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MODIFICATION OF TRACK-ETCHED MEMBRANES WITH OLIGOMERIC BIANCHOR COMPOUNDS AND ITS EFFECT ON THEIR SEPARATING PROPERTIES

Abstract

A study was conducted on the adsorption process of bianchor surfactants from water solutions onto the surface of micro-filtration track-etched membranes, and their functional properties were investigated. The effects that several extraneous factors, such as concentration and component ratio, have upon the membranes modification were demonstrated. It was established that electrochemical interactions play the main role in electrolyte retention within the investigated concentrations range on the original and modified membranes.

Introduction

Hydrophobic membranes manufactured from chemically stable and thermo-resistant polymers (e.g., polypropylene, polytetrafluoroethylene, polyethylene terephthalate [PET], etc.) are extensively used in membrane technology. However, despite the valuable processing properties of such membranes, their hydrophobic nature has sometimes a significant negative impact on their use for certain practical applications. Chemical and physical-chemical modification of hydrophobic membranes (1) allows to both aid their surface wetting (including the pore surfaces), and to impart specific separating properties to the membranes due to formation of certain functional groups on their surfaces (2). Besides, it has been known (3) that modification of membranes often leads to a significant change in their structural and transport properties. Among the variety of available methods to aid surface wetting of hydrophobic membranes, surfactant treatment is one of the most effective and simple ones (4). However, use of the traditional low molecular weight surfactants has a short-term effect.

As we demonstrated (5), adsorption of bianchor surfactants (BAS) from water solutions onto the membranes surface leads to a significant change in their separating properties. Therefore, it would be reasonable to expect that adsorption of BAS having ionic groups in the molecule will have a significant influence on both the hydrophilic properties of the membranes, and their rejection, pore structure, and nature of the surface. Due to their simple geometry, it is most practical to use track-etched (T-E) membranes as the material for studying adsorption properties. Their pores are shaped as cylindrical capillaries. Narrow pore distribution allows precluding the problems related to tortuosity of polymeric membranes manufactured by other methods (6). The goal of this study was to investigate the pattern of bianchor surfactants adsorption from water solutions onto the surface of micro-filtration PET T-E membranes and to examine their separating properties.

Methods

In the study conducted, surface wetting of micro-filtration PET T-E membranes with pore diameter of 0.05 and 0.08 μm was aided by oligomeric surfactants such as cation-active and anion-active urethane bianchor surfactants (subsequently referred to as "oligomeric BAS"), which are characterized by presence of a hydrophobic hetero-chain macromolecule of branching structure; the macromolecule ends with three pyridine chloride groups $\text{N}^+\text{C}_5\text{H}_5$ (Cl^-) in cation BAS, and with three saline groups OSO_3K (7). Molecular weight of BAS is 4 200 g/mol. For BAS adsorption, membrane samples with an area of $26.4 \cdot 10^{-4} \text{ m}^2$ were

held in water solutions of BAS with initial concentrations of 0.025 %, 0.1 %, 0.3 %, and 1%. The above concentrations are derived from the necessity not to exceed the critical micelle concentration (CMC). Adsorption process duration was from 5 minutes to 30 days, and the modifying BAS solution volume was 20 cm³. For the duration of adsorptive modification, the membranes were periodically removed from the BAS solutions, washed with distilled water, and the bulk flow of de-ionized water through the membrane was measured. The amount of BAS adsorbed onto the membrane surface and pores was determined by measuring electrical conductivity of BAS solutions before and after adsorption with a conductivity meter HI 9032 (HANNA INSTRUMENTS). Selectivity of membranes modified with anion-active BAS was determined based on retention of SO₄²⁻ (K₂SO₄) ions, and that of the membranes modified with cation-active BAS – from retention of Ca²⁺ (CaCl₂) ions; the solution concentrations were 1.0 · 10⁻³, 3.3 · 10⁻³, and 1.0 · 10⁻² kmol/m³. The experiments were conducted with the use of an ultra-filtration cell of the FM-02-200 type, at a pressure of 0.05 MPa and mixing speed of 500 rpm. Electrolyte concentration in the initial solution and in the filtrate was measured with a flame photometer, model PAZh-3. In order to determine the change of the membrane selectivity regarding non-ionic substances, retention of polyethylene glycols (PEG) having molecular weights of 1500, 3000, 6000, 12000, and 35000 from their water solutions with a concentration of 3 kg/m³ was determined; in doing so, the experiment results of both the original and the modified membranes were compared. PEG concentration in the initial solution and in the filtrate was measured with an interference meter ITR-2.

Results

It is known (8) that BAS adsorption onto the membrane surface and pores leads to reduction of its pores' effective radius, and therefore reduces the bulk flow through the membrane. Accordingly, the degree of the membrane modification by the bianchor surfactants can be characterised through the change of bulk flow of water through the membrane before and after the BAS sorption. As Fig. 1 illustrates, volumetric water flux through the modified membranes decreases with increase of the modification process duration and of the initial BAS concentration in the solution. This is typical of the membranes modified with both anion-active (Figs. 1a, 1b), and cation-active BAS (Figs. 1c, 1d) with different pore sizes. It was established that bulk flow decrease with duration of modification is more significant for the membranes with pore size of 0.08 mcm (Figs. 1b, 1d), than for the ones with pore size of 0.05 mcm (Figs. 1a, 1c). As Fig. 1 demonstrates, bulk water flow through all the modified membranes decreases only to a certain point, and after that remains constant.

Fig.1(a, b). Dependence of bulk water flow value (J_v , l/m²·h) on duration of anionic BAS sorption (τ , h) from water solutions. Pore size of PET T-E membrane is: a-0,05mcm, b-0,08 mcm. P = 0,01 MPa

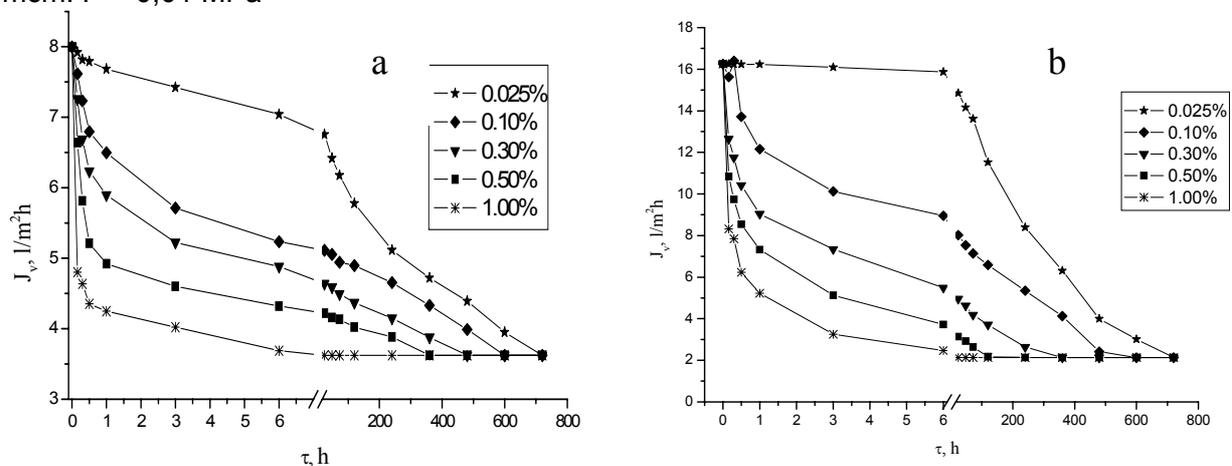
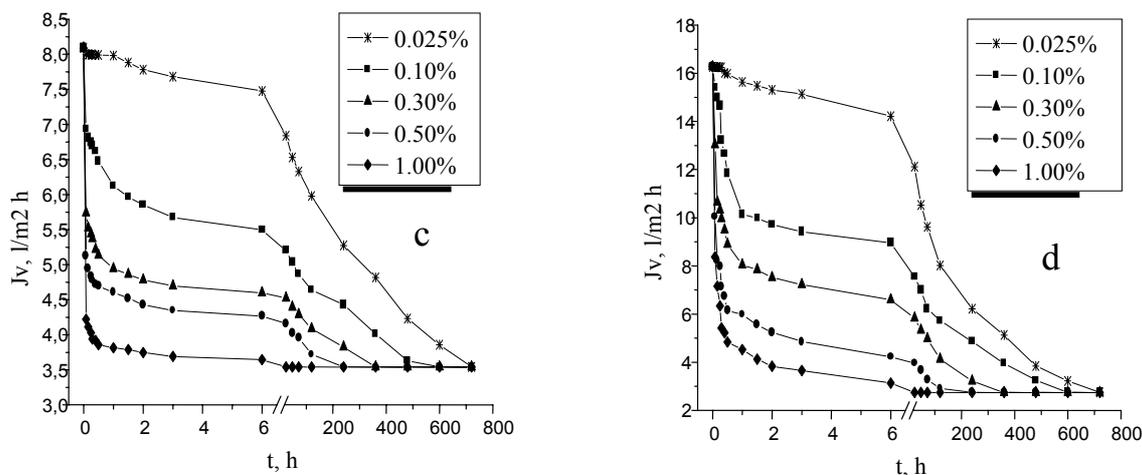


Fig.1 (c, d). Dependence of bulk water flow value (J_v , $l/m^2 \cdot h$) on duration of cationic BAS sorption (τ , h) from water solutions. Pore size of PET T-E membrane is: a-0,05mcm, b-0,08 mcm. P = 0,01 MPa



This behavior of the curves could be attributed to the fact of complete adsorptive saturation of the outer surface of the membrane and its pores with bianchor surfactants, after which no oligomer sorption follows. In this process, the higher is the initial solution concentration, the faster is the sorption. For example, when conducting a study of BAS sorption from a 1 % solution, the complete adsorptive saturation (stabilization of bulk water flow through the membrane with sorption time) is reached within 24 hours of sorption, whereas with BAS solution concentration of 0.025 % it is only achieved in 30 days.

Taking into account such factors as concentration and colloidal-chemical state of the BAS solution, sorption duration, change of productivity and selectivity of modified membranes with time, it may be concluded, that the BAS concentration of 0.5 % is optimal for modification of the T-E membranes under consideration.

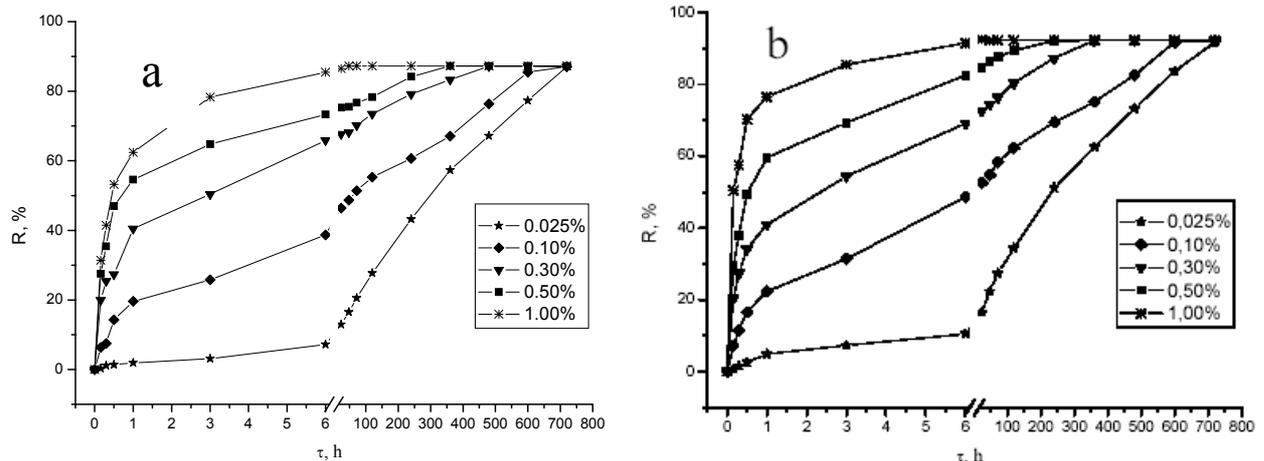
This conclusion clearly demonstrates the amount of BAS adsorbed vs. sorption duration; the data was calculated from the electrical conductivity change of modifying BAS solutions. The maximum amount of anion-active BAS adsorbed by a membrane with a pore diameter of 0.08 mcm is 0.63 g/m^2 , and for a membrane with a pore diameter of 0.05 mcm the amount is 0.43 g/m^2 . Whereas cation-active BAS is sorbed by a membrane with a pore diameter of 0.08 mcm in the amount of 0.41 g/m^2 , and in the amount of 0.31 g/m^2 by a membrane with a pore diameter of 0.05 mcm, which could be attributed to the bigger-sized membrane pores being more permeable for the BAS molecules and to the lessened effect of electrostatic repulsion between the adsorbed surfactants and the ones being adsorbed.

Presence of ionic groups in the BAS let us assume a significant change in separating properties of the modified membranes towards the ionic substances, such as low molecular weight electrolytes.

To support the above assumption, a study was conducted on selective retention of SO_4^{2-} ions (for anion-active BAS-modified membranes), and of Ca^{2+} ions (for cation-active BAS-modified membranes) during filtration of $1.0 \cdot 10^{-3}$, $3.3 \cdot 10^{-3}$ $1.0 \cdot 10^{-2}$ M solutions of potassium sulphate (1-2) and calcium chloride (2-1) through modified membranes, since retention of such electrolytes by the charged membranes is a manifestation of the electrochemical process of retention. It is apparent that the bigger is the membrane charge, the better will SO_4^{2-} ions be retained, and accordingly Ca^{2+} ions for cation-active BAS-modified membranes. When comparing the resulting data, it could be seen that in modifying the membranes with the initial BAS solution concentration of 0.025%, retention of SO_4^{2-} and Ca^{2+} ions gradually increases with the increase of solution contact duration with the membranes modified with anion-active and cation-active BAS respectively, whereas the 1% concentration of the initial modifying solutions produces a sharp spike of rejection (almost by 30%) within the first 10 minutes of contact (Figs. 2a, 2b, Tab.1). Retention factor of the

electrolytes in question on the membrane with larger pore size (diameter D of 0.08 mcm) is higher, than that on the membrane with a pore size D of 0.05 mcm, regardless of the sorption duration. This fact further supports significance of the effect BAS concentration and membrane pore size have on the modification process.

Fig. 2 (a, b). Dependence of SO_4^{2-} rejection coefficient (R , %) on duration (τ , h) of BAS sorption from water solutions determined by filtration of K_2SO_4 solutions through modified by anionic BAS T-E membranes with different pore size: a) 0,05 mcm, b) 0,08 mcm. Ions concentration $1,0 \cdot 10^{-3}$ M.



As Table 1 illustrates, the higher is the electrolyte concentration, the lower is the retention factor for Ca^{2+} ions, which is related to the phenomenon of compression of the dual electric layer under the influence of the electric field of the electrolytes' dissociated ions.

Table 1. Dependence of Ca^{2+} rejection coefficient (R , %) on CaCl_2 solution concentration. The PET T-E membrane was modified with 0,5% cationic BAS solution (duration of sorption – 10 days).

CaCl ₂ water solution concentration											
1.0 · 10 ⁻³ kmol/m ³				3.3 · 10 ⁻³ kmol/m ³				1.1 · 10 ⁻² kmol/m ³			
0.05 mcm		0.08 mcm		0.05 mcm		0.08 mcm		0.05 mcm		0.08 mcm	
I , l/m ² h	R , %	I , l/m ² h	R , %	I , l/m ² h	R , %	I , l/m ² h	R , %	I , l/m ² h	R , %	I , l/m ² h	R , %
3.516	87.2	2.134	92.1	3.509	67.2	2.129	72.6	3.505	59.8	2.124	65.6

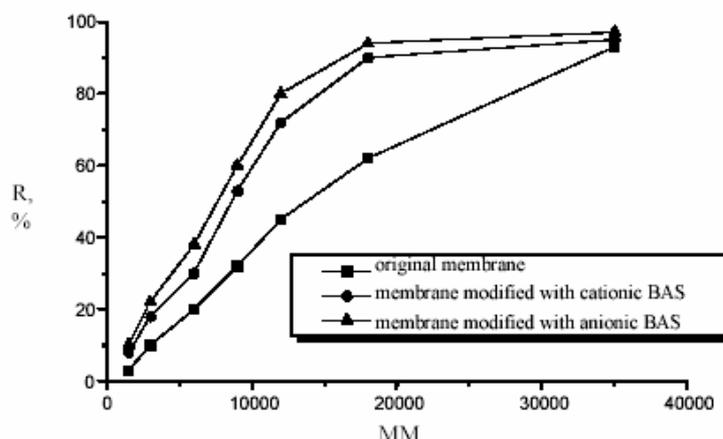
Thereby, the data received attest to the fact that electrochemical interactions contribute significantly to electrolyte retention by a modified membrane within the whole range of examined concentrations.

Membrane modification leads to decrease of their productivity in CaCl_2 and K_2SO_4 solutions, which is due to decrease of the modified membranes' effective radius; moreover, as in the case of the distilled water bulk flow, it decreases with increase of the initial BAS concentration and modification process duration.

Membranes' pore size change could also be judged from measurements of the retention factor of low and high molecular weight substances of various chemical natures, such as PEGs with different molecular weights. PEGs are water-soluble nonionic substances poorly adsorbed onto the membranes; they produce no electrochemical interaction during their filtration, and, in low concentrations and at operating pressures, almost no gel formation, deformation, or macromolecular coil orientation is apparent (9). Based on the studies of the

membranes' separating properties towards the PEG water solutions, the curves of molecular-mass retention (MMR) were generated, which allows determining the membranes' cut-off, as well as their pore size distribution. It was discovered that modification of the membranes leads to a reduction of their permeability and an increase of the PEG retention factor.

Fig. 3. PEG molecular-mass retention curves for membranes with 0,05 mcm pore size modified with 0,5 % BAS water solution; sorption duration - 10 days.



MMR curves of the PEGs shift towards the lower molecular weights (Fig. 3); besides, the higher is the BAS initial concentration and the duration of the membrane samples modification, the higher the above effects are.

Conclusions

Modification of the T-E membrane surface with oligomeric bianchor compounds dramatically changes their separating properties (retention factor and permeability) due to both the change of the membrane pore size as a result of BAS sorption, and the manner of interaction between the dissolved substance and the membrane in the case of filtration of electrolytes water solutions.

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