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Redox-Responsive Gels with Tunable Hydrophobicity for Controlled Solubilization and Release of Organics

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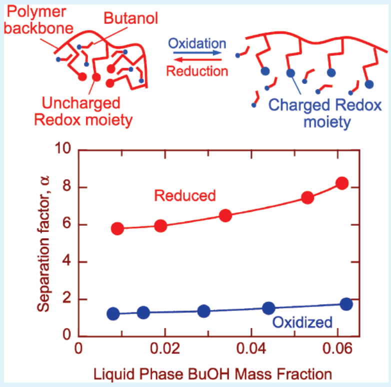
Supporting Information

ABSTRACT: The hydrophobicity of the chemical environment within a redox-responsive polymer gel synthesized by copolymerization of hydroxybutyl methacrylate (HBMA) and vinylferrocene (VF) can be controlled by tuning the oxidation state of the redox-responsive moiety, ferrocene. When ferrocene is in the uncharged reduced state, the gel is hydrophobic and selectively extracts butanol from aqueous solution. Upon oxidation to ferricenium ions, charge is induced at the ferrocene sites making the gel hydrophilic, with a reduced capacity for butanol relative to water. Equilibrium distribution coefficients and separation factors provide quantitative evidence for this changing preference for butanol depending on oxidation state. The selection of the monomer constituting the polymer backbone, HBMA, was based on an initial screening using the Hansen solubility parameters of commercially available monomers. The effect of the various constituents of the gel on the gel's butanol extraction ability has been ascertained experimentally.



KEYWORDS: redox-responsive, gel, hydrophobicity, hydrophilicity, butanol extraction

1. INTRODUCTION

Synthetic systems capable of responding to stimuli in a controllable and predictable fashion have found widespread application, and have therefore been an active field of scientific inquiry. The majority of these systems are based on polymeric materials because the control of the composition and architecture of polymers is well understood.[1] Incorporating stimuli-responsive moieties in polymer gel systems has been particularly attractive because gels have the unique ability to display liquid-like behavior at the molecular scale and solid-like macroscopic properties, such as, for instance, maintaining a rigid shape.[2] Stimuli-responsive polymer gels have been applied in many diverse areas such as biosensor design,[3,4] biomaterial synthesis,[5] microfluidics,[6] actuators,[7] and separation systems,[8] to name a few. The change in interactions within a gel system can be triggered by applying an appropriate stimulus such as temperature,[9,10] pH,[11−13] light,[14,15] or magnetic field.[16] Reviews by Ahn et al.[17] and Shibayama and Tanaka[18] discuss stimuli-responsive gels in detail.

Species which can undergo reversible oxidation−reduction reactions have also been incorporated in polymer gel systems to render the polymers responsive to the application of an electric potential. In particular, several reports show that the properties of ferrocene-containing redox molecular systems can be manipulated by altering the oxidation state of redox-active ferrocene moieties.[4,19−29] Charging and discharging of the redox active moiety in such polymers has been used successfully to control the phase transition temperature of gels[30−32] and to prepare self-oscillating gels.[7] The change in the properties of these redox gels as a function of the oxidation state of the redox species reflects the differences in the hydrophobicity of the gel in the reduced and oxidized states; the presence of charges on moieties within the gel makes the gel environment more hydrophilic. In this paper, we demonstrate that the switchable properties of such gels can be exploited in the removal or recovery of organic compounds, specifically butanol, from aqueous solution, with potential applications in the treatment of wastewater, or for recovery of desired products from an aqueous stream.

The purification of water by the removal of dissolved contaminants is a challenge of global dimensions. In particular, removal of organics becomes critical for treatment of water for drinking purposes, treatment of industrial effluents and sewage before discharge into natural water bodies, and separation of organic compounds produced industrially in an aqueous medium. Strict regulations, such as the Safe Drinking Water Act in the USA, enforce a maximum allowable concentration of organic contaminants in water. To comply with these regulations, a number of technologies including biological degradation,[33,34] steam stripping,[35] adsorption on activated carbon,[36] membrane filtration,[37] and pervaporation[38] have been reported in literature. The most popular method among these has traditionally been the use of activated carbon because of its low cost and high capacity. However, the difficulties associated with the regeneration of carbon and low mechanical strength make this technology less attractive.[39] Another promising technology, solvent extraction,[40,41] also suffers from drawbacks, including emulsification with the feed phase, and counter-contamination of the feed by the solvent. This motivates the need for the development of new techniques for removal of organic compounds from aqueous solutions.

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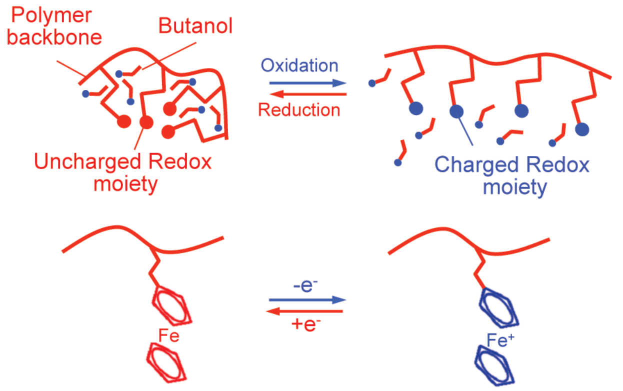

Figure 1. Schematic diagram showing the absorption of organic molecules (e.g., butanol as shown here) by the polymer in the uncharged state and the subsequent release of the organic molecules on oxidation of the ferrocene groups in the polymer.

The production of biofuels is another area in which effective recovery of organic compounds from aqueous streams is an important issue. The ever increasing human thirst for energy combined with the limited availability of fossil fuels has spurred the development of alternative, renewable fuels. Low molecular weight alcohols such as ethanol and butanol produced from biomass are expected to be good substitutes for gasoline.[42−44] The fermentation process by which they are produced, however, suffers from product inhibition[45,46] necessitating the development of separation technologies to remove the fermented alcohol from the aqueous fermentation broth as it is formed to maintain noninhibitory concentration levels. Conventional distillation has limitations in that it requires significant energy input to carry out this separation, reducing the commercial viability of the alcohols as substitutes for gasoline.[47] Liquid−liquid extraction, on the other hand, has been found to be an attractive technique for removing alcohol from broths,[47−53] but again, extraction using a solvent leads to problems of solvent emulsification and contamination. There is clearly scope for the development of new separation technologies that have the advantages of traditional separations, but which avoid their difficulties.

The goal of this paper is to report on the development of stimuli-responsive materials with selectivity and capacity for desired compounds similar to those of liquid−liquid extractants but with none of their drawbacks. We exploit the reversible control of the hydrophobicity of a polymer gel that can be achieved by manipulation of the oxidation state of a redox-active constituent of the gel to design a polymer gel system capable of undergoing a two step process in which an organic compound is first extracted from an aqueous solution, and then released into a second medium on change in the oxidation state of the gel. This can be achieved by maintaining all the redox moieties in the gel in the uncharged state during the first step. Once the gel is saturated with the organic compound, by the use of a suitable electrochemical reaction as the second step of the process, charge can be induced on the redox active moieties leading to an increase in the hydrophilic character of the gel and consequent decrease in its preference for the organic compound. The organic compound which had been preferentially extracted during the first step is expected to be released from the gel during the second step into a medium of choice. A schematic of this proposed process is presented in Figure 1.

2. EXPERIMENTAL METHODS

Materials. Hydroxybutyl methacrylate (HBMA) (94%, mixture of isomers), hydroxybutyl acrylate (HBA) (90%), 2-hydroxyethyl acrylate (HEA) (96%), methyl methacrylate (MMA) (99%), butyl acrylate (BuAc) (99+%), ethyleneglycol dimethacrylate (EGDMA) (98%), vinylferrocene (VF) (97%), 2,2′-azobis(isobutyronitrile) (AIBN) (98%), N,N′-methylenebisacrylamide (BIS) (98+%), ferric chloride ($FeCl_3$) (97+%, anhydrous), ferrous sulfate heptahydrate ($FeSO_4.7H_2O$) (99+%), ammonium sulfate ($(NH_4)_2SO_4$) (99+%), sodium chloride (NaCl) (98+%), L-ascorbic acid (99+%), and 1-butanol (99+%) were purchased from Sigma-Aldrich and used as received without further purification. Ethanol (200 proof, absolute, anhydrous) was purchased from Pharmco-Aaper and used as received.

Synthesis of Polymer Gel. Polymer gels were synthesized in bulk via free radical polymerization. HBMA and VF constituted the polymer backbone, with AIBN as the initiator, and either BIS or EGDMA as the cross-linker.

The desired molar composition of the gel determined the amount of each of the reactants needed for the reaction. The required amounts of VF and EGDMA (or BIS) were added to a reaction test tube, which was then sealed using a rubber septum and deaerated by bubbling dry nitrogen gas through the contents of the tube for 30 min. VF was dissolved by ultrasonication of the suspension. In parallel, a weighed quantity of AIBN was added to the test tube containing 1 mL HBMA, and the test tube was sonicated to dissolve the AIBN. Thereafter, the solution of AIBN in HBMA was injected into the reaction tube through which dry nitrogen gas was passed continuously. The reaction tube was placed inside an oven preheated to 70 °C, for 4 h, following which the solid redox gel was removed from the tube and placed in a beaker containing 1,4-dioxane to wash away the unpolymerized monomers. Finally, the gel was dried in a vacuum oven and stored in a sealed tube for further characterization and studies.

Measurement of Solvent Uptake By Gel. The solvent uptake by the redox gel was measured by recording the change in its weight when it was allowed to equilibrate with excess volume of the solution of interest. The swelling of the gel in pure water, pure butanol, and butanol-water solutions of intermediate compositions was investigated. A gel sample was weighed and immersed in a test tube filled with the solvent. The change in weight of the gel was measured at regular intervals by removing the gel from the test tube, wiping the solvent droplets on its surface using a Kimwipe, and then weighing it. The gel was subsequently reimmersed in the solvent. The weight change was recorded until no further change in the weight was observed for three successive measurements.

Chemical Oxidation and Reduction of Redox Gel. The ferrocene moieties in the redox gel were oxidized chemically to investigate the effect of their oxidation on the solvent uptake behavior of the gel. $FeCl_3$ was selected as the oxidizing agent because of literature reports of the successful oxidation of ferrocene moieties by $FeCl_3$.[54] A 0.1 g/mL stock solution of $FeCl_3$ was prepared in the solvent (water, butanol, or butanol-water solution) to be used in the solvent uptake study. A sample of redox gel was weighed and immersed in the solvent. A small volume of the stock solution of $FeCl_3$ was added to the test tube containing the solvent and the gel; the volume added was determined to ensure that the equivalents of $FeCl_3$ were in excess of the stoichiometric amount needed to oxidize the ferrocene groups in the gel sample being oxidized. The swelling of the gel in the solvent containing $FeCl_3$ was determined following the procedure described above.

The chemically oxidized gel was reduced by reaction with L-ascorbic acid using a procedure analogous to that used for oxidation of the gel. The gel after oxidation by $FeCl_3$ was carefully immersed in solvent containing dissolved L-ascorbic acid and allowed to equilibrate. After the gel reached equilibrium swelling, its color was noted and solvent uptake in the reduced state was determined following the procedure described in the preceding section.

Measurement of Butanol Concentration in the Liquid Phase. The butanol concentration in water was determined by gas chromatography using a Varian CP3800 GC (Varian, Inc.) equipped with a PoraBOND Q fused silica column (25 m × 0.32 mm ID), a CP8400 autosampler and a flame-ionization detector (FID).

The injection temperature was set at 200 °C, and the injected sample was diluted by mixing with the carrier gas using a split ratio of 100. The oven in which the column was located was programmed to heat the column from 50 to 250 °C with a linear ramp of 16 °C/minute and to hold the temperature at 250 °C for 150 s. The detector was set at 280 °C. Nitrogen was used as the carrier gas and air and hydrogen were used for combustion of the eluted sample in the detector.

Ethanol was added as the internal reference to the samples of butanol-water solution to be analyzed. A sample of volume 0.5 μL was injected into the column using the autosampler. The peaks in the chromatograms were identified using the Galaxie software which was also used for determining the area under the peak and for carrying out baseline correction.

Calculation of Equilibrium Distribution Coefficients and Separation Factors. The equilibrium distribution coefficients for butanol and water between the gel and the liquid solution were determined by equilibrating a butanol-water solution of known concentration with a gel of known initial weight. Measurements of the mass of solvent uptake by the gel and of the final concentration of butanol in the liquid phase were used to estimate the mass of butanol inside the gel. Since water constituted the remainder of the solvent phase both inside and outside the gel, the mass fraction of water was calculated by difference. The ratios of the mass fractions of butanol and water between the gel and the liquid phases were used to calculate the values of the equilibrium distribution coefficient (K_D) and separation factor (α) defined by

$$K_D = \frac{x_{gel}}{x_{liq}} \text{ and } \alpha = \frac{K_{D,\,BuOH}}{K_{D,\,water}} \qquad (1)$$

where x denotes the mass fraction of the species of interest. The mass fraction in the gel phase, x_{gel}, is defined on a gel-free basis, i.e., by dividing the mass of the component of interest (butanol or water) in the gel phase by the total mass of solvent absorbed by the gel.

3. RESULTS AND DISCUSSION

Selection of Monomer Constituting the Polymer Backbone. Hansen solubility parameters (HSP) quantifying the solvency behavior of solvents were used for the selection of the monomer forming the polymer gel backbone. The closer any two molecules are in the three-dimensional "Hansen solubility space", the greater are the chances of their mutual miscibility.[55] Molecular Modeling Pro software was used to estimate the HSPs of different molecules, which in turn were used to calculate their "distance", R, in the solubility space from molecules of interest using the equation[55]

$$R^2 = 4(\delta_{D2} - \delta_{D1})^2 + (\delta_{P2} - \delta_{P1})^2 + (\delta_{H2} - \delta_{H1})^2 \qquad (2)$$

where δ_{Di}, δ_{Pi}, and δ_{Hi} denote the dispersion, polar, and hydrogen bonding components of solvent i, respectively.

The calculation of HSPs of the solvents used by Offeman and co-workers[51] for liquid−liquid extraction of alcohols from water led to the observation that in the "solubility space", good extractants for alcohols were separated from water by a "distance" greater than or equal to 30 MPa$^{1/2}$, from ethanol by a "distance" less than or equal to 12 MPa$^{1/2}$, and from butanol by a "distance" less than or equal to 8 MPa$^{1/2}$. This heuristic was tested by calculating the "distances" of a series of commercially available monomers from water, ethanol, and butanol in the "solubility space", and then independently measuring solvent uptake behavior of their gels when immersed in water, ethanol, and butanol. The "distances" of five sample monomers from the three solvents are presented in Table 1, and the solvent uptake by their homopolymer gels is plotted in Figure 2. HBMA and HBA satisfy the three "distance"-based heuristics discussed earlier and are therefore expected to show preferential selectivity for the alcohols, whereas the proximity of HEA to water and ethanol in the solubility space indicates its hydrophilic character. BuAc and MMA are distant from all the three solvents and satisfy none of the three conditions. Thus, they may be expected to have low preference for all three solvents.

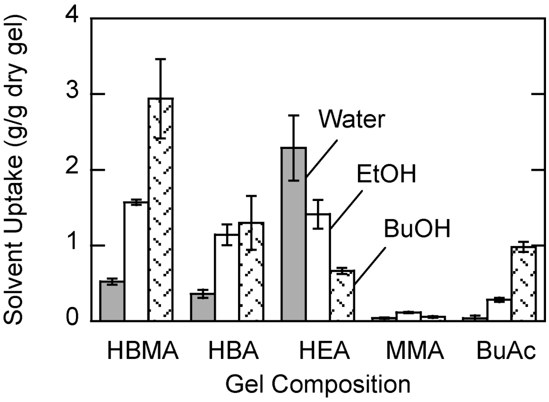

Figure 2. Uptake of water, ethanol, and butanol by homopolymer gels of HBMA, HBA, HEA, MMA, and BuAc.

The swelling results confirm the preferential selectivity of HBMA and HBA gels for butanol and ethanol over water, as reflected in the large alcohol uptake by these gels and low uptake of water. Similarly, the experimental results show that HEA gel swells more in water than in the alcohols while MMA gel does not have preference for any of the three solvents. These results are in agreement with the predictions made on the basis of the solubility parameters of the monomers. The swelling results for the BuAc gel, on the other hand, show that it has selectivity for the alcohols over water, which is not completely in line with the inferences drawn from its location in the solubility space. Nonetheless, the good match between the HSP-based prediction and the solvent uptake behavior indicates the utility of HSP as a first-order screening method for monomers for the synthesis of polymers designed to have selectivity for a molecule of interest.

Because of the high preferential selectivity for butanol observed for HBMA gels, HBMA was selected as the VF comonomer in the synthesis of the polymer gels used in this study.

Oxidation of Ferrocene Moieties in the Gel by $FeCl_3$. The results obtained by Nguyen et al.[54] demonstrating the oxidation of ferrocene moieties by $FeCl_3$ were confirmed by independent experiments in this study by monitoring the changes in the UV−visible (UV−vis) absorption spectrum of a solution of ferrocene in butanol following the addition of $FeCl_3$ to the solution, which resulted in the solution turning blue. Details are given in the Supporting Information.

In the case of ferrocene-containing gels, successful oxidation of the ferrocene moieties when a piece of the gel was immersed in a solution of $FeCl_3$ was concluded based on the observance of

Table 1. HSP and "Distances" of Five Sample Monomers—HBMA, HBA, HEA, MMA, and BuAc—from Water, Ethanol, and Butanol in the Hansen Solubility Space Calculated Using Molecular Modeling Pro

monomer	δ_D (MPa$^{1/2}$)	δ_p (MPa$^{1/2}$)	δ_H (MPa$^{1/2}$)	Hansen distance from water (MPa$^{1/2}$)	Hansen distance from ethanol (MPa$^{1/2}$)	Hansen distance from butanol (MPa$^{1/2}$)
HBMA	17.25	9.55	10.60	32.52	9.31	6.86
HBA	17.95	10.84	13.24	29.89	7.82	6.82
HEA	18.11	15.91	13.96	28.78	10.11	11.14
MMA	16.82	12.88	4.79	37.72	15.31	13.23
BuAc	16.73	9.75	4.17	38.70	15.37	12.38

Table 2. Molar Composition of Different HBMA-VF Polymer Gels Synthesized in This Study to Determine the Optimum Composition

	mole % of constituents				
name of gel	HBMA	VF	BIS	EGDMA	AIBN
A	95.60		2.27		2.13
B	95.42	1.40	1.64		1.54
C	93.94	2.35	1.88		1.83
D	66.97	19.85		8.37	4.81
E	72.91	21.61		3.04	2.44
F	74.04	21.94		1.54	2.48
G	73.47	21.77		2.30	2.46
H	72.36	21.44		3.77	2.43

Table 3. Properties of HBMA-VF Gels Synthesized in This Study

name of gel	α^{red}_{sat}	ψ_{sat}	Δ
A	12.0		4.50
B	10.0	1.0	4.15
C	9.5	1.0	4.35
D	6.5	5.5	0.25
E	7.7	4.1	0.81
F	8.2	4.3	1.53
G	8.1	4.4	1.27
H	7.8	4.2	0.54

changes in the color of the bulk gel from an initial orange color to blue. The known ability of ferrocene gels to undergo chemical oxidation[30] along with the observed change in color of the gel to the same color as that of ferrocene solution upon oxidation by $FeCl_3$ (see the Supporting Information) were used to conclude that ferrocene moieties in the gel were oxidized successfully by reaction with the oxidizing agent $FeCl_3$.

Reversible Reduction of Oxidized Ferrocene Moieties in the Gel Using Chemical Agents. The change in color of the ferrocene containing gel from orange to blue upon oxidation by $FeCl_3$ was found to be reversible. The blue-colored oxidized gel, when allowed to equilibrate with solvent containing dissolved L-ascorbic acid, was observed to regain its original orange color, a color change that was attributed to chemical reduction of the ferricenium ions in the gel back to ferrocene. Kuramoto et al.[30] have previously demonstrated that L-ascorbic acid can act as a reducing agent for ferrocene containing gels. The gels after reduction by L-ascorbic acid could again be oxidized using $FeCl_3$ thus establishing the reversibility of the chemical redox reaction.

Effect of Gel Constituents on Butanol Capacity and Selectivity. The relative proportions of the four constituents in the gel (the monomer constituting the polymer backbone, HBMA, the redox-active monomer, VF, the cross-linker, EGDMA or BIS, and the initiator, AIBN) will affect the gel properties. In particular, the desired properties of the gel include a high capacity for absorbing butanol, and a preferential selectivity for butanol over water, in the reduced state, and a decrease or even reversal in this selectivity for butanol when the ferrocene moieties in the gel are oxidized. Gels with the compositions listed in Table 2 were synthesized as part of this study.

The preferential selectivity of a gel for butanol in the reduced state is reported in terms of the separation factor determined following equilibration with a saturated solution of butanol in water (mass fraction of butanol equal to 0.066), α^{red}_{sat}. The decrease in the selectivity of the gel for butanol when it is oxidized is characterized by the ratio of the separation factor for the gel in the reduced state to that in the oxidized state when the gel is brought to equilibrium with a saturated solution of butanol in water

$$\psi_{sat} = \frac{\alpha^{red}_{sat}}{\alpha^{ox}_{sat}} \tag{3}$$

where α^{red} and α^{ox} denote the separation factors in the reduced and oxidized states of the gel, respectively. The capacity of the gel for butanol, denoted by Δ, was measured as the fractional increase in the mass of the gel on equilibration with excess butanol. Table 3 lists the values of the three quantities, α^{red}_{sat}, ψ_{sat}, and Δ for the gels synthesized in this study.

Gels with low ferrocene and high HBMA content have a very high capacity and selectivity for butanol in the reduced state. However, the selectivity for butanol did not decrease significantly on oxidation of the ferrocene moieties, as is evident from the values of ψ_{sat} close to 1 obtained for these gels. The charge on the ferrocene moieties when they are oxidized is expected to lead to an increase in the hydrophilic environment in a region around the pendant ferrocene group. However, if the ferrocene content of the gels is low, the presence of charge on the oxidized ferrocene moieties will not lead to significant changes in the chemical environment within the bulk of the gel. Therefore, the low values of ψ_{sat} obtained for gels *B* and *C* were attributed to the ferrocene content in these gels being less than that which would be required for an appreciable reduction in the preference for butanol on oxidation. On increasing the ferrocene content to close to 20 mol %, as in gel *E*, the selectivity for butanol was found to decrease when the gels were oxidized indicating that the significantly larger percentage of ferrocene makes the gel prefer water over butanol when the ferrocene groups are charged. At these high ferrocene concentrations, however, the capacity of the gel was found to

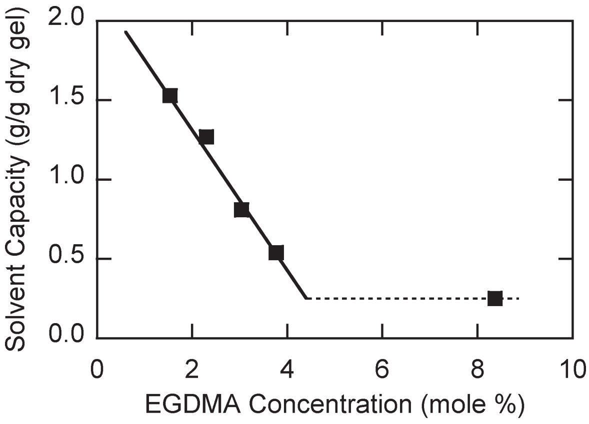

Figure 3. Swelling of gels in the presence of saturated butanol/water solutions as affected by cross-link density.

decrease by a factor of 5 and the selectivity for butanol in the reduced state also decreased. Alcohols, like methanol, are known to be nonsolvents for poly(vinylferrocene)[56] and the reduction in the selectivity and capacity for butanol on increasing the ferrocene content is consistent with this observation. These trade-offs in the selectivity and capacity of the gels with increasing ferrocene content indicate an optimum ferrocene content for a specific application.

The cross-linker, e.g., BIS or EGDMA, leads to interconnection of the polymer chains and gelation on polymerization of the monomer solution. The polymer gel thus formed can have high mechanical rigidity, and does not disintegrate or dissolve when equilibrated with solvents, a critical property in the study of solvent uptake by the gel. Gels were synthesized with different molar percentages of the cross-linker, all less than 4 mol % except in the case of gel *D*, where it was above 8 mol %. At these low concentrations, the cross-linker was not expected to influence the selectivity of the gel for butanol significantly. The solvent uptake by the gels, on the other hand, was found to depend strongly on the cross-linker concentration; the solvent capacity, Δ, decreased almost linearly with the increase in the cross-linker concentration up to a value of about 4%, above which the solvent uptake did not appear to change much, as shown in Figure 3. It was observed that gels with cross-linker concentrations of less than that in *F* (1.54 mol %) had extremely poor mechanical properties, and samples of such gels crumbled into a powder during experiments unless handled very carefully. Therefore, although a gel with low cross-linker concentration and consequently high solvent capacity is desired, cross-linker concentrations below 1.54 mol % were considered to be unsuitable from a practical application perspective.

Thus, in summary, a high ferrocene content in the gel is required for the extraction of butanol in the reduced state and release of butanol in the oxidized state, but at very high ferrocene contents both the selectivity and capacity for butanol are compromised. The solvent uptake capacity of the gel can be increased by reducing the cross-linker concentration, but reducing it below a critical value compromises the mechanical strength of the gel. With these considerations in mind, the composition of gel *F* was deemed to be the best among the gels synthesized in this study. Gels with composition identical to gel *F* were used for the subsequent butanol extraction experiments.

Capacity and Selectivity of Gel for Butanol and Water in the Reduced and Oxidized State. The selectivity of gel *F* for butanol and water in its reduced and oxidized states was quantified in terms of the equilibrium distribution coefficients of the two species between the gel and solvent phases, and the separation factor, which were measured as a function of the butanol concentration in the liquid phase. The results are shown in Figure 4.

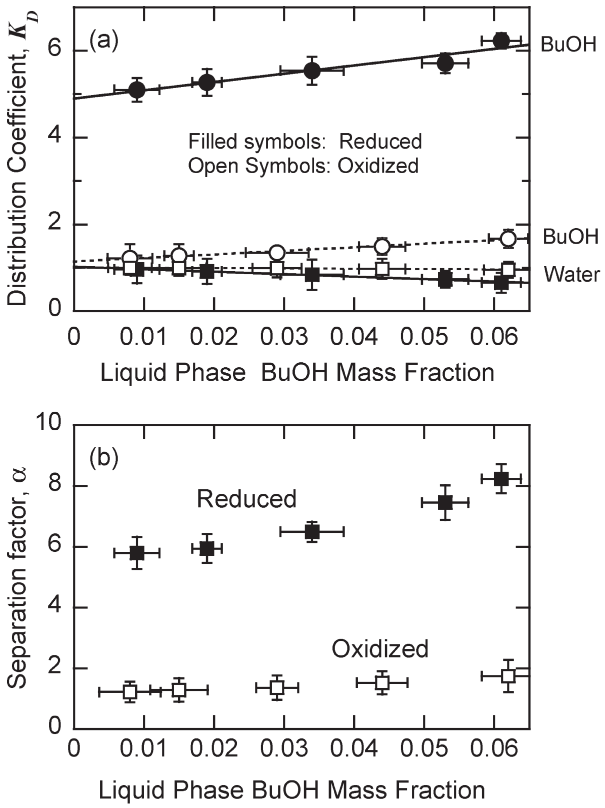

Figure 4. (a) Equilibrium distribution coefficient for butanol and water between the HBMA-VF gel (with composition identical to F) and aqueous solution when the gel is in the reduced and the oxidized state (b) Separation factor for butanol and water between the HBMA-VF gel (with composition identical to F) phase and aqueous phase when the gel is in the reduced and the oxidized state.

The distribution coefficient for water was found to be different, but close to unity, in the reduced and oxidized states of the gel, as seen in Figure 4a, and to vary slightly with butanol concentration. The distribution factor for butanol also changed slightly with butanol concentration in the solvent, but, in contrast to water, changed dramatically with the oxidation state of ferrocene in the gel. When the ferrocene moieties in the gel were in the reduced state, the distribution coefficient for butanol, $K_{\mathrm{D,BuOH}}^{\mathrm{red}}$, was nearly five times greater than that for water at low butanol mass fraction, and increased with increasing butanol concentration. $K_{\mathrm{D,H_2O}}^{\mathrm{red}}$ decreased by up to 30% with increasing butanol concentration. When the solvent phase was saturated with butanol, the butanol distribution coefficient was measured to be 6.2, or roughly nine times the distribution coefficient of water. The increase in the distribution factor of butanol is clearly reflected in the plot of the separation factor, α, of the gel in the reduced state (Figure 4b). The increase in butanol distribution coefficient with an increase in butanol concentration in a butanol-water solution is in agreement with similar results reported by Offeman et al.[51] for the solvent extraction of ethanol from aqueous solutions. The increasing butanol and decreasing water distribution coefficients, and therefore the increasing separation factor, with higher butanol loadings indicate that the hydrophobic environment in

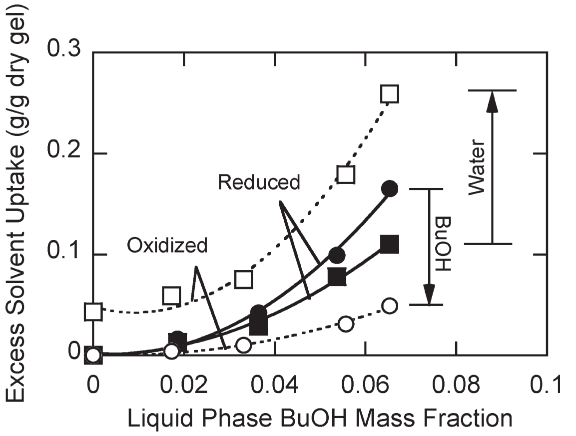

Figure 5. Excess uptake of water and butanol relative to a reduced, water-saturated, butanol-free gel. Solid and broken lines (and filled and open symbols) indicate the reduced and oxidized states, respectively, while circles and squares denote butanol and water. The changes in solute uptake upon oxidation under butanol-saturated conditions are indicated by the arrows.

the gel becomes increasingly more favorable for the hydrophobic component of the solution, butanol, as the butanol content in the gel goes up.

The selectivity of the gel for butanol is altered dramatically in the oxidized state. The distribution coefficient for butanol between the oxidized gel phase and the solvent is considerably lower than the distribution coefficient when the gel is in the reduced state (Figure 4a). Since the distribution coefficient of water increases under the same conditions, the net result is a much lower value of the separation factor when the gel is oxidized (Figure 4b). This result clearly demonstrates that the gel phase has lower selectivity for butanol upon oxidation.

The oxidation was achieved by the addition of $FeCl_3$, which altered the ionic strength of the solvent phase, and hence potentially also the distribution of the solvent components between the liquid and gel phases. The activity coefficient of butanol at different concentrations in water in the presence of $FeCl_3$ was calculated using the Electrolyte NRTL model with the Redlich−Kwong equation of state in ASPEN and found to be only 0.5% to 2% lower than the activity coefficients in binary butanol-water solutions, indicating that the distribution coefficients were not affected significantly by the addition of the oxidizing agent. In addition, it was shown experimentally that the solution ionic strength did not affect gel swelling; control experiments measuring the solvent uptake by a reduced gel in solutions of other salts such as $FeSO_4.7H_2O$, $(NH_4)_2SO_4$ and NaCl, which do not act as oxidizing agents, resulted in swelling that was almost identical to the swelling of the reduced gel in pure solvent without the added salts.

The lower selectivity on oxidation is a result of an increase in the hydrophilicity of the environment within the gel upon oxidation of the ferrocene moieties to form ferricenium ions, and the simultaneous migration of negatively charged counterions from the bulk solvent phase to the vicinity of the ferrocene site. The presence of charged species within the gel phase increases the need for hydration of the gels, and thereby decreases the preference of the gel for the more hydrophobic butanol, resulting in lower distribution coefficient. Similar increases in the hydrophilicity, or decreases in the hydrophobicity, of redox gels have been reported by Kuramoto et al.,[30] Oyama et al.[32] and Tabata et al.[7] Although the former two research groups used the oxidation of ferrocene-containing polymer gels to alter the gel phase transition temperature by changing the gel hydrophobicity, Tabata and co-workers exploited the hydrophobic−hydrophilic transitions to cause swelling and deswelling of a self-oscillating gel. The results obtained in this study further corroborate the idea that the control of the oxidation state of redox species in a polymer gel matrix can be used to alter the hydrophobicity of the chemical environment within the gel. More importantly, the reversible nature of the redox reaction can be used to switch back and forth between the hydrophobic and hydrophilic states.

In the reduced state, and in the absence of butanol, the gel is swollen with 0.135 g of water/g of dry gel; under all other conditions the solvent uptake is larger. This swollen gel is, in effect, the actual separation medium, or base case, rather than just the cross-linked polymer itself. The effect of butanol addition and ferrocene oxidation on the changes in the uptake of water and butanol, i.e., the excess solvent uptake, by this redox-active absorbent (polymer plus initial water) is reported in Figure 5, in which it is clear that increasing butanol concentration leads to an increase in uptake of both water and butanol by the gel, no matter its oxidation state. The effect of changes in oxidation state on solvent uptake, however, is dramatically different for the two components, as indicated by the magnitudes and directions of the changes in excess solvent uptake for water and butanol when the liquid phase is saturated with butanol. On oxidation, the water uptake increases significantly at the expense of butanol, whose uptake decreases to almost the same extent, in accordance with our assertion that the changes in hydrophilicity/hydrophobicity upon changing the oxidation state favor one or the other of the components, depending on the direction of the redox reaction .

The equilibrium distribution coefficient of butanol and the separation factors were found to remain unchanged when butanol was dissolved in a defined medium used for the fermentative production of butanol (with the composition given by Yang and Tsao[57]) instead of in simple binary butanol−water solutions. Thus, a separation system based on redox-responsive polymer gels as developed in this study can be integrated with a butanol fermentation reactor for continuous removal of butanol from the aqueous fermentation broth to overcome product inhibition effects.

4. CONCLUSION

We have demonstrated the reversible control of the hydrophobicity of an HBMA polymer gel through control of the oxidation state of the ferrocene groups covalently attached to the polymer backbone. When the ferrocene moieties are in the reduced state, the gel environment is hydrophobic, whereas upon oxidation of ferrocene to ferricenium ions, charges are induced inside the gel to render the gel hydrophilic. The tunable hydrophobicity of the gel system developed in this study has been used successfully for extracting butanol from its aqueous solution when the gel is in the reduced state and then releasing it when the gel is oxidized. The reversibility of the preference of the gel for an organic compound dissolved in water can be extended to other gel systems having preferential selectivity for other organics.

The redox polymer developed during the course of this work can form the basis of novel separation systems for the removal of organics from water. Although oxidation of the polymer was carried out using a chemical agent in the experiments reported here, the attachment of the polymer to conducting substrates to form redox polymer electrodes (RPEs) would allow the use of electric potential to induce similar reversible changes in the oxidation state of the ferrocene moieties in the gel. These RPEs can then be used in a separation system which can be operated continuously to separate the desired organic from water. In particular, a separation system based on electrodes with the HBMA-VF redox polymer synthesized in this paper that can be integrated with a butanol fermentation reactor to continuously remove butanol from the broth and diminish the product inhibition effects, is expected to have a significant impact in enhancing the productivity of butanol fermentation processes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. The successful oxidation of ferrocene dissolved in butanol by $FeCl_3$ was confirmed independently in this study using UV−visible spectrophotometry. The results are discussed and presented. This material is available free of charge via the Internet at http://pubs.acs.org/.

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