Gels as Size Selective Extraction Solvents

We have successfully used cross-linked, partially-hydrolyzed, polyacrylamide gels to concentrate solutions of high molecular weight solutes. The gels are size-selective, concentrating solutes whose diameter exceeds 3 nm. They can be easily regenerated by means of pH-induced changes in gel swelling; this regeneration is consistent with that inferred from existing theories of gel swelling. The resulting separation process is a good alternative to ultrafiltration.

E. L. CUSSLER,
M. R. STOKAR,
and J. E. VARBERG

Department of Chemical Engineering and Materials Science
University of Minnesota
Minneapolis, MN 55455

SCOPE

Separation processes are a key aspect of the chemical industry. In the past, these processes were dominated by distillation, reflecting the key role played by petroleum. More recently, alternative separations have been more widely practiced: two good examples are the dewaxing of lubricants by mixed extraction solvents and the separation of gaseous mixtures using membranes (King, 1979).

However, there are an emerging group of separation problems for which current technology is expensive or clumsy. These problems center around dilute solutions of organic or biological materials. Examples include the removal of water from starch and cheese whey, the concentration of antibiotics in fermentation beers, and the recovery of protein products of genetically-engineered microorganisms. This paper, the first of a series, explores new separation methods for these systems.

The particular idea developed here is the use of gels as extraction solvents. Such gels have two advantages over conventional solvents:

1) They can be easily regenerated.

2) They can separate by molecular size.

Disadvantages include the gel's uncertain mechanical integrity.

Past experiments have emphasized different aspects of these gels. Changes in gel swelling basic to regeneration have been studied largely as an example of a new type of critical phenomenon (Dušek and Patterson, 1968; Tanaka 1981; Ilavský, 1981). While the results are fascinating, they are not directly applicable to this work. Similarly, separations using gels have centered on gel permeation chromatography (Kremmer & Boros, 1979). There, the separation is of very small amounts of similar high molecular weight solutes in a packed bed of gel swollen to a constant extent. In our work, the separation is of potentially large amounts of a high molecular weight solute and water, using a gel whose swelling is deliberately altered. Past efforts of this type are scattered and make no effort to regenerate the gel (Flodin et al., 1960; Fanta et al. 1978; Anderson et al., 1979).

CONCLUSIONS AND SIGNIFICANCE

We have successfully used polyelectrolyte gels to concentrate macromolecular solutions by as much as twenty times. This concentration is selective for solutes greater than 3 nm in diameter, but not for solutes less than 1 nm in diameter. Solutes concentrated include polystyrene latex, polyethylene glycol, and hemoglobin.

The gel emphasized is a hydrolyzed, cross-linked polyacrylamide, which can reach its equilibrium swelling in a few minutes, so that separations are potentially fast. Moreover, the surface of the gel is not sticky, so that it is easily handled. The separations depend on gel swelling changing sharply as a function of pH. At pH 7, the gel absorbs twenty times its weight in water but it does not absorb macromolecules. At pH 5, the gel releases 85% of the absorbed water. These changes in gel volume result from gel ionization and can be quantitatively explained using an extended Flory-Huggins theory for the swollen gel.

This gel-based separation forms an interesting counterpoint to ultrafiltration (Lonsdale, 1982). In ultrafiltration, a polymer membrane separates a solution at high pressure from a solvent at low pressure. Solvent is forced through the membrane from high to low pressure, while solutes are retained and thus concentrated. This one-step process is conceptually simpler than that proposed here. However, it is compromised by concentration polarization near the membrane, which necessitates large pressure drops and expensive equipment.

In contrast, the separation described in this paper involves several steps: the gel is added to a solution, filtered off to leave a concentrated raffinate, and then regenerated. Nonetheless, the gel has significant advantages. Because it has a large surface area per volume, it does not show as major concentration polarization and can operate at atmospheric pressure. As a result, equipment cost is less. We look forward to discovering how future developments clarify the comparison of these two processes.

INTRODUCTION

This paper reports the use of cross-linked gels as size-selective extraction solvents. The gels are effective because they absorb a low molecular weight solvent like water but not high molecular weight solutes like proteins. They can be easily regenerated because their swelling is a very strong function of the pH of the surrounding solution. As a result, these gels represent an attractive new separation process.

The way in which the gels function is shown schematically in Figure 1. Small gel spheres are added to a dilute solution. The spheres swell, absorbing the low molecular weight solvent but excluding high molecular weight solutes. The raffinate, now concentrated in the high molecular weight solutes, can then be separated from the swollen gel by filtration.

The swollen gel must now be regenerated. We use gels whose swelling is a very strong function of pH, so adding acid collapses the gel volume and releases much of the absorbed solvent. The

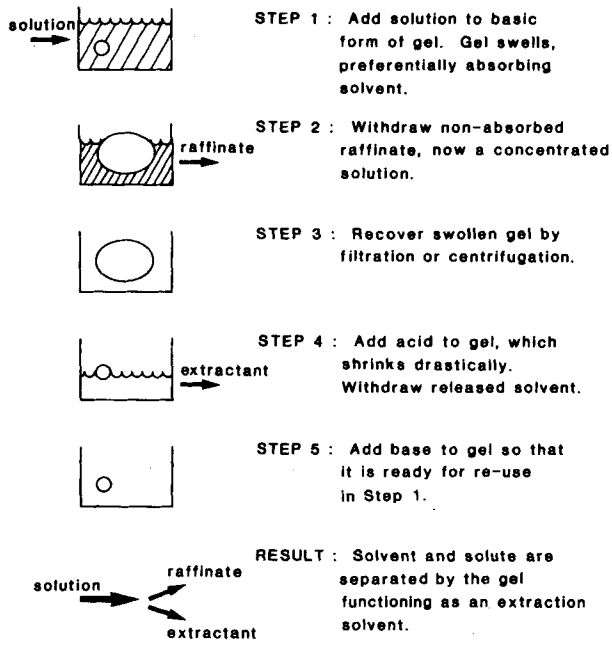

Figure 1. Gels as extraction solvents. Cross-linked polymer gels absorb small molecular weight species, but not large ones. Because this absorption can be a strong function of variables like pH and temperature, the gels can be regenerated and reused.

collapsed gel is separated from the released solvent by filtration and added to a small amount of base. The gel can then be added to fresh solution, where it will swell again.

The value of this separation depends on two characteristics of the gel which make it different than other separations. First, it absorbs according to molecular size. For example, if the gel interacts equally with water and with a protein solute, it will still absorb only the water because the protein is too large to diffuse between the gel's crosslinks. As a result, gels are like extraction solvents whose selectivity depends on differences in diffusion. They are like absorbants whose capacity is over ten times their mass.

The second interesting characteristic of these gels is the ease with which they can be regenerated. In the experiments reported here, the gels used are hydrolyzed polyacrylamide, which undergoes a variety of phase transitions and critical phenomena (Hochberg et al., 1979). In particular, the swelling of such gels can be a violent function of temperature (Ilavský et al., 1982), pH (Hasa & Ilavský, 1975), solvent concentration (Tanaka et al., 1980), and electric field (Tanaka et al., 1982). Such violent changes make the gel regeneration straightforward.

In the following sections, we first develop a theory which explains why the gel swelling changes so dramatically. We next describe our experiments. Finally, we show that these separations are effective for a variety of macromolecular species and that the changes of gel volume are consistent with the theory developed below.

THEORY

The separation process proposed in this paper relies on regenerating the gel by changing its volume via decreasing the pH. This variation of gel volume with pH can be estimated using a form of Flory-Huggins theory for polymer solutions (Dušek, 1971; Hasa et al., 1975; Ilavský et al., 1981). In the following, we extend the theory to predict that change in gel volume which is effected by the addition of a known amount of sodium hydroxide. This change is easily measured experimentally.

This calculation begins with the expected equilibrium of the solvent *1* across the gel-solution interface

$$\mu_1(\text{in solution}) = \mu_1(\text{in gel}) \tag{1}$$

We expect that the surrounding solution will be dilute, so that the chemical potential of the solvent will be close to its standard state value. We also assume that the chemical potential of the solvent in the gel is approximately (Flory, 1953; de Gennes, 1978):

$$\mu_1 = \mu_1^0 + RT\{ln\phi_1 + \phi_2 + \chi\phi_2^2 + k\phi_2^{1/3}\} \tag{2}$$

in which ϕ_1 and ϕ_2 are the volume fractions of the solvent and the gel, respectively; χ is an average enthalpy of interaction between the solvent and the gel; and k is a measure of gel elasticity. The right-hand side of this equation involves major approximations: for example, the effect of non-Gaussian chains and of the entropy of crosslinks are both ignored (Ilavský, 1982). Whether these approximations are justified must be checked by experiments.

A central feature of the gels used here is that they are polyelectrolytes. As a result, part of the gel is ionic, and associated with counterions:

$$\phi_1 + \phi_2\{1 + Z\zeta\} = 1 \tag{3}$$

where ζ is the degree of ionization, and Z is the maximum concentration of counterions produced by a mole of gel. If we insert Eq. 3 into Eq. 2, expand the logarithm as a power series and neglect all but the lowest-order terms, we obtain

$$0 = -\zeta Z\phi_2 + k\phi_2^{1/3} + \ldots \tag{4}$$

This equation includes only ionic and elastic effects.

We now must calculate the degree of ionization ζ as a function of pH, or more specifically, of the amount of added base. To do so, we assume that the gel reacts as follows:

$$RCOOH + OH^- \rightleftarrows RCOO^- + H_2O \tag{5}$$

so

$$[RCOO^-] = K[RCOOH][OH^-] \tag{6}$$

where K is an equilibrium constant and $[RCOO^-]$ and $[RCOOH]$ are the concentrations of ionic and potentially ionic groups in the gel. We also expect that the gel is subject to two otther restraints. The first represents a mass balance on all carboxylic groups in the gel:

$$[\bar{R}] = [RCOO^-] + [RCOOH] \tag{7}$$

where $[\bar{R}]$ is the total concentration of potentially ionic groups. The second, the statement of electroneutrality, implies no added small electrolyte:

$$[Na^+] = [RCOO^-] + [OH^-] \tag{8}$$

Combining Eqs. 6–8, we find

$$\zeta = \frac{[RCOO^-]}{[\bar{R}]} \tag{9}$$

$$= \frac{1}{2}\left[1 + \frac{[Na^+]}{[\bar{R}]} + \frac{1}{K[\bar{R}]}\right] \cdot \left\{1 - \sqrt{1 - \frac{4[Na^+]/[\bar{R}]}{\left(1 + \frac{[Na^+]}{[\bar{R}]} + \frac{1}{K[\bar{R}]}\right)^2}}\right\}$$

For small ζ, this becomes

$$\zeta = \frac{[Na^+]}{([\bar{R}] + K^{-1}) + [Na^+]} \tag{10}$$

We now comine this result with Eq. 4 to find that

$$\phi_2^{-2/3} = \frac{Z}{k}\left(\frac{[Na^+]}{[\bar{R}] + [Na^+] + K^{-1}}\right) \tag{11}$$

Since the volume of the swollen gel V is inversely proportional to the gel volume fraction ϕ_2, this predicts that

$$V^{-2/3} \propto \left(1 + \frac{([\bar{R}] + K^{-1})}{[Na^+]}\right) \tag{12}$$

i.e., the gel volume to the $(-\frac{2}{3})$ power should vary linearly with the reciprocal of the amount of added sodium. This prediction is tested experimentally in the discussion section below.

EXPERIMENTAL

Two gels were used in these experiments. The first gel, used in most experiments, was made by hydrolyzing cross-linked polyacrylamide beads produced commercially as packing for gel permeation chromatography (Bio-Rad Laboratories, Richmond, CA). The gel emphasized, sold as Bio-Gel P-6 has a particle size in water of $150–300·10^{-6}$ m. It was hydrolyzed for 24 hours at 323 K in 0.50 M $NaHCO_3$ (Jacobson and Branton, 1977). The second gel (CM-Sephadex C-50, Pharmacia Fine Chemicals, Piscataway, NJ), used in occasional experiments, is also made as a packing for gel permeation chromatography. The material, which has a dry particle size of $60–120·10^{-6}$ m, is already weakly ionic, and so was used as received.

Sugar, urea, and sodium chloride were reagent grade (Fisher) and were used as received. Polystyrene latex particles 910 nm in diameter were purchased commercially (Duke Scientific, Palo Alto, CA). Polystyrene latex particles 34.6 nm in diameter were a gift of Hamish Small (Dow Chemical Co., Midland, MI). Colloidal silica particles (Nalco Chemical, Chicago, IL) were 5 nm in diameter. Bovine serum albumin (Sigma Chemical, St. Louis, MO) was dialyzed and then recrystallized. Hemoglobin was a highly purified sample obtained from Rufus Lumry (University of Minnesota). The sample of polyethylene glycol used (J. T. Baker, Phillipsburg, NJ) is sold as having 68–84 monomer units and a molecular weight of 3,000–3,700 dalton.

The basic apparatus used in the measurements of gel volume is shown in Figure 2. It consists of a centrifuge tube with an internal basket; the result is a tube with two compartments. These compartments are separated by a hydrophobic filter (Whatman PS). To make an experiment, we placed about 0.005 kg of gel and 0.02 kg of basic solution in the upper compartment. We mixed the compartment on a wrist action shaker, and then centrifuged the tube for 300 s at 17 rpm. Originally, we waited at least six hours for equilibration, but we later discovered that a few minutes was sufficient. We removed and weighed both the gel and the raffinate. Gel volumes were calculated from measured density data. The gel was shrunk by washing with a small volume of 0.1 N HCl at room temperature; washing at higher temperatures tended to cause further hydrolysis. Raffinate concentrations were measured by evaporation to dryness, by spectrophotometry (Perkin-Elmer model 139) or by refractive index (Brice-Phoenix differential refractometer). More details of this technique are given elsewhere (Stokar, 1982).

To check this technique, we also made a smaller number of measurements of gel size by microscopy. We took a small sample of polyacrylamide gel and measured the diameters of over 300 particles, using a stereoscopic microscope (Wild, Heerbrugg, Swiz) fitted with a 35 mm camera (Canon). We then allowed these beads to swell in water, and measured the diameters again. Interestingly, the particle distribution was non-Gaussian, with larger numbers of larger particles. We used these data to find that the gel volume had increased (19.2 ± 0.9) times. When we repeated this measurement using centrifugation, we found a volume increase of (20.0 ± 0.3) times. This minor difference is probably caused by the retention of small amounts of raffinate in the filter cake. We conclude that the tedious microscopic measurements are equivalent to the straightforward centrifugation.

RESULTS AND DISCUSSION

This work includes three different kinds of measurements, all of which are required to show that gels can function as size-selective extraction solvents. The first shows that gel absorption is selective, for the gels absorb the low molecular weight solvent but not high molecular weight solutes. The second shows how the gels can be regenerated and reused; this regeneration exploits the large changes of gel volume with small variations in pH. The third kind of measurement shows that the gels are sufficiently strong to be used repeatedly. These three kinds of measurements are discussed sequentially in the following paragraphs.

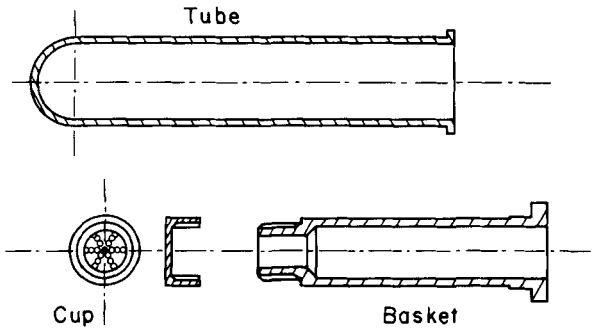

Figure 2. Centrifuge tube used in gel experiments. The cup and basket fit into the centrifuge tube to give a tube containing two compartments. The gel and a test solution are first mixed in the basket. Centrifugation forces the raffinate into the bottom of the tube but retains the swollen gel in the basket.

TABLE 1. CONCENTRATION OF DILUTE AQUEOUS SOLUTIONS USING HYDROLYZED POLYACRYLAMIDE GELS

Solute	Mol. wt. Dalton	Solute Size, nm	Feed Conc.[a]	Raffinate Conc.[a]	% Eff.[b]
Polystyrene Latex	—	990[c]	0.21	0.35	85
Polystyrene Latex	—	34.6[c]	0.91	1.40	82
			0.50[f]	1.23[f]	93[f]
Silica	—	5.0	1.82	3.03	80
Bovine Serum Albumin	66,000	7.2[d]	0.082	0.183	93
Hemoglobin	64,500	6.2[d]	0.73	1.26	91
Polyethylene Glycol	3000–3700	3.8[e]	0.56	1.09	91
Sucrose	342	0.84[d]	1.00	1.09	6
Urea	60	0.53[d]	3.00	3.00	0

[a] As weight percent.
[b] Defined as (measured increase in concentration) × (raffinate volume)/(initial solution volume).
[c] Measured by electron microscopy.
[d] Estimated from the diffusion coefficient in water using the Stokes-Einstein equation (Cussler, 1984).
[e] Reported by the manufacturer from light scattering.
[f] Obtained with a dextran gel (Sephadex C-50).

Gel Selectivity

That the gel can function as a size-selective extraction solvent is shown by the experiments reported in Table 1. The gel used in these experiments was the hydrolyzed polyacrylamide. The first three columns in the table identify the solutes to be concentrated. Columns 4–5 give the initial and final concentrations of the solution; they give the increases in concentration achieved with the small amount of gel used. Finally, the last column in Table 1 gives the efficiency of the extraction, expressed as the ratio of final to initial concentration compared with that expected from the altered raffinate volume. For example, if the solution volume was reduced by a factor of two, and the solute concentration was increased by a factor of 1.8, then the efficiency would be (1.8/2.0), or 90%.

The results in Table 1 show that solutes which are greater than 3 nm in diameter can be concentrated with an efficiency of at least 80%. These efficiencies are compromised by weak solute adsorption on the surface of the gel spheres. For example, for the 34.6 nm latex, some latex adhered weakly to the gel. When this latex was removed by washing, the extraction efficiency increased to 97%. In this sense, the gel extractions are similar to freeze-concentration techniques used in the food industry, where solutes can adhere to ice crystals.

The cut-off of 3 nm found in these extractions can presumably be decreased by increasing the density of cross links in the gel. While we have not studied this systematically, we have seen some evidence of this selectivity in experiments with concentrated orange juice by a factor of 2.5. We then diluted the concentrated raffinate 2.5 times. Total solids in the rediluted sample were within 1% of those in the original sample (as determined by the Majonnier method, Majonnier, 1978). The concentrations of volatile flavors in the reconstituted juice were 35% less than in the original samples when measured by gas chromatography.

There is one major limitation of the results in Table 1: the solutes involved are all neutral or negatively charged. When we tried to

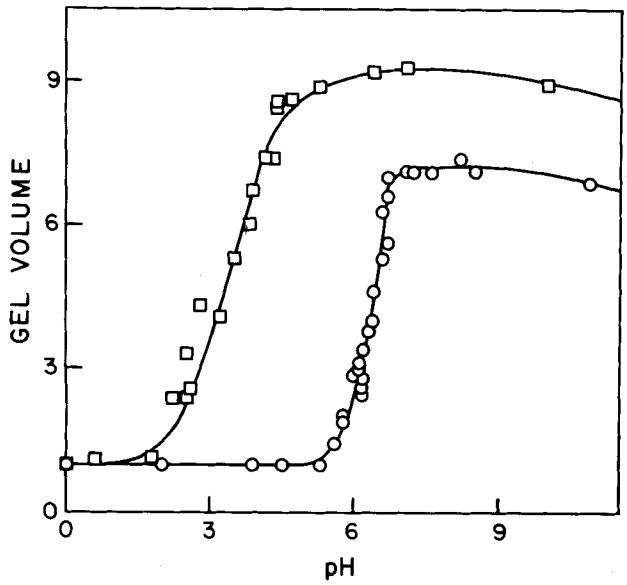

Figure 3. Relative gel volume vs. pH. The gel volume shown is that relative to the volume at pH = 1. The circles are for the hydrolyzed polyacrylamide gel while the squares are for the dextran gel. The results shown were found by centrifugation, but essentially identical results can be found by microscopy (Stokar, 1982).

concentrate cationic proteins like lysozyme and cytochrome C, we found that these solutes precipitated on the gel. This electrostatic interaction may compromise separations. Interestingly, the gel's swelling seems to be largely unaffected by these reactions.

Gel Regeneration

To be used for separations, gels must absorb selectively and be regenerated. In the above, we showed that the absorption is size-selective; we now want to show that the gels used are easily regenerated.

The regeneration depends on large changes of gel volume with small changes in process conditions like temperature and pH (cf. Figure 1). The variation of gel volume with pH for the two gels used in this work is shown in Figure 3. At low pH, the gel volume is constant; over some intermediate pH range, it increases sharply; and at high pH, it goes through a soft maximum. The sudden increase in volume occurs at pH 5–6 for the hydrolyzed polyacrylamide gel and at pH 2–3 for the dextran gel. These pH ranges are those measured outside of the gel, and may be somewhat different than the pH inside the gel because of Donnan equilibrium (Tanford, 1960).

For a separation to be effective, the sudden increase in gel volume must occur at a lower pH than that of the solution being separated. However, we should emphasize that these separations need not involve changing the pH of the solution. As shown in Figure 1, the gel can be added to the solution and removed from it at the solution's pH. It is only the gel regeneration which involves adding acid or base, and not the separation itself.

The changes of gel volume shown in Figure 3 may result in a variety of thermodynamic nonidealities (Rogovina and Slovimskii, 1974). We believe that gel ionization is the most important factor involved. On this basis, we developed the theory given above, which predicts that the $(-\frac{2}{3})$ power of the gel volume should vary linearly with the reciprocal of the total amount of sodium hydroxide added to the gel (cf. Eq. 12). This prediction is verified by the results in Figure 4. At the same time, we expect that more accurate experiments will report cases where other factors are significant. We expect that counterion bonding will be especially important because it is central to the chemistry of ionic micelles. We also expect that Donnan equilibrium will be important. Both these phenomena are probably involved in the soft maximum in gel volume at high pH (cf. Figure 3).

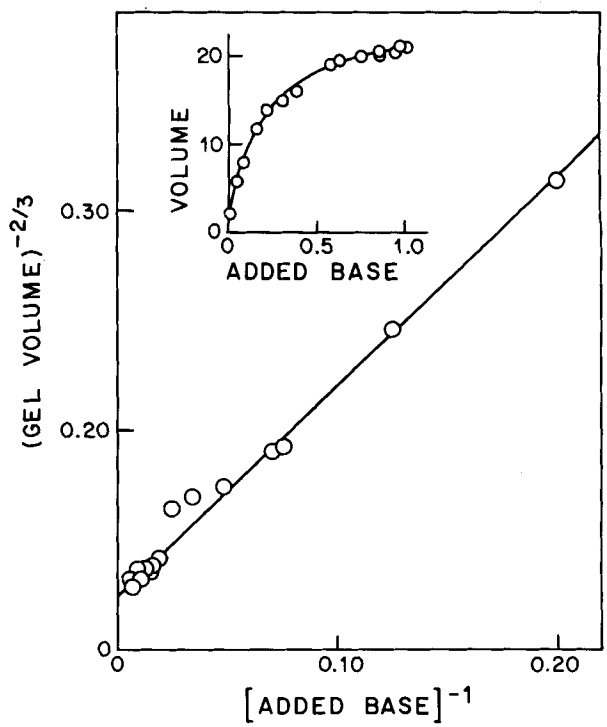

Figure 4. Relative gel volume vs. added base. The gel volume, defined as in Figure 3, may also be measured as a function of added base in moles as shown in the inset. If gel ionization is the chief factor controlling gel volume, the volume is predicted to vary with added sodium hydroxide as shown by the solid line (cf. Eq. 12). The units of the added hydroxide are arbitrary.

Gel Reuse

To test the repeated use of these gels, we prepared a dilute suspension of the 34.6 nm polystyrene latex described above. We removed a fraction of the water in this latex using a small amount of the dextran gel, and we then measured the raffinate concentration. We then added acid to shrink the dextran gel, filtered the resulting suspension, added a drop of base to the filter cake, and again treated the raffinate with the same gel. From a mass balance, we expect that the final raffinate concentration c after n treatment cycles should be

$$c = \frac{m}{v_o - nv} \tag{13}$$

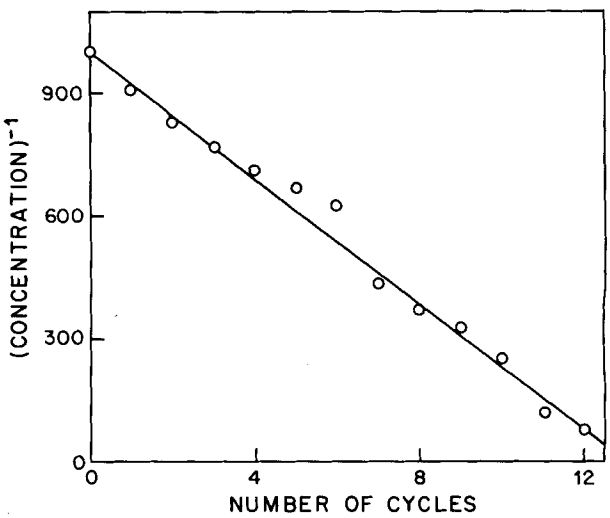

Figure 5. Latex concentration over several gel extractions. The latex concentration is given in weight percent. These results show that a small amount of gel can be used repeatedly over many extraction cycles.

where m is the initial mass of latex, v_o is the initial volume of solution, and v is the volume removed by one treatment cycle of gel absorption. Thus the reciprocal of concentration c should vary linearly with the number of cycles n.

The results given in Figure 5 show that this is true. These results have two important corollaries. First, there is little cumulative loss due to latex adsorption on the gel. This adsorption, which is responsible for the inefficiencies reported in Table 1, is apparently most significant for the first cycle and is much less important as the gel is reused.

The second corollary of the results in Figure 5 is that the gel is removing the same amount of water on the tenth cycle as on the first cycle. This implies that the gel is remaining intact over all cycles, and hence can be routinely reused. To be sure, reuse in practice must involve hundreds of cycles, and we have not made such extensive long term tests. Nonetheless the results in Figure 5 and the other experiments reported in this paper all illustrate the promise of gels as size-selective extraction solvents.

ACKNOWLEDGMENTS

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NOTATION

c	= raffinate concentration (Eq. 13)
k	= gel elasticity (Eq. 2)
K	= equilibrium constant (Eq. 6)
m	= latex mass (Eq. 13)
n	= number extraction cycles (Eq. 13)
$[Na^+]$	= sodium ion concentration (Eq. 8)
$[OH^-]$	= hydroxyl ion concentration (Eq. 6)
R	= gas constant (Eq. 2)
$[\bar{R}]$	= total concentration of carboxyl groups in gel (Eq. 7)
$[RCOO^-]$, $[RCOOH]$	= concentrations of ionized and unionized carboxyl groups, respectively (Eq. 6)
T	= temperature (Eq. 2)
v	= solution volume (Eq. 13)
v_o	= initial solution volume (Eq. 13)
V	= gel volume (Eq. 12)
Z	= maximum charge on gel (Eq. 3)
ζ	= degree of gel ionization (Eq. 3)
μ_i	= chemical potential of species i (Eq. 1)
μ_i^o	= chemical potential of species i in the standard state (Eq. 1)
ϕ_i	= volume fraction of species i (Eq. 2)
χ	= interaction parameter (Eq. 2)

LITERATURE CITED

Anderson, N. G., et al., "Analytical Techniques for Cell Fractures. XXV: Concentration and Two-Dimensional Electrophoretic Analysis of Human Urinary Proteins," *Anal. Biochem.*, **95**, p. 48 (1979).

Cussler, E. L., *Diffusion*, Cambridge University Press, London, Section 5.2 (1984).

Dušek, K., and D. Patterson, "Transition in Swollen Polymer Networks Induced by Intramolecular Condensation," *J. Polym. Sci.*, **A2, 6**, p. 1209 (1968).

Dušek, K., "Inhomogeneities Induced by Crosslinking in the Course of Crosslinking Copolymerization," *Polymer Networks: Structural and Mechanical Properties*, A. J. Chompff, Ed., Plenum Press, New York, p. 245 (1971).

Fanta, G. F., R. C. Burr, W. M. Doane, and C. R. Russell, "Absorbent Polymers from Starch and Flour Through Graft Polymerization of Acrylonitrile and and Comonomer Mixtures," *Starch/Starke*, **30**, p. 237 (1978).

Flodin, P., B. Gelotte, and J. Porath, "A Method for Concentrating Solutes of High Molecular Weight," *Nature*, **188**, p. 493 (1960).

Flory, P. J., *Principles of Polymer Physics*, Cornell Univ., Ithaca (1979).

de Gennes, P. G., *Scaling Concepts in Polymer Physics*, Cornell Univ. (1979).

Hasa, J., M. Ilavský, "Deformational, Swelling, and Potentiometric Behavior of Ionized Poly (Methacrylic Acid) Gels. II: Experimental Results," *J. Poly. Sci.*, **13**, p. 263 (1975).

Hasa, J., and M. Ilavský, and K. Dŭsek, "Deformational, Swelling, and Potentiometric Behavior of Ionized Poly(Methacrylic Acid) Gels. I: Theory," *J. Poly. Sci.*, **13**, p. 253 (1975).

Hochberg, A., T. Tanaka, and D. Nicoli, "Spinodal Line and Critical Point of an Acrylamide Gel," *Phys. Rev. Letters*, **43**, p. 217 (1979).

Ilavský, M., "Effect of Electrostatic Interactions on Phase Transition in the Swollen Polymeric Network," *Polymer*, **22**, p. 1687 (1981).

Ilavský, M., J. Hrouz, and K. Dušek, "Inhomogeneities and Deviations from the Gaussian Photoelastic Behavior of Networks," *J. Macromol. Sci.*, **B19**, p. 227 (1981).

Ilavský, M., J. Hrouz, and K. Ulbrich, "Phase Transition in Swollen Gels. III: The Temperature Collapse and Mechanical Behaviour of Poly(N,N-diethylacrylamide) Networks in Water," *Polymer Bull.*, **7**, p. 107 (1982).

Jacobson, B. S., and D. Branton, "Plasma Membrane: Rapid Isolation and Exposure of the Cytoplasmic Surface by Use of Positively Charged Beads," *Sci.*, **195**, p. 302 (1977).

King, C. J., *Separation Processes*, 2nd Ed., McGraw-Hill, New York (1979)

Kremmer, T., and L. Boros, *Gel Chromatography*, Wiley-Interscience, New York (1979).

Lonsdale, H. K., "The Growth of Membrane Technology," *J. Membrane Sci.*, **10**, p. 81 (1982).

Mojonnier Bros. Co., "Directions for Making Total Solids Test Using the Mojonnier Tester" (1978).

Rogovina, L. Z., and G. L. Slonimskii, "Formation, Structure, and Properties of Polymer Gels," *Russian Chem. Revs.*, **43** (6), p. 503 (1974) [translated from *Uspekhi Khimii*, **43**, p. 1102 (1974)].

Stokar, M. R., "Gels as a Size-Selective Extraction Solvent," M.S. Thesis, University of Minnesota (1982).

Tanaka, T., et al., "Phase Transitions in Ionic Gels," *Phys. Rev. Letters*, **45**, p. 1636 (1980).

Tanaka, T., "Gels," *Scient. Amer.*, **224**, p. 124 (1981).

Tanaka, T., I. Nishio, S. T. Sun, and S. Ueno-Nishio, "Collapse of Gels in an Electric Field," *Sci.*, **218**, p. 467 (1982).

Tanford, C., *The Physical Chemistry of Macromolecules*, Wiley, New York (1960).

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