Simplex Membranes of Sulphoethylcellulose and Poly(diallydimethylammonium chloride) for the Pervaporation of Water–Alcohol Mixtures

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ABSTRACT: Polyelectrolyte complex membranes were prepared by simultaneous interfacial reaction of aqueous solutions of two oppositely charged polyions. The cellulose derivative sulphoethylcellulose (SEC) was used as the polyanionic component and poly(diallyldimethylammonium chloride) as the polycationic component. Characterization of molecular parameters of SEC were determined by size exclusion chromatography coupled with light scattering, viscosimetry, and rheology, and then correlated with membrane properties. Pervaporation investigations together with measurements of swelling behavior and network structure indicate that the membranes can be successfully used for dehydration of alcoholic solvents since they show excellent separation properties. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 3169–3177, 2000

Key words: polyelectrolyte complex; sulphoethylcellulose; membrane; dehydration of organics; pervaporation

INTRODUCTION

Membrane technology is gaining increasing importance as an innovative, reliable, and cost-effective alternative to conventional processes. One area of membrane technology is the dehydration of alcoholic solutions. This is based on the fact that alcohols form azeotropes with water that cannot be separated by conventional methods. A large number of materials have been used in order to improve the dehydration effect, as e.g., cellulose, polyvinyl alcohol, polyamides and polyelectrolyte complexes. The use of hydrophilic polyelectrolytes as a component of the membranes yields better separation parameters because of the presence of highly hydrophilic hydroxyl groups. Polyelectrolyte complexes (simplexes) provide an elegant method of rendering these water-soluble systems insoluble, and are now useful in solving dehydration problems. But for all known membrane systems the selectivity is quite low if the permeation rate reaches an acceptable value and the permeation rate of high selective membranes is low. Therefore the development of novel polymer membranes for separating alcohol water mixtures is still important.[1-4]

In this investigation the cellulose derivative sulphoethylcellulose (SEC, Fig. 1) was to be used as a component of simplex membranes. SEC is easily accessible by polymer-analogous substitution reactions of cellulose, adjusting the molecular parameters as molar mass and degree of substitution (DS) as desired. It is an anionic cellulose derivative that is water soluble even at low DS between 0.2 and 0.5.
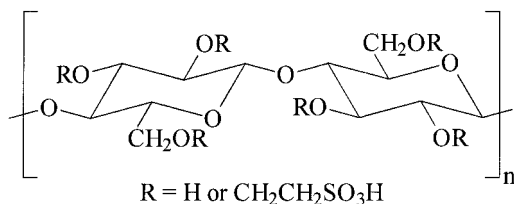
Figure 1   Repeating unit of sulphoethylcellulose.

The aim of the present investigation was to introduce SEC as a suitable new raw material for simplex membranes in dehydration problems. Pervaporation membranes based on SEC and poly(diallydimethylammonium chloride) (PDADMAC) were prepared. Different SEC samples with variable molar mass M and degree of substitution DS were used because the molecular parameters of the educts influence their properties as well as those of the membranes. However, only one PDADMAC sample was used to reduce the properties of the respective membranes to the effect of SEC. So the SEC is characterized in terms of molar mass, degree of substitution, and flow properties. Further, the properties of the membranes produced were studied with respect to the separation process and the separation properties themselves.

EXPERIMENTAL

Materials

Sulphoethylcellulose was produced industrially by sulphoethylation of cellulose with the sodium salt of vinylsulphonic acid. PDADMAC was obtained commercially and used without any further purification. Solutions with a content of 2–6% polyanionic polyelectrolyte or 4% polycationic polyelectrolyte respectively were obtained by dissolving the samples in water at room temperature.

Characterization of the Components

The molar mass of sulphoethylcellulose was determined by size exclusion chromatography coupled with light scattering. The eluent was aqueous $0.1M$ $NaNO_3$ solution. The solvents and solutions were filtered through 0.02 μm filters. TSK columns from Toso Haas were used for separation. The light scattering measurements were performed with a Wyatt light scattering photo-

meter at 633 nm and 25°C. As refractive index increment (dn/dc) 0.136 mL/g was used.[5–7]

The charge density was determined by polyelectrolyte titration and a standard PDADMAC solution as titrant. To identify the end of titration, a particle charge detector from Mütek was used.[8]

Rheological measurements of SEC solutions with differing concentrations were carried out on a shear-stress-controlled Bohlin CS50 rheometer at room temperature in order to determine the viscous and elastic properties of SEC.[9,10]

Further details about the methods above can be found in Refs. 11–15.

Synthesis of Membranes

To prepare simplex membranes, a simultaneous interfacial reaction of aqueous solutions of the two oppositely charged polyions was used. The solution of sulphoethylcellulose was spread as a 0.5 mm thick film on a glass plate and carefully put into a solution of PDADMAC. A spontaneous surface reaction between the two components led to formation of the polyelectrolyte complex membrane. After a reaction time of 1 h, the membrane on the glass plate was washed with distilled water to remove the adjacent unreacted polycationic compound. The membrane was loosened from the support and dried. The thickness of the membranes obtained was in the range of 10–30 μm and dependent upon the SEC concentration in the casting solution.

Characterization of the Membranes

The degree of membrane equilibrium swelling was determined according to

$$SD(\%) = 100\% \cdot (m_s - m_d)/m_d$$

where m_s and m_d are the weights of membrane strips in the swollen and dried states respectively. The swelling degree was measured at room temperature in pure water, ethanol, and aqueous solutions of different salts at different concentrations.

Rheological oscillation measurements of the swollen membranes were carried out on the Bohlin CS 50 stress-controlled rheometer with a plate-plate geometry. The plate-plate distance was determined by the membranes thickness in the swollen state.[16,17]

Table I Molecular Parameters of the Samples Used

Sample	DS	$[\eta]$ (mL/g)	M_w (g/mol)[a]	M_w (g/mol)[b]	M_w (g/mol)[c]
SEC 1	0.36	482	210,000	170,000	550,000
SEC 2	0.28	524	230,000	160,000	1,200,000
SEC 2 methylated[d]	0.28	533	230,000	220,000	220,000
SEC 3	0.39	374	160,000	190,000	370,000
SEC 4	0.35	432	190,000	170,000	710,000
PDADMAC 1	—	80	60,000	—	—

[a] Calculated from $[\eta]$: $[\eta] = 4.28 \times 10^{-3} \times M_w^{0.95}$ (SEC). $[\eta] = 7.06 \times 10^{-3} \times M_w^{0.85}$ (PDADMAC).
[b] Determined with size exclusion chromatography, dissolved directly in the solvent.
[c] Determined with size exclusion chromatography, dissolved in water and salt added.
[d] DS (methyl) = 0.85.

Pervaporation experiments were carried out with a laboratory scale apparatus using a P28 stainless steel measuring cell supplied by Celfa AG, Switzerland. The effective membrane area is 17 cm². Water–isopropanol mixtures at 50°C were used for membrane testing. The permeate flux was determined gravimetrically and the compositions of feed and permeate by density measurements. The separation efficiency is described by mainly two values[18]:

- Separation capacity: described by the permeation rate J

$$J = \frac{\text{mass}}{\text{time} \cdot \text{area}}$$

- Separation selectivity: described with separation factor α

$$\alpha = \frac{c(\text{H}_2\text{O})_{\text{feed}}/c(\text{alcohol})_{\text{feed}}}{c(\text{H}_2\text{O})_{\text{permeat}}/c(\text{alcohol})_{\text{permeat}}}$$

RESULTS AND DISCUSSION

Characterization of SEC

The properties of the membranes are dependent upon the molecular parameters of the base materials. Therefore the samples are characterized to determine them. Table I summarizes several molecular parameters of the samples used.

Molar Mass

The molar mass was determined by means of size exclusion chromatography in aqueous 0.1M

NaNO₃. The results of average molar mass differ according to the type of sample preparation and are not comparable with those calculated from intrinsic viscosities (Fig. 2). If the samples are dissolved directly in the eluting solvent, the molar masses then determined are too low and only about the half of the injected mass is detected. It can be assumed that large aggregates exist and that these are separated during the ultracentrifugation before the measurements. If the samples are first dissolved in water before the NaNO₃ is added, nearly all the injected mass is detected but the molar masses determined for the samples are too large. In this case there are supposed to be fewer large aggregates but many small aggregates with a compact structure. A methylated sample of SEC 2, which should not form any aggregates at all because of the suppression of hydrogen bonds, shows no dependence upon sample preparation.

A comparison of the elutions diagrams of differently prepared solutions of Sample 2 and the methylated sample (Fig. 3) clearly illustrates the different aggregation behavior. The methylation conditions were very mild so that the sample would not degrade during the reaction. The molar mass and the molar mass distribution should be similar to those of sample 2, but without the presence of aggregates. In actual fact, the methylated sample exhibits no aggregates, and the elution pattern is the same as for that of a molecularly disperse sample. The directly dissolved sample has some aggregates that elute at the beginning with size exclusion, which can be seen by the molar mass plateau at the shoulder of the concentration signal. The rest of the sample elutes in exactly the same way as the methylated pattern
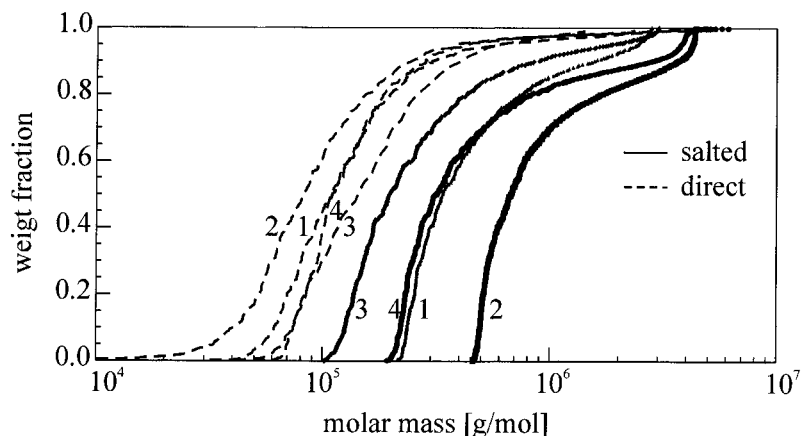
Figure 2 Molar mass distributions as a function of sample preparation—dissolved directly in the eluent solvent $0.1M$ NaNO$_3$ solution—first dissolved in pure water with salt added later to give the same NaNO$_3$ concentration as in the eluent.

with no more disturbing aggregates. The salted sample also displays size exclusion at the beginning of elution, but there are more aggregates than in the directly dissolved sample, which can be seen in the larger concentration signal. The molar masses are larger than those of the other samples over the whole elution range. This indicates the presence of small compact aggregates which interfere with the precise determination of molar mass for the single chains.

Rheology

Rheology describes the flow properties of polymer solutions.[12] These rheological properties are im-

portant for membrane synthesis because they affect the spreading behavior of solutions. If the viscosity is too low, too high, or the solution too elastic, a suitable surface cannot be prepared when spreading the solution. Shear stress and oscillation measurements were performed. The results for Samples 2–4 are shown in Figure 4.

As the concentration of SEC increases, the viscosity increases too. The Newtonian level at low shear stress is only evident in Sample 3 and at low concentrations of Sample 4. All the samples are pseudoplastic and the viscosity decreases with increasing shear stress. The viscosity yield of the samples decreases in the order $2 > 1 > 4$
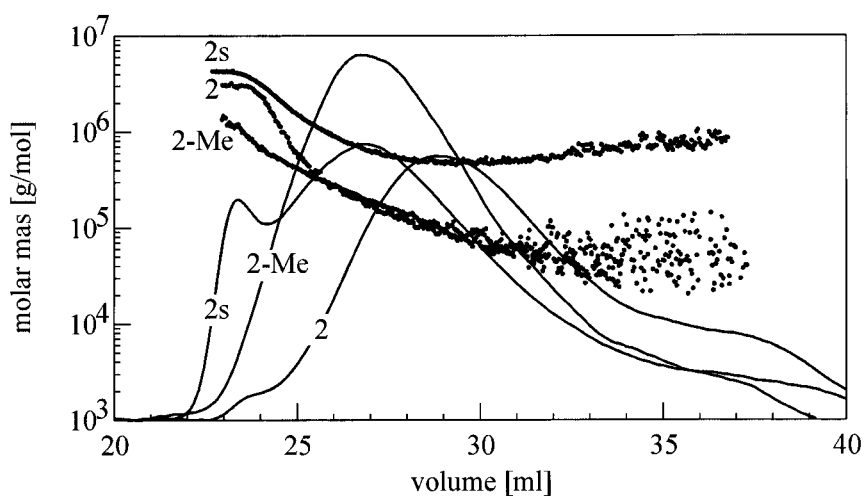

Figure 3 Comparison between the elution behavior of a directly dissolved sample (2), a sample dissolved in water with subsequent salt addition (2 s) and a methylated sample of SEC 2 (2-Me).
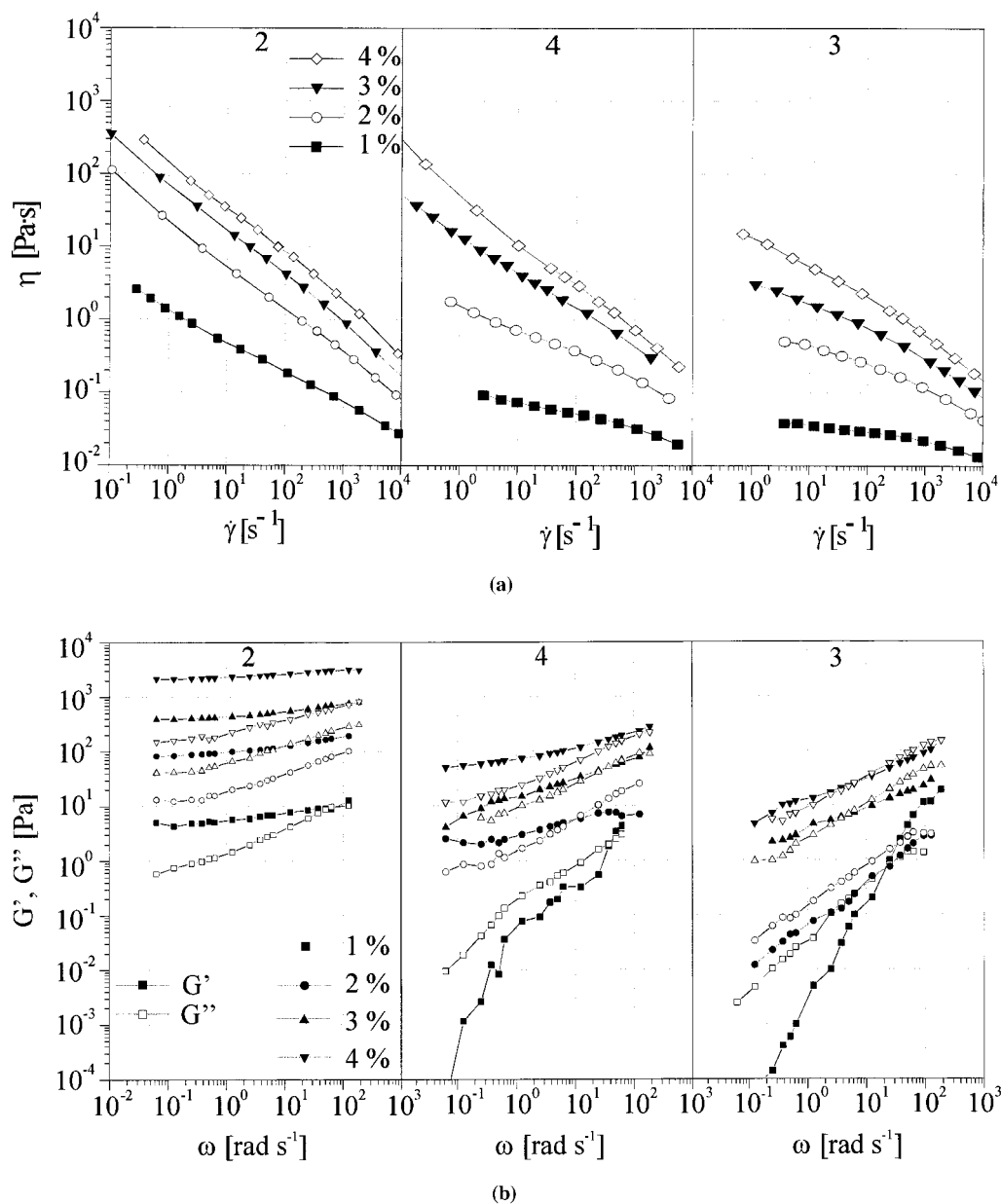
Figure 4 (a) Comparison of the shear measurements of Samples 2–4. (b) Comparison of the oscillation measurements of Samples 2–4.

> 3. With increasing concentration and molar mass, the solutions take on more and more the character of network solutions. The gel-like part of the solutions interferes with the synthesis of membranes because it is more difficult to spread a film on the glass plates. In order to have a suitable viscosity range for synthesizing membranes, the solutions of Sample 2 have to be less concentrated (about 2%) and solutions of Sample 3 more concentrated (about 4%).

Characterization of Membranes

Degree of Swelling

The swelling behavior can be correlated with the pervaporation properties because the ability of the medium to dissolve in the membrane is very important for the separation process. The swelling ratio and the differences between the membranes decreased with increasing ethanol concentration in the medium. In 100% ethanol, the
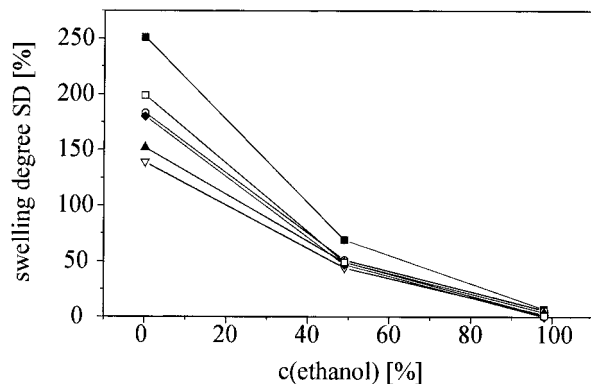
Figure 5 Dependence of the degree of swelling upon the ethanol concentration for various membranes of Sample 4.

membranes are not swollen at all (Fig. 5). Ethanol is dissolved less than water in the membrane so that ethanol should not permeate the membrane as well as water.

The dependence of swelling behavior in pure water on SEC concentration in the casting solution is shown in Figure 6. The swelling ratio first decreases and then increases again with increasing SEC concentration. The largest degree of swelling is exhibited by the membranes of Sample 2, which have the longest chain length. The greater the chain length, the greater the meshes of the membrane network are, and the more the membrane may swell. In the presence of salts, the swelling behavior changes as a function of charge and concentration of the salt used (Fig. 7). The salt ions diffuse and intercalate into the membrane and expand the morphological structure so
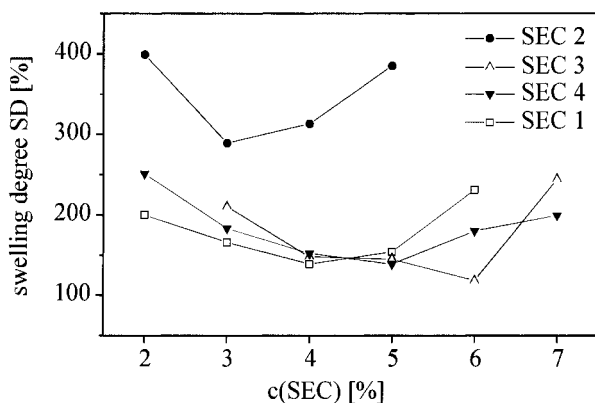

Figure 6 Dependence of the degree of swelling in water upon the SEC concentration in the casting solution.
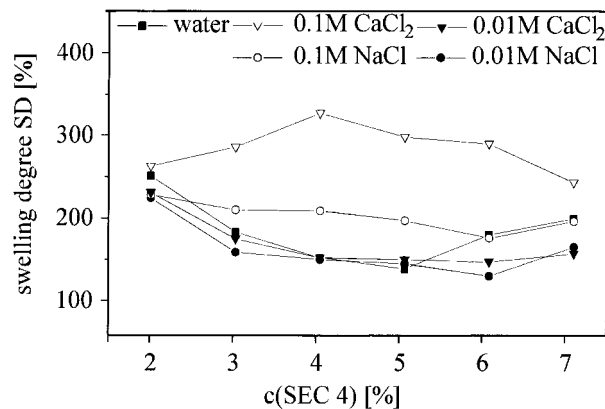

Figure 7 Dependence of the degree of swelling upon the SEC concentration of Sample 4 in different solvents.

that the *SD* increases. This effect is stronger with increasing charge and salt concentration.

Rheology

The membranes are a network system and can be characterized by means of rheological oscillation measurements. In the case of networks, as shown in Figure 8, the loss modulus G'' is about one decade lower than the storage modulus G' and the complex viscosity $|\eta^*|$ has the slope -1. A plateau modulus G'_P from which the molar mass between two crosslinks M_e can be calculated exists.[17]
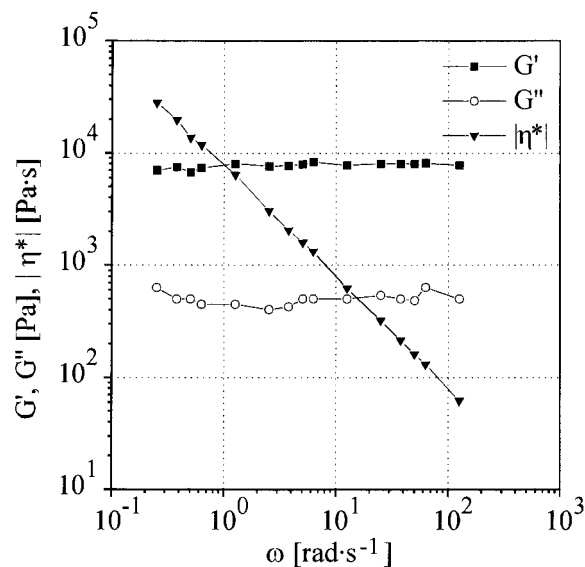

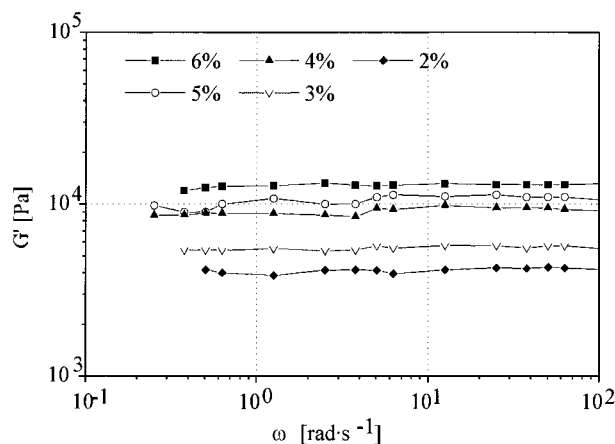**Figure 8** Oscillation measurement of a swollen membrane to determine the plateau modulus $G'_P = G'$.

Figure 9 Dependence of the plateau modulus G'_P upon SEC concentration in the casting solution.

Figure 10 Scanning electron microscopy on a cross-section of a simplex membrane.

$$M_e = \frac{\rho \cdot R \cdot T}{G'_P}$$

Figure 9 shows the plateau modulus dependence of the SEC concentration in the membrane. The plateau modulus increases with increasing concentration and the molar mass between two crosslinks decreases. The membranes become more compact, which should influence the separation properties. Table II shows the dependence of mesh size and network density upon some molecular parameters.

Morphology

The structure of the membranes can be examined by scanning electron microscopy. A cross-sectional view of a freeze-dried simplex membrane shows that the membranes are dense, homogeneous and symmetric (Fig. 10). There is also no difference between the top and the bottom of the membrane surface.

Table II Dependence of Network Properties Upon Molecular Parameters of SEC[a]

Increasing	Mesh Size $\equiv M_e$	Network Density
c(SEC)	↓	↑
M	↑	↓
DS	↓	↑

[a] ↑ = increasing, ↓ = decreasing.

Separation Efficiency

The properties of the membranes based on SEC and PDADMAC are in principle comparable to those based on other cellulose derivatives and PDADMAC.[18] The water content in the permeate reaches 99% in most cases. It is supposed that with increasing temperature the flux increases and the selectivity decreases. The performance data are nearly independent of time. The chemical stability of the membranes to organic solvents was found to be sufficient but they are disintegrated by low-molar-mass electrolytes due to the suppression of coulombic interactions. Table III summarises the results obtained from pervaporation experiments. In Figure 11 the permeation rate and separation factors of some membranes are clarified. They have excellent separation performances with high separation factors and high permeate fluxes. With increasing water concentration in the feed mixture, the separation factor decreases and the permeation rate increases. This is caused by the correlation between permeation and swelling. The more a membrane is swollen, the better a solution can permeate, because of increasing meshes. But this also implies that the separation efficiency decreases, because the alcohol molecules can also permeate better.

The membranes of Sample 4 show different separation properties as a function of the SEC concentration in the casting solution: the permeation rate J decreases and the separation factor α increases. With increasing concentration, the membrane structure becomes more compact, which was already indicated by the rheological

Table III   Performance of Pervaporation Properties of Different Simplex Membranes

Components	c(SEC) (%)	$c(H_2O)_{feed}$ (%)	$c(H_2O)_{permeate}$ (%)	α	J (kg/h $\cdot$ m^2)
SEC 1[a]	4	18.25	99.25	593	1.67
SEC 2[a]	3	18.15	93.00	60	1.71
SEC 4[a]	3	17.28	99.30	446	2.10
SEC 4[a]	4	18.15	99.00	679	2.02

[a] With PDADMAC as polycation.

measurements. The larger the molecules are, the more time they need to permeate, which improves the separation efficiency. But the different SEC concentration also influences the thickness of the membranes and flux J is influenced by this thickness: the more concentrated the casting SEC solution is, the thicker the relating membrane will be, and the thicker the membrane, the lower J will be. To eliminate this problem, thinner membranes with the same high SEC concentration in the casting solution can be produced by spreading a thinner film. This membrane should have a similar α but higher J.

The membranes of Sample 2 do not exhibit particularly good separation parameters: the flux J and the separation factor α are lower than those of the other membranes. Because of the long chains and the low charge density of the SEC, the mesh size is quite large so that the solvent mixture can permeate without separation. In this case, the solvent should permeate the material very well. However, the flux J is lower than the permeation rate of the other membranes, a phenomenon not well understood at the moment. Further investigations are therefore necessary.
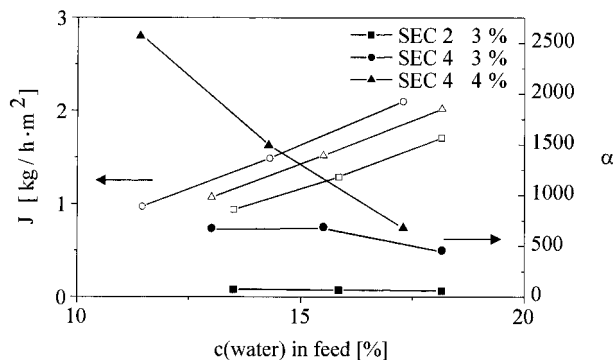

Figure 11   Separation parameters of different simplex membranes.

CONCLUSIONS

1. Sulphoethylcellulose is a suitable raw material for synthesising simplex membranes.
2. Characterization of SEC by customary methods for characterizing polymers give informations about its solution structure. It shows that the tendency to aggregate due hydrogen bonds decreases as the DS increases.
3. These membranes are dense, homogeneous, and symmetrical. They swell in water but not in alcoholic solutions. Salt ions intercalate into the membrane and destroy them due to suppression of coulombic interactions.
4. With increasing SEC concentration in the casting solution the membranes become more compact. This influences the plateau modulus in oscillation measurements and the separation parameters.
5. The membranes show good separation factors at high permeation rates and are so suitable for the dehydration of alcoholic solutions.

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