

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 ($\ll 4\mu\text{F cm}^{-2}$) 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

$$C_d = C_{del} (1-\theta) + \theta C_{dsat}$$

where C_{del} is the capacity of the double layer in the absence of organics and $C_{d sat}$ the capacity when the surface is saturated with the organic molecules. The capacity can be obtained from the experimental values of the capacitive current (|2|).

The previous expression assumed a model of two parallel capacitors for mercury/water interface, one due to the water molecules at the interface and the other due to the organics adsorbed (|3|).

In this study two mechanisms have been tried in order to interpret the experimental results of adsorption of PEG 8000:

- 1) adsorption controlled by the diffusion step
- 2) adsorption controlled by diffusion and kinetics at the interface

The mathematical treatment for each one led to the following expressions:

1 - diffusion controlling step

From:

- a) Cottrell equation for linear and spherical diffusion (|4|)

$$\frac{d\Gamma}{dt} = \frac{D}{\delta} (C - C^0) \quad (1)$$

$$\frac{d\Gamma}{dt} = D (C - C^0) \left(\frac{1}{\delta} + \frac{1}{R} \right) \quad (2)$$

with Γ - n° of adsorbed molecules per unit area, D - diffusion coefficient, A - drop area, δ - thickness of the diffusion layer ($\delta = \sqrt{D\pi t}$ for non stirring medium), C - bulk solution concentration, C^0 - solution concentration at the interface ($C^0 \ll C$ up to saturation for strong adsorption).

$$b) \theta \text{ definition: } \theta = \Gamma / \Gamma_{max} \quad (3)$$

and assuming that $C^0 \ll C$, the following expressions can be derived:

1.1 - non stirred medium

A - linear diffusion

$$\theta = (t/t_{sat})^{1/2} \quad (4)$$

$$C = \frac{1}{2} \pi^{1/2} D^{-1/2} \Gamma_m t_{sat}^{-1/2} \quad (5)$$

with: t_{sat} - time required to attain saturation, where $\Gamma = \Gamma_m$

B - spherical diffusion

$$\theta = \left(\frac{2R + \sqrt{D\pi t}}{2R + \sqrt{D\pi t_{sat}}} \right) \frac{t^{1/2}}{t_{sat}^{1/2}} \quad (6)$$

$$C = \frac{\pi^{1/2} D^{-1/2} R \Gamma_m}{(2R + \sqrt{D\pi t_{sat}})} \times t_{sat}^{-1/2} \quad (7)$$

with: R - mercury drop radius

1.2 - stirred medium with linear diffusion

$$\theta = t/t_{sat} \quad (8)$$

$$C = D^{-1} \Gamma_m \delta t_{sat}^{-1} \quad (9)$$

2 - diffusion and kinetics controlling steps

From:

- a) diffusion and kinetics at the interface equations:

$$\frac{d\Gamma}{dt} = \frac{D}{\delta} (C - C^0) \quad (10)$$

$$\frac{d\Gamma}{dt} = (k_a C^0 (1-\theta) - k_d \theta) \quad (11)$$

k_a and k_d being respectively the adsorption and desorption rate constants and

$$b) \text{ Langmuir isotherm } \theta/(1-\theta) = \beta \times C$$

one can derive

$$\frac{d\theta}{dt} = \frac{C - \theta / ((1-\theta) \beta)}{\Gamma_m / ((1-\theta) k_a) + \frac{\Gamma_m}{D} \delta} \quad (12)$$

where β is the equilibrium adsorption constant ($\beta = k_a/k_d$). When there are interactions between adsorbed molecules, eq. (12) can still be applied, but β , k_a and k_d depend on θ :

$$\beta = \beta_0 e^{b\theta} \quad (13) \quad k_a = k_a^0 e^{\lambda\theta} \quad (14) \quad k_d = k_d^0 e^{(1-\lambda)b\theta} \quad (15)$$

where b is the Frumkin parameter related to the interaction forces ($b > 0$ ($b < 0$) for attractive (repulsive) forces), and λ is a parameter between 0 and 1.

EXPERIMENTAL RESULTS

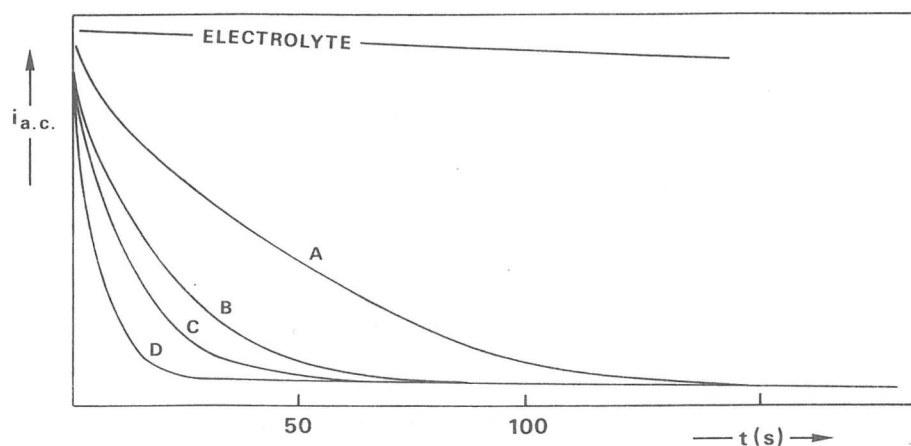


Fig. 1 - Capacitive current versus time (curves A,B,C,D), in a non stirred medium, 0.5 M NaF, for PEG 8000 concentrations (2,4,5,10) $\times 10^{-7}$ M.

For a given concentration of PEG 8000 the capacitive current decreases with time due to the adsorption process. The constant i_{ac} value obtained after a certain time is the same for different concentrations, which means that saturations of the mercury drop is attained. However, the time for saturation to be reached decreases with the increase of concentration and/or the stirring speed.

The linearity of θ vs $t^{1/2}$ for $\theta < 0.8$ and $C \geq 5 \times 10^{-7}$ (Fig. 2) suggests that the linear diffusion is the controlling step (eq. (4)).

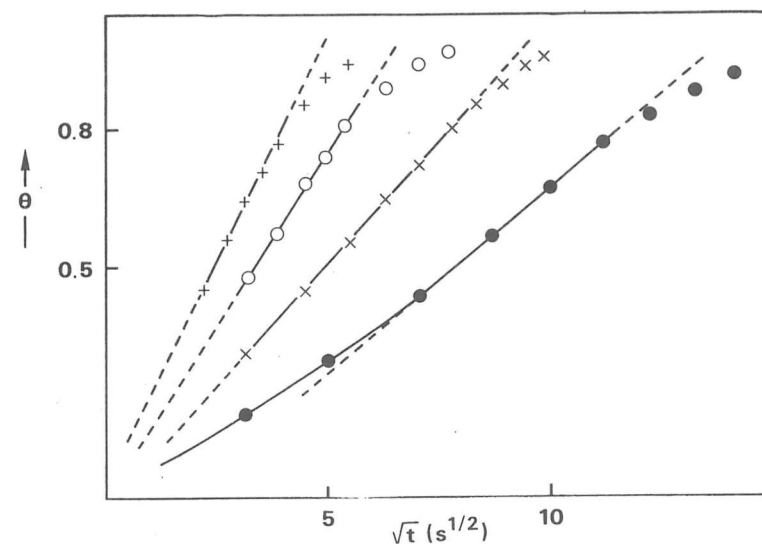


Fig. 2 - θ vs $t^{1/2}$ for PEG 8000 concentrations (\bullet - 3, \times - 5, \circ - 7.5, $+$ - 10) $\times 10^{-7}$ M, in a non stirred medium, 0.5 M NaF.

For concentrations lower than 5×10^{-7} M spherical diffusion has to be considered, which explains the deviation from the linearity of θ vs $t^{1/2}$.

Γ_m can be obtained from exp. (5) (or (7)), using saturation times calculated from eq. (4) (or (6)). The diffusion coefficient was estimated from the empirical expression

$$\bar{D} = \frac{10^{-4}}{(PM)^{1/2}} \quad (|5|)$$

The Γ_m value determined was:

$$\Gamma_m = (7.8 \pm .2) \times 10^{-12} \text{ mols/cm}^2$$

with good agreement for linear and spherical diffusion.

In a stirred medium an approximately linear relationship of θ vs t for each stirring rate and concentration is observed for $\theta \leq 0.8$, which indicates that diffusion should still be the controlling process (eq.(8)).

The thickness of the diffusion layer - δ - was determined for each

stirring rate from eq. 9, using t_{sat} determined with eq. 8 and Γ_m value determined in a non stirring medium. The values obtained were compared with δ values for cadmium (obtained from the limiting current of its faradic reduction), for each stirring rate, through the expression

$$\left(\frac{\delta_{PEG}}{\delta_{Cd}}\right) = \left(\frac{D_{PEG}}{D_{Cd}}\right)^\alpha$$

where α should be independent of the stirring rate (theoretically $\alpha = 0.3$ for pure spherical diffusion (6)).

The mean α value obtained from five different stirring rates was $= 0.50 \pm 0.02$, quite reasonable since the electrode geometry and convection currents cause deviations from a pure spherical diffusion.

In order to interpret the shifts from the linearity for $\theta > 0.8$, both steps - diffusion and kinetics adsorption at the interface - have to be considered.

Assuming Langmuir isotherm ($b = 0$), it is found from the experimental values that k_a^0 increases with the stirring rate. This seems to indicate that there should be some attractive forces between adsorbed molecules, i.e., $b > 0$.

The best fitting of experimental points $d\theta/dt$ to the theoretical expression - eq. 12 - was obtained for $b = 2.0$, $\lambda b = 1.4$ and Γ_m , k_a^0 , $\log \beta^0$ given in Table 1.

STIRRING	CONC. (M)	Γ_m (moles/cm ²)	$\log k_a^0$ (cm s ⁻¹)	$\log \beta^0$
WITHOUT	7×10^{-7}	5×10^{-12}	- 3.1	9.7
STIRRING	12×10^{-7}	5×10^{-12}	- 3.2	9.6
POS. 1	3×10^{-7}	4×10^{-12}	- 3.2	10.1
POS. 2	3×10^{-7}	3×10^{-12}	- 3.3	10.4
POS. 3	2×10^{-7}	5×10^{-12}	- 2.8	10.5
	3×10^{-7}	4×10^{-12}	- 3.0	10.3
POS. 4	2×10^{-7}	4×10^{-12}	- 3.0	10.6
POS. 4	3×10^{-7}	4×10^{-12}	- 2.9	10.3
POS. 5	3×10^{-7}	4×10^{-12}	- 2.9	10.3

Table 1 - PEG 8000 adsorption values determined considering both steps - diffusion + kinetics adsorption at the interface - using Frumkin parameters of: $b = 2.0$, $\lambda b = 1.4$.

From this table it can be noticed that Γ_m is about half the value obtained from the diffusion controlling step. This seems to indicate that even a small contribution of adsorption kinetics at the interface for the overall process significantly affects Γ_m value but not the linearity of θ vs $t^{1/2}$ (or θ vs t) for $\theta < 0.8$ in a non stirring (or stirring) medium.

CONCLUSION

Adsorption of PEG 8000 should be interpreted considering both steps - diffusion and kinetics adsorption at the interface - with attractive forces between adsorbed molecules.

The adsorption values found for this compound are:

$$b = 2.0 \quad \lambda b = - 1.4$$

$$\Gamma_m = (4 \pm 1) \times 10^{-12} \text{ moles cm}^{-2} \quad k_a^0 = (8 \pm 3) \times 10^{-3} \text{ cm s}^{-1} \quad \log \beta^0 = 10.2 \pm 0.4$$

It should be emphasized that saturation is attained for all concentrations ($15 \times 10^{-7} \geq C \geq 2 \times 10^{-7}$ M), which accounts for the low precision of $\log \beta^0$. Lower concentrations (to avoid saturation) cannot be used due to the competition of the impurities of the medium.

Acknowledgement - This work is under research project nº 87.48 of Junta Nacional de Investigação Científica e Tecnológica.

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