Grafted Polypropylene Membranes for Purification of Water Containing Sodium Alkylbenzenesulfonate

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Synopsis

The possibility of eliminating sodium alkylbenzenesulfonate (ABS) from water by reverse osmosis was examined by operating with polypropylene membranes grafted with poly(acrylic acid). Flux through the membranes decreases with increasing thickness. For 23μ thickness and 0.5 l./hr-m² flux, the rejection is 100% (operating pressure, 50 atm; concentration, 1 g ABS/l.). For 5μ thickness the rejection is lower and is related to ABS concentration: rejection increases with increasing concentration and reaches 60% for concentrations higher than 5 g ABS/l. (flux, 5 l./hr-m²; operating pressure, 50 atm). This is ascribed to the prevailing ultrafiltration as regards the reverse osmosis. ABS, at higher concentrations than the critical value, gives micelles whose dimensions might be compared to pores. The membrane behavior is influenced by previous treatments; when the membrane has been conditioned in NaCl solution, it is more selective and more permeable; the rejection reaches 90% with fluxes of 6.8 l./hr-m² for concentrations of 5 g ABS/l. (operating pressure, 50 atm). In order to relate the properties to the structure of membranes, we have examined them by electron microscope. The ion exchange which takes place between membrane and NaCl and between membrane and ABS has also been studied.

INTRODUCTION

Branched sodium alkylbenzenesulfonate (ABS) is a polluting agent found in waste water and is slowly degradable.[1] We have used polypropylene (PP) membranes grafted with poly(acrylic acid) (PAA), prepared in our laboratory, for purifying water containing ABS.

Only one reference[2] is concerned with the application of membranes for this purpose, and it is related to low ABS concentrations (100 ppm). Our paper deals with higher concentrations (between 500 and 10,000 ppm) whose range is useful for treatment of water flowing from industrial factories such as tensioactive manufacturers, producers of emulsion polymers, and so on.

EXPERIMENTAL

The preparation, structure, and physicochemical properties of PP membranes grafted with PAA were previously described by us.[3] Grafted

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PP has been prepared in homogeneous phase[4,5] by dissolving polypropylene in o-dichlorobenzene at 120°C and adding a peroxide agent and acrylic acid. From the reacted polymeric solution, membranes were prepared by extraction of a glass cylinder. After immersion into water, the membrane can be easily removed from the glass. Membrane thickness depends mainly on the solution viscosity and on the extraction rate of the glass cylinder.

The membranes used were substantially of two series: the first series was 23 μ thick; the second series, 5 μ thick. All membranes contained 33% grafted PAA and a small amount of PAA homopolymer (about 3%).

After preparation, the membranes were stored in distilled water. Some of the 5-μ-thick membranes were stored in a 3.5% NaCl solution.

The apparatus used for testing the membranes is the same as that utilized for reverse osmosis operation and consists of a cell (volume 1200 ml) continuously fed with an ABS solution and is supplied with an internal magnetic stirrer in order to decrease polarization phenomena.

The membranes (75 cm² area) were supported at the cell bottom by a synterized steel plate below which the permeate was recovered and readded to the ABS solution. The operating pressure was regulated with a needle valve. For operating pressures of 50 atm, the fluctuations were less than 0.5 atm.

ABS concentration was measured by a colorimetric method based on methylene blue,[6,7] using a Lumekron colorimeter spectrophotometer, at a wavelength of 650 millimicrons. ABS was branched pure sodium dodecylbenzenesulfonate of K & K Laboratories.

Ion exchange experiments were carried out for practical reasons on molded samples of PP grafted with PAA, according to a previously described method.[8] The samples under examination, swollen in water, were put into NaCl or ABS solutions ($1.45 \times 10^{-2}M$). The pH variation of the solution versus time, was followed during exchange at 23°C with a GK 235113 electrode and a pH meter Radiometer Model 26 with 0.01 pH-unit sensitivity.

The solutions were stirred before each measurement in order to help the diffusion processes. The surface tension measurements were carried out with a semiautomatic Tensiomat 51 Fischer apparatus. The experimental values were obtained at 20°C using a Pt-Ir ring having a 6.025-cm circumference, and are reported without the contribution of correction coefficients.

The membrane morphology was studied with a Siemens transmission electron microscope Model Elmiskop IA; cross sections and replicas of the membrane surface were examined.

RESULTS

Compaction and Structure

Flux is defined as volume of permeated liquid in unit time and unit of membrane area.

TABLE I
Flux and Rejection for Grafted Membranes[a]

	23 μ[b]	5 μ[b]	
Conditioning	In H_2O	In H_2O	In 3.5% NaCl solution
Flux, l./hr-m²	0.5	7	12.8
Rejection, %	100	33.3	36.7

[a] 50 atm, 1 g ABS/l., 25°C.   Per cent grafted PAA, 33%.
[b] Membrane thickness.

Rejection (%) is defined as

$$\%R = \frac{C_A - C_P}{C_A} \cdot 100$$

were C_A is the feed concentration and C_P is the permeate concentration.

Flux and rejection values reported in the text are values obtained under stationary conditions.   Flux and rejection both change with time until practically constant values are reached.

Flux decrease versus time is related to membrane compaction, which is a phenomenon due to the deformation of the composite system.   PP is a stiff matrix which contains domains of the amorphous polymer (PAA).

In Figure 1a, two phases (PP and PAA) can be seen; black areas correspond to the PAA domain.   This assertion is based on the osmium affinity of polyacid as well as on comparative investigations carried out on membranes having a different PAA percentage.

Both phases can also be seen in Figure 1b, which shows the membrane surface: the spots which can be seen correspond to the PAA domains. This assertion may be justified by a linear-type relationship between the number of spots and the PAA per cent, as well as by the equality of the black areas dimensions which can be seen in transmission micrographs, as well as of the spots seen on the surface.   These spots and black areas have an average diameter of about $5 \times 10^{-2} \mu$.

When the membrane comes into contact with water, PAA swells and causes internal forces; consequently, it is probable that microfracture takes place in the polypropylene matrix.   The possibility that these microfractures may be passing in a continuous way through the membrane (passing channels) is lower the higher the membrane thickness.

The high fluxes obtained using low-thickness membranes should be of bulk type; that is, the passage might take place through the passing channels; rejection has consequently low values.   In the case of high-thickness membranes, water can permeate through the PAA hydrophilic regions, preferentially by a solution and diffusion mechanism, instead of going directly through the passing channels; under these conditions, we can expect a higher rejection (see Table I).
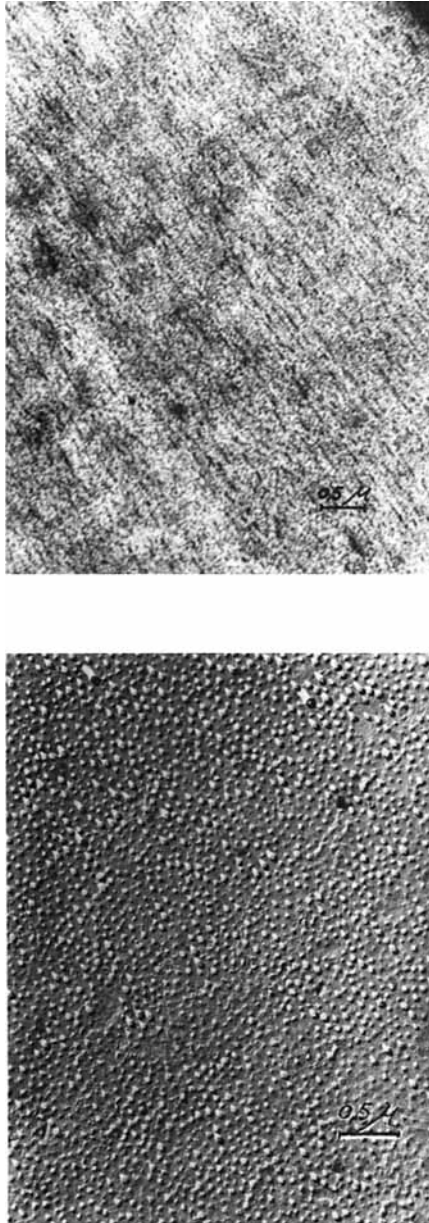
Fig. 1. Polypropylene membrane grafted with 57% poly(acrylic acid): (a) cross section; (b) replica of surface.

While the run continues, the water-swollen PAA and PP domains can undergo relaxation; the composite structure becomes more compact; passing channels and porosity gradually close, and therefore bulk-type passage decreases. Because of the compaction, flux decreases and goes preferentially through the PAA domains so that rejection increases.

Influence of ABS Concentration

Using the highest-thickness membranes (Table I), the ABS rejection is 100%, and flux is 0.5 l./hr-m². Our work particularly concerns membranes of lower thickness, with which we can obtain higher fluxes without sacrificing good rejection.

Since ABS in solution can have different aggregation states ranging from dissociated molecule to micelles according to concentration,[10] we first examined ABS concentration influence on the process.

Figure 2 (curve cd H$_2$O, concerning water-conditioned membranes) shows stationary rejection values versus ABS concentration. Figure 3 (curve cd H$_2$O) shows corresponding flux values versus ABS concentration. Flux has a fast initial decrease and a sucessive slow decrease when ABS concentration increases.

Rejection versus ABS concentration is characterized by nonmonotonic behavior. This fact could be related to the existence of a critical micelle concentration (CMC). It is in fact known[10] that the surface tension of a tensioactive solution decreases when concentration increases down to a critical concentration value (CMC) and then remains practically constant. CMC corresponds to the point where the formation of micelles begins.

From Figure 4, which shows surface tension under static conditions of ABS solutions, we can notice that the critical concentration for the formation of micelles is 1.1 g ABS/l. This CMC value corresponds to the beginning of the plateau of Figure 2 (curve cd H$_2$O). It is however, difficult to give a sure interpretation of this phenomenon because the conditions
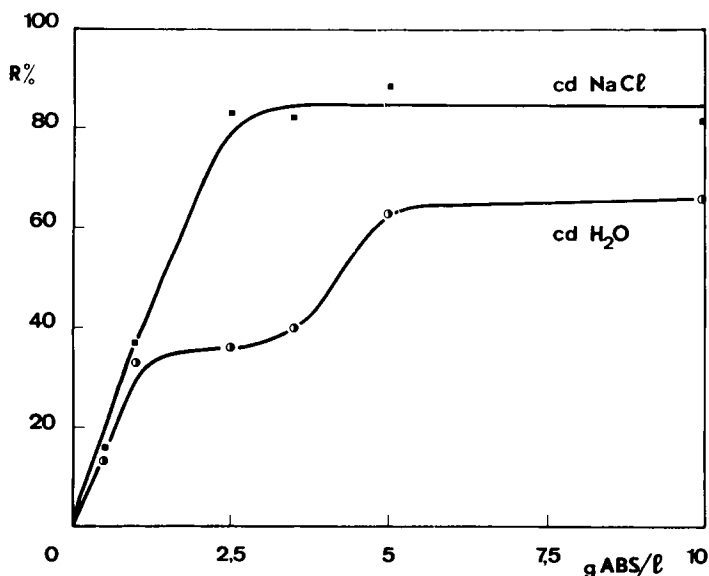

Fig. 2. Comparison of rejection vs. ABS concentration for differently conditioned membranes 5μ thick ($P = 50$ atm, 25°C).
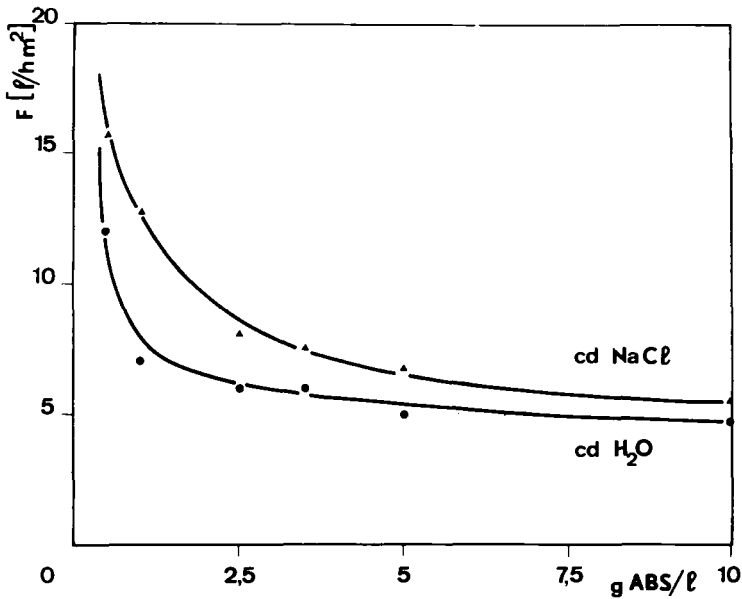
Fig. 3. Comparison of flux vs. ABS concentration for differently conditioned membrane 5 μ thick (50 atm, 25°C).
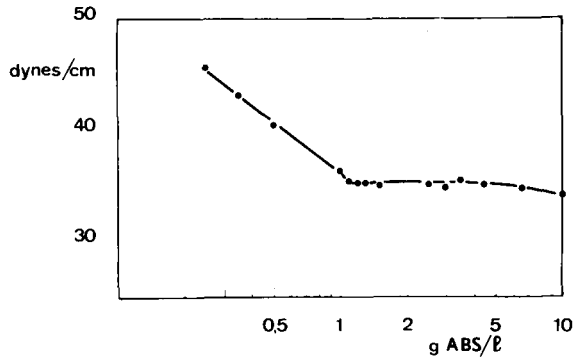

Fig. 4. Uncorrected surface tension at 20°C vs. ABS concentration.

in the tensiometer and inside the osmosis cell, where the solution is under pressure and flows, are not comparable.   It is known[11] that the formation of micelles inside water solutions of tensioactive agents is hindered by the movement of the liquid.

The transition from the first to the second plateau (Fig. 2) is difficult to be interpreted;   it could be related to the form and to the dimensions of the micelles which, as is known[10] change with the concentration;   or to other factors, such as the occupation of pores or especially of channels by an ever increasing number of micelles.   The attainment of a certain asymptotic value in the rejection could be explained on the base that micelles are in equilibrium with nonaggregated tensioactive molecules and

that the concentration of these latter does not vary very much when the concentration increases.[10]

For low-thickness membranes, an ultrafiltration mechanism should be responsible for rejection, at least in part.

Above CMC, rejection increase is due to the dimension of micelles larger than the channels. The average diameter of the membrane channels ranges within the initial equivalent diameter of the micelles.

According to Mankowich,[12] this value is 48 Å; it must be considered as only indicative, of course.

The Conditioning Influence of NaCl Solutions

Whenever the membrane is conditioned before use in a NaCl solution, its behavior is quite different. In Figure 2 (curve cd NaCl), we can notice that the rejection increases monotonically and is higher than in the case of water-conditioned membranes. We can also notice that in the NaCl-conditioned membranes (curve cd NaCl Fig. 3), the flux is always higher than in the case of water-conditioned membranes.

In order to give an explanation of this phenomenon, it might be useful to observe (Fig. 5) the approach to steady state conditions of rejection and flux for the two differently conditioned membranes. In the case of NaCl-conditioned membranes, stationary conditions are reached only after a few hours, much faster than in the other case. Besides, while the initial behavior of water-conditioned membranes is much different from the stationary one, in the other case this difference is much less. This is related probably to the fact that the polyacid chains in contact with NaCl extend themselves.[13] When the polyacid chains are extended, a better occlusion
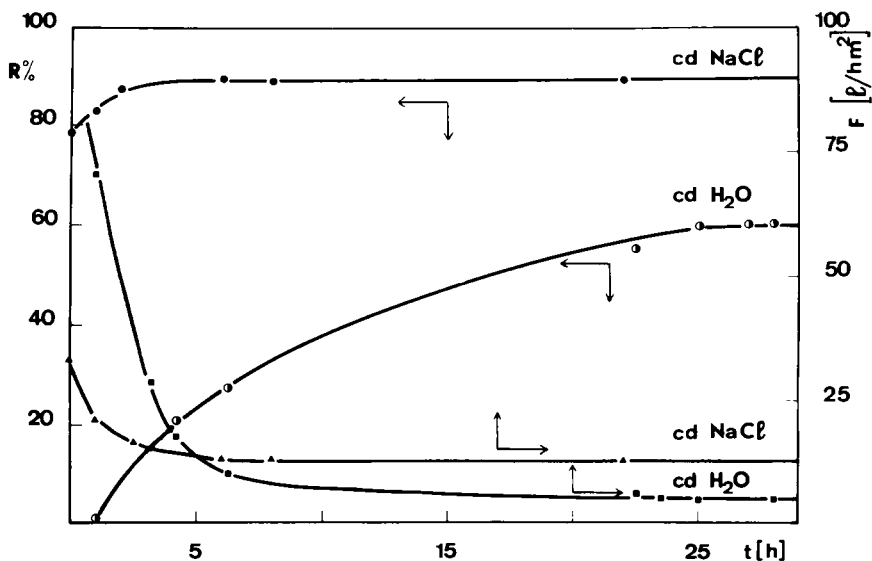

Fig. 5. Rejection and flux variation vs. time for differently conditioned membranes 5 μ thick (5 g ABS/l., 50 atm, 25°C).
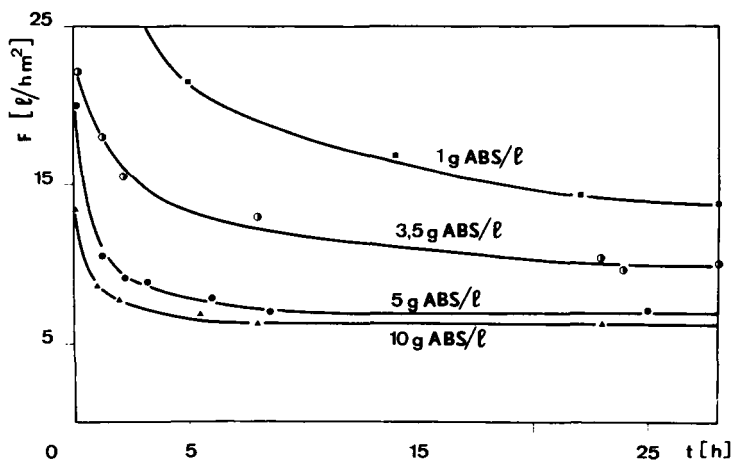
Fig. 6. Flux variation vs. time at different ABS concentrations for NaCl-conditioned membranes 5 μ thick (50 atm, 25°C).

of channels and a lower initial flux are possible.   That is also confirmed by our dilatometric measurements which point out that the polyacid increases in specific volume when it is put into contact with NaCl solution.   Improvement in rejection may partly be attributed to the transition from ultrafiltration to a solution diffusion mechanism due to channel occlusion. NaCl-conditioned membranes do not compact so much as water-conditioned ones: flux, as time goes on, can therefore be larger.

Another reason for the different behavior may be the different PAA homopolymer solubilities either in water or in NaCl solution.[14]   Actually, the membranes made from the reaction raw material contain a small amount of PAA homopolymer[5] (in our case about 3%).   When the membranes are stored in water, the PAA homopolymer can spread from inside to outside the membranes, leaving pores.   On the other hand, for membranes stored in NaCl solution, the PAA homopolymer is less soluble[14] and therefore it can remain inside the membrane.   We have noticed that ABS, too, reduces the solubility of PAA.

Times necessary for the attainment of the stationary conditions, also depend on the ABS concentration.   From Figure 6 we can, in fact, notice that the higher the ABS concentration, the shorter is the time to reach stationary conditions.   This behavior may be related to the fact that when concentration increases, we have a higher number of micelles and micelles of ever-increasing dimensions[10];   these may occlude the pores and channels in a shorter time and cause also lower fluxes.

Membrane Exchange Reaction

The PAA which is present in the membranes can only partially salify in the presence of Na$^+$:

$$R-COOH + Na^+ \rightleftharpoons RCOONa + H^+$$
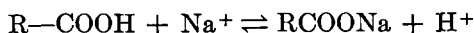
We have already studied[8,15] the exchange reaction with NaCl: it takes place until equilibrium conditions are reached.
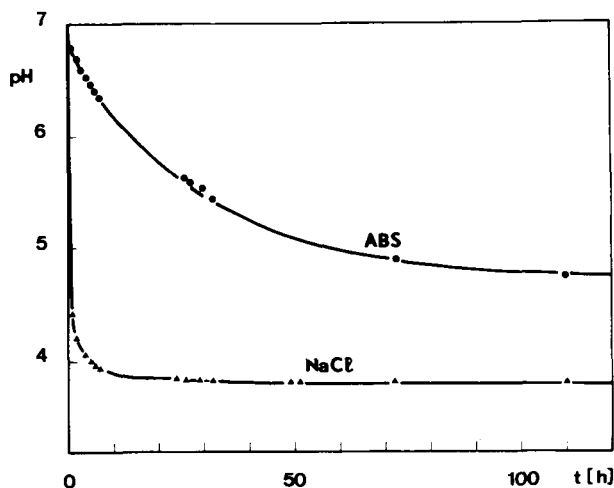
Fig. 7. pH variation vs. time of $1.45 \times 10^{-7}M$ solutions of NaCl and of ABS put into contact with molded 1.38-g samples of polypropylene containing 57% grafted PAA. Dimensions: thickness 2 mm, total surface 12.4 cm^2.

Ion exchange takes place, of course, also with ABS, as can be seen in Figure 7, where pH is plotted against time in the case of equimolecular NaCl and ABS solutions put into contact with an equal amount of PP grafted with PAA. From the comparison between the two curves, we can notice that with ABS ion exchange is much slower. In any case, polyacid salifies during the runs both when the membrane is water conditioned or when it is NaCl conditioned.

CONCLUSIONS

The differences previously registered between the water-conditioned membranes and the NaCl-conditioned ones are put into evidence in Figure 8. Here, we can notice that the NaCl-conditioned membranes are more efficient than the water-conditioned ones. The reason for this behavior
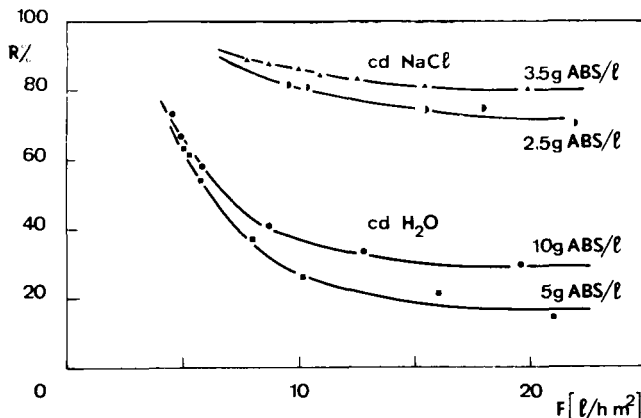

Fig. 8. Rejection vs. flux for differently conditioned membranes 5 μ thick (50 atm, 25°C).

could not yet completely be clarified; it is probably related to the NaCl influence on the polyacid structure, to the PAA homopolymer insolubility in the presence of NaCl and ABS, and to the NaCl and ABS influence on the mechanical properties of composite membranes.

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