

Facilitated transport near the carrier saturation limit

Anawat Sungpet¹, Songpol Wongirung²,
Veerapol Seearamroongruang², and Natcha Kamphangseree²

Abstract

Sungpet, A., Wongirung, S., Seearamroongruang, V., and Kamphangseree, N.
Facilitated transport near the carrier saturation limit
Songklanakarin J. Sci. Technol., 2002, 24(Suppl.) : 907-913

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

¹Ph.D. (Chem. and Petro. Ref. Eng.), Asst. Prof., ²B.E. (Chem. Eng.), Department of Chemical Engineering, King Mongkut's University of Technology Thonburi, Bangmod, Thung Khru, Bangkok 10140, Thailand.
Corresponding e-mail : anawat.sun@kmutt.ac.th

Received, 14 January 2003

Accepted, 13 June 2003

บทคัดย่อ

อนวัช สังข์เพชร ทรงพล วงศ์จิริง วีรพล สือรัมย์รุ่งเรือง ณัชชา กำแพงเสรี
การถ่ายโอนเชิงแพซิทีเทตในช่วงใกล้กับการอิ่มตัวของตัวพา
ว.สงขลานครินทร์ วทท. 2545 24(ฉบับพิเศษ): 906-912

งานวิจัยนี้ศึกษาการแพร่ของเอทิลเบนซีน, สไตรีนและ 1-เฮกซีนผ่านเพอร์ฟลูออโรซัลโฟเนต ไอโอโนเมอร์ เมมเบรนที่ความเข้มข้นสารป้อนตั้งแต่ 1 โมลาร์ถึงสารบริสุทธิ์ ผลจากการทดลองกับเมมเบรนที่อยู่ในรูป Ag^+ แสดงให้เห็นว่าเอทิลเบนซีนมีค่าฟลักซ์ต่ำที่สุด และฟลักซ์จะเพิ่มขึ้นเล็กน้อยเมื่อความเข้มข้นมีค่าเกิน 3 โมลาร์ซึ่งแสดงให้เห็นถึงการเกิดการอิ่มตัวของตัวพา ส่วนการเพิ่มขึ้นของฟลักซ์ของสไตรีนนั้นลดลงเช่นกัน ณ ความเข้มข้นของสารป้อนสูง ๆ ในทางตรงกันข้าม ฟลักซ์ของ 1-เฮกซีนมีค่าสูงที่สุดและยังคงเพิ่มขึ้นเรื่อย ๆ เมื่อความเข้มข้นของสารป้อนเพิ่มขึ้น จากการวิเคราะห์ความเข้มข้นของตัวถูกละลายที่อยู่ในเมมเบรนที่ใช้ในการทดลองกับสารป้อนที่เป็นสารบริสุทธิ์แสดงให้เห็นว่าเปอร์เซ็นต์ของ Ag^+ ในเมมเบรนที่ทำปฏิกิริยากับ 1-เฮกซีนเป็น 62.5% ในขณะที่ของสไตรีนและเอทิลเบนซีนนั้นเป็น 40.6% และ 28.9% ตามลำดับ ส่วนค่าคงที่สมดุลของการเกิดสารประกอบเชิงซ้อนของ 1-เฮกซีน, สไตรีนและเอทิลเบนซีนคือ 129, 2.2 และ 0.7 โมลาร์⁻¹ ตามลำดับ ซึ่งแสดงให้เห็นว่าความเสถียรของสารประกอบเชิงซ้อนเป็นปัจจัยสำคัญประการหนึ่งซึ่งส่งผลกระทบต่อเกิดการอิ่มตัวของตัวพา

ภาควิชาวิศวกรรมเคมี มหาวิทยาลัยเทคโนโลยีพระจอมเกล้าธนบุรี ทุ่งครุ กรุงเทพฯ 10140

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 isooctane, and the receiving side was isooctane. 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 isooctane to remove solute from the surface. The film was then put into 30 ml of pure isooctane. 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.

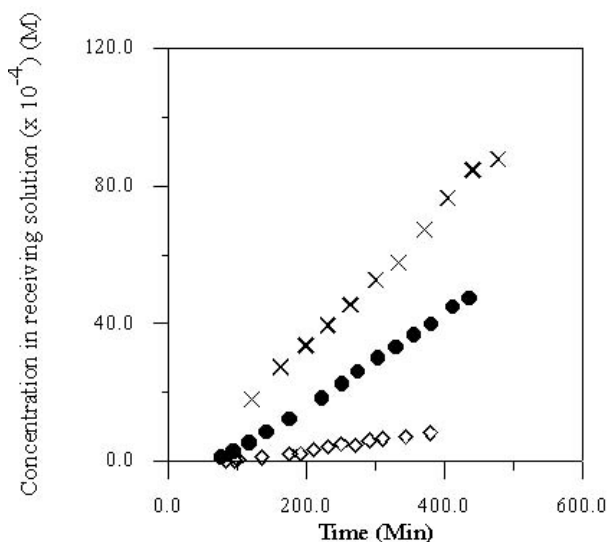


Figure 1. The concentration of solutes in the receiving side as a function of time obtained from the experiments with 1M feed solutions: styrene (●), ethylbenzene (◇), 1-hexene (×)

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 isooctane. 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.

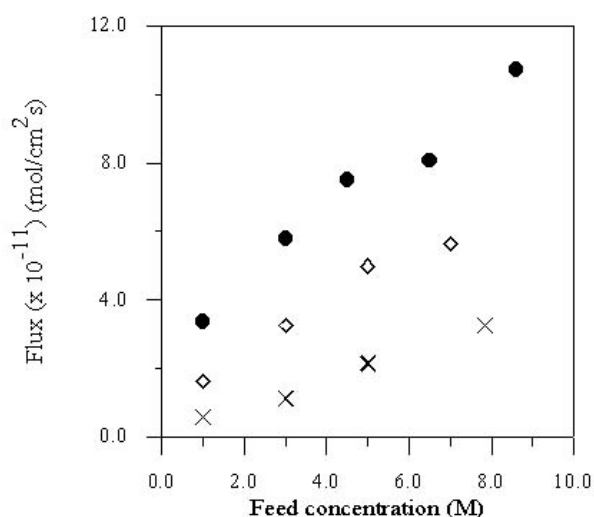


Figure 2. Flux of styrene (●), ethylbenzene (◇), 1-hexene (×) through Na^+ -form Nafion[®] 117.

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-

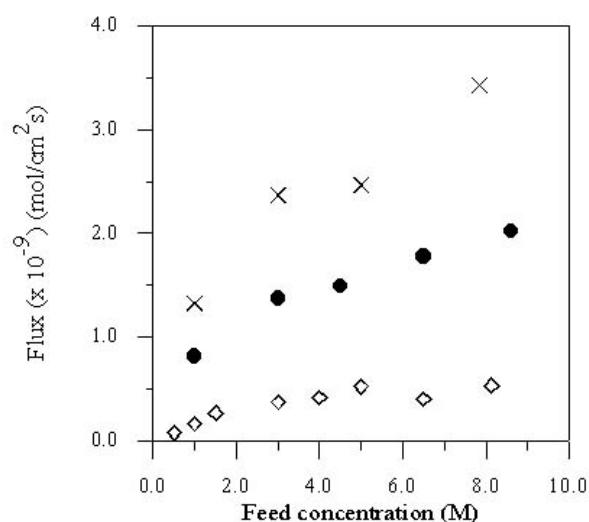


Figure 3. Flux of styrene (●), ethylbenzene (◇), 1-hexene (×) through Ag^+ -form Nafion[®] 117.

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.

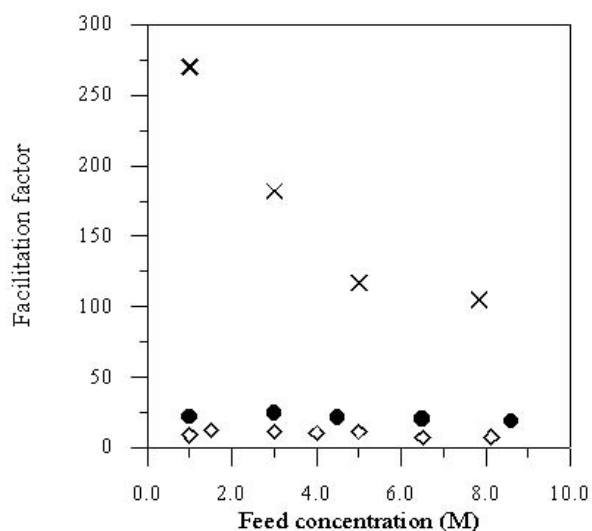


Figure 4. Facilitation factor of styrene (●), ethylbenzene (◇), 1-hexene (×).

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.

Acknowledgment

The authors would like to thank Mr. Panya Meesilpa for his help on the experiments.

References

- Beverwijk, C.D.M., Van Der Kerk, G.J.M., Leusink, A.J. and Noltes, J.G. 1970. Organosilver chemistry. *Organometal. Chem. Rev. A. 5*: 215-280.
- Goering, R.M., Bowman, C.N., Koval, C.A., Noble, R.D. and Ashley, M.E. 2000. Complexation structure and transport mechanism of 1,5-hexadiene and 1-hexene through silver facilitated transport membranes. *J. Membrane Sci.* 172: 49-57.
- Goering, R.M., Bowman, C.N., Koval, C.A., Noble, R.D. and Williamson, D.L. 1998. Role of ion-exchange membrane morphology and sorption properties in facilitated transport di-olefin/mono-olefin separations. *J. Membrane Sci.* 144: 133-143.
- Hartley, F.R. 1973. Thermodynamic data for olefin and acetylene complexes of transition metals. *Chem. Rev.* 73(2): 163-190.
- Kohls, S.L., Noble, R.D. and Koval, C.A. 1997. Effects of molecular structure and equivalent weight on facilitated transport of alkenes in Ag(I)-PFSI membranes. *J. Membrane Sci.* 125: 61-73.
- Koval, C.A. and Spontarelli, T. 1988. Condensed phase facilitated transport of olefins through an ion exchange membrane. *J. Am. Chem. Soc.* 110: 293-295.
- Koval, C.A., Spontarelli, T. and Noble, R.D. 1989. Styrene/ethylbenzene separation using facilitated transport through perfluorosulfonate ionomer membranes. *Ind. Eng. Chem. Res.* 28: 1020-1024.
- Koval, C.A., Spontarelli, T., Thoen, P. and Noble, R.D. 1992. Swelling and thickness effects on the separation of styrene and ethylbenzene based on facilitated transport through ionomer membranes. *Ind. Eng. Chem. Res.* 31: 1116-1122.
- Sungpet, A., Way, J.D., Koval, C.A. and Eberhart, M.E. 2001. Silver doped Nafion-poly(pyrrole) membranes for facilitated permeation of liquid-phase olefins. *J. Membrane Sci.* 189: 271-279.
- Sungpet, A., Pimsert, A., Jiratananon, R. and Way, J.D. 2002. Facilitated transport of unsaturated hydrocarbons through crosslinked-poly(sulfonated styrene). *Chem. Eng. J.* 87: 321-328.

- Sungpet, A., Saithong, T. and Kalapanulak, S. 2002. Blocking phenomenon in permeation of amines through perfluorosulfonate ionomer containing metal(II) ions. *J. Membrane Sci.* 202: 81-87.
- Thoen, P.M., Noble, R.D. and Koval, C.A. 1994. Unexpectedly large selectivities for olefin separations utilizing silver ion in ion-exchange membranes. *J. Phys. Chem.* 98: 1262-1269.
- Way, J.D., Noble, R.D. 1992. Chapter 44 Facilitated transport. **In** *Membrane Handbook*. pp. 833-866. (eds. W.S. Ho and K.K., Sirkar), New York : Van Nostrand Reinhold.
- Winstein, S. and Lucas, H.J. 1938. The coordination of silver ion with unsaturated compounds, *J. Am. Chem. Soc.* 60: 836-847.