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A R T I C L E S

Self-Cleaning Resins

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Abstract: This paper introduces a fundamentally new concept in adsorbents, whereby the sorption of an aqueous solute by a cross-linked polymer is controlled by a gel to liquid-crystalline phase transition. To demonstrate proof of principle, a bilayer forming surfactant, *N*,*N*-dioctadecyl,*N*,*N*-dimethylammonium bromide (DODAB) has been immobilized onto a cation exchange resin, Dowex 50WX2, and its thermotropic phase behavior and solute-adsorption properties have been investigated. Examination by a combination of differential scanning calorimetry and X-ray scattering has confirmed the retention of a gel to liquid-crystalline phase transition of the surfactant, occurring between 296 and 318 K. Adsorption measurements that were made for 4-chlorotetrahydropyran, 1,2-dichloroethane, and benzyl alcohol have also confirmed uptake by the resin in the liquid-crystalline phase and release in the gel phase.

Introduction

The removal of organic contaminants from water sources is a growing environmental problem that is attracting new chemistries and new engineering approaches.[1-6] In principle, the creation of new classes of adsorbents that can adsorb organic compounds at one temperature and release them at another would represent attractive new materials for such purposes. In a broader context, thermally controllable adsorbents could be considered for a variety of other applications: for example, as "temporary solvents" (i.e., catalysts) for concentrating organic reactants, as thermally responsive chromatographic materials for molecular separations, as carriers of drugs, etc.[7,8]

In the work that is reported herein, our primary aim was to provide proof of principle for a fundamentally new concept in adsorbents, whereby adsorption is controlled by a gel to liquid-crystalline phase transition. Specifically, we sought to demonstrate the feasibility of creating cross-linked polymers, bearing bilayer-forming surfactants, which would adsorb organic solutes from water in their liquid-crystalline phase and release them in their gel phase. Thus, we sought to create a new class of polymeric materials that we term "self-cleaning resins" or SCRs.

Our concept of SCRs is a direct outgrowth of work that we previously reported, in which a synthetic ionophore was found to be "squeezed out" of a lipid bilayer when the membrane was converted from the fluid-like to the solid-like state.[9,10] The driving force for such expulsion was presumed to be due to strong van der Waals association between the acyl chains of neighboring phospholipids relative to weaker phospholipid–ionophore association. On the basis of this observation, we hypothesized that cross-linked polymers, bearing pendent bilayer-forming surfactants, might exhibit similar behavior. Specifically, we postulated that at elevated temperatures, these polymer-bound surfactants would form fluid-like regions within the resin, having a relatively high affinity toward organic solutes. At reduced temperatures, solid-like regions would then form, having reduced affinity toward these same solutes.

Experimental Section

General. Commercial samples of DOWEX 50WX2 (50–100 mesh, H^+ form) and DODAB were obtained from Supelco (Bellefonte, PA) and Kodak (Rochester, NY), respectively. Amberlyst A26 (hydroxide form) and CTHP were obtained from Aldrich (Milwaukee). Prior to use, Amberlyst A26 was washed, sequentially, with 1 M aqueous NaOH, water, and methanol/water (1/1, v/v). All gas chromatographic analyses were performed using a Shimadzu model 17A gas chromatograph equipped with a flame ionization detector. Swelling was determined from height measurements using 2 mm diameter glass capillary tubes. Differential scanning calorimetry measurements were made using a Shimadzu DSC-60 calorimeter, which was equipped with a thermal analyzer, TA 60 WS. DSC scans were made from 10 to 65 °C using a scan rate of 2 °C/min.

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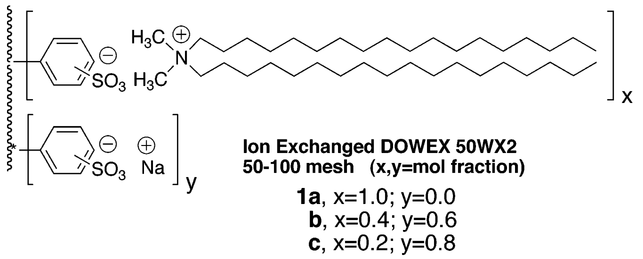
10.1021/ja068679f CCC: $37.00

Chart 1



Ion Exchanged DOWEX 50WX2
50-100 mesh (x,y=mol fraction)
1a, x=1.0; y=0.0
b, x=0.4; y=0.6
c, x=0.2; y=0.8

Preparation of Polymer-Bound Surfactants. The preparation of **1b** was carried out as follows: DODAB (2.6 g, 4.12 mmol) was dissoved in 10 mL of methanol at 35 °C. This solution was then cooled to room temperature and passed through a column containing 21 g of Amberlyst A26. A portion of the filtrate was analyzed for hydroxide content by titration with 0.1 M aqueous HCl. This methanolic solution of *N*,*N*-dioctadecyl,*N*,*N*-dimethylammonium hydroxide (DODAH) was then used, directly, to immobilize the cationic surfactant onto DOWEX 50WX2 via acid/base reaction as follows.

A 2.02 g sample of DOWEX 50WX2 (50−100 mesh, H^+ form) was washed, sequentially, with water (4 × 20 mL) and CH_3OH/water (1/1, v/v) (2 × 20 mL) and suspended in 10 mL of CH_3OH/water (1/1, v/v). This resin was then treated with 0.4 equiv of a stock (0.6 M) methanolic solution of DODAH. Analysis of the external solution confirmed that all of the DODAH had been taken up by the resin, as evidenced by its neutral pH. Titration of the resulting dispersion with aqueous 1 M NaOH solution converted the remaining 0.6 equiv of sulfonic acid groups to sodium sulfonate groups. The dispersion was then centrifuged, the excess solvent was removed, and the resin was washed, sequentially, with CH_3OH/water (1/1, v/v), methanol, and water. Subsequent freeze-drying (48 h) afforded 0.865 g (98%) of **1b**. Anal. Calcd: N, 1.34. Found: N, 1.36. Resin **1c** was prepared in a similar manner (Anal. Calcd: N, 0.89. Found: N, 0.90). For the preparation of **1a**, treatment with the 1 M NaOH solution was omitted (Anal. Calcd: N, 1.95. Found: N, 1.90). In all cases the isolated yields, based on the expected weight gain, were between 96% and 100%.

Solute Adsorption and Release. In a typical experiment, a 4-mL vial equipped with a Teflon-lined screw cap was charged with 20 mg of dry polymer. An aqueous solution of 4-chlorotetrahydropyran (CTHP, 300 μL of a 5 mM aqueous solution) was then added, and the resin was allowed to equilibrate at the desired temperature for 3 h with gentle agitation using an Environ Shaker (model 3527). Removal of a 50 μL aliquot from the external aqueous solution and injection into 50 μL of an aqueous solution containing CH_3CN (internal standard), followed by gas chromatographic analysis, allowed for a quantitative assessment of the extent of CTHP that was removed from solution. Specifically, the moles of adsorbed CTHP were calculated from the difference between the solution concentrations of CTHP in the absence and in the presence of the polymer. In all cases, adsorption equilibrium was reached within 3 h. Experiments that were carried out with **1a** (and also with **1b**) showed complete reversibility; samples that were first equilibrated at 323 K and subsequently equilibrated at 296 K (3 h) gave concentrations of CTHP in the external solution that were the same as those found at 296 K in the absence of this 323 K equilibration.

To determine maximum capacity, typically, 10 mg of **1a** was added to a 4-mL vial equipped with a Teflon-lined screw cap. Initially, 80 μL of a stock solution of CTHP (190 mM) was added to the vial and equilibrated at 296 °C for 3 h with gentle agitation using an Environ Shaker (model 3527). A 40 μL aliquot was then withdrawn and analyzed for CTHP remaining in solution. The amount of adsorbed CTHP was then determined by the amount of CTHP remaining in solution. Three additional increments of this stock solution were added, sequentially, in volumes of 270, 280, and 640 μL. After addition of each increment and equilibration for 3 h, the solution phase was analyzed by withdrawing 40 μL and analyzing for CTHP by gas chromatography.

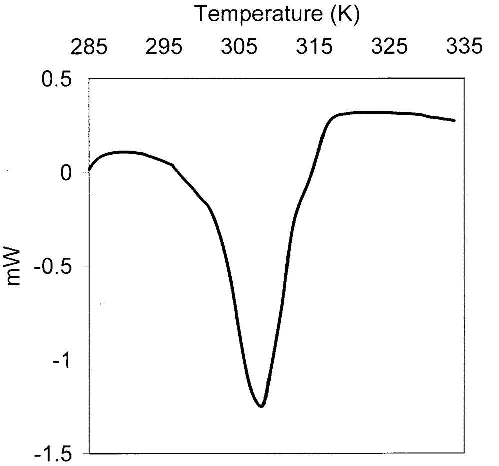


Figure 1. DSC trace for **1b** in the presence of excess water; $\Delta H = 40$ J/g of polymer or 42 kJ/mol of surfactant.

X-ray Scattering. All X-ray scattering measurements were conducted in transmission mode, with Cu Kα radiation (wavelength $\lambda = 0.15418$ nm) produced by a PANalytical PW3830 generator with a PW 2773/20 tube. Wide-angle X-ray scattering (WAXS) was conducted with a pinhole camera (Statton camera with hot stage, W. H. Warhus) flushed with helium. Monochromatization was achieved with a planar pyrolytic graphite monochromator (Huber 151) in the incident beam. WAXS patterns were recorded on image plates (Kodak) read with a Molecular Dynamics PhosphorImager SI, providing a digital version of the diffraction pattern directly.[11] Small-angle X-ray scattering (SAXS) patterns were acquired with an Anton-Paar compact Kratky camera flushed with helium, a Braun OED-50M one-dimensional position-sensitive detector, and a custom-built hotstage.[12] Data were corrected for empty beam scattering and absorption, normalized for sample thickness, placed on an absolute intensity scale with a polyethylene strip traceable to a Kratky Lupolen standard, and desmeared for slit length, all as described elsewhere.[13] Absolute SAXS intensities I/I_eV are plotted against the magnitude of the momentum transfer vector $q = (4\pi/\lambda) \sin \theta$, where θ is one-half the scattering angle.

Results and Discussion

Resin-Bound *N*,*N*-Dioctadecyl,*N*,*N*-dimethylammonium Ions. For proof of principle, we prepared a series of resins from a cation exchange resin, Dowex 50WX2 (H^+ form), and a bilayer forming surfactant, *N*,*N*-dioctadecyl,*N*,*N*-dimethylammonium bromide (DODAB). Specifically, we immobilized *N*,*N*-dioctadecyl,*N*,*N*-dimethylammonium (DODA) ions onto DOWEX 50WX2 at three different loadings, to give **1a**, **1b**, and **1c** (Chart 1). Initial attempts that were made at direct ion exchange, using the sodium form of the resin plus 1 equiv of DODAB in methanol, proved unsuccessful; that is, none of the surfactant was immobilized on the support after 24 h at 296 K as evidenced by quantitative TLC. However, acid−base reaction of the H^+ form of the resin with *N*,*N*-dioctadecyl,*N*,*N*-dimethylammonium hydroxide in methanol/water (1/1, v/v) led to quantitative, titratable conversions.

In their dry state, **1a** and **1b** (but not **1c**) exhibited a distinct waxy appearance. When contacted with water at 323 K, **1a** showed no detectable swelling as determined by height mea-

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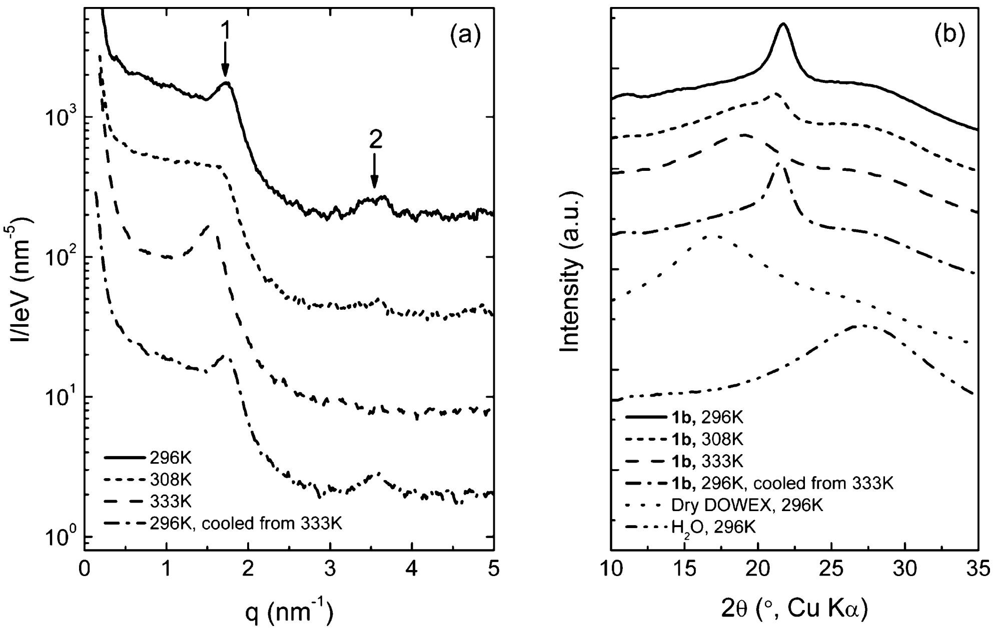

Figure 2. (a) SAXS and (b) WAXS patterns for **1b** through a heating/cooling cycle. From top to bottom: 296 K (below transition), 308 K (halfway through transition), 333 K (above transition), and then cooled to 296 K and held at that temperature for 1 h. Patterns are shifted vertically for clarity. The bottom two traces in panel (b) are the room-temperature WAXS patterns of dry DOWEX 50X2 (Na^+ form) and water, whose broad signatures can be seen in all of the WAXS patterns.

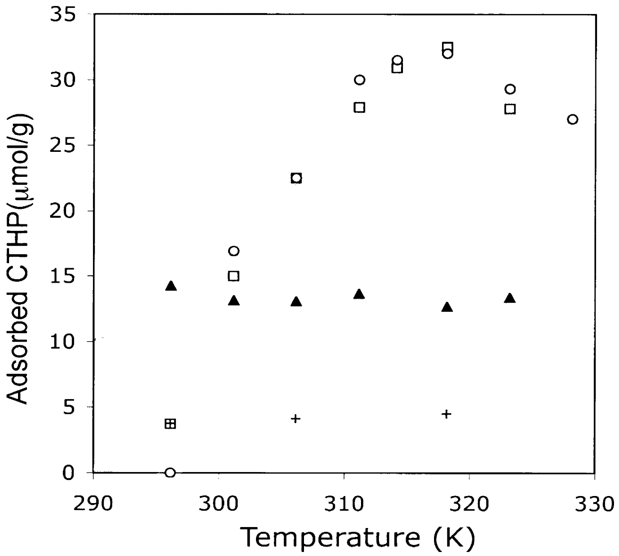

Figure 3. Plots of μmoles of adsorbed CTHP/g of resin as a function of temperature for **1a** (○), **1b** (□), and **1c** (▲) and Dowex 50WX2 (Na^+ form) (+). For each experiment, 20 mg of resin was equilibrated with 300 μL of a 5 mM aqueous solution of CTHP at a given temperature.

Table 1. Maximum Adsorption onto **1a** and XAD-4[a]

	4-chlorotetrahydropyran		1,2-dichloroethane		benzyl alcohol	
temperature (K)	**1a**	XAD-4	**1a**	XAD-4	**1a**	XAD-4
296	0.19	5.60[b]	0.16	4.0[b]	0.60	2.90[b]
318	4.90[c]	4.80	4.40[c]	3.9	2.80[c]	2.40

[a] All values listed are the number of millimoles of adsorbed solute per gram of dry polymer. [b] Value obtained upon cooling a suspension at maximum adsorption from 318 to 296 K. [c] The moles of adsorbed 4-chlorotetrahydropyran, 1,2-dichloroethane, and benzyl alcohol per mole of resin-bound DODA were 3.58, 3.21 and 2.04, respectively.

surements; **1b** showed only slight (ca. 10%) swelling. In sharp contrast, under the same conditions, **1c** swelled by ca. 300%! No significant changes in swelling were detected for each of these polymers when the temperature was then lowered to 296 K. To confirm that resins of this type are stable in the presence of high aqueous salt concentrations, we suspended **1a** in a 1 M NaCl solution for 8 h at 50 °C. Examination of the aqueous phase by thin layer chromatography showed no detectable release of DODA from the resin.

Gel to Liquid-Crystalline Phase Transition Behavior. Examination of **1b** by differential scanning calorimetry (DSC) in the presence of excess water showed a broad endotherm between ca. 296 and 318 K (Figure 1). A very similar endotherm was observed for **1a** (not shown). The thermal behavior of **1c** proved to be irreproducible; some DSC scans showed a very weak endotherm within this temperature region, while others showed no endotherm at all. Control experiments that were carried out with Dowex 50WX2 (Na^+ form) did not reveal an endotherm over this temperature range. In the absence of water, an initial heating scan of **1a** and **1b** showed an endotherm that was similar to that found in the presence of water. However, subsequent heating scans did not show an endotherm. Thus, the presence of water appears to be essential for the reversibility of this transition.

Recent studies have shown that the DSC behavior of multilamellar vesicles of DODAB depends, in large part, on their thermal history.[14,15] In contrast, sonicated DODAB vesicles generally exhibit one broad endotherm between ca. 306 and 318 K.[14,15] This endotherm corresponds to a gel to liquid-crystalline phase transition that has been characterized by enthalpies ranging from 26 to 41 kJ/mol.[14,15] The similarity of the DSC behavior of **1b** (and also of **1a**) to that of sonicated DODAB vesicles led us to postulate that a similar phase transition was taking place within the polymer beads.

This hypothesis was verified by the small-angle X-ray scattering (SAXS) data for **1b** shown in Figure 2a, and the wide-

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angle X-ray scattering (WAXS) data shown in Figure 2b. At 296 K, the ordered lateral packing of the DODA acyl chains is reflected by the WAXS peak at 21.7°, which disappears upon heating to 333 K. The SAXS pattern at 296 K shows two reflections corresponding to a lamellar structure of limited coherence length and a periodicity of 3.63 nm, essentially identical to bulk DODAB.[16] Heating to 333 K leads to a broader SAXS peak at 9% larger spacing, concomitant with the disordering of the acyl chains. At 308 K, halfway through the transition, the SAXS and WAXS patterns are essentially linear combinations of those at 296 and 333 K, as expected for a first-order phase transition. The changes in the WAXS and SAXS patterns are fully reversible upon cooling to room temperature and holding for 1 h.

Solute Adsorption and Release. The ability of **1a**, **1b**, and **1c** to bind and release organic solutes as a function of temperature was first assessed by measuring the adsorption of 4-chlorotetrahydropyran (CTHP) from water. As discussed previously, CTHP is attractive as a model solute because of its moderate solubility in water, its inability to associate, ionically, with polyelectrolytes, and its relatively high lipophilicity.[17] Specific experimental procedures that were used were similar to those previously reported.[17]

In Figure 3 are shown plots of μmoles of adsorbed CTHP/g of resin versus temperature for **1a**, **1b**, **1c**, and the sodium form of Dowex 50WX2. In the case of **1a**, no adsorption could be detected at 296 K. As the temperature was increased to 318 K, however, a steady increase in adsorption was observed; further increases in temperature resulted in a modest decrease in adsorption. Lowering the temperature from 318 to 296 K led to the complete release of CTHP; that is, this thermally induced adsorption was completely reversible. Similar results were found for **1b**.[18] In contrast, moderate adsorption of CTHP onto **1c** was found, which was independent of temperature. Similarly, adsorption of CTHP onto the sodium form of Dowex 50WX2 was also independent of temperature, and the extent of adsorption was relatively low (Figure 3).

To test for generality, and also to demonstrate the feasibility of binding larger quantities of solute, we examined the adsorption and release behavior of **1a** with respect to 1,2-dichloroethane and benzyl alcohol as well as CTHP, using higher solute concentrations. Thus, when 20 mg of **1a** was exposed to 0.3 mL of 190 mM of CTHP at 318 K, we found that 1.24 mmol of CTHP was adsorbed per gram of **1a** of dry polymer after 3 h. When the temperature was reduced to 296 K, 44% of this solute was released after 6 h. In the case of 1,2-dichloroethane, using a 81 mM solution of this solute in water, the extent of adsorption at 318 K corresponded to 1.02 mmol per gram of **1a**; returning the temperature to 296 K led to a 54% release of the solute after 6 h. Finally, using a 300 mM aqueous solution of benzyl alcohol, we found that 2.05 mmol of solute was adsorbed per gram of **1a** at 318 K and that 15% of it was released after 3 h at 296 K. Extending the desorption time to 24 h resulted in the release of 63% of the solute.

To estimate adsorption capacities, aqueous solutions of CTHP, 1,2-dichloroethane, or benzyl alcohol were added, incrementally, to **1a** so that the percentage of solute remaining in solution could be accurately determined by measuring differences in solution concentrations. Table 1 summarizes our principal findings. In this table, we also report maximum quantities of solute that were adsorbed onto Amberlite XAD-4 (a common nonionic polymeric adsorbent) under similar conditions. The maximum capacities are similar, but while XAD-4 shows the conventional slow and smooth decrease in adsorption capacity as the temperature is raised, **1a** is qualitatively different in both the direction of the change (increased adsorption with increased temperature) and the relatively abrupt nature of the change, allowing temperature to be used as a "switch" for adsorption/desorption.

Conclusions

In this study, we have demonstrated the feasibility of immobilizing a bilayer-forming surfactant onto an ion-exchange resin with retention of gel to liquid-crystalline phase transition behavior. We have also shown that three organic solutes of varying polarity (4-chlorotetrahydropyran, 1,2-dichloroethane, and benzyl alcohol) can be adsorbed onto such resins while in the liquid-crystalline phase, and released when converted into the gel phase. When a moderate concentration of 4-chlorotetrahydropyran (i.e., 5 mM) was equilibrated with **1a**, release from the polymer was found to be quantitative; when a high concentration was used (i.e., 190 mM), a significant amount of the solute was retained by the resin. How much of this retention is due to kinetic or thermodynamic factors, however, remains to be established. Finally, it should be noted that the mechanism by which this adsorption occurs is fundamentally different from that found with lower critical solution temperature (LCST) polymer gels. With the latter, a large increase in adsorption is found as the critical temperature is reached, which is accompanied by a large decrease in volume (e.g., 30−40%) due to the loss of imbibed water.[6] In sharp contrast, the swelling of **1a**, **1b**, and **1c** is virtually unchanged across the gel to liquid-crystalline transition.

Efforts currently in progress are aimed at exploring the full scope of SCRs where the kinetics and thermodynamics of solute adsorption/desorption are being investigated as a function of the structure and composition of the solute, the surfactant, and the cross-linked polymer employed. Comparisons are also being made between ionically and covalently bound surfactants as well as liposomal analogs. The results of these studies will be reported in due course.

Acknowledgment. We are grateful to the National Science Foundation (CHE-0345248 and DMR-0505940) for support of this research.

JA068679F

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