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Properties and Transport Behavior of Perfluorotripentylamine (FC-70)-Doped Amorphous Teflon AF 2400 Films

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Abstract: Teflon AF 2400 films are known to imbibe solvents, making films in the presence of solvents less fluorous than they might otherwise be. Herein, we demonstrate that doping films with perfluorotripentylamine (Fluorinert FC-70) maintains the fluorous nature of Teflon AF 2400 and improves transport selectivity for fluorine-containing organic compounds. Density measurements on the FC-70-doped films reveal that free volume decreases dramatically as the dopant concentration increases (0−12 wt %) and then increases to approach that of pure FC-70. Remarkably, films from 0 to 12 wt % FC-70 have the same w/v concentration of Teflon AF 2400, indicating that FC-70 fills the free volume of Teflon AF 2400. This is consistent with the observed increased storage modulus and significant decrease (compared to undoped films) of solute diffusion coefficients in the same range of FC-70 concentrations. In contrast, FC-70 at concentrations greater than 12 wt % dilutes Teflon AF 2400, leading to a decrease of storage modulus and dramatic increase in solute diffusion coefficients. Sorption of chloroform decreases from 11.8 g of chloroform/100 g of film (pure Teflon film) to 3.8 g of chloroform/100 g of film (27 wt % FC-70-doped Teflon film), less than the solubility of chloroform in pure FC-70 (4.06 g of chloroform/100 g of FC-70). Solute partition coefficients from chloroform to FC-70-doped films generally decrease with increased dopant concentration. However, within a series of toluenes and nitrobenzenes, selectivity for F-containing solutes over analogous H-containing solutes increases as dopant concentration increases if the substitution is on the aromatic ring but not if it is on the methyl group (toluene). Transport (partitioning × diffusion) rates, as they involve both thermodynamic and kinetic factors, are not simply related to composition.

1. Introduction

Polymer membranes and films are widely applied in gas separations,[1−5] ion separation/ion exchange,[6,7] liquid-phase extraction/separation of organic compounds of biological and environmental interest,[8] sensor materials,[9−11] and as coatings to improve or create functionality such as electrowetting,[12] avoidance of biofouling,[13] improving biocompatibility,[14] and growing stem cells[15] and as composites with nanomaterials.[16,17] Fluorocarbon polymers are well represented in several of these applications. The development of fluorous media is of special interest for the selective partitioning of fluorinated substances.[18,19] Highly fluorinated hydrogen bonding,[20−24] coordination,[25] and

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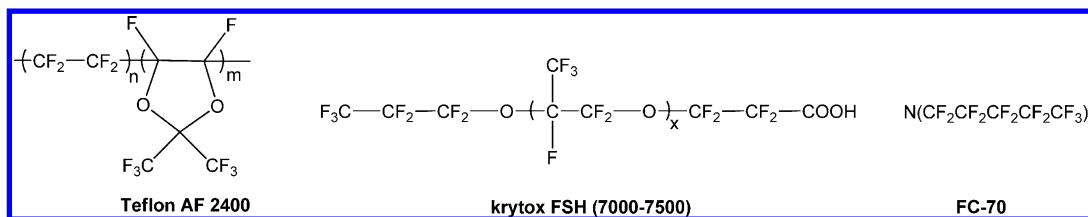
Figure 1. Structures of polymer and dopants: Teflon AF 2400 ($n = 13$ mol %, $m = 87$ mol %), Krytox FSH (7000−7500), and FC-70.

ionic receptors[26] have been shown to impart selectivity to fluorous phases for complementary target species. Notably, the partitioning of fluorinated solutes into fluorous media is preferred even without specific interactions, due to weak van der Waals interactions per molecular contact area.[27] This unique property renders fluorocarbons to be the basis of a distinctive platform for selective extraction and transport.[27,28] In many cases, covalent modification of reaction participants with fluorous tags facilitates product purification and catalyst recycling in synthetic chemistry.[29−32] Fluorous-supported liquid membranes have been recognized as promising platforms for sensors and separations.[33−36] As alternative fluorous media, perfluoropolymers attracted our attention given their potential value for selective transport. Dimensionally stable perfluoropolymers are promising matrices for membrane separations due to their low activation energy of diffusion and unique solubility/partitioning behavior.[37] In addition, strong carbon−fluorine and carbon−carbon bonds give perfluoropolymers extraordinary thermal and chemical stability, thereby yielding a long lifetime in hostile environments.[37,38]

Among commercially available perfluoropolymers, Teflon AF 2400 is an unusual amorphous glassy copolymer with a high fractional free volume (FFV).[39−41] This intrinsic feature is probably due to the rigid structure of the dioxolane ring in Teflon AF 2400 and the weak van der Waals interactions between fluorous polymeric chains, Figure 1.[41] The free volume size distributions of amorphous Teflon AF 2400 determined by various techniques are in substantial agreement (radius ranges from 3 to 8 Å) based on spherical or cylindrical assumptions of microcavity geometry.[39,40,42] Theoretical modeling indicates the bimodal distribution of microvoids and their partial con-

nectivity in Teflon AF 2400.[43] Due to the significant free volume, the gas permeability of Teflon AF 2400 is second only to poly(1-trimethylsiyl-1-propyne) (PTMSP).[40,44] Thus, Teflon AF 2400 has been widely investigated as the matrix for gas transport (light gases, C1−C4 hydrocarbons, and C1−C3 fluorocarbons),[45−50] pervaporation (acetone, chlorinated hydrocarbons, hydrocarbons, and lower alcohols),[51−54] and gas sensors (H_2S, NO_2, Cl_2, and CO_2).[9,55,56]

We initiated an investigation of Teflon films as matrices for liquid-phase selective transport with an eye on extraction, separations, and applications in synthesis and analysis.[57,58] Teflon AF 2400's high FFV and large Henry's constant[59] for chloroform result in strong sorption of chloroform, which decreases free volume and enhances segmental movement plasticizing the polymer.[57] Thus, the permeability of a solute (dissolved in chloroform) across the film deviates from the ideal prediction from the reported pervaporation results.[57] In this sense, Teflon AF 2400 films in contact with organic liquids become less fluorous and more "organic like". In order to maintain the fluorous nature of Teflon AF 2400 (π^*: −0.28), we tried to dope the films with perfluorinated compounds. Attempts to dope 50 wt % Krytox 157FSH (MW 7000−7500) in Teflon AF 2400 lead to significantly decreased solute permeability, even though the film was plasticized by the dopant.[57,58] This was attributed to a trade-off between the enhancement of segmental movement and the viscous environ-

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ment.[58] Therefore, we attempted to modulate the chemical environment within Teflon films by doping them with a lower molecular weight perfluorinated liquid, which is much less viscous yet has a high boiling point. Perfluorotripentylamine (Fluorinert FC-70, bp 215 °C, π^*: −0.23) was chosen as a dopant due to its considerable stability, compatibility, and solvophobicity.

In this context, we systematically investigated the physical and chemical properties of Teflon AF 2400 films doped with various amounts of FC-70. We provide experimental evidence on the "FC-70-like" property of Teflon AF 2400 films doped with a large weight percentage of FC-70 (>20 wt %). Antiplasticization and plasticization effects were observed, respectively, for Teflon films doped with low and high weight percentages of FC-70. Transport behavior of solutes can be related to the independently established film properties.

2. Experimental Section

2.1. Materials. Teflon AF 2400 was purchased from DuPont (Wilmington, DE). Fluorinert FC-72 (a mixture of perfluorohexanes, bp 56 °C) and Fluorinert FC-70 (perfluorotripentylamine, bp 215 °C) were purchased from 3M (Minneapolis, MN). Probe solutes used in transport experiments (toluene, α,α,α-trifluorotoluene, 2,3,4,5,6-pentafluorotoluene, octafluorotoluene, nitrobenzene, and pentafluoronitrobenzene) were purchased from Sigma-Aldrich (St. Louis, MO). Chloroform was obtained from Fisher Scientific and used as received. Water was purified with a Milli-Q Synthesis A10 system (Millipore, Bedford, MA). Tygon Chemfluor FEP tubing, resistant to vapor chloroform, was purchased from United States Plastic Corp. (Lima, OH).

2.2. Preparation of the Films. Pure films of Teflon AF 2400 were cast from a 12 mg/mL solution of amorphous Teflon AF 2400 polymer dissolved in FC-72. A defined amount of solution was transferred into an optical flat-bottomed glass Petri dish with an i.d. of 6.0 cm. The dish was covered with a piece of weighing paper and a glass cover. The solvent, FC-72, was allowed to evaporate at room temperature until a constant weight of the film was reached. Three milliliters of Milli-Q water were added to the Petri dish to enable the film to float on top of the water within several minutes. The film was then oven dried at 110 °C for 2 h to remove water residue and stored at room temperature.

To prepare FC-70-doped Teflon AF 2400 films for both density measurement and dynamic mechanical analysis (DMA), FC-70 was weighed and mixed with a 12 mg/mL solution of Teflon AF 2400 polymer in FC-72 in the calculated proportions. Doped Teflon films were formed under the same conditions as described above for the pure films with one difference. They were readily peeled off using a scalpel with the addition of 0.4 mL of ethanol rather than using water for this step. The doped films were not oven dried because FC-70 could be lost. They were stored in a covered container with an FC-70-saturated atmosphere.

The FC-70-doped Teflon AF 2400 films used in the transport experiments were prepared by soaking a piece of pure Teflon AF 2400 film in a chloroform solution containing a defined amount of FC-70 (including 0 wt %) with stirring (200 rpm) at 20.0 ± 1.0 °C. The FC-70 content in the film was evaluated by FT-IR absorbance analysis to determine when the two phases reached equilibrium. The resulting chloroform solution containing FC-70 was used as the receiving phase and to prepare the source phase solution in the transport experiments. The equal chemical potential of FC-70 in the source phase, polymer phase, and receiving phase prevented the potential loss or gain of FC-70 in doped films during the transport experiments. There is no significant difference of solute permeabilities in oven-dried pure Teflon AF films compared to pure Teflon AF films that were not oven dried. Thus, differences between pure Teflon AF films and FC-70-doped films are not caused by the difference in preparation procedures.

For all FC-70-doped Teflon AF 2400 films, the amount of dopant in the film was evaluated by FT-IR absorbance analysis. Films were cut into small pieces (0.8 cm ×0.8 cm) for both density measurement and transport experiments. A Starrett micrometer (Athol, MA) with an accuracy of ±1 μm was used to measure film thickness.

2.3. Scanning Electron Microscopy (SEM). The morphology of the films was investigated using a Philips XL-30 field emission SEM. FC-70-doped Teflon AF 2400 films were fractured in liquid nitrogen and sputter coated with palladium to enhance surface conductivity.

2.4. Film Density Measurement and Fractional Free Volume. The hydrostatic weighing method was used to determine film density (ρ). A film (mass, m) was hung on the hook of a suspension system in silicon oil (ρ_s), which was chosen because of its high boiling point. The mass change of the suspension system with and without the film ($W − W_0$) was recorded by a XS105 DualRange analytical balance (Mettler Toledo, Columbus, OH). The hydrostatic density after correction (the density of air at 20 °C, $\rho_A = 0.00129$ g/cm³) is given by eq 1:[60,61]

$$\rho = \frac{m}{(W - W_0)/\rho_s} + \rho_A \qquad (1)$$

On the basis of measured densities, the FFV of the FC-70-doped Teflon films can be calculated according to eq 2[62]

$$FFV = \frac{V_F}{V} = \left(\frac{V - V_0}{V}\right) = 1 - \rho \cdot V_0 \qquad (2)$$

where the specific free volume (V_F) is the difference between the experimentally determined specific volume (V) and the estimate of specific volume at absolute zero (V_0). V equals the reciprocal of measured film density (ρ). As suggested by Lee, V_0 is 1.3 times the van der Waals specific volume,[63] which can be obtained according to a group contribution method.[64] For a polymer−dopant system, V_0 can be estimated based on the weight fraction of each component:[65]

$$V_{0,mixture} = V_{0,polymer} \cdot wt \%_{polymer} + V_{0,additive} \cdot wt \%_{additive} \qquad (3)$$

2.5. Dynamical Mechanical Analysis (DMA). Dynamical mechanical analysis was carried out using a Q800 DMA (TA Instruments, New Castle, DE). DMA was performed on a piece of film cut and mounted between the tensile mode clamps of the instrument. The dimensions of films were approximately 9 mm long by 0.53 mm wide by 0.02 mm thick. The sample was prestretched under a preload force of 0.01 N. A sinusoidal strain deformation (0.3%) of 1 Hz was applied during a temperature sweep from −100 to 300 °C at a rate of 3 °C/min.

2.6. Sorption and Desorption of Chloroform in FC-70-Doped Teflon AF 2400 Films. A FT-IR gas flow cell was utilized to measure the sorption of chloroform in the FC-70-doped Teflon AF 2400 films. Saturated chloroform vapor was carried into the IR flow cell (containing two lead spacers sandwiched between two KBr windows) by nitrogen gas with a pressure of 15 psi (20 °C) at a flow rate of 0.1 LPM. The tail gas was absorbed by *n*-butanol. IR absorbance of chloroform in the flow cell was continuously monitored by an FT-IR spectrometer (Bio-Rad Excalibur FTS 3000 Spectrometer, DigiLab, Randolph, MA). In order to measure the sorption of chloroform in an FC-70-doped Teflon AF film, a piece

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of the film with the same diameter as the KBr window was placed between the two lead spacers in the flow cell for IR measurement (after 30 min equilibrium had been reached). The IR absorbance of the flow cell without a film was monitored as the control experiment. The net sorption of chloroform in the film was obtained from the difference between the IR absorbance with and without the film. Since the C−Cl vibration shifted from 772 cm^{-1} for the vapor chloroform to 768 cm^{-1} for the chloroform saturated in the film, the peak area of the C−Cl vibration was used for IR quantification.

To determine the diffusion coefficient of chloroform in FC-70-doped Teflon AF 2400 film, a film in equilibrium with liquid chloroform was set in the FT-IR window for kinetic measurement. The FT-IR absorbance (3025 cm^{-1}, C−H stretch) was continuously acquired with a time interval of 1 min. Assuming that the concentration of chloroform on the film surfaces is zero ($D_{\text{chloroform in film}} \ll D_{\text{chloroform in air}}$), the portion of chloroform remaining in the film can be theoretically described by eq 4[66,67]

$$\frac{M_t}{M_0} = \frac{A_t}{A_0} = \frac{8}{\pi^2} \cdot \sum_{k=0}^{\infty} \left(\frac{1}{2k+1}\right)^2 \cdot e^{-(2k+1)^2 \pi^2 \cdot D \cdot t / l^2} \quad (4)$$

where M_0 is the initial total amount of chloroform inside the film, M_t is the amount of chloroform remaining in the film at time t, A_0 corresponds to the initial IR absorbance, whereas A_t is the absorbance at time t. l is the film thickness. D denotes the diffusion coefficient of chloroform in the film, which can be obtained from nonlinear fitting by Mathcad 14 ("infinity" in the sum was set to 100).

2.7. Transport of Solutes through Films. Transport experiments were conducted with a homemade, three-phase transport device at 20.0 ± 1.0 °C.[68] The film was mounted between two quartz cuvettes (path length = 1.0 cm, Starna Cells, Atascadero, CA) with holes (0.5 cm in diameter) to define the effective transport area. Two pieces of Viton gasket were placed in between the film and the cuvettes to prevent leaking. The eight-position multicell transport holder was used to hold eight cells (four pairs) in a rack, which were kept at constant temperature by water circulation from a thermostatic water bath. The stirring module for the multicell transport holder could control the stirring speed at the same rate for the eight cells. The volume of the source phase containing the solute and receiving phase was 3.00 mL in all the transport experiments. Solute concentration in the receiving phase was continuously monitored by a UV spectrophotometer (Hewlett-Packard 8452A UV−visible diode array spectrophotometer, Palo Alto, CA). The steady-state flux, J, of a solute through the film is given by eq 5[58]

$$J = \frac{dC_r}{dt} \cdot \frac{V}{A} (\text{mol} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}) \quad (5)$$

where dC_r/dt is the accumulation rate of solute in the receiving phase, V is the volume of the receiving phase (3.00 mL), and A is the effective transport area (0.196 cm^2). The permeability coefficient, P, can be deduced from the flux[58]

$$P = \frac{J \cdot l}{C_s - C_r} \approx \frac{J \cdot l}{C_{sI}} (\text{cm}^2 \cdot \text{s}^{-1}) \quad (6)$$

where l is the film thickness and C_s and C_r represent the concentration of the solute in the source phase and receiving phase, respectively. In our experimental duration, C_r is negligible compared to C_s. Thus, $C_s - C_r$ can be simplified to the initial concentration of the solute in the source phase, C_{sI}. Selectivity of a film is defined

as the permeability ratio of a fluorinated compound over its hydrogen-containing control:

$$S = \frac{P_F}{P_H} \quad (7)$$

2.8. Determination of Solute Diffusion Coefficients (D) and Partition Coefficients (K). In order to clearly observe the lag phase prior to the solute flux reaching the steady state, FC-70-doped Teflon AF films with various thicknesses (36−127 μm) were employed in the transport experiments. The concentration of source phase solutions (e.g., toluene, 1.0 M; α,α,α-trifluorotoluene, 0.3 M; 2,3,4,5,6-pentafluorotoluene, 0.5 M; octafluorotoluene, 0.1 M; nitrobenzene, 0.5 M; pentafluoronitrobenzene, 0.2 M) was chosen based on solute absorptivity. UV absorbance of the receiving phase was recorded continuously at a time interval of 20 s in order to measure the solute accumulation. For a transport system that starts with "zero" solute concentration in both the film and the receiving phase, the accumulation of solute molecules can be theoretically described by eq 8[66]

$$Q_t = K \cdot C_s \cdot l \cdot \left(\frac{D \cdot t}{l^2} - \frac{1}{6} - \frac{2}{\pi^2} \cdot \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \cdot e^{-D \cdot n^2 \cdot \pi^2 \cdot t / l^2}\right) (\text{mol} \cdot \text{cm}^{-2}) \quad (8)$$

where Q_t denotes the accumulation of the solute in the receiving phase (substance passed through the film) per transport area within the time range t. K is the partition coefficient of the solute from chloroform to the film. C_s is the concentration of the solute in the source phase solution. l represents the thickness of film. D is the average diffusion coefficient of the solute in the film. Thus, the diffusion coefficients and partition coefficients can be obtained by nonlinear fitting eq 8 to experimental data using Mathcad 14 ("infinity" in the sum was set to 100).

The partition coefficients of octafluorotoluene and 2,3,4,5,6-pentafluorotoluene from chloroform to pure FC-70 were determined from the liquid−liquid partitioning experiments. The solution of 1 mM octafluorotoluene or 5 mM 2,3,4,5,6-pentafluorotoluene in chloroform (750 μL/500 μL) mixed with FC-70 (750 μL/1 mL) was placed in a VWR GC-autosampler vial (1.8 mL, West Chester, PA) and shaken at 1300 rpm for 30 min at 20 °C (Bioshaker, BIONEXUS Inc., Oakland, CA). The chloroform layers were then quantitatively analyzed by UV spectrophotometry at 267 and 258 nm.

The partition coefficients of toluene, α,α,α-trifluorotoluene, nitrobenzene, and pentafluoronitrobenzene from chloroform to pure FC-70 were determined from head space gas chromatography (HSGC). The instrument combines the inherent sensitivity of modern capillary gas chromatography with computer-controlled gas sampling, injection, sample equilibration, and data handling techniques. The details of a custom-built HSGC have been described elsewhere.[69] The instrument was used to precisely sample the vapor phase in equilibrium with the solution phase and analyze the vapor phase by a gas chromatographic technique.

In a typical experiment, a standard mixture of four solutes was added to 10.0 mL of FC-70 solvent by using a calibrated auto syringe into a thermostatted (±0.1 °C) glass cell. The solute's mole fraction range was toluene 0.001−0.007, α,α,α-trifluorotoluene 0.001−0.005, nitrobenzene 0.001−0.009, and pentafluoronitrobenzene 0.001−0.004, each added over 10−20 increments.

Once the vapor−liquid equilibrium is established, 50 μL of the vapor was sampled and injected by using the automated valve system on-column into a capillary GC for analysis. This procedure was continued after each aliquot addition to obtain a series (10−20 additions) of concentration-dependent vapor pressures. Assuming

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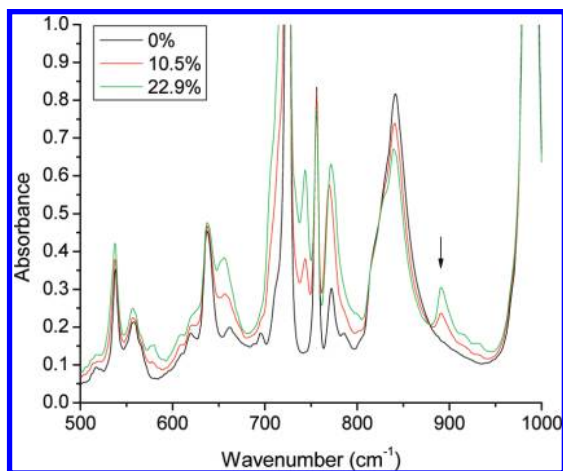
Figure 2. FT-IR spectra of Teflon AF films doped with various amounts of FC-70 (wt %).

ideal gas, the response peak areas can be used to calculate the activity coefficients of the solute, γ_i, in a solvent by the equation

$$\gamma_i = A_i/(A_i^{\circ} x_i) \tag{9}$$

where A_i is the peak area for the solute, A_i° is the peak area for pure solute (measured separately), and x_i is the mole fraction of the solute in the solvent. The γ_i values are therefore referenced to the pure solute as the standard state. The infinite dilution activity coefficient was obtained from extrapolation of γ_i vs x_i curve to x_i = 0, and the mole-fraction-based partition coefficient was determined from the vapor−liquid composition.

2.9. Recycling of Teflon AF 2400. FC-70-doped Teflon AF 2400 films after usage have been recycled as follows. First, small pieces of used films were dissolved in FC-72 to cast large films in order to allow the IR quantification of remaining FC-70 conveniently. Second, the film was heated to approximately 160 °C in an oven with vacuum for several days until the characteristic peak of FC-70 (891 cm^{-1}) could no longer be observed by IR. After treatment, the films were redissolved in FC-72. Filtration was carried out to remove the dust attracted by static electricity. Finally, clean Teflon AF 2400 was recovered after evaporation of FC-72.

3. Results and Discussion

3.1. Characterization of FC-70-Doped Teflon AF 2400 Films. FC-70 (0−40 wt %) doped Teflon AF 2400 films were prepared as transparent and homogeneous films. As shown in Figure 2, FT-IR spectra of FC-70-doped Teflon films show the characteristic peak of FC-70 at 891 cm^{-1}. The peak magnitude is dependent on the weight percentage of FC-70; thus, it is used to verify the composition of FC-70-doped Teflon films.

SEM was used to determine the macroscopic homogeneity of FC-70-doped Teflon films. Both films display satisfactory homogeneity through the cross-section, as shown in Figure 3. The morphology of 30 wt % FC-70-doped Teflon is very similar to that of the pure Teflon film. As confirmed by SEM, the films are free from detectable pinholes or cracks.

3.2. Density and Free Volume of FC-70-Doped Teflon AF 2400 Films. Doping miscible low molecular weight additives in a polymer film should result in the change of both physical and chemical properties of the film.[70] Dopants may decrease FFV and substantially reduce gas permeabilities.[65,71] The effect

of FC-70 content on the film's free volume can be seen in Figure 4, showing the density of Teflon AF 2400 films containing various amounts of FC-70. The film density increases significantly (in the range of 0−12 wt % dopant) and then decreases gradually along with the FC-70 content (12−40 wt %) in the film. Interestingly, the peak density of the doped film (2.06 g/cm^3) is significantly higher than both pure Teflon film (1.82 g/cm^3) and pure FC-70 liquid (1.94 g/cm^3). This indicates the volumetric shrinkage of FC-70-doped Teflon AF 2400 film, usually a phenomenon accompanying antiplasticization.[72]

To understand the role of the dopant, the concentration of Teflon AF 2400 in the doped films (C) over a pure film (C_0) was plotted against FC-70 content (Figure 5). Teflon AF 2400 concentration is almost a constant in films containing 0−12 wt % FC-70. This observation indicates that FC-70 mainly fills in the existing free volume of the Teflon polymer in this range of compositions. Having 12 wt % FC-70 in 88 wt % Teflon AF 2400 requires that 44.6% of the free volume in Teflon is occupied by FC-70. Hoffman and co-workers[43] used two models to describe the experimentally determined free volume distribution in Teflon AF 2400. In one, called R_max, the measured sizes correspond to the size of a feature in what may be a larger, irregular void. In the other, called V_connect, the measured size corresponds to the size of the complete void. An analogy may help. In a simple image of a flower, the R_max approach would characterize the flower by the size of the petals, whereas the V_connect would characterize the size of the void by the size of the whole flower. According to Hofmann and co-workers, 44.6% of the free volume in Teflon AF 2400 corresponds to cavities with a feature size larger than 8−9 Å in the R_max approach. Interestingly, the critical diameter is equal to the length of the side chain (r) in FC-70 calculated by Gaussian.[73] In contrast, according to V_connect approach, 75% of the free volume can accommodate FC-70. We would have observed the transition from filling the void volume to dissolving the polymer (Figure 5) at 20 wt %, which is significantly larger than the experimentally determined value.[43] Such inconsistency could be due to the topological complexity of free volume elements which cannot accommodate FC-70, even though those elements have larger feature size than FC-70. In summary, the data for the FC-70/Teflon AF 2400 system shows that the accessible free volume distribution based on the R_max approach is more appropriate than the V_connect approach.

The FFV of FC-70-doped Teflon AF 2400 films was calculated from the measured film densities based on empirical methods (Figure 6). The FFV of doped films decreases in the range of 0−12 wt % dopant and then increases gradually to approach the FFV of pure FC-70. Similar phenomena have been reported in other polymeric materials doped with small molecule additives.[65,74−76] A turning point of the FFV change is probably due to the transition of the chemical environment of FC-70-doped Teflon AF 2400 films. Since FC-70 (0−12 wt %) fills in the existing microvoids within the Teflon AF 2400 polymer, the decrease of free volume will lead to subsequently reduced

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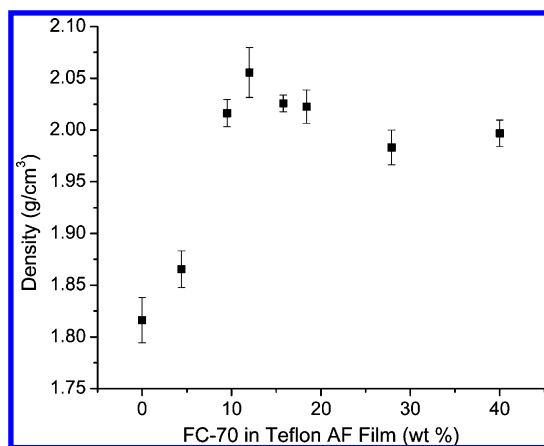
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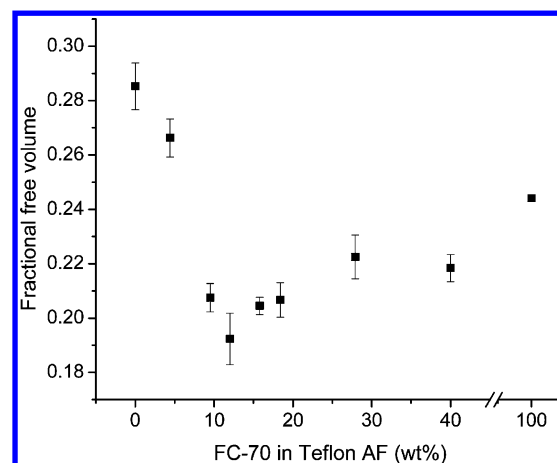
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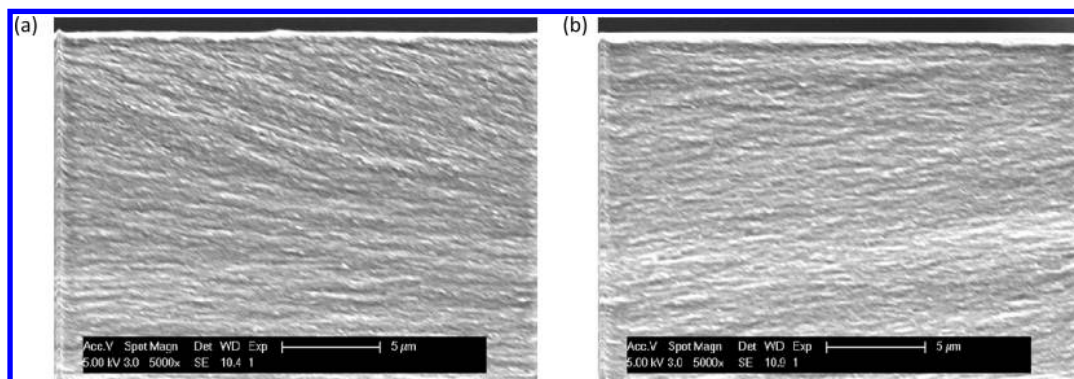
Figure 3. Cross-section SEM micrographs of (a) a pure Teflon AF film and (b) a Teflon AF film doped with 30 wt % FC-70.

Figure 4. Dependence of film density (20.0 ± 1.0 °C) on FC-70 content (wt %). The number of measurements for each data point are: 5 (0 wt %), 8 (4.4 wt %), 8 (9.5 wt %), 9 (12.0 wt %), 11 (15.8 wt %), 9 (18.4 wt %), 6 (27.9 wt %), and 10 (40.0 wt %). The error bars represent the standard error of the mean. Pure films were oven dried to remove water residue, while doped films were air dried to remove ethanol residue.

Figure 5. Concentration ratio of Teflon AF 2400 polymer in the doped films over a pure film was plotted against the weight percentage of FC-70 in the film. Error bars represent the standard error of the mean. Pure films were oven dried to remove water residue, while doped films were air dried to remove ethanol residue. Note: C/C_0 also equals the ratio of volume of the pure film (V_0) to the volume of the doped film (V) containing the same amount of Teflon AF 2400.

polymeric chain mobility. When the microvoids in the polymeric matrix are saturated with FC-70 (12−40 wt %), adding more FC-70 will dilute the polymer chains. Thus, a polymeric chain unit of Teflon AF 2400 has fewer polymeric segments and more
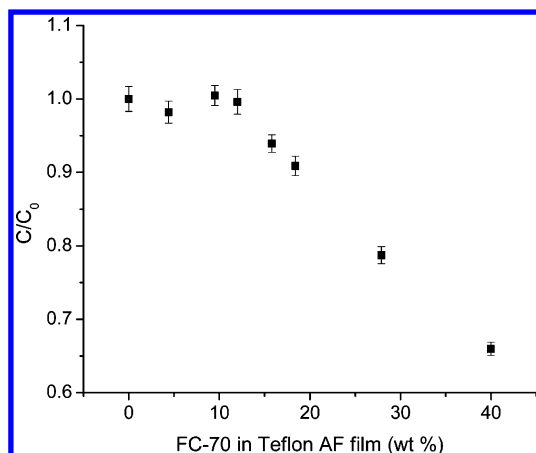

Figure 6. Dependence of FFV on FC-70 content (wt %). Error bars are the standard error of the mean. Pure films were oven dried to remove water residue, while doped films were air dried to remove ethanol residue.

Table 1. Storage Modulus of FC-70-Doped Teflon AF Films[a] at 20.0 °C

FC-70 (wt %)	storage modulus (MPa)
0	1122
10	1439
18	1085
26	836
35	593

[a] Pure films were oven dried to remove water residue, while doped films were air dried to remove ethanol residue.

FC-70 molecules in its vicinity. Its local friction may be significantly reduced, which results in easier thermal motion of polymeric segments. Overall, changes in FFV would lead one to predict an antiplasticization effect on the films with less than 12 wt % dopant due to void filling by FC-70 and a plasticization effect on the films with more than 12 wt % dopant due to chain dilution.

In order to determine the influence of FC-70 on antiplasticization/plasticization effects, we monitored the viscoelastic properties of FC-70-doped Teflon AF films by dynamic mechanical analysis (DMA). Table 1 shows the storage modulus (E') of FC-70-doped Teflon AF films at the temperature for transport experiments (20 °C). The 10 wt % FC-70 shows the antiplasticization effect, with the storage modulus E' 1.3 times higher than that of pure Teflon AF. Further increase of FC-70 content leads to a decrease of the storage modulus, indicating plasticization. This is confirmed by the emergence of two low-temperature transitions in the DMA for 26 (4 and 134 °C) and

Table 2. Summary of the Physical and Chemical Properties of FC-70-Doped Teflon AF Films at 20.0 °C

	Teflon AF 2400 doped with FC-70	
property	0−12 wt % FC-70 content	>12 wt % FC-70 content
free volume	decreasing, FC-70 fills the free volume of Teflon AF 2400	increasing, FC-70 dilutes Teflon AF 2400
storage modulus	increasing	decreasing
sorption of $CHCl_3$	decreasing and approaching the solubility of $CHCl_3$ in FC-70	
permeability coefficients	decreasing	increasing
diffusion coefficients	decreasing	increasing
partition coefficients	decreasing trend in general	
partitioning selectivity (8F/8H, 5F/5H)[a]	increasing trend in general	
partitioning selectivity (3F/3H)[a]	no increase	

[a] Partition coefficient of a fluorous compound with the stated number of F atoms divided by the partition coefficient of the analogous hydrogen-containing compound.

Table 3. Comparison of Permeability Coefficients through Fresh Pure Teflon Film and Chloroform-Soaked Pure Teflon Film at 20.0 ± 1.0 °C

| solutes	permeability through fresh Teflon AF film (P_f, cm^2/s)[a]	permeability through soaked Teflon AF film (P_s, cm^2/s)[a]	P_s/P_f
nitrobenzene	$(1.05 \pm 0.003) \times 10^{-9}$	$(2.53 \pm 0.10) \times 10^{-9}$	2.4 ± 0.10
pentafluoronitrobenzene	$(4.98 \pm 0.05) \times 10^{-9}$	$(1.06 \pm 0.002) \times 10^{-8}$	2.1 ± 0.02

[a] The permeability coefficients are the mean values of duplicate experiments. Errors indicated in the table are the standard error of the mean.

35 wt % (−10 and 117 °C) FC-70-doped Teflon AF 2400 films that are not present in films that contain 0, 10, and 18 wt % FC-70. The presence of two low-temperature transitions was also observed by Lugert and co-workers[77] while studying the plasticization of Teflon AF 2400 by perfluoroperhydrophenanthrene, perfluoro(1-methyldecalin), and 2*H*-perfluoro-5,8,11-trimethyl-3,6,9,12-tetraoxapentadecane. The extent of polymeric chain mobility indicated by the antiplasticization/plasticization effect is an important influencing factor for solute transport through films.

In what follows, we present a considerable number of experimental data showing how the physical changes just described influence the thermodynamic (partitioning) and transport properties of these films. As a guide, we present a broad overview of the results in Table 2.

3.3. Sorption of Chloroform in Doped Films. Our previous study found that pure Teflon AF 2400 films in equilibrium with chloroform contain 1.13 M chloroform.[57] There is ongoing interest in the analysis of how chloroform may influence solute transport. We compared the permeability coefficients of nitrobenzene and pentafluoronitrobenzene through a fresh pure Teflon AF film (P_f) and a film from the same batch soaked in fresh chloroform for 4 days (P_s). As shown in Table 3, P_s is significantly larger than P_f for each solute. This could be interpreted as enhanced solute diffusivity due to the plasticization of Teflon by chloroform.[57] Moreover, the ratio of permeability coefficients (P_s/P_f) for nitrobenzene is slightly higher than pentafluoronitrobenzene. Obviously, the Teflon film in equilibrium with chloroform becomes more "organic like", which is less favorable for the selective partitioning of fluorocarbons than the corresponding hydrocarbon counterparts.

We doped films with FC-70 to reduce the sorption of organic solvents in the Teflon matrix for the purpose of achieving selective transport of fluorocarbons over hydrocarbons. The chloroform sorption in Teflon AF films doped with FC-70 was investigated by means of gas-phase IR experiments. As shown in Figure 7, the amount of chloroform absorbed in doped films decreases along with the increase of FC-70 wt % and then levels off. This phenomenon could be a result of the free volume change inside the film and the enhanced fluorophilicity of the

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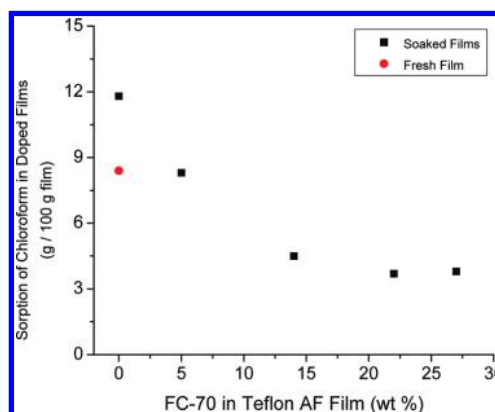
Figure 7. Sorption of chloroform in FC-70-doped Teflon AF films.

Teflon matrix doped with FC-70. According to the dual-sorption model, sorption of chloroform in FC-70-doped Teflon AF films contains the sorption into both the free volume and the polymeric matrix.[48,59] The variation of sorption into free volume is roughly parallel to the change of FFV, whereas the matrix sorption would decrease in Teflon films doped with FC-70 because of the increased fluorophilicity. The amount of chloroform absorbed in Teflon films doped with more than 20 wt % FC-70 approaches the solubility of chloroform in pure FC-70 (4.06 g of chloroform per 100 g of FC-70). Therefore, Teflon AF 2400 films doped with more than 20 wt % FC-70 appear to behave more "FC-70 like".

We noticed that the amount of chloroform absorbed by a fresh pure Teflon film is significantly lower than in a soaked pure film. This indicates that the chloroform imbibed by the film during the soaking process could change the film's properties and then enhance its sorption capacity. Similar effects were reported for the sorption and desorption isotherms of some gaseous hydrocarbons and fluorocarbons in Teflon AFs.[59] Gas desorption isotherms were found to be higher than sorption isotherms in Teflon AFs. This effect is especially pronounced for gases which are more soluble in the Teflon matrices.[59] It could be attributed to the plasticization of Teflon film caused by the sorption of molecules in high concentration, which may

effectively decrease the matrix cohesive energy to more easily accommodate more molecules.[78]

The desorption of chloroform from FC-70-doped Teflon AF films in equilibrium with liquid chloroform was also observed by FT-IR. The diffusion coefficient of chloroform in a 5 wt % FC-70-doped film was determined to be 9.3×10^{-9} cm$^2 \cdot$s^{-1} at 20.0 ± 1.0 °C. This value is about 20% of the diffusion coefficient of chloroform in pure Teflon AF film from a pervaporation study (4.22×10^{-8} cm$^2 \cdot$s^{-1} at 25 °C),[52] indicating the restricted mobility of chloroform in the Teflon film anti-plasticized by FC-70.

3.4. Dependence of Permeability Coefficients (*P*) on Film Composition. The dependence of permeability coefficients on film composition was investigated using aromatic compounds as probe molecules. Recall that permeability coefficients are products of partition coefficients and diffusion coefficients. As shown in Figure 8, solute permeability coefficients are sensitive to FC-70 content in Teflon AF films. Six probe solutes (toluene (TOL), α,α,α-trifluorotoluene (TFT), 2,3,4,5,6-pentafluorotoluene (PFT), octafluorotoluene (OFT), nitrobenzene (NB), and pentafluoronitrobenzene (PFNB)) show similar trends in the plots. The permeability coefficients decrease as FC-70 content increases when films are doped with less than 15 wt % FC-70. The permeability coefficient of each solute through the pure Teflon AF films is around 10 times larger than through the films doped with 15 wt % FC-70. The trend of the permeability coefficient is reversed when films are doped with more than 15 wt % FC-70. Films containing more than 30 wt % FC-70 can transport solutes as effectively as the pure film. The SEMs of permeability coefficients through pure Teflon films of different thicknesses is never greater than 6% for each solute. Thus, film thickness has no measurable influence on permeabilities.

A plot of log *P* versus log *MW* of aromatic hydrocarbon solutes is linear with a negative slope—larger homologues permeate more slowly than smaller homologues.[58] Among six probe solutes in the present work, toluene and nitrobenzene contain no fluorine and fit the linear relationship well. However, the fluorinated solutes with a higher weight percentage of fluorine have logarithmic values of permeability (through pure Teflon AF film) which depart positively (higher *P*) from the hydrocarbon line. This is consistent with the preferred transport of fluorocarbons through pure Teflon AF 2400 films. For each composition of FC-70 (0−30 wt %) doped Teflon AF 2400 film, the permeability coefficients of the toluene series can be arranged in decreasing order $P_{OFT} > P_{PFT} > P_{TFT} > P_{TOL}$, despite the fact that the molar mass/critical volumes decrease in the same order. This observation demonstrates that the increase in partition coefficient that accompanies the replacement of a hydrogen atom by a fluorine atom in a solute is greater than the decrease of the diffusion coefficient of the solute. We decided to investigate this in a little more detail.

3.5. Dependence of Diffusion Coefficients (*D*) on Film Composition. The diffusion coefficients of six solutes in FC-70-doped Teflon AF 2400 films are plotted against the film composition, as shown in Figure 9. For all the solutes, the diffusion coefficients decrease as the amount of FC-70 is increased in the low weight percentage range (0−10 wt %), and then the trend is reversed at the high FC-70 content (10−30 wt %). Factors that influence the diffusion in the doped films include (1) the local viscosity, (2) the tortuosity of the diffusion

path which is directly related to the concentration of amorphous Teflon in the film,[79] and (3) the polymeric chain mobility. We showed above that chloroform sorption decreased in Teflon films with more FC-70 dopant. Because chloroform (dynamic viscosity at 20 °C, 0.573 cP)[80] is less viscous than FC-70 (dynamic viscosity at 25 °C, 24 cP), solute diffusion will be slower in the more viscous environment created by FC-70. According to the Teflon concentration in doped films (refer to Figure 5), the tortuosity is similar in films doped with less than 12 wt % FC-70 and then significantly decreases with a further increase of FC-70 content. Thus, solutes would experience a shorter pathway when diffusing across the films doped with more than 12 wt % FC-70. In addition, the mobility of the polymer chain decreases first at the low FC-70 content (<12 wt %) and then increases at the high FC-70 content (>12 wt %). Solute diffusion through a polymer is easier when the chain mobility increases, and becomes more difficult when the chain mobility decreases. Therefore, in the range of compositions with FC-70 less than 12 wt %, all three factors become less favorable for diffusion as the FC-70 concentration increases. Thus, diffusion coefficients show a decreasing trend in this range. Meanwhile, diffusion coefficients increase along with the increased dopant amount in films containing more than 12 wt % FC-70. This indicates that the influence of the tortuosity and polymer chain mobility are more important than the viscosity of the additive on solute diffusivity in this system. The diffusion coefficients in films containing approximately 30 wt % FC-70 are larger than in a pure Teflon film, showing the possibility to improve the transport efficiency by doping a large amount of FC-70.

3.6. Dependence of Partition Coefficients (*K*) on Film Composition. It is helpful to understand the partitioning of solutes from chloroform to pure FC-70 before we investigate solute partitioning from chloroform into FC-70-doped Teflon AF films. Octafluorotoluene and 2,3,4,5,6-pentafluorotoluene have relatively large partition coefficients and thus can be accurately measured by the liquid−liquid partitioning experiment. The partition coefficients of the other four solutes were obtained from the measurement of activity coefficients by head space gas chromatography (HSGC). The partition coefficients (based on molar concentration ratio) are summarized in Table 4. In general, substitution of fluorine increases the partition coefficients from chloroform to FC-70. Compared with the methyl group, the nitro group is more polar. Therefore, the nitrobenzene series exhibits lower partition coefficients than the analogous toluenes.

The partition coefficients and diffusion coefficients of the solutes from chloroform to FC-70-doped Teflon films have been determined simultaneously from the transport experiments with thick films. As shown in Figure 10, the partition coefficients of all the solutes show a decreasing trend in general along with the increase of FC-70 wt % and eventually approach their partition coefficients from chloroform to pure FC-70. Therefore, Teflon films doped with larger amounts of FC-70 behave more "FC-70 like". A descending order of partition coefficients ($K_{OFT} > K_{PFT} > K_{TFT} > K_{PFNB} > K_{TOL} > K_{NB}$) is common for the Teflon films with different amounts of dopant.

Since fluorine substituents contribute to the selective partitioning from chloroform to FC-70-doped Teflon films, it is worthwhile to compare the outcomes of the solutes with different substitutions. Six solutes were classified into three categories:

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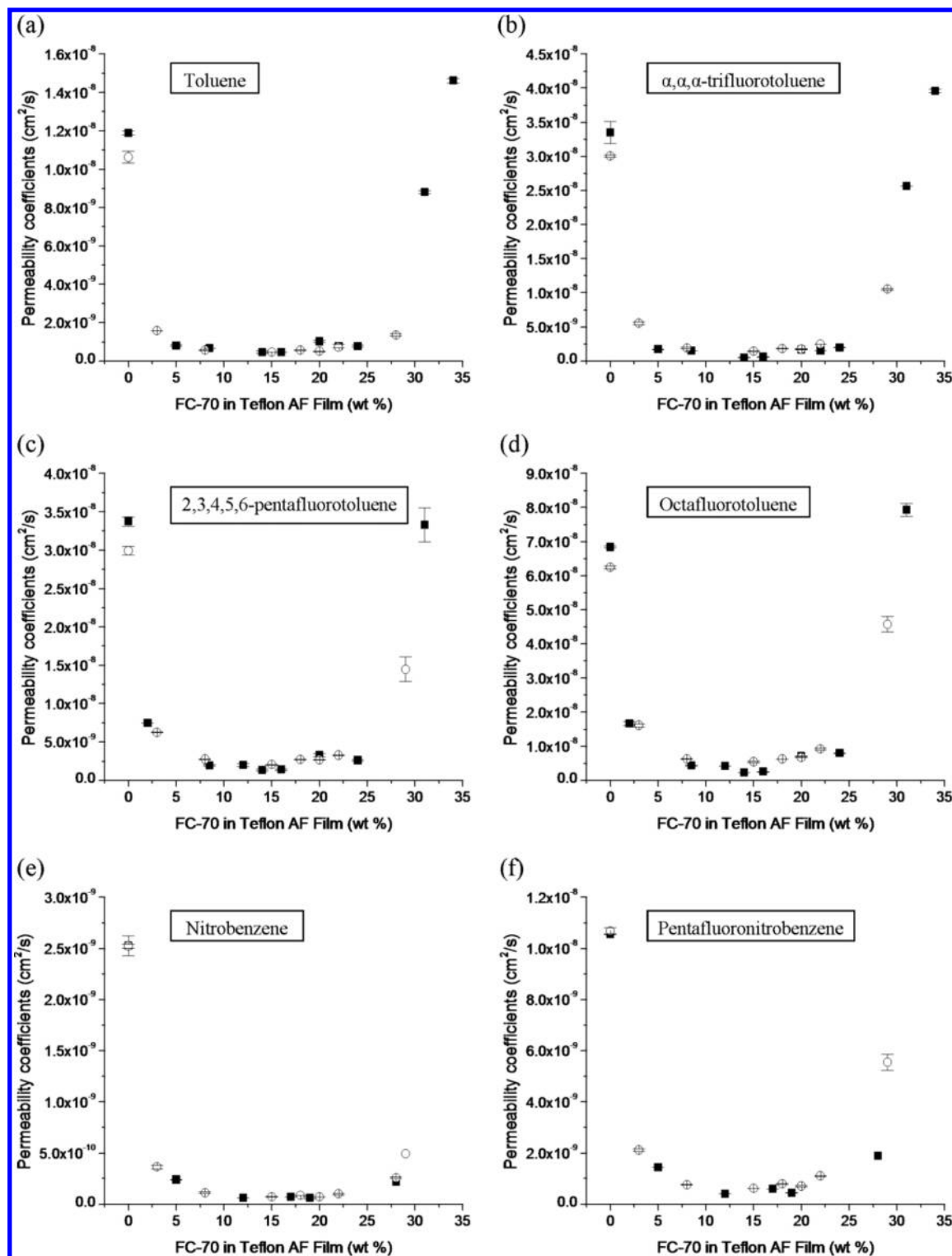
Figure 8. Permeability coefficients of solutes in FC-70-doped films at 20.0 ± 1.0 °C: (a) toluene; (b) α,α,α-trifluorotoluene; (c) 2,3,4,5,6-pentafluorotoluene; (d) octafluorotoluene; (e) nitrobenzene; (f) pentafluoronitrobenzene. For all dark squares (■), the source phase concentration is 0.1 M; the film thickness is between 18 and 33 μm. (○) Film thickness ranges from 36 to 127 μm and the source phase concentration varies: (a) 1.0, (b) 0.3, (c) 0.5, (d) 0.1, (e) 0.5, (f) 0.2 M. The error bars represents the standard error of the mean for two measurements.

substitution of three methyl hydrogen atoms with fluorine (3F/3H), substitution of five phenyl hydrogen atoms with fluorine (5F/5H), and substitution of eight hydrogen atoms with fluorine (8F/8H). On the basis of different substitutions with fluorine, the selectivities of partitioning from chloroform to doped Teflon films are plotted in Figure 11. Interestingly, the partitioning selectivities of 2,3,4,5,6-pentafluorotoluene/toluene are close to

those of octafluorotoluene/α,α,α-trifluorotoluene. In addition, α,α,α-trifluorotoluene/toluene and octafluorotoluene/2,3,4,5,6-pentafluorotoluene pairs also have similar partitioning selectivities. If indeed the effects of a particular substitution pattern, e.g., 3F/3H, on partition coefficients is independent of the remainder of the molecule, then the product of the selectivities for the substitutions 3F/3H and 5F/5H should predict the
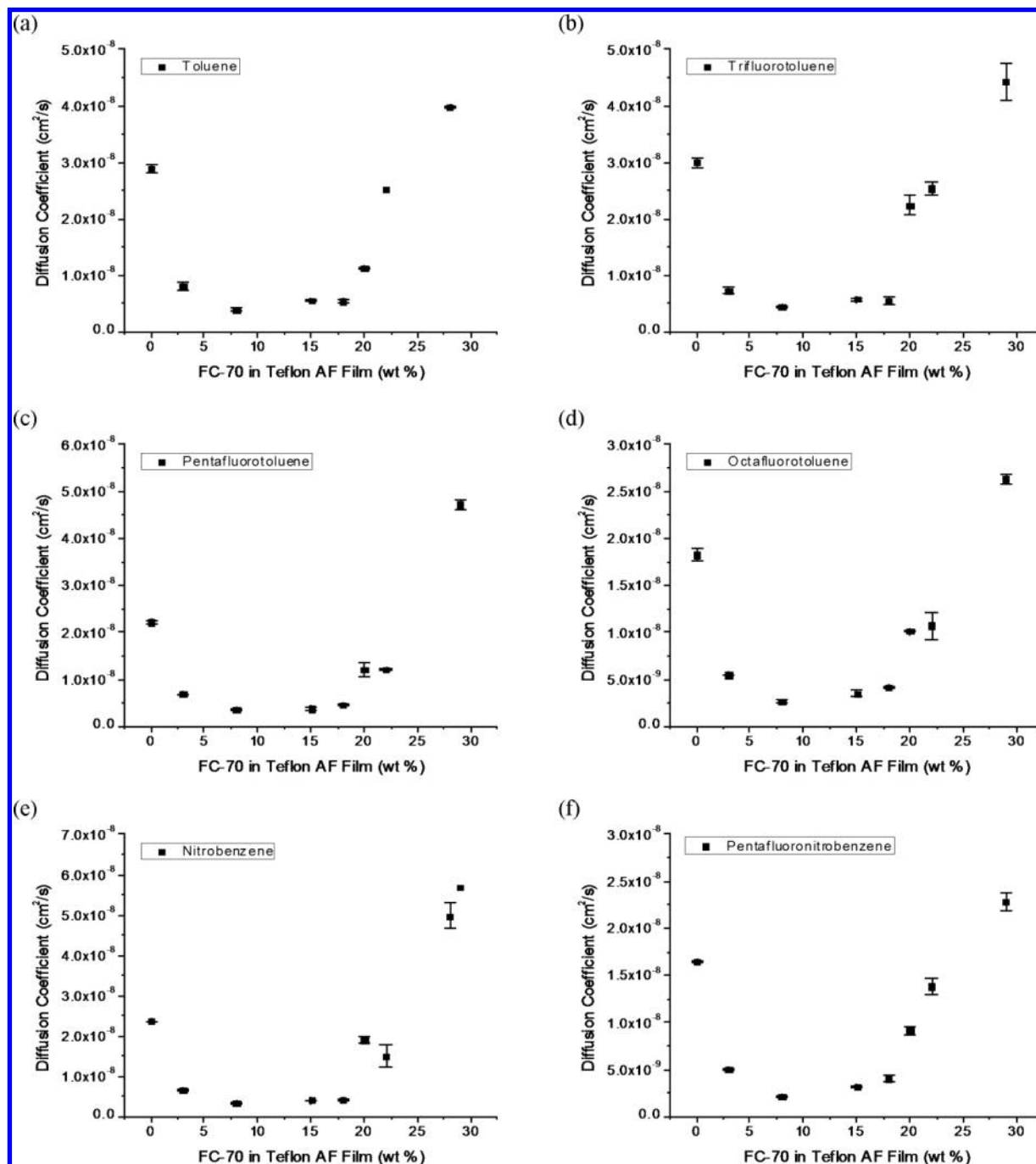
Figure 9. Diffusion coefficients of solutes in FC-70-doped Teflon AF 2400 films at 20.0 ± 1.0 °C: (a) toluene, C_s = 1.0 M; (b) α,α,α-trifluorotoluene, C_s = 0.3 M; (c) 2,3,4,5,6-pentafluorotoluene, C_s = 0.5 M; (d) octafluorotoluene, C_s = 0.1 M; (e) nitrobenzene, C_s = 0.5 M; (f) pentafluoronitrobenzene, C_s = 0.2 M.

Table 4. Solute Partition Coefficients (FC-70/CHCl₃) at 20 °C

solutes	$K_{F/C}$
toluene[a]	0.011 ± 0.001
α,α,α-trifluorotoluene[a]	0.060 ± 0.004
2,3,4,5,6-pentafluorotoluene[b]	0.108 ± 0.002
octafluorotoluene[b]	0.616 ± 0.006
nitrobenzene[a]	0.006
pentafluoronitrobenzene[a]	0.045

[a] Data were obtained from HSGC. [b] Data were obtained from solute partitioning (triplicate measurements). The errors indicated in table are the standard error of the mean.

selectivity for the substitution 8F/8H. Thus, partitioning selectivities, $S_{k\text{-}CF_3/\text{-}CH_3}$ and $S_{k\text{-}C_6F_5/\text{-}C_6H_5}$, were calculated from the

average of the partitioning selectivities of the solute pairs with the corresponding substitutions. The product of the two partitioning selectivities is very close to the partitioning selectivity of the octafluorotoluene/toluene pair ($S_{kC_6F_5CF_3/C_6H_5CH_3}$) at each film composition. A linear relationship (R^2 = 0.9964) was obtained with a slope of 1.009 ± 0.025 and an intercept of -0.368 ± 0.444, when $S_{kC_6F_5CF_3/C_6H_5CH_3}$ is plotted against $S_{k\text{-}CF_3/\text{-}CH_3} \times S_{k\text{-}C_6F_5/\text{-}C_6H_5}$ (Figure 12). Statistical analysis shows no significant difference between the slope and the ideal value of unity (p = 0.723). The difference between the intercept and the ideal value of zero is not significant either (p = 0.446). This correlation in the toluene series indicates that neither the substitution of fluorine on the methyl group nor that on the
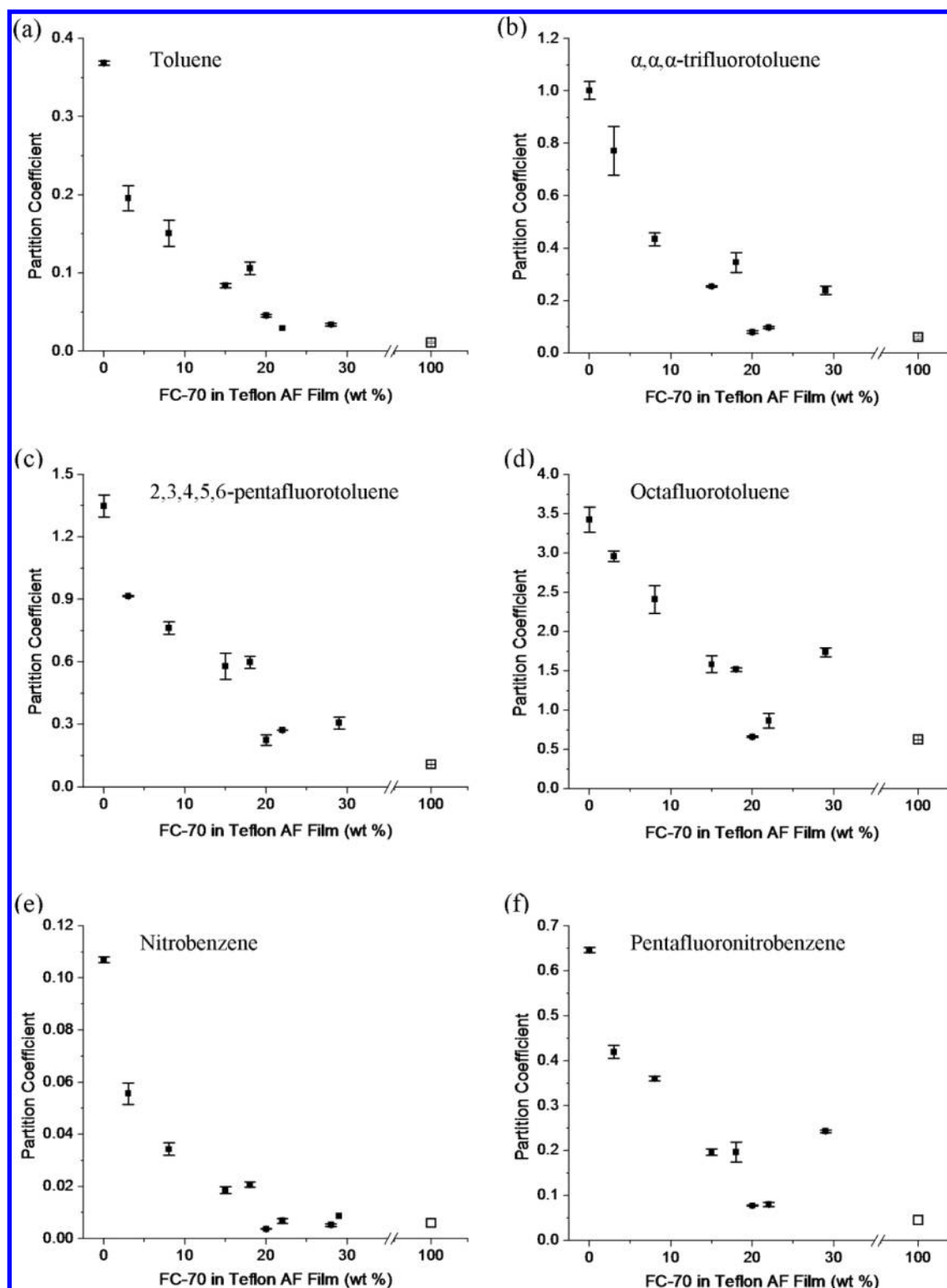
Figure 10. Partition coefficients of solutes in FC-70-doped films at 20.0 ± 1.0 °C: (a) toluene, C_s = 1.0 M; (b) α,α,α-trifluorotoluene, C_s = 0.3 M; (c) 2,3,4,5,6-pentafluorotoluene, C_s = 0.5 M; (d) octafluorotoluene, C_s = 0.1 M; (e) nitrobenzene, C_s = 0.5 M; (f) pentafluoronitrobenzene, C_s = 0.2 M. Partition coefficients of toluene, α,α,α-trifluorotoluene, nitrobenzene, and pentafluorotoluene from chloroform into pure FC-70 were obtained from head space gas chromatography. Liquid−liquid partitioning experiments were performed to get those values for 2,3,4,5,6-pentafluorotoluene and octafluorotoluene.

phenyl group will significantly change the partitioning properties of other substructures in the solutes.

For the nitrobenzene pair, the partition ratio of pentafluoronitrobenzene over nitrobenzene is much higher than the ratios of toluene pairs with the same substitution. This probably results from the strong electron-withdrawing effect of the F/H substitu-

tion on the nitro group. Nitrobenzene is not only highly polar but also highly polarizable.[81] Substitution of five hydrogen atoms on the phenyl group with fluorine atoms may significantly

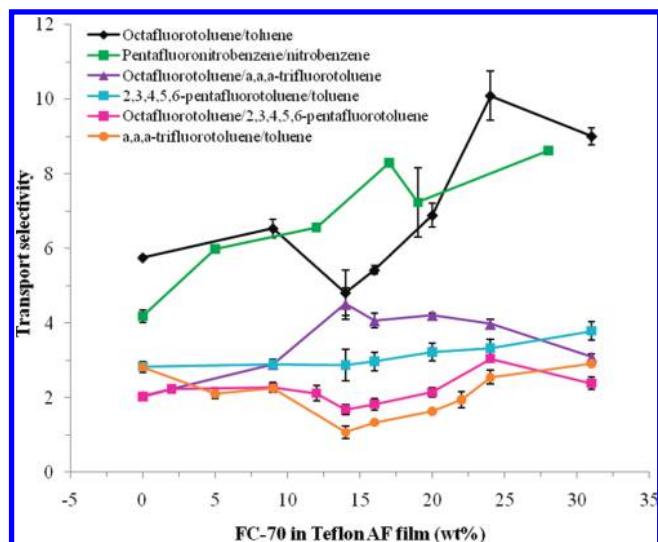(81) Vlasov, V. M.; Khalfina, I. A. *J. Phys. Org. Chem.* **2000**, *13*, 630– 633.
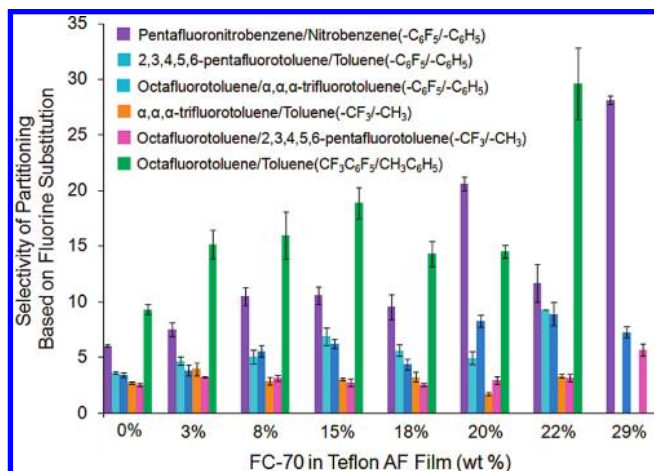
Figure 11. Selectivity of partitioning based on different fluorine substitutions. The error bars are the standard error of the mean.
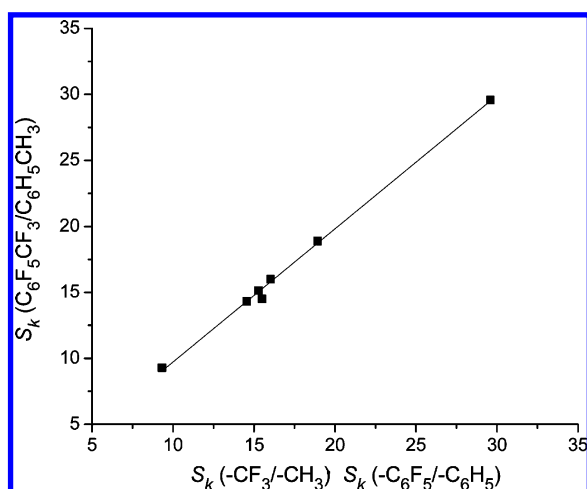
Figure 12. Partitioning selectivities of octafluorotoluene over toluene in FC-70-doped (0−30 wt %) Teflon AF films were plotted against the product of partitioning selectivities of trifluoromethyl/methyl and perfluorophenyl/phenyl groups ($y = 1.009x - 0.368$, $R^2 = 0.9964$).

decrease the electron density on the nitro group, thus decreasing its polarizability. Recently, Amemiya's group reported that the lipophilic nature of perfluoroalkyl surfactants originates from the electron-withdrawing effect of a perfluoroalkyl group on its adjacent oxoanion groups.[82] The decrease in the charge density on the carboxylate functional group is responsible for the significant solubility of perfluorooctanoate in octanol. In a similar way, therefore, the intermolecular interactions between pentafluoronitrobenzene and solvent are weaker than those of nitrobenzene. Confirmation of this notion can be seen in the relatively large difference of the boiling points of the two liquids (52 °C). In comparison, the differences of boiling point between the toluene and 2,3,4,5,6-pentafluorotoluene pair as well as the α,α,α-trifluorotoluene and octafluorotoluene pair are 6 and 2 °C, respectively. In addition, an FT-IR study of nitrobenzene in chloroform indicates a strong hydrogen-bond formation.[83] However, the nitro group in pentafluoronitrobenzene will be a much weaker hydrogen-bond acceptor due to the decreased

(82) Jing, P.; Rodgers, P. J.; Amemiya, S. *J. Am. Chem. Soc.* **2009**, *131*, 2290–2296.
(83) Nyquist, R. A.; Settineri, S. E. *Appl. Spectrosc.* **1990**, *44*, 1552–1557.

Figure 13. Transport selectivity based on the substitution of fluorine atoms (8F, 5F, 3F) at 20.0 ± 1.0 °C. The error bars represent the standard error of the mean.

electron density. Thus, the 5F/5H substitution on the phenyl group significantly changes the electronic properties of the nitro group.

3.7. Transport Selectivity of FC-70-Doped Teflon AF Films Based on Different Substitutions. The transport selectivities based on different substitutions (3F, 5F, 8F) are plotted against the composition of FC-70-doped films (Figure 13). Usually, longer fluorous ponytails, more ponytails, and/or a higher weight percentage of fluorine lead to larger partition coefficients into fluorous media and thus better selectivity in partitioning dominated selective transport. There is a general increasing trend for the selectivities of 8F- and 5F-substituted pairs. Among all the solute pairs we studied, the octafluorotoluene and toluene pair has the largest difference in fluorine content; thus, the partitioning of octafluorotoluene compared with toluene (K_{OFT}/K_{TOL}) into doped film is more favorable than into the pure Teflon AF film. However, the relatively large size of octafluorotoluene leads to slower diffusion. Nonetheless, the selectivity of this pair increased using Teflon AF films doped with larger FC-70 content. For the solute pairs with the same substitution of five fluorine atoms on the phenyl ring, the selectivity increased most significantly for the pentafluoronitrobenzene/nitrobenzene pair followed by the octafluorotoluene/α,α,α-trifluorotoluene and 2,3,4,5,6-pentafluorotoluene/toluene pairs. For the solute pairs with substitution of three fluorine atoms, no obvious increase on selectivity was observed using FC-70 (≤30 wt %) doped Teflon AF film. Further increase of the FC-70 wt % in Teflon film can be beneficial to increase the transport selectivity. However, a Teflon AF 2400 film containing FC-70 larger than a weight percentage of 35 wt % is difficult to handle practically due to the reduced mechanical properties.

3.8. Recycling of Teflon AF 2400. Teflons are normally not considered to be easily degraded. The recycling of Teflons can reduce not only the production of waste but also the cost of our separation system. As shown in Table 5, the recycled Teflon AF 2400 films have a similar film density to that of the fresh films with no significant difference ($p = 0.553$). The practicality of the recycled Teflon AF 2400 for the transport application has been verified. The relative errors of permeability coefficients for toluene and α,α,α-trifluorotluene through recycled films and fresh films are 22% and 13%, respectively, which fall within

Table 5. Properties of the Fresh Teflon AF 2400 Film and Recycled Teflon AF 2400 Film

	fresh Teflon AF 2400 film	recycled Teflon AF 2400 film
density (g/cm^3)	1.816 ± 0.022 ($n^a = 5$)	1.822 ± 0.017 ($n^a = 10$)
$P_{toluene}$ (cm^2/s)	$(1.19 \pm 0.01) \times 10^{-8}$	$(0.953 \pm 0.040) \times 10^{-8}$
$P_{\alpha,\alpha,\alpha\text{-trifluorotoluene}}$ (cm^2/s)	$(3.35 \pm 0.16) \times 10^{-8}$	$(2.94 \pm 0.02) \times 10^{-8}$
selectivity	2.82 ± 0.14	3.08 ± 0.13

^{a} n is the number of measurements.

the margin of error in our long-term study.[58] The selectivity of α,α,α-trifluorotluene over toluene has 9% relative error through the recycled Teflon films and fresh ones. Therefore, the FC-70-doped Teflon AF 2400 used in this work could be recycled for practical use.

4. Summary

Perfluorotripentylamine-doped Teflon AF 2400 matrices transport fluorinated organic compounds with considerable selectivity compared to their organic counterparts. Less chloroform paritions into Teflon AF films containing FC-70 than into undoped films. The amount of chloroform absorbed in Teflon films with larger than 20 wt % FC-70 is close to the solubility of chloroform in FC-70. Moreover, solute partition coefficients from chloroform to Teflon films doped with more FC-70 approach the partition coefficients from chloroform to pure FC-70. Both the sorption behavior of chloroform and the solute partitioning pattern indicate that doped Teflon films have FC-70-like properties. The permeabilities of six solutes through Teflon films doped with various amounts of FC-70 (0−30 wt %) show a similar pattern as FC-70 content is changed due to the integrated effect of solute diffusion and partitioning. FC-70-doped films show increasing selectivity for transport of 8F/8H- and 5F/5H-substituted solute pairs as FC-70 content increases.