigations.

Remarkable observations were made regarding the voltammetric behavior of quinhydrone in these three media. The ΔE_{p} values for this compound decrease from 1.0 V in TBAP/CH_3CN to around 0.8 V in TEA.3HF/CH_3CN. A further significant decrease to ΔE_{p} values of 0.3 V is noticed in TEA.3HF medium (Table 4). This observation is once again true for all three electrodes. It appears that in the case of quinhydrone oxidation, which involves inner-sphere electron transfer, the fluoride film on electrode surfaces indeed, enhances the electron transfer rate and hence decreases the ΔE_{p} values. It should also be noted that the decrease in ΔE_{p} values are mainly due to the decrease in E_{pa} values or change in the oxidation potential of the redox system (Table 4).

The same trend seems to prevail in the case of oxidation of methyl phenyl sulfide as well. The decrease in the E_{pa} value from 1.7 V to as low as 1.0 V in TEA.3HF may once again be due to the kinetic influence of fluoride films (Table 1). The exact cause for such significant effect of fluoride films on slow inner sphere electron transfer reaction deserves further investigation.

4. Conclusions

The present investigations indicate that the electrochemical behavior of organic compounds on Pt as well as carbon electrodes would be quite similar in CH_3CN medium whether fluoride ions are present or not. At low concentrations of TEA.3HF in CH_3CN, the effect of fluoride ions is not significant on the voltammetric behavior. Analytical technique can be used with equal degree of sensitivity in this type of fluoride containing CH_3CN medium.

In the absence of CH_3CN, triethylamine-3HF room temperature melt behaves in a significantly different manner. The background currents are considerably higher in this medium. Hence, reasonable level of analytical sensitivity could be achieved only when the reactant concentration exceeds 20 mM. The kinetics of the charge transfer processes is also significantly influenced by the high concentration of fluoride medium. The oxidation peak potentials for quasireversible and irrreversible charge transfer reaction decreases substantially.

These differences need to be taken into consideration whenever electroanalysis is attempted on such media of high fluoride ion concentration. From analytical perspective, both Pt and carbon electrodes may be employed. However, Pt may be preferably used in TEA.3HF medium. Care should also be taken while comparing voltammetric responses of electroactive species in fluoride media with widely different fluoride content since this can influence voltammetric parameters especially peak potentials.

5. Acknowledgements

The authors thank Director, CECRI, Karaikudi for his keen encouragement in doing this work. The authors acknowledge the assistance of Mr. R. Ravichandran and Mr. S. Ravishankar during the preliminary stages of this investigation. The authors thank Volkswagen Stiftung, Germany for the financial support of this work. V.S. and R.S. thank CSIR, New Delhi for award of fellowships.

6. References

[1] A.G. Doughty, M. Fleischmann D. Pletcher, *J. Electroanal Chem.* **1974**, *51*, 456.
[2] J.P. Masson, J. Devynck, B. Tremillon, *J. Electroanal Chem.* **1974**, *54*, 232.
[3] J.P. Masson, J. Devynck, B. Tremillon, *J. Electroanal Chem.* **1975**, *64*, 193.
[4] J.P. Masson, J. Devynck, B. Tremillon, *J. Electroanal Chem.* **1975**, *64*, 175.
[5] P.L. Fabre, J. Devynck, B. Tremillon, *J. Electroanal Chem.* **1980**, *113*, 251.
[6] M. Chandrasekaran, M. Noel, V. Krishnan, *Talenta* **1990**, *37*, 695.
[7] E. Laurent, B. Marquet, R. Tardivel, *Tetrahedron* **1989**, *45*, 4431.
[8] E. Laurent, B. Marquet, R. Tardivel, *J. Fluorine Chem.* **1990**, *49*, 115.
[9] T. Fuchigami, *Reviews on Heteroatom Chem.* **1994**, *10*, 155.
[10] A.J. Calandra, C.M. Ferro, C.P. Castellano, *Electrochim. Acta* **1980**, *25*, 201.
[11] O.R. Brown, M.J. Wilmott, *J. Electroanal. Chem.* **1986**, *106*, 313.
[12] H. Gronet, D. Devillers, S. Duran-vidal, F. Nicholas, M. Gunbel, *Electrochim. Acta* **1999**, *44*, 2793.
[13] M. Noel, R. Santhanam, M.K. Ravikumar, M. Francisca Flora, *Electroanalysis* **1995**, *7*, 170.
[14] G.M. Swain, *J. Electrochem. Soc.* **1994**, *14*, 3382.
[15] K. Gatner, G. Zabinskaolszak, *Polish J. Chem.* **1993**, *67*, 281.
[16] K. Gatner, *Polish J. Chem.* **1993**, *67*, 1155.
[17] F. Huba, E.B. Yeager, G.A. Olah, *Electrocheim. Acta* **1979**, *24*, 489.
[18] V. Surynarayanan, M. Noel, *J. Fluorine Chem.* **1998**, *92*, 177.
[19] S.Q. Chen, T. Hatakeyema, F. Fukuhara, S. Hara, N. Yoneda, *Electrochim. Acta* **1997**, *43*, 1951.
[20] K. Momota, M. Morita, Y. Matsuda, *Electrochim. Acta* **1993**, *38*, 1123.
[21] K. Momota, K. Kato, M. Morita, Y. Matsuda, *Electrochim. Acta* **1989**, *39*, 681.
[22] D.T. Sawyer, A. Sobkowiah, J.L. Roberts. Jr., *Electrochemistry for Chemists*, 2nd ed. Wiley, New York **1995**, ch. 13, p. 469.
[23] R.S. Nicholson, *Anal. Chem.* **1965**, *37*, 1351.
[24] M. Noel, K.I. Vasu, *Cyclic Voltammetry and the Frontiers of Electrochemistry*, Oxford IBH, New Delhi, India **1990**, ch. 4.
[25] R.H. Wopschall, I. Shain, *Anal. Chem.* **1967**, *39*, 1514.
[26] M. Noel, K.I. Vasu, *Cyclic Voltammetry and Frontiers of Electrochemistry*, Oxford IBH, New Delhi, India **1990**, ch. 7.
[27] A.D. Goolsby, D.T. Sawyer, *J. Electroanal Chem.* **1965**, *19*, 405.
[28] M. Heyrovsky, S. Vavricka, *Collect. Czeh. Chem. Commun.* **1969**, *34*, 1204.
[29] M. Noel, P.N. Anantharaman, *Analyst* **1985**, *110*, 1095.