

SEPARATIONS

Zeolite/Polyelectrolyte Multilayer Pervaporation Membranes for Enhanced Reaction Yield

Peter M. Budd,^{*,†} Nágila M. P. S. Ricardo,[‡] Jalal J. Jafar,[†] Ben Stephenson,[†] and Ron Hughes[§]

Department of Chemistry, University of Manchester, Manchester M13 9PL, UK,

Department of Organic and Inorganic Chemistry, Federal University of Ceará, PO Box 12.200 CEP 60455-760, Brazil, and Chemical Engineering Unit, University of Salford, Salford M5 4WT, UK

Multilayer membranes were prepared by alternating adsorption of a cationic polyelectrolyte, chitosan, and an anionic polyelectrolyte, poly(4-styrene sulfonate), onto zeolite A films formed on porous supports in sheet and tube form. The multilayer membranes are shown to exhibit the high selectivity for water over alcohols associated with zeolite A but to be considerably more stable under acidic conditions than a pure zeolite A membrane. The membranes were successfully applied to the selective removal of water by pervaporation in the esterification of lactic acid with ethanol, catalyzed by *p*-toluenesulfonic acid. For esterification at 70 °C, yields of about 60% without the membrane were increased to >80% with pervaporation, and for esterification at 100 °C, yields of about 70% without the membrane were increased to >90% with pervaporation.

Introduction

Membrane processes offer the potential to enhance the yield of equilibrium-limited reactions by selective removal of a reaction product, e.g. the removal of water from an esterification reaction. Important membrane processes are pervaporation, in which the feed is a liquid mixture, and vapor permeation, in which the feed is a mixture of vapors. In both cases, the driving force for transport through the membrane is the removal of vapor from the permeate side by application of vacuum or use of a sweep gas. We have previously demonstrated that zeolite A membranes have a very high selectivity for water over alcohols¹ and that in vapor permeation mode they can give substantially enhanced yields of ethyl lactate from the esterification of lactic acid.² The use of zeolite membranes for dehydration of solvents and for treatment of waste streams has been investigated,^{3–6} and a large-scale plant has been constructed in Japan.⁷ However, a major drawback of zeolite A membranes is their acid-sensitivity, which forbids their use as pervaporation membranes in direct contact with mixtures containing lactic acid or other organic acids or even in vapor permeation with more volatile acids such as acrylic acid. One solution to this problem is the use of a less acid-sensitive zeolite, such as zeolite T.^{8–10} An alternative approach, explored in the present work, is to incorporate zeolite A into an acid-resistant multilayer membrane.

Composite membranes comprising a polymer filled with a ceramic or zeolite have been investigated previ-

ously.^{11,12} Also, thin polyelectrolyte multilayers have been shown to act as effective pervaporation membranes.^{13–16} The membrane described here consists of a continuous, polycrystalline zeolite A layer, grown on a macroporous support from a homogeneous hydrothermal system,^{1,17} onto which is adsorbed, from solution, alternating layers of a cationic and an anionic polyelectrolyte. Since cationic polyelectrolytes adsorb extremely strongly onto the external surfaces of the negatively charged zeolite A framework, and since polyelectrolyte multilayers are capable of a high degree of ion-selectivity,¹⁸ it should be possible to inhibit the ion-exchange process that is presumed to lead to zeolite degradation. The cationic polyelectrolyte utilized in this study was chitosan, which has previously been studied as a membrane material for pervaporation.^{19–24} However, a pure chitosan membrane suffers from the drawback that it is a semicrystalline polymer with two crystalline morphologies,²⁵ which may interconvert under pervaporation conditions so that the membrane properties change in use. When chitosan is incorporated into a multilayer, its crystallinity should be suppressed. The anionic polyelectrolyte used in this work was sodium poly(4-styrene sulfonate) (PSS). Zeolite/polyelectrolyte multilayer membranes were prepared in both sheet and tubular forms and tested as pervaporation membranes in the esterification of lactic acid with ethanol to give ethyl lactate:



Experimental Section

Membrane Preparation. Zeolite A membranes were formed on sheet (Ceramesh, Acumen Ltd.) and tube

* To whom correspondence should be addressed. Tel.: +44-161-275-4711. Fax: +44-161-275-4598. E-mail: Peter.Budd@man.ac.uk.

[†] University of Manchester.

[‡] Federal University of Ceará.

[§] University of Salford.

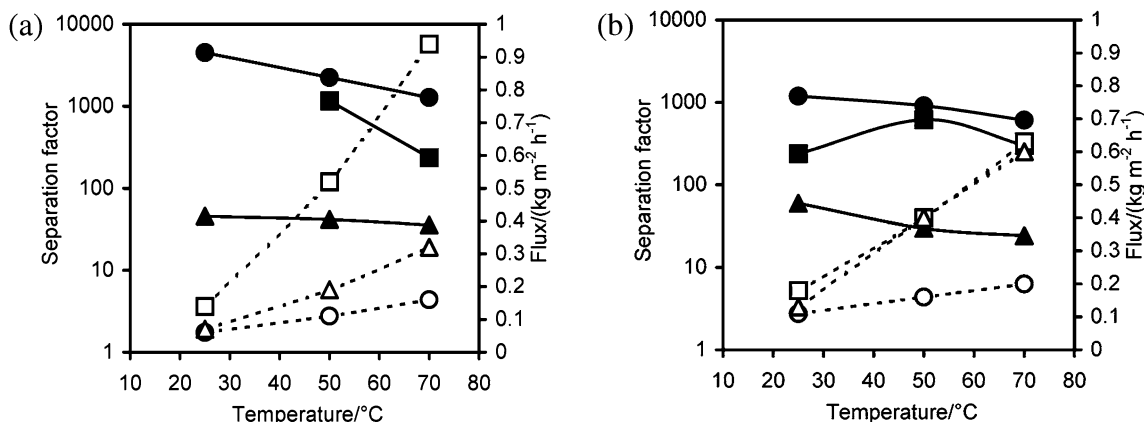


Figure 1. Dependence of the separation factor, α (solid symbols, left-hand axis), and flux (open symbols, right-hand axis) on temperature for pervaporation of (a) 10 wt % aqueous 2-propanol and (b) 10 wt % aqueous ethanol, with sheet (■, □) and tube (●, ○) zeolite/chitosan/PSS multilayer membranes and with a chitosan/PSS membrane (▲, △). Data points are averages for three separate experiments (Uncertainty: $\pm 15\%$ in α , $\pm 6\%$ in flux).

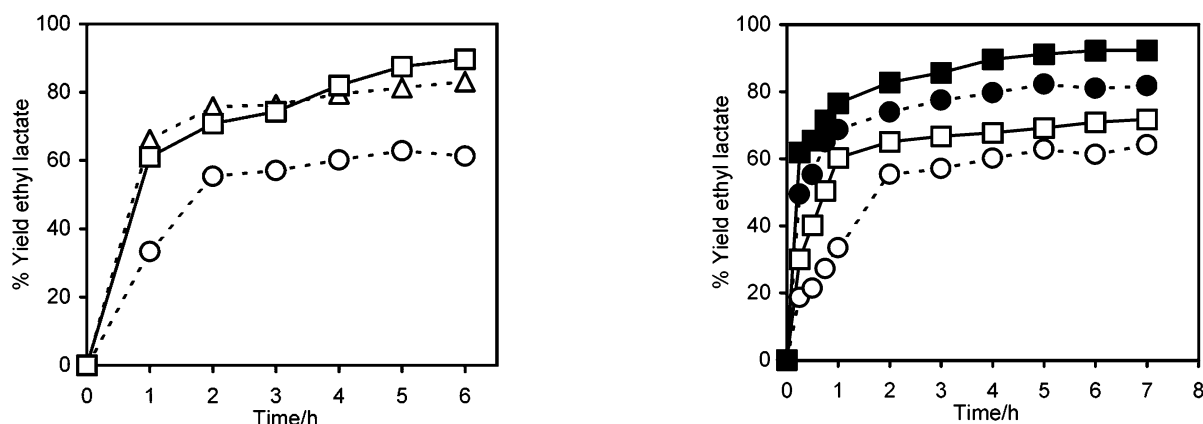


Figure 2. Dependence of the yield of ethyl lactate on time for the catalyzed esterification of lactic acid at 70 °C carried out (○) without a pervaporation membrane in place and assisted by pervaporation using (□) sheet zeolite/chitosan/PSS multilayer membrane and (△) sheet chitosan/PSS multilayer membrane. Data points are averages of three separate experiments (Uncertainty: $\pm 7\%$ in yield).

(Carbosep M14, Ultra Tech Services Ltd.) porous supports as described previously.¹ Chitosan solution (2% w/v for the sheet membrane, 1% w/v for the tube membrane) was prepared by dissolving chitosan powder (91.04% deacetylated chitosan, Polymar, Brazil) in aqueous acetic acid (1% v/v), and the solution was filtered after 5 h to remove any residual particles. PSS solution (1% w/v) was prepared by dissolving sodium poly(4-styrene sulfonate) (molar mass ca. 70 000 g mol⁻¹, Aldrich) in distilled water. The supported zeolite membrane was immersed in chitosan solution, dried, neutralized with aqueous NaOH (0.5 mol dm⁻³), washed, dried, then immersed in PSS solution, and dried. The tube membrane was subjected to a further nine cycles of treatment with chitosan and PSS. A chitosan/PSS membrane (3 cycles) was also formed directly onto a Ceramesh support without zeolite.

Pervaporation. Pervaporation experiments were carried out batch-wise on a laboratory scale. Membranes were first tested for the separation of 2-propanol/water and ethanol/water mixtures, to confirm they functioned as expected, then were utilized in lactic acid esterifications. Most experiments were carried out with an integrated reactor/pervaporation system, in which the membrane was in direct contact with the reaction mixture. For the sheet membrane a stainless steel

Figure 3. Dependence of the yield of ethyl lactate on time for the catalyzed esterification of lactic acid at (○, ●) 70 °C and (□, ■) 100 °C carried out (○, □) without a pervaporation membrane in place and (●, ■) assisted by pervaporation using tube zeolite/chitosan/PSS multilayer membrane. Data points are averages of three separate experiments (Uncertainty: $\pm 7\%$ in yield).

pervaporation cell was utilized with an effective membrane area of 0.00159 m².¹ For the tube membrane, a glass cell was used with an effective membrane area of 0.005 m². For esterification, the cell was filled with a 25 g reaction mixture containing 0.125 mol of lactic acid (13.25 g of 85 wt % aqueous lactic acid solution, Acros), 0.250 mol of ethanol, and *p*-toluenesulfonic acid catalyst (3 wt % relative to lactic acid, Aldrich). Esterification reactions were performed at 70 °C and 100 °C. Samples of the permeate and the reaction mixture were taken at intervals and analyzed by gas chromatography, as described previously.² Experiments were also undertaken with an alternative (coupled) arrangement in which vapor from the reaction was condensed into a separate pervaporation unit, incorporating a tube membrane, and the nonpermeating components were cycled back into the reactor. In this latter case, the reactor temperature was 100 °C, and the membrane temperature was 70 °C.

Results and Discussion

Results of initial pervaporation experiments at temperatures in the range of 25–70 °C are shown in Figure 1a for 10 wt % 2-propanol/water mixtures and in Figure 1b for 10 wt % ethanol/water mixtures. For the tube zeolite/chitosan/PSS membrane, which was prepared

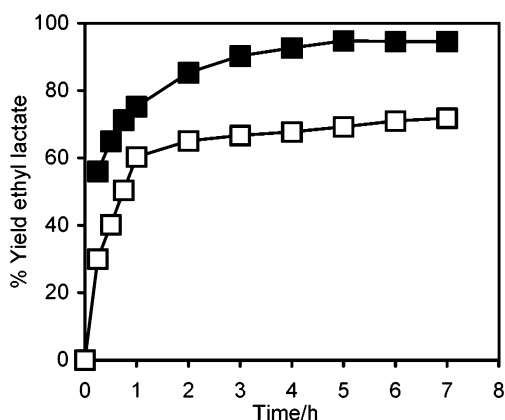


Figure 4. Dependence of the yield of ethyl lactate on time for the catalyzed esterification of lactic acid at 100 °C (□) without pervaporation and (■) coupled with a tube zeolite/chitosan/PSS multilayer membrane operating in a separate unit at 70 °C. Data points are averages of three separate experiments (Uncertainty: $\pm 7\%$ in yield).

with 10 layers of each polyelectrolyte, values of the separation factor (α = weight ratio of water to alcohol in permeate/weight ratio of water to alcohol in feed) and flux are comparable to those obtained previously for zeolite A membranes and indicate a highly selective membrane with a good quality zeolite layer.² For the sheet zeolite/chitosan/PSS membrane, which was prepared with a single layer of each polyelectrolyte, lower

values of α and higher flux suggest a less perfect membrane or less effective sealing around the membrane. Nevertheless, it was considered suitable for use in the present work, since in pervaporation it may be more important to achieve high flux than high selectivity. The chitosan/PSS membrane (3 layers of each polyelectrolyte) formed without zeolite gave substantially lower values of α , demonstrating that the zeolite layer significantly increases selectivity.

In the catalyzed esterification of lactic acid with ethanol, use of the pervaporation process to preferentially remove water from the system gave substantially enhanced yields of ethyl lactate, as can be seen in Figure 2 for sheet membranes. A control experiment at a reactor temperature of 70 °C without a membrane gave no more than about 60% yield, whereas up to 90% yield was achieved after 6 h when assisted by pervaporation with a sheet zeolite/chitosan/PSS multilayer membrane. At this temperature, a similar performance was obtained with a sheet chitosan/PSS membrane formed without zeolite, despite the lower selectivity of that membrane, demonstrating the importance of achieving high flux in this type of application. When the experiments were repeated at a higher reactor temperature of 100 °C, the membrane formed without zeolite disintegrated, whereas the membrane incorporating zeolite survived. The zeolite/polyelectrolyte composite therefore appears more robust than a pure polyelectrolyte membrane. In a single run, catalyzed esterification at 100

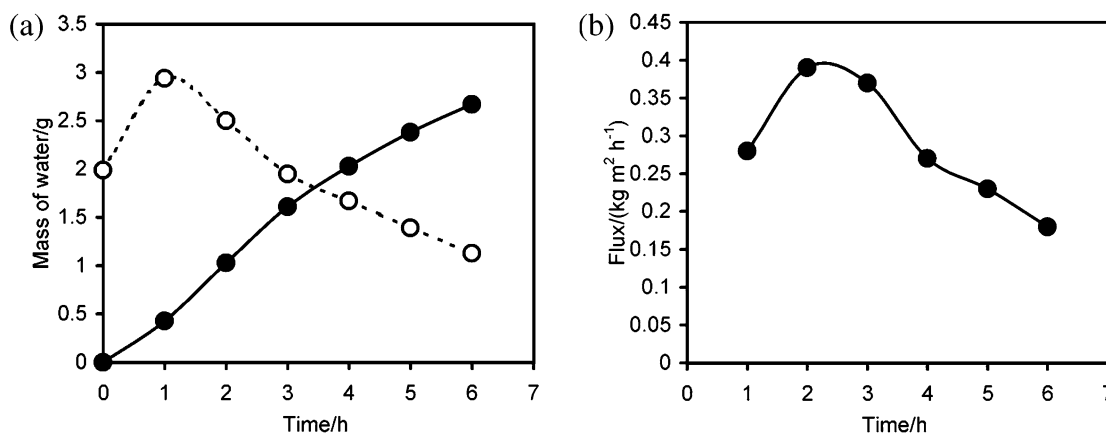


Figure 5. Integrated esterification/pervaporation with a sheet zeolite/chitosan/PSS multilayer membrane at 70 °C: (a) Dependence on time of (○) the mass of water in the reactor and (●) the cumulative mass of water removed by pervaporation. (b) Dependence on time of the total flux through the membrane. Data points are averages of three separate experiments.

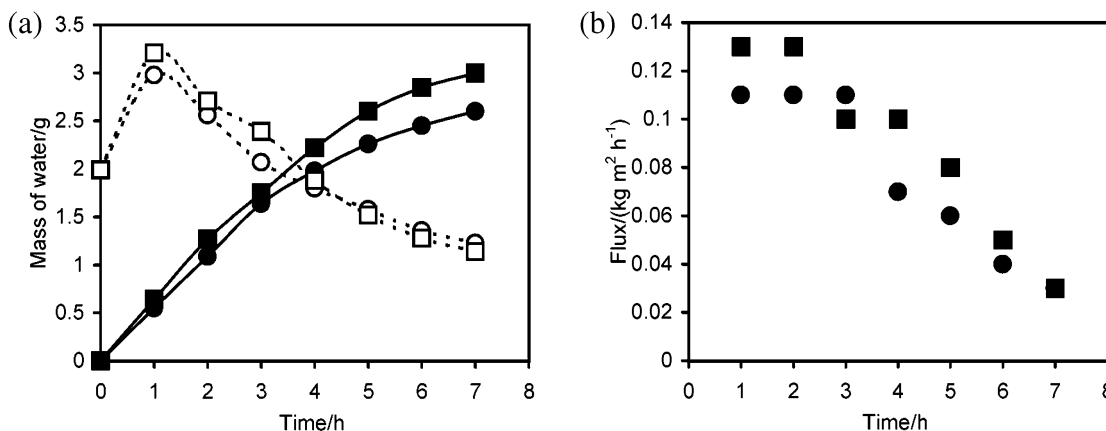


Figure 6. Integrated esterification/pervaporation with a tube zeolite/chitosan/PSS multilayer membrane at (○,●) 70 °C and (□,■) 100 °C: (a) Dependence on time of (○,□) the mass of water in the reactor and (●,■) the cumulative mass of water removed by pervaporation. (b) Dependence on time of the total flux through the membrane. Data points are averages of three separate experiments.

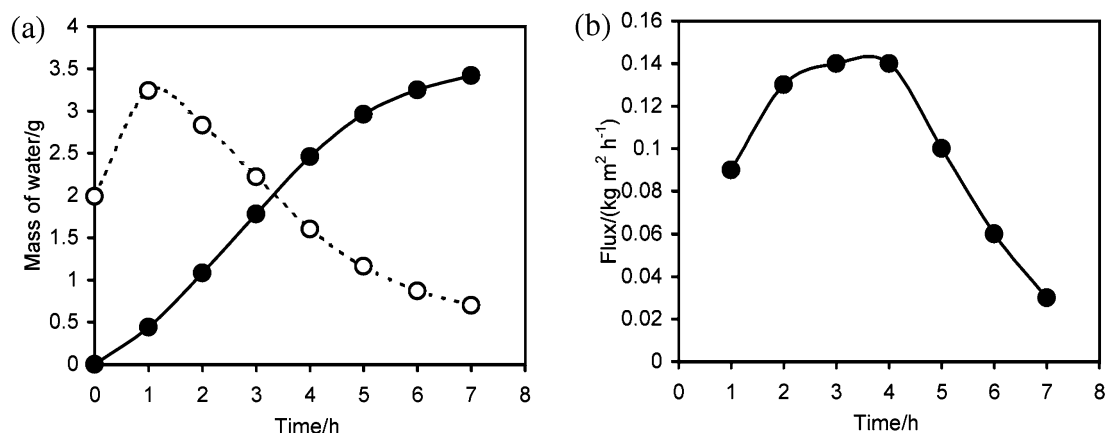


Figure 7. Esterification coupled to a separate pervaporation unit with a tube zeolite/chitosan/PSS multilayer membrane (reactor temperature 100 °C; membrane temperature 70 °C): (a) Dependence on time of (○) the mass of the water in the reactor and (●) the cumulative mass of water removed by pervaporation. (b) Dependence on time of the total flux through the membrane. Data points are averages of three separate experiments.

°C with a sheet zeolite/chitosan/PSS multilayer pervaporation membrane gave a yield approaching 100% within 4 h.

The tube zeolite/chitosan/PSS multilayer membrane also gave substantially enhanced yields of ethyl lactate in the catalyzed esterification of lactic acid, as can be seen in Figure 3. For esterification at 70 °C, yields of about 60% without the membrane were increased to >80% with pervaporation, and for esterification at 100 °C, yields of about 70% without the membrane were increased to >90% with pervaporation. Slightly lower yields were attained than with the sheet membrane, reflecting the lower flux. The results presented here illustrate the importance of achieving high flux for this type of membrane application, even at the expense of some selectivity. The membrane survived repeated use in direct contact with the reaction mixture, even at 100 °C. Such conditions lead to very rapid dissolution of a pure zeolite A membrane, which demonstrates that the addition of a polyelectrolyte multilayer enormously improves the acid-resistance. However, a detailed examination of the data revealed a slight decrease in performance each time it was used at the higher temperature of 100 °C.

Results for an alternative experimental arrangement are shown in Figure 4. In this system, the pervaporation unit is separate from the reactor, and nonpermeating components are cycled back into the reactor. The membrane does not come into direct contact with the involatile lactic acid, and pervaporation takes place at a temperature lower than that of the reactor. As with the integrated reactor/pervaporation system, a substantial increase was achieved in the yield of ethyl lactate. The results are comparable to those obtained previously using a zeolite A membrane in a vapor permeation mode, with a reactor temperature of 100 °C and a membrane temperature of 70 °C.²

The effectiveness of the pervaporation process in removing water during esterification is seen in Figures 5–7 for the integrated system with a sheet membrane, the integrated system with a tube membrane, and the coupled system, respectively. These figures show the mass of water in the reactor, the mass of water removed by pervaporation, and the total flux through the membrane at various times throughout the reaction period. Water is initially present in the commercial 85% lactic acid, and the pervaporation process needs to remove as

much as possible of this as well as the water produced by reaction. With the small membrane areas utilized in this work, there is in the first hour an increase in the water content of the reactor, associated with a high initial rate of reaction, but over a longer period of time the pervaporation process reduces the amount of water to well below that originally present. As would be expected, the permeate flux decreases as the water content drops.

Conclusions

This work has demonstrated that zeolite/polyelectrolyte multilayer membranes retain the high selectivity for water over alcohols exhibited by zeolite A but offer much greater resistance to acid attack than the pure zeolite and can survive at higher temperatures than an equivalent polyelectrolyte multilayer. The zeolite/polyelectrolyte multilayer membranes were successfully employed in pervaporation mode in the esterification of lactic acid to remove water preferentially from the system and so improve the yield of ethyl lactate.

Acknowledgment

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