

## How Fluorous Is Poly(2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxide-co-tetrafluoroethylene) (Teflon AF)?

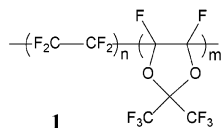
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Simple partitioning of solutes, with or without the aid of synthetic receptors,<sup>1</sup> is of inestimable value in chemistry. Selective partitioning, with solvents and/or synthetic receptors that solvate/bind to specific types of compounds, is particularly reliable. Fluorous liquids are selective solvents for fluorous compounds, a property that is useful in synthesis.<sup>2</sup> In practical situations, dimensionally stable solvents, such as polymer supported liquids,<sup>3</sup> are advantageous. With this in mind, we investigated poly(2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxide-co-tetrafluoroethylene (Teflon AF), a stable fluorous polymer, as a transport/extraction medium for solutes.

Teflon AF 2400 (**1**) contains 13 mol % tetrafluoroethylene and has a  $T_g$  of 240 °C.<sup>4</sup> **1** is moderately soluble in some fluorinated solvents at room temperature, which allows thin and dimensionally stable films to be cast easily. Films have been studied for their



suitability for gas separation<sup>5-10</sup> and pervaporation.<sup>11</sup> Films of **1** are highly permeable to gases apparently because of their high free volume. Some reports have shown gas-pressure-dependent transport, suggesting that the films are plasticized under these conditions.<sup>6,8,9</sup> There is no work of which we are aware that specifically looks at this important material as a solvent or transport medium of *solutes*. How fluorous is Teflon AF? We will first show that films of **1** are influenced by the solvent to which they are exposed. We then show that, as a result of imbibing organic solvent, films of **1** are not as dramatically different from organic solvent as is the fluorous solvent FC-72 (a mixture of perfluorohexanes).

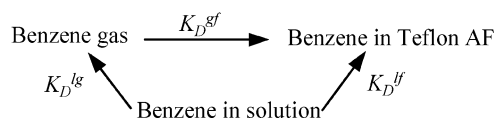
Table 1 shows the permeabilities of a series of organic solutes in chloroform through Teflon AF films.<sup>12</sup> The concentration independence of the permeability of benzene and pyrazine is consistent with a diffusion-controlled mechanism of mass transfer in which permeability ( $P$ ) is the product of diffusion coefficient ( $D$ ) and partition ratio ( $K_D$ ). We note that the films are somewhat selective. The solute  $\alpha,\alpha,\alpha$ -trifluorotoluene is preferred over its nonfluorinated counterpart. Less polar molecules pass more readily than the more polar ones ( $P_{\text{toluene}} > P_{\text{pyrazine}} > P_{\text{pyridine}}$ ). Thus, in this limited perspective, the permeability behavior qualitatively reflects the fluorous nature of the films.

Clues about the chemical nature of these films in equilibrium with solvent can be deduced from a comparison of diffusion coefficient and partition ratio for a solute, benzene, to the same parameters for “dry” films. Diffusion coefficients came from analysis of transport data for benzene (solute in  $\text{CHCl}_3$  solvent).<sup>12,13</sup> Benzene has a diffusion coefficient of  $(1.2 \pm 0.3) \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$  and a partition ratio ( $K_D^{\text{lf}}$ , from  $\text{CHCl}_3$  to **1**) of  $0.040 \pm 0.011$

**Table 1.** Permeability Coefficients ( $P$ ) of Solutes in Teflon AF Films

analyte	$P/(10^{-8} \text{ cm}^2 \cdot \text{s}^{-1})$
$\alpha,\alpha,\alpha$ -trifluorotoluene	4.7
benzene	3.3
toluene	2.4
pyrazine	2.0
pyridine	1.4

### Scheme 1



$$K_D^{\text{gf}} = V_g \rho_s \quad (1)$$

(SEM:  $n = 7$ ). The diffusion coefficient of benzene in **1** in a pervaporation study (film between pure liquid and gas phase) was reported to be  $1.9 \times 10^{-7} \text{ cm}^2 \cdot \text{s}^{-1}$ .<sup>11</sup> However, the diffusion coefficient of the gas vapor of benzene in Teflon AF 1600 is only  $10^{-10} \text{ cm}^2 \cdot \text{s}^{-1}$ .<sup>14</sup> The diffusion of gases in Teflon AF 1600 is about a factor of 10 slower than in **1**. Thus, the diffusion coefficient of the solute benzene is remarkably 2–3 orders of magnitude larger than that of the gaseous benzene.

To assess the partition ratio for a solute to a “dry” film, it is helpful to consider Scheme 1. We will compare measured  $K_D^{\text{lf}}$  for benzene (solute) to the value of  $K_D^{\text{lg}} K_D^{\text{gf}}$ . The latter product is a hypothetical  $K_D^{\text{lf}*}$  for benzene (solute) to a “dry” film. The partition ratio  $K_D^{\text{gf}}$  comes from inverse gas chromatography (benzene vapor sorption into **1**). Using eq 1 with a net retention volume,  $V_g$ , of  $600 \text{ cm}^3 \cdot \text{g}^{-1}$  (at room temperature from the plot of  $V_g$  vs temperature reported by Bondar et al.<sup>15</sup>) and a density,  $\rho_s$ , of  $1.73 \text{ g} \cdot \text{cm}^{-3}$ , the partition ratio  $K_D^{\text{gf}}$  is 1038.  $K_D^{\text{lg}}$  is  $3.32 \times 10^{-4}$  from the partial pressure of 0.1 M benzene solution at 298 K. (Refer to Supporting Information.) Thus, the partition ratio of benzene from chloroform solution to the *chloroform-free* Teflon AF film,  $K_D^{\text{lf}*}$ , is 0.34. This is about 8 times larger than  $K_D^{\text{lf}}$  we measured, which is only 0.040.

$$K_D^{\text{gf}} = V_g \rho_s \quad (1)$$

We therefore measured the extent of solvent uptake in film **1**. Films were monitored by infrared spectroscopy while in contact with flowing saturated vapor of chloroform. The concentration of chloroform in **1** in equilibrium with saturated vapor at room temperature is  $1.13 \pm 0.04 \text{ M}$  ( $n = 5$ ), which is a 100-fold concentration of the vapor on a molar basis. This value is close to the value recently reported in a pervaporation study (1.3 M).<sup>11</sup> The surprisingly strong sorption of solvents in Teflon AF films is

**Table 2.** Vibrational Frequencies of  $\text{CHCl}_3$ 

chloroform	$\nu$ ( $\text{cm}^{-1}$ )
gas <sup>16</sup>	3034
liquid	3020
1% solution in FC-72	3034
in <b>1</b>	3025

**Table 3.** Partition Ratio of 3-hydroxypyridine and Its Association Constant with **2** in Fluorous Media

	$K_D^a$	$K_f^a$
<b>1</b>	0.02	840
FC72	$6.7 \times 10^{-5}$	$4.3 \times 10^6$

<sup>a</sup>  $K_D$ : partition ratio.  $K_f$ : association constant. The association constant is calculated by taking the stoichiometry of the complex as 1:1 as measured from Job's plot of **3** with perfluorodecanoic acid.<sup>18</sup>

consistent with the dual sorption model describing the gas behavior in Teflon AF,<sup>9,15</sup> in which **1** was demonstrated to have high Langmuir sorption capacity and Henry constants compared to other glassy polymers. The Langmuir sorption capacity represents saturable partitioning into voids, while the Henry constant represents dissolving in the polymer matrix.

The C–H stretch is known to be solvatochromic.<sup>16</sup> Interestingly, the IR spectra of chloroform as gas vapor, as liquid, as a solute in FC-72, and in film **1** show marked differences (Table 2). The spectroscopic evidence demonstrates that chloroform is not in an environment like bulk chloroform; neither is it in an environment like a fluorous solvent.

We conclude that, because the film sorbs solvent, it becomes more organic-like, though the solvent is not identical to the bulk solvent. Extrapolating published data<sup>15</sup> for small gases leads to estimates of Henry's constant and Langmuir sorption for  $\text{CHCl}_3$ . They predict that, of the sorbed  $\text{CHCl}_3$  from exposure of **1** to saturated vapor or pure liquid, about 40% is dissolved while 60% is sorbed into the free volume. Sorption of solvent decreases the  $K_D$  of benzene (solute) compared to benzene vapor because the large free volume, which is void space for benzene vapor, is chloroform-filled. At the same time, partitioning of chloroform into the film matrix (Henry's law) plasticizes the film, dramatically increasing the diffusion coefficient of benzene (solute) vs benzene (vapor).

We have, for the first time, demonstrated plasticization of **1** with a  $T_g$  measurement. A nonvolatile, –COOH terminated perfluoroether, Krytox FSH (**2**, MW 7500, Dupont), plasticizes **1**:  $T_g$  is  $-40$  °C for **1** containing 50% **2** (w/w) compared to  $240$  °C for pure **1**. Remarkably, small solute diffusion coefficients decrease dramatically in the plasticized film compared to the glassy film from pure **1**. For example, the diffusion coefficient of benzene (solute) changes from  $(1.2 \pm 0.3) \times 10^{-6}$  ( $n = 7$ ) to  $(2.8 \pm 0.2) \times 10^{-9}$   $\text{cm}^2 \cdot \text{s}^{-1}$  ( $n = 3$ ); the diffusion coefficient of 3-hydroxypyridine (**3**) decreases from  $(3.3 \pm 0.4) \times 10^{-8}$  ( $n = 7$ ) to  $(8.9 \pm 2.0) \times 10^{-11}$  ( $n = 3$ )  $\text{cm}^2 \cdot \text{s}^{-1}$ . Like  $\text{CHCl}_3$ , **2** decreases free volume, but it is more viscous than  $\text{CHCl}_3$ . So, while it plasticizes **1** (increasing segmental chain motion), it does not increase the mobility of small solutes. This observation contrasts with antiplasticization<sup>17</sup> in which additives to organic polymers decrease free volume while decreasing segmental chain motion. The result is lower penetrant permeability accompanied by increased film stiffness.<sup>17</sup>

It is informative to compare directly polar solute partitioning and hydrogen bonding in a fluorous solvent and in a **1** film. Chloroform solutions of 3-hydroxypyridine were extracted by FC-72 or **1** films with or without **2** (0.13 M) (Table 3).

The fluorous FC-72 cannot dissolve the polar 3-hydroxypyridine. H-bond based association, which is highly solvent dependent,<sup>19</sup> is very strong in FC-72. The noncovalent association between Krytox and 3-hydroxypyridine increases the extractability of the polar solute by 15 000 times in FC-72 as opposed to 41 times in **1**.

Solvent-saturated Teflon AF films are not truly fluorous. The solvent creates a supported-liquid membrane. The sorption of solvents changes the diffusion and partitioning properties of solutes in the films.

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**Supporting Information Available:** Equations and MathCAD nonlinear fit of the transport curve of benzene; calculation of  $K_D$ <sup>18</sup>; spectra of chloroform in solution and in film **1**; determination of the stoichiometry of the complex between 3-hydroxypyridine and perfluorodecanoic acid. This material is available free of charge via the Internet at <http://pub.acs.org>.

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