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Carbon-13 Nuclear Magnetic Resonance Study of the Separation of Styrene from Ethylbenzene by Dense Polymer Films

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We have discovered a simple correlation between the ability of a dense polymer film to separate styrene from ethylbenzene and the observed ^{13}C nmr line widths of the absorbed species. The correlation for the seven polymers listed in Table I is shown in Figure 1. The greater the observed ^{13}C nmr line widths for both styrene and ethylbenzene the larger the separation factor for the film.

The separation factor, β, for two components absorbed in a dense polymer film is defined as

$$\beta = (C_1{}^0/C_2{}^0)(C_2{}^e/C_1{}^e)$$

where $C_i{}^0$ is the concentration of the ith (of two) species in the initial feed, and $C_i{}^e$ is the concentration of the ith species in the effluent. In Table I, ethylbenzene is component 1 and styrene component 2. The separation factors were measured on intact polymer films about 5 mils in thickness by classical pervaporation experiments,[1] in which the relative effluent concentrations of styrene and ethylbenzene were determined chromatographically. The relation of the relative solubilities of the permeants in a given film to the separation factor for that film was determined by a desorption procedure, in which the steady state concentrations[1] of styrene and ethylbenzene in the film at the conclusion of a pervaporation experiment were also determined chromatographically. The latter experiment leads to a quantity defined as

$$\beta_c = (C_1{}^0/C_2{}^0)(C_2{}^f/C_1{}^f)$$

where $C_i{}^f$ is the steady state concentration of the ith species within the film. As shown in Table I, β_c is not simply proportional to the separation factor. For example, the separation factors for polyethylene, poly(p-xylene), and nylon-11 increase in that order, even though the corresponding values for β_c do not.

Samples were prepared for the ^{13}C nmr experiments by cutting 15-mm strips of each film and wrapping these around a central Teflon spoon. The outside diameter of the entire assembly was made sufficiently less than the inside diameter of the 13-mm nmr tube to allow for swelling when the styrene and ethylbenzene were added. Both styrene and ethylbenzene were added at levels well below their solubilities in the films. The initial ratio of concentrations was chosen as the steady state ratio established in the separation experiments. Upon addition of the permeants, the nmr tube was sealed and the spectrum obtained after equilibrium was reached. The time to reach equilibrium at room temperature varied from a few days for polyethylene to a few months for the acrylonitrile copolymer.

Fourier transform ^{13}C nmr spectra were obtained using a Bruker spectrometer operating at 22.6 MHz with single-phase detection and with field stabilization provided by an external time-shared ^{19}F field-frequency lock.[2] A typical spectrum is shown in Figure 2. Since the α carbons of both the styrene and the ethylbenzene used in the nmr experiments were specifically enriched at the 90% level, these are the only lines observed in the spectrum. (The enriched styrene, with 50–100 ppm 4-*tert*-butylpyrocatechol added to inhibit polymerization, and enriched ethylbenzene were obtained from Merck Sharp and Dohme, Canada, Ltd., as custom syntheses.) The low-field olefinic methine-carbon line of styrene is asymmetric and about 50% broader than the high-field methylene-carbon line of ethylbenzene. These results are typical of those obtained for films showing separation factors larger than 1.5.

The separation factor for a dense polymer film depends upon *both* the relative solubilities of the pair of permeants in the film and the relative diffusional mobilities of the permeants within the film. In general, nmr line widths can be associated with characterizations of molecular mobility. However, the ^{13}C nmr line widths observed in these experi-

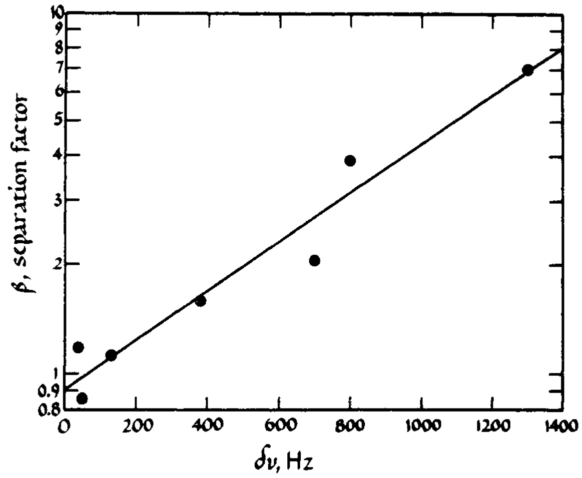

Figure 1. A plot of the separation factor for styrene and ethylbenzene absorbed in some dense polymer films as a function of the ^{13}C line width (full width at half-height) of the absorbed isotopically enriched styrene. The films are identified in Table I.

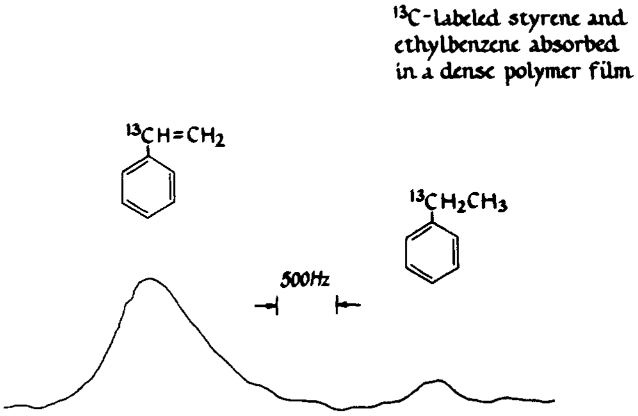

Figure 2. The ^{13}C nmr spectrum of isotopically enriched styrene and ethylbenzene absorbed in a film of cyanoethylated cellulose.

ments are not measures of *differential* mobilities since the ratio of the line width of styrene to that of ethylbenzene is about the same from film to film. Rather, for any particular film, the ^{13}C nmr line widths of styrene and ethylbenzene are a measure of the extent to which the two permeants have become polymer like, that is, the extent to which both styrene and ethylbenzene have avoided isolating voids and channels and have instead become involved with motions associated with long correlation times similar to those describing the motions of the host polymer matrix. As the permeants become polymer like, their characteristic line widths increase reflecting the increased intramolecular dipolar broadening (and possibly intrinsic or extrinsic chemical shift dispersions[3]) associated with the inhibited microscopic motion[4] of a genuinely absorbed state. Once the permeants have become intimately involved with the host polymer chains, differences in the subtle chemical and physical interactions which distinguish the pair can come into play, and these lead to a separation of the two by the film. By this reasoning, it is clear that no large separation factor will exist for two very similar molecules if their ^{13}C nmr line widths are small. We feel that this is the basis of the empirical correlation shown in Figure 1.

Table I
Separation Factors for Styrene and Ethylbenzene and the ^{13}C Nmr Line Width for Styrene Absorbed in Some Dense Polymer Films

Polymer	β	β_c	$\delta\nu$, Hz
Copolymer: acrylonitrile/ 2-methyl-5-vinyl pyridine (68:32 mol ratio)[a]	6–8	4	1300
Cyanoethylated cellulose (DS = 2.5)[b]	3.9	1.92	800
Nylon-11[c]	2.05	1.48	700
Poly(*p*-xylene)	1.59	2.25	380
Polyethylene	1.18	1.33	40
Poly(vinyl chloride)	1.12	1.39	130
Silicone rubber	0.86	1.09	50

[a] W. F. Strazik and E. Perry, U. S. Patent 3,726,934 (1974).
[b] W. F. Strazik and E. Perry, U. S. Patent 3,733,677 (1974).
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It is possible, of course, that broad ^{13}C nmr lines may be observed even though the absolute separation factor is small, simply because of a lack of any substantial differences in the strong interactions of styrene and ethylbenzene with the film. We have found no example of this behavior. Naturally, a simple correlation between just line width and separation factor is inherently incapable of *predicting* whether the separation factor is, in fact, greater or less than one. Perhaps the observation that the styrene line is consistently broader than the ethylbenzene line for those films of Table I with separation factors substantially greater than one is, actually, related to such a prediction. With the experimental evidence presently available, however, this kind of argument must be considered strictly speculative.

The determination of the ^{13}C nmr line widths of absorbed styrene and ethylbenzene is a far simpler experiment than the determination of the separation factor, mainly because the nmr experiment does not depend critically upon having an *intact* polymer film, free from holes, cracks, or other macroscopic defects. (A genuine film is required, of course, rather than, say, a powder, to ensure that the morphology of the system is represented.) In practice, one can use the observed ^{13}C nmr line width as a guide to which of a variety of experimental polymer films are most likely ultimately to produce membranes capable of high separation factors. We feel that the nmr line width analysis of ^{13}C labels should be generally useful in the search for polymer films with the potential to separate close-boiling pairs of similar molecules, assuming the labels can be incorporated at or near the structural point of difference between the two molecules.

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