

References

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SIMULATION OF A NATURAL WATER INTERFACE

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For a better understanding of adsorption of organic matter on particles in natural waters in terms of kinetics and equilibrium, adsorption studies of single compounds and their mixtures on a mercury/aqueous solution interface are being done using alternating current voltammetry^{1,2}. This interface has been chosen since the behaviour of tensioactive compounds on natural hydrophobic interfaces is similar to the one shown on the mercury/water interface. The species adsorbed, the concentration below which there is no adsorption, the time required to attain equilibrium as a function of concentration, and adsorption constants are the major parameters to be determined.

In this context studies were carried out on the adsorption of :
a) some aminoacids existing in natural waters, with a relatively long aliphatic hydrocarbonated chain or π bonds, namely, lysine and phenylalanine, b) some aromatic organic ligands, chelating parts of humic and fulvic acids, namely, benzyliminodiacetic, pyridine-2,6-dicarboxylic and pyridine-2 carboxylic acids, c) mixtures of polyethyleneglycol with a molecular weight of about 8000 and phthalic acid.

The experimental results presented were obtained by ac voltammetry, at 25°C, in KNO₃ medium 1.0 M. This technique is widely used in adsorption studies because it allows the determination of capacitive currents directly related to the capacity of the double layer.

For all the ligands studied the adsorption is maximum at the potential of zero charge ($E_{pzc} \approx -0.55V$) which corresponds to the adsorption of neutral groups. The results presented in this paper were obtained for this potential.

For the aminoacids and aromatic ligands, the total adsorption equilibrium attained when the concentration at the electrode surface before saturation is equal to the bulk concentration is reached in some seconds for concentrations higher than 10⁻³M. This is experimentally checked from the constancy of the capacitive current after some seconds, at E_{pzc} . It is worthwhile emphasizing that the time required for the equilibrium depends on the adsorption constant and on the concentration of the ligand, decreasing with the increase of each one of these.

In equilibrium conditions the capacitive current decreases, i.e., the adsorption increases when the ligand concentration increases, up to the limit of the total saturation of the electrode. From this decrease the surface degree of coverage of the electrode can be determined for each ligand concentration ($\theta \approx \Delta i / \Delta i_{max}$, where Δi is the capacitive current decrease from the electrolyte currents and Δi_{max} the maximum value of Δi , i.e., when saturation is attained).

Table 1 shows the adsorption constant values obtained by fitting the experimental points to a Langmuir isotherm, using bulk ligand concentrations since the total equilibrium is reached. If the molecule is charged it

would be better, in principle, to use the Frumkin isotherm, which takes into account the interactions between molecules. However, for these ligands, molecular interactions should be very small since the fitting to a Frumkin isotherm gives the same order of magnitude for adsorption constants and a value for b parameter within the experimental errors.

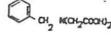
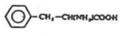
Ligand	pH	Species in Solution	$K(n^{-1})$ at E_{pzc}	$C_{pzc}^0(H)$ (for $\theta = 12$)
 pyridine - 2 - carboxylic acid	3.0	H L ⁰	0.8x10 ²	5x10 ⁻⁶
	7.5	L ⁻	not adsorbed	—
 pyridine - 2,6 - dicarboxylic acid	1.0	H ₂ L ⁰	2.0x10 ³	2x10 ⁻⁶
	8.5	L ²⁻	not adsorbed	—
 benzylaminoacetic acid	1.0	H ₂ L ⁰	2.0x10 ³	1x10 ⁻⁶
	8.5	L ²⁻ + HL ⁻	0.9x10 ³	2x10 ⁻⁵
 lysine	7.8	H ₂ L ⁰	1x10 ²	0.7x10 ⁻⁶
	9.5	HL ⁰	2x10 ²	0.5x10 ⁻⁶
	11.0	L ⁻	1.5x10 ²	0.7x10 ⁻⁶
 phenylalanine	7	HL ⁰	0.7x10 ³	2x10 ⁻⁵
	11	L ⁻	0.5x10 ³	2x10 ⁻⁵

Table 1

From Table 1 one can see that the values of adsorption constants are in the range of 10² - 10³ M⁻¹, being higher at pH values where the molecule is neutral. However, while the charged groups of pyridinic acids, directly bound to the aromatic ring, hinder the adsorption of the hydrophobic part of the molecule, for the other ligands the adsorption constant doesn't change significantly with pH. For these compounds the charged groups (hydrophilic groups) are well separated from the hydrophobic groups and do not greatly affect the adsorption of the latter ones on mercury.

The fulvic acids, consisting of complex mixtures of compounds, need much more time to attain total adsorption equilibrium than the ligands

studied above, due to their lower diffusion rate (high molecular weight) and slower adsorption kinetics (conformational changes take place along the time, tending to expell the hydrophilic groups^{3,4} from the surface.

For an approach closer to the reality of fulvic acids, we have studied the adsorption of organic mixtures where a more strongly adsorbed surfactant can displace one with a higher diffusion coefficient but less strongly adsorbed.

The results obtained on the competitive adsorption of a mixture of polyethyleneglycol (PEG) with a molecular weight of 8000 and phthalic acid will be presented. However, it is important, first of all, to have an insight into the behaviour of the PEG itself. From the surface coverage degree versus the square root of time, in non equilibrium conditions, Fig. 1a, one can determine the time required for the saturation of the mercury surface in adsorption processes if the diffusion is the limiting step and the ligand concentration in solution at the interface is negligible compared with the bulk concentration up to saturation. Indeed, in these conditions the degree of surface coverage is a linear function of the square root of time and from the slope one can determine the saturation time⁵. For the hanging mercury electrode one has:

$$\tau = 4.84 \times 10^{-4} \times D^{1/2} \times C_L^{bulk} \times t^{1/2} \quad \text{and} \quad \theta = \frac{t^{1/2}}{t_{sat}^{1/2}}$$

where $D(\text{cm}^2 \text{s}^{-1})$, $C_L(\text{M})$, $t(\text{s})$. From the slope of the linear relationship of ligand concentration versus the inverse of the square root of saturation time, Fig. 1b, the area of the adsorbed molecule can be determined if the diffusion coefficient is known⁵

$$C_L^{bulk} = 2.07 \times 10^3 D^{-1/2} \frac{1}{A} t_{sat}^{-1/2}$$

where $A(\text{cm}^2)$ is the surface covered by one mole.

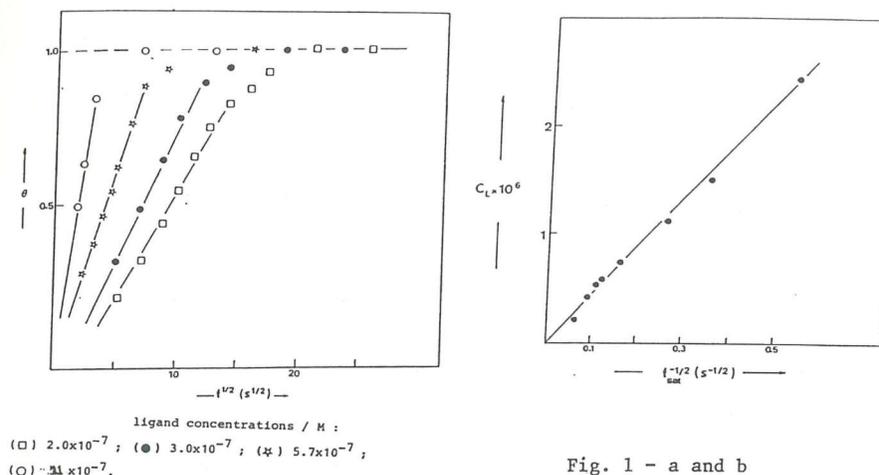


Fig. 1 - a and b

In the presence and absence of phthalic acid, the evolution of the capacitive current for PEG along the time is quite different - Fig. 2. The competitive adsorption between PEG and phthalic acid depends on the species present and their concentration. As the concentration of phthalic acid increases, the capacitive current decreases at the beginning of the contact mercury/solution due to the adsorption of this ligand, with a higher diffusion coefficient. However, as time increases, phthalic acid is being replaced by PEG (which has a lower diffusion coefficient but a higher adsorption constant) until full coverage of the electrode is attained.

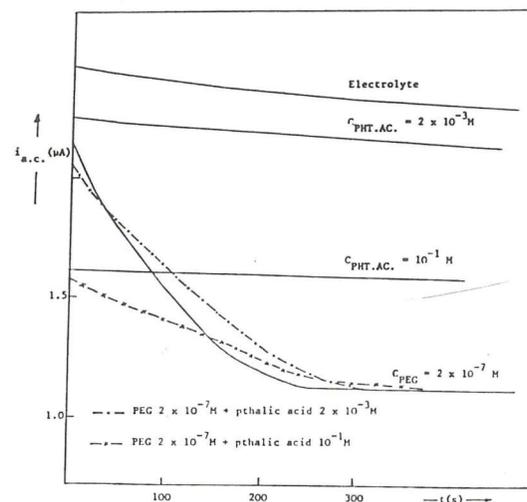


Fig. 2

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ULTRAMICROELECTRODES: SMALL IS BETTER

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In recent years, microelectrodes have attracted attention in many fields of electrochemistry and their popularity has grown rapidly due to a recognition of the significant advantages to be derived from their applications^(1,2).

The use of very small electrodes made of carbon fibre or a thin metal wire has several advantages as a result of their very specific properties, (i) since they are very small (diameter < 100 μm) they draw very small currents, thus decreasing the effect of uncompensated iR drop and allowing measurements to be made in very concentrated solutions of electroactive species, or in highly resistive media; (ii) high rates of steady state diffusion can be obtained allowing the study of fast electron transfer reactions and coupled chemistry, (iii) the faradaic/charging current ratio is enhanced.

We have been interested in applying microelectrodes to a series of systems in order to determine the kinetics of fast heterogeneous electron transfer reactions by using fast sweep cyclic voltammetry⁽³⁾. In very short timescale experiments, the linear diffusion flux totally predominates over the spherical diffusion field and it is possible to use the equations and dimensionless plots of Nicholson and Shain to obtain the kinetic parameters.