gradient within the mercury film limits the maximum scan rate to around 20mV s^{-1}. Good reproducibility was found with experiments at the rotating disc and at the wall-jet disc electrode. At the former excellent agreement was found between experiment and theory at a variety of rotation speeds and scan rates. However, at the wall-jet electrode, broader peaks were found except at very high flow rates (>0.125 cm^3 s^{-1}) and low scan rate, although the asymmetric wave shape typical of convective stripping was still apparent. Two factors can be invoked to explain the differences, reflecting the non-applicability of assumptions in the model at the wall-jet:

(i) The non-uniform accessibility implies the possibility of different electrode kinetic regimes over the electrode surface. This will be more accentuated the lower the flow-rate.

(ii) Diffusion parallel to the electrode surface is significant at low flow rates, since radial convection is low.

Despite the broader peaks at the wall-jet electrode advantages in peak resolution, due to peak asymmetry, and the good reproducibility are to be gained from convective stripping. This is important for the on-line use of these electrodes.

Similar considerations can be applied to tubular and channel electrodes, which are more uniformly accessible than the wall-jet electrode.

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THE GLASSY CARBON ELECTRODE/TETRABUTYLAMMONIUM ELECTROLYTE SOLUTION INTERFACE IN N,N-DIMETHYLFORMAMIDE SOLVENT

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Carbon electrodes have the advantage of being usable over a wide potential range in a variety of solvents, that has made their application widespread. However, owing to the existence of surface groups on the carbon, they cannot be regarded as inert, which is often manifested by significant background currents.

Studies previously undertaken by ourselves using glassy carbon (GC) electrodes in tetraalkylammonium electrolytes in *N,N*-dimethylformamide (DMF) [1] have shown the large background currents obtained in supporting electrolyte only at negative applied potentials. Additionally, cyclic voltammograms show variation with the anion and, as shown in Fig.1, small peaks can appear, in this case for chloride anion at -0.7V.

In this work the glassy carbon electrode/tetrabutylammonium (TBA) electrolyte interface in DMF was further studied for perchlorate (TBAP), bromide (TBAB) and chloride (TBAC) salts at varying concentrations from 0.01M → 0.20M and over the potential range 0.0 → -2.0V vs SCE. The structure of the interface was probed using the ac impedance technique with a Solartron 1250 Frequency Response Analyser coupled to a 1286 Electrochemical Interface and HP9816 computer. A sinusoidal perturbation of 5mV rms was superimposed on top of the dc

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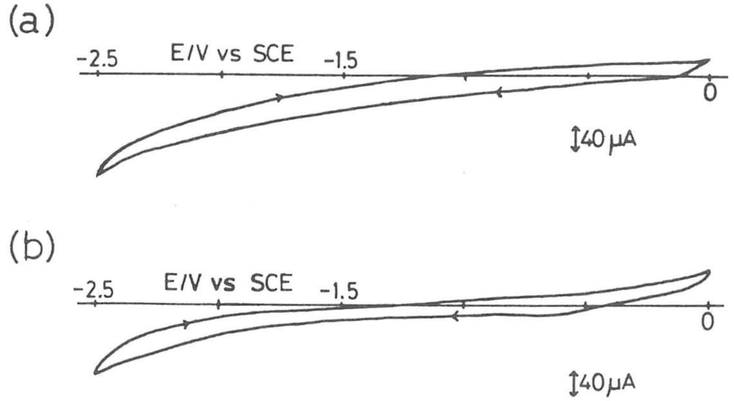

Fig.1 Cyclic voltammograms of 0.1M tetrabutylammonium electrolyte in DMF at GC electrode (area 0.38^2). Scan rate 100 mV s^{-1}. Deoxygenation 1 hr. (a) perchlorate; (b) chloride.

polarisation for frequencies varying between 0.1Hz and 65kHz. TBAP and TBAB (purissimum) and TBAC (purum) were obtained from Fluka and carefully dried; analytical grade DMF was dried, distilled and stored over Linde 4A molecular sieves in the dark before being used (within 48hr.). Solutions were deoxygenated with oxy-free, DMF-saturated N_2 for 1hr. before and during experimental runs. The GC electrode was polished with diamond paste down to 1μm and rinsed in DMF before use.

A typical impedance frequency spectrum, in the complex plane, is given in Fig.2 for TBAB, showing clearly the existence of faradaic processes, and in Fig.3 the variation of the high frequency part with TBAB concentration. The low frequency part of the spectrum is virtually the same for the three TBA salts and is not affected by salt concentration; only the high frequency part changes. With respect to the high frequency feature, was found:

(i) Variation with anion identity and electrolyte concentration;

(ii) No variation of impedance with applied potential.

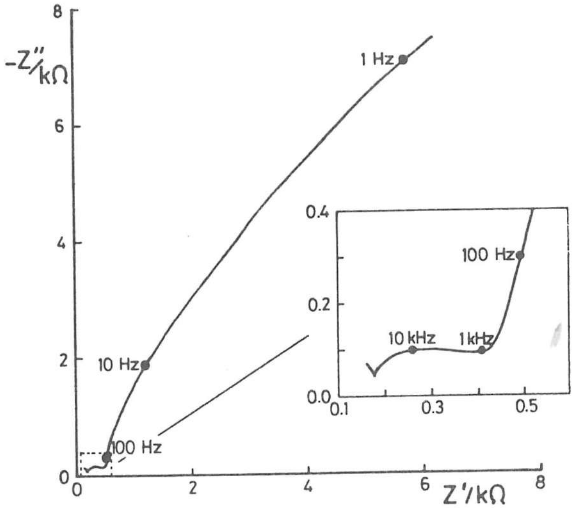

Fig.2 Complex plane impedance spectrum of 0.05M TBAB in DMF at GC electrode. E = -1.5V vs SCE.

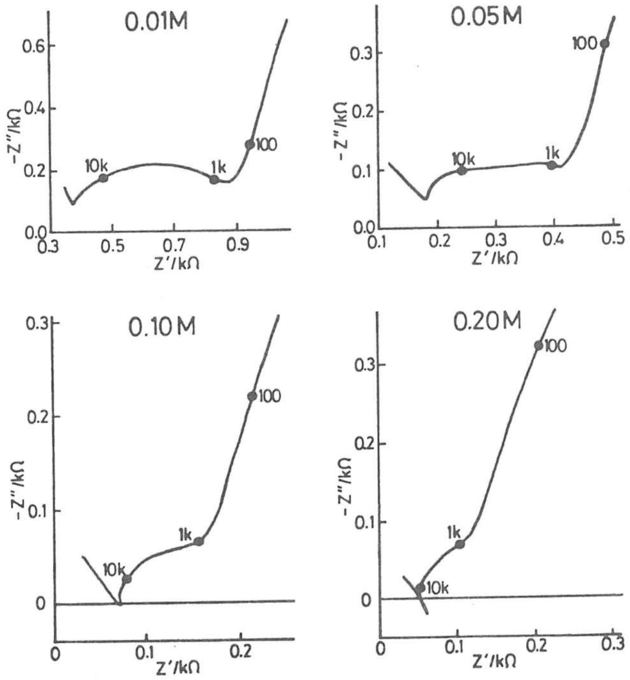

Fig.3 Impedance spectra for various [TBAB]. Other conditions as Fig.2.

This second observation is perhaps rather surprising since the dc currents are anodic at 0V, pass through zero at -1.0V and are significantly cathodic at -2.0V.

In explaining these results we must consider the porous nature of glassy carbon, and that at these potentials the main species attached to the GC electrode will be DMF molecules with a lesser quantity of bulky TBA$^+$ cations, the anion effect being secondary. Thus the low frequency behaviour probably involves the pores and solvent molecules. Even though DMF is aprotic, it has a dielectric constant of 37 and donor number 26.6. The high frequency part is probably due to processes occurring on the more accessible surface outside the pores of the glassy carbon electrode. Calculation of the double layer capacitance from the semicircles gives low values ($<4\mu F\ cm^{-2}$) with values for TBAB<TBAP<TBAC and increasing with concentration [2]. Although chloride gives the highest values as would be predicted, it is surprising that perchlorate leads to higher values than bromide, contrary to expected. It is intended to include other salts in this study in order to take more complete conclusions.

Acknowledgement. An equipment grant from the Calouste Gulbenkian Foundation and Instituto Nacional de Investigação Científica is gratefully acknowledged.

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ADSORPTION KINETICS OF POLYETHYLENE POLYMERS AT THE MERCURY/ELECTROLYTE INTERFACE

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SUMMARY

Adsorption mechanism of polyethyleneglycol 8000 on mercury/water interface is discussed on the basis of kinetics and diffusion steps. The maximum number of adsorbed molecules per unit area, the rate constant of adsorption and the equilibrium adsorption constant are determined using a.c. voltammetry, at the potential of zero charge of the electrolyte (NaF), where neutral molecules are strongly adsorbed.

INTRODUCTION

For a better understanding of adsorption of organic matter on particles in natural waters in terms of kinetics and equilibrium, adsorption studies of models of fulvic components are being done on a mercury/water interface (Buffle et al. |1|). This interface has been chosen because it simulates the behaviour of tensioactive compounds on natural hydrophobic interfaces and is very convenient in electrochemical terms.

Although a large number of small and well defined organic molecules was studied during the 1960's and 1970's, only a few studies exist about adsorption of macromolecules and their mixtures due to the higher complexity of the process.

THEORY

The degree of coverage is expressed by

$$C_d = C_{del}\ (1-\theta) + \theta\ C_{d\,sat}$$

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