Membrane Materials as Ligands for Ag(I) Ions: Design and Use for Hydrocarbon Separations.

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Summary: The selectivity and reversibility of the reaction with Ag(I) makes it potentially interesting for separating alkenes and arenes from hydrocarbon mixtures, which is an energy-intensive industrial process. Adaptation of Ag(I) complexation chemistry for use in membrane separations has many challenges. We have investigated many aspects of Ag(I)-containing facilitated transport membranes. Recent results on the preparation and characterization of composite membrane materials are described.

Motivation/Membrane Processes

Their reversible complexation reaction with Ag(I) (1, 2) can be used to separate unsaturated hydrocarbons (alkenes and arenes) from their saturated analogs. At present, the separation of saturates from unsaturates is carried out on distillation columns which require large inputs of energy. At present, distillation is the main industrial process for performing separations of unsaturates from saturates. There are over 40,000 distillation columns in the USA performing 95 % of all industrial separations (3). Table 1 points out

Table 1. Examples of Separations of Unsaturated Hydrocarbons (Chemical and Engineering News, April 8, 1996)

Compound	Rank	'95 Production (billion of lb)	Boiling Points (C)
Ethene	4	47.0	-104
Ethane	-		-88
Propene	9	25.7	-48
Propane	-		-42
Butadiene	36	3.7	-4.5
1-Butene	-		-6.3
Butane	-		-.05
Benzene	16	16.0	80
Cyclohexane	47	2.1	81
Ethylbenzene	19	13.7	136
Styrene	20	11.4	145

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to a few statistics on chemicals that are mass produced in the USA. Due to similar boiling points for groups of chemicals listed in this table (ethene/ethane, propene/propane, etc.), the energy penalty paid to separate close boiling hydrocarbons using distillation is enormous. In contrast to distillation, membrane separations can be very selective and energy-efficient. For this reason, there is current interest in developing membrane materials that can perform separations of unsaturated hydrocarbons so that distillation can be replaced or modified in a membrane/distillation hybrid process (4).

As shown in Table 2, the ability of a membrane to perform a particular separation is usually characterized by three different factors: productivity, selectivity and cost. In many cases, implementation of membrane processes is limited by the stability of the membrane under industrial conditions which results in an unacceptably high cost.

Table 2. Membrane Performance Characteristics

Productivity
- Proportional to the fluxes (mol cm^{-2} sec^{-1} or kg m^{-2} hr^{-1}) through membranes
- Increases with increasing concentration driving force
- Inversely proportional to membrane thickness

Selectivity
- How fast one component goes through compared to other components
- Usually a trade-off with productivity

Cost (Stability)!!!
- Includes the costs of manufacturing and periodically replacing the membrane
- Generally, the biggest problem with facilitated transport membranes

Complexation-Based/Facilitated Transport Membranes (FTMs)

There are three basic types of membrane materials (5). Filtration membranes achieve separations based on filtration of species with different molecular sizes. Filtration membranes, especially those manufactured from porous inorganic materials, can be very stable even at elevated temperatures. However, filtration membranes can not achieve high selectivity for many hydrocarbon separations. These separations are performed using dense, non-porous membranes that separate solutes according to a solution/diffusion mechanism. For hydrocarbon separations, non-porous polymer membranes often become plasticized, which usually results in decreased selectivity. Furthermore, the difference in solubility and diffusion coefficient for the components in many hydrocarbon mixtures is not great. Facilitated transport membranes (FTMs) operate by a carrier mediated transport mechanism. The simplest type of FTM contains a carrier dissolved in a liquid which is supported physically on a macroporous support. Although the performance of liquid FTMs is usually acceptable in terms of productivity and selectivity, they usually exhibit very poor stability which translates into high cost.

In addition to improving stability, there are issues related to choosing the appropriate complexing agent to act as the carrier in an FTM. These issues are well understood due to modeling optimization studies (6). As shown in Table 3, the choice of carrier must be optimized with respect to dimensionless parameters related to the thermodynamics, kinetics and mobility of the species involved in the separation process.

Table 3. Dimensionless Parameters That Effect the Choice of Carriers for FTMs

Thermodynamic Ratio

-A_o = concentration of A in membrane due to partitioning from feed phase should be low for high selectivity from carrier

- $K_d = A_o\,Keq = [AC] / [C]$ = complexed carrier/uncomplexed carrier; should have a value of about 10

Kinetic Ratio

- D = diffusion coefficient; L = membrane thickness
- $D_{AC} / k_{-1}L^2$ = reaction time / diffusion time
- should be << 1, but high productivity only if L is small

Mobility Ratio

- $D_{AC}\,[C]_{tot} / (D_A{*}A_o) = \dfrac{\text{diffusion rate times total carrier concentration}}{\text{diffusion rate times solute concentration in membrane}}$
- should be >> 1 (more carrier than solute)

Polar Polymer and Ionomer Membrane Based FTMs

Although the soft Lewis acid/base interactions between Ag(I) ions and the double- or triple bonds in unsaturated hydrocarbons are weak, these reactions often satisfy the criteria listed in Table 3 fairly well. Therefore, most of the attempts to develop FTMs for hydrocarbon separations have involved Ag(I) ions. Although early work in this area involved supported liquid membranes (7, 8, 9), most of the recent reports involve the use of polar polymers containing Ag(I) salts (10, 11), or Ag(I) ions exchanged into ionomer membrane materials. The obvious advantage of polymer membranes with respect to supported liquid membranes is improved stability. Polymer membranes are mechanically stable and in some cases are fairly resistant to the loss of water or other solvents which are necessary for high productivity. Furthermore, loss of Ag(I) from ionomer membranes is prevented by electrostatic forces in the absence of other exchangeable cations.

What is even more interesting is that the environment of Ag(I) in these materials is often altered significantly from free solution. Therefore, one occassionally observes the ability to perform separations that would not be possible for Ag(I) supported liquid membranes. Over the past decade, our group has documented a variety of "unexpected" separations involving Ag(I) in perfluorosulfonic acid ionomer membranes such as DuPont's Nafion (12). As a result of attempts to understand these unusual results, we have obtained evidence suggesting that the morphology and interfacial area present in these materials has dramatic effects on the Ag(I) complexation reactions and on the mechanism of transport of unsaturated hydrocarbons (13, 14). Although these results were interesting, the high cost and low porosity for the ionomer materials make them impractical for commercial applications. Therefore, our recent research has involved attempts of prepare composite membrane materials which will, hopefully, display useful abilities to separate unsaturated hydrocarbons but will be more productive and less expensive.

Preparation of AMPSA/PE Composite Membranes

Current research focuses on understanding and developing composite facilitated transport membranes (FTMs) using thin, hydrophobic, porous supports filled with cation exchange polymers. Due to the variety of porous support materials and monomer molecules that can be placed and polymerized inside these supports, FTMs are excellent candidates for a variety of studies. For example, thin sheets of porous polyethylene (PPE) are available in different pore sizes and different pore densities, enabling us to study the effects of interfacial area (area between the support and polymer) on membrane performance. Membrane support morphology, pore geometry, and monomer choice are some additional variables that might affect membrane efficiency. Table 4 lists a number of PPE supports used in our lab. They are obtained from 3M corporation.

Table 4: Porous Polyethylene Supports obtained from 3M

Membrane type	Thickness (microns)	Percent Void Space	Pore diameter (microns)
933-1A	**53.3**	**84**	**0.75**
1167-1E	**53.3**	**80**	**0.22**
1246-5-9	**45.7**	**69**	**0.12**
R1192-4	20.3	81	0.14
R1240-4C	127	88	1.10
R839-3B	6.4	76	0.62

Ultimately, we want to understand the effect of each variable on FTM performance and be able to tailor FTMs based on the need to separate specific compounds. Most of the composite FTMs used in our lab are prepared by polymerizing and crosslinking 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPSA) inside porous polyethylene (PPE) supports. This is accomplished by dissolving the monomer in an appropriate solvent, painting the PPE support with the monomer mixture, and then placing the monomer containing support in a polyethylene bag flushed with nitrogen (15). Thereafter, the sample is exposed to UV radiation (365 nm) which starts the polymerization of AMPSA. Solvent choice is very important not only because it has to dissolve the monomer, crosslinker, and initiator molecules, but also because it has to wet the highly hydrophobic polyethylene support. Even though the membrane preparation process is very simple and straightforward, a few steps need to be taken in order to obtain functional membranes. First, the solvent has to be a relatively non-volatile substance in order to avoid solvent evaporation before exposing the membrane to light. Second, wiping procedures used to remove excess monomer solution from the surface of the PPE have to be gentle enough in order to avoid wicking the monomer solution from the pores of the PPE support. Similarly to Nafion membranes, AMPSA-PPE membranes are readily exchangeable with silver ions and stable over periods of, at least, three weeks. Typical concentrations of silver ions in AMPSA-PPE membranes range from 3-5 M. Currently, membrane characterization is performed using middle and near infrared (IR) spectroscopy and scanning electron microscopy (SEM).

Preliminary Transport Experiments

Transport experiments are performed in a U-shaped glass cell that is split along the middle to allow for membrane placement. One side of the cell contains isooctane as the receiving solution (sweep side), while the other side of the cell (feed side) contains solutes dissolved in isooctane. Transport of solutes occurs from the feed to the sweep side of the cell. As shown in Table 5, fluxes of olefins through silver exchanged AMPSA-PPE membranes increase substantially upon exchanging the membrane with silver ions. Most promising separation factors were obtained for mixtures of 1,5-hexadiene/1-hexene, and benzene/cyclohexane. Even though Ag+ form AMPSA-PPE membranes showed a 4-fold increase in separation factors for styrene/ethylbenzene mixtures, the absolute value of this number was too low for any practical applications. The increase in separation factors for mixtures containing 1-hexene/n-hexane were negligible.

Table 5. Separation Factors for Na+ and Ag+ AMPSA-PPE membranes

Feed Mixture	Membrane	Competitive Separation Factors*	
		Na+	Ag+
1,5-hexadiene/1-hexene	AMPSA-PPE	3.30	15.80
Benzene/cyclohexane	AMPSA-PPE	6.00	11.20
Styrene/ethylbenzene	AMPSA-PPE	1.56	5.30
1-hexene/n-hexane	AMPSA-PPE	3.10	4.00

* Obtained by performing transport experiments with two compounds in the feed.

Next, AMPSA-PPE membranes prepared on supports having different pore sizes were used to study the effects of pore surface area on membrane performance. As a natural extension of studies performed on Nafion membranes, present research tries to precisely determine the effect of interfacial area between the polymer and the support material on membrane fluxes and separation factors. Preliminary transport experiments for 1,5-hexadiene/1-hexene and benzene/cyclohexane mixtures were performed on three, silver and sodium exchanged AMPSA-PPE membranes having different pore sizes. All three membranes (boldfaced characters in Table 4) contained approximately the same silver and sodium ion concentrations (~3.5M) and were, approximately, the same thickness. Separation factors for both mixtures followed a trend quite opposite of what we expected. Figure 1 shows that the separation factors for 1,5-hexadiene/1-hexene mixtures decreased as the interfacial area increased (pore size decreased). This observation was in contrast to the expectation that smaller pore sizes (larger surface areas) should provide greater interfacial area for alkene transport and, therefore, greater separation factors. The same was observed for mixtures of benzene/cyclohexane. Either we were not forming a defined interfacial area consisting of sulfonate groups oriented towards the PPE, or the role of interfacial area was not as important as we thought it to be. In order to investigate the first point, a detailed look at the polymerization process was needed.

Use of Grafting Polymerization to Modify Interface

Polymerization of AMPSA molecules in the pores of PPE supports can follow two paths. Depending on the photoinitiator choice, AMPSA molecules can either react with each other to give a homopolymer of AMPSA (bulk polymerization), or they can react with the hydrophobic PPE support and other AMPSA molecules to give a combination of grafted AMPSA polymer and AMPSA homopolymer. Modifications of membranes using graft and bulk polymerization have been done in the past using a variety of acrylate-based monomers (16, 17, 18). Grafted polymerization is usually accompanied by bulk polymerization and the final yield of bulk AMPSA polymer vs. grafted AMPSA polymer depends on the kinetics of the two processes. Due to lack of any specific interactions between the sulfonate groups of AMPSA and the PPE, a

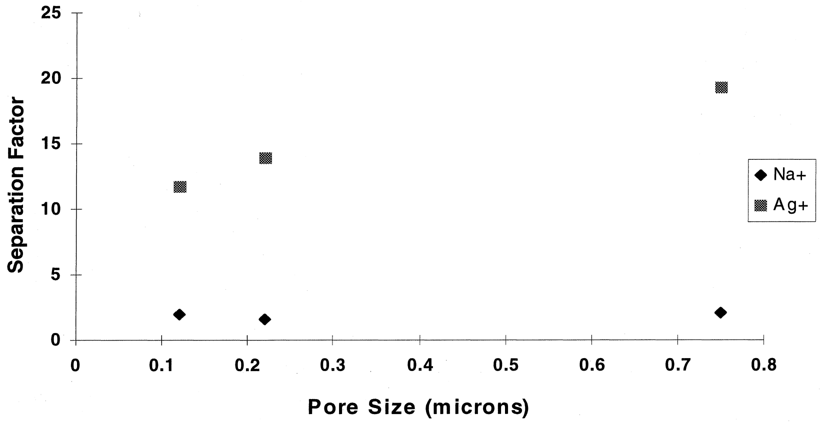

Figure 1: Plot of 1,5-hexadiene/1-hexene separation factors vs. membrane pore size through silver and sodium exchanged AMPSA-PPE membranes.

homopolymer of AMPSA will exhibit a random distribution of sulfonate groups throughout the pore volume. The lack of a well defined interfacial area, characterized by a high density of exchangeable sulfonate groups along the PPE pore walls, is one possible reason why there is no effect of pore size on separation factors for the bulk polymerized AMPSA-PPE membranes.

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