

Voltammetric behavior of perfluorocarboxylic acids and their corresponding ethyl esters on glassy carbon electrode: surface effects

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Abstract Voltammetric responses of trifluoroacetic acid, perfluorobutyric acid, perfluorohexanoic acid, and perfluorooctanoic acid (PFOA) were studied in acetonitrile/tetra-*n*-butylammonium perchlorate medium on glassy carbon electrode. All the four acids gave two voltammetric waves. PFOA exhibits blocking effects. In the presence of excess water, the first cathodic peak current increases, and the second peak disappeared. Very small quantity of triethylamine (TEA; 1–2 mM) was found to be effective in suppressing the first cathodic peak. Both the peak current and peak potential values were sensitive to water and TEA content. The ester derivatives of all the four perfluorocarboxylic acids (PFCAs), however, gave well-defined cathodic reduction peak around -2.3 V. This peak appears to be the best choice for quantitative estimation of PFCAs.

Keywords Perfluorocarboxylic acids · Voltammetry · Glassy carbon electrode · Trifluoroacetic acid · Perfluorobutyric acid · Perfluorohexanoic acid · Perfluorooctanoic acid

Introduction

Due to their low surface tension characteristics, perfluoroalkyl groups are likely to exhibit significant adsorption and related surface effects in electrochemical processes. However, there are only few reports on the electroreduction of perfluorinated and polyfluorinated organic compounds. Both aliphatic [1] and aromatic [2] carbon–fluorine bonds are found to undergo two-electron reduction leading to the

formation of C–H bond in aprotic medium. Fluorinated carboxylic acids undergo proton discharge while their corresponding esters undergo carbon–fluorine bond reduction at alpha position in the absence of proton donors on mercury electrode [3]. In the presence of protons, the ester group is reduced to aldehyde group. The electroreduction process occurs at lower reduction potentials with increasing chain length of the perfluoroalkyl group [4]. Perfluorocarbons containing double bonds or branched chains undergo facile polymerization in addition to carbon–fluorine bond reduction on glassy carbon electrode (GCE) [5]. Carbon–fluorine bonds of trifluoromethyl [6,7] and other perfluoroalkyl groups [8] attached to aromatic ring also undergo similar reduction process. Electroreduction of perfluoroalkyl iodides in presence of CO₂ or SO₂ leads to the formation of carboxylic acids or sulfonic acids [9–11], respectively.

In this work, an effort was made to develop a simple voltammetric approach for the analysis and quantitative estimation of perfluorocarboxylic acids in aprotic medium. The glassy carbon electrode was selected due to its highly reproducible voltammetric responses in protic as well as aprotic solvents. Preliminary investigations, however, suggested significant surface effects. The causes for these surface effects were investigated in some detail. A simple voltammetric approach developed using ethyl ester derivatives of perfluorocarboxylic acids is also described here.

Experimental

Cyclic voltammetric studies were carried out using Wenking Model LB 75 L potentiostat made in Germany. A homemade 10-ml capacity undivided cell with provisions for working, counter and reference electrode, and deaeration was employed. The solutions were thoroughly degassed for at

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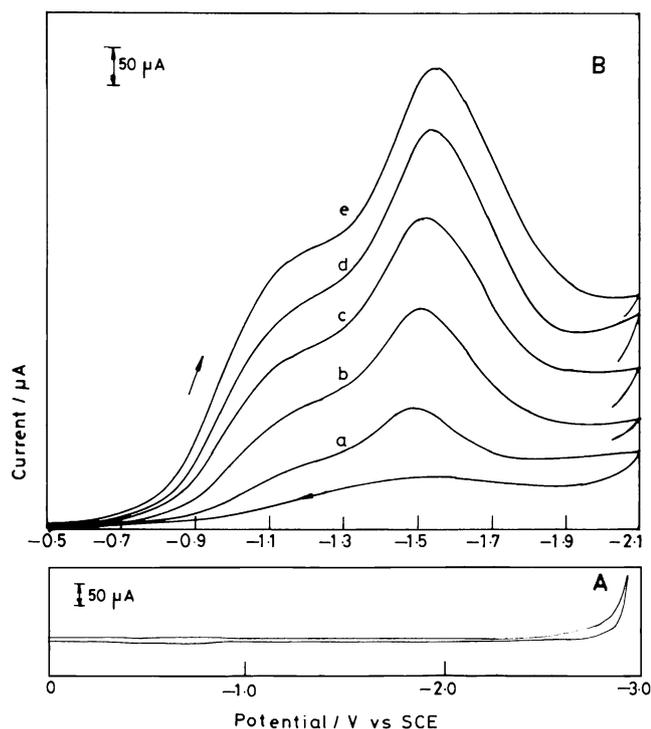


Fig. 1 Cyclic voltammograms of (A) residual current and (B) different concentration of TFA in 0.1 M $(\text{Bu})_4\text{NClO}_4/\text{CH}_3\text{CN}$ medium at 40 mV s^{-1} on GCE. *a–e* = 3.85, 7.4, 10.7, 13.8, and 16.7 mM, respectively

least 15 min prior to measurements by slow bubbling of high pure nitrogen passing through several traps sulfuric acid, molecular sieves, indicator silica gel (blue), and finally the trap containing solvent-supporting electrolyte system. A 5-mm diameter glassy carbon (0.1964 cm^2) served as working electrode and platinum foil was used as counter electrode. Saturated calomel electrode connected through intermediate solvent-supporting electrolyte medium using two salt bridges served as reference electrode. Solvent-supporting electrolyte is dried overnight using molecular sieves. All the experiments were carried out at room temperature ($25^\circ\text{C} \pm 2$).

Analytical grade trifluoroacetic acid (TFA) and perfluorobutyric acid (PFBA) obtained from Merck and Acros Organics, respectively, were used as such. Perfluorohexanoic acid (PFHA) and perfluorooctanoic acid (PFOA) were synthesized in this laboratory by electrochemical fluorination of acid chlorides and distilled twice before use. Acetonitrile, potassium ferricyanide, and tetra-*n*-butylammonium perchlorate were of analytical grade obtained from Aldrich. Analytical grade potassium chloride and sulfuric acid were procured from Ranbaxy chemicals. Moisture-free molecular sieves and indicator silica gel (blue) were purchased from Qualigens chemicals.

The glassy carbon electrode was electrochemically activated in 0.1 M aqueous KCl medium, and the activity was evaluated

using voltammetry of ferricyanide-ferrocyanide system in the same medium [12].

The perfluorocarboxylic acids were converted into their corresponding ethyl esters by conventional sulfuric acid catalyzed esterification [13].

Results and discussion

Voltammetric behavior of perfluorocarboxylic acids

Typical cyclic voltammetric responses of different concentrations of TFA at a constant sweep rate of 40 mV s^{-1} are presented in Fig. 1. A cathodic wave around -1.2 V followed by a distinct cathodic peak at -1.5 V is noticed in all concentrations. This type of voltammetric response was found for all the four perfluorocarboxylic acids (PFCAs) investigated, and it is quite common. Typical linear sweep voltammograms obtained for 3.85 mM PFBA at different sweep rates are presented in Fig. 2 as an example. The double peak response prevails at high sweep rates as well.

The cathodic peak current and peak potential values for all the four perfluorocarboxylic acids under identical concentration and sweep rate values are presented in Table 1. The first cathodic peak appears as wave, and the peak potential could only be estimated approximately. The second cathodic peak potential shifts in the positive direction from C_2 to C_6 PFCAs and once again shifts to a more negative potential for C_8 PFCA. This suggests some blocking adsorption for C_8 carboxylic acid namely PFOA.

The first cathodic peak current value could also be estimated only approximately. From an analytical stand point, the total peak current value for different concentration of all the four PFCAs at the same sweep rate are presented in Fig. 3. The peak current values for C_2 to C_6 acids are found to vary only slightly. However, the peak

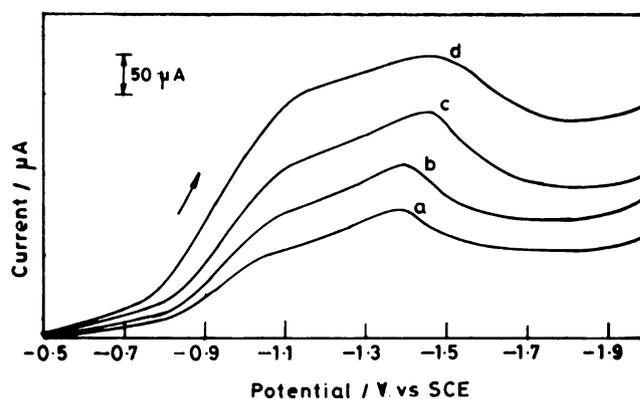


Fig. 2 Linear sweep voltammograms of 3.85 mM PFBA in 0.1 M $(\text{Bu})_4\text{NClO}_4/\text{CH}_3\text{CN}$ medium on GCE at different sweep rates. *a–d* = 40, 80, 160, and 320 mV s^{-1} , respectively

Table 1 Peak potential and peak current density values of 16.7 mM perfluorocarboxylic acids and their corresponding ethyl esters at 40 mV s⁻¹

Compound	Peak potential (-E _p ^c ; V)		Peak current density (mA/cm ²)	
	Acid	Ester	Acid	Ester
TFA	-1.55	-2.70	3.00	5.60
PFBA	-1.51	-2.62	3.34	8.91
PFHA	-1.45	-2.66	3.11	11.40
PFOA	-1.56	-2.75	1.27	12.93

TFA trifluoroacetic acid, PFBA perfluorobutyric acid, PFHA Perfluorohexanoic acid, PFOA perfluorooctanoic acid

current value for C₈ is found to be substantially lower, indicating once again the blocking type of adsorption effect.

According to earlier reports, the electroreduction of TFA [3] and other PFCAs [4] on mercury electrode gave rise to only a single cathodic peak. It is quite interesting to note two distinct peaks for the same compound on glassy carbon electrode. From an analytical point of view, two indistinguishable peaks would be quite inconvenient for quantitative estimation. Hence, some efforts were made to determine the cause of this surface effect and evolve possible methods for obtaining a well-defined single voltammetric peak for analytical purposes.

Quite similar surface effects were reported earlier for the reduction of carbonyl compounds on glassy carbon electrode [14–17] from this laboratory in aprotic solvents. In addition to the main reduction peak, a small prewave was noticed for carbonyl compounds including benzaldehyde [14], benzophenone, [15] vanillin [16], and benzyl [17].

The prewave was attributed to the hydrophilic and protonating surface functional groups present on glassy carbon electrode. The heterogeneous glassy carbon surface also contains oxidized hydrophilic regions and relatively hydrophobic regions. These regions would influence the adsorption and electroreduction of perfluoroalkyl com-

pounds. The peak separation between the first and the second cathodic peaks in the case of PFCAs is found to be significantly higher (greater than 300 mV) when compared to carbonyl compounds (less than 200 mV). In the case of carbonyl compounds, the prewave reached a limiting value below 2 mM concentration, beyond which, only the main cathodic peak current increased with reactant concentration [14–17]. In contrast to this, the first cathodic peak current values for PFCAs were found to increase with reactant concentration even at the higher concentration values investigated.

Small concentration of water would be expected to improve the hydrophilicity of the electrode surface and, hence, the reactivity of PFCAs. Water may also act as proton donor. The effect of direct addition of small concentrations of water on the voltammetric behavior of 10.7 mM TFA is shown in Fig. 4. The peak current in the first peak potential region increases during initial addition of water, and the peak current in the second peak potential

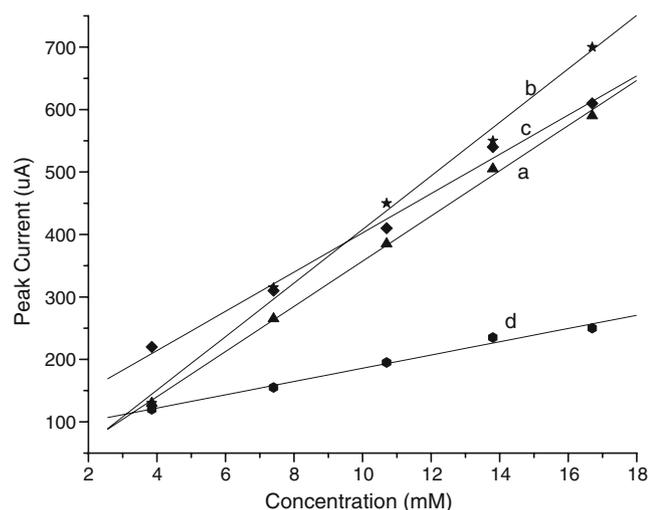


Fig. 3 A plot of concentration of perfluorocarboxylic acids against cathodic peak current at 40 mV s⁻¹; TFA (a), PFBA (b), PFHA (c), and PFOA (d)

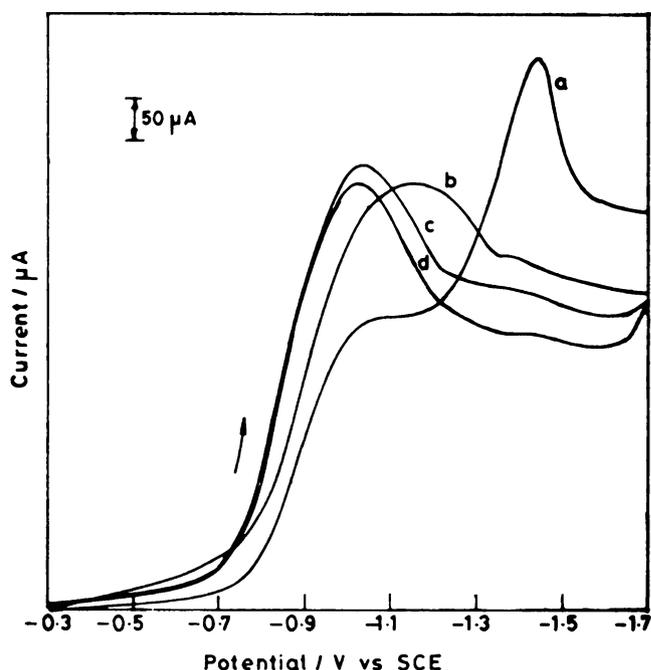


Fig. 4 Effect of water in the linear sweep voltammograms of 10.7 mM TFA in 0.1 M (Bu)₄NClO₄/CH₃CN medium at 40 mV s⁻¹ on GCE; a–d=0, 2, 4, and 6 M water, respectively

region almost disappear. The first cathodic peak potential also shifts to less negative values with increasing water content.

In the presence of excess water, the first cathodic peak current was found to increase with increasing concentration of TFA, as shown in Fig. 5. If the condition of excess water is not maintained, the carboxylic acids once again exhibit the second cathodic peak (Fig. 5).

Triethylamine (TEA), a base, was found to influence the voltammetric response in a much more significant fashion. On addition of less than 1 mM TEA, the first cathodic peak disappears completely. A single well-defined cathodic peak appeared at a more negative potential as shown in Fig. 6. With further increase in TEA concentration, the cathodic peak current decreases slightly, and the cathodic peak potential shifts towards a more negative region (Fig. 6). TEA appears to be a better reagent for bringing out surface uniformity on glassy carbon electrode. On a comparative basis for 10 mM TFA, around 6 M water is required to achieve a single cathodic peak around -1.0 V (Fig. 4). Less than 1 mM TEA would be sufficient to achieve a single

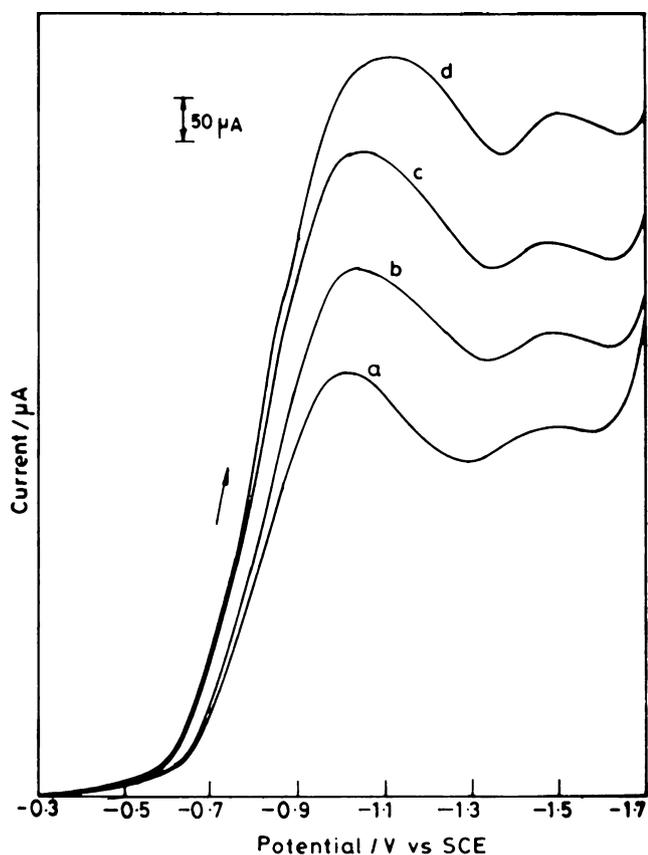


Fig. 5 Linear sweep voltammograms of TFA in excess water (4 M) in 0.1 M $(\text{Bu})_4\text{NClO}_4/\text{CH}_3\text{CN}$ medium at 40 mV s^{-1} on GCE showing the influence of TFA; $a-d=10.7, 13.8, 16.7,$ and 19.3 mM TFA, respectively

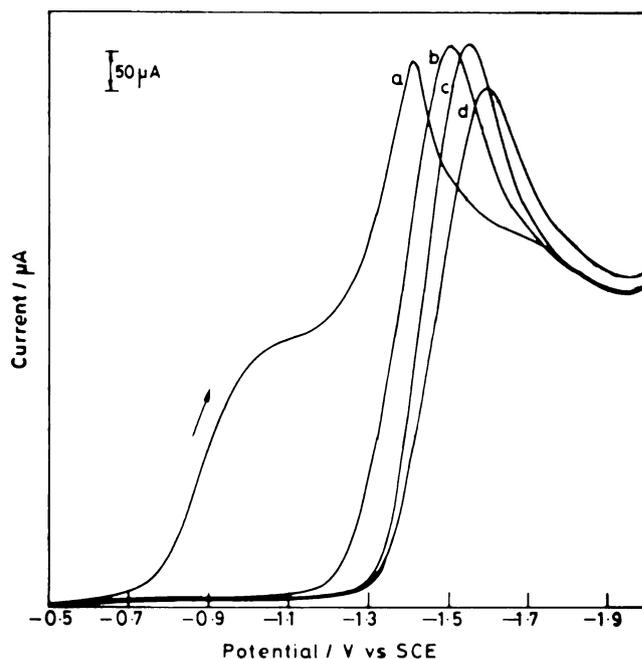


Fig. 6 Effect of TEA in the linear sweep voltammograms of 10.7 mM TFA in 0.1 M $(\text{Bu})_4\text{NClO}_4/\text{CH}_3\text{CN}$ medium at 40 mV s^{-1} on GCE; $a-d=0, 0.27, 0.53,$ and 0.8 mM TEA, respectively

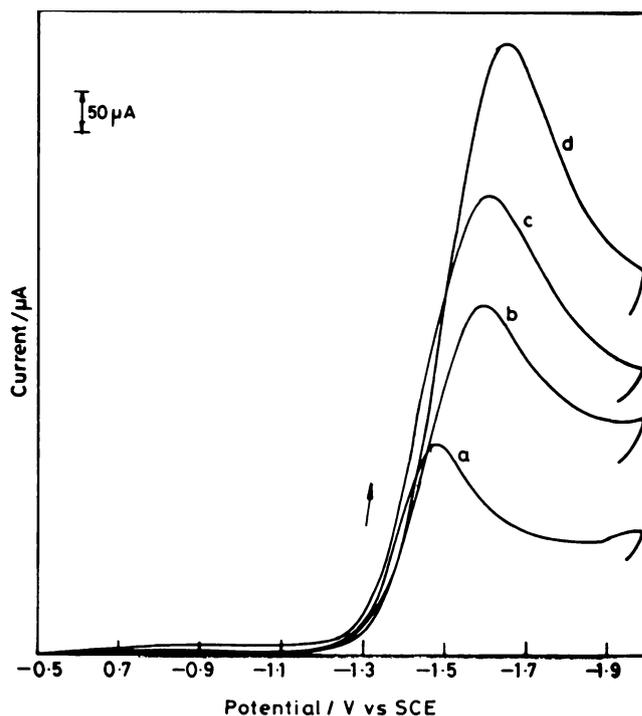


Fig. 7 Linear sweep voltammograms of TFA in excess TEA (1.2 mM) in 0.1 M $(\text{Bu})_4\text{NClO}_4/\text{CH}_3\text{CN}$ medium at 40 mV s^{-1} on GCE showing the influence of TFA; $a-d=3.85, 7.4, 10.7,$ and 13.8 mM TFA, respectively

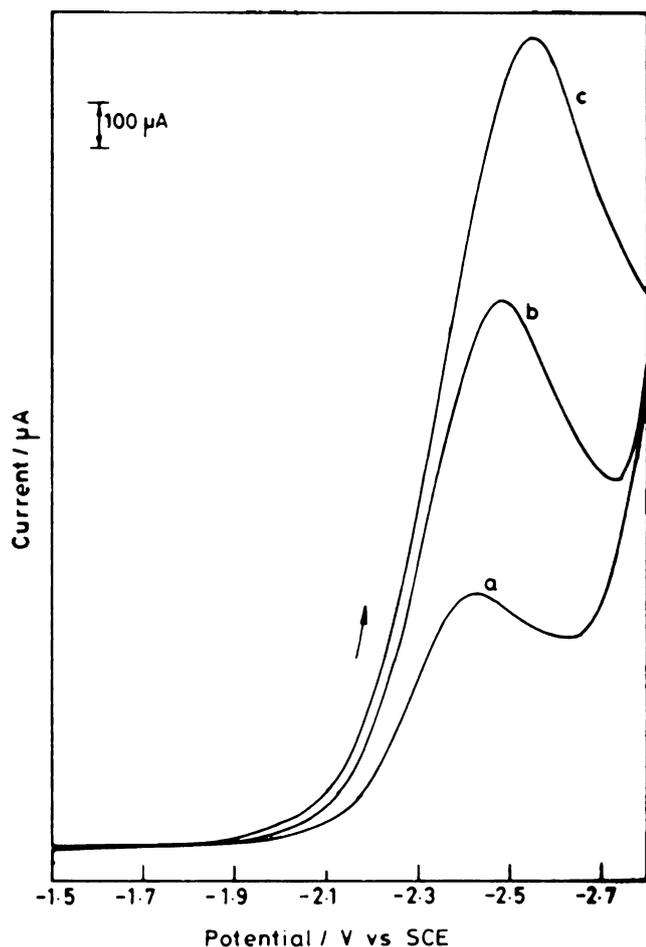


Fig. 8 Linear sweep voltammograms of ethyl perfluorohexanoate in 0.1 M $(\text{Bu})_4\text{NClO}_4/\text{CH}_3\text{CN}$ medium at 40 mV s^{-1} on GCE at different concentrations; *a–c*=3.85, 7.4, and 10.7 mM ethyl perfluorohexanoate, respectively

cathodic peak around -1.5 V for the same TFA. (Low concentrations of TEA were added from stock solution of 100 mM TEA solvent supporting electrolyte mixture.) In the presence of TEA, the cathodic peak current was also found to increase linearly with increase in concentration of TFA (Fig. 7).

The above experiments indicate that the two cathodic peaks observed during the electroreduction of PFCAs on glassy carbon electrode are most probably due to the reduction of single reactant species. The splitting of the cathodic peak is probably due to the existence of surface heterogeneity on glassy carbon electrode. This surface heterogeneity may be due to hydrophilic/hydrophobic regions or acidic/neutral surface functional groups. Water can enhance the hydrophilicity or acidity, leading to enhancement of the peak current in the first potential region. TEA can enhance hydrophobicity or eliminate surface acidity, leading to single cathodic peak in the more negative potential region.

In aprotic media, the electroreduction of these acids occurs through the reduction of C–F bond as reported in many such cases earlier [4].



If the proton is available on the glassy carbon electrode surface as carboxylic or phenolic surface functional groups, the first cathodic reduction peak is noticed around -1.0 V . If these surface protons are quenched by TEA through an acid-base reaction, the reduction occurs at a more reduction potential around -1.5 V .

Voltammetric behavior of ethyl esters of perfluorocarboxylic acids

From the above investigations, it is apparent that carboxylic acid can be estimated using linear sweep voltammetry in the

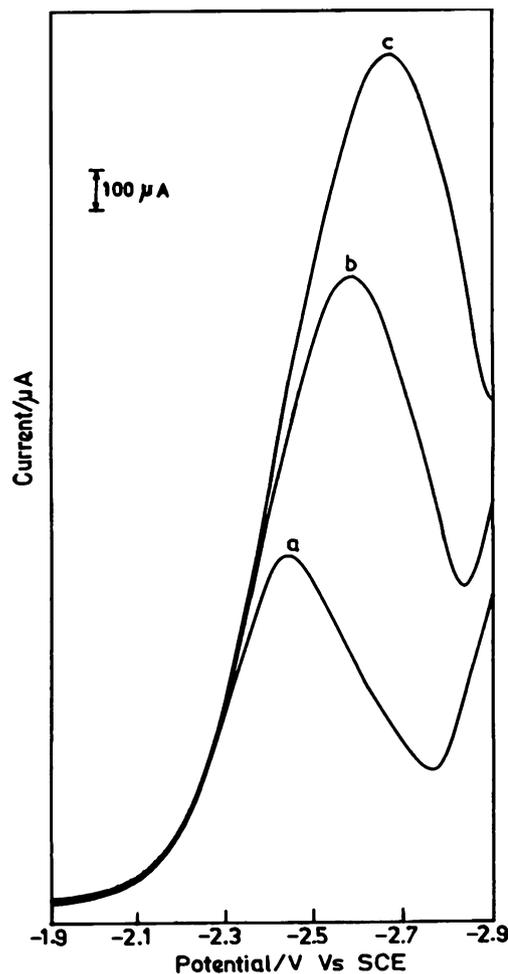


Fig. 9 Linear sweep voltammograms of ethyl perfluorooctanoate in 0.1 M $(\text{Bu})_4\text{NClO}_4/\text{CH}_3\text{CN}$ medium at 40 mV s^{-1} on GCE at different concentrations; *a–c*=3.85, 7.4, and 10.7 mM ethyl perfluorooctanoate, respectively

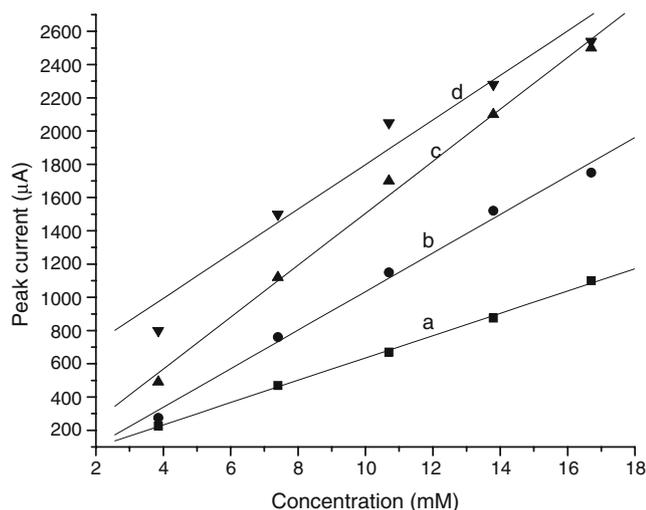


Fig. 10 A plot of concentration of ethyl perfluorocarboxylates against cathodic peak current at 40 mV s^{-1} ; ethyl trifluoroacetate (a), ethyl perfluorobutyrate (b), ethyl perfluorohexanoate (c), ethyl perfluorooctanoate (d)

presence of 1 mM TEA (Fig. 7). However, even in this medium, the cathodic peak current as well as peak potentials around -1.5 V is quite sensitive to TEA concentration as shown in Fig. 6.

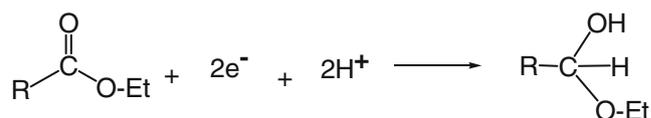
From an analytical stand point, it may be easier to convert the PFCAs into their ethyl esters if higher sensitivity and reproducibility are achievable from the reduction of these perfluorocarboxylic acid esters. The present experiments indeed suggest such a possibility.

Typical linear sweep voltammograms of ethyl ester of PFHA (Et-PFHA) are shown in Fig. 8. A single well-defined cathodic peak around -2.4 V is obtained. The cathodic peak current increased linearly with reactant concentration. Figure 9 shows the effect of sweep rate on the voltammetric response of 3.85 mM ethyl ester of PFOA (Et-PFOA). Once again, the cathodic peak current increases linearly with square root of sweep rate suggesting overall diffusion control nature of the process. Typical voltammetric data for all the four ethyl esters of PFCAs under identical condition are summarized in Table 1.

Quite interestingly, the voltammetric peaks of the ethyl esters are indeed found to be much more sensitive to reactant concentration. The peak current values at constant sweep rate of 40 mV s^{-1} for all the four compounds at

different concentrations are compared in Fig. 10. The peak current values for different esters are found to be at least three to four times higher than the peak current (both the peaks) values of their corresponding PFCAs (compare Figs. 3 and 10). It is also interesting to note that for the same concentration, the peak current values for the esters increase with increasing chain length. Based on molecular weight, molecular size, and diffusion coefficient correlations, one would indeed expect the diffusion-limited peak current to decrease with molecular weight. The exact cause for the inverse relationships observed in the present study is not known. This is, however, due to weaker adsorption with increasing molecular weight also contributing to the cathodic peak current in the same potential region [18–20].

However, other possibilities also exist. Earlier studies of electroreduction of perfluorocarboxylic acid esters suggest an overall two-electron, two-proton reduction of the ester group to the hemiacetal group [4].



If the reduction process changes with increase in chain length from one-electron process (say dimerization) to two-electron process, such increase in peak current values with increase in chain length can occur.

Quantitative analysis requires a single peak with higher peak current. Among the PFCAs and esters, acids gave single reduction peak in the presence of water and TEA. However, peak current values are smaller than the corresponding esters. Typical peak potential and peak current values for TFA in the absence and in the presence of water or TEA are compared with the same values for Et-TFA in Table 2. The peak potential values are substantially more negative for Et-TFA. However, the peak current values for TFA increase significantly in the presence of water and even to a greater extent in the presence of TEA. However, the peak current values are significantly higher for Et-TFA, suggesting that this derivative would give the highest signal to noise ratio for electroanalysis.

Table 2 Peak potential and peak current density values of 10.7 mM ethyl trifluoroacetate (Et-TFA) with TFA in the presence of water and TEA

Compound	Peak potential ($-E_{\text{p}}^{\text{c}}$; V)	Peak current density (mA/cm^2)
TFA	-1.52	1.96
TFA + water (4 M)	-1.04	2.29
TFA + TEA (1.03 mM)	-1.40	3.11
Et-TFA	-2.67	3.41

Conclusions

Perfluorocarboxylic acids exhibit sufficient surface effects during their electroreduction on GCE. The surface effects probably linked with the surface heterogeneities. Very small quantities of TEA and a significantly higher concentration of water were found to eliminate such surface effects, suggesting that surface acidity and surface hydrophobicity play an important role in exhibiting such surface effects for the estimation of PFCAs. Voltammetric reduction of their corresponding ester derivatives appeared to be a much better choice.

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