Article

Fluorophobic Effect Promotes Partitioning of Organics into Macroporous Organic Polymers: A Method for Achieving High Local Concentrations

Shannon M. Leeder, and Michel R. Gagn

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 1 articles that cite this article, as of the time of this article download
- Access to high resolution figures

- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

Fluorophobic Effect Promotes Partitioning of Organics into Macroporous Organic Polymers: A Method for Achieving High Local Concentrations

Shannon M. Leeder and Michel R. Gagné*

Contribution from the University of North Carolina at Chapel Hill, Department of Chemistry, Chapel Hill, North Carolina 27599-3290

Received March 28, 2003; E-mail: mgagne@unc.edu

Abstract: The efficiency for partitioning small organic compounds from fluorinated solvents of varying quality into highly cross-linked, macroporous, and insoluble organic polymers is described. The solvating qualities of the poly(acrylates) together with the solvating quality of the solvent are key to describing the partitioning thermodynamics. Partitioning measurements for 9-anthracene methanol **1** are reported as a function of fluorous content in perfluoromethylcyclohexane (PFMC):hexanes mixtures, comonomer structure and loading, and temperature. The best comonomer for the sorption of **1** is methacrylamide. Concentration enhancements of up to ~200-fold are obtainable, and are proposed to account for previously observed rate accelerations in catalyst-containing porous polymers. Partition efficiency (PE) measurements, described as the ratio of polymer to original solution concentrations, are presented for a variety of organic compounds. The PE is sensitive to analyte structure and ranges from 1 to 170 (180 being the maximum under the conditions employed), with linear alkanes at the low end of the spectrum and polar functional groups at the opposite.

Introduction

Over the past decade, the use of fluorinated solvents and reagents for solving sophisticated problems in synthesis,[1] catalysis,[2] and molecular recognition/assembly[3] has grown. The clever utilization of this "third phase" has led to numerous solutions to problems that would otherwise be difficult to achieve using conventional solvents and reagents. Fundamental studies examining the unusual effects that can be achieved with fluorinated solvents, catalysts, and reagents promise to expand these benefits into new areas.

As part of a study examining the ability of unusual solvents to penetrate and access the interior volume of catalyst-containing, insoluble porous polymers, we recently observed that when the solvent was a mixture of fluorous and organic (perfluoromethylcyclohexane (PFMC) and toluene), the reactivity of the imbedded hydrogenation catalyst *increased* with the volume fraction of the fluorous solvent component (Figure 1).[4] This observation was unusual because most "pony-tail" derivatized catalysts function more poorly in fluorous environments.[5]
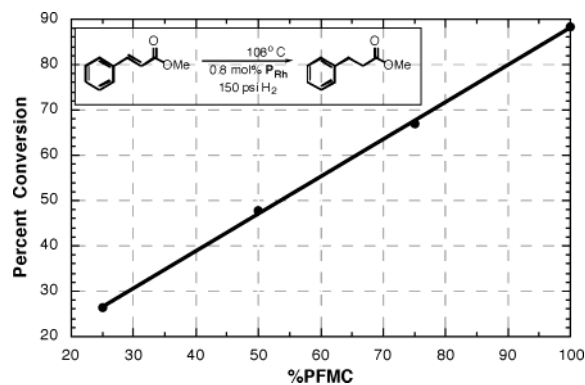

Figure 1. Conversion (1 h) versus %PFMC in toluene.

In the reported case, we traced the rate acceleration to higher concentrations of the reactant (methyl-*trans*-cinnamate) in the organic (catalyst-containing) polymer phase as the fluorous content of the continuous phase increased and its solvency decreased.[6,7]

Recognizing the intrinsic merit of a phenomenon that sorbs and concentrates a reactant into a small volume,[8-10] we examined the factors controlling the kinetics and thermo-

(1) (a) Curran, D. P. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1174−1196. (b) Luo, Z.; Zhang, Q.; Oderaotoshi, Y.; Curran, D. P. *Science* **2001**, *291*, 1766−1769. (b) Zhang, W.; Luo, Z.; Chen, C. H.-T.; Curran, D. P. *J. Am. Chem. Soc.* **2002**, *124*, 10 443−10 450. (c) Ryu, I.; Matsubara, H.; Yasuda, S.; Nakamura, H.; Curran, D. P. *J. Am. Chem. Soc.* **2002**, *124*, 12 946−12 947. (d) Luo, Z.; Swaleh, S. M.; Theil, F.; Curran, D. P. *Org. Lett.* **2002**, *4*, 2585−2587.
(2) For reviews, see: (a) Hope, E. G.; Stuart, A. M. *J. Fluorine Chem.* **1999**, *100*, 75. (b) Barthel-Rosa, L. P.; Gladysz, J. A. *Coord. Chem. Rev.* **1999**, *190−192*, 587−605. (c) Fish, R. H. *Chem. Eur. J.* **1999**, *5*, 1677. (d) Horváth, I. *Acc. Chem. Res.* **1998**, *31*, 641−650. (e) de Wolf, E.; van Koten, G.; Deelman, B.-J. *Chem. Soc. Rev.* **1999**, *28*, 37−41.
(3) Yoder, N. C.; Kumar, K. *Chem. Soc. Rev.* **2002**, *31*, 335−341.
(4) Vinson, S. L. and Gagné, M. R. *Chem. Commun.* **2001**, 1130−1131.

(5) (a) Richter, B.; Spek, A. L.; van Koten, G.; Deelman, B.-J. *J. Am. Chem. Soc.* **2000**, *122*, 3945−3951. (b) Rutherford, D.; Jiliette, J. J. J.; Rocaboy, C.; Gladysz, J. A. *Catal. Today* **1998**, *42*, 381−388.
(6) For several recent examples of reaction rate accelerations due to fluorous-induced, substrate phase preferences, see: (a) Pace, A.; Clennan, E. L. *J. Am. Chem. Soc.* **2002**, *124*, 11 236−11 237. (b) Morphy, J. R.; Rankovic, Z.; York, M. *Tetrahedron Lett.* **2001**, *42*, 7509−7511.
(7) For a rate acceleration in fluorous media ascribed to differential solvation in the transition state of the Diels−Alder reaction, see: Myers, K. E.; Kumar, K. *J. Am. Chem. Soc.* **2000**, *122*, 12 025−12 026.

dynamics of partitioning organic compounds from fluorinated solvents into the pores of insoluble porous organic polymers (many examples are known of sorbing organic compounds from aqueous solutions[11,12]). Our experiments were designed around the simple notion that the phase preference (insoluble organic polymer versus fluorous solvent, eq 1) of an analyte could be understood as a competition between two phases for "dissolving" it.

$$\text{Analyte}_{solvent} + \text{Polymer} \underset{}{\overset{P}{\rightleftharpoons}} \text{Analyte}_{polymer} + \text{Solvent} \quad (1)$$
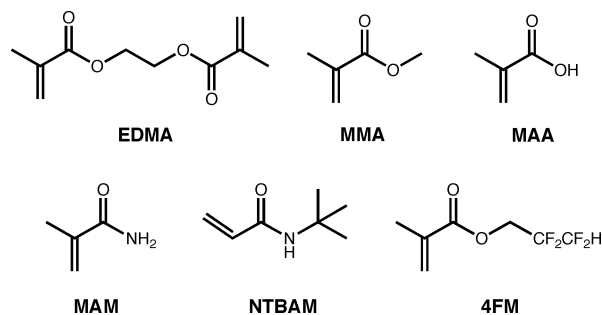
This simple analysis obviously suggests that decreasing the quality of a solvent will reduce the analyte's (or reactant's) thermodynamic preference for that phase, and that a better "quality" polymer should better *solubilize* (and concentrate) it.[13] Thus, the partitioning equilibrium (*P*) should depend on the balance between fluorous solvent and polymer quality. Our experiments were designed to test this hypothesis and establish the sensitivity of these two factors on the partitioning of test organic compounds. Our ultimate goal was a procedure for generating large local concentrations capable of enhancing a wide variety of chemistries; for example, bimolecular rate accelerations (catalysis and stoichiometric), concentration dependent equilibrium shifts (homo- or heterodimerization for molecular recognition etc.), or even in the remediation/sorbing of undesirable solution contaminants from fluorous waste streams resulting from new fluorous technologies.

To systematically determine the effect of fluorous content on partitioning kinetics and thermodynamics, we utilized solvent mixtures (PFMC:hexanes and PFMC:ether) that were miscible in all proportions at room temperature.[2b] These solvent mixtures provided a readily controllable model of the higher temperature miscing behavior of PFMC:toluene, the solvent mixture used in the original hydrogenation experiments, and in numerous biphase reaction protocols.[2] With room-temperature miscing, UV−vis spectroscopy (on the supernatant solution) conveniently provided kinetic and thermodynamic partitioning information on chromophore-containing compounds. For compounds lacking a chromophore, GC measurements proved most useful for measuring thermodynamics.

To probe the effect of polymer structure and morphology on partitioning, a number of modifications were made to the parent polyethylene dimethacrylate (pEDMA) porous polymer. Most

(8) Quaternized polymer latexes can significantly accelerate reaction rates by both partition induced concentration enhancements and intrinsic rate constant increases, see: Ford, W. T. *React. Funct. Polymers* **1997**, *33*, 147−158.

(9) De Vos has quantified the effect of substrate partitioning from dilute solutions (chromatographically) into zeolites and correlated these effects to the catalytic reactivity of the zeolite. See, for example: Langhendries, G.; Vos, D. E. D.; Baron, G. V.; Jacobs, P. A. *J. Catalysis* **1999**, *187*, 453−463.

(10) Micelles will also partition organics from aqueous solutions with consequent increases or decreases in chemical reactivity. For classic examples of rate enhancements, see for example: (a) Menger, F. M.; Portnoy, C. E. *J. Am. Chem. Soc.* **1967**, *89*, 4698−4703. (b) Yatsimirski, A. K.; Martinek, K.; Berezin, I. V. *Tetrahedron* **1971**, *27*, 2855−2868. (c) Romsted, L. S.; Bunton, C. A.; Yao, J. *Curr. Opin. Colloid Interface Sci.* **1997**, *2*, 622−628. For a recent example where rate acceleration and decelerations result, see: Davies, D. M.; Stringer, E. L. *Langmuir* **2003**, *19*, 1927−1928.

(11) (a) Azanova, V. V.; Hradil, J. *React. Funct. Polymers* **1999**, *41*, 163−175. (b) Martel, B.; Morcellet, M. *J. Appl. Polym. Sci.* **1994**, *51*, 443−451.

(12) (a) Hradil, J.; Wojaczynska, M.; Svec, F.; Kolarz, B. N. *Reactive Polymers* **1986**, *4*, 277−283. (b) Podlesnyuk, V. V.; Hradil, J.; Marutovskii, R. M.; Klimenko, N. A.; Fridman, L. E. *React. Funct. Polymers* **1997**, *33*, 275−288.

(13) These effects are well documented in sorption studies from aqueous solutions, see for example footnote 11a.

Scheme 1

notable were materials synthesized with variable quantities of a functionalized comonomer, chosen to vary the interior functionality of the polymer's pores, and thereby probe the effect of polymer *quality* on partitioning magnitudes.

Results

A. Polymer Synthesis and Characterization. Access to monolithic bulk polymers with permanent pores[14,15] was most conveniently achieved by combining ethylene dimethacrylate (EDMA) with chlorobenzene (1:1 by weight) and heating the mixture in unstirred 20 mL scintillation vials for 24 h (60 °C) with 1 wt % AIBN. Chlorobenzene was chosen as the porogenic solvent because it yields monolithic polymers with high surface areas ($\sim$480 m^2/g).[16] The resulting monoliths were coarsely crushed and Soxhlet extracted with CH$_2$Cl$_2$ (6 h), followed by solvent removal under vacuum (60 °C, 6 h). The dried polymers were ground and sieved and the 425−500 micron sized particles collected for analysis.[17]

A number of polymers were synthesized with different comonomer additives to vary the functional groups present in the final polymers (Scheme 1). Operationally, a specific weight percent of comonomer was added to the EDMA followed by AIBN and chlorobenzene. This procedure was followed for all monomers except methacrylamide (MAM), which required the porogen to contain 50 wt % methanol for complete solubility.

Polymer Surface Area (BET). Table 1 lists polymer surface areas (SA) obtained by N$_2$ BET for 100% pEDMA obtained using 50 wt % chlorobenzene as porogen during polymerization. As expected chlorobenzene is a "good" solvent for the polymer and high surface areas are obtained.[14,16] By substituting part of the EDMA with 5% of a comonomer a series of functionalized

Table 1. Surface Areas (N$_2$ BET) for Comonomer-Containing pEDMA Polymers[a]

entry	comonomer (5 wt %)	surface area[b]
1	100% EDMA	443
2	MMA	399
3	MAM[c]	405
4	NTBAM	423
5	4FM	389

[a] Chlorobenzene porogen (50 wt % in polymerization solution) unless noted. [b] N$_2$ BET measurements. [c] Porogen is 1:1 MeOH:ClPh by weight.

(14) Sherrington, D. C. *Chem. Commun.* **1998**, 2275−2286.

(15) For classic papers in this area see, for example: (a) Kunin, R.; Meitzner, E.; Bortnick, N. *J. Am. Chem. Soc.* **1962**, *84*, 305−306. (b) Kun, K. A.; Kunin, R. *Polymer Lett.* **1964**, *2*, 587−591. (c) Millar, J. R.; Smith, D. G.; Marr, W. E.; Kressman, T. R. E. *J. Chem. Soc.* **1963**, 218−225.

(16) (a) Santora, B. P.; Gagné, M. R.; Moloy, K. G.; Radu, N. S. *Macromolecules* **2001**, *34*, 658−661. (b) Sellergren, B.; Shea, K. J. *J. Chromatogr.* **1993**, *635*, 31.

(17) This size range proved most convenient for UV−vis studies because interference with the light path was low.

Table 2. Surface Area (N_2 BET) Measurements as a Function of MAM Content

entry	EDMA (%)	MAM (%)[a]	surface area (m^2/g)[b]
1	100	0	443
2	95	5	405
3	90	10	363
4	85	15	280
5	80	20	175
6	75	25	178

[a] The porogen for entries 2−6 was 1:1 methanol:chlorobenzene. [b] N_2 BET measurements.
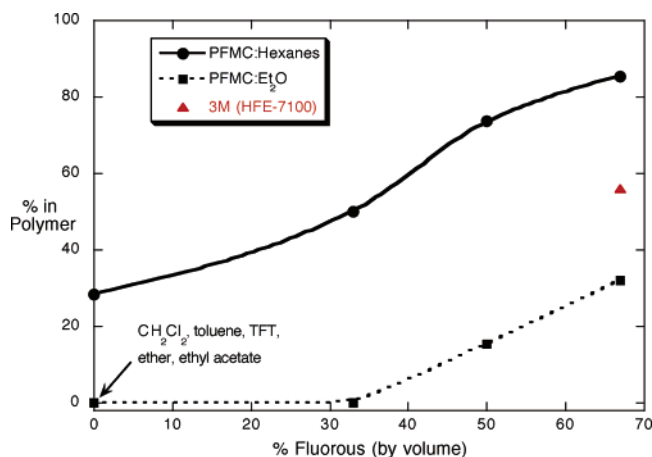
Figure 2. Effects of solvent on the percent of **1** to uptake into pEDMA. The % in polymer was determined by the difference in solution concentration before and after polymer addition: ($[1]_{initial} - [1]_{final})/[1]_{initial}$. HFE-7100 is 68.38% fluorine by weight.

polymers were obtained and similarly analyzed by N_2 BET. At 5 wt % comonomer, the surface areas were insensitive to comonomer structure, which provided material for assessing the functional group effects on partitioning free of SA variability complications (vide infra).[11b] For MAM, SAs were also measured as a function of comonomer content (Table 2). As expected, the SAs of the bulk materials decreased with the cross-link density.[18]

SEM images of sieved 425−500 micron sized particles of 100% pEDMA show highly irregular and jagged polymer pieces, which result from the grinding and sieving process (see the Supporting Information).

B. Partitioning Studies. Fluorinated Solvents and Mixtures. In the hydrogenation experiments where a fluorophobic driven partitioning of methyl trans-cinnamate was first observed, the solvent was a mixture of perfluoromethylcyclohexane (PFMC) and toluene, which misced at ~105 °C in the presence of substrate.[19] To avoid the complications of making measurements at elevated temperatures, we examined fluorous/organic solvent mixtures that were monophasic over a wide range of compositions at room temperature. Viable candidates included PFMC:hexanes and PFMC:ether.[2b] Figure 2 compares the uptake of 9-anthracenemethanol **1** into pEDMA as a function of

(18) For recent references on the effect of cross-link density on surface area see: (a) Sellergren, B. *Makromol. Chem.* **1989**, *190*, 2703. For poly-(divinylbenzene) polymers (c) Law, R. V.; Sherrington, D. C.; Snape, C. E. *Macromolecules* **1997**, *30*, 2868. (d) Xie, S.; Svec, F.; Fréchet, J. M. J. *Chem. Mater.* **1998**, *10*, 4072−4078. For multifunctional methacrylate polymers (e) Rohr, T.; Knaus, S.; Gruber, H.; Sherrington, D. C. *Macromolecules* **2002**, *35*, 97, (f) Steinke, J. H. G.; Dunkin, I. R.; Sherrington, D. C. *Macromolecules* **1996**, *29*, 5826.

(19) In the absence of substrate, this mixture misces at 89 °C, 104 °C if the mixture is 0.25 M in methyl *trans*-cinnamate.
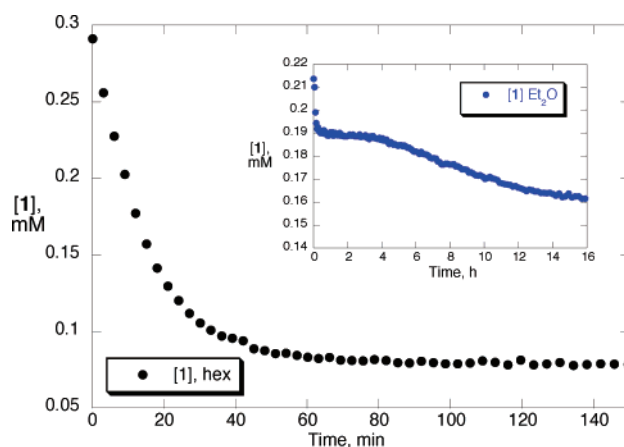
Figure 3. Sorption of **1** into pEDMA from 3.0 mL of 50% PFMC:hexanes and 50% PFMC:ether: $[1]_{0,Hex} = 0.34$ mM; $[1]_{initial,Ether} = 0.17$ mM; 17.0 ± 0.5 mg polymer, 40 °C.

fluorous content in these mixtures and several organic solvents (dichloromethane, toluene, trifluorotoluene, ether, and ethyl acetate) and the partially fluorinated methyl nonafluorobutyl ether ($CH_3O(CF_2)_3CF_3$, HFE-7100).

1
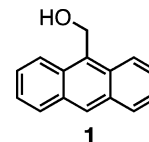
Similar to the observation made in the hydrogenation of methyl trans-cinnamate (reactivity increased with increased fluorous content, Figure 1) the percent of **1** to partition into the polymer also increased as the solvent's fluorous content was increased.[20] In contrast, no measurable partitioning occurs when CH_2Cl_2, toluene, Et_2O, EtOAc or TFT are the solvent. Hexanes was the only purely organic solvent that promoted the partitioning of **1**,[21] though the HFE-7100 (3M), which is a single component solvent and ~68% fluorine by weight, was an excellent performer. Figure 3 shows the solution concentration profile of **1** as it migrates from 50% PFMC:hexanes and 50% PFMC:Et_2O solutions into the pEDMA phase. The faster equilibration kinetics of PFMC:hexanes mixtures and the higher partitioning led us to focus on this solvent mixture.

The raw data for the concentration plot in Figure 3 was obtained by UV−vis spectroscopy, which proved convenient for measuring both the kinetics and thermodynamics of analyte uptake. In cases where a chromophore was lacking, GC analysis proved useful, though less convenient due to solvent volatility. Modeling of the uptake kinetics with simple reversible first-order relaxation to equilibrium expressions were successful,[22,23] and first-order rate constants describing diffusion in and out of the polymer were obtained under a variety of conditions. Gross kinetic rates were found to depend on particle size (smaller = faster),[24] fluorous content, and whether the particles were sinking or floating in the solution. A thorough and careful analysis of uptake kinetics is outside the scope of this investigation,

(20) For a similar phenomenon in $scCO_2$ where increasing pressure (increasing solvency) decreases the partitioning of small molecules into cross-linked siloxane polymers, see: Brantley, N. H.; Bush, D.; Kazarian, S. G.; Eckert, C. A. *J. Phys. Chem. B* **1999**, *103*, 10 007−10 016.

(21) Paleos documented this phenomenon 30 years ago, see: Paleos, J. *J. Colloid Interface Sci.* **1969**, *31*, 7−18.

Table 3. Forward Rate Constants (k_1) and Polymer Behavior for Partitioning of **1** in PFMC:Hexanes and Et$_2$O Mixtures

%PFMC by vol	k_1 (s^{-1}) hexanes	polymer behavior	k_1 (s^{-1}) Et$_2$O	polymer behavior
0	0.074	sink		sink
33	0.14	sink		sink
50	0.066	mix → float	0.00042	float
67	0.024	float	0.033	float

[a] The forward rate constants were directly calculated from the integrated first-order rate equation.[22]

however, rate constants for partitioning from solution to polymer were obtained for comparative purposes, keeping the particle sizes constant (425−500 μm) and varying the solvent ratios. As shown in Table 3, increasing the fluorous content from 33 to 67% actually decreases the rate of establishing equilibrium (∼6-fold), even though the driving force is larger in each instance. In the case of Et$_2$O/PFMC, however, the rate increased significantly on going from 50 to 66% PFMC. Additional experiments are needed to understand these data.

Differences in polymer density were apparent as the density of the PFMC:hexanes mixture was varied. In the lighter solvents (hexanes and 33% PFMC) all the polymers sank, while they all floated in the 67% system.[25] In the 50% mixture, pEDMA and 5% MAM floated to the surface, whereas the higher MAM content polymers (15−25%) and the 5% MAA each sank. The 10% MAM polymer's density was sufficiently matched to the solvent that it could be made to float or sink with tiny changes in solvent composition. Interestingly, this polymer initially sinks in 1:1 PFMC:hexanes as do the higher MAM materials, but after 1−2 min changes its density so that it floats to the surface. This density change must be a result of a shifting in the solvent composition in the pores of the polymer and will be discussed separately (vide infra).

Comonomer Effects. The effect of the polymer's interior composition/functionality on the partitioning of **1** was determined by examining pEDMA polymers with different comonomer additives.[26,27] Materials containing 2,2,3,3-tetrafluoropropyl methacrylate (4FM), methacrylic acid (MAA), methacrylamide (MAM), *tert*-butylacrylamide (NTBAM), and methyl methacrylate (MMA) (Scheme 1) were tested. Figure 4 shows the calculated polymer concentration of **1** ([**1**]$_{polymer}$ = Molal$_1$ = (moles$_1$/kg polymer) as a function of the fluorous content of the solvent and the comonomer identity. The horizontal dotted
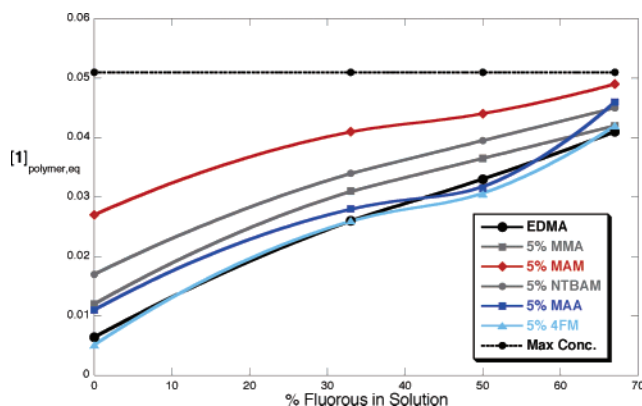
Figure 4. Effect of comonomer (5 wt %) on the equilibrium of [**1**] in pEDMA. [**1**]$_{polymer}$ is in units of moles/kg polymer. Experimental conditions: 3.0 mL of 0.30 mM **1**, 17.0 ± 0.5 mg polymer, 40 °C, 4 h.
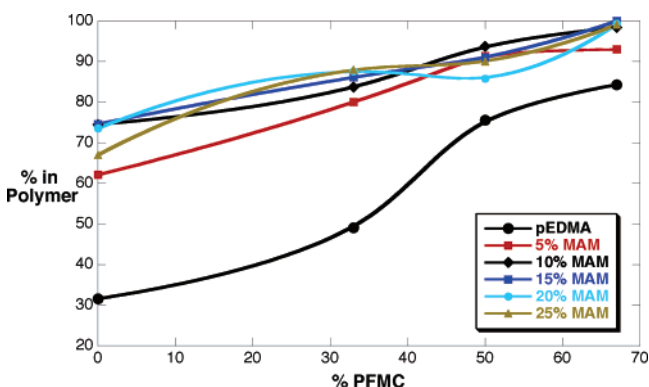

Figure 5. Effect of MAM comonomer content on the uptake of **1** into pEDMA (3.0 mL of 0.30 mM **1**, 17.0 ± 0.5 mg polymer, 29 °C, 4 h); [**1**]$_{initial}$ = 0.35 mM for 67% PFMC.

line represents the maximum concentration of **1** if all of it were to partition into the polymer. From these data it is evident that acrylamide comonomers, especially MAM, significantly enhance the partitioning of **1** and that this effect is magnified at higher fluorous concentrations. At 67% fluorous [**1**]$_{polymer}$ is 175× greater than its initial solution concentration, which approaches the maximum possible enhancement (180×) under these conditions.

Because the 5% MAM copolymer displayed the greatest concentration enhancements (red line), several additional copolymers of varying MAM content (5 to 25 wt %) were prepared and their uptake efficiencies compared. As Figure 5 indicates, increasing the MAM content significantly increased the degree of partitioning of **1**, though the largest benefit is obtained with the first 5%. Anomalously low uptakes (apparently) were observed for 20 and 25% MAM at 50% fluorous content. The source of this dip may be artifactual as density differences cause the 15, 20, and 25% materials to sink and the 5 and 10% materials to float (vide supra). All polymers sink at 0 and 33% PFMC and all polymers float at 67%.

Defining Partition Efficiencies (PE). At this point it was determined that the most informative way to report on the partitioning of analytes was to use a partition efficiency (PE), which we define as the equilibrium concentration of the analyte in the polymer phase divided by the initial solution concentration (eq 2). This value best reflects the enhancements in local concentration that occur upon the addition of polymer. Partition coefficients (*P*) describing the thermodynamics of partitioning

(22) Laidler, K. J. *Chemical Kinetics*, 3rd ed.; Harper & Row: New York, 1987. For a similar approach to modeling the kinetics of uptake of organic compounds from aqueous solutions into polyacrylate coated silica fibers, see: Vaes, W. H. J.; Hamwijk, C.; Errestarazu Ramos, E.; Verhaar, H. J. M.; Hermens, J. L. M. *Anal. Chem.* **1996**, *68*, 4458−4462.

(23) Several more sophisticated approaches to modeling analyte uptake have been used to separate diffusion into macro-, micro-, and bulk polymer diffusion phases. See, for example: (a) Hradil, J.; Svec, F.; Podlesnyuk, V. V.; Marutovskij, R. M.; Friedman, L. E.; Klimenko, N. A. *Ind. Eng. Chem. Res.* **1991**, *30*, 1926−1931. (b) Wang, C.; Xu, M.; Shi, Z.; Fan, Y.; Ji, C. *Chinese J. React. Polym.* **2000**, *9*, 81−89.

(24) Tomoi, M.; Ford, W. T. *J. Am. Chem. Soc.* **1981**, *103*, 3821−3828.

(25) For measurements of particle and skeletal densities of macroporous polymers, see: Vlad, C. D.; Milhailescu, S. *Eur. Polym. J.* **2001**, *37*, 71−77.

(26) Functional group like amines have been observed to enhance the partitioning of phenols from aqueous solutions into EDMA-type materials, see for example footnotes 11b and 12.

(27) A reviewer correctly pointed out that monomer reactivity ratio differences might not necessarily lead to interior surface functionalizations that are identical to the feed ratios. For several recent examples of derivatizing the interior surface of a porous monolithic polymer through a functional comonomer, see: Viklund, C.; Nordström, A.; Irgum, K.; Svec, F.; Fréchet, J. M. J. *Macromolecules* **2001**, *34*, 4361−4369, and footnote 18d.
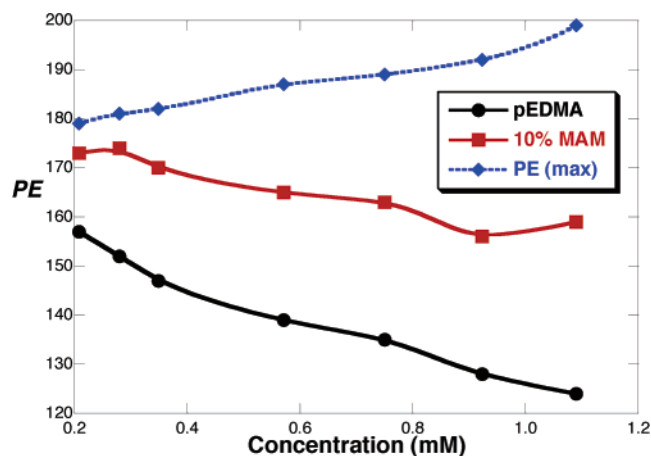
Figure 6. PE of **1** in pEDMA and 10% MAM as a function of [**1**]$_{initial}$. Reaction conditions: 3.0 mL of desired [**1**], 40 °C, 17.0 ± 0.5 mg polymer, 4 h.

Table 4. Partition Efficiency (PE) and Forward Rate Constant (k_1) vs Temperature^a

T (°C)	PE	k_1 (s^{-1})
35	138	0.050
40	135	0.069
45	131	0.078
55	115	0.13
60	96	0.22

^{a} Analysis conditions: 3.0 mL of 0.30 mM **1**, 1:1 PFMC:hexanes, 17.0 ± 0.5 mg pEDMA, 4 h.

(eq 3), are avoided because they do not quantify the concentration enhancements and at high fluorous contents the final solution concentrations are sufficiently low that the *P*'s get large (>20 000) and have unacceptably large errors.

$$PE = \frac{[\text{Analyte}]_{\text{Polymer}} \text{ (mol/kg polymer)}}{[\text{Analyte}]_{\text{initial}} \text{ (M)}} \qquad (2)$$

$$P = \frac{[\text{Analyte}]_{\text{Polymer, equilibrium}}}{[\text{Analyte}]_{\text{Solution, equilibrium}}} \qquad (3)$$

How Initial Concentration Affects PE. To determine if the MAM content also affected the polymer's capacity for sorbing the test analyte **1**, the uptake for pEDMA and 10% MAM materials was measured as a function of [**1**]$_{initial}$ (Figure 6). If the porous polymers had an infinite capacity for sorbing the analyte, the PE would track with the dotted max PE line in Figure 6. Obviously, the data indicate that in these concentration ranges the materials are not infinitely sorbing, and the PEs slowly drop as more analyte is introduced into the system. The 10% MAM polymer has a clear advantage over pEDMA in PE magnitude and in response to loading, the flatter line representing more ideal behavior. Despite the negative slopes, at ~1 mM the PE for both systems is still >120 suggesting that concentration enhancement effects will continue to be operative at this and higher concentrations.

Temperature. The effect of temperature on the partitioning of **1** from a 50% PFMC solution into pEDMA is summarized in Table 4. Not surprisingly,[11a] the PE decreased with increasing temperature, which is most likely a result of the increased solubility of **1** in the fluorous solvent mixture. Large solubility increases with temperature[28] (e.g., the miscing of toluene and

Table 5. Partitioning of Anthracene Derivatives into pEDMA and 10% MAM Polymers^a

		EDMA			10% MAM		
		% sorbed	[ ]^b	*PE*	% sorbed	[ ]^b	*PE*
1		82	147	**147**	86	225	**161**
2		22	12	**40**	35	18	**63**
3		75	50	**134**	82	54	**150**
4		67	51	**121**	73	112	**138**
5		16	16	**28**	19	20	**34**

^{a} Analysis conditions: UV−vis, 0.40 mM substrate in 3.0 mL 1:1 PFMC: hexanes, 17.0 ± 0.5 mg polymer, 40 °C, 4 h equilibration time. ^{b} [ ]$_{polymer}$ is in units of mmoles/kg polymer (mmolal).

PFMC at 90 °C) are not unusual in fluorinated solvents[2b,29] and so the significant drop in PE is not surprising. The rate of sorbing (k_1) also increased with increasing temperature, indicating that the reverse rate constant k_{-1} (polymer → solvent) must increase even more quickly to achieve the overall lowering of the PE.[30]

Fluorous Induced Partitioning of Different Substrates. After determining what factors affected the partitioning of **1** (solvent, temperature, and polymer functionality), standard conditions for comparing **1** to other organic compounds were chosen (0.40 mM in 3 mL of 1:1 PFMC-hex, 40 °C, 17.0 ± 0.5 mg polymer). Two polymers were examined, pEDMA and 10% MAM, pEDMA because it is the primary control polymer, and 10% MAM because of its significantly enhanced partitioning of **1**. Although the greatest degree of partitioning occurs with 2:1 PFMC:hexanes, the 1:1 PFMC:hexanes mixture was used to facilitate the detection of residual substrate in solution after equilibration and enable a relative ranking of analytes. Table 5 lists data for several anthracene derivatives; it tabulates the percent of analyte to partition into the two polymers, the concentration of each substrate in the polymer (mmoles/kg of polymer), and the PE.
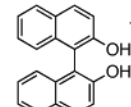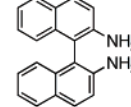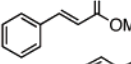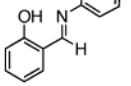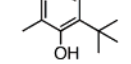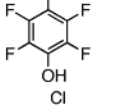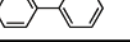
By comparing these analyte structures, the effect of a single functional group on partitioning can be ascertained. Clearly, the sensitivity of the partitioning phenomenon to functional groups is high as methylating the alcohol in **1** reduced the amount of solution material to partition by 4-fold and the resulting concentration in the polymer by >12-fold (entries 1 and 2).

(28) Wende, M.; Meier, R.; Gladysz, J. A. *J. Am. Chem. Soc.* **2001**, *123*, 11 490−11 491.

(29) This effect is also the basis of thermomorphic catalysts, which are soluble at high temperatures and then phase separate upon cooling. For fluoro-based methodologies, see: (a) Rocaboy, C.; Gladysz, J. A. *New J. Chem* **2003**, *27*, 39−49. (b) Rocaboy, C.; Gladysz, J. A. *Org. Lett.* **2002**, *4*, 1993−1996. For examples of this approach in nonfluorous systems, see: (c) Bergbreiter, D. E. *Chem. Rev.* **2002**, *102*, 3345−3384. (d) Bergbreiter, D. E.; Osburn, P. L.; Frels, J. D. *J. Am. Chem. Soc.* **2001**, *123*, 11 105−11 106. (e) Bergbreiter, D. E.; Osburn, P. L.; Wilson, A.; Sink, E. M. *J. Am. Chem. Soc.* **2000**, *122*, 9058−9064. (f) Bergbreiter, D. E.; Liu, Y.-S.; Osborn, P. L. *J. Am. Chem. Soc.* **1998**, *120*, 4250−4251.

(30) At high concentrations of **1** (>1.0 mM) the partitioning is insensitive to temperature (~85% for 26−46 °C, and ~83% for 51−66 °C). Sorption thermodynamics have been analyzed by both Frendlich and Langmuir isotherm models, see for example footnote 11.

Table 6. Partitioning of Small Aromatic Compounds into pEDMA and 10% MAM Polymers[a]

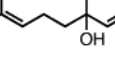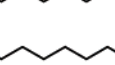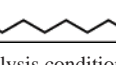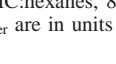|		EDMA			10% MAM		
		% sorbed	[ ][c]	**PE**	% sorbed	[ ][c]	**PE**
6[a]		84	60	**155**	93	66	**170**
7[a]		80	57	**146**	91	64	**165**
8[a]		28	13	**51**	31	13	**54**
9[a]		18	8.2	**32**	69	33	**121**
10[b]		15	15	**28**	27	30	**51**
11[b]		87	92	**164**	88	98	**164**
12[b]		14	7.2	**13**	17	9.4	**16**
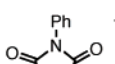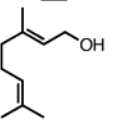
[a] Analysis conditions: UV–vis, 0.40 mM substrate in 3.0 mL 1:1 PFMC:hexanes, 17.0 ± 0.5 mg polymer, 40 °C, 4 h equilibration time. [b] GC conditions: 0.5–0.6 mM substrate in 1.5 mL 1:1 PFMC:hexanes, 8.4 ± 0.3 mg polymer, RT, 18 h equilibration time. [c] [ ]$_{polymer}$ are in units of mmoles/kg polymer (mmolal).

Capping the alcohol with an acetyl group also reduced the partitioning however the polar oxygens partially compensate and only a small decrease is observed. A similar effect is seen with the other polar functional groups, with unadorned anthracene (entry 5) reinforcing the notion that polar functional groups provide the largest driving force for partitioning. As indicated in the second column of data, the PEs of the 10% MAM polymers are all higher than the pEDMA, suggesting that the functional group enhancement of partitioning is a general phenomena and strategy for enhancing further the concentration of an analyte in the polymer.

In fact, all the cases in this study have the 10% MAM polymer providing a stronger driving force for partitioning (Tables 5–7). In some cases, this can be attributed to specific partition enhancing H-bonding interactions. But because some substrates lack H-bonding sites, we surmise that the methacrylamide comonomer also provides a more nonspecific increase in the polymer medium's polarity, and that this enhancement also contributes to the thermodynamics of partitioning. This analysis is completely in line and supportive of our working hypothesis that the thermodynamics of partitioning would be a balance of polymer and solution solvency.

Table 6 lists data on several additional aromatic compounds (entries 6–12). Most noteworthy in these data is the spread from strong to weaker partitioning as the structure is modified. Consistent with arguments that H-bonding is an important contributor to partitioning is pentafluorophenol (entry 11), which although being nearly 52% fluorine by weight is one of the

Table 7. Partitioning of Nonaromatic Compounds into EDMA and 10% MAM Polymers[a]

		EDMA			10% MAM		
		% sorbed	[ ][b]	**PE**	% sorbed	[ ][b]	**PE**
13		61	56	**98**	80	81	**140**
14		37	42	**67**	63	72	**117**
15		12	13	**23**	43	51	**80**
16		0	0.5	**1**	0	0.5	**1**
17		0	0.4	**1**	17	16	**22**
18		0	0.5	**1**	0	0.5	**1**

[a] Analysis conditions: GC conditions: 0.5–0.6 mM substrate in 1.5 mL 1:1 PFMC:hexanes, 8.4 ± 0.3 mg polymer, RT, 18 h equilibration time. [b] [ ]$_{polymer}$ are in units of mmoles/kg polymer (mmolal).

most strongly sorbed compounds, presumably a result of strong H-bonding between the acidic phenol OH and the polymer carbonyls.

In nonaromatic cases (Table 7), the dominant contributor to partitioning is the presence or absence of polar functional groups. In cases where alcohols or amides are present, the partitioning is relatively high, though straight chain saturation has a compensating effect. Illustrative is the case of hydroxy decene, which has no measurable partitioning in pEDMA, but a PE of 22 in the 10% MAM porous polymer (entry 17). The ketone is unaffected by the comonomer (entry 18) and has a PE of 1 in both polymers.

Discussion

The ability to sorb organic compounds from partially fluorinated solvents into the described polymers is made possible by the permanent pore structure of these low-swelling macroporous polymers. A great deal of literature (much of it patent) is available for manipulating porosity (e.g., pore size distribution),[31] though the focus of this contribution is more on describing the partitioning phenomenon itself, and how it responds to chemical rather than physical or morphological changes in the polymer structure. The data presented herein convincingly demonstrate that a solvento phobic effect (in this case fluorophobic) can be harnessed to provide large (up to 200-fold) increases in local concentration of analyte, reactant, or substrate (depending on the application). Because concentration is a fundamental component of the kinetics and thermodynamics of matter, the ability to locally control and manipulate it will provide many avenues for exploiting this effect.

Overall, the data is consistent with the notion that the partitioning process is governed by a balance of forces, which include the solvency of the fluorous phase along with the solvency and physical properties (less emphasized) of the polymer phase. As observed in Tables 5–7, this balance is subject to the analyte's structure and functionality, especially

(31) See, for example: (a) Peters, E. C.; Svec, F.; Fréchet, J. M. J. *Adv. Mater.* **1999**, *11*, 1169–1181. (b) Svec, F.; Fréchet, J. M. J. *Chem. Mater.* **1995**, *7*, 707–715.

important being the presence or absence of polar groups. The first-order picture has polymer addition to a solution of analyte leading to a filling of the pores of the polymer with the bulk solution.[32] Because the walls of the cavity enhance the polarity of the medium, the internal volume becomes more accommodating to organic analytes and favors their partitioning into the polymer. Direct association of the analyte with the polymer surface functionality may also be important, especially in the case of specific interactions such as H-bonding.

Several considerations, however, lead us to think that the picture may be more complex, particularly with regards to the nature of the solvent within the pores. Revealing was the observation that in 1:1 PFMC:hexanes the 10% MAM polymer first sinks as do the other higher acrylamide content materials, but changes its density and begins to float after 1−2 min. Because polar organic addends can increase the consolute temperature[2b] (temperature of miscing) of fluorous/organic solvent mixtures this observation suggests that the polarity of the pore wall may sufficiently affect the thermodynamics of PFMC/hexanes mixing that a fraction of the fluorous solvent is favored to exit the polymer phase (demix).[20] Demixing results in a polymer interior that is more organic and reinforcing of the preference of an organic analyte for this medium. Like the effect of methyl *trans*-cinnamate on the consolute temperature of PFMC/toluene, higher concentrations of the analyte could also contribute to an increase in the consolute temperature of the mixture and further favor the local demixing of the fluorous and organic components.

The migration of fluorous solvent out of the interior would also result in a less dense particle (ρ for PFMC and hexanes are 1.787 and 0.659 g mL^{-1}, respectively), and explain the observation that in 1:1 PFMC:hexanes the 10% MAM particle initially sank, but that after a period of time floated. This sinking/floating observation could be reproduced with 10% MAM in solutions whose densities ranged from 1.16 to 1.30 g/mL (43−57% PFMC), and similarly observed with pEDMA in a density range of 1.14 to 1.16 g/mL (37−43% PFMC). In both cases, an equilibrium point could be reached with a nearly perfect density match with the solvent, 41% (1.14 g/mL) and 43% PFMC (1.16 g/mL) for pEDMA and 10% MAM, respec-

tively (see the Supporting Information). The range of solution densities where polymer net buoyancy changes were observed is broader with the 10% MAM material, in part because of its higher skeletal density, but just as likely because the polar acrylamide units are more efficient at promoting solvent demixing.

Finally, as a model for the behavior of the common toluene and PFMC biphase mixtures, these data further suggest that in cases where the consolute temperature is relatively high (89 °C for toluene/PFMC) and sensitive to organic addends, that a combination of polymer functionality and substrate preconcentration could cause significant demixing of the PFMC and toluene in the pores (especially the micropores) of the polymer. Naturally, this would further reinforce the desire of the analyte to occupy these toluene rich regions of the polymer.[6b] Because "pony-tailed" catalysts typically function more poorly in fluorinated solvents,[5] it is also conceivable that this pore demixing could also insulate any polymer-immobilized catalysts from a fluorous-related attenuation in activity.

Thus, we conclude that the enhanced activity of our rhodium hydrogenation catalysts with increasing fluorous content of the solvent (Figure 1) is due to a combination of effects, the most important being the concentration enhancement of the substrate in the catalyst-containing polymer phase. Many applications of an up to 200-fold increase in local concentration can be envisioned; the data and analysis described herein provide the fundamental basis for designing and implementing these new experiments.

Supporting Information Available: Experimental procedures, SEM image of ground and sieved polymers, tables of pEDMA and 10% MAM sinking/floating behavior, along with PFMC/hexanes solvent density data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA0353558

---

(32) The filling of the pores with solvent is accompanied by a rapid displacement of the air (seconds) in the interior pores, which is accompanied by the liberation of small air bubbles.