small pieces and was then continuously extraced with ether for 15 h. The polymer was dried under reduced pressure. Run 5, Anal. Calcd for $(C_6H_8O_2)_n$: C, 64.27; H, 7.20. Found: C, 63.99; H, 7.33 (no residue).

Group-Transfer Polymerization. To a solution of 48 mg (0.27 mmol) of 1-methoxy-1-(trimethylsiloxy)-2-methyl-1-propene and 2.7 μL (2.7×10^{-3} mmol) of a 1 M acetonitrile solution of tris(dimethylamino)sulfonium bifluoride in 8.7 mL of THF under argon at −78 °C in a reaction flask (flamed under argon) was quickly introduced 2.0 g (18 mmol) of lactone. Within a few minutes, the reaction mixture became a gel. After 24 h, the gel was allowed to warm to ambient temperature. Methanol was added and the gel was broken into small pieces by stirring. The polymer was continuously extracted with ether for 15 h and then dried under reduced pressure. Run 7, Anal. Calcd for $(C_6H_8O_2)_n$: C, 64.27; H, 7.20. Found: C, 64.04; H, 7.29 (no residue).

NMR. ^{1}H NMR spectra were taken on Me_2SO polymer solutions at 160 °C with a JEOL FX-100 spectrometer at 100 MHz. ^{13}C spectra were obtained on Me_2SO solutions containing 7.5 wt % polymer (runs 1–4 and 6) or 5 wt % polymer (runs 5 and 7) at 100 °C using an IBM WP-200 (50.288 MHz) with a broad-band variable-temperature 10-mm probe. Generally, 20000–40000 scans were accumulated, depending on the sample concentration and the region of the spectrum observed.

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Swelling of Ionic Gels: Quantitative Performance of the Donnan Theory

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ABSTRACT: This study investigates the quantitative consistency of the Donnan theory of swelling of weakly charged ionic gels. Instead of the usual a priori assumptions about the volume dependence of the swelling pressure of the neutral network, this function is obtained as one of the results of the study. The theory is applied to predict quantitatively the swelling of a polyacrylamide–acrylic acid copolymer gel as a function of ionic composition of the solvent. No free parameters are used. As long as no multivalent ions are involved, the changes in swelling and swelling extrema occur exactly at predicted ion concentrations in the solutions. The extent of swelling is also satisfactorily predicted. In solutions containing divalent cations, significant quantitative discrepancies between the theory and the experiment are observed, but qualitative features are adequately described.

1. Introduction

The interest in ionic gels has been revived since the observation of the phenomenon of phase transition in such systems by one of the authors.[1] A partially hydrolyzed acrylamide gel can change its volume discontinuously when the solvent composition is continuously varied. Charged groups attached to the network play an essential role in this phenomenon.[2-4] The transition can be induced by changing the pH of the solvent, by changing salt concentrations, or by applying an electric field.[2,5,6] A complete description of such phenomena depends on an understanding of the role of charges in the system.

Theories on swelling of ionic gels are reviewed in ref 7. Most of the theories tend to be quite complex, attemping to combine the description of the contractile force of the network (network swelling pressure) and the electrostatic interactions (ion swelling pressure) in one model. Such theories contain many free parameters and their experimental verification is therefore difficult.

The simplest of the theories attributes the ion swelling pressure to the difference between the osmotic pressure of freely mobile ions in the gel and in the outer solution.[8-10] The distribution of the ions between the gel and the outer solution is obtained from Donnan equilibrium. Within this theory the ionic forces depend only on the ionic composition of the solvent and on the concentration of fixed ionizable groups in the gel but not on the properties of the neutral network.

We will take advantage of this simplification and proceed according to the following concept. First we use the ion pressure to swell gels in a desired extent. We do perform the experiments using acrylamide–acrylic acid copolymer gels in one solvent having a simple ionic composition. We adjust the ion swelling pressure by varying the amount of fixed charges in the gel. This pressure, which can be calculated under the assumption of the validity of the Donnan theory, is equal to the negative of the swelling pressure of the neutral network at the given equilibrium volume.

We next use the data on the network thus obtained to predict quantitatively the swelling of a gel in solutions with varying ionic composition. When the prediction turns out

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to be quantitatively correct in a wide range of ion concentrations, we will regard it as an evidence for the consistency of the theory.

To illustrate the relevance of the study to the phenomenon of the phase transition, we will also present an example of discontinuous swelling induced by changes in ion concentration.

2. Theoretical Considerations

Consider a flexible polymer network immersed in a solvent, i.e., a gel. The network concentration is low. In our case the volume fraction of the network at synthesis is 5%. The degree of cross-linking is also low and the network can swell as much as 100 times. Typically, 5% of the monomers are modified to carry an ionizable group, which in our case is acrylic acid. The network is immersed in a large reservoir of heat (temperature T), solvent (chemical potential μ_s') and ions or neutral molecules at low concentration (chemical potentials μ_i' and μ_n', respectively). For simplicity we assume only one type of ion can bind chemically to the network-fixed carboxylate, in our case hydrogen. Such a system will be in equilibrium when the chemical potentials of mobile components within the gel are equal to those in the reservoir (osmotic equilibrium), and simultaneously, the chemical potential of free hydrogen ions in the gel equals that of carboxylate-bound hydrogen (chemical equilibrium).

To obtain the equilibrium conditions, we need to know the Gibbs free energy of the gel. It is assumed to be a sum of several terms

$$G = G_{\mathrm{net}} + G_{\mathrm{sol}} + G_{\mathrm{dis}} + G_{\mathrm{coul}} \tag{1}$$

Here G_{net} is the free energy contribution of the neutral network. This term contains the entropy of network conformation and the enthalpy and entropy changes due to interactions between the network and the solvent. An approximate expression for G_{net} has been derived,[10] but in our treatment we do not need to be concerned with the explicit form of this term. We neglect the interactions between the network and the solute. This approximation is justified because the concentrations of both solute and network are low.

The second term G_{sol} represents the familiar free energy of a dilute solution of ions or neutral molecules within the gel.

The term G_{dis} is introduced to account for the dissociation of the acid groups. They are assumed to be far apart in the chain, and interactions between them are neglected. G_{dis} is similar to G_{sol}, but instead of the dilution entropy, we include the entropy of distributing the number of dissociated and undissociated acid groups on the available sites in the network.

Finally G_{coul} represents the free energy contribution associated with Coulombic interactions within the system. One important contribution to G_{coul} can be deduced from the resemblance between a gel and a semipermeable membrane. The gel is assumed to be electrically neutral, but some of the mobile cations can diffuse into the outer solution. The cations are, however, attracted by the network-fixed negative groups. The result is a formation of a charged bilayer which in turn creates a Donnan potential U. Since we are dealing with macroscopic gels, we neglect the contribution from ions in the surface bilayer. The potential is constant throughout the gel and does not affect the mobility of the internal ions. Their electrostatic energy in U is the only Donnan contribution to G_{coul}, and we have

$$G_{\mathrm{coul}} = \sum_{\mathrm{i}} n_{\mathrm{i}} z_{\mathrm{i}} e U + n_{\mathrm{a}} z_{\mathrm{a}} e U \tag{2}$$

Here n is the number and z the valency of ions in the gel (subscript i refers to free ions of type i and a to the dissociated acrylic acid), and e is the elementary charge.

In G_{coul} we have neglected a term which would take into account interactions between the ions within the gel (both mobile and fixed). This term appears to be controversial. Theories dealing with this problem[11-13] suggest a contribution from the repulsion of the fixed charges which would enhance the gel expansion (the polyelectrolyte term). This is realistic in strongly charged polyelectrolyte gels where the charged groups are forced to remain in proximity by the chain constraints.

On the other hand, in two well-investigated ionic systems, the ordered ionic crystal and the disordered ionic solution, such ion interactions result in an attractive contribution to free energy rather than a repulsive one. We can expect a weakly ionic, neutral, and flexible gel to represent an intermediate case between the extremes of a crystal and a solution. A rigorous theoretical description is yet to be developed.

We will briefly investigate the limit of extremely flexible gels where the network-attached groups can be considered to be almost freely mobile. In such a system the resemblance to an ionic solution surrounded by a membrane should be close enough to include the well-known Debye–Hückel contribution[14,15] to the free energy of the gel and the outer solution. It will be shown (section 4.5) in the present case the quantitative improvement in the theory is negligible. Therefore, we neglect the Debye–Hückel contribution in further considerations for the sake of simplicity.

With the assumptions discussed above and with the familiar expressions for the chemical potentials in the outer solution, the equilibrium conditions can be expressed as follows:

$$\frac{c_{\mathrm{n}}}{c_{\mathrm{n}}'} = 1 \tag{3}$$

$$\frac{c_{\mathrm{i}}}{c_{\mathrm{i}}'} = \exp\left(-\frac{z_{\mathrm{i}} e U}{k_{\mathrm{B}} T}\right) = K^{z_{\mathrm{i}}} \tag{4}$$

$$-\Pi_{\mathrm{net}} = \Pi_{\mathrm{ion}} = RT \sum_{\mathrm{i}} (c_{\mathrm{i}} - c_{\mathrm{i}}') \tag{5}$$

$$\frac{c_{\mathrm{a}} c_{\mathrm{h}}}{c_{\mathrm{ah}}} = K_{\mathrm{a}} \tag{6}$$

Equation 3 is trivial, stating simply the concentration of the neutral solute of type n is the same in the gel (c) and in the outer solution (c'). In eq 4, which describes the distribution of mobile ions of type i between the gel and the solution, we have introduced the Donnan ratio K. K is always larger than 1 when the network-fixed charges are negative. In eq 5, Π_{net} represents the swelling pressure of the network defined as

$$\Pi_{\mathrm{net}} = -\frac{1}{v_{\mathrm{s}}} \left.\frac{\partial G_{\mathrm{net}}}{\partial n_{\mathrm{s}}}\right|_{p,T,n_{\mathrm{i}},n_{\mathrm{n}}} \tag{7}$$

where n_{s} is the number and v_{s} is the volume of the solvent molecules. In equilibrium, Π_{net} is balanced by the swelling pressure of the ions Π_{ion}. The latter is, of course, the difference between the osmotic pressures due to the ionic solute in the gel and in the solution (R is the gas constant).

Equation 6 describes the dissociation equilibrium of the fixed acid groups under the assumptions only hydrogen ions (molar concentration c_{h}) can associate with the carboxylate (molar concentration c_{a}) and the acrylic acid content in gel is low. The dissociation constant K_{a} may differ from that of the monomeric acid but should be close to it, providing the attachment to the polymer chain does not distrub the electronic structure of carboxylate substantially.

Inserting (4) and (6) into the charge balance equation in the gel, we obtain an equation for the Donnan ratio K

$$\sum_{i} z_i K^{z_i} c_i' + z_a \frac{c_0(V)}{1 + K c_h'/K_a} = 0 \qquad (8)$$

Here $c_0(V)$ is the total concentration of acid $c_a + c_{ah}$. It varies with the volume of the gel V. Equation 5 can be expressed in terms of the Donnan ratio as

$$-\Pi_{net}(V) = \Pi_{ion} = RT\sum_{i} c_i'(K^{z_i} - 1) \qquad (9)$$

Equations like (8) and (9) can be solved algebraically only in special cases or only approximately. A numerical solution is, however, straightforward and that is all we need for comparison with experiments. When the Debye–Hückel contribution is included, eq 4–9 will be modified.[14,15] The numerical solution becomes somewhat more tedious but is still feasible.

3. Sample Preparation and Experiments

Gels were prepared by radical copolymerization of acrylamide, *N,N'*-methylenebis(acrylamide) (both Bio-Rad, electrophoresis purity), and acrylic acid (reagent grade). Total monomer concentration in reaction solution (water) was 700 mM, the concentration of bis(acrylamide) was 8.6 mM, and the concentration of acrylic acid was varied between 0 and 146 mM. Water used in preparation and in swelling experiments was Millipore purified (resistivity 18 MΩ cm). Acrylic acid was distilled to remove polymerization inhibitor.

The gelation reaction, initialized by ammonium persulfate, took place in micropipets of 1.33-mm inner diameter. Instead of using the usual accelerator TEMED, the gelation was performed at elevated temperature (70 °C). Gelation occurred within 3 min. Gels were then kept at 70 °C for 1 h and subsequently at room temperature for 1 day to ensure completion of the reaction.

After removal from the micropipets, the gels were dialyzed against a large amount of pure water (no membrane is necessary) to remove impurities and possible mono- or oligomers not incorporated into the network. Water was changed every 48 h, and the gels were monitored for changes in swelling. The gels were considered to be purified when the swelling ceased to change (after approximately 1 week).

The swelling behavior was investigated in solutions of various neutral salts and simple bases and acids. All chemicals were of reagent grade quality and used without further purification.

Because of the gels' ion-exchange properties, precautions must be taken to ensure the gels are indeed in equilibrium with the known, originally prepared, salt concentration. It is important to realize that 40 L of 10^{-8} M salt solution would be necessary to supply the cations needed to exchange H^+ ions contained in 10 μL of gel having an acrylic acid concentration of 40 mM. Even if the salt concentration is sufficiently high, a decrease of pH in the outer solution, which is associated with the ion exchange, must be taken into account. To avoid the use of such impractically large containers, the swelling experiments were performed in several steps. The gels were repeatedly immersed for 2 days in fresh solutions (200 mL per 10 μL of gel) with the given salt concentration until the gel diameter ceased to change. The ion-exchange effects are particularly important for divalent cations. Data for such solutions in concentrations below 10^{-7} M are likely to be of limited quantitative reliability.

The experiments were carried out in Pyrex Erlenmeyer flasks, filled with nitrogen and sealed to avoid dissolution of CO_2. Changes in pH which nevertheless did occur in the neutral salt solutions after completion of the ion exchange (a decrease of 0.5 unit over 4 days) were taken into account in the analysis of experiments.

The diameter of the gels was measured by using a microscope with a calibrated eyepiece. From the diameter, the swelling ratio X, i.e., the ratio of equilibrium volume V to the volume after the preparation V_0, was calculated.

Table I
Swelling of a Gel in Aqueous Solutions Containing Different Electrolytes[a]

electrolyte	concn, 10^{-2}/mM	swelling ratio[b]
$MgCl_2$	3	16–18
$CaCl_2$	3	15–17
$BaCl_2$	3	15–17
$BaSO_4$	3	17–19
NaCl	8	34–36
LiCl	8	33–35
KCl	8	35–37
NaBr	8	33–35
KBr	8	34–36
NaF	8	35–37
base	pH	swelling ratio[b]
NaOH	8.7	51–53
triethanolamine	8.7	51–53

[a] Initial acrylic acid concentration is 36.5 mM. [b] $X = V/V_0$.

4. Testing the Theory

4.1. Consistency of Some Basic Assumptions. A premise of the present theory is that the swelling of a charged gel should depend only on the valency and concentration of the ions in the solution but not on their size and chemical properties. (Exceptions include H^+ and other species which can associate with the carboxylate group of acrylic acid.) To test this assumption, we have investigated the swelling in neutral solutions of various salts. As seen in Table I, this simple but important assumption is well fulfilled for salts of alkali metals and alkaline-earth metals. This finding indicates we do not have to deal with phenomena such as ion binding, which would depend on the size of the ions.[15,16]

Note also in Table I, the gel swells to the same extent at pH 8.7 in both the NaOH solution as well as in the solution of the weaker base, triethanolamine (TEA). Apparently, the cation H^+(TEA) does not associate with carboxylate, and the neutral TEA molecule does not influence the swelling. Therefore, TEA, being a weak base, is convenient to use to adjust the pH in the range above 7.

To justify the assumption of no interaction between the neutral network and the ionic solute, we have investigated the swelling of a charge-free acrylamide gel. In water, the volume swelling is approximately 1.7 and shows a negligible dependence on the ion concentration in the solution, in particular its pH. (In strongly basic or acidic solutions, however, hydrolysis will occur.[4])

4.2. Measuring the Network Swelling Pressure. Consider a series of gels having varying amounts of acrylic acid (initial concentration c_0^i) but otherwise identical network parameters. We assume that in all the gels the network contribution Π_{net} to the swelling pressure is the same function of swelling ratio X. In other words, the properties of the neutral network remain unchanged as long as the ratio of acrylic acid monomer to acrylamide is low.

The gels are swollen to equilibrium in a solution of TEA at pH 8.7. From the equilibrium volumes, we can calculate the equilibrium acid concentrations $c_0 = c_0^i V_0/V$ within each gel. The ion concentration in the outer solution is known, and we chose for K_a the value for the monomeric acid (5.6×10^{-5}). Having all parameters, we can apply the theory discussed in section 2 (eq 8 and 9) to calculate the ion swelling pressure Π_{ion} for each gel. In Figure 1 Π_{ion} is

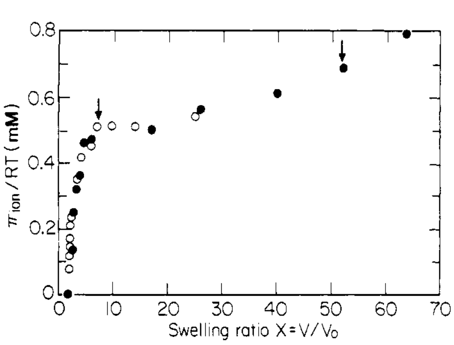

Figure 1. Ion swelling pressure calculated from the measured swelling ratio $X = V/V_0$ of gels with varying initial concentration of acrylic acid. The dissociation constant of the acid monomer $K_a = 5.6 \times 10^{-6}$ was used in the calculations. Open circles: water pH ≈6.5. Solid circles: solution pH 8.7. The points marked with arrows (initial acrylic acid concentration 36.5 mM) correspond to the gel used in subsequent swelling experiments. Assuming the neutral network of all gels is not altered by small amounts of acidic groups, the resulting curve is a graphical representation of the function $-\Pi_{net}(X)$.

plotted as a function of the equilibrium swelling ratios $X = V/V_0$ of the gels (solid circles). Under the assumption discussed above and since

$$\Pi_{ion} + \Pi_{net} = 0 \qquad (10)$$

the resulting curve can be regarded as a graph of the function $-\Pi_{net}(X)$. We have obtained a representation of the equation of state of the nonionized network.

We have chosen the value of the dissociation constant K_a somewhat deliberately. We will verify it in the next section. At any rate, numerical calculations show any value of K_a larger than 5×10^{-6} would change the results in Figure 1 unperceivably. At the given pH of the outer solution, the swelling is insensitive to K_a because 95% of the network acid groups would be dissociated even if K_a is as low as 5×10^{-6}.

4.3. Dissociation Equilibrium. The determination of the dissociation constant of acidic groups bound to the network is not easy because of the problems associated with the measurement of the hydrogen ion concentration within the gel. A pH meter measures essentially the chemical potential of H^+, which in equilibrium is the same as in the outer solution. Indicator dyes, on the other hand, are themselves ionic and will thus disturb the equilibrium unless used in extremely low concentrations.

When using potentiometric titration,[11,13] one must take into account changes of the volume of the gel during the titration process. It would be necessary to assume the validity of a theory of the swelling pressure of the network (free parameters) and this contradicts our present concept. To obtain the dissociation constant from titration without such an assumption, one would have to measure the absolute volumes of the gel and also the outer solution and the outer solution concentrations of both H^+ and the base cation. This would be a rather impractical procedure, considering the long equilibration times needed in every step of titration.

We chose therefore a somewhat indirect but simple method to estimate the dissociation constant. We use again the assumption that the neutral network contribution to the swelling pressure does not depend on the amount of acrylic acid as long as it remains low. In other words, when two gels swell to the same extent (in two different solutions) their Π_{net} is assumed to be the same, independent of their acrylic acid content.

Therefore, when the experiments as described in the preceding section are performed in pure water, and the data are analyzed and plotted in the same way, the resulting curve should be congruent with the previous one. In contrast to the case of pH 8.7, in water the calculated Π_{ion} is very sensitive to K_a. Only when the correct value is used, we obtain the expected congruence. As can be seen in Figure 1 (open circles), the assumed $K_a = 5.6 \times 10^{-5}$ matches the data very well.

4.4. pH Dependence of Swelling. The following qualitative considerations will be useful in understanding the experimental results. Consider a gel being prevented by some means from adjusting its volume upon changes in ion swelling pressure. The concentration of acrylic acid is then constant. In water at pH 7 the only mobile ions in the system are H^+ and OH^-. In this case eq 8 is simply a charge balance equation for a solution of a weak acid at concentration c_0 and dissociation constant K_a. Hydrogen ion concentration in the gel can be easily calculated. It is much larger than the outer concentration 10^{-4} mM (Donnan ratio K is large) and thus determines the ion swelling pressure. When the pH is decreased, we should take into account the acid anion A^-. Since, however, K is large, A^- is excluded from the gel. The charge balance equation remains approximately unchanged and thus also the H^+ concentration within the gel (c_h). As long as c_h' (H^+ concentration outside) remains low compared to c_h, the ion swelling pressure remains approximately constant.

When c_h' approaches c_h, the ion swelling pressure will drop, as it is the difference of the two concentrations. The drop will be ehnanced by the association of surplus H^+ ions, now entering the gel together with the counterions to the acid, with the carboxylate groups. Concentration of fixed charges in the gel will decrease and we end up with an uncharged gel.

The opposite behavior occurs in basic solutions in the pH range 7–8. As the pH increases, the concentration of base cations in the outer solution will also increase. Those cations will be attracted into the gel and will replace the mobile H^+ ions. The gel of course acts as an ion exchanger. New H^+ ions will be supplied by the yet undissociated acrylic acid. The concentration of mobile ions in the gel will thus increase more rapidly than in the outer solution, and the ion swelling pressure will increase.

The supply of H^+ ions is, however, limited. Eventually, all the acrylic acid will be dissociated. Any further increase of pH will decrease the Donnan ratio K. (In this limit the term on the right side of eq 8 will be approximately constant and the equation can be easily solved.) The Donnan ratio K approaches 1 rapidly. There will always remain an excess of cations and a deficit of anions in the gel but those two contributions to Π_{ion} will cancel. With increasing pH, the ion swelling pressure will begin the drop again.

We can now anticipate the tendencies in the swelling behavior of the gel. At very low pH it will deswell to the volume of an uncharged gel. In the pH range 5.5–7 it will maintain approximately a constant volume. In basic solutions it will first swell as the pH is increased and then deswell again at still higher pH.

To quantitatively predict the dependence of swelling ratio on pH of the solution, we use the results obtained in sections 4.2 and 4.3. We apply standard numerical procedures to obtain a (physically meaningless) analytical representation (e.g., linear combination of polynomials) of the data in Figure 1 and thus of the function $\Pi_{net}(X)$. We then insert this function into eq 9 and solve the system of equations [(8) and (9)] numerically for X and K at a given value of pH. (Ion concentrations in the outer solution and K_a are known.)

In Figure 2 the theoretical prediction is confronted with the experimental data.[17] The agreement is very good. All

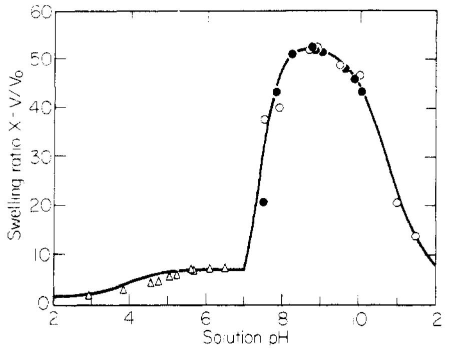

Figure 2. Swelling in solutions of varying pH. Initial acrylic acid concentration of the gel is 36.5 mM. Solid curve: Theoretical swelling[17] calculated by using $\Pi_{\text{net}}(X)$ obtained from Figure 1. Triangles: observed swelling in solutions of acetic acid. Open circles: swelling in solutions of NaOH. Solid circles: swelling in solutions of triethanolamine.

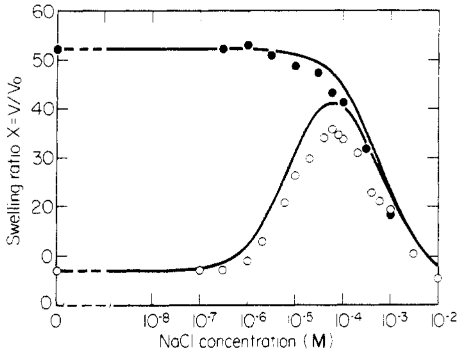

Figure 3. Dependence of swelling on concentration of NaCl. Open circles: observed swelling in neutral solutions at pH ≈6.5. Solid circles: swelling in basic solutions pH 8.7. Solid lines: predicted swelling.

the features discussed above are observed, and the volume changes occur at predicted pH values. The results are thus consistent with the Donnan equilibrium theory.

4.5. Swelling in Salt Solutions. The same considerations as in the preceding section can be applied to understand the swelling behavior in solutions with varying salt concentrations. Consider first a gel with fixed acrylic acid concentration in a solution of an uni-univalent salt, such as NaCl, at pH 7. As we increase the salt concentration from zero, H^+ ions in the gel will be exchanged for the salt cation. The ion swelling pressure will increase due to the increasing production of free counterions by dissociation of acrylic acid. When the acrylic acid is completely dissociated, any further increase of salt concentration will reduce the ion swelling pressure as in a gel at high pH. (It does not matter if the involved anion is OH^- or Cl^-.) We can expect a maximum in swelling at some intermediate salt concentration.

The same swelling behavior should occur in solutions of an uni-bivalent salt such as $MgCl_2$. Here, however, only half as much of the divalent cation Mg^{2+} will be needed to maintain the charge balance in a gel with completely dissociated acid groups. The maximum swelling will occur at lower salt concentrations, and the gel will swell to a lesser extent.

When the pH of the salt solutions is increased to 8.7, all the acrylic acid in the gel is completely dissociated, even at very low salt concentrations. The maximum in the swelling curve will disappear, the swelling pressure simply decreases with increasing salt concentration. Because, again, less divalent than monovalent cations are needed to maintain the charge balance, the drop will occur at lower salt concentrations in the divalent case.

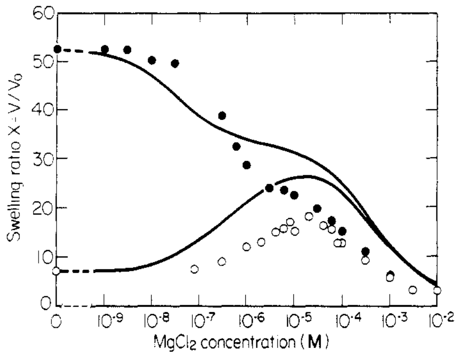

Figure 4. Swelling in solutions of $MgCl_2$. Open circles: observed swelling in neutral solutions at pH ≈6.5. Solid circles: swelling in basic solutions pH 8.7. Solid lines: predicted swelling.

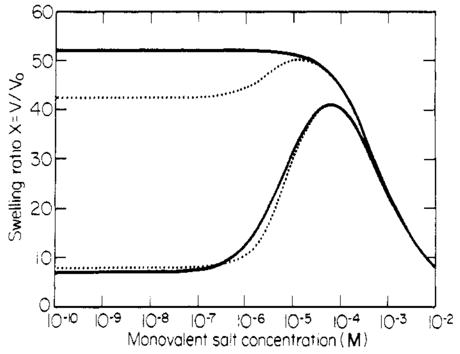

Figure 5. Influence of a trivalent cation impurity on the swelling in solutions of a uni-univalent salt. Solid lines: theoretical curves from Figure 3. Dots: theoretical swelling in presence of 10^{-7} mM of a uni-trivalent salt.

As in the preceding section, we can calculate the theoretical curves for the swelling ratio X as a function of salt concentration. The results, together with the corresponding experimental data are shown in Figures 3 and 4. In the case of the monovalent salt (Figure 3), the agreement between theory and experiment is very good. Volume changes and swelling maximum occur at predicted salt concentrations. The prediction for the extent of swelling at the maximum is not as good but is still satisfactory considering no free parameters were used in the calculations.

In the case of divalent cations (Figure 4), the predicted qualitative features are again observed. In neutral solution there is a swelling maximum. In basic solution we observe first, a deswelling at low salt concentration, then a plateau, and then a further deswelling at still higher salt concentrations. Quantitative agreement is not as good. The first volume change with increasing salt concentration is observed at considerably higher concentrations than predicted. Also, again the extent of swelling at maximum is too low.

The limitations of the theory thus become apparent. It is conceivable the neglected interactions between the localized fixed charges and the dibalent cations may result in formation of new weak cross-links.

When the Debye–Hückel correction is used, the theoretical curves are altered in the right direction. However, the correction is too small to account for the observed discrepancies.

4.6. Effects of Impurities. Considering the increase in sensitivity to monovalent over divalent cations, we can anticipate what happens when small amounts of cations with still higher valencies are present in the system. In Figure 5, the theoretical dependence of swelling on the concentration of monovalent salt (neutral and basic solu-

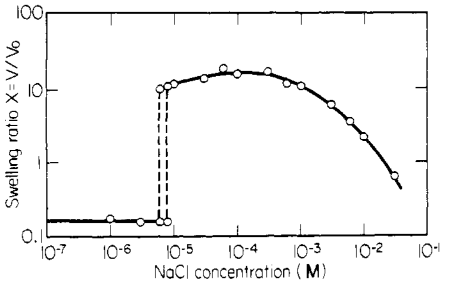

Figure 6. An example of discontinuous swelling in neutral solutions of NaCl in a water–acetone mixture (acetone concentration 45%). The solid line is to guide the eye. The vertical dashed lines indicate the narrow salt concentration range in which both phases, the swollen and the shrunken, are observed.

tion) is compared with results obtained when the solution also contains 10^{-7} mM of a trivalent salt. In the neutral solution, the qualitative features of the swelling curve remain unchanged. At pH 8.7, the situation is very different. Instead of a monotonically decreasing swelling, a distinct maximum appears.

This finding suggests a convenient method to detect the presence of multivalent impurities. One only has to measure the dependence of swelling on the concentration of a monovalent salt at pH 8–9. The method is, however, not foolproof. A likely trivalent impurity is Al^{3+} (Pyrex glassware used in our experiments contains a considerable amount of aluminum). The aluminium cation behaves as weak acid. In a basic solution it is converted into a divalent hydroxide and as a divalent cation it would remain undetected to much higher concentrations.

The sensitivity of the swelling to multivalent impurities indicates the experimental difficulties one would encounter when attempting to test a more sophisticated theory of the ion swelling pressure.

5. Ion Swelling Pressure and the Phase Transition

In the previous experiments the gel swelling varied continuously with changes of the ionic composition of solvent. The situation becomes more complicated when a water–acetone mixture is used as a solvent instead of water. It has been shown[5] the volume changes may become discontinuous.

In Figure 6 the swelling of a gel as a function of NaCl concentration in a neutral water–acetone mixture (45% acetone) is shown. The gel remains shrunken up to 10^{-2} mM NaCl and then swells discontinuously. In a narrow range of salt concentration, both the swollen and the shrunken phase are observed. At higher salt concentrations the gel deswells, this time continuously. (In some situations the deswelling at high salt concentrations may be also discontinuous.[5]) It is interesting to note that states which are unstable at low salt concentration become accessible when the concentration is increased.

The present results (Figure 6) differ somewhat from those previously reported.[5] There the first transition at low salt concentration was not observed. This is understandable since in these preliminary experiments the usual accelerator TEMED was used in gel preparation. TEMED is basic, and the pH of the solution was probably quite high.

At the present stage we will not interpret the discontinuous swelling quantitatively, as we do not know the dissociation constant K_a in water–acetone mixtures.

6. Conclusions

A simple theory based on Donnan equilibrium was found to describe the swelling behavior of weakly charged ionic gels in a surprisingly consistent way as long as no divalent ions are involved. We have tested the consistency of the theory without using any free parameters and without assumptions about the network contribution Π_{net} to the swelling pressure of the gel. Rather, we have obtained an approximation for the dependence of Π_{net} on the swelling ratio as one of the results of our study.

We have been able to predict quantitatively with a high precision the ionic solvent compositions at which the swelling of gels will change or reach an extremum. The extent of swelling is not as well, but still satisfactorily, described. Discrepancies between the theory and the experiment are observed in solutions of multivalent salts. Qualitatively, however, the observed behavior is described well. To judge the performance of an imporved theory, further efforts would be necessary to ensure the absence of multivalent impurity ions.

We would also point out the importance of choosing appropriate experimental conditions when dealing with ionic gels. The ionic composition of the solvent should be chosen to minimize the effect of impurities or to make them easily detectable. Furthermore, the gel should be insensitive to parameters which are not well-known, such as the dissociation constant. Finally, small variations of solvent composition should not affect the swelling state of the gel. In the present case of a weakly charged acrylamide gel, these requirements are met when the experiments are performed in a solution of a weak base at pH between 8 and 9. Unless such conditions are fulfilled, it is difficult to obtain meaningful quantitative results.

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(17) The discontinuity of the slope of the calculated curve in Figure 2 at pH 7 may first appear peculiar. The curve describes actually two experiments. In acidic solutions we vary concentrations of H^+, OH^-, and of an acid anion, which is replaced by a base cation above pH 7.