

Effect of Poly(styrenesulfonic Acid) on the Electret Effect in Cellulose Acetate Membranes

INTRODUCTION

Foulant deposits frequently build up on cellulose acetate reverse osmosis membranes during desalination of saline water. These foulant deposits are due to colloidal contaminants. Wallace and Gable¹ have recently shown that cellulose acetate reverse osmosis membranes can store considerable electric charge. These heterocharged membrane electrets interact electrostatically with charged colloidal particles to produce self-cleaning or antifouling membranes.

The electric fields of heterocharged membrane electrets are thought to be due to dipole orientation and ionic impurity separation within the membrane. To what extent ionic polymer additions increase the electret effect in cellulose acetate has not been reported. If the charge separations that occur during electroformation at elevated temperatures remain stable at room temperature, then large electret potentials could be generated by these ionic membrane electrets. The increase in electret potential will increase the antifouling capabilities of these membranes.

Wallace² and Forgacs³ have reported on the electret behavior of electro dialysis membranes which consist of 25 wt-% sulfonated polystyrene in a matrix of polyethylene. The present paper reports on the effect of the addition of poly(styrenesulfonic acid) on the electret behavior of cellulose acetate membranes. Thermal depolarization⁴ was used to measure the stored heterocharge released from the membrane electrets.

EXPERIMENTAL

Materials

Poly(styrenesulfonic acid) (PSA) was prepared from 40-mesh linear polystyrene powder, average molecular weight of 35,000. Polystyrene was sulfonated with 5 to 10 times its weight of concentrated sulfuric acid and 1% its weight of silver sulfate as catalyst. The sulfonation was carried out at 100°C for 3 hr with continuous stirring. Complete sulfonation was indicated by total solubility of the sulfonated polystyrene in water.

The PSA was precipitated by the addition of limited amounts of water to the sulfonation mixtures. Excess sulfuric acid was then poured off the top of the mixture. The concentrate was further purified by repeated dialysis across cellophane membranes. The PSA solutions were then evaporated to dryness at 105°C. The dried sulfonated polystyrene was completely resolvable in water. The average molecular weight of the PSA was computed to be 63,000 assuming no degradation.

Cellulose acetate, average molecular weight 54,000 and acetyl number 2.5, was obtained from Eastman Kodak. Dimethylformamide (Baker Analyzed Reagent Grade) was used as a solvent.

Membrane Preparation

Casting solutions were prepared using cellulose acetate as the matrix and PSA as the polyelectrolyte, with dimethylformamide as the solvent. The solutions contained 95 wt-% dimethylformamide, 4 wt-% cellulose acetate, and 1 wt-% PSA.

Membranes were cast on glass plates and dried at 75°C for 96 hr, then stripped from the plates after soaking in distilled water for 10 min. The membranes were then redried in vacuo for 24 hr at 60°C and stored in a desiccator.

Heterocharge Measurement

Membranes were electroformed using methods developed by Wallace.² Samples 1.0 in. in diameter were coated with silver paint on both surfaces and placed between carbon

electrodes in a shielded vacuum measuring cell. The measuring cell had controlled heating and cooling rates. Inert atmospheres were introduced into the cell.

The samples were subjected to the following steps: (a) heating to an electroformation temperature of 60°C; (b) applying a polarizing voltage for 3.0 hr; (c) cooling to 25°C in the applied electric field; (d) short-circuiting the sample at 25°C for 24 hr, and finally (e) measuring the thermal depolarization current as the sample is linearly heated while shorted through an electrometer ammeter.

Depolarization currents were measured with a Cary Model 31 vibrating reed electrometer with a 10 in. ohm input resistor. Sample current and temperature were recorded simultaneously on a Honeywell X-Y recorder.

RESULTS AND DISCUSSION

Typical thermal depolarizations for unmodified cellulose acetate membranes and also for cellulose acetate membranes incorporated with 20% PSA are presented in Figure 1. Both membranes were polarized at the same temperature and with the same electric field strength of 11.4 kV/cm. The charge stored in the membranes was calculated using the relationship

$$Q = \frac{1}{b} \int_{T_{\text{initial}}}^{T_{\text{final}}} J(T) dT$$

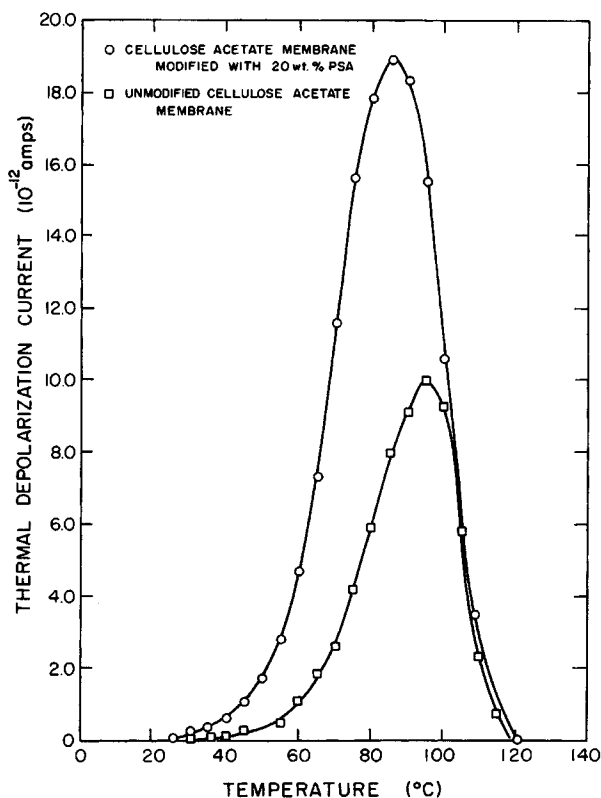


Fig. 1. Thermal depolarization peaks of unmodified cellulose acetate membranes and cellulose acetate membranes containing 20 wt-% poly(styrenesulfonic acid).

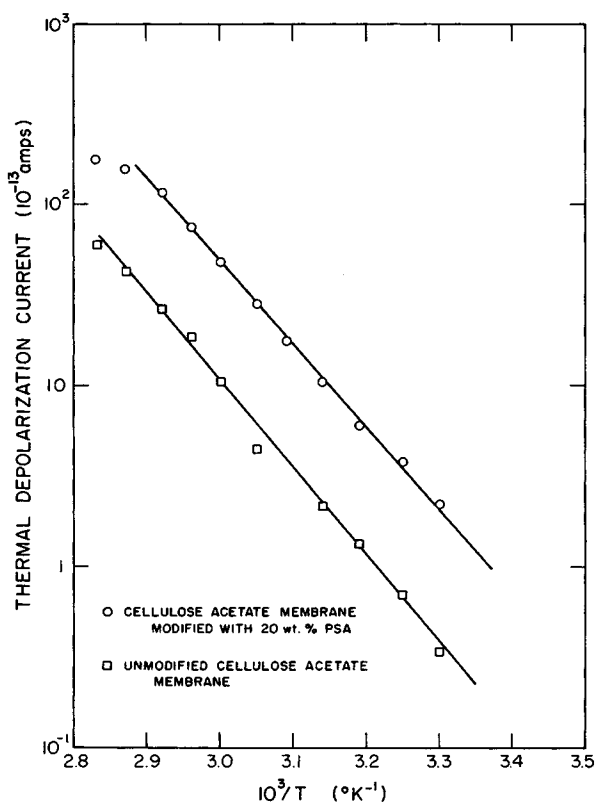


Fig. 2 Logarithmic plot of initial rise in thermal depolarization current for peaks of unmodified cellulose acetate membranes and cellulose acetate membranes modified with 20 wt-% poly(styrenesulfonic acid).

where Q is the charge in coulombs, $J(T)$ is the discharge current in amps, b is the linear heating rate of $0.034^{\circ}\text{C}/\text{sec}$, and T is the temperature in degrees centigrade.

The total charge stored in the unmodified cellulose acetate membrane was 8.7×10^{-10} coulombs, while that stored in the cellulose acetate membrane containing 20 wt-% PSA was found to be 2.1×10^{-9} coulombs. The cellulose acetate membrane with the incorporated PSA stores over twice the electric charge. Figure 1 clearly illustrates the large increase in electret effect produced by adding ionic polymer additives.

If during depolarization the internal electric field is constant, the initial rise method⁴ can be used to determine the activation energy for depolarization. The depolarization current is then given by

$$i = i_0 \exp(-E/kT).$$

The activation energies were calculated from the logarithmic plots shown in Figure 2. The activation energy for polarization decay in unmodified cellulose acetate was 0.413 eV, while for cellulose acetate incorporating 20 wt-% PSA the activation energy was 0.393 eV.

CONCLUSIONS

The incorporation of poly(styrenesulfonic acid) greatly increases the stored heterocharge in cellulose acetate membranes. Thermal depolarization data indicates that

the addition of 20 wt-% PSA to cellulose acetate membranes increases the stored charge by 2.4 times. This large increase in stored heterocharge can lead to an increase in the antifouling behavior of cellulose acetate reverse osmosis membrane electrets.

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