

## Olefin/paraffin solubility in a solid polymer electrolyte membrane

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The addition of silver tetrafluoroborate to a nylon-12/tetramethylene oxide block copolymer (PA12-PTMO) dramatically reduces paraffin solubility in the polymer electrolyte, contributing significantly to overall olefin/paraffin selectivity.

The potential for facilitated transport methods to efficiently perform industrially-important olefin/paraffin separations has resulted in considerable effort to harness this technology as a replacement for traditional distillation.<sup>1</sup> One of the most promising means of implementing such facilitated separation is based on solid polymer electrolyte membranes. These thin-film, solid-state devices offer mechanical stability, high gas fluxes, and an olefin carrier that remains active even in a water-free environment. Our original approach<sup>2</sup> of dissolving olefin-coordinating silver salts in polyether-based polymers continues to be expanded upon in recent work.<sup>3</sup>

While a number of reports have described the olefin/paraffin permeability and selectivity of solid polymer electrolyte membranes, there is surprisingly little solubility data for these systems. The few solubility studies available in the literature focus almost exclusively on olefin sorption, which is enhanced over that of the pure polymer due to complexation of olefin molecules with the carrier species (usually silver ions).<sup>4,5</sup> The effect of carrier addition on paraffin solubility, its impact on selectivity, and the extent to which solid polymer electrolyte membrane selectivity is controlled by elevated sorption or enhanced mobility of the olefin species are largely unknown.

In this work, we report a systematic investigation of ethylene and ethane solubility in a nylon-12 (20 wt%)/tetramethylene oxide (80 wt%) block copolymer (PA12-PTMO) containing varying amounts of AgBF<sub>4</sub>. These data provide fundamental insight into the operation of solid polymer electrolyte membranes.

Dense, isotropic films of PA12-PTMO/AgBF<sub>4</sub> were prepared by dissolving the polymer in ethanol to form a 2 wt% solution. The desired amount of AgBF<sub>4</sub> was added to this solution and mixed thoroughly. Films were solution-cast into a ring on a glass plate and dried at ambient conditions for 24 h. Nascent films were further dried under vacuum at 50 °C for 3 days before starting sorption experiments. Pure-gas ethylene and ethane solubility data were obtained with a dual-cell barometric sorption apparatus as described elsewhere.<sup>6</sup>

As illustrated in Figs. 1 and 2, addition of AgBF<sub>4</sub> has a dramatic effect on both ethylene and ethane solubility in PA12-PTMO. Sorption levels for ethylene increase systematically and substantially with increasing AgBF<sub>4</sub> content in the polymer. For example at 1 atm, the 50 wt% AgBF<sub>4</sub> sample sorbs 73 times more ethylene than pure PA12-PTMO. Such solubility enhancement for samples containing AgBF<sub>4</sub> is attributed primarily to the capacity of disassociated silver ions to form coordinate bonds with ethylene molecules.<sup>5</sup> In contrast, ethane solubility decreases significantly with increasing AgBF<sub>4</sub> concentration in PA12-PTMO. For example, the same 50 wt% AgBF<sub>4</sub> sample sorbs nearly an order of magnitude less ethane than the pure polymer. This 'salting-out' behavior for the solid polymer electrolyte seems reasonable given that the addition of silver salt likely increases the cohesive energy density of the

polymer matrix, undoubtedly rendering it less inviting to a nonpolar gas such as ethane. The resultant reduction in ethane solubility, previously overlooked, contributes significantly to the overall ethylene/ethane selectivity of the polymer electrolyte.

This point is demonstrated quantitatively in Table 1, which presents solubility coefficients and selectivities for ethylene and ethane in PA12-PTMO as a function of AgBF<sub>4</sub> content. In the absence of specific interactions between gases and a sorbing media, relative solubility typically scales with a measure of gas volatility, such as critical or boiling temperature. Ethylene and ethane solubility coefficients in pure PA12-PTMO are nearly equivalent, consistent with their similar relative volatilities.

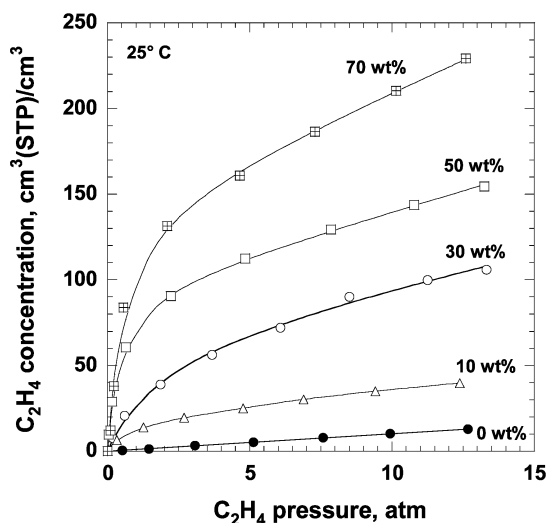


Fig. 1 Ethylene sorption isotherms in PA12-PTMO containing varying amounts of AgBF<sub>4</sub>.

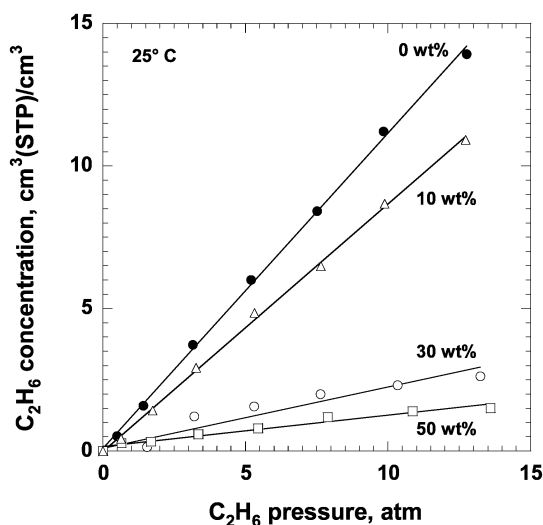


Fig. 2 Ethane sorption isotherms in PA12-PTMO containing varying amounts of AgBF<sub>4</sub>.

**Table 1** Ethylene/ethane solubility selectivity of PA12-PTMO at 25 °C and 1 atm

AgBF <sub>4</sub> content, wt%	Solubility, cm <sup>3</sup> (STP)/(cm <sup>3</sup> atm)		Selectivity
	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>4</sub> /C <sub>2</sub> H <sub>6</sub>
0	1.0	1.1	0.91
10	13	0.87	15
30	28	0.19	150
50	73	0.13	560
70	102	nd <sup>a</sup>	> 1000

<sup>a</sup> Not detectable — the sorbed amount is below the detection limit of our sorption system, which is approximately 0.10 cm<sup>3</sup>(STP)/(cm<sup>3</sup> atm).

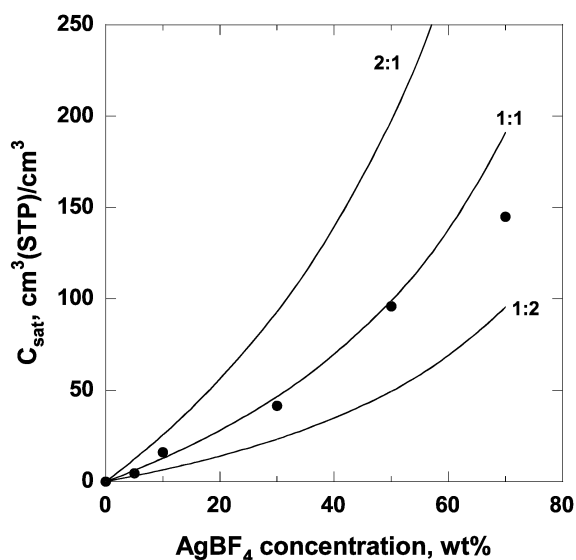
However, as silver concentration increases to the maximum loading, ethylene solubility is enhanced more than 100 times, whereas ethane solubility decreases nearly 10 times, finally dropping below experimental detection limits at 70 wt% AgBF<sub>4</sub>.

The sorption isotherms for ethane in all of the solid polymer electrolyte samples and ethylene in pure PA12-PTMO are linear, consistent with Henry's law and previous reports of gas solubility in this polymer.<sup>6</sup> In contrast, ethylene sorption isotherms in the silver containing samples are concave to the pressure axis and this curvature increases with increasing AgBF<sub>4</sub> content. Such behavior may be described by a dual sorption mechanism. In addition to Henry's law dissolution of ethylene into the polymer matrix, the olefin is also sorbed by the silver ions in Langmuir fashion; that is:

$$C = kp + C_{\text{sat}}bp/(1 + bp)$$

Here,  $C$  is the concentration of ethylene in the solid polymer electrolyte,  $p$  is the ethylene pressure in the contiguous gas phase,  $k$  is Henry's law constant,  $C_{\text{sat}}$  is the carrier saturation capacity, and  $b$  is an equilibrium constant. As AgBF<sub>4</sub> concentration in PA12-PTMO increases, ethylene sorption becomes increasingly dominated by Langmuir-type uptake caused by silver complexation.

From the ethylene isotherms in Fig. 1 and a dual-mode sorption analysis,  $C_{\text{sat}}$  may be calculated as a function of AgBF<sub>4</sub> content. These values from solubility measurements are compared in Fig. 3 to theoretical  $C_{\text{sat}}$  values based on silver loading and different ethylene-silver coordination numbers. For the theoretical  $C_{\text{sat}}$  values, each mole of silver loaded in PA12-PTMO was assumed to coordinate with two (2 : 1), one (1 : 1), or 0.5 (1 : 2) moles of ethylene. As illustrated, the measured



**Fig. 3** Carrier saturation ethylene capacity as a function of AgBF<sub>4</sub> content. The solid lines represent theoretical capacity for various ethylene : silver coordination numbers.

solubility data closely follow the theoretical line for 1 : 1 ethylene to silver coordination. This result suggests that at sorption equilibrium each mole of silver, loaded into the solid polymer electrolyte as AgBF<sub>4</sub>, is able to form coordinate bonds with one mole of ethylene molecules. Such behavior is consistent with silver-olefin complexation stoichiometry known to predominate in dilute aqueous salt solutions.<sup>7</sup>

Recently, we have reported that mixed-gas ethylene and ethane fluxes decrease as AgBF<sub>4</sub> content in PA12-PTMO membranes increases from 0 to roughly 65 wt%.<sup>8</sup> This result is initially surprising in light of the solubility data discussed above. Molecular transport through dense membranes generally follows a solution-diffusion mechanism, whereby the trans-membrane flux is a product of penetrant solubility in the membrane and penetrant mobility within the membrane. The fact that ethylene flux decreases over a silver content range where ethylene solubility increases 100-fold suggests that sorbed ethylene molecules have very low diffusivity in these membranes.

Such low olefin mobility may partially explain why the ethylene/ethane selectivity of PA12-PTMO membranes remains below 2 for AgBF<sub>4</sub> loadings of less than 65 wt%<sup>8</sup> in spite of the high ethylene solubility selectivities recorded in Table 1. An additional effect that could detract from ethylene/ethane selectivity is the impact of mixture conditions. The solubility selectivities recorded in Table 1 are taken from pure-gas measurements. Under mixture conditions, swelling of the membrane induced by high ethylene uptake will likely allow a greater amount of ethane to sorb than in the pure-gas experiments, thereby lowering the actual solubility selectivity.

The ethylene/ethane selectivity of PA12-PTMO membranes increases dramatically at silver loadings above 70 wt% AgBF<sub>4</sub> as the result of a sudden upturn in ethylene flux.<sup>8</sup> This percolation-type threshold, in concert with the low mobility of complexed ethylene below the threshold, lends credence to the theory that facilitated transport occurs in this solid polymer electrolyte only when the dissolved carrier species are sufficiently close to allow hopping of ethylene molecules from one carrier site to another.<sup>9,10</sup>

In summary, we have found that ethylene solubility is significantly increased while ethane solubility is dramatically reduced upon AgBF<sub>4</sub> addition to PA12-PTMO. The paraffin solubility reduction substantially enhances the olefin/paraffin solubility selectivity of the solid polymer electrolyte. Analysis of ethylene sorption data indicates that dissolved silver species form 1 : 1 coordinate bonds with ethylene molecules. These complexed ethylene molecules exhibit low mobility until the silver salt concentration exceeds 70 wt%, suggesting that this is the point at which the distance between carrier species is short enough to allow site to site hopping of ethylene molecules.

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