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Chemical Engineering Journal 87 (2002) 321–328

Chemical Engineering Journal

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Facilitated transport of unsaturated hydrocarbons through crosslinked-poly(sulfonated styrene)

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Received 12 March 2001; received in revised form 16 July 2001; accepted 12 September 2001

Abstract

Permeation of ethylbenzene, styrene and cyclohexene through CR 61-CMP-447, a crosslinked-poly(sulfonated styrene) ion-exchange membrane, was investigated. The experiments were performed with single-component and bicomponent feeds with solute concentrations ranging from 0.5 to 2.0 M. The Na^+-form membrane was highly permeable to the aromatics, while giving a much lower flux for cyclohexene. The magnitude of solute flux correlated well with the swelling degree of membrane by the solute. An additional experiment was carried out with the Na^+-form membrane incorporated with poly(pyrrole) and 2.0 M styrene as a feed. The presence of poly(pyrrole) in the membrane resulted in a significant flux decline. As Ag^+ ions were exchanged for Na^+ ions, the solute fluxes were increased through the reversible complex formation. It was found that the solute flux attributed to the facilitated transport closely related to the diffusional flux. The styrene/ethylbenzene separation factors observed with single-component and bicomponent feeds were much the same, indicating a lack of competitive transport.

Keywords: Facilitated transport membranes; Competitive transport; Crosslinked-poly(sulfonated styrene); Poly(pyrrole)

1. Introduction

Considerable research in separations of alkenes and aromatics through facilitated transport membranes containing Ag^+ has been done [1–7]. Based on the flux measurements carried out with single-component feed solutions, the separation factor of a bicomponent feed is likely to be small. Nevertheless, unexpectedly large selectivities for the separation of certain unsaturated hydrocarbon mixtures were observed. The competitive facilitated transport of styrene and ethylbenzene through Ag^+-Nafion® 117 was first reported by Koval et al. [1]. Although each component in the feed solution was able to complex with Ag^+, a styrene/ethylbenzene separation factor of 36 was obtained for the feed containing 0.1 mol/l of each aromatic. In a subsequent study, the effect of permanent swelling of the membrane on the separation were explored [2]. The expansion of the cluster network allowed the membrane to absorb more water. The effective Ag^+ concentration in the membrane was reduced, which resulted in the lower facilitation of aromatic transport. The more open membrane structure also led to the higher permeation through solution-diffusion pathway. As a consequence, the styrene/ethylbenzene separation factor decreased dramatically, i.e., the effect of competitive transport was less pronounced. Koval and Spontarelli [3] also observed the enhancement of 1-hexene and 1,5-hexadiene transport rates across Nafion® 111 by factors of several hundred when Ag^+ was exchanged for Na^+.

An in-depth study of the separations of linear C_5–C_{10} dienes from monoenes using hydrated Nafion® was performed by Thoen et al. [4]. Selectivities much larger than predicted from measurements involving single-component feed solutions were obtained. For the separation of 1,5-hexadiene from 1-hexene, the separation factor obtained from an equimolar, bicomponent experiment was 43, 10 times higher than the number predicted from the single-component experiments. It was found that fluxes of the solutes related closely to their concentrations in the membrane, clearly indicating that the large selectivity resulted from competitive absorption. However, it was demonstrated that competitive absorption did not occur for liquid membranes composed of aqueous salts. To explain the unexpected large separation factors for the diene/monoene mixtures, the complexation of dienes to two Ag^+ was proposed. Kohls et al. [5] reported that further investigation into the effects of various

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PII: S1385-8947(01)00243-1

properties of C_6 alkene and dienes, such as bond spacing and position, on their competitive permeation. Competitive transport through Nafion® was also observed with gas-phase olefins [6]. The competitive effect slightly increased the *cis*-2-butene/*trans*-2-butene selectivity from the ideal value of 1.4 calculated from pure gas fluxes to about 1.9–2.7, depending on the feed composition. Recently, absorption and transport experiments in Ag^+-exchanged Neosepta® CM-1 suggested the transport through the membrane occurred predominantly through the 1:1 1,5-hexadiene/Ag^+ complexation mechanism [7].

In the present work, facilitated transport of styrene, ethylbenzene and cyclohexene through crosslinked-poly (sulfonated styrene) containing Ag^+ was investigated. The chemical structure and morphology of the membrane was different from Nafion® and led to intriguing results. The permeation through the crosslinked-poly(sulfonated styrene) incorporated with poly(pyrrole), a positively charged polymer, was also carried out. In addition, the effects of temperature and feed concentration were also studied.

2. Experimental

2.1. Materials

Crosslinked-poly(sulfonated styrene), commercially designated as CR 61-CMP-447, was kindly donated by Ionics. The 22.5 Mils thick membrane was reinforced with polypropylene. An ion-exchange capacity of 2.2 meq/dry gram was reported by the manufacturer. Sorbic acid or 2,4-hexadienoic acid (99% purity) and ethanol (99.5% purity) were used to prepare the membrane storage solution. The purity of silver nitrate and sodium nitrate was higher than 99%. Ethylbenzene, 98+%, was purchased from Fluka. Cyclohexene, styrene, and isooctane (2,2,4-trimethylpentane), all 99+% grade, were used. Pyrrole, 98%, was purchased from Aldrich. Aqueous hydrogen peroxide 40 m/v in water was used. All chemicals were used without further purification. Purified and deionized water was used in all experiments.

2.2. Membrane preparation and characterization

The as-received H^+-form membrane was kept in 0.1% aqueous solution of sorbic acid and ethanol. Conversion to a Na^+-form membrane was done by first thoroughly washing the as-received membrane with water. The membrane was then immersed in a 1 M aqueous sodium nitrate solution for 6 h. The film was subsequently rinsed with water. The membrane was converted to Ag^+-form by ion-exchanging in a 1 M aqueous silver nitrate solution for 6 h. The membrane was then repeatedly rinsed with water to remove the excess solution.

Water content of the membrane was obtained by first weighing a fully hydrated H^+-form membrane. The membrane was dried in a vacuum oven at 60 °C for 6 h, and then placed in a desiccator. A constant weight of the membrane was reached after several days. Water content of the membrane found by this procedure was 32.9 wt.%. The water content reported by manufacturer is 44% of wet resin only.

The preparation of the membrane incorporated with poly(pyrrole) was similar to our procedure described previously [8]. To polymerize pyrrole into a H^+-form film, an aqueous solution of 0.01 M pyrrole was prepared. A H^+-form crosslinked-poly(sulfonated styrene) film was placed in the solution for 12 h. Then, approximately 0.25 cm^3 of hydrogen peroxide, 40 m/v in water, was subsequently added to the solution. The mixture was continuously and gently stirred for about 5 min. A black film of the H^+-form crosslinked-poly(sulfonated styrene)–poly-(pyrrole) composite polymer was obtained. The film was rinsed with water. The ion-exchange procedures used to convert these membranes to the Ag^+- or Na^+-form were the same as those described earlier. The membranes were thoroughly washed prior to transport measurements.

The amount of poly(pyrrole) in the membrane was obtained from the weight difference between the dry H^+-form membrane containing poly(pyrrole) and the dry H^+-form membrane. Before impregnation with poly(pyrrole), a wet H^+-form membrane was weighed. The weight of the dry H^+-form membrane was obtained by subtracting the calculated weight of water in the membrane from weight of the wet H^+-form membrane. Poly(pyrrole) was subsequently polymerized into the membrane. The composite membrane was dried in an oven and a desiccator until a constant weight was obtained. The membrane was found to contain ca. 1.1 wt.% poly(pyrrole). The water content of the composite membrane, obtained by the same procedures described earlier, was 31.0 wt.%.

2.3. Transport measurements

The flux measurement cell was similar to the one described previously [9]. The two compartments of the cell were separated by the membrane which was held in place with O-rings and a joint clip. The surface area of the membranes exposed to the solutions, measured from the O-ring joint diameter, was approximately 4.52 cm^2. The experiments were performed with liquid phases in both feed and receiving (sweep) solutions, referred to as the perstraction mode of operation. The feed side compartment contained 15 cm^3 of solute in water-saturated isooctane. The receiving compartment consisted of 15 cm^3 of water-saturated isooctane. Both cell compartments were mechanically stirred by magnetic stirrers.

After the cell was assembled, the permeation measurement was done in a room whose temperature was constant at 25 °C. To investigate the mass transfer at low temperature, the cell was placed in a refrigerator providing the temperature of 10 ± 1 °C. Aliquots (ca. 1 μl) of the receiving solution were removed periodically with a syringe and analyzed for permeates by gas chromatography. The gas chromatograph was a Shimadzu 14B with a flame ionization detector. Separations were performed with a packed column (BX-10). Solute fluxes were obtained by calculating the concentration of olefin appearing in the receiving reservoir per unit time and unit area of membrane. The experiments involving Ag^+-form membranes were performed in a way as to minimize exposure to light.

3. Results and discussion

3.1. Na^+-form membranes

To investigate the Fickean mass transport of ethylbenzene, styrene and cyclohexene, the permeation measurements were carried out with the Na^+-form CR 61-CMP-447 membrane. Fluxes through the membrane obtained from the single-component feeds, i.e., the feeds consisted of either ethylbenzene, styrene or cyclohexene in isooctane, are shown in Fig. 1. The membrane exhibited very large fluxes for ethylbenzene and styrene, the aromatics, while giving a much lower flux for cyclohexene, an alkene. The very large fluxes were possibly attributed to the high solubilities of the aromatics into the membrane. The degree of solubility was investigated by immersing hydrated membranes in the 2 M solutions of aromatics and cyclohexene for 24 h. Sorption of ethylbenzene and styrene into the membrane increased volume of the membrane by 9.1–9.6% as shown in Table 1. The swelling was mainly induced by the aromatics as isooctane increased volume of the membrane by less than 3%. Cyclohexene swelled the membrane by a lesser extent which was consistent with its lower flux.

Further investigation on solution-diffusion of styrene through CR 61-CMP-447 was done by incorporating poly(pyrrole) into the membrane. In an oxidized-form, poly(pyrrole) contains positive charges and requires the presence of anions as counter ions. In this case, the sulfonate groups in CR 61-CMP-447 served as the counter ions for the positive charges of poly(pyrrole). Embedded in the hydrophilic region, poly(pyrrole) decreased the water content of the membrane from 32.9 to 31.0 wt.%. It was possible that poly(pyrrole) replaced water originally

Table 1
Percent volume change of the membrane immersed in various solutions for 24 h

Solutions	Volume change (%)	
	CR 61-CMP-447	CR 61-CMP-447/poly(pyrrole)
Pure isooctane	2.7	2.3
2 M styrene in isooctane	9.6	4.5
2 M ethylbenzene in isooctane	9.1	–
2 M cyclohexene in isooctane	7.3	–
Mixture of 2 M ethylbenzene and 2 M styrene in isooctane	12.0	–

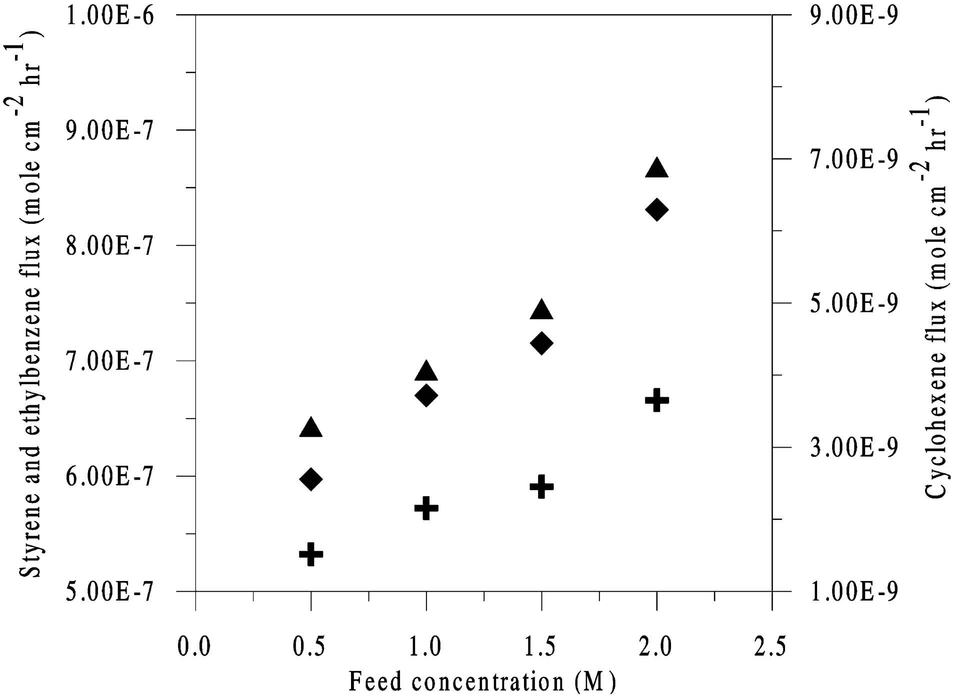

Fig. 1. Flux of styrene, ethylbenzene and cyclohexene through Na^+-form membrane obtained from single-component feed (mol cm^{-2} h^{-1}) at 25 °C: (▲) styrene, (◆) ethylbenzene, (✚) cyclohexene.

forming the hydration shell around the sulfonate groups. Furthermore, there was strong evidence that poly(pyrrole) served as an additional crosslinker within the membrane matrix. As listed in Table 1, volume change of the membrane swollen with styrene was significantly reduced when incorporated with poly(pyrrole). It was most likely that positive charges on a poly(pyrrole) chain simultaneously bound with sulfonate groups within the range of the chain length, limiting the membrane from swelling. The membrane was tested with 2.0 M styrene as a feed. The flux of styrene was 7.34×10^{-7} mol cm^{-2} h^{-1}, approximately 15.4% lower than flux of the poly(pyrrole)-free membrane. This was possibly due to a decrease in the free-volume of the membrane. The flux decline in the presence of poly(pyrrole) suggested that the solution-diffusion transport also took place in the hydrated region.

Permeation measurements of ethylbenzene and styrene were also performed with the equimolar binary mixture feeds. The fluxes of the aromatics, as listed in Fig. 2, were slightly greater than those obtained from the single-component feed. This could result from the higher concentration of aromatic in the feed side in the bicomponent experiments. The membrane was then swollen to a greater degree as indicated by the percent volume change. This allowed the solutes to diffuse more freely through the membrane with the consequentially increasing fluxes. Reducing temperature resulted in the decreasing solution-diffusion flux. At 10 °C, ethylbenzene and styrene fluxes were 3–4 times lower than those obtained from the experiments done at 25 °C.

In comparison with Nafion®, the CR 61-CMP-447 membrane was more permeable to ethylbenzene and styrene. With the feed composed of 1.0 M of each aromatic, ethylbenzene and styrene fluxes through Nafion® 117 were 1.19×10^{-8} and 3.96×10^{-8} mol cm^{-2} h^{-1}, respectively [1]. Evidently, the aromatic fluxes of Nafion® 117 were several times lower than those of CR 61-CMP-447. A direct comparison was, however, not possible as CR 61-CMP-447 was approximately 3.25 times thicker than Nafion® 117. By taking the membrane thickness into account, permeability coefficients of the aromatics were then calculated by multiplying flux with membrane thickness. The permeability coefficients shown in Table 2 clearly indicated that CR 61-CMP-447 had a much larger solution-diffusion aromatic transport than Nafion® 117.

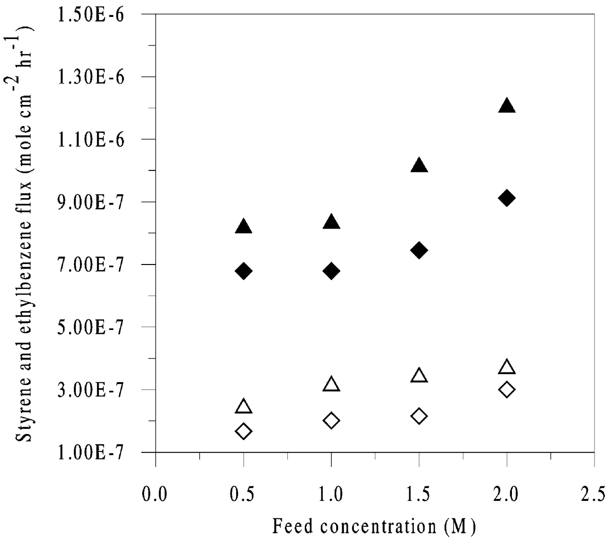

Fig. 2. Flux of ethylbenzene and styrene through Na$^+$-form membrane obtained from bicomponent feed (mol cm^{-2} h^{-1}): (▲) styrene 25 °C, (△) styrene 10 °C, (◆) ethylbenzene 25 °C, (◇) ethylbenzene 10 °C.

Table 2
Comparison between ethylbenzene and styrene permeability coefficients through Na$^+$-form membranes (mol cm cm^{-2} h^{-1})

Compound	Koval et al. [1]	This work
Styrene	7.92×10^{-10}	5.45×10^{-8}
Ethylbenzene	2.38×10^{-10}	4.41×10^{-8}

3.2. *Ag$^+$-form membranes*

The reversible reaction between carrier and penetrant provides another transport pathway through the membrane in addition to the solution-diffusion mechanism [10]. Ag$^+$ ion is mostly used as the carrier for the facilitated transport of unsaturated hydrocarbons because of its effectiveness in forming a complex with the penetrant. In the present study, Ag$^+$ ions were ion-exchanged into the membrane, which could be expected that they had no mobility within the film.

There are a number of mathematical models in the literature which describe mechanisms of facilitated transport in a fixed site carrier membrane where the carriers are immobile [11–16]. One of the widely accepted models for the facilitated transport mechanism in a fixed site carrier membrane was provided by Noble [14–16]. The main feature of the theory was that a penetrant had weak interactions with the polymer linkages between carrier sites and could migrate along the polymer chain. Flux of a penetrant through the membrane was the sum of the diffusion flux and the flux attributed to the complexation reaction. The flux of solute through the facilitated transport pathway or facilitated flux could therefore be calculated by subtracting flux of the Na$^+$-form membrane from flux of the Ag$^+$-form membrane. In the region between two carrier sites, the diffusive flux of solute was approximately the same as the solute flux through the carrier-free membrane.

The necessity of the solute diffusion between carrier sites for the facilitated transport to occur could be a result of a low carrier concentration and a limited mobility of carrier. The concentration of Ag$^+$ ion in CR 61-CMP-447 was less than 2.8 M, while other membranes usually possessed a higher concentration [1–7,17,18]. In addition, for a crosslinked membrane, the mobility of carrier sites was reasonably limited. Consequently, there was a strong possibility that the diffusion of solute between carrier sites was

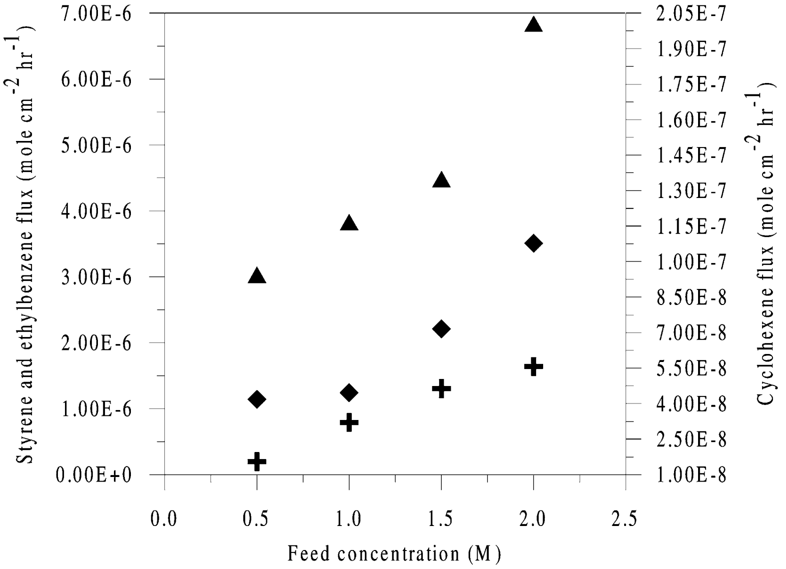

Fig. 3. Flux of ethylbenzene, styrene and cyclohexene through Ag^+-form membrane obtained from single-component feed (mol cm^{-2} h^{-1}) at 25 °C: (▲) styrene, (◆) ethylbenzene, (✚) cyclohexene.

essential to the facilitated transport in CR 61-CMP-447. An objective of the present study was to explore the effect of the diffusion of solute between the carrier sites on the facilitated transport.

Facilitated transport of ethylbenzene, styrene and cyclohexene through the Ag^+-form CR 61-CMP-447 was investigated. Fluxes observed with the single-component feed solutions are reported in Fig. 3. Facilitated flux of each component was calculated by subtracting flux of Na^+-form membrane from flux of Ag^+-form membrane and shown in Table 3. By considering the diffusion fluxes of ethylbenzene, styrene and cyclohexene reported in Fig. 1, it was evident that the magnitude of the facilitated transport flux corresponded to the diffusional flux. The Na^+-form membrane exhibited the largest flux for styrene, while the Ag^+-form membrane also gave the highest facilitated flux. On the other hand, both diffusion and facilitated fluxes of cyclohexene were lowest. The correspondence between facilitated flux and diffusion flux suggested a correlation between the transport through reactive and diffusive mechanisms.

The correlation could be established through the mathematical analysis by Noble [14]. According to the model, the transport of solute through the reversible complexation pathway was described by the "effective" diffusion coefficient (D_{AB}). When the spacing between fixed sites was large, the facilitated transport required the diffusion of solute between carrier sites. As a consequence, D_{AB} was primarily dependent on the diffusion coefficient of solute between fixed sites (D_{DD}). In the present study, the correlation between the facilitated and diffusive fluxes suggested that a high D_{DD} enhanced the facilitation effect. High water content and the appreciable swelling of the membrane by the solute probably accounted for a large diffusion coefficient of solute in the hydrophilic region of the membrane, where the carriers were located.

The permeation of aromatic was also done with the bicomponent feeds, and their fluxes are listed in Fig. 4. In comparison with the single-component permeation, flux of each aromatic was slightly reduced due to the presence of another component in the feed. This was probably because both aromatics were able to complex with Ag^+ in the membrane. The available carriers for each aromatic might therefore be reduced, which was the cause of a decrease in the facilitation effect.

The styrene/ethylbenzene separation factor, defined as the ratio of styrene flux to ethylbenzene flux, is a parameter that quantifies the effectiveness of the membrane in its selective permeability. The separation factor observed with

Table 3
Facilitated fluxes of styrene, ethylbenzene and cyclohexene (mol cm^{-2} h^{-1})

Compound	Concentration (M)			
	0.5	1.0	1.5	2.0
Styrene	2.39×10^{-6}	3.14×10^{-6}	3.74×10^{-6}	5.97×10^{-6}
Ethylbenzene	5.43×10^{-7}	5.70×10^{-7}	1.50×10^{-6}	2.68×10^{-6}
Cyclohexene	1.39×10^{-8}	2.99×10^{-8}	4.40×10^{-8}	5.20×10^{-8}

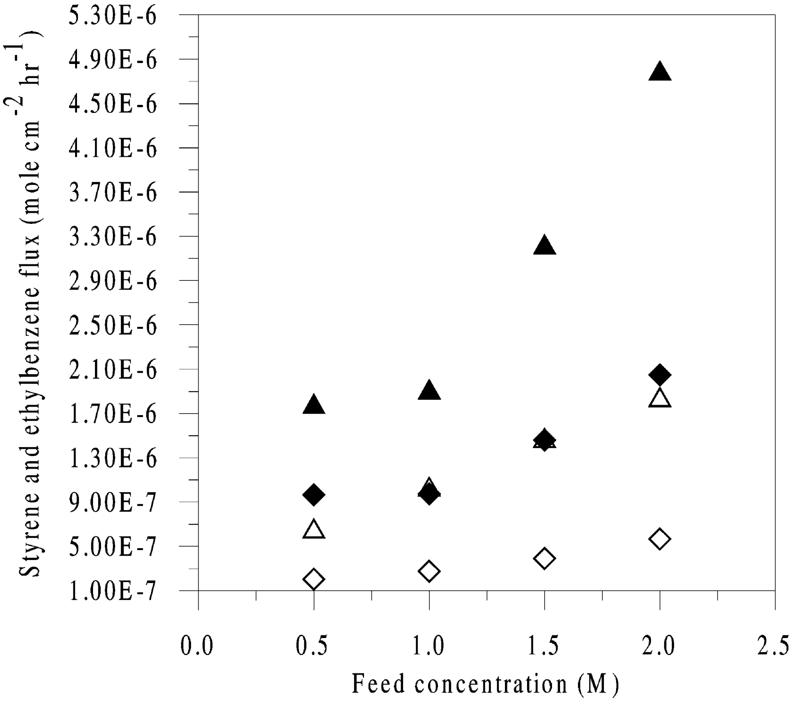

Fig. 4. Flux of ethylbenzene and styrene through Ag^+-form membrane obtained from bicomponent feed (mol cm^{-2} h^{-1}): (▲) styrene 25 °C, (△) styrene 10 °C, (◆) ethylbenzene 25 °C, (◇) ethylbenzene 10 °C.

Ag^+-form CR 61-CMP-447 was only about 2. This ratio was much the same as that observed with the single-permeation measurements, indicating that facilitated transport of each aromatic was not affected by the presence of the other. In contrast, the styrene/ethylbenzene separation factor of the Ag^+-form Nafion® was as high as 16 for the feed composed of 0.5 M of each aromatic [4]. It was higher than the separation factor of 3.5 calculated from the measurements involving single-component feed solutions. The reason for the very high separation factor was that, for a bicomponent feed, both components were competitively absorbed into the membrane.

A plausible explanation for the low separation factor of CR 61-CMP-447 was concerned with morphology difference between Nafion® and CR 61-CMP-447. The ion-exchange sites in Nafion® aggregated into clusters [19–21]. The polymeric side chain ionic groups and absorbed water were separated from the fluorocarbon backbone in approximately spherical clusters connected by short narrow channels. The cluster diameter was approximately 40 Å and the channel diameter was about 10 Å. Providing that the fixed anions were located in the narrow channels, the facilitated transport of aromatics across the membrane has to occur through these inter-cluster regions. However, only a small number of H_2O molecules, ions, and aromatics could occupy this small volume of approximately 1 nm^3. Preferential absorption of styrene in these cluster-connecting pores could block ethylbenzene from accessing the carriers that mostly locate in the clusters. This could effectively exclude ethylbenzene from the membrane. Unlike Nafion®, ion-exchange sites in CR 61-CMP-447, a crosslinked-poly(sulfonated styrene) membrane, were uniformly distributed. The absorption of ethylbenzene was not affected by the presence of styrene in the feed. As a consequence, the styrene–ethylbenzene competitive transport was not observed with CR 61-CMP-447.

By considering the amount of carrier in the membrane, the effect of Ag^+ carrier distribution on the lack of competitive transport in CR 61-CMP-447 could be pointed up. The concentration of Ag^+ ion in CR 61-CMP-447 was less than 2.8 M while that of Nafion® was about 6–7 M depending on water content of the membrane. The low availability of carrier should promote the exclusion of ethylbenzene from absorption into the membrane as the carriers were rapidly used up by styrene. However, as CR 61-CMP-447 showed a very small selectivity, the dispersion of Ag^+ carriers within the membrane matrix evidently was more important to the competitive transport. This finding was consistent with the suggestion provided by Thoen et al. [4] that large separation factor due to competitive absorption would not be observed for liquid membranes composed of aqueous silver salts. With the uniform distribution of carrier and large quantities of water, CR 61-CMP-447 probably behaved like the aqueous solution and exhibited only small difference in the styrene and ethylbenzene transport rates.

Compared with styrene, decreasing temperature from 25 to 10 °C reduced flux of ethylbenzene by a slightly greater degree. The separation factor consequently increased from about 2 at 25 °C to 3–4 at 10 °C.

4. Conclusions

Much research has been done to investigate the facilitated transport of unsaturated hydrocarbons across the membrane containing Ag^+ ions. Nearly, all the studies involving in liquid phase olefins such as styrene, ethylbenzene, monoenes and dienes, were performed by using Nafion®, a perfluorosulfonate ionomer. In the present work, permeation measurements of styrene, ethylbenzene and cyclohexene through Na^+- and Ag^+-form CR 61-CMP-447 ion-exchange membranes were carried out. CR 61-CMP-447, kindly given by Ionics, was a crosslinked-poly(sulfonated styrene) membrane.

Studies of the solution-diffusion transport were performed with the membrane in Na^+-form. CR 61-CMP-447 exhibited very high aromatic fluxes, while giving a lower flux for cyclohexene. The styrene-based structure of the membrane most likely contributed to the very high solubilities of the aromatics in the membrane. The solution-diffusion transport was further explored by incorporating poly(pyrrole) into the membrane. The styrene flux, obtained from a 2.0 M feed, decreased by about 15.4%. Reduction in the water content and swelling ability of the membrane due to the presence of poly(pyrrole) were responsible for the flux decline.

When Ag^+ ions were exchanged for Na^+ ions, a study of facilitated transport under conditions of very high solution-diffusion transport was possible. It was found that there was a correlation between the magnitude of flux attributed to the facilitated transport and the diffusional flux. Based on the mathematical model by Noble [14], it was probable that a fast diffusion of solute between the carrier sites enhanced the transport rate through the facilitated transport pathway.

The phenomenon of competitive facilitated transport could selectively enhance flux of a certain component in a mixture. However, CR 61-CMP-447 showed a very low styrene/ethylbenzene separation factor, indicating the absence of the competitive transport. It was likely that morphology of the membrane was mainly responsible for the low separation factor. With the homogeneous distribution of Ag^+ ions within the membrane matrix, the carriers were accessible for ethylbenzene although styrene was present in the feed. In addition, it could be rationalized that, relative to the amount of carrier in the membrane, the distribution of carrier was more important to the competitive transport.

Finally, although decreasing temperature from 25 to 10 °C resulted in a lower diffusive flux, an increase in facilitation effect was almost negligible. This was because the facilitated flux was also reduced by the similar degree.

Acknowledgements

Acknowledgement is made to The Thailand Research Fund for the support of this work through the postdoctoral grant No. PDF/05/2542. The authors gratefully acknowledge the kindness of the Ionics, for providing us with the membranes used in this study.

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