Application of Jojoba Wax Bound to Polyethylene Membranes and Hollow Fibers in Ion-Exchange and Pervaporation Processes

M. SHEVACHMAN,[1] S. BELFER,[2] S. BINMAN,[1],* A. SHANI[1]

[1] Department of Chemistry, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel

[2] The Institutes for Applied Research, Ben-Gurion University of the Negev, Beer-Sheva 84105, Israel

ABSTRACT: Chlorosulfonated polyethylene membranes and hollow fibers were reacted with allylic amino jojoba to bind the wax chemically to the polymer. The modified membranes and hollow fibers were then tested in the ion-exchange and pervaporation processes, respectively. The jojoba-bound polyethylene membranes were selective in preventing transfer of divalent ions such as Ca^{2+} and Mg^{2+}, while monovalent ion such as K^+ and Na^+ could penetrate the membranes. The flux of the monovalent ions depended on the amount of jojoba bound to the polymer, which acted as a barrier to the ions (the monovalent ions could be eluted by acid washing). The concentration of ions (in the range of 0.05–1.0 N) in the feed solution had little effect on the flux. Preliminary results of pervaporation of a dioxane/water mixture through hollow fibers made of jojoba-bound chlorosulfonated polyethylene show separation of the dioxane from the water with a separation factor of 6. This technique can be applied to remove residual organic solvents in the purification of industrial waste water. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 763–768, 2001

Key words: jojoba wax chemically bound to polyethylene; membranes; hollow fibers; selective ion exchange; pervaporation

INTRODUCTION

Ion-exchange, dialysis, and pervaporation applications require materials based on solid substrates that are readily available, cheap, easy to work with, and selective. Polyethylene, which is commercially available in sheet, film, and hollow fiber forms, answers the first three demands, but its hydrophobicity and lack of selectivity preclude its application in separation processes. The introduction of more polar or Lewis base or acid frag-

ments (such as carbonyl, double bond, ether, amine, or complexing entities containing P or S atoms) into the polymer chain could change the properties of the material, hence making it suitable for the required applications. We have successfully tested such an approach on polystyrene: chemical bonding of jojoba wax (Scheme 1) to polystyrene beads produced a solid extractant that was selective for a number of metal ions.[1–6]

In this article, we apply the same approach to polyethylene in film and hollow fiber form. To change the hydrophobicity of the material, chlorosulfonation with SO_2 and Cl_2 was used to introduce SO_2Cl groups into the polymeric chain (PE–SO_2Cl).[7,8] These groups can be hydrolyzed to form strong acids such as —SO_3H, which can be utilized in ion-exchange processes.

(Z,Z)-$CH_3(CH_2)_7CH=CH(CH_2)_mCOO(CH_2)_nCH=CH(CH_2)_7CH_3$
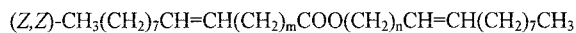
Jojoba wax (I)

m = 7, 9, 11, 13   n = 8, 10, 12, 14

average composition (%)   11, 71, 14, 1   1, 44, 45, 9
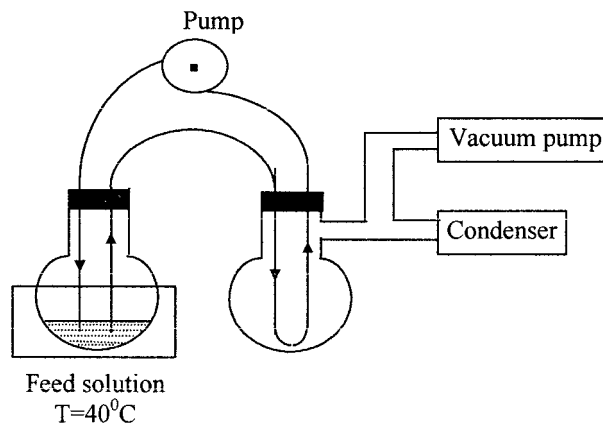
Scheme 1

By analogy with our previous work, we predicted binding jojoba wax (which is hydrophobic by itself) to PE–SO$_2$Cl, followed by hydrolysis, would produce a modified membrane with unique properties for ion exchange or dialysis processes. By the same token, the modified material in hollow fiber form would be suitable for application in pervaporation processes for separation between polar and nonpolar molecules in pervaporation process. The chemical binding of jojoba liquid wax to chlorosulfonated polyethylene gave a stable polymer, as is described elsewhere.[9] The material was prepared by reacting allylic amino jojoba (I, II) with PE–SO$_2$Cl via sulfonamide bonds, as illustrated in Scheme 2.

From analytical results, it was estimated that some amino jojoba molecules reacted with one SO$_2$Cl group, while others reacted with two SO$_2$Cl groups, either on the same chain or crosslinked to another chain (Scheme 2). The efficacy of the chemical binding depended primarily on the solvent [dimethyl formamide (DMF) being a better solvent than chloroform or dioxane], but also to some extent on the concentration of the amino derivative in the reaction mixture and the amount of SO$_2$Cl groups on the polymer.[9]

For this study, two different jojoba-bound PE–SO$_2$Cl materials were prepared as described above: J2NP11, containing 41% (w/w) of jojoba (prepared in DMF) and J2NP12, containing 16% (w/w) jojoba (prepared in dioxane). Membranes of both types were tested in the selective separation of mono- from divalent metal ions and J2NP11 was used as the hollow fiber to separate an or-
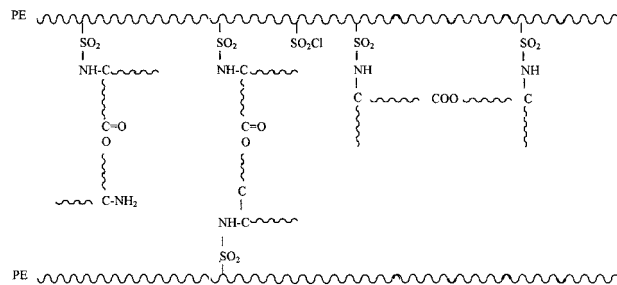
Scheme 3

ganic solvent (dioxane) from water in a pervaporation process.

EXPERIMENTAL

Materials

Crude jojoba wax was used in all the experiments without purification [iodine number (Wijs) 84; acid number 2.7; saponification number 93]. Low-density polyethylene (density 0.922g/cm^3; thickness 50 μm; melting index 0.3) was purified before use by Soxhlet extraction with hexane. Modified membranes J2NP11 and J2NP12 were prepared as described elsewhere.[9] Dioxane (Frutarom) was distilled and dried over NaOH; dimethyl formamide (DMF, 99.8%, Aldrich) was dried over A4 molecular sieves. All other solvents were CP grade (Frutarom), and were used without further purification.

Basic Hydrolysis of Chlorosulfonated Polyethylene and the Modified Membranes

Hydrolyses were performed as described previously.[10]

Pervaporation

The design of the system is presented in Scheme 3 (adapted from ref. 11).

RESULTS AND DISCUSSION

Properties of the Modified Polymer

Some physicochemical properties of the PE–SO$_2$Cl-based materials, J2NP11 and J2NP12, are

Scheme 2

Table I Properties of Modified Polyethylene

Membrane	Electrical Resistance (Ω^*cm^2)	Permselectivity (mV)	IEC^b Q_{H^+} (mEq/g)
PE-SO$_2$Cl	53942.9	0.2	—
J2NP11	38124.9	0.4	—
J2NP12	49719.1	0.3	—
J2NP11h^a	2535.5	1.8	0.01
J2NP12h^a	205.5	8.7	0.32
PE-SO$_3$H	22.7	16.0	2.01

^{a} Products of J2NP11 and J2NP12 after hydrolysis.
^{b} IEC—ion exchange capacity of membrane.

summarized in Table I. Base hydrolysis of the three products (to give PE–SO$_3$H, J2NP11h, and J2NP12h, respectively) dramatically changed their characteristics: enhancement of hydrophilicity was attributed to the SO$_3$H groups formed from unreacted SO$_2$Cl entities. Free amino groups along the jojoba chains also contributed to increased hydrophilicity. Careful inspection of the results presented in Table I shows that the properties of J2NP12, which contains less jojoba and, therefore, more unreacted SO$_2$Cl, are closer to those of PE–SO$_2$Cl than to those of J2NP11, and hence, after hydrolysis, J2NP12h is more hydrophilic (and much closer in properties to PE–SO$_3$H) than J2NP11h.

Ion Exchange Across the Modified Membranes

Base hydrolysis of PE–SO$_2$Cl to yield sulfonic groups (PE–SO$_3$H) resulted in nonselective ion transport across a membrane of this material, allowing both mono- and divalent ions to pass freely. On the other hand, the modified membranes after base hydrolysis contained both a small number of ionogenic SO$_3$H groups and hydrophobic jojoba chains bearing some free amino groups. This combination conferred of both hydrophilic and hydrophobic properties on the modified products, which enabled them to differentiate between of mono- and divalent ions, which exhibit differences in their hydration envelopes as well as in their charges. Thus, J2NP12h, blocked the passage of Ca^{2+} (Fig. 1) but allowed free passage of K$^+$ ions (Fig. 2). Similar results were obtained with Mg^{2+} and Na$^+$ (Fig. 3). All experiments were conducted for 24 h, but no significant increases in ion transport were detected after the first 6 h of each run; the results presented are confined to this period of 6 h.
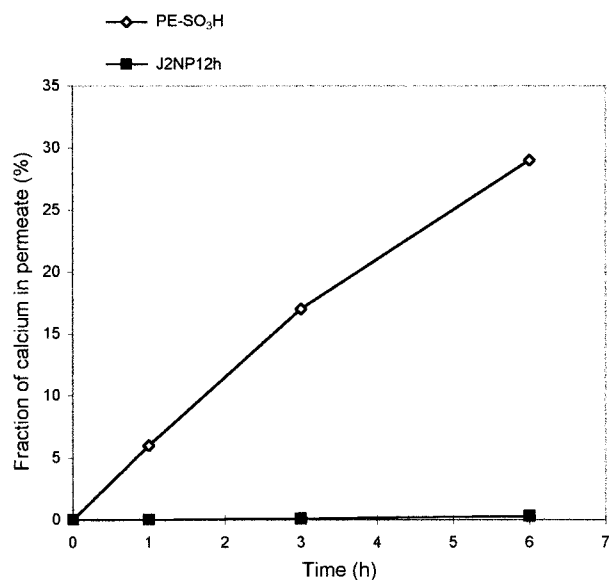

Figure 1 Passage of Ca^{2+} across the base-hydrolyzed membranes PE–SO$_3$H and J2NP12h.

Cation exchange is controlled by electrostatic forces, and the charges and ionic radii of the exchanged ions. For cations in dilute solution, the lyotropic (or Hofmeister) series for ion-exchange affinity takes the following order:[12]

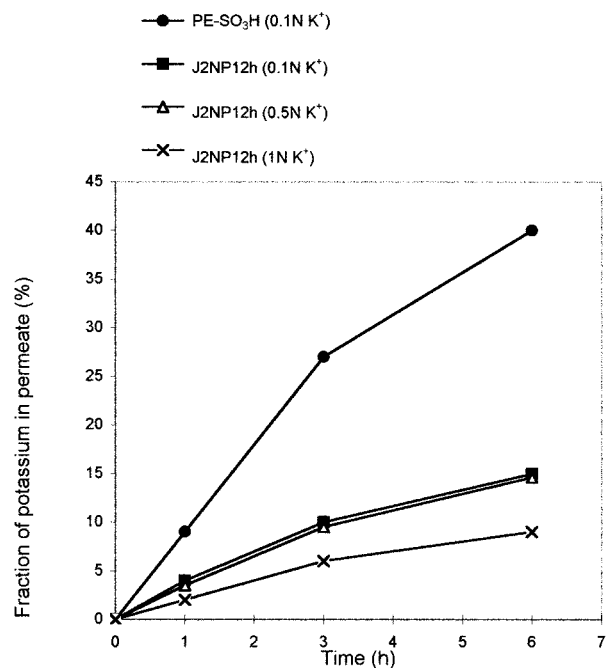Li < Na < K < Rb < Cs, Mg < Ca < Sr < Ba < Al < Sc < Y < Eu < Sm < Nd < Pr < Ce < La.

Figure 2 Passage of K$^+$ across the base-hydrolyzed membranes PE–SO$_3$H and J2NP12h.
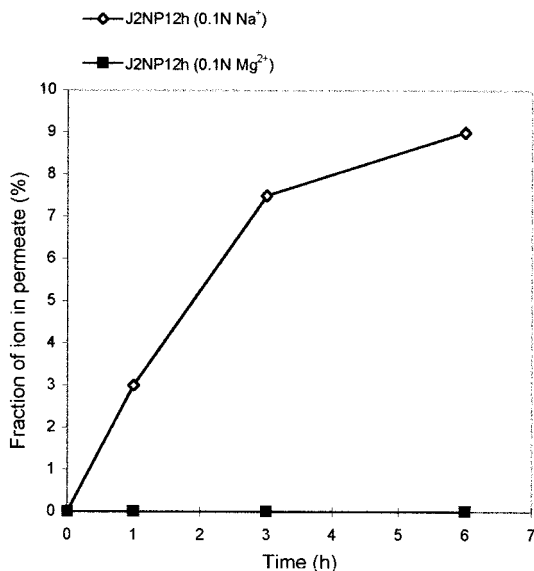
Figure 3 Passage of Na^+ and Mg^{2+} across the base-hydrolyzed membrane J2NP12h.

In aqueous solution, the ions are hydrated, and the degree of hydration is proportional to charge of the ion, i.e., the degree of hydration is highest for ions with largest charges. Because the attraction of the metal ions to the active anionic groups (SO_3^-) depends on the charge of the cation, Ca^{2+}
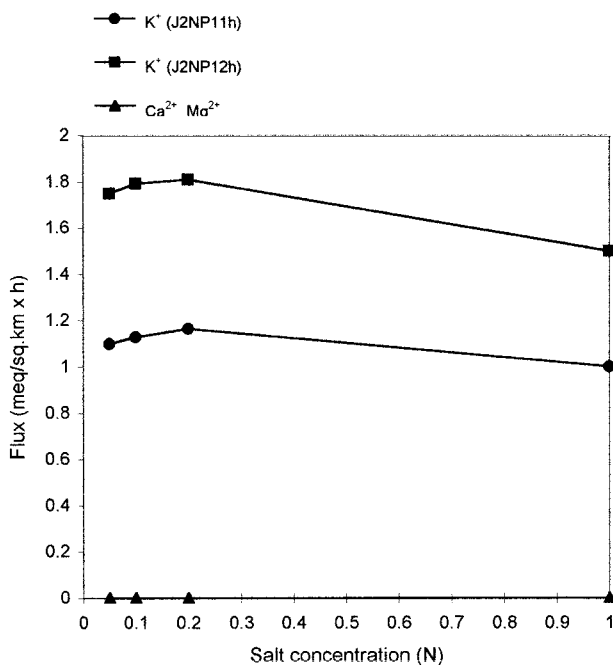

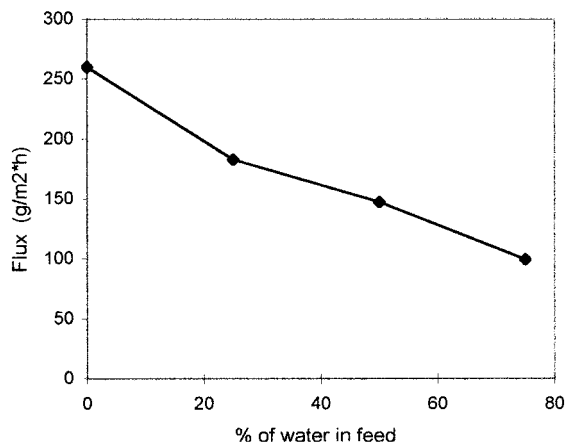**Figure 4** Cation-exchange flux as a function of solution concentration.

Figure 5 Change of dioxane flux as a function of water concentration.

and Mg^{2+} were attracted more strongly to the membrane than the monovalent ions Na^+ and K^+. However, because calcium and magnesium ions have larger hydration radii than that of monovalent ions (3.1 Å for Ca^{2+} and 4.6 Å for Mg^{2+} vs. 1.8 Å for K^+ and 2.2 Å for Na^+),[13] they are stopped at the boundary layer of membrane and do not pass across the membrane. Monovalent ions, on the other hand, having a relatively small hydration radius, can migrate to the other side of the membrane. It is interesting to note that K^+ ion, with its smaller hydration radius, is better transported across the membrane than Na^+ (compare Figs. 2 and 3).

Effect of the Jojoba Content in the Polymer on the Ion-Exchange Flux

The fluxes of the monovalent cations across J2NP11h differed from those across J2NP12h (Fig. 4), the membrane richer in jojoba (J2NP11h) having the lower flux. The relatively higher content of PE-SO_3H in J2NP12h is probably the factor enhancing the ion exchange through the membrane. For the membrane that contained the smaller amount of jojoba (J2NP12h), the number of monovalent ion equivalents that disappeared from the feed solution was equal to the number of ion equivalents appearing in the removal solution. In contrast, for the membrane containing the larger amount of jojoba (J2NP11h), only 41% of the monovalent ions removed from the feed solution reappeared in the removal solution, more than half of the ions being trapped in the membrane. After extensive washing for 24 h of the latter membrane with dilute HCl, the trapped

ions were eluted. Thus, the membrane acts both as a barrier and as a selective border through which only the smaller ions can penetrate.

From Figure 4, it is evident that the higher the jojoba content in the membrane (J2NP11h) the lower the flux of K^+ is obtained.

In summary, the hydrophobic layer constitutes a block to the transport of divalent vs. monovalent ions across the membrane. However, a thick layer of jojoba on the membrane that transports monovalent ions also adsorbs much of the monovalent ion passing, and thus acts as a barrier as well. Therefore, for practical application the amount of bound jojoba should be tailored to that required for efficient and complete ion separation and transport.

Separation of an Organic Solvent from Water by Pervaporation

Separation by pervaporation is based on differences in the permeability of the pervaporation membrane to various materials as well as on volatility of the liquids to be separated.[14] Thus, pervaporation can be used to separate a more volatile compound or a less volatile compound from a feed mixture (such as an azeotropic mixture), to separate an organic compound from water, or to dehydrate from wet organic solvents.

The pervaporation experiment was conducted with hollow fibers made of J2NP11 (41% of jojoba) as the pervaporation membranes. The system chosen for the pervaporation experiment was dioxane/water, because the two liquids are miscible, form an azeotrope of 18.6% (w/w) of water in dioxane, and have very close boiling points [dioxane 101.3°C water (100°C)]. For such a system, it is likely that the separation would depend on a difference in polarity, namely, the more hydrophobic molecules (dioxane) would have a better chance of penetrating the wall of the modified polymer.

The selectivity is calculated from the formula:

$$\alpha = (C'_D/C'_W)/(C_D/C_W)$$

where C'_D and C'_W are the concentrations of dioxane and water in the evaporated mixture, and C_D and C_W are the concentrations of dioxane and water in feed mixture.

The pervaporation was applied to aqueous solutions containing 25–75% dioxane and to pure dioxane. The results presented in Figure 5 show that the flux of dioxane increased with a decreas-
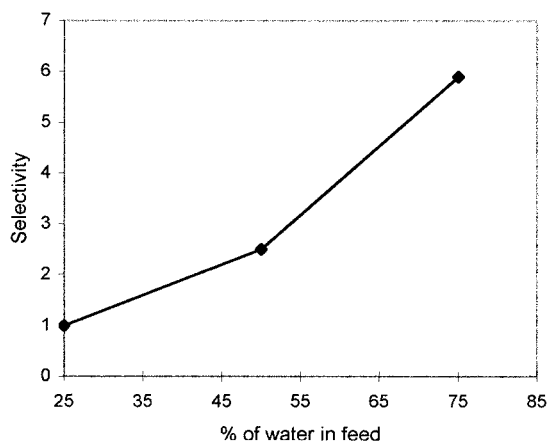

Figure 6 Selectivity of J2NP11 membrane as a function of water content in feed mixture.

ing content of water in the feed mixture. The more important finding was that the selectivity for dioxane (separation factor) increased sixfold as its content in feed solution decreased (Fig. 6), i.e., the membrane effectively separated the rest of dioxane from water. This may be explained in terms of the hydrophobic nature of the jojoba chains, which favor dioxane over the polar molecules of water. It is thus reasonable to assume that the separation would be even more effective in aqueous solutions containing just a few percent of dioxane. The advantages of a process in which it is possible to remove residues of dioxane from aqueous solutions are self-evident.

Because dioxane is relatively polar and more hydrophilic than other organic solvents, it is likely that separation of residues of solvents such as dichloromethane, chloroform, ether, and toluene, which are less hydrophilic, will be even more efficacious.

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