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**ADSORPTION OF LONG CHAIN CARBOXYLATES ON
MEMBRANE MATERIALS**

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Abstract

A batch adsorption procedure for adsorption isotherm measurements has been developed, using direct contact of six metallic oxides powders with a mix of different sodium carboxylates. The amount of adsorbed solutes are determined after solvent extraction and GC quantification. Isotherms modelling according to Langmuir and B.E.T. models suggest the existence of multilayer adsorption. Binding constants (K_n) range from 0.053 to 0.210 $l.mmol^{-1}$, which is consistent with a weak binding. Total adsorption sites number (A_t) range from 1.61 to 18.51 $mmol.m^{-2}$ and vary both with membrane material and carboxylate nature. In all cases the amount of adsorbed solutes is quite small, and do not explain, alone, fouling of membranes.

I. INTRODUCTION

In the field of micro and ultrafiltration, adsorption of solutes is always described as a major factor for membrane fouling and flux decrease (1,2,3). This phenomenon has been studied, especially during protein filtration (4,5,6). Nevertheless, we lack information about basic mechanisms of solutes membranes interactions. In a recent study, a method for measuring adsorption isotherms of proteins has been described (7,8); the results proved to be relevant to explain filtration results. In this latter study(7), the major factor involved in protein adsorption was the pH, that influences solutes-membrane interactions by means of modifying protein and membrane charge. Therefore, if the pH of the solution can not be modified for any reason, changing membranes surface charge density can actually result in separation improvement (9).

Ceramic is emerging as an advantageous material for membrane manufacturers, in regard to its chemical, mechanical, and thermic resistances. Recently new kinds of ceramic membranes, of which zero point charge has been modified, have entered membrane market. These membranes have been reported to be usefull in some separation applications, in regard to their surface charge modifications (10). Nevertheless, complete characterization

of their surface reactivity is needed to have a better understanding of their behaviour during filtration experiments.

In the present study, ceramic powders used in Membralox membranes production, have been studied, in regard to their adsorption properties. A batch procedure for carboxylates isotherms measurements has been developed, using direct contact between ceramic powders and solutes. The results clearly proved the occurrence of interactions between ceramic materials and carboxylates. This adsorption phenomenon do not explain previous results obtained with microfiltration experiments.

II. MATERIAL AND METHODS

II.1. Solutions

Fatty acids, C12:0, C16:0, C18:0, C18:1, were purchased from Prolabo (France). The initial solution was composed respectively of: laurate 2.5 mM, palmitate 1.8 mM, stearate 1.3 mM, and oleate 1.6 mM. It was prepared as follows: fatty acids were mixed with hot distilled water (65°C) and then neutralized with 10N NaOH. Resulting pH was 11.5. This solution was then diluted with distilled water to reach appropriate concentration for isotherm measurements (dilution factor from 0.025 to 1).

II.2. Fatty acids quantification

Sodium soaps in solutions were quantified using a hexane extraction procedure at acid pH value, and GC measurements: 10 ml of aqueous solution were mixed with 10 ml of hexane containing C9 as internal standard (0.5 g.l⁻¹) and with 0.25 ml of HCl 37% (w/v). After 30 min stirring, an aliquot of the hexane phase was collected and submitted to BF₃/methanol 14% as reagent (11), for fatty acid methyl esters (FAME) obtention.

The FAME were then injected into a Varian GC apparatus. The chromatographic conditions were: injection; split ratio 1/20, injector temperature 250°C, carrier gas hydrogen, flow velocity 27 cm.s⁻¹, column FFAP Nukol (Supelco, France) length 30 m, internal diameter 0.32 mm, phase thickness 0.25 μm; detection flame ionization detector, temperature 260°C; elution temperature profile, isotherm 5 min, 120°C, 120 to 200°C, 5°C per min, isotherm 5 min at 200°C.

II.3. Ceramic powders

Six different powders have been provided by the Société des Céramiques Techniques (S.C.T., France). The different materials were: Standard alumina (St), Zirconia powder (Zr), and modified aluminas type A (AA), B (AB), C (AC), and D (AD)

If necessary, membranes powders were cleaned before use. Membranes powders cleaning was achieved as follows: powders in glass tubes were washed successively with NaOH 1% and HNO₃ 1% under stirring at 50°C for 30 min in a stirred thermostated bath. After each cleaning step, powders were washed with distilled water until pH reached neutrality. Membranes powders were dried 7 h at 100°C before use.

II.4. Batch adsorption procedure

Five gram of ceramic powder were added to 10 ml of carboxylates solution at 50°C in a glass tube. After 3 h stirring at 50°C, the glass tube was centrifuged at 2000 g, 10 min. The supernatant (S_0) was removed and the sediment was washed with distilled water and centrifuged again. This latter stage was repeated. The resulting supernatants were S_1 and S_2 . The washed sediment was dried at 100°C, during 7 h. Hexane/acetic acid (97/3) containing C9 as internal standard was used to desorb carboxylates from the powder. In order to check total recovery of carboxylates, quantification was performed on every supernatant (S_0, S_1, S_2), and on the hexane/acetic acid extract (Ep). For routine determinations only the Ep fraction was quantified.

II.5. Isotherm modelization

Two different models have been used for isotherms modelization:

$$\text{Langmuir modelling: } 1/[CS] = 1/(K [At] [S]) + 1/[At] \quad [1]$$

$$\text{B.E.T. modelling: } 1/[CS] = 1/At - Kn. [S]/ [At] \quad [2]$$

[S] soaps in solution (mmol.l^{-1}), [CS] amount of adsorbed soaps (mmol.m^{-2})

At, total available adsorption sites number (mmol.m^{-2})

K and Kn, affinity constants (l.mmol^{-1})

Langmuir model is based on a simple equilibrium between free and adsorbed solutes and concerns only adsorbant-solute interactions. This model is therefore suitable for monolayer coverage. This model will be valid if a plot of $1/[CS]$ versus $1/[S]$ is a straight line. On the contrary, B.E.T. model describes multilayer adsorption; this model is valid if a plot of $1/[CS]$ against [S] is linear.

III. RESULTS AND DISCUSSION

III.1. Fatty acids recovery

Table 1 presents results obtained after 3 repetitions of the batch adsorption procedure. It is observable that fatty acids are almost totally recovered. Confidence intervals appear to be rather wide, and proportional to soaps amount.

The mechanism involved in soaps adsorption remains unclear since powders and solutes have a negative charge at basic pH values (12). In fact, because of the amphoteric nature of ceramics (13), some positive charges may still exist despite a total negative charge and can interact with negative charged solutes. However adsorption of an anionic surfactant has been observed on zirconia membranes (15).

Table 1: fatty acids recovery = $\frac{\text{amount of soaps extracted}}{\text{total amount of soaps}} \times 100$

	S ₀	S ₁	S ₂	Ep	Total
C12:0	89.0 ± 4.6	7.0 ± 2.8	2.0 ± 1.6	0.8 ± 0.2	98.8
C16:0	84.0 ± 8.3	6.7 ± 2.4	4.6 ± 1.0	10.2 ± 2.1	105.5
C18:0	79.0 ± 11.8	5.5 ± 5.1	4.7 ± 1.2	16.9 ± 2.7	106.1
C18:1	85.0 ± 10.0	5.6 ± 2.5	2.9 ± 0.6	3.3 ± 0.6	96.8

III.2. Langmuir and B.E.T. modelling on Standard membrane

The modelisation according to Langmuir has been tested on standard ceramic powder. Figure 1a. presents the curve obtained for this material. The model is not valuable within the interval studied. Therefore, Langmuir basic hypothesis are not valid, i.e. there is a multilayer adsorption or there are several kinds of binding sites. Such behaviour has been observed previously (7).

B.E.T. model fits the observed data with significative correlation at 5% level. Thus, the hypothesis of multilayer adsorption seems to be valid. This has been confirmed on every ceramic material. A typical B.E.T. plot is presented figure 1b.

III.2. B.E.T. parameters Kn and At

B.E.T. modelling has been applied to each material isotherm. The influence of cleaning has been investigated. B.E.T. parameters vary both with carboxylate and material. In fact, amounts of C16 and C18 adsorbed soaps are the highest.

Binding constant (Kn) values are consistent with a weak binding (around 0.1 l.mmol⁻¹). They are not significantly different from a material to another, thus the reactivity of each material is quite equal. Furthermore this reactivity is not influenced by cleaning.

Total adsorption sites numbers are much more different from a material to another (At results are presented figure 2). The lowest adsorption sites number is obtained for Zr powder and C 12 soap, the highest for AD powder and C16 soap. It is rather difficult to compare these values with those obtained from litterature since very often solutes are proteins, which have a much higher molecular weight. The differences in total adsorption sites number between soaps is therefore rather surprising since their molecular weight are

slightly different. The influence of cleaning results in total adsorption sites number decrease, particularly with AD powder. The cleaning process reduces the quantity of adsorption sites without changing their solutes affinity.

All these results clearly prove the occurrence of interactions occurring between carboxylates and ceramics. The amount of adsorbed soaps is small if compared to results obtained with chromatographic adsorbants (16). In fact, alpha alumina is well known to have low sorptive ability compared to chromatographic gamma alumina.

During microfiltration experiments, high rejection levels of C16:0, C18:0, C18:1 micellized soaps have been observed, while C12:0 soap was hardly rejected. Membrane fouling was well described by an adsorption model. The results observed in this study are very different. First, there is no evidence of micellization effect on adsorption results (figure 1b). Secondly, C12:0 soap which is known to be unmicellized, behave just like micellized soaps. Therefore the adsorption phenomenon is not sufficient to explain fouling of membranes.

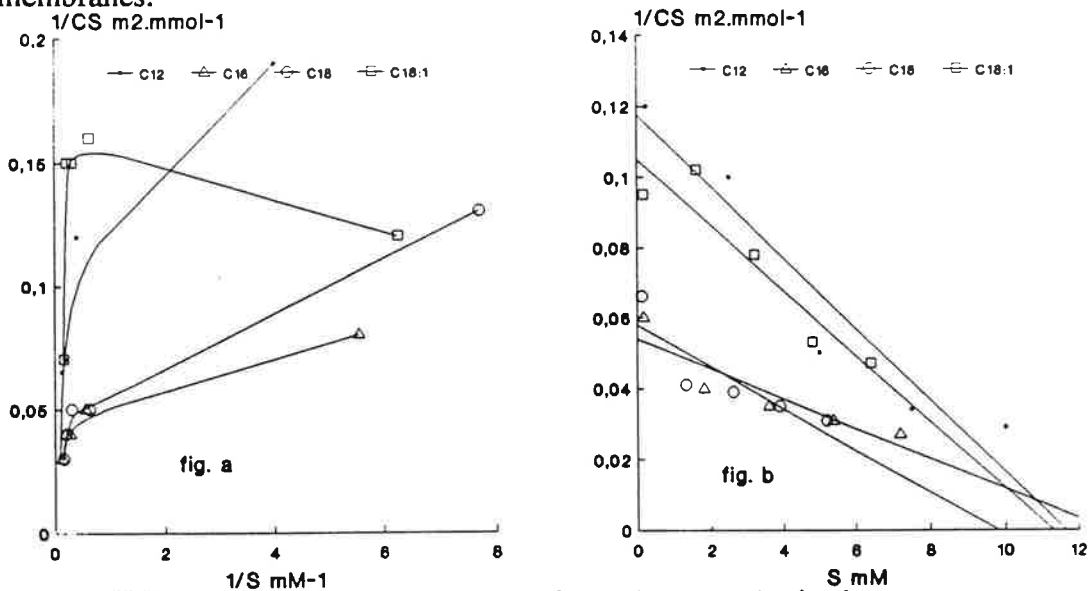


Figure 1 a & b: Langmuir and B.E.T. plot of Standard powder isotherm

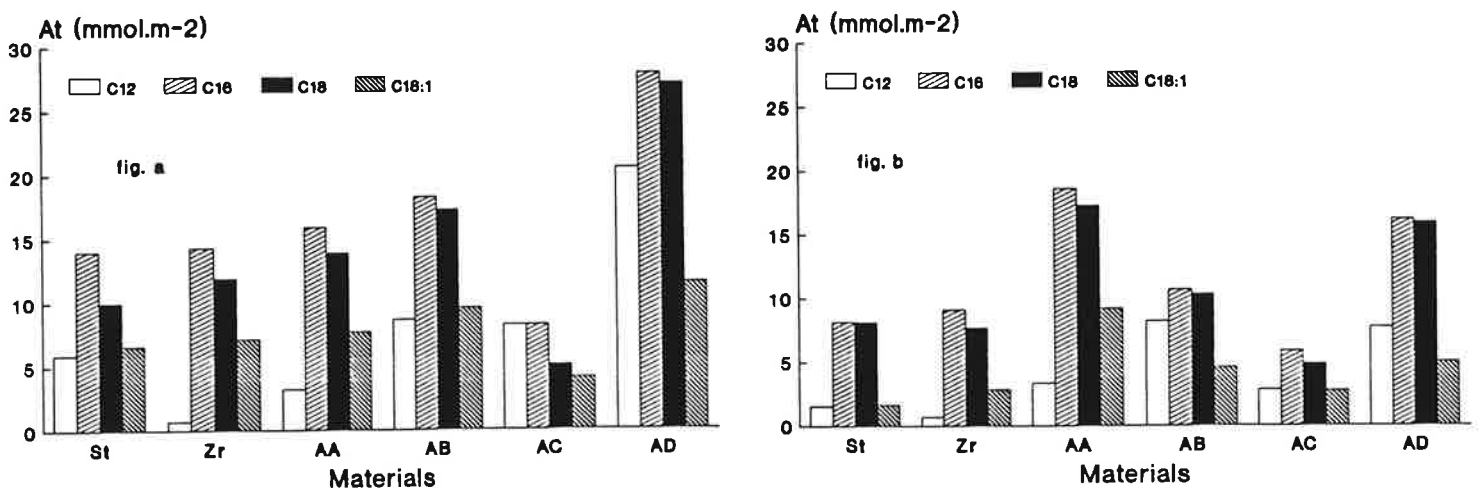


figure 2 a & b: Total adsorption sites number A_t without (a) or with (b) cleaning

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