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Hydrophobic Sponges: Resin-Bound Surfactants as Organic Scavengers[†,‡]

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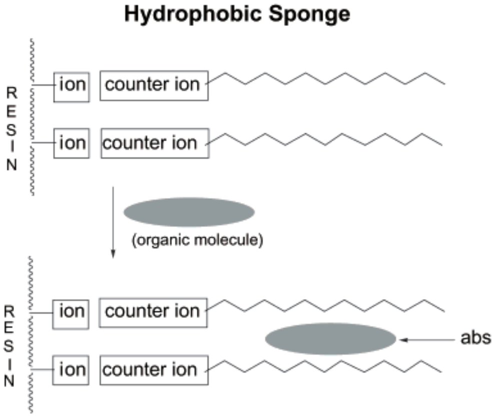
In this paper, we describe the immobilization of single-chain and double-chain (gemini) surfactants onto a cation-exchange resin and show how the resulting polymers are capable of functioning as "hydrophobic sponges". Specifically, we report the synthesis of **1a**, **1b**, **1c**, **2**, and **3** and quantify their ability to absorb 4-chlorotetrahydropyran from water (Chart 1).

The removal of organic contaminants from water sources is a major environmental issue that continues to attract new chemistries and new engineering approaches.[1−10] From a materials science standpoint, the creation of novel solids that can bind a wide range of organic compounds, having tunable affinities, are of special interest. Here, we report the synthesis of resin-bound surfactants (i.e., "hydrophobic sponges") that combine the absorptive properties of the surfactant with the insolubility of a cross-linked polymeric support (Scheme 1). We also show that the affinity of such polymers can be modulated by varying the loading of the amphiphile within the support, as well as the amphiphile's chain length.

Resins **1a**, **1b**, **1c**, **2**, and **3** were prepared by ion exchange of **1d** with the appropriate quaternary ammonium bromide using aqueous solutions that were kept below their critical micelle concentrations. The progress of the ion exchange, in all cases, was monitored by determining the concentration of Na$^+$ that was released from the polymer using a Na$^+$ electrode. The error of this Na$^+$ analysis, over the concentrations used, was $\pm$4.5%. Specific values of *X* and *Y* that are shown in Chart 1 refer to the mole fractions of the quaternary ammonium and sodium ions that are present, respectively; *Z* indicates the corresponding resin capacites.

Scheme 1



Resins **1a**, **1b**, and **1c** were obtained by stirring 3.00 g of a cation-exchange resin **1d**, (Dowex 50X2, Na$^+$ form, 50−100 mesh; 95% ring substitution) with 0.3, 0.6, and 1.0 equiv of dodecyltrimethylammonium bromide, respectively. In each case, an aqueous solution of the surfactant was added, dropwise, to a stirred suspension of the resin such that submicellar concentrations were maintained; the total volume of water used was ca. 1 L. Analysis of the Na$^+$ that was released from the polymer (Na$^+$ electrode) indicated that ion exchange was quantitative within 3 h. The accuracy of this analysis, based on the use of Na$^+$ electrodes, was confirmed in the case of **1c**, where elemental analysis showed the expected nitrogen and bromine content; i.e.: Anal. Calcd: N, 3.42; Br, 0.00. Found: Calcd: N, 3.38; Br, 0.00. Resin **2** was prepared by treating **1d** with 0.3 equiv of an analogous gemini surfactant (bromide salt), corresponding to 0.15 mol of the "double-tailed" surfactant per mole of sulfonate.[11] In this case, the ion exchange was allowed to proceed for 24 h. Analysis of the Na$^+$ that was released indicated that the ion exchange was complete; i.e.: Anal. Calcd: N, 1.52; S, 10.69; Br, 0.00. Found: N, 1.56; S, 10.68; Br, 0.00. Resin **3** was prepared by treating **1d** with 1.0 equiv of tetradecyltrimethylammonium bromide for 24 h, which was sufficient for a quantitative ion exchange. Increased loadings of dodecyltrimethylammonium ions resulted in decreased swelling in water. Thus, whereas the pure Na$^+$ form of the resin (**1d**) absorbed 3.74 g of water/g of dry resin, **1a**, **1b**, and **1c** absorbed 2.11, 1.16, and 0.53 g of water/g of dry resin, respectively. Resin **2** and **3** were both found to absorb 1.99 g of water/g of dry polymer.

To characterize the ability of these resins to absorb organic molecules on the basis of hydrophobic forces, we examined their ability to absorb 4-chlorotetrahydropyran (CTHP). Our choice of CTHP as a model solute was based on three considerations. First, CTHP is nonionic. Thus, solute binding through ion exchange—a process that would add complexity to our interpretation of structure−activity relationships—is avoided. Second, CTHP has moderate solubility in water. One would expect, therefore, that a significant fraction of CTHP would remain in solution. If only a negligible concentration of CHTP remained in solution, this would make it difficult, if not impossible, to quantify differences among these polymers, in terms of their absorption characteristics. Third, CTHP has a relatively high

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[†] S.L.R., concept, experimental design, wrote paper; V.J., preparation of **1a**, **1b**, **1c**, **2**, and **3**, the shorter-chain analogues of **1a**, and swelling measurements; X.Y., Figure 2 and experimental design.

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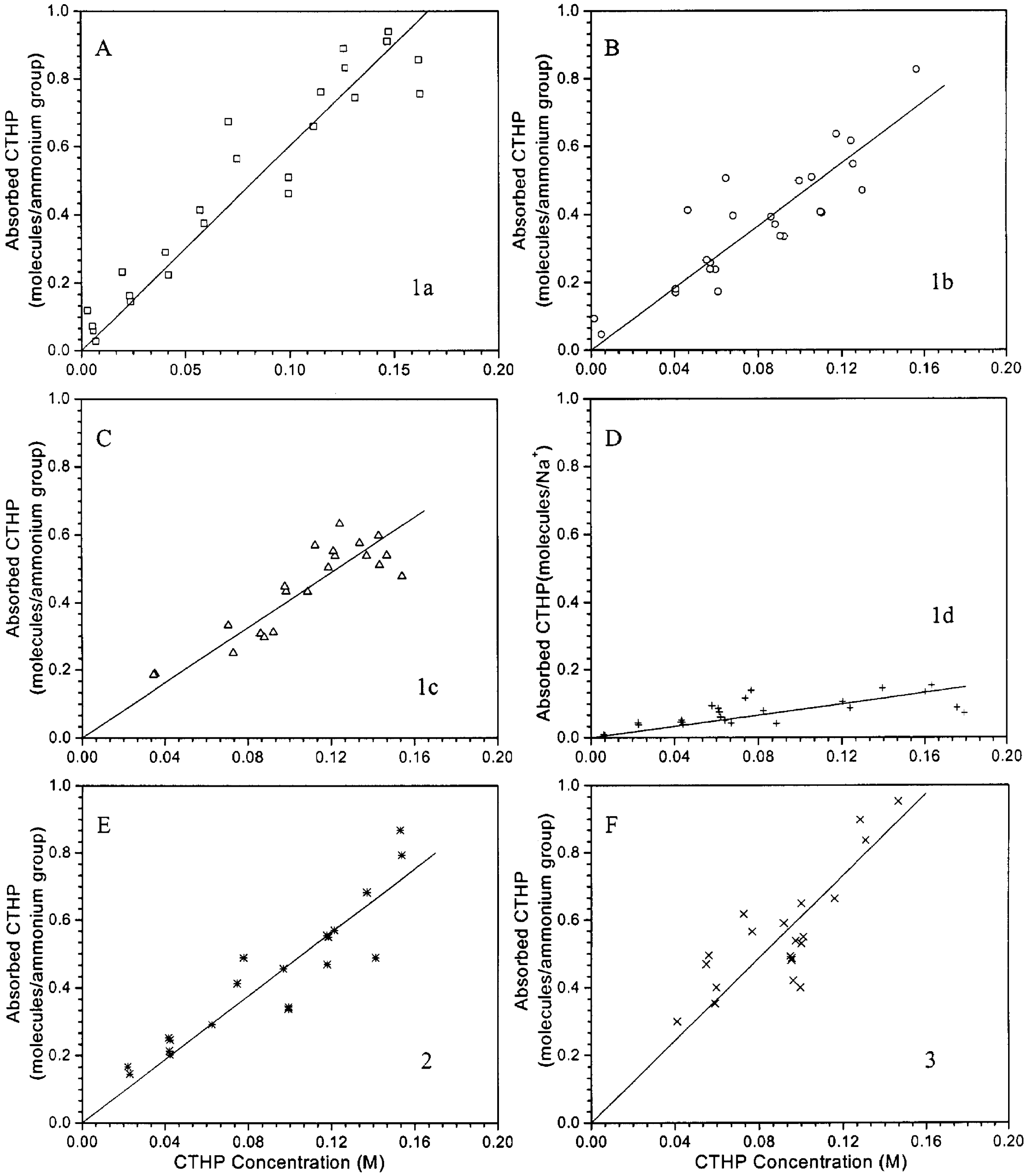


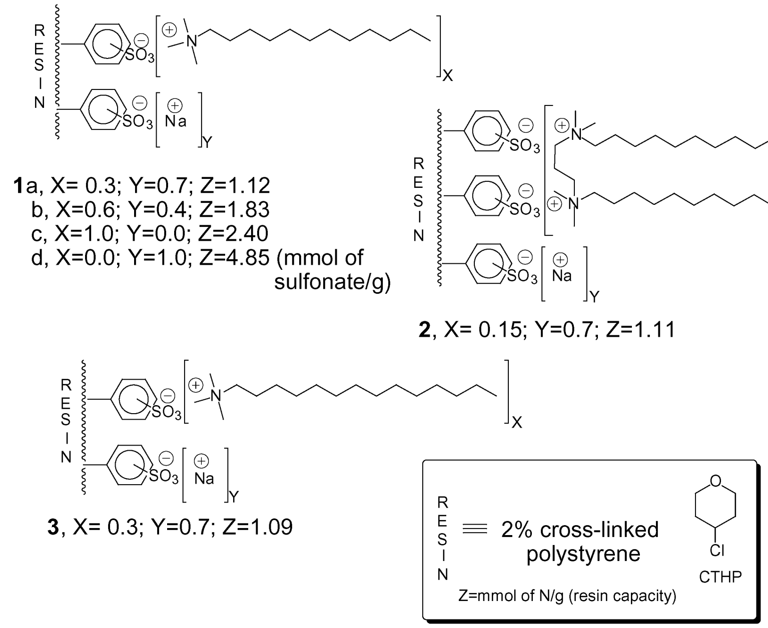
Figure 1. Plots of molecules of absorbed CTHP per ammonium (or sulfate) group as a function of CTHP concentration in the external aqueous phase for (A) **1a**, (B) **1b**, (C) **1c**, (D) **1d**, (E) **2**, and (F) **3**. Each data point represents a single experiment.

lipophilicity. Thus, the partitioning of CTHP between 1-octanol and water, as determined by gas chromatography, yielded a value of log *P* (octanol−water partition coefficient) that was 1.20.

In a typical experiment, a 4-mL vial, equipped with a Teflon-lined screw cap, was charged with 100.0 mg of dry resin. An aqueous solution of CTHP (3.0 mL, 0.150 M) was then added, and the resin was allowed to equilibrate for 3 h at 23 °C with gentle agitation (Environ Shaker, Model 3527). Removal of a 0.200 mL aliquot from the external aqueous phase and injection into 1.0 mL of ethanol containing chlorobenzene (internal standard) allowed for a quantitiatve assessment to be made of the extent of CTHP absorption (gas−liquid chromatography). Specifically, the moles of absorbed CTHP were calculated from the difference between the solution concentrations of CTHP in the absence and in the presence of a given resin. In all cases, absorption equilibrium was reached within 3 h.

The absorptive characteristics of **1a**, **1b**, **1c**, **1d**, **2**, and **3** are shown in Figure 1 as plots of absorbed molecules of CTHP per ammonium group (or per sulfonate group in the case of **1d**) vs the CTHP concentration remaining in solution. In brief, polymers **1a**, **1b**, **1c**, **2**, and **3** showed a significant and linear increase in absorption as the concentration of CTHP was increased; with **1d**, the extent of absorption was relatively low at all CTHP concentrations. From the slopes of these plots, it is clear that the affinity of the resin-bound surfactant toward CTHP increases as the loading of the amphiphile within the polymer decreases; that is, the slopes for **1a**, **1b**, **1c**, and **1d** were 6.0 ± 0.3, 4.6 ± 0.2, 4.1 ± 0.1, and 0.8 ± 0.1, respectively. Whereas extending the dodecyl chain by two methylene groups had no significant influence on the resin's absorptive propertes, when 30% of the Na$^+$ in the polymer was replaced with ammonium groups (i.e., the slope of **3** was 6.1 ± 0.3), covalently

Chart 1



linking two quaternary ammonium surfactants together signficantly lowered their affinity toward CTHP; that is, the gemini-based analogue (**2**) had a slope of 4.7 ± 0.2.

The decrease in the absorption of CTHP that accompanies the increase in loading of *n*-dodecyltrimethylammonium ions is a likely consequence of a more tightly packed assembly of surfactants. Thus, at higher loadings, hydrophobic interactions between the hydrocarbon chains of the amphiphilic counterions are enhanced at the expense of hydrophobic interactions with the CTHP molecules. Similarly the lower affinity of the gemini-based analogue toward CTHP may be accounted for by enhanced van der Waals forces between neighboring alkyl chains. In this case, a covalent bond permanently fixes two tetraalkylammonium ions as nearest-neigbors. The fact that both polymer swelling and absorption efficiency decrease with increased loadings of *n*-dodecyltrimethylammonium ions supports a shift toward a more hydrophobic resin that is more compact in character. Whether or not micellar-like structures are formed within these resins is not presently clear.[2] Thus, one could also describe these differences in absorption properties in terms of loosely and tightly packed micelles; the former being better able to accommodate the CTHP molecule.

To further demonstrate the tunability of a hydrophobic sponge, we measured the absorptive properties of analogues of **1a**, in which the length of the *n*-dodecyl chain was shortened. Thus, using *n*-octyltrimethylammonium, *n*-hexyl-trimethylammonium, and tetramethylammonium ions as counterions (i.e., analogues of **1a** having carbon chain lengths of 8, 6, and 1, respectively), and using a solution concentration of CTHP of 0.13 M, the extent of adsorption was found to decrease, as shown in Figure 2.[12] Swelling capacities of these resins, bearing *n*-octyltrimethylammonium, *n*-hexyl-trimethylammonium, and tetramethylammonium ions, were 3.01, 3.50, and 3.57 g of water/g of dry polymer, respectively.

In summary, we have demonstrated the feasibility of combining simple cationic surfactants with cross-linked polymers to produce resins having absorption properties that are tunable. In principle, hydrophobic sponges, of the type reported herein, may find use not only in the area of water treatment but also as novel media for carrying out organic reactions.[13]

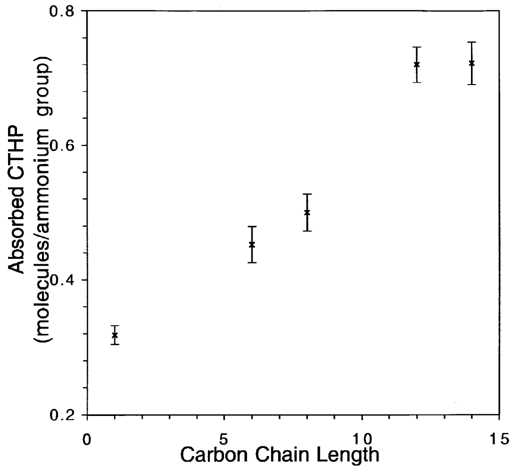


Figure 2. Plots of molecules of absorbed CTHP per ammonium group as a function of carbon chain length (n) for $(CH_3)_3N^+(CH_2)_nH$, using 0.13 M CTHP, and a level of ion exchange of 30%. Error bars are for duplicate experiments.

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