Swelling and shrinking of a polyelectrolyte gel induced by a salt solution

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The stability of a polyelectrolyte gel in solution results from a delicate balance between several competing thermodynamic forces, viz.

  (i) osmotic pressure of free ions in the gel,
 (ii) molecular interaction of solvent and polymer molecules,
(iii) network elasticity,
(iv) Debye-Hückel interaction of ions.

That balance may be upset by a decrease of temperature and by the addition of salt to the solvent. This results in a decrease of osmotic pressure and collapse of the gel to a small fraction of the initial volume. The effect can be reversed by increasing temperature and by removing salt from the solution. This paper presents an attempt to describe swelling and shrinking quantitatively and to understand the nature of the opposing forces. The volume of a particular polyacrylamide gel in a water acetone solution is represented as a function of the salt content and of temperature.

1 Introduction

A gel consists of a network of polymer molecules which are surrounded by a solvent. The molecules move easily through the solvent and thus, macroscopically, the gel appears as a soft, elastic solid with little compressibility. The mass of the solvent in the gel may be several hundred times as big as the mass of the polymer.

    The polymer network may be endowed with ionizable groups of molecules. In the presence of the solvent such groups will split into network ions, bound to the network, and counterions, that move freely in the solvent. The gel as a whole will be electrically neutral; it is called a polyelectrolyte gel.

If the gel is immersed in a bath of solvent of the same type that is contained in the gel, solvent molecules may be exchanged between the bath and the gel. The counterions, however, are constrained to the network by electrostatic forces. In their tendency to reach equidistribution over the whole system of gel and bath they exert an osmotic pressure that expands the gel. The expansion is counteracted by the network elasticity.

When salt is added to the solvent of the bath, the salt ions have a tendency to migrate into the gel. The migration comes to an end when the so-called "Donnan equilibrium" is reached. That equilibrium does *not* mean equal distribution of salt ions through the system. The distribution of ions has a considerable effect on the volume of the gel: an increase of salt makes the gel shrink. Usually the shrinking process occurs smoothly. But under proper conditions the process may be discontinuous in that a tiny addition of salt leads to a collapse of the gel, i.e. a drastic decrease of volume to a fraction of 1/100 (say) of its initial value. This process is reversible; a decrease of the salt concentration makes the gel swell again. The onset of shrinking and swelling depends strongly on temperature.

All these phenomena are akin to thermodynamic phase transitions in other branches of physical chemistry. Accordingly in this paper we construct a free energy as a function of salt concentration in the bath and of temperature. This free energy has a nonconvex character in the proper range of variables and thus it identifies competing ionic equilibria and the corresponding volumes.

In contrast to previous works on the same subject (e.g. [1], p. 584ff.; [9]) we do not simplify the problem excessively. Therefore an analytic exploitation of the equilibrium conditions is impossible and we have to enlist the help of a proper numerical method. However, we shall put particular emphasis on suggestive interpretation of the results by trying to identify the competing effects which set themselves into equilibrium in this complex system.

2 Composition

A typical polyelectrolytic gel consists of an acrylamide-sodiumacrylate-NN'-methylenebisacrylamide copolymer network in a water-acetone mixture as solvent. The network ions are carboxylate groups COO^- and the counterions are Na^+ ions. A network junction consists of a covalent binding of four chain molecules to a NN'-methylenebisacrylamide molecule.

The salt added to the bath surrounding the gel will here be taken to be NaCl. Note that thus the counterions and the cations of the salt are identical.

We shall ignore the small concentration of H_3O^+- and OH^--ions present in the water, so that the whole system contains only two types of movable ions, viz. Na^+ and Cl^-. Sodium chloride and sodium acrylate are taken to be fully ionized.

We know that the gel and the bath are electrically neutral to an excellent approximation. Therefore the cations Na^+ and the anions Cl^- can pass the interface gel-bath only in *pairs*.

3 Free energy

3.1 Constituents of the system. Contributions to the free energy

We envisage a gel in a bath whose pressure is kept constant at the value p_0 by a piston, see Fig. 1. The temperature is constant in time and throughout the system.

Under those circumstances thermodynamic stability requires that the free *enthalpy* $F + p_0 V$ have a minimum in equilibrium. However, in the case under consideration we may as well say that the free *energy* F be minimal, because the exchange of solvent and ions between the gel and the bath occurs isochorically to an excellent approximation.

Quantities referring to the gel and the bath will be characterised by $'$ and $''$ respectively. We have three constituents: solvent, polymer and salt and we assume that the salt is fully ionized. Therefore the gel consists of

n_L' moles of solvent,
n_P moles of polymer chains,
n_A' moles of mobile anions,   (3.1)
n_K' moles of cations,

and the bath consists of

n_L'' moles of solvent,
n_A'' moles of anions,   (3.2)
n_K'' moles of cations.

There are three contributions to the free energy of the gel and they are due to mixing, electrostatic interaction and network elasticity. In the bath of course the network contribution is missing. Thus we write

$$F' = F_M' + F_E' + F_N', \qquad F'' = F_M'' + F_E''.$$ (3.3)

We proceed to calculate the contributions to the free energy in terms of the mole numbers of the constituents.

3.2 Free energy of mixing

The free energy of mixing will be given in two parts. The first one is based on the entropy of mixing of an ideal mixture and the second one accounts for the non-ideal character of the mixture.
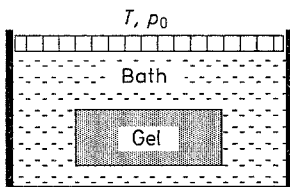

Fig. 1. Gel and bath

The first term has the conventional form

$$-TS_M = RT \left(n'_L \ln \frac{n'_L}{n'} + n'_K \ln \frac{n'_K}{n'} + n'_A \ln \frac{n'_A}{n'} \right.$$

$$\left. + n''_L \ln \frac{n''_L}{n''} + n''_K \ln \frac{n''_K}{n''} + n''_A \ln \frac{n''_A}{n''} \right), \tag{3.4}$$

where n stands for $n_L + n_K + n_A + xn_p$. R is the gas constant. Although this expression is familiar to everybody who knows the basics of physical chemistry, it merits a remark in the present context, because there is no term representing the polymer network. Indeed, in a mixture containing unlinked polymer chains of x monomeric segments each, there should be a contribution of the form (see [1], p. 502)

$$-Rn_P \ln \frac{xn_P}{n'} \tag{3.5}$$

to the entropy of mixing. However, if the chains are linked together in a network — as they are in the gel — the polymer constituent consists of one big macromolecule and the mole number n_P tends to zero (see again [1], p. 577). Therefore the network contribution becomes negligible and we ignore it.

The second part of the free energy of mixing is due to the change of intermolecular potential energy of the van der Waals forces and to the small-scale arrangement of adjacent molecules. We assume that only pairs of the xn_P polymer segments and the n'_L solvent molecules provide a sizable contribution of this type. Therefore we take this part of the free energy of mixing to be proportional to the expected number

$$n'_L \frac{xn_P}{n'}$$

of such pairs and write

$$\frac{F_M}{RT} = \chi n'_L \frac{xn_P}{n'} - \frac{S_M}{R}, \quad \text{or by (3.4)}$$

$$\frac{F_M}{RT} = \chi n'_L \frac{xn_P}{n'} + \left(n'_L \ln \frac{n'_L}{n'} + n'_K \ln \frac{n'_K}{n'} + n'_A \ln \frac{n'_A}{n'} \right.$$

$$\left. + n''_L \ln \frac{n''_L}{n''} + n''_K \ln \frac{n''_K}{n''} + n''_A \ln \frac{n''_A}{n''} \right). \tag{3.6}$$

The coefficient χ consists of two terms, one constant and the other one inversely proportional to temperature. We write

$$\chi = \chi_s + \frac{\chi_e}{RT}. \tag{3.7}$$

χ_e determines the heat of mixing of polymer segments and solvent molecules and χ_s determines the decrease of entropy associated with the formation of a pair of such particles.

χ_e and χ_s must be measured. For polyacrylamide in a 30% aceton-water mixture χ has a value of about 0.5 at 30°C (see [3]). On the other hand the measured values of χ_s are known to range from 0.1 to 0.4 for any polymer solution (see [2]). For the calculations of this paper we choose $\chi_s = 0.2$ and $\chi = 0.65$ for $T = 300$ K, implying that the solvent contains more than 30% acetone. These values will be seen to provide qualitative agreement with the observed phenomena. Thus we have

$$\chi = 0.2 + \frac{135 \text{ K}}{T}. \tag{3.8}$$

In the calculations of (3.4) through (3.6) one assumes that the ions, the polymer segments and the solvent molecules all have approximately the same size (see [1], p. 498). In the sequel we shall refer to these ions, segments and molecules as *particles*, and we shall assume that they have the molar volume

$$V_M = 1.8 \cdot 10^{-5} \text{ m}^3/\text{mol}, \tag{3.9}$$

which is the value for water.

3.3 Free energy of the network

Flory ([1], p. 464 ff.) has calculated the entropy of a homogeneously strained polymer network in isotropic deformation with the deformation gradient α. He obtains[1]

$$S_N = -\tfrac{3}{2}Rn_P^e(\alpha^2 - 1 - 2\ln\alpha). \tag{3.10}$$

n_P^e is the number of elastically effective polymer chains; it is different from n_P, because there are always chains with free ends and closed loops. In the subsequent calculations we shall take $n_P^e = 0.5n_P$. α^3 is the ratio of the actual volume V' of the gel and of the volume V_0' which the gel had before it was in contact with the bath. Since all particles are assumed to have the same molar volume, it follows that $\alpha^3 = V'/V_0'$ may be written as n'/n_0', where n_0' is the number of moles in the gel before immersion in the bath. Thus we have for the free energy of the network

$$\frac{F_N}{RT} = \tfrac{3}{4}n_P\left[\left(\frac{n'}{n_0'}\right)^{2/3} - 1 - \tfrac{2}{3}\ln\left(\frac{n'}{n_0'}\right)\right]. \tag{3.11}$$

3.4 Free energy of electrostatic interaction

In this paper we assume that the network ions of the polyelectrolyte contribute to the electrostatic interaction in the same manner as would the free ions in a normal electrolyte. In view of the fact that the network is quite a flexible structure

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[1] Flory has a factor 1, instead of 2, in front of the logarithmic term. That factor cannot be correct in our opinion, because it requires a non-zero stress in the reference state $\alpha = 1$

this assumption may be justified, at least for the small fraction of 1.25 % of ionic network segments, on which subsequent calculations are based.

The ions in an electrolyte interact by electrostatic fields and the energy of those fields must be taken into account in the internal energy of the electrolyte. In addition, as a result of the electrostatic interaction the particle distribution becomes ordered in the sense that each ion surrounds itself by a "cloud" of other ions, the net charge of that cloud being the negative of the charge of the central ion. Such small-scale order results in a decrease of entropy. The energetic and entropic contributions of the electrostatic field to the free energy are calculated in the Debye-Hückel theory (e.g. see [4], p. 767 ff.). That theory leads to a free energy of the form

$$\frac{F_E}{RT} = - \sum_s \sum_j \frac{C_j^s}{a_j} \left(\frac{1}{2} - \frac{\beta^s}{a_j} + \left(\frac{\beta^s}{a_j} \right)^2 \ln \left(1 + \frac{a_j}{\beta^s} \right) \right), \tag{3.12}$$

$$C_j^s = \frac{A n_j^s (z_j e)^2}{4 \pi \varepsilon}, \qquad \beta^s = \sqrt{\frac{\varepsilon k T V^s}{A \sum_j n_j^s (z_j e)^2}}.$$

The index j denotes the different types of ions of which we have three, viz. COO^-, Na^+ and Cl^-. The index s refers to gel or bath (' or ") and a_j are the radii of the ions. e is the elementary charge and z_j are the numbers of elementary charges of an ion of type j. A is the Avogadro number and ε the dielectric constant. β^s is called the Debye radius. Thus, if i is the number of ionized segments in one chain, we have

$$\sum_j n_j^s z_j^2 = \begin{cases} i n_P z_P^2 + n_K' z_K^2 + n_A' z_A^2 & \text{for the gel} \\ n_K'' z_K^2 + n_A'' z_A^2 & \text{for the bath.} \end{cases} \tag{3.13}$$

V in (3.12) may be replaced by $n V_M$.

3.5 Sum of all free energies

Summing (3.6), (3.11) and (3.12) we obtain the total free energy of the system of gel and bath, viz.

$$\begin{aligned} F = RT \Bigg\{ & \chi n_L' \frac{x n_P}{n'} + \left(n_L' \ln \frac{n_L'}{n'} + n_K' \ln \frac{n_K'}{n'} + n_A' \ln \frac{n_A'}{n'} \right. \\ & + n_L'' \ln \frac{n_L''}{n''} + n_K'' \ln \frac{n_K''}{n''} + n_A'' \ln \frac{n_A''}{n''} \Bigg) \\ & + \tfrac{3}{4} n_P \left(\left(\frac{n'}{n_0'} \right)^{2/3} - 1 - \tfrac{2}{3} \ln \left(\frac{n'}{n_0'} \right) \right) \Bigg\} \\ & - \sum_s \sum_j \frac{C_j^s}{a_j} \left(\frac{1}{2} - \frac{\beta^s}{a_j} + \left(\frac{\beta^s}{a_j} \right)^2 \ln \left(1 + \frac{a_j}{\beta^s} \right) \right). \end{aligned} \tag{3.14}$$

There are 6 variables in this function, viz.

$$n_L', \quad n_L'', \quad n_K', \quad n_K'', \quad n_A', \quad n_A'', \tag{3.15}$$

but these are not all independent. Indeed, we have only two independent variables, because

$$n_L = n_L' + n_L'', \quad n_K = n_K' + n_K'', \quad n_A = n_A' + n_A'' \tag{3.16}$$

are all constant and because both phases are electrically neutral so that we have the conditions

$$in_P z_P + n_K' z_K + n_A' z_A = 0, \quad n_K'' z_K + n_A'' z_A = 0. \tag{3.17}$$

Note that one of the restrictions (3.17) is redundant. because the system as a whole must also be neutral.

4 Equilibrium conditions

4.1 Formulation

As independent mole numbers we choose n_L' and n_K', the mole number of solvent molecules in the gel and the mole number of cations (viz. Na$^+$) in the gel. Necessary conditions for an equilibrium then read

$$\left(\frac{\partial F}{\partial n_L'}\right)_{n_K'} = 0 \quad \text{and} \quad \left(\frac{\partial F}{\partial n_K'}\right)_{n_L'} = 0. \tag{4.1}$$

More explicitly from (3.14) through (3.17) we obtain

$$RT\left\{\chi\left(\frac{xn_P}{n'} - n_L'\frac{xn_P}{n'^2}\right) + \ln\frac{n_L'}{n'} - \ln\frac{n_L''}{n''} + \frac{xn_P}{n'} + \frac{n_P^e}{n_0'}\left[\left(\frac{n_0'}{n'}\right)^{1/3} - \frac{n_0'}{n'}\right]\right\}$$

$$+ \frac{1}{2a}\left(1 - 2\frac{\beta'}{a}\ln\left(1 + \frac{a}{\beta'}\right) + \frac{1}{1 + \frac{a}{\beta'}}\right)\frac{\beta'}{a}\sum_k\frac{C_k'}{n'}$$

$$- \frac{1}{2a}\left(1 - 2\frac{\beta''}{a}\ln\left(1 + \frac{a}{\beta''}\right) + \frac{1}{1 + \frac{a}{\beta''}}\right)\frac{\beta''}{a}\sum_k\frac{C_k''}{n''} = 0, \tag{4.2}$$

$$RT\left\{2\frac{xn_P}{n'}\left(1 - \chi\frac{n_L'}{n'}\right) + \ln\frac{n_K'/n'}{n_K''/n''} + \ln\frac{n_A'/n'}{n_A''/n''} + \frac{n_P^e}{n_0'}\left[\left(\frac{n_0'}{n'}\right)^{1/3} - \frac{n_0'}{n'}\right]\right\}$$

$$- \frac{Ae^2}{4\pi\varepsilon a}\left\{\left(1 - 2\frac{\beta'}{a}\ln\left(1 + \frac{a}{\beta'}\right) + \frac{1}{1 + \frac{a}{\beta'}}\right)\frac{\beta'}{a}\frac{n_L' + (x - i)n_P}{n'}\right.$$

$$- \left(1 - 2\frac{\beta''}{a}\ln\left(1 + \frac{a}{\beta''}\right) + \frac{1}{1 + \frac{a}{\beta''}}\right)\frac{\beta''}{a}\frac{n_L''}{n''}$$

$$\left. + 2\left(\tfrac{1}{2} - \frac{\beta'}{a} + \left(\frac{\beta'}{a}\right)^2\ln\left(1 + \frac{a}{\beta'}\right)\right) - 2\left(\tfrac{1}{2} - \frac{\beta''}{a} + \left(\frac{\beta''}{a}\right)^2\ln\left(1 + \frac{a}{\beta''}\right)\right)\right\} = 0. \tag{4.3}$$

For simplicity we have set all ionic radii equal in these formulae, so that $a_K = a_A = a_N = a$. In the numerical calculations below we have used the value for a sodium ion: $a = 2.4 \cdot 10^{-10}$ m. For the ionic charges we have assumed $z_K = -z_A$.

4.2 Discussion

The equilibrium conditions (4.2) and (4.3) express in explicit form the requirement that the chemical potentials of the solvent and of the cations are equal in the gel and the bath in equilibrium. Apart from the Debye-Hückel term the condition (4.2) has already been written down by Flory ([1], p. 587) and subsequently by many authors. The condition (4.3) on the other hand appears here for the first time to my knowledge in its full generality. That condition is normally truncated to contain only the two underlined terms (e.g. see [9]) and it is usually written in the form

$$\frac{n_K' n_A'}{n'^2} = \frac{n_K'' n_A''}{n''^2} \, . \tag{4.4}$$

Equation (4.4) is known as the Donnan equation (e.g. see [5]); it describes the equilibrium of mobile cations and anions at a membrane in the presence of a third ionic constituent that cannot pass the membrane, here the ionic segments of the network.

Comparison of (4.3) and (4.4) shows that the following items are missing from (4.4)

 (i) the Debye-Hückel term,
 (ii) the network elasticity, and
 (iii) the effect of the intermolecular potential energy.

It cannot a priori be decided weather the additional terms give negligible contributions. Only a comparison of the results from the exact formula and from the truncated one can decide that question.

5 Exploitation of equilibrium conditions

5.1 Graphical representation of the solutions of the eqs. (4.2) and (4.3)

The system of eqs. (4.2), (4.3) was solved numerically for many different salt concentrations in the bath and for many different temperatures. For the graphical representation of the results we introduce normalized variables as follows.

   The normalized salt concentration in the bath is defined as

$$\hat{c}_s = \frac{\overset{0,\prime\prime}{n_K}/\overset{0,\prime\prime}{n}}{\overset{0,\prime}{n_K}/\overset{0,\prime}{n}} \, .$$

$\overset{0,\prime\prime}{n_K}, \overset{0,\prime\prime}{n}$ are the mole numbers of cations Na$^+$ in the bath and the mole numbers of particles at all in the bath respectively before the bath is in contact with the gel.

$n_K^{0'}$, $n^{0'}$ are the corresponding mole numbers in the gel. In order to give some understanding of the significance of this variable we note that $\hat{c}_s = 1$ means that the cation concentration in the bath and the concentration of counter ions in the gel was equal before contact was established. We shall see that the interesting phenomena occur for $\hat{c}_s < 1$.

The normalized mole number of the solvent in the gel is defined as

$$\hat{n}_L' = \frac{n_L'}{x n_P}.$$

For a better understanding of this value we note thiat $\hat{n}_L' = 1$ means that the number of solvent molecules in the gel equals the number of polymer segments in the gel. We shall see that the interesting range of $\hat{n}_L'$ is the one between 1 and 100.

We also introduce a normalized mole number of the cations Na$^+$ in the gel by the definition
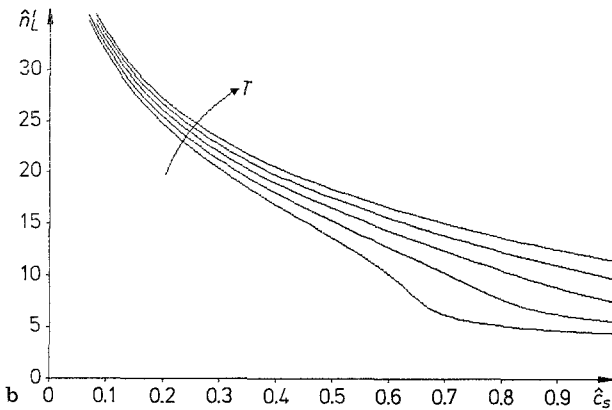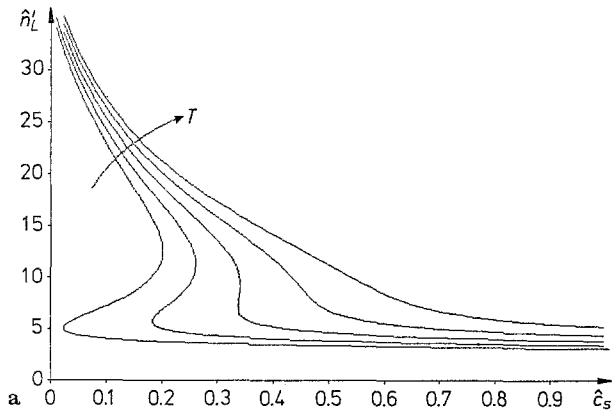
$$\hat{n}_K' = \frac{n_K'}{i n_P}.$$

Fig. 2. a Number of solvent molecules in the gel versus salt concentration of the bath. b Same as a but with Debye-Hückel term in Eq. (4.2) omitted and Eq. (4.3) truncated to contain only the underlined terms

If $\hat{n}'_K$ equals 1, the number of Na$^+$ ions equals the number of ionized polymer
segments. This is of course the situation before the gel is immersed in the bath.
Therefore we shall be interested in values of $\hat{n}'_K$ that exceed 1, and it will turn out
that the interesting range of $\hat{n}'_K$ is between 1 and 1.15.

The Figs. 2a and 3a represent the solutions of Eqs. (4.2) and (4.3). Curve
parameter is the temperature which ranges over the values $T = 21°$, $25°$, $29°$,
$33°$ and $37°$C.

The Figs. 2b and 3b give an impression of the importance of the terms of
Eqs. (4.2) and (4.3) that are neglected in most parts of the relevant literature.
As was mentioned before, the Debye-Hückel term in Eq. (4.2) usually is missing
and the Eq. (4.3) is usually truncated to contain only the two underlined terms.
This simplification has a drastic qualitative and, of course, quantitative effect
on the predicted values of the equilibrium concentrations $\hat{n}'_L$ and $\hat{n}'_K$. Comparison
of the curves of Fig. 2a and b and of Fig. 3a and b illustrates this point.

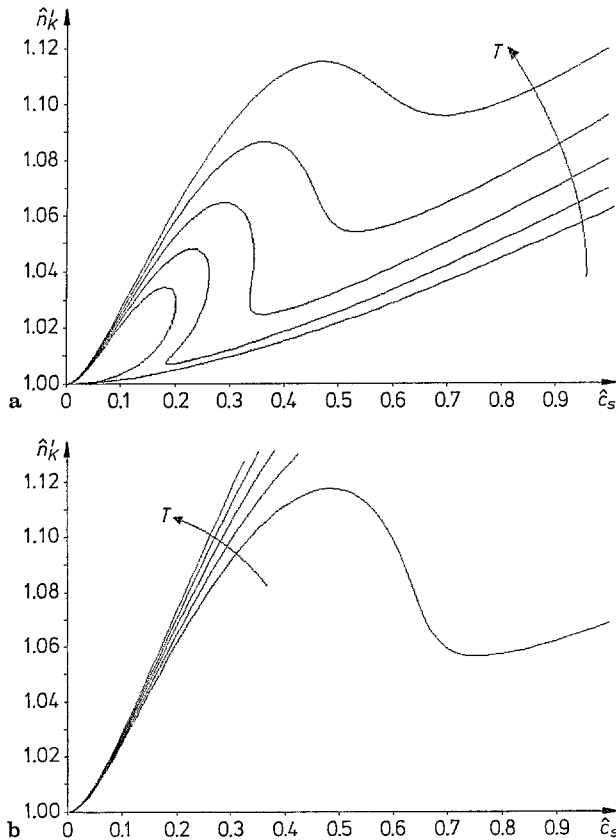An interpretation of the curves of Figs. 2a and 3a will follow in Sect. 6.1.

Fig. 3. a Number of cations in the gel versus salt concentration of the bath. b Same as
a but with Debye-Hückel term in Eq. (4.2) omitted and Eq. (4.3) truncated to contain
only the underlined terms

5.2 Graphical representation of the free energy

Inspection of Figs. 2a und 3a shows that in a certain range of temperature T and salt concentration $\hat{c}_S$ we have three equilibrium values of solvent mole number $\hat{n}'_L$ and cation mole number $\hat{n}'_K$. The question arises which one of these solutions are stable.

Geometrically the solutions of (4.2) and (4.3) may be minima, maxima or saddle points of the free energy as a function of $\hat{n}'_L$ and $\hat{n}'_K$. Only the minima correspond to stable equilibria.

The Fig. 4a–g shows contour diagrams of the free energy as a function of $\hat{n}'_K$, $\hat{n}'_L$ for different salt concentrations $\hat{c}_S$ and for $T = 25\,°C$. The position of the deepest minimum is marked by a dot which thus identifies the stable minimum. In many of the figures we see two minima seperated by a saddle point and we also see that the stable position $\hat{n}'_L$, $\hat{n}'_K$ shifts at $\hat{c}_S = 0.24$, because the minimum for large values of $\hat{n}'_L$ loses its role as the deeper one to the minimum for small values of $\hat{n}'_L$.

Note from Fig. 4a that at $\hat{c}_S = 0.1$ the gel contains 24 times as many solvent molecules as polymer segments. On the other hand from Fig. 4g we conclude that for $\hat{c}_S = 0.3$ most of the solvent has been pushed out of the gel. It contains only 4.5 times as many solvent molecules as polymer segments.

Figure 4e shows that the switch between the minima, which occurs at $\hat{c}_S \approx 0.24$ is associated with a drop in $\hat{n}'_L$ from 17 to 4.6. This drop is connected with a collapse of the gel to roughly 30 % of its volume, because it is essentially $\hat{n}'_L$ which determines the size of the volume. The collapse has great similarity with a thermodynamic *phase transition* in that it occurs at a fixed value of a parameter, here $\hat{c}_S$.

Since two minima coexist over a wide range of $\hat{c}_S$, it is conceivable that metastable states might be observed. I.e. the gel might stay in a minimum although there exists a deeper one which, however, cannot be reached, because the saddle point is too high. To my knowledge such metastable states have not been observed.

The Fig. 5a–f represents contour lines of the free energy in the same range of salt concentrations as in Fig. 4a–g but for 37°C. We see now that there is no "phase transition"; rather the transition from the swollen state with $\hat{n}'_L$ large to the shrunken state with $\hat{n}'_L$ small occurs continuously as $\hat{c}_S$ grows.

6 Discussion of results

6.1 The $(\hat{n}'_L, \hat{c}_S)$-isothermes

A little reflection is needed to see the connection between Figs. 4a–g and the $(\hat{n}'_L, \hat{c}_S)$-isotherm of Fig. 2a for 25°C; The isotherm describes the ordinates of the minima and of the saddle point of the free energy for a given value of $\hat{c}_S$. The parts of the isotherm that have negative slopes correspond to minima and the part with a positive slope corresponds to the saddle point.

We ignore the unstable saddle points and the metastable minima and connect the two branches of the isotherm corresponding to stable minima by a vertical line at the value of $\hat{c}_S$ where the minima exchange their roles as deepest minima. This has been done in Fig. 6 for $T = 21°$, $25°$ and $29°C$. The isotherms for $T = 33°$ and $37°C$ have no unstable or metastable parts.

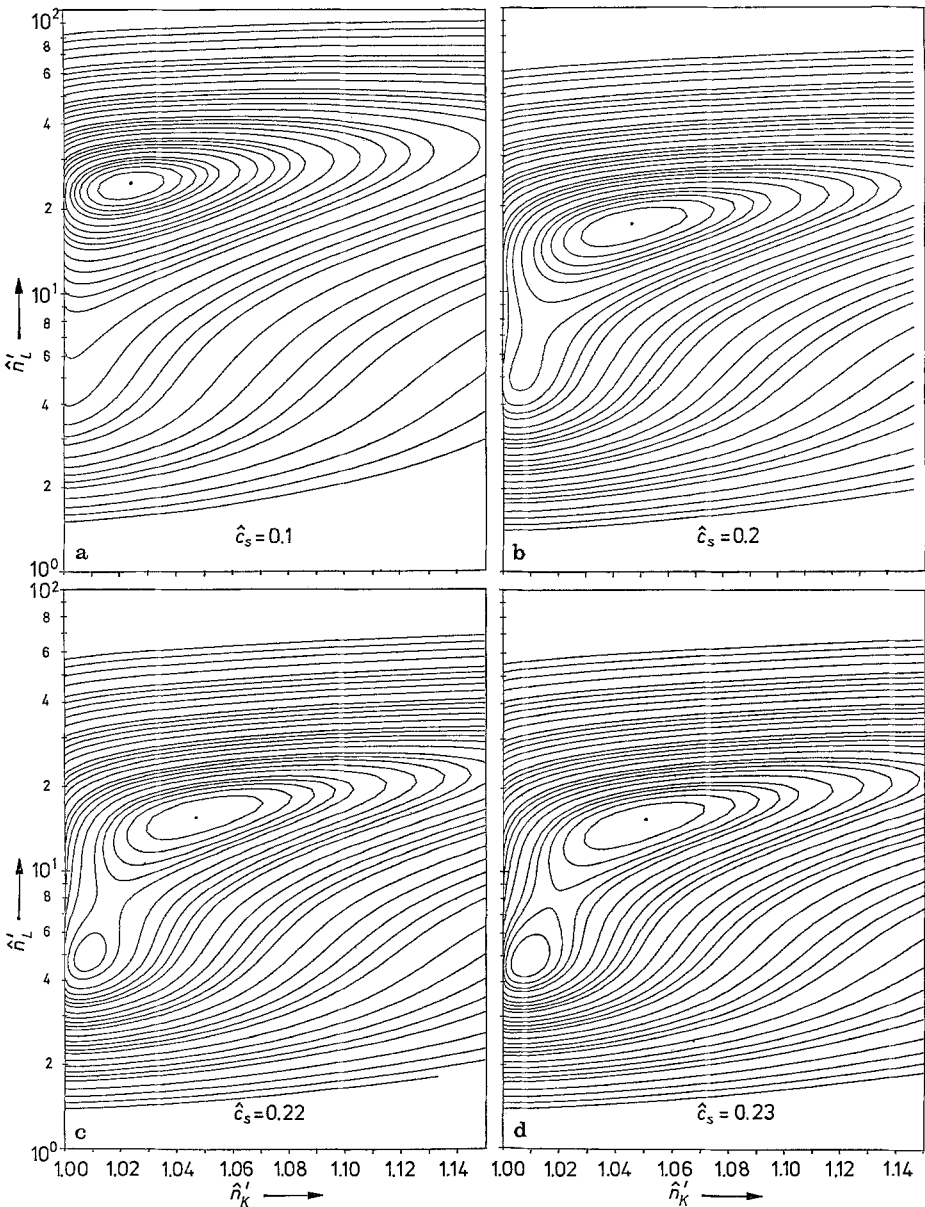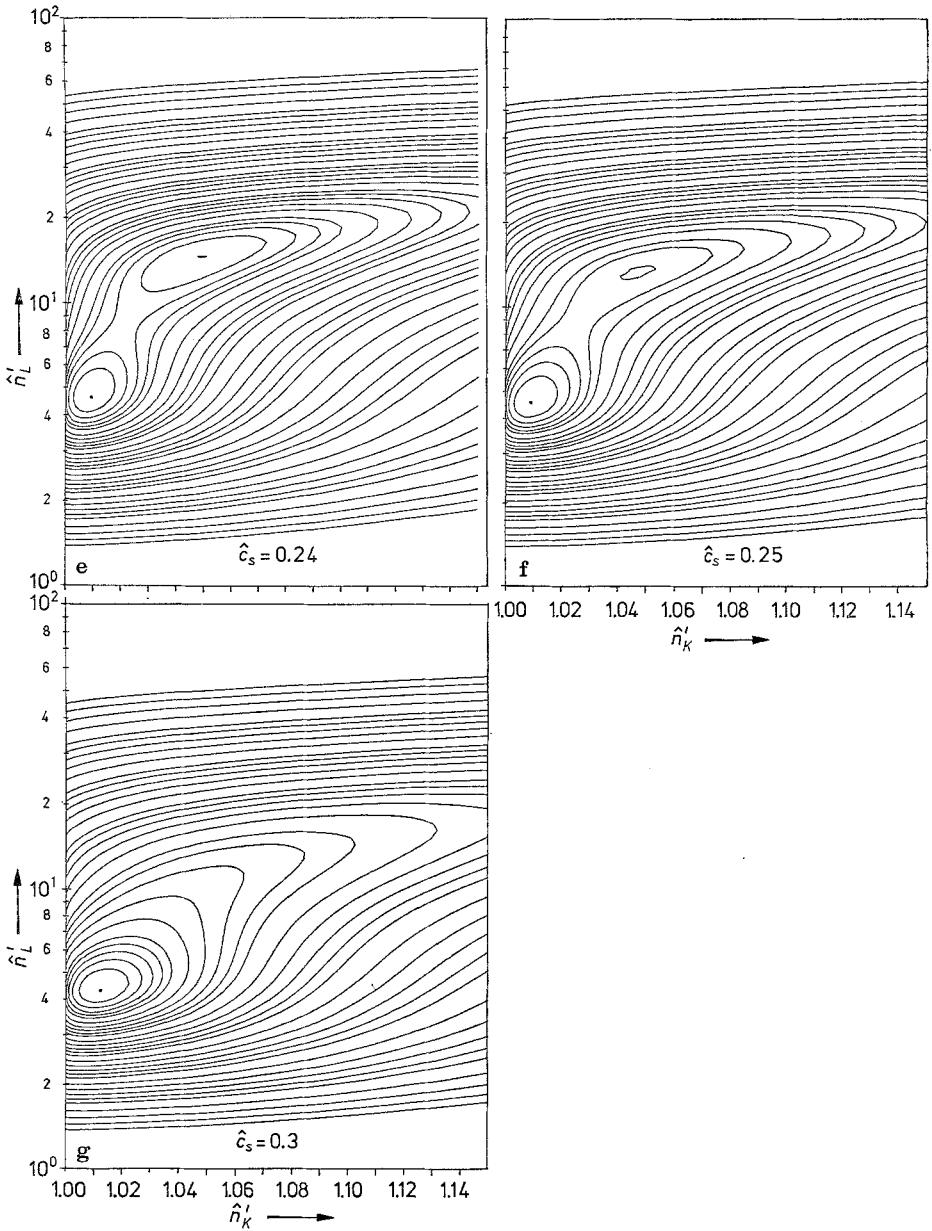Fig. 4a—d

Fig. 4e–g

Fig. 4a–g. Contour lines of the free energy $F(\hat{n}'_K, \hat{n}'_L)$ at $T = 25\,^{\circ}\text{C}$. The lower minimum is marked by a dot. The first 5 contour lines around the dot have a difference of ΔF, the following 5 have the difference $2\Delta F$, and the ones, that follow after that, have a difference of $4\Delta F$

Also in Fig. 6 there is a second ordinate giving the values of the volume V of the gel normalized by V_0, the volume of the gel before it made contact with the bath. As we had already anticipated, V increases with $\hat{n}'_L$, nearly linearly, albeit not quite, because there is also some migration of salt ions into the gel as we can see from Fig. 3.

Inspection of Fig. 6 shows that in a bath with $\hat{c}_S \approx 0.01$ at a temperature of $T = 21\,°C$ the volume ratio V/V_0 is roughly 2, while at $\hat{c}_S \approx 1$ we have
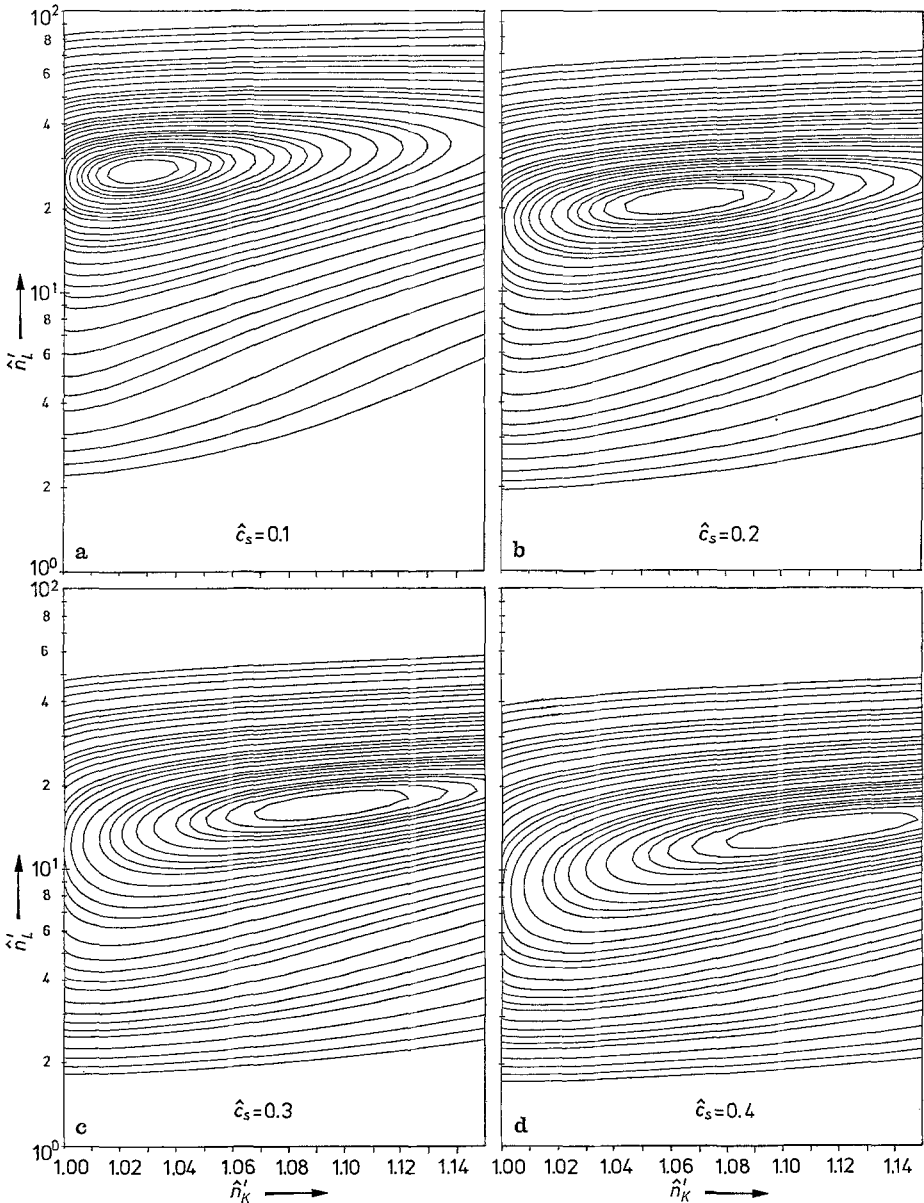

Fig. 5a—d

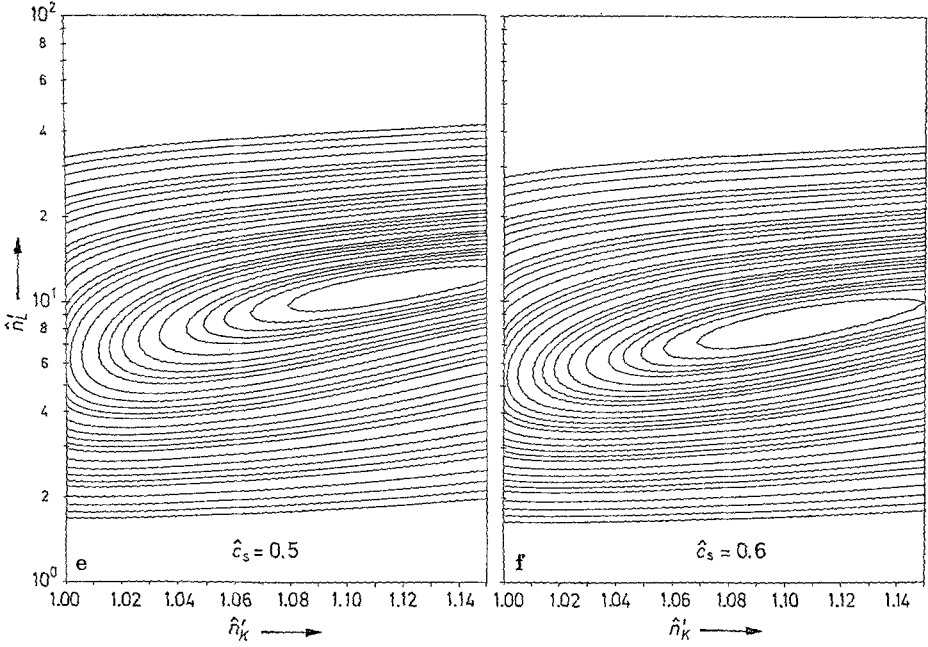**Fig. 5e–f**

Fig. 5a–f. Contour lines of the free energy $F(n'_K, n'_L)$ at $T = 37\,°C$. The differences of F for the different lines are as in Fig. 4
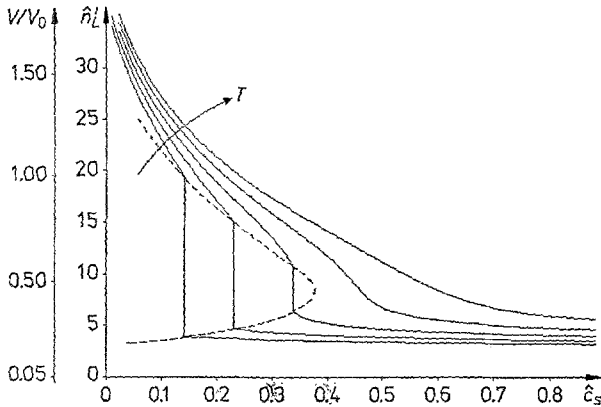

Fig. 6. Gel volume and number of solvent moles in the gel versus salt concentration of the bath

$V/V_0 \approx \frac{1}{6}$. Thus the volumetric swelling ratio is 12. Much bigger swelling ratios are reported in the literature. But the present calculations are valid for weakly ionized networks and for a fairly small solvent content during polymerisation. The values chosen are $in_P/xn_P = 1.25 \cdot 10^{-2}$ and $\overset{0,}{n_L}/xn_P = 19$. This makes for only moderate swelling.

In analogy to the terminology of phase transition we may call the isotherms for $T = 21°$, $25°$ and $29°C$ subcritical while the isotherms for $T = 35°$ and $37°C$ are supercritical. The critical isotherm lies somewhere between $T = 29°C$ and $T = 33°C$. The subcritical isotherms run through a two-phase region in which the gel consists of swollen and shrunken domains that are in equilibrium. The two phase region is bounded by the dashed curve in Fig. 6.

6.2 The Donnan exclusion effect

In the previous section we have seen that the increase of the salt concentration of the bath lets the gel shrink, either smoothly or discontinuously in the way of a phase transition, depending on the temperature. We shall now attempt a suggestive interpretation of the acting mechanisms.

For that purpose it is appropriate to introduce the number n'_A of movable anions Cl⁻ in the gel. Figure 7 shows the relative numbers n^s_A/n^s in the gel and the bath for 5 different temperatures. Note that n'_A is also the surplus of the number of cations in the gel over the number in_P of ionized polymer segments: this is so since the salt ions Na⁺ and Cl⁻ can only enter the gel jointly because of electro-neutrality.

Comparison of the curves for n''_A/n'' and n'_A/n' shows that the anions are not distributed evenly over the gel and the bath: while in the bath the curve n''_A/n'' versus $\hat{c}_S$ is linear, the fraction n'_A/n' starts out very flat. This observation represents the Donnan exclusion effect which was first described in 1911 by F. G. Donnan [8] for ionic equilibria at membranes that are impermeable for one ionic constituent. The effect occurs here, because the ions on the polymeric network cannot leave the gel.
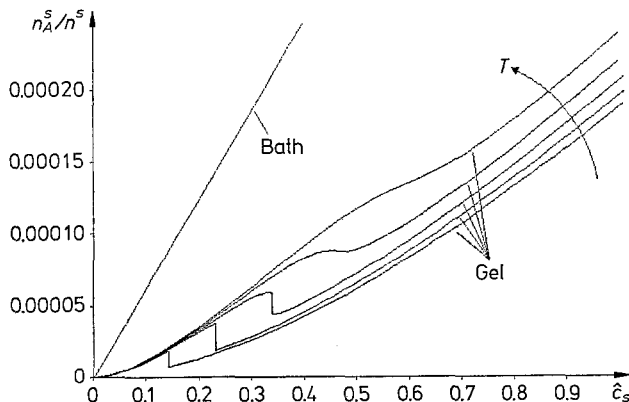

Fig. 7. Concentrations of anions Cl⁻ versus salt concentration

An intuitive understanding of the Donnan effect can be gained as follows. The anions Cl^- of the salt added to the solvent have the tendency to migrate into the gel, because the gel is devoid of them. But to do so they have to carry along a cation Na^+ because of electroneutrality. However, there are already many cations as counterions in the gel, many more than in the bath. Therefore the cations that migrate into the gel along with the anions are unwelcome and develop a tendency to return to the bath taking along the anions, again for electroneutrality. Thus the anions are effectively barred from the gel, at least as long as the salt concentration is small.

For higher salt concentrations the exclusion is less effective for two reasons: (i) the anions push more strongly into the gel when more are present, and (ii) the surplus of cations in the gel over the bath becomes less pronounced. Therefore the curves n_A'/n' pick up for higher values of $\hat{c}_S$ as can be seen in Fig. 7. Also we see in Fig. 7 that the collapse of the gel enhances the Donnan exclusion. This is easily understood, because the collapse increases the density of counterions, i.e. cations in the gel and those are the ones that are responsible for the exclusion.

6.3 Influence of van der Waals interaction, network elasticity, osmotic pressure and electrostatic interaction on the volume of the gel

6.3.1 On the van der Waals interaction

The van der Waals term in the free energy of the system is

$$F_{\text{v.d.w.}} = RT\chi n_L' \frac{xn_P}{n'}.$$

Differentiation of this expression with respect to $V' = n'V_M$ for a fixed number n_K' of cations gives

$$\left(\frac{\partial F_{\text{v.d.w.}}}{\partial V'}\right)_{n_K'} = \frac{1}{V_M}\left(\frac{\partial F_{\text{v.d.w.}}}{\partial n'}\right)_{n_K'} = \frac{RT}{V_M}\chi\frac{xn_P}{n'}\left(\frac{xn_P + n_K' + n_A'}{n'}\right).$$

This expression has the dimension of a pressure and we therefore call it the van der Waals pressure in the gel. For $\chi > 0$ we have $\left(\frac{\partial F_{\text{v.d.w.}}}{\partial V'}\right) > 0$ so that a decrease of the gel volume decreases the part of the free energy that is due to van der Waals interaction. Another way of saying this is that the van der Waals forces are contractive.

The interpretation is clear: The polymer molecules have the tendency to stick together because of the attractive van der Waals forces and to force the solvent out of the gel. The van der Waals pressure is inversely proportional to n'^2 and therefore inversely proportional to the square of the volume of the gel. This too is easy to understand, because in a swollen gel most of the polymer chains are beyond the range of their van der Waals forces.

6.3.2 On network elasticity

The network contribution to the free energy of the system is

$$F_N = RT \frac{n_P^2}{2} \left[3 \left(\frac{n'}{n_0'} \right)^{3/2} - 3 - 2 \ln \frac{n'}{n_0'} \right].$$

Differentiation of this expression with respect to V' gives

$$\left(\frac{\partial F_N}{\partial V'} \right)_{n_K'} = \frac{RT}{V_M} \frac{n_P^2}{n_0'} \left[\left(\frac{n_0'}{n'} \right)^{1/3} - \frac{n_0'}{n'} \right].$$

We call this expression the network pressure: its sign determines whether the network forces tend to increase the volume of the gel or decrease it. We distinguish three cases

$$\left(\frac{\partial F_N}{\partial V'} \right)_{n_K'} - \begin{cases} > 0 & \text{for } n' > n_0', \\ = 0 & \text{for } n' = n_0', \\ < 0 & \text{for } n' < n_0'. \end{cases}$$

Therefore the network elasticity is contractive for the swollen gel. In fact the network elasticity aims at keeping the gel in the state which it had before contact with the bath.

6.3.3 On osmotic pressure

The term in the free energy of the system that is due to the entropy of mixing reads

$$F_M = RT \left(n_L' \ln \frac{n_L'}{n'} + n_K' \ln \frac{n_K'}{n'} + n_A' \ln \frac{n_A'}{n'} \right.$$

$$\left. + n_L'' \ln \frac{n_L''}{n''} + n_K'' \ln \frac{n_K''}{n''} + n_A'' \ln \frac{n_A''}{n''} \right)$$

and we obtain upon differentiation

$$\left(\frac{\partial F_M}{\partial V'} \right)_{n_K'} = \frac{RT}{V_M} \left(\ln \frac{n_L'}{n'} - \ln \frac{n_L''}{n''} + \frac{x n_P}{n'} \right) \approx - \frac{RT}{V_M} \left(\frac{n_K' + n_A'}{n'} - \frac{n_K'' + n_A''}{n''} \right).$$

The latter approximate equation holds for $n_K^s \ll n^s, n_A^s \ll n^s$. We denote the two terms on the right hand side by $p_{osm.}'$ and $p_{osm.}''$ respectively and call them the osmotic pressures of the gel and the bath.

In Fig. 8 we have plotted $(n_K^s + n_A^s)/n^s$ versus $\hat{c}_S$. Inspection shows that this expression is bigger for the gel than for the bath for all values of $\hat{c}_S$. Therefore $p_{osm.}'$ is greater than $p_{osm.}''$, and we conclude that the osmotic pressures always act expansively upon the gel.
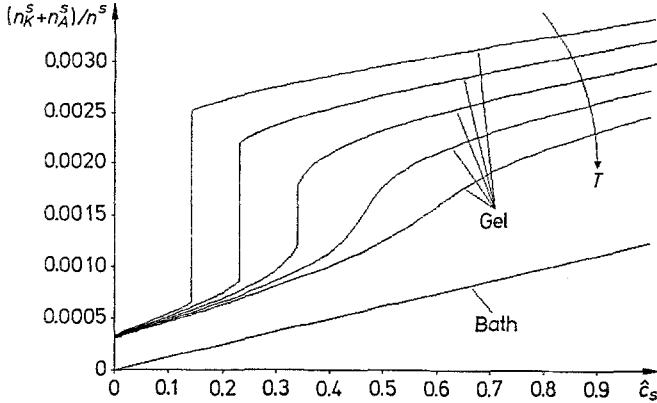
Fig. 8. Concentrations of movable ions in the gel and the bath versus salt concentration in the bath

6.3.4 On the electrostatic interaction

The Debye-Hückel term in the free energy is given by equation (3.12). Differentiation with respect to V' leads to

$$\left(\frac{\partial F_D}{\partial V'}\right)_{n_K'} = \frac{1}{2aV_M}\left(1 - 2\frac{\beta'}{a}\ln\left(1 + \frac{a}{\beta'}\right) + \frac{1}{1 + \frac{a}{\beta'}}\right)\frac{\beta'}{a}\sum_k \frac{C_k'}{n'}$$

$$- \frac{1}{2aV_M}\left(1 - 2\frac{\beta''}{a}\ln\left(1 + \frac{a}{\beta''}\right) + \frac{1}{1 + \frac{a}{\beta''}}\right)\frac{\beta''}{a}\sum_k \frac{C_k'}{n''}.$$

We denote this expression the Debye pressure; once again we realize that its sign determines in which direction it acts on the gel. Thus, if F_D decreases with decreasing V' we conclude that the electrostatic forces act contractively upon the gel; if F_D increases with decreasing V' they tend to expand the gel. We proceed to find out which of these possibilities infact occurs.

First of all we have

$$\sum_j \frac{C_j'}{n'} = \frac{Ae^2}{4\pi\varepsilon}\sum_j \frac{n_j'}{n'}z_j^2 = \frac{Ae^2}{4\pi\varepsilon}\frac{in_P + n_K' + n_A'}{n'}$$

and

$$\sum_j \frac{C_j''}{n''} = \frac{Ae^2}{4\pi\varepsilon}\frac{n_K'' + n_A''}{n''}.$$

Inspection of Fig. 8 shows that $(n_K^s + n_A^s)/n^s$ is bigger in the gel than in the bath, therefore

$$\sum \frac{C_j'}{n'} > \sum \frac{C_j''}{n''}. \tag{6.2}$$

Secondly

$$f\left(\frac{\beta}{a}\right) := \left(1 - 2\frac{\beta}{a}\ln\left(1 + \frac{\beta}{a}\right) + \frac{1}{1 + \dfrac{a}{\beta}}\right)\frac{\beta}{a}$$

can be shown to be a monotonically decreasing function in the relevant range where $\beta/a > 1$ holds. On the other hand because of the definition of β [Eq. (3.12)] and because of

$$\sum_j \frac{n_j'}{n'} > \sum_j \frac{n_j''}{n''}$$

(see Fig. 8), we have

$$f\left(\frac{\beta'}{a}\right) > f\left(\frac{\beta''}{a}\right). \tag{6.3}$$

From (6.1) through (6.3) we conclude that $\left(\dfrac{\partial F_D}{\partial V'}\right)_{n_K} > 0$ holds, so that the Debye contribution to the free energy represents a contractive effect on the gel.

   This result merits a short discussion which is motivated by the frequent remark in the literature (e.g. see [1], p. 584f.; [6], [7]) that the dramatic swelling of poly-electrolyte gels is due to the electrostatic *repulsion* of the network ions. In contrast to this the Debye-Hückel thory shows that the electric field of a network ion is effectively shielded by the oppositely charged cloud consisting of all other ions, and that there is an *attractive* force between the network ion and this cloud. Hence a contractive effect of the electrostatic interaction is plausible and that is what our formal calculation has indeed given.

6.4 Influence of salt concentration on the volume of the gel

Among the 4 pressures which we have identified in the previous section the osmotic pressure is the only expansive one. Therefore, since swelling may be induced by lowering the salt concentration, we should like to obtain an intuitive understanding of how the decrease of the salt concentration affects the osmotic pressure.

   For that purpose we consider a gel in equilibrium with a bath consisting of the pure solvent at the supercritical temperature $T = 37\,°C$ (say). This equilibrium we propose to disturb by adding salt to the bath so that $\hat{c}_S$ assumes the value 0.05. This starts a process which consists of two interconnected parts.

   A part of the salt ions migrates into the gel, but that part remains small because of the Donnan exclusion. This means that at the end of the migration the concentration of salt ions in the gel is much smaller than in the bath. For illustration see Fig. 7.

   The salt ions in the bath exert an osmotic pressure on the gel which we call the external osmotic pressure. Therefore the gel shrinks. In the process of shrink-

ing the density of movable ions in the gel increases and so does their osmotic pressure, which we call the internal osmotic pressure. The shrinking proceeds until a new equilibrium with the changed osmotic pressures is established.

Figure 8 shows that the internal osmotic pressure has risen by practically the same amount as the external one. This follows from the fact that the initial slopes of $(n_K^s + n_A^s)/n^s$ are roughly equal in the gel and in the bath. Indeed, the osmotic pressure is proportional to $(n_K^s + n_A^s)/n^s$ as we have seen in Sect. 6.3.3 for small concentration of ions.

Next we disturb the new equilibrium by adding enough salt to make $\hat{c}_S$ equal to 0.9. There upon the same process occurs again but with a new ingredient. As the mean distance of the polymer molecules shrinks the van der Waals interaction between them grows. The resulting contractive van der Waals pressure gains influence and enhances the shrinking. Figure 8 shows that now the osmotic pressure of the gel must increase more rapidly so as to be able to counteract the effect of the van der Waals pressure (for simplicity the Debye pressure and the network pressure have not been mentioned here).

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