

Facilitated transport near the carrier saturation limit

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Abstract

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Permeation of ethylbenzene, styrene and 1-hexene through perfluorosulfonate ionomer membranes was carried out with the feed concentrations ranging from 1 M to pure. On comparison, fluxes of ethylbenzene through the Ag⁺-form membrane were the lowest. Only a small increase in ethylbenzene flux was observed after the feed concentration exceeded 3 M, indicating the existence of carrier saturation. The increase in styrene flux was suppressed to some degree at high concentration driving forces. In contrast, 1-hexene flux was the highest and continued to increase even at very high feed concentrations. After the experiments with pure feeds, extraction of the solutes from the membranes revealed that 62.5% of Ag⁺ ions reacted with 1-hexene as against 40.6% for styrene and 28.9% for ethylbenzene. Equilibrium constants, determined by distribution method, of 1-hexene, styrene and ethylbenzene were 129, 2.2 and 0.7 M⁻¹ respectively, which suggested that stability of the complex was a key factor in the carrier saturation phenomenon.

Key words : facilitated transport, Nafion[®], carrier saturation, equilibrium constant

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การถ่ายโอนเชิงแฟชิลิเตตในช่วงใกล้กับการอิ่มตัวของตัวพยา
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งานวิจัยนี้ศึกษาการแพร่ของเอทิลเบนซีน, สไตรีนและ 1-ເເກซື່ນຜ່ານເພວົ້າຟຸອອໂຮ້ລິໂພເນັດ ໂອໂໂນໂນເມວ່າ
ເມນເບຣນທີ່ຄວາມເຂັ້ມຂັ້ນສາງປົ້ນຕັ້ງແຕ່ 1 ໂມລາຣີ້ສິງສາງວິສຸກີ້ ພລຈາກການທົດລອງກັນເມນເບຣນທີ່ອູ້ຢູ່ໃນຮູບ Ag^+ ແສດ
ໄທ້ເຫັນວ່າເອທີເບນເບນເບນມີຄໍາຟລັກໜ້າຕໍ່ທີ່ສຸດ ແລະຟລັກໜ້າຈະເພີ່ມນ້ອຍນາກເນື້ອຄວາມເຂັ້ມຂັ້ນມີຄໍາເກີນ 3 ໂມລາຣີ້ສິ່ງແສດໄກ້
ເຫັນລຶ່ງການເກີດການອື່ນຕັ້ງອອງຕົວພາ ສ່ວນການເພີ່ມເຂັ້ນອອງຟລັກໜ້າຂອງສໄຕຣີນ້ຳລົດລອງເຫັນກັນ ດ້ວຍຄວາມເຂັ້ມຂັ້ນອອງສາງປົ້ນ
ສູງ ຈຸນໃນທາງທຽບກັນຂ້າມ ຝລັກໜ້າຂອງ 1-ເເກຊື່ນມີຄໍາສູງທີ່ສຸດແລະຍັງຄອງເພີ່ມເຂັ້ນເຮືອງ ຈຸນເນື້ອຄວາມເຂັ້ມຂັ້ນອອງສາງປົ້ນເພີ່ມເຂັ້ນ
ຈາກການວິເຄາະທີ່ຄວາມເຂັ້ມຂັ້ນອອງຕົວລູກລະຄາທີ່ອູ້ຢູ່ໃນເມນເບຣນທີ່ໃຫ້ໃນການທົດລອງກັນສາງປົ້ນທີ່ເປັນສາງວິສຸກີ້ແສດ
ໄທ້ເຫັນວ່າເປົອຮັ້ນຕົ້ນຂອງ Ag^+ ໃນເມນເບຣນທີ່ທຳປົງກິກິວິຍາກັນ 1-ເເກຊື່ນເປັນ 62.5% ໃນຂະໜາດຂອງສໄຕຣີນແລະເອທີ
ເບນເບນເບນນັ້ນເປັນ 40.6% ແລະ 28.9% ຕາມລຳດັບ ສ່ວນຄໍາຄົງທີ່ສົມຄຸລູດອອງການເກີດສາງປະກອນເຊີ້ງຂ້ອນຂອງ 1-ເເກຊື່ນ,
ສໄຕຣີນແລະເອທີເບນເບນເບນຄືອ 129, 2.2 ແລະ 0.7 ໂມລາຣີ-1 ຕາມລຳດັບ ຈິ່ງແສດໄກ້ໄທ້ເຫັນວ່າຄວາມເສີ່ຍ່າຍອອງສາງປະກອນ
ເຊີ້ງຂ້ອນເປັນປັງຈິຍລຳຄັ້ນປະກາດທີ່ສ່ວງຜົກກະທຸນທີ່ອ່ານວິເຄາະ

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A reversible complexation between the solutes and the carriers, which are embedded within the polymer matrix, preferentially enhances the solute flux through the facilitated transport membranes. Because of the reversible reaction, permeation flux of a facilitated transport is not always proportional to the concentration driving force across the membrane (Way and Noble, 1992). At very high driving forces, the number of carriers complexed with solutes approaches the upper limit. A further increase in the driving force can only increase the flux through the solution-diffusion pathway. Under these conditions, known as carrier saturation, separations by facilitated transport membranes become less effective.

An application of the facilitated transport membranes that has long been of interest for many years is the separation of unsaturated hydrocarbons. Ag^+ is most used as the carrier in the membrane because of its effectiveness in facilitating the transport of unsaturated hydrocarbons. The membrane, however, requires the presence of a polar solvent such as water to promote the reaction between Ag^+ ions and the solutes. Despite extensive research on the facilitated

olefin transport using Ag^+ -containing membranes (Koval and Spontarelli, 1988; Koval *et al.*, 1989; Koval *et al.*, 1992; Thoen *et al.*, 1994; Kohls *et al.*, 1997; Goering *et al.*, 1998; Goering *et al.*, 2000), an in-depth study of carrier saturation phenomenon has not been reported.

In the present work, facilitated transport of liquid-phase unsaturated hydrocarbons at very high concentration driving forces was investigated. The experiments were performed with the aim of obtaining knowledge of the effect of complex stability on carrier saturation.

Materials and Methods

Chemicals

Perfluorosulfonate ion-exchange membrane, commercially known as Nafion®, was purchased from Aldrich (Milwaukee, WI). Equivalent weight, defined as grams of dry Nafion per mole of exchange sites, was 1100. Silver nitrate, 99+, sodium nitrate, 99%, and sodium hydroxide, 97+, were certified A.C.S. grade. Purity of styrene, ethylbenzene, and 1-hexene was 99%, 99.5%, and 98% respectively. Isooctane (2,2,4-

trimethylpentane) 99% was used as a solvent for the unsaturated hydrocarbons. Purity of glycerol used for heat-treatment of the membrane was 99+. Purified and deionized water was used in all experiments.

Membrane preparation and characterization

The membrane was prepared by thoroughly washing an as-received H⁺-form Nafion® with water. The membrane was then immersed in a 1 M aqueous NaOH solution for 6 hours to obtain a Na⁺-form membrane. After being rinsed with water, the membrane was immersed in glycerol at 130 °C for 15 minutes and allowed to cool slowly, at the rate of about 1 °C/min to room temperature. The membrane was subsequently heated in boiling water for 30 minutes to remove glycerol. The membrane was converted to Ag⁺-form by ion-exchanging in a 1 M aqueous AgNO₃ solution for 6 hours. The film was repeatedly rinsed with water to remove the excess solution.

The water content of the membrane was obtained by first weighing a dry membrane, which was placed in a vacuum oven at 50 °C for 5 hours. The membrane was hydrated by immersing in DI water until a constant weight was reached. The weight of water in the membrane was obtained from the weight difference between the water-saturated and the dry films. Water content, calculated as the weight ratio of water to hydrated membrane, was 22.4%. Given the Nafion® equivalent weight of 1100, the calculated concentration of Ag⁺ in the membrane was 3.15 M.

Transport measurements

The flux measurement cell was described previously (Sungpet *et al.*, 2002). All permeation tests used single feed solutions and were done at 25 °C. The feed side was the solution of unsaturated hydrocarbon in isoctane, and the receiving side was isoctane. Both feed and receiving solutions were saturated with water, preventing the loss of water from the membrane during the operation. The two compartments of the flux measurement cell were separated by Nafion® 117 membrane. The area of the membranes exposed

to the feed and receiving solutions was 4.524 cm². The solute concentration in the receiving side was analyzed by periodically injecting 1 µl of the receiving solution into a gas chromatograph. The solute fluxes were obtained by calculating the concentration of the hydrocarbons appearing in the receiving reservoir per unit time and unit area of membrane. Figure 1 shows typical data for the concentration of solute in the receiving side as a function of time.

Solute extraction

After the flux measurement with pure feeds, the concentration of solute in Nafion® was determined by first rinsing the membrane with isoctane to remove solute from the surface. The film was then put into 30 ml of pure isoctane. The extract was analyzed using gas chromatography until the concentration of the extract remained unchanged. The solute concentration in the film was calculated by assuming that the solutes resided only in the water-containing regions of the membrane.

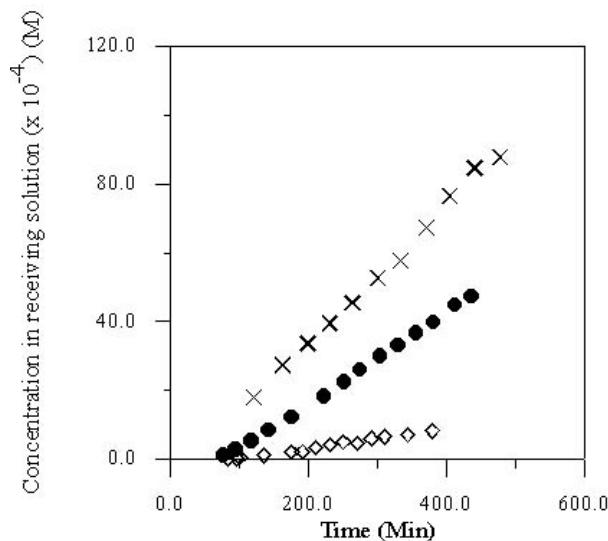


Figure 1. The concentration of solutes in the receiving side as a function of time obtained from the experiments with 1M feed solutions: styrene (●), ethylbenzene (◇), 1-hexene (X)

Determination of equilibrium constants

The equilibrium constants of the complexation between the unsaturated hydrocarbons and Ag^+ at 25 °C were determined by distribution method (Hartley, 1973; Winstein and Lucas, 1938). Briefly, 3 cm³ of 1 M aqueous AgNO_3 solution was mixed with 3 cm³ of 0.1 M of unsaturated hydrocarbon in isoctane. The mixture was settled for 5 hours, allowing the reaction to reach equilibrium. The concentration of the unsaturated hydrocarbon in the organic phase was then analyzed by gas chromatography. To obtain the distribution ratio, 1 M solution of NaNO_3 was used as the aqueous phase.

Results and discussion

Na^+ -form membranes

As Na^+ ions were unable to react with the unsaturated hydrocarbons, the permeation measurements carried out with the Na^+ -form membrane served as the control experiments. Fluxes of ethylbenzene, styrene and 1-hexene linearly increased with the feed concentration as shown in Figure 2, indicating the mass transfer through solution-diffusion mechanism.

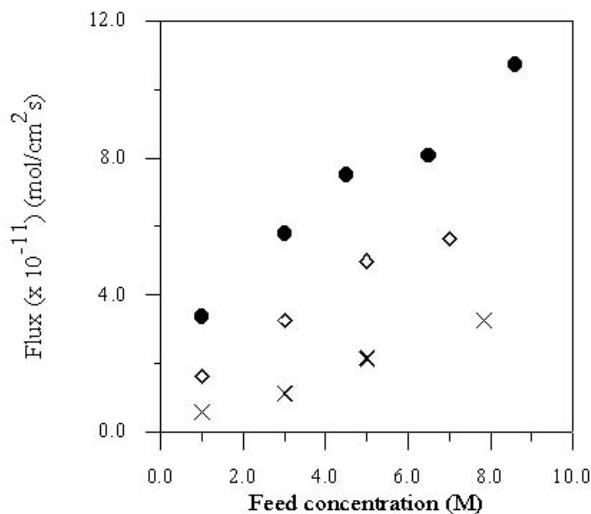


Figure 2. Flux of styrene (●), ethylbenzene (◇), 1-hexene (×) through Na^+ -form Nafion[®] 117.

It was very likely that the transport of solutes occurred in the hydrated region because fluorocarbon-natured polymer of Nafion[®] had very little affinity for the hydrocarbons. There was strong evidence to suggest that the hydrocarbons were not highly soluble into the fluorocarbon backbone. Upon contacting with the hydrocarbons, the water-free membrane was swollen to negligible degree. In addition, it was previously found that permeability of olefin through the dry Na^+ -form Nafion[®] was exceedingly low (Sungpet et al., 2001).

Ag^+ -form membranes

Figure 3 presents the fluxes through the Ag^+ -form membrane, which are significantly higher than those obtained from the Na^+ -form membrane. Increase in the driving force beyond 3 M had very little effect on ethylbenzene flux, suggesting the onset of carrier saturation. A similar flux characteristic was also found with styrene. Nevertheless, it was probable that the carriers were not completely saturated. Close examination of the data would reveal that, in comparison with the Na^+ -form membrane, the Ag^+ -form membrane showed a slightly greater in-

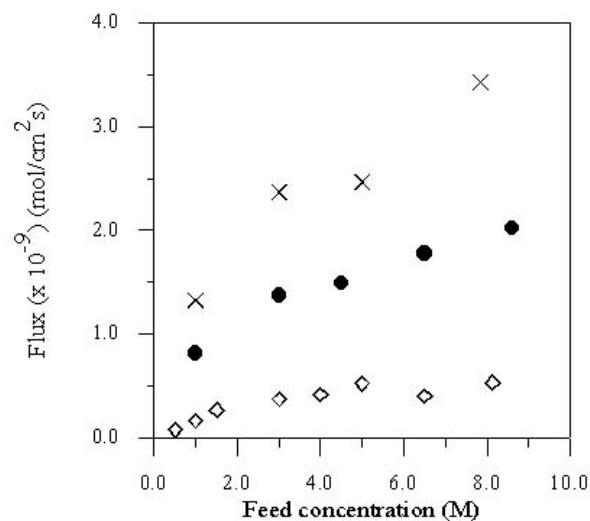


Figure 3. Flux of styrene (●), ethylbenzene (◇), 1-hexene (×) through Ag^+ -form Nafion[®] 117.

crease in the styrene flux upon the increase in the feed concentration. This indicated that the carriers were able to further enhance the transport of styrene across the membrane. On comparison, 1-Hexene showed the highest flux. In addition, the flux continued to significantly increase even at high feed concentrations. It was evidence that facilitation effect had not reached its maximum capability.

The effectiveness of the facilitated transport could be quantified by facilitation factor, calculated as the ratio of the total flux with the Ag^+ carrier present to the diffusional flux. As shown in Figure 4, the facilitation factors of 1-hexene were the highest, indicating that 1-hexene was effectively transported by the carriers.

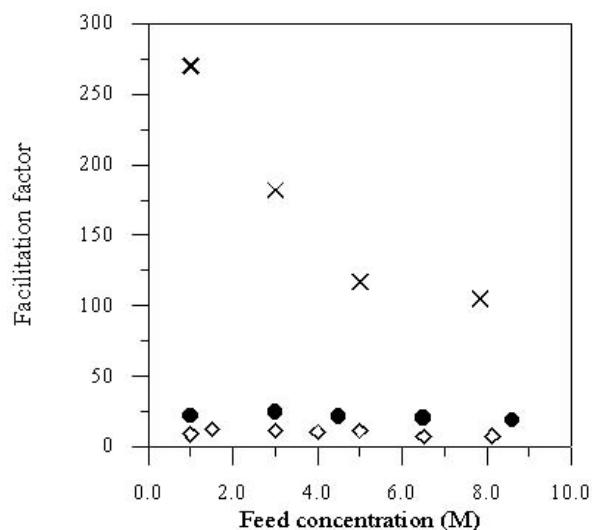


Figure 4. Facilitation factor of styrene (●), ethylbenzene (◇), 1-hexene (×).

In contrast, the facilitation factors of ethylbenzene were the lowest.

Extraction of the solutes from the membranes provided an insight into the amount of carriers taking part in facilitated transport. Table 1 presents the concentrations of solutes in the membranes from the experiments carried out with pure feeds. Providing that the carriers and solutes likely formed 1:1 complexes (Beverwijk *et al.*, 1970), the percentage of Ag^+ ions reacting with the solutes was reasonably estimated as the difference between the solute concentration in Ag^+ and Na^+ -form membranes. The results revealed that not all carriers involved in the transport even at very high feed concentrations. Only a small proportion of Ag^+ ions in the membrane complexed with ethylbenzene even though there was an indication of carrier saturation. Apparently, the condition for the carrier saturation to occur was not that all the carriers were occupied by the solutes.

There was a good correlation between the flux characteristic and equilibrium constant, K_{eq} , of the complex formation. The equilibrium constant of Ag^+ -1-hexene complexation, determined by distribution method, was 129 M^{-1} , while those of styrene and ethylbenzene were 2.2 and 0.7 M^{-1} respectively. On comparison, 1-hexene formed the most stable complex with Ag^+ and correspondingly showed the highest flux and facilitation factor. In contrast, the low stability of the ethylbenzene- Ag^+ complex was unfavorable for the facilitated transport. The results also suggested that the solute complexed weakly with the carrier was susceptible to the carrier saturation. However, it should be noted that if a solute formed a highly

Table 1. Solute concentrations in Ag^+ and Na^+ -form membranes and the amount of Ag^+ ions complexed with solutes

Solute	Concentration of solute in Ag^+ -form membrane (M)	Concentration of solute in Na^+ -form membrane (M)	Concentration of complexed Ag^+ ions (M)	Percentage of Ag^+ complexed with solute (%)
1-Hexene	2.19	0.22	1.97	62.5
Styrene	1.62	0.34	1.28	40.6
Ethylbenzene	1.14	0.23	0.91	28.9

stable complex with carrier, the solute would not be rapidly released from the carrier. Under this condition, the effective diffusion coefficient of the solute was greatly reduced and facilitation effect could be minimal. In fact, it was previously found that a highly stable complexation was responsible for a lack of facilitation effect (Sungpet *et al.*, 2002).

Conclusions

Facilitated transport of styrene, ethylbenzene and 1-hexene at high driving forces was investigated by using Nafion® incorporated with Ag⁺ ions as carriers. Experiments carried out with the Na⁺-form membranes provided information on the solution-diffusion permeation.

A high correlation between the facilitated flux characteristics and stability of the complex was found. Based on the equilibrium constant of 0.7 M⁻¹, ethylbenzene weakly formed complex with Ag⁺ and was not effectively transported by reactive pathway. At high feed concentrations, a very small increase in ethylbenzene flux was observed, which was an indication of carrier saturation. After the experiments with pure feed, extraction of ethylbenzene from the membranes revealed that there were a large number of unoccupied carriers in the membrane. Styrene had a slightly higher equilibrium constant, 2.2 M⁻¹, but to a degree underwent a decline of the increase in flux at high feed concentrations. In contrast, 1-hexene was able to form a relatively more stable complex with Ag⁺ and its transport showed no evidence of carrier saturation. Furthermore, the number of Ag⁺ ions taking part in the transport of 1-hexene was much greater than that of ethylbenzene. The number of Ag⁺ ions reacting with the solutes was evidently dependent on the stability of the complexes.

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