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Porous alumina-based fluorous liquid membranes: Dependence of transport on fluorous solvent

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ABSTRACT

We report here the properties of supported fluorous liquid membranes based on porous alumina. The alumina is first rendered compatible with fluorous solvents by surface modification with an oligomeric perfluoropropylene oxide-based carboxylic acid, Krytox 157FSH. After modification, simply dipping the porous alumina membrane into a perfluorinated solvent results in a supported liquid membrane with high selectivity for fluorous compounds. Two homologous series of compounds differing in the number of $-CF_2-$ groups were investigated, namely esters of cinnamyl alcohol and the analogous naphthyl derivative with 2H,2H,3H,3H-perfluoroalkanoic acids ($HOOC\text{-}(CH_2)_2\text{-}(CF_2)_{m-1}CF_3$, $m = 2, 4, 6$ and 8). Four perfluorinated membrane solvents (FC-77, PF-5080, FC-3283 and FC-43) were investigated. In FC-3283, the permeabilities, which are the products of a diffusion coefficient and a partition coefficient in the solution–diffusion model, of cinnamyl alcohol derivatives are 3.62 ± 0.36 times greater than those of the analogous naphthyl compounds for the solutes containing the same perfluorinated chain. Permeability, P, increases as the perfluorinated chain length increases in all of the perfluorinated solvents. Values of $\log(P)$ vs m are linear with a slope of 0.147 ± 0.002 but with different intercepts for the various solvents. Independent measurements of the partition coefficients of the solutes between the source/receiving phase solvent, ethanol, and the fluorous solvents reveal that the selectivity behavior is dominated by partitioning rather than diffusion. The free energy of transfer of a $-CF_2-$ group (ethanol to perfluorinated solvents) is -1.1 kJ/mol. Despite the fact that the solvents are mixtures, not pure liquids, the partition coefficients are well correlated with values calculated based on group contributions with 'mobile order and disorder' theory. The diffusion coefficients of four solutes in four membrane solvents were also determined based on the solution–diffusion model. The Stoke–Einstein equation shows satisfactory estimation of experimental results.

1. Introduction

A successful supported liquid membrane (SLM) [1–3] requires a proper combination of porous support and a liquid phase to achieve high selectivity, high permeability, and desirable stability. To date, organic solvents have been used widely as the supported liquid because the common application is the separation of solutes based on lipophilicity. Here, our strategy is to use perfluorocarbons or related fluorous materials to replace the commonly used organic solvents. Fluorous liquids such as perfluorinated alkanes, perfluorinated oligoethers or polyethers and perfluorinated trialkylamines are inert [4,5], nonpolar and hydrophobic as well as oleophobic. The attraction of perfluorocarbons has been recognized by the organic synthesis community in biphasic synthesis, catalysis and extraction [6–8]. The driving force in those techniques arises from the fact that the fluorinated compounds have weaker van der Waals interactions with solvent per molar volume than organic compounds [9]. Typically, a fluorous tag is covalently attached to the target species to give it some solubility in fluorous solvents. Other synthetic applications such as the phase-vanishing or bulk membrane techniques [10–12] use a fluorous layer but not necessarily fluorous reagents or catalysts. There is a small but growing interest in using noncovalent interactions in fluorous media for synthetic chemistry [13], selective extractions [14–16], and potentiometric sensors [17,18]. In these applications, the permeability of the solutes (reagents, catalysts, analytes) through the fluorous medium is an important parameter in dictating the function of the fluorous phase.

We have previously worked on the transport of solutes through Teflon AF 2400 membranes, which are readily cast, thin, and mechanically strong. The preferential transport of

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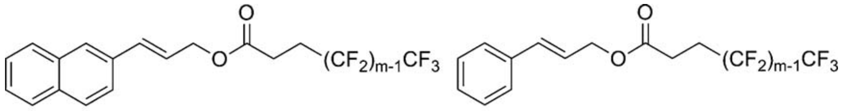

2
2a (*m* = 2)
2b (*m* = 4)
2c (*m* = 6)
2d (*m* = 8)

3
3a (*m* = 2)
3b (*m* = 4)
3c (*m* = 6)
3d (*m* = 8)

Fig. 1. Structures of solutes studied.

α,α,α-trifluorotoluene over toluene was demonstrated in Krytox 157FSH (**1**)-doped polymeric Teflon AF 2400 membranes [19].

$$\underset{\mathbf{1}}{CF_3{-}CF_2{-}CF_2{-}O{-}\,[CF(CF_3)CF_2{-}O{-}]_nCF(CF_3)COOH}$$

However, solute transport through Teflon AF 2400 membranes is slow. Also, Teflon AF imbibes the solvent from the source/receiving phase (chloroform) and as a result becomes less fluorous [20,21]. To create a membrane that is more fluorous than Teflon AF, we have developed fluorous SLMs [22] based on porous alumina [23–25]. In the work presented here, we have determined permeabilities and partition coefficients for two homologous series in SLMs with four different fluorous solvents. Diffusion coefficients were determined from the permeabilities and partition coefficients. We find that the transfer free energy for the $-CF_2-$ group (from source/receiving phase, ethanol) is the same for all four fluorous solvents investigated, however the affinity of the fluorous solvents for an organic moiety varies considerably. There are a few approaches to determine partition coefficients in fluorous systems based on empirical relationships [9,26–31]. This effort is largely focused on the perfluoro(methylcyclohexane)/toluene solvent system and the notion of 'fluorophilicity'. It is necessary to expand the range of applicability of empirical approaches. Thus, using the SLMs, we determined permeability coefficients of the solutes through four fluorous solvents. Independent measurements of the partition coefficients in the biphasic systems fluorous solvent/ethanol (where 'fluorous solvent' represents the four solvents used) allow estimation of diffusion coefficients. Partition coefficients and diffusion coefficients are well predicted by convenient approaches using group additivity methods.

2. Results and discussion

2.1. Dependence of permeability coefficients on the solute properties

Two homologous series of solutes (Fig. 1) were used to investigate the influence of solute properties on transport through the fluorous SLMs (FSLMs). Data are listed in Table 1. Inspection of Table 1 shows that the permeability for each member of the **3**-series is about 3∼4 times higher than that for the corresponding **2**-series. The average ratio of the permeabilities of members in the **3**-series over the corresponding members in the **2**-series is 3.62 ± 0.36. The insertion of an organic group is known to decrease partition coefficients in similar solvent systems [32]. Of course, the addition of an organic group leads to a larger molecular volume, and hence a lower diffusion coefficient as well. Thus, it is clear that the lower permeabilities of the **2**-series are expected. Increasing the number of $-CF_2-$ groups hastens transport through the FSLMs, as shown in Table 1. Solutes with a longer perfluoroalkyl tail have a larger partition coefficient into a fluorous phase. However, the addition of a $-(CF_2)_2-$ unit no doubt increases molecular size, resulting in a decreased diffusion coefficient. Table 1 indicates that the permeability increases with an increasing length of perfluoroalkyl tail. In this case it is the effect of adding a $-(CF_2)_2-$ unit increases the partition coefficient more than it decreases the diffusion coefficient.

Table 1
Logarithmic values of *P* for **2**- and **3**-series solutes.

n	$\text{Log}(P/10^{-7}\,\text{cm}^2\,\text{s}^{-1})$[a]	
	2-Series	**3**-Series
2	-8.18 ± 0.04	-7.66 ± 0.01
4	-7.88 ± 0.06	-7.22 ± 0.02
6	-7.48 ± 0.12	-6.90 ± 0.09
8	-7.25 ± 0.02	-6.79 ± 0.02

[a] Average permeabilities based on duplicate or triplicate measurements through **1**-modified 100 nm alumina membranes filled with FC-3283.

2.2. Dependence of permeabilities on membrane solvent

Permeabilities and partition coefficients of the **3**-series for various membrane solvents are reported in Table 2. The properties of these perfluorinated solvents are listed in Table 3. The properties of the solutes are listed in Table 4. These solvents were chosen based on a compromise. Lower molecular weight solvents have lower viscosity, which increases permeabilities, however they also have lower boiling points which decreases their attractiveness. This set of solvents has on average a fairly low viscosity and a fairly high boiling point. The slope of a plot of log *K* vs the number of $-CF_2-$ groups, *m*, is directly proportional to the free energy of transfer of the $-CF_2-$ group. Slopes of such plots based on the data in Table 2 give rise to similar slopes for **3**-series partitioning into the four membrane solvents. The average slope of the log(*K*) vs *m* plot (partitioning) is 0.188 ± 0.003. Thus, the free energy of transfer of a $-CF_2-$ from ethanol to these perfluorinated solvents is −1.1 kJ/mol. The average slope of the log(*P*) vs *m* plot (permeability) is 0.147 ± 0.002. Thus, the addition of a $-CF_2-$ unit increases the transport rate by a factor of 1.4. The permeability shows a strong dependence on the membrane solvents in the order of FC-77 > PF-5080 > FC-3283 > FC-43. For example, the permeability of **3d** in FC-77 is about seven times that in FC-43. The great variation in permeability goes beyond the influence of partition coefficients (Table 2) resulting from the different membrane solvents. For instance, the measured partition coefficient of **3d** in FC-77 is twice that in FC-43. Hence, we postulate that the extra variation in the permeability is caused by the effect of solvent on the solute diffusion coefficients. We defer a detailed discussion of diffusion. For now, it is sufficient to point out that the ratio of viscosities for the same two solvents (FC-77 and FC-43) is about 4. Thus, the large dependence of permeability on solvent can be rationalized.

2.3. Predicting solute behavior

There is a justifiable tendency to shun the use of solvent mixtures such as FC-72, FC-77, PF-5080, and FC-3283, and use solvents like perfluoromethylcyclohexane. Important quantities such as molar volume are necessarily less well defined in the

Table 2
Logarithmic values of *P* and *K* for the **3**-series in different membrane solvents.

n	$\log(P/10^{-7}\,cm^2\,s^{-1})$[a]				$\log(K)$[b]			
	FC-77	PF-5080	FC-3283	FC-43	FC-77	PF-5080	FC-3283	FC-43
2	-7.31 ± 0.05	-7.43 ± 0.08	-7.66 ± 0.01	-8.09 ± 0.03	-1.57 ± 0.11	-1.63 ± 0.03	-1.79 ± 0.14	-1.87 ± 0.16
4	-7.02 ± 0.04	-7.06 ± 0.02	-7.22 ± 0.02	-7.89 ± 0.02	-1.24 ± 0.10	-1.22 ± 0.06	-1.25 ± 0.04	-1.55 ± 0.11
6	-6.68 ± 0.05	-6.82 ± 0.04	-6.90 ± 0.09	-7.44 ± 0.02	-0.78 ± 0.04	-0.91 ± 0.02	-0.95 ± 0.04	-1.04 ± 0.01
8	-6.41 ± 0.01	-6.54 ± 0.01	-6.79 ± 0.02	-7.27 ± 0.08	-0.44 ± 0.02	-0.51 ± 0.01	-0.62 ± 0.04	-0.74 ± 0.02

[a] The permeabilities are based on duplicate or triplicate measurements.
[b] The partition coefficients are based on triplicate measurements.

former solvents compared to the latter solvent. On the other hand, in the world of applied chemistry, there is a tendency to use solvents based on criteria other than whether a solvent is a mixture or not. We note the large difference of a factor of two in the partition coefficients mentioned above. We had not anticipated such a difference among nominally similar solvents. We therefore sought to understand whether approaches to understanding partition coefficients and diffusion coefficients based on group contribution approaches would apply to the current data. While we recognize that our data set is limited, we point out that the few computational treatments that exist focus on 'fluorophilicity' which is related to partitioning between perfluoromethylcyclohexane and toluene [26,29,30,33,34].

de Wolf et al. established a general relationship for the partition coefficient, *K*, based on the mobile order and disorder (MOD) theory [33].

$$\log K = 0.2171\ln\left(\frac{V_o}{V_F}\right) - 0.217\,V_b\left(\frac{1}{V_o} - \frac{1}{V_F}\right) + 0.0522\left(\frac{V_b}{T}\right)\left(\frac{\delta_o^2}{\delta_F^2}\right) - 0.1045\left(\frac{V_b\delta_b}{T}\right)(\delta_o - \delta_F) \qquad (1)$$

T is the experimental temperature (Kelvin). V_b is the molar volume of the solute. V_o and V_F are the molar volumes of the organic and the fluorous solvent, respectively. δ_b is the modified nonspecific cohesion parameter of the solute. δ_o and δ_F are the modified nonspecific cohesion parameters of the organic and the fluorous solvents. Modified nonspecific cohesion parameters account for only the nonspecific force exhibited between molecules in liquids [29]. Generally, group contribution methods [33,35] can be used to estimate the value of molar volume for solutes and solvents. Similarly, δ can be calculated from the molar volume and the molar nonspecific vaporization energy. Hence, the values of *V* and δ can be determined for the fluorous solutes and the organic phase, ethanol. For the fluorous solvents it is not so simple. Some approximations are required when using the group contribution approach for these fluorous solvents. For example, PF-5080 and FC-3283 are each mixtures; PF-5080 is a mixture of perfluorooctanes and FC-3283 is a mixture of perfluorononanes. The values of V_F were estimated based on the perfluorinated *n*-octane and *n*-nonane respectively. A comparison between the calculated values of V_F and the values determined by dividing molecular weight by density demonstrates that reasonable accuracy can be achieved following this procedure. Therefore, the same chemical structures were used to calculate the values of δ_F for PF-5080 and FC-3283. FC-43 is not a mixture. However there is no group contribution for the nitrogen group in a perfluorotrialkylamine for estimating the value of δ_F. Considering that no specific interactions such as dipole–dipole and H-bonding exist in FC-43, the solubility parameter and the modified nonspecific cohesion parameter should be identical. Thus, we used the vaporization energy [35] to estimate the δ_F for FC-43. The most complicated case is FC-77 which is a mixture of C_8F_{18} and cyclic $C_8F_{16}O$. The molar volume can be calculated by dividing molecular weight by density. Furthermore, the δ_F for the oxygen group in perfluoroethers is small (0.03 kJ/mol), so we assumed that the incorporation of oxygen would not alter the vaporization energy significantly. Therefore, for FC-77's value of δ_F we used the value established for PF-5080. All of the values of V_F and δ_F are shown in Table 3.

Table 3
Properties of perfluorinated membrane solvents used.

Name	Boiling point (°C)	Viscosity (cP)	V_F (cm^3/mol)	δ_F (MPa$^{1/2}$)
FC-77	97	1.28	233[c]	10.5[b]
PF-5080	101	1.36	248[a]	10.5[d]
FC-3283	128	1.37	271[a]	10.6[b]
FC-43	174	5.26	356[e]	10.2[f]

[a] Increment values for the molar volume (cm^3/mol) obtained from Ref. [33], unless noted otherwise.
[b] Increment values for the nonspecific part of the molar vaporization energy used to calculate δ_F obtained from Ref. [31] unless specified otherwise.
[c] The molar volume of FC-77, a mixture, was determined from the molecular weight (415 g/mol) divided by the density.
[d] The values of δ_F for FC-77 and PF-5080 are the same.
[e] The increment value for the molar volume of nitrogen in perfluorotrialkylamines is from Ref. [35].
[f] The molar vaporization energy of nitrogen in triperfluoroalkyl amines from Ref. [35] was used to calculate the value of δ_F for FC-43.

Table 4
Properties of fluorous esters **3**.

Name	Melting point (°C)	V_b (cm^3/mol)[a,c]	δ_b (MPa$^{1/2}$)[b,d]
3a	–	258	15.6
3b	–	304	15.1
3c	33	350	14.6
3d	66	396	14.3

[a] Increment values for the molar volume (cm^3/mol) obtained from Ref. [33].
[b] Increment values for the nonspecific part of the molar vaporization energy used to calculate δ_b obtained from Ref. [33].
[c] Increment value for the molar volume of $-CH{=}CH_2$ was used for the substitute $-CH{=}CH-$.
[d] The calculated values of δ_b for $-CH{=}CH_2$ was employed as the values of δ_b for $-CH{=}CH-$.

The comparison of these calculated values from Eq. (1) and measured values from Table 2 are shown in Fig. 2. A good linear relationship with a slope of 1.01 ± 0.06 (SEM) and an intercept value of −0.15 ± 0.06 (SEM) is achieved when experimental log(*K*) was plotted vs calculated log(*K*). The statistical analysis shows that there is no significant difference between the slope and the ideal value of unity ($p = 0.870$). There is a marginally significant difference between the intercept and the ideal value of zero ($p = 0.027$).

This good correlation demonstrates the validity and applicability of Eq. (1) to fluorous solvents that are mixtures as well as to a fluorous system with an associating solvent. The work published to date concerns solvents perfluoromethylcyclohexane and toluene. Thus, while the data set is of limited size it is nonetheless encouraging that established approaches to partitioning based on group contributions seem applicable to a broader set of solvents than heretofore realized. It is interesting to note that, despite the different solvent structures represented here, the MOD treatment is satisfactory. Thus, the molar volume and the modified nonspecific cohesion parameter are adequate for a good estimation of the solvating properties of these solvents.

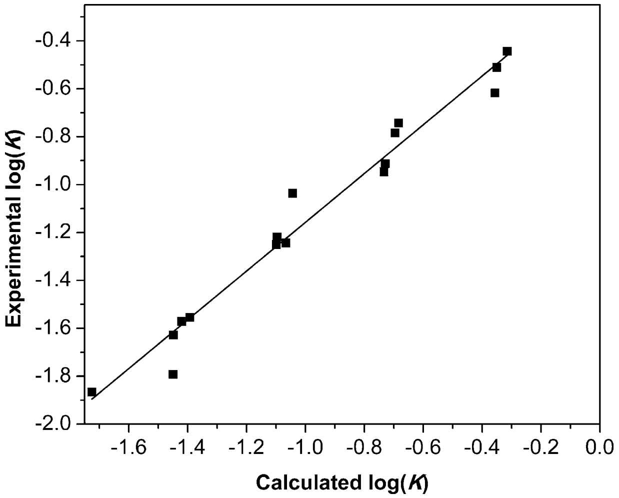

Fig. 2. Experimental vs calculated values of log(K) for the fluorous esters **3a–d** partitioning from ethanol to the fluorous solvents. The points represent the averages of duplicate or triplicate measurements.

We are not aware of measurements of diffusion coefficients of large molecules in fluorous solvents. The diffusion coefficients of solutes in the membrane solvents can be calculated from the measured partition coefficients (K) and permeabilities (P) corrected by porosity (ϕ) as shown in Eq. (2).

$$D = \frac{P}{K\phi} \qquad (2)$$

Table 5 shows these diffusion coefficients in the four perfluorinated solvents. We used a value for the porosity of 0.28 determined by voltammetry at the interface between two immiscible electrolyte solutions (ITIES) [36], which is a very similar system to ours. As for the partition coefficients, it would be helpful to have evidence that an established approach can predict the diffusion coefficients. We have used the Stokes–Einstein equation. The radius of each solute was calculated from the molar volume based on the group increment method [33]. The calculated diffusion coefficients are listed in Table 5, along with the experimental values. Here, we would like to point out the influence of the experimental error on our results. The average relative error for the diffusion coefficients was calculated from those for the permeability and partition coefficients. Both of the latter errors were about 10%. Therefore, the average relative error of the diffusion coefficients is about 15%. The solutes containing longer perfluoroalkyl groups gave us less relative error for permeability and partition coefficients compared to those with shorter perfluoroalkyl groups. Considering these errors, the agreement between the calculated and experimental values is satisfactory, especially for the solutes with longer perfluoroalkyl tags.

SLMs have been used widely for separation of ions or small organic molecules from aqueous or organic mixtures [37–41]. Hydrophobic SLMs based on organic solvents are the most common type. Carriers are typically dissolved into the membrane liquid to improve the separation selectivity. To our knowledge, there are no reports of FSLMs. We can compare range of permeabilities of the FSLMs reported here to a similar system, a mineral oil filled octadecyltrimethyoxylsilane (ODS) modified alumina membrane [25]. The investigators applied this system to the transport of small organic solutes such as phenol and its relatives. The permeabilities they achieved were in the range of $\sim 10^{-7}$ cm^2/s. The permeabilities reported here for our FSLMs for larger solutes are comparable. We have previously investigated transport through films of Teflon AF2400. Permeabilities of small organic solutes were about an order of magnitude smaller than the permeabilities mentioned above in the mineral oil SLM [19]. Hence, the FSLMs appears to provide permeabilities that are greater than or at least equal to the ODS modified SLMs and the Teflon AF2400 membranes.

We have demonstrated that the modified alumina membranes impregnated with perfluorinated solvent are effective fluorous membranes. The increase of the organic domain of the solute molecules significantly decreases the permeabilities for the identical length of fluorous tag. Lengthening the perfluoroalkyl chain on the solutes shows a strong influence on the permeability and partition coefficients. The free energy of a –CF2– group from ethanol into the four perfluorinated solvents is −1.1 kJ/mol. Diffusion coefficients were calculated from the measured permeabilities and partition coefficients. The Stokes–Einstein equation was also used to estimate the diffusion coefficients in the membrane solvents. A group contribution approach was used to determine the molar volume, and thus the effective molecular radius for the Stokes–Einstein equation. Satisfactory agreement was achieved for all solutes in each perfluorinated solvent.

3. Experimental

3.1. Materials

All the chemicals, unless specified otherwise, were obtained from Aldrich (Milwaukee, WI) or Sigma (St. Louis, MO). Krytox 157FSH with a carboxylic acid end group was obtained from Miller–Stephenson Chemical Co. (Morton Grove, IL). In previous work, we estimated the value of n to be 29 [15] and 33 [14] by ^{19}F NMR for two separate lots, both of which were used in this work. Fluorous-tagged solutes were gifts from FTI (Pittsburgh, PA). Alumina membranes (100 nm pore size, 13 mm diameter and 60 μm thickness) were obtained from Whatman (Florham Park, NJ). Hydrofluoroether-7100 (HFE-7100) (a mixture of methyl nonafluorobutyl and nonafluoroisobutyl ethers) was obtained from 3 M (Minneapolis, MN). FC-3283 Fluoroinert Electronic Liquid (a mixture of perfluorononanes), FC-43 Fluoroinert Electronic Liquid (perfluorotributylamine), FC-77 Fluoroinert Electronic Liquid (a mixture of C_8F_{18} and cyclic $C_8F_{16}O$) and PF-5080

Table 5
Diffusion coefficients for the **1**-modified 100 nm membranes.

Solute	FC-77		PF-5080		FC-3283		FC-43	
	D_{exp}[a] (/10^{-6} cm^2/s)	D_{cal} (/10^{-6} cm^2/s)	D_{exp}[a] (/10^{-6} cm^2/s)	D_{cal} (/10^{-6} cm^2/s)	D_{exp}[a] (/10^{-6} cm^2/s)	D_{cal} (/10^{-6} cm^2/s)	D_{exp}[a] (/10^{-6} cm^2/s)	D_{cal} (/10^{-6} cm^2/s)
3a	6.6	4.4	5.7	4.1	4.8	4.1	2.2	1.1
3b	6.0	4.2	5.2	3.9	3.8	3.9	1.7	1.0
3c	4.5	4.0	3.9	3.7	3.4	3.7	1.4	1.0
3d	3.8	3.8	3.4	3.6	2.4	3.5	1.1	0.9

[a] Porosity adopted here is 0.28 [36].

Performance Fluid (a mixture of perfluorooctanes) were purchased from 3 M (Minneapolis, MN).

3.2. Membrane modification

All 100 nm alumina membranes were pretreated by sequentially sonicating them in 30% H_2O_2 for 30 min, H_2O for 15 min and absolute ethanol for 30 min, and then drying at 100 °C for 30 min. Pretreated membranes were vertically mounted into a homemade Teflon rack. The rack of membranes was immersed in 60 mL of a 3 mM solution of 1 in HFE-7100 and refluxed for 3 h. After 3 h, the modified membranes were then thoroughly rinsed with HFE-7100, absolute ethanol and dried at 80 °C for 45 min.

3.3. Transport experiments

Transport measurements were made using a two-compartment system at $22 \pm 2^{\circ}$, measuring UV absorbance in the receiving phase. The membrane was dipped in a perfluorinated solvent and then mounted between two quartz cuvettes with holes in them [42]. Viton gaskets were required to prevent leaking. The transport area was defined by the holes in the gaskets/cuvettes with a diameter of 0.5 cm. A modified eight-position cuvette holder (Agilent) held four transport experiments in a rack. Each of the eight cuvettes was stirred magnetically with same stirring speed controlled by a stirring module. Typically, the four transport units were used for duplicate transport experiments conducted for two related solutes simultaneously. The source phase containing 3 mL of 1 mM solute in ethanol (saturated with the perfluorinated solvent used in the membrane) was introduced to one of the cuvettes, while the receiving phase contained 3 mL ethanol saturated with the corresponding perfluorinated solvent. To prevent any loss of perfluorinated solvent in the membrane, the identical membrane solvent (20 μL) was added to the source and receiving phases. The concentration of solutes in the receiving phase was monitored by a Hewlett-Packard 8452A UV–vis diode array spectrophotometer (Palo Alto, CA). The steady state flux, J, of a solute is given by Eq. (3):

$$J = \left(\frac{dC_r}{dt}\right)\left(\frac{V}{A}\right)(\mathrm{mol\,s^{-1}\,cm^{-2}}) \tag{3}$$

where A is the effective area of the membrane for transport, V is the volume of the receiving phase and dC_r/dt is the steady state accumulating rate of the solute in the receiving phase. The permeability, P, can be calculated from the flux using Eq. (4) as follows.

$$P = \frac{Jl}{C_s - C_r} \approx \frac{Jl}{C_{s_0}}\ (\mathrm{cm^2\,s^{-1}}) \tag{4}$$

l is the thickness of the membrane. C_s and C_r are the concentrations of the solute in the source phase and the receiving phase, respectively. $C_s - C_r$ is close to C_{s_0}, the initial concentration of the solute in the source phase, since C_r is negligible at the beginning of the experiment.

3.4. Determination of partition coefficients

Solute was dissolved in ethanol at the concentration of 1 mM. Solute/ethanol solution (70 μL) and perfluorinated solvent (140 μL) were placed in a VWR GC-autosampler vial (1.8 mL, West Chester, PA), shaken with the Bioshaker (distributed by BIONEXUS, Inc., Oakland, CA) at 1000 rpm and 25 °C for 30 min. The layers were physically separated and the ethanol layer was quantitatively analyzed by Jasco XLC (Easton, MD). Before injection, each sample was diluted five times with ethanol and 0.14 mM cinnamyl acetate was used as internal standard. A step gradient method was employed using Acquity UPLC^{TM} BEH C18 1.7 μm (1.0 × 50 mm) reversed-phase column from Waters (Milford, MA). Mobile phase was increased from 20% acetonitrile/80% H_2O (v/v) at 0.1 min to 95% acetonitrile/5% H_2O (v/v) at 0.2 min and remained at 95% acetonitrile/5% H_2O (v/v) for 8.8 more min. Finally, 20% acetonitrile/80% H_2O (v/v) was used to flush the column for 5 min in order to bring the column back to its initial state. The flow rate was maintained at 0.1 mL/min. The column temperature was kept at 40 °C. A Jasco XLC^{TM} 2077 Plus acted as the detector at 250 nm. The peak areas were integrated by the software after manually defining the baseline. For calibration curves, we used a series of five standard solutions with concentrations ranging from 0.02 to 0.18 mM solutes plus 0.14 mM cinnamyl acetate in ethanol. These standard solutions were used to create the calibration curves for each solute by plotting the peak area ratio of solute/cinnamyl acetate vs solute concentration.

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