Mechanical Stress in Immobilized Polycation Thin Films Induced by Ion-Exchange

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ABSTRACT: The exchange of one counterion with another, perchlorate with chloride, induces mechanical stress in polycation matrices. The magnitude of the stress decreases with increasing hydrophobicity of the matrix. Thin films of cross-linked poly-(vinylbenzyl chloride) are reacted with trialkylamines to give immobilized poly(vinylbenzyltrialkylammonium chloride) matrices. Mechanical stress in films is measured using a scanning laser apparatus. Each material exhibits tension upon exchange from chloride to perchlorate form, consistent with matrix dehydration. Data are fit to a chemical equilibrium model assuming proportionality between stress and conversion to perchlorate form. Maximum changes in biaxial stress range from 3.1 MPa for a tributylamine-modified film to 16.6 MPa for a trimethylamine-modified film. Selectivity coefficients range from 43 for the trimethylamine-modified film to 370 and 450 for the tributylamine- and tripropylamine-modified films, respectively, indicating greater selectivity for perchlorate in more hydrophobic matrices. These results help clarify the physical origins of perchlorate selectivity in anion-exchange resins.
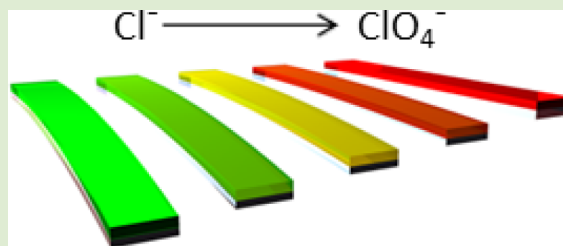
Solid-state polyelectrolytes are a useful class of materials due to their ability to exchange counterions with an adjacent medium.[1,2] Hydrophobic polycations have emerged as an important subclass of polyelectrolytes due to their propensity to selectively bind perchlorate (ClO_4^-) and pertechnetate (TcO_4^-) from complex environmental matrices.[3,4] The EPA issued a final decision in February 2011 to regulate ClO_4^- in drinking water because ClO_4^- is a potent inhibitor of iodide uptake in the human thyroid.[5] Anion-exchange resins containing hydrophobic fixed ions such as quaternary ammonium derivatives of tributylamine or trihexylamine are known to exhibit high selectivity for ClO_4^- and have emerged as a promising treatment option for contaminated drinking water.[3,6] Selectivity in these systems is generally understood to be dictated by the free energy associated with hydration and dehydration of the exchanging anions.[3,7] However, this model has yet to be adequately validated through experiments; in light of the pending EPA regulation, there is an urgent need for improved understanding of the origins of perchlorate selectivity in anion-exchange resins.

We recently reported an observation of mechanical stress associated with water uptake in cross-linked poly-(vinylbenzyltrialkylammonium chloride) (PVBTC) matrices[8] induced by adsorption of water produced by changes in relative humidity (RH). In the present study we measure mechanical stresses induced by ion-exchange in aqueous solutions. As shown in Figure 1, exchange of anionic counterion from chloride (Cl^-) to ClO_4^- is an inherently stoichiometric process due to charge neutrality. Water-swollen matrices are generally expected to dehydrate with the forward process,[9] as represented by Δn_w, the ratio of water molecules expelled by the matrix to

the number of ionogenic sites. Essentially, while our previous study was limited to observation of matrices containing a single species of counterion, the present study enables us to observe the path each material takes from the initial to the final (i.e., Cl^- and ClO_4^-) state.

We prepared cantilevers for measurements of stress induced by ion-exchange using the same synthetic route described recently.[8] Briefly, Au (50 nm)/Cr (20 nm)-coated microscope cover glasses were functionalized with aminopropyltriethoxysilane to give an amine-terminated surface. Poly(vinylbenzyl chloride) and diazabicyclo[2.2.2]octane (DABCO) were spin-coated onto the nonmetalized side of the cover glass. After curing, the PVBCl coatings were reacted by nucleophilic substitution with tertiary amines including trimethylamine (TMA), triethylamine (TEA), tripropylamine (TPrA), and tributylamine (TBA) to give PVBTC films. Conversion of the vinylbenzyl chloride groups to their corresponding quaternary ammonium chlorides is approximately 40% of the theoretically expected value.[8] Swollen thicknesses are estimated to range from 440 to 580 nm on the basis of previous water vapor uptake measurements. Sample thickness was not measured directly in liquid water; however, because liquid water and saturated water vapor are thermodynamically equivalent, swelling in each medium is expected to be comparable.[2,10] Uncertainty in thickness measurements for films in liquid water made direct measurements impractical. After reaction, canti-
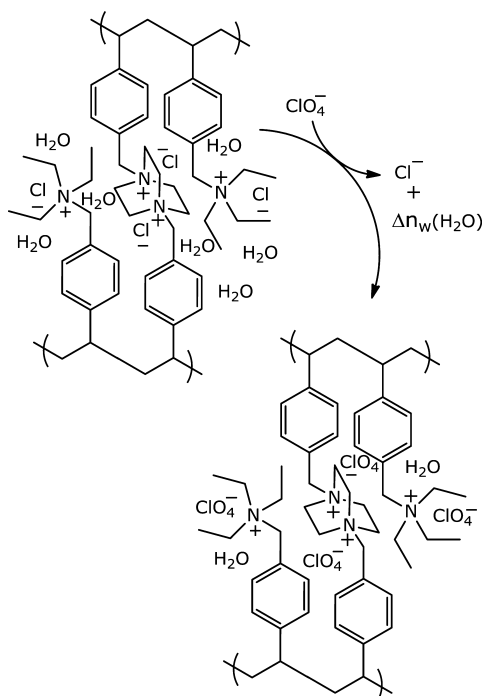
Figure 1. Exchange of a poly(vinylbenzyltrialkylammonium chloride) (PVBTC) matrix, shown as modified by TEA, from Cl^- to ClO_4^- form. Ion exchange is accompanied by dehydration of the matrix due to the relative hydrophobicity of ClO_4^-.
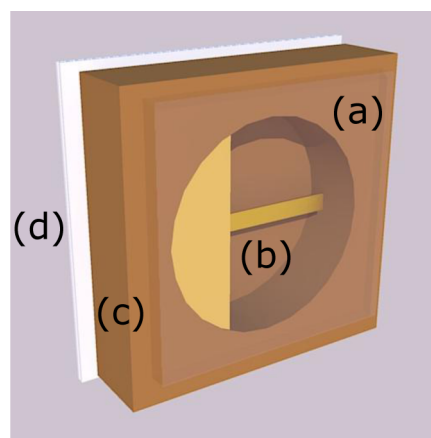

Figure 2. Diagram of the sample cell used for measuring changes in biaxial stress in PVBTC films due to ion-exchange: (a) quartz window, (b) coated glass cantilever, (c) PEEK cell, and (d) thermoelectric chiller used for temperature control. Aqueous solutions are pumped through the cell in between measurement intervals.

maintain consistency with our previous report of humidity-induced stress.[8]

Temperature of the sample cell was varied in order to determine how changes in temperature propagate into changes in the stress state of the films. As shown in Figure 3, each
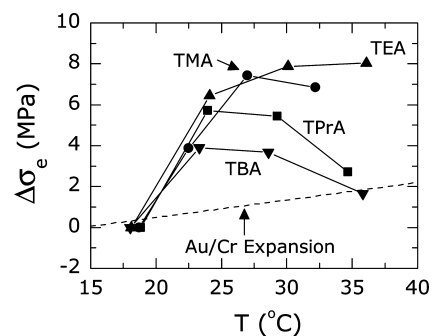

Figure 3. Change in biaxial stress ($\Delta\sigma_e$) plotted against temperature for PVBTC films. The expected response due to expansion of the Cr/Au coating is also shown, where the compressive stress in the metal layer leads to an apparent tensile stress in the polymer coating. Each of the four materials undergo relative tensile stress, from an expected initial compressive stress, due to an increase in temperature, with a plateau or drop-off above 27 °C.

levers approximately 10 × 1 mm were then cut from the cover glasses using a diamond-tipped pen. As before, the thickness of the cover glass is 150 μm and the cantilever dimensions meet the limiting requirements of Stoney's equation.[11,12] Moreover, Stoney's equation is an expression of mechanical equilibrium as it concerns the substrate. Slow viscous or viscoelastic response in the coating does not affect the functional relationship between interfacial stress and curvature in the substrate. We previously demonstrated kinetic effects to have a minor impact on the measured stress and expect these effects to be insignificant.[8]

Samples were mounted in a cell constructed from polyetheretherketone (PEEK), as shown in Figure 2. Temperature was monitored using a thermistor and stabilized at 18 ± 0.2 °C with a thermoelectric element mounted on the backside of the cell. The sample cell was purged in between sampling intervals with a minimum of 20 times the cell volume of a given solution. Curvature of the cantilevers was measured using a scanning-laser optical apparatus described previously.[8,13] Changes in glass-film interfacial stress, Δg, are derived from the rms voltage output ΔV from the lock-in amplifier using

$$\Delta g = \frac{Y_s d^2}{6(1-\gamma_s)} \frac{\sqrt{2}\,\Delta V}{wF\beta} \tag{1}$$

where Y_s, γ_s, and d are the Young's modulus (75.9 GPa), Poisson ratio (0.22), and thickness (150 μm) of the glass cantilever substrate, respectively, β is the calibration constant of a position sensitive detector (1000 V m^{-1}), F is the primary lens focal length (0.5 m), and w is the laser scanning width on the cantilever (4 mm). Dividing Δg by the dry film thickness (h_0) gives the change in biaxial engineering stress ($\Delta\sigma_e$). We use the dry film thickness in our calculation of stress to

material follows the same general pattern: relative tensile stress is observed as temperature is raised until a plateau or a reversal to relative compressive stress is reached at temperatures greater than 25−30 °C. Each material exhibits a change in stress of approximately 1 MPa °C^{-1} from 18 to 24 °C, which suggests errors due to temperature variation are approximately ±0.2 MPa. Also shown in Figure 3 is the expected response due to differential expansion of the Cr/Au coating (thermal expansion coefficients: Au, 14.2 ppm K^{-1}; Cr, 5.9 ppm K^{-1}; glass, 7.5 ppm K^{-1}) relative to the substrate.[14] Assuming the materials are all initially in a state of compression due to swelling from the water, the observed tensile stresses generally represent partial relaxation from the swelled state. The nonmonotonic stress response in some of the materials suggests temperature dependence above 24 °C is due to a complicated combination of swelling and changes in the mechanical properties (i.e.,

modulus, yield strength) of the films. Understanding the temperature dependence of the response may be valuable in its own right and may be further explored in the future.

Changes in biaxial stress in each material due to ion exchange are shown in Figure 4. Each of the four materials exhibits
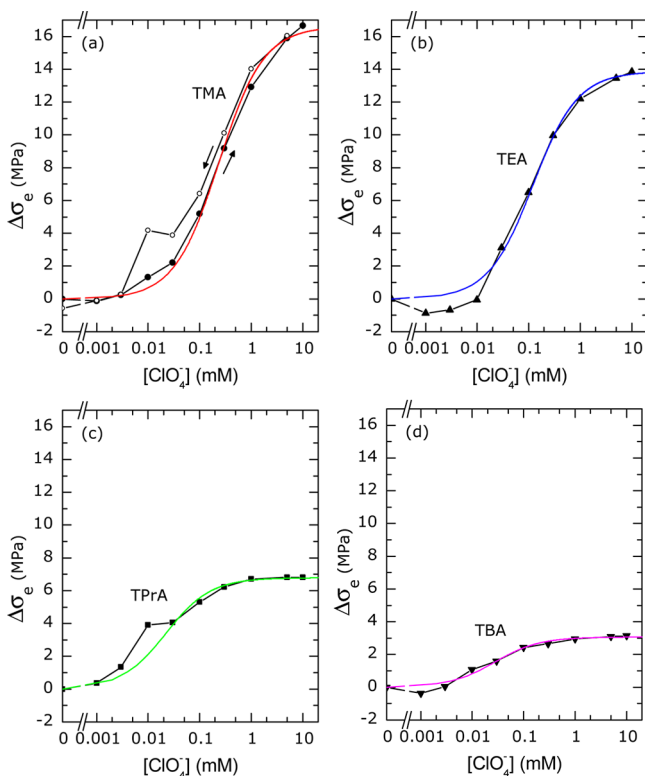

Figure 4. Change in biaxial stress ($\Delta\sigma_e$) plotted against ClO_4^- concentration for PVBTC films modified with (a) TMA, (b) TEA, (c) TPrA, and (d) TBA. Tensile stress is positive. Total concentration of the external solution is constant at 10 mM, with Cl^- making up the balance; both Cl^- and ClO_4^- are present as Na^+ salts. Colored lines represent fits to a chemical equilibrium model assuming a proportional relationship between $\Delta\sigma_e$ and conversion between Cl^- and ClO_4^- forms. More hydrophobic materials display progressively higher selectivity toward ClO_4^-, as indicated by the onset, midpoint, and saturation of ion-exchange induced stress at lower concentrations.

relative tensile stresses upon exchange of Cl^- for ClO_4^-. Tensile stresses are consistent with volume loss due to matrix dehydration. The TBA- and TMA-modified films display the smallest and largest changes in stress, respectively. The changes in stress are approximately 5−10 times lower than those observed upon exposure of a dry film to nitrogen nearly saturated with water vapor.[8] The concentration range over which stress is induced varies among the materials; while the onset of stress is ambiguous, collectively, the onset, midpoint, and saturation of stress all occur at higher ClO_4^- concentrations in the TMA- and TEA- modified films than in the TPrA- and TBA-modified films.

Each data set was fit according to a model involving exchange of ions as shown in eq 2,

$$R^+Cl^- + ClO_4^- \rightleftharpoons R^+ClO_4^- + Cl^- + m_w + \Delta n_w$$

$$(2)$$

where the notation R^+X^- indicates a counterion bound to a fixed cation, and $\Delta n_w = n_w - m_w$ is the change in absorbed water molecules per fixed ion site, also shown in Figure 1. In

this model, ion exchange is considered a chemical reaction with an equilibrium coefficient (K) corresponding to the distribution of ions according to

$$K = \frac{[R^+ClO_4^-][Cl^-]}{[R^+Cl^-][ClO_4^-]}$$

$$(3)$$

where the notation [ ] refers to the concentration of each species. Larger values of K indicate greater selectivity for ClO_4^- relative to Cl^-. If the change in stress is directly proportional to the degree of conversion from ClO_4^- to Cl^- form, then the stress data should fit

$$\Delta\sigma_e = \alpha \frac{[R^+ClO_4^-]}{[R^+Cl^-] + [R^+ClO_4^-]}$$

$$(4)$$

where α is a proportionality constant. Eqs 3 and 4 combine to give

$$\Delta\sigma_e = \alpha K \frac{x}{1 - x + Kx}$$

$$(5)$$

where x is the ClO_4^- concentration divided by the total concentration of the external solution. As defined in this model, K is equivalent to the $ClO_4^- - Cl^-$ selectivity coefficient.[2]

Maximum changes in biaxial stress ($\Delta\sigma_{e,max}$) are summarized for each material in Figure 5, where they are plotted against the

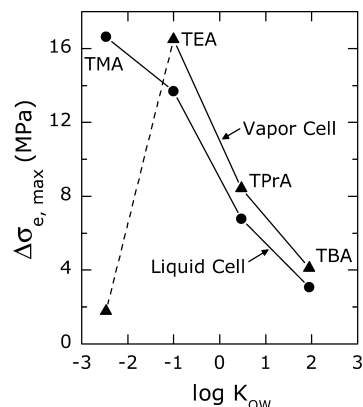**Figure 5.** $\Delta\sigma_{e,max}$ plotted against log K_{OW}, the estimated octanol−water partition coefficient for the benzyltrialkylammonium chloride salt derived from each tertiary amine precursor. Data are shown for both the present study (i.e., "liquid cell") and our recent report (i.e., "vapor cell") of mechanical stress due to water uptake from a mixture of nitrogen and water vapor (i.e., the difference in maximum changes in stress between Cl^- and ClO_4^- forms assuming the dry states are identical). Maximum changes in stress correlate well between these experiments, suggesting the absolute stress in the dry state for each material is similar regardless of counterion species.

log octanol−water partition coefficients (log K_{OW}) for analogous benzyltrialkylammonium chloride salts calculated based on an atom/fragment contribution method.[5,15] The magnitude of the change in stress varies from 3.1 to 16.6 MPa in the TBA- and TMA-modified films, respectively, indicating greater dehydration in the more hydrophilic materials.

For comparison, data from our recent report[8] of stress due to water vapor absorption are also shown in Figure 5. These data are calculated based on the assumption that the absolute state of stress under dry nitrogen is identical in both Cl^- and ClO_4^- forms; if this assumption holds, then the differences in stress observed at high RH for each ionic form should roughly

correlate to those observed in the present experiment. Indeed, the data match quite well for all but the TMA-modified film. However, as noted in our previous report, the Cl⁻-form, TMA-modified material is a peculiar case because it most likely does not fully dehydrate under dry nitrogen. Residual water in the matrix leads to uncertainty in our determination of the appropriate "dry" reference state. Aside from uncertainty regarding the TMA-modified film, the data support our assumption that the state of stress is similar in each dry material irrespective of counterion form.

Changes in stress are due to hygroscopic strain or the volume change in the film (ΔV_f) due to water content and the difference in volume occupied by Cl⁻ and ClO$_4^-$ ions. In eq 5 we have assumed stress is proportional to the extent of ion exchange. The magnitude of this stress may be used to estimate ΔV_f and develop new insights into the physical process of ion exchange.

To estimate the change in volume due to exchange of anions, we calculated the biaxial modulus (B) for each material from the difference in stress ($\Delta\sigma_e$) and volume measured at approximately 83 and 90% RH,

$$B = \frac{3V_0\Delta\sigma_e}{\Delta V_f} \tag{6}$$

where V_0 is the dry volume of the film and $\Delta V_f/3V_0$ is equivalent to strain in the present geometry. Changes in volume due to water vapor uptake are calculated from the fractional mass uptake (ϕ), specific volume of water (v_s), and density of the material (ρ_0),

$$\frac{\Delta V_f}{V_0} = \Delta\phi v_s \rho_0 \tag{7}$$

Combined, eqs 6 and 7 give

$$B = \frac{3\Delta\sigma_e}{\Delta\phi v_s \rho_0} \tag{8}$$

which, assuming $v_s = 1$ cm^3 g^{-1}, yields the following B for each amine-modified film: 0.33 GPa (TMA), 0.58 GPa (TEA), 1.8 GPa (TPrA), and 1.7 GPa (TBA). The moduli of the more hydrophilic materials (i.e., TMA and TEA) are substantially lower than the others because they are plasticized due to higher water content.[8]

Equation 6 may be used to calculate $\Delta V_f/V_0$ from B and $\Delta\sigma_e$. Microscopic volume changes (i.e., volume per fixed ion) are calculated from $\Delta V_f/V_0$ according to eq 9

$$\Delta\bar{V} \equiv \frac{\Delta V_f}{n_{ion}} = \frac{\Delta V_f}{V_0}\frac{1}{N_A\rho_0 C} \tag{9}$$

where N_A is Avogadro's constant and C is the ion exchange capacity (mmol g^{-1}) of each material. Lastly, eqs 6 and 9 combine to give

$$\Delta\bar{V} = \frac{3\Delta\sigma_e}{B}\frac{1}{N_A\rho_0 C} \tag{10}$$

which is used to calculate $\Delta\bar{V}$ for each of the materials.

Estimated changes in volume due to ion-exchange are shown in Figure 6. Positive values of $\Delta\bar{V}$ indicate dehydration. In the example of the TMA-modified film, $\Delta\sigma_e = 16.6$ MPa gives a $\Delta\bar{V}$ of 80 Å^3. As shown in Figure 6, the TMA-modified film exhibits the highest $\Delta\bar{V}$, while the TBA-modified film is the lowest at 4 Å^3. For comparison, the ionic volumes of Cl⁻ and ClO$_4^-$ are 21
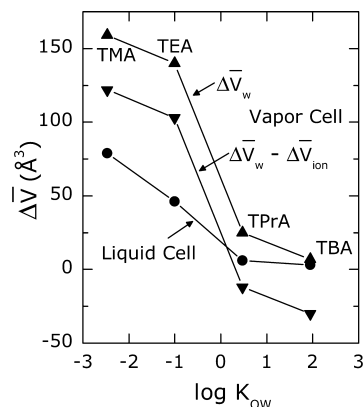

Figure 6. Changes in volume ($\Delta\bar{V}$) per ionogenic site in each matrix plotted against log K_{OW}, the estimated octanol−water partition coefficient for analogous benzyltrialkylammonium chloride salts. Data are shown for both the present study (i.e., "liquid cell") and our recent report[8] of water relative humidity-induced water absorption (i.e., "vapor cell"). The expected change in volume due to absorbed water ($\Delta\bar{V}_w$) is calculated from Δn_w, the difference in number of absorbed water molecules per ionogenic site when each material contains Cl⁻ versus ClO$_4^-$ ions. A correction for the difference in ionic volume between Cl⁻ and ClO$_4^-$, $\Delta\bar{V}_{ion}$, is shown as well.

and 58 Å^3, respectively, as calculated from their thermochemical radii.[16] Also, for reference, the volume of an individual water molecule is 30 Å^3 in bulk liquid water.

Values of Δn_w were calculated from the maximum amount of water absorbed in each film at high RH,[8] allowing us to estimate $\Delta\bar{V}_w$, the change in volume expected on the basis of dehydration. The TMA-modified film, for example, absorbs $n_w = 7.8$ in Cl⁻ form and $n_w = 2.5$ in ClO$_4^-$ form. Again, assuming absorbed water molecules occupy the same volume as in bulk liquid water, $\Delta n_w = 5.3$ equates to $\Delta\bar{V}_w = 160$ Å^3.

As shown in Figure 6, values of $\Delta\bar{V}$ from the present study follow the same general trend expected on the basis of our previous report of water absorption induced by changes in RH. The magnitudes of $\Delta\bar{V}$ are roughly 30−70% lower in the present study than predicted for the TMA- and TEA-modified films. Such discrepancies in the magnitude of $\Delta\bar{V}$ are unsurprising given uncertainty in v_s and the use of B, which may differ somewhat from the modulus of each film in contact with a 10 mM aqueous salt solution.

More surprising, however, each of the four materials exhibits a loss in volume or net contraction upon exchange of Cl⁻ for ClO$_4^-$. The TPrA- and TBA-modified films are predicted to exhibit relatively small $\Delta\bar{V}_w$. If the difference in ionic volume between Cl⁻ and ClO$_4^-$ ($\Delta\bar{V}_{ion}$) is then considered, net expansion would also be expected for each of these two more hydrophobic materials. The exact cause for this discrepancy is unclear but may be due to differences in how each anion is accommodated by the larger quaternary ammonium cations.

Selectivity data are summarized in Figure 7 along with values of K reported in the literature.[7,17] The more hydrophobic materials display higher selectivity for ClO$_4^-$, consistent with several other reports on the selectivity of bulk anion-exchange resins.[3,4,7] However, even the most hydrophilic TMA-modified film exhibits a strong preference for ClO$_4^-$ over Cl⁻. Each of the four materials exhibits lower K than expected on the basis of previous reports.[7,17] Possible explanations for the lower selectivity include reduced cross-linking density[7] and our use of DABCO instead of divinylbenzene to cross-link the
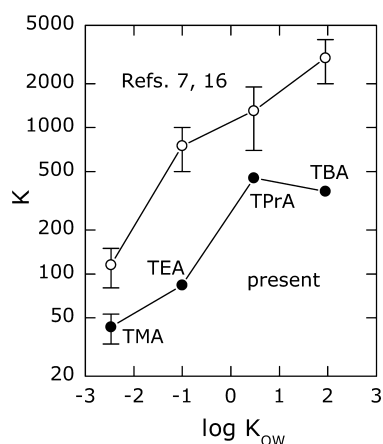
Figure 7. Selectivity coefficient (K) plotted against K_{OW}, the estimated octanol−water partition coefficient for analogous benzyltrialkylammonium chloride salts. Values reported in the literature[7,17] are shown for comparison. Higher values of K indicate greater selectivity for ClO_4^-. Despite lower overall values the trend is consistent with that previously observed for anion-exchange resins.[4,19]

materials. DABCO-based quaternary ammonium sites, for example, are expected to increase the resin hydrophilicity relative to divinylbenzene groups. Mechanical stress or pressure-volume related energy is itself known to have only a negligible influence on selectivity.[18]

The general selectivity of these materials for ClO_4^- may be rationalized by considering the free energies of hydration (ΔG_h) of ClO_4^- (-205 kJ mol^{-1}) and Cl^- (-340 kJ mol^{-1}) derived from lattice energies.[16] Anions bound in the matrix are forced to accept a lower level of hydration than those in the adjacent aqueous solution and, consequently, the more hydrophobic ClO_4^- ions have a strong tendency to displace Cl^- ions in the matrix. The relative selectivity of the four materials studied is consistent with this concept, as the more hydrophobic matrices (TPrA and TBA) are expected to be less accommodating of counterion hydration than the more hydrophilic matrices. Because of the large difference in ΔG_h between ClO_4^- and Cl^-, extreme selectivity might be expected for even small differences in ion hydration. However, other contributions such as electrostatic interaction also factor heavily into the overall free energy of ion exchange, as evidenced by the preference of conventional (TMA-based) anion exchangers for SO_4^{2-} ($\Delta G_h = -1295$ kJ mol^{-1}) over Cl^- despite the large difference in ΔG_h. The TMA-modified material (see Figure 4a) is the only system for which we collected data for the reverse process. Similar $\Delta\sigma_e$ is observed at each ClO_4^- concentration for both the forward and reverse processes. Experimental difficulty prevented reintroducing Cl^- into the more highly ClO_4^--selective films.

In conclusion, polycationic PVBTC films modified with TMA, TEA, TPrA, or TBA each exhibit tensile stress upon uptake of ClO_4^-, an indication that matrix dehydration dominates any mechanical compression that may be expected from insertion of an anion larger than Cl^-. The magnitudes of stress observed in the present study show a similar trend to what we predict based on our recent report of mechanical stress induced by absorption of water vapor.[8] Selectivity of each material for ClO_4^- over Cl^- is consistent with literature reports involving ClO_4^- selective anion-exchange resins: the more hydrophobic materials exhibit greater selectivity for ClO_4^-.[3,4,7] Moreover, these results reinforce the theory that selectivity for

monovalent anions is largely dictated by variations in the free energy of hydration. Increasing hydrophobicity causes the matrices to be less accommodating of anion hydration. As a result, hydrophilic anions preferentially exchange into an adjacent aqueous solution, where they are fully hydrated.

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Notes
The authors declare no competing financial interest.

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