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Osmotic properties of poly(ethylene oxide) gels with localized charged units

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Abstract

Polyelectrolyte gels consisting of neutral poly(ethylene oxide) chains and charged polymethacrylate chains were studied at equilibrium in aqueous salt solutions. The swelling degree Q increases with the fraction of charged monomer units β however this growth is considerably weaker ($Q \sim \beta^{0.23}$ in 10^{-4} mol dm^{-3} NaCl) than the expected one. The shear modulus G varies with Q approximately according to the classical prediction $G \sim Q^{-1/3}$ and does not depend on β. This indicates that the neutral network chains determine the modulus and, hence, the elastic contribution to the swelling pressure. The osmotic contribution found from the data on free swelling and osmotic deswelling was separated into polymer and ionic parts. The polymer part scales as $Q^{-9/4}$ like the osmotic pressure of semidilute aqueous solutions of poly(ethylene oxide). The ionic part is far less than the ideal-gas pressure of counterions, and this discrepancy increases with β. This is explained by two causes: localization of charged units within the network, resulting in the counterion condensation, and the electrostatic interactions in the gel. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polyelectrolyte gels; Poly(ethylene oxide); Osmotic pressure contributions

1. Introduction

Polyelectrolyte gels — polymer networks with charged groups have attracted much attention during the past few decades due to their unique properties. One of the most important properties of such gels is the ability of enormous swelling in water or aqueous solutions, which is caused by the high osmotic pressure of counterions of the charged network. Owing to this property, polyelectrolyte gels are widely used as superabsorbent materials in agriculture (water retention in soil), hygiene (disposable diapers, sanitary napkins), etc. [1,2].

The swelling properties of polymer gels have long been understood in terms of the balance between the osmotic pressure π_{osm} acting to swell the gel and the elastic response of the cross-linked polymer chains π_{el} [3–5]. The osmotic pressure in polyelectrolyte gels consists of two contributions: the polymer one π_{pol} arising from the polymer–solvent interactions and the ionic one π_{ion}, which mainly comes from the translational entropy of mobile ions confined in the gel volume. The latter is often much higher than the polymer contribution and, hence, plays a dominant role in the behavior of polyelectrolyte gels.

The ionic contribution is usually deduced from the Donnan equilibrium, which suggests that all mobile ions freely move in the overall gel volume and contribute to the osmotic pressure as an ideal gas [3]. This seems justified as, in many cases, the swelling degree [6–8] and the value of π_{ion} [9–11] are satisfactorily predicted. However, it has been also shown that the ionic pressure observed experimentally may be significantly lower than the value of π_{ion} calculated within the Donnan framework [12,13].

A lower osmotic efficiency of mobile ions can be caused by different reasons discussed in a number of theoretical studies [14–17]. First, these ions can behave as a non-ideal gas due to electrostatic interactions between them and the charged polymer chains [14,15]. Second, some counterions can be osmotically passive, i.e. do not contribute to the osmotic pressure. An obvious reason for this is a Manning condensation of counterions on the highly charged network chains [16]. The other reason is related to the inhomogeneous distribution of charged units within the gel. It has been suggested that, in the relatively highly charged regions, the local potential wells be formed, which additionally entrap some of the counterions [17]. The effect of the charge distribution on the swelling behavior of polyelectrolyte gels was observed experimentally [18].

In our previous study [19], the polyelectrolyte gels consisting of neutral and charged polymer chains were

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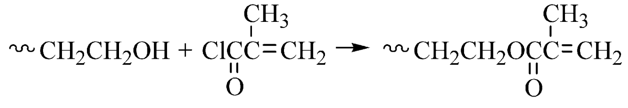


$$\sim CH_2CH_2OH + ClC(=O)C(CH_3)=CH_2 \rightarrow \sim CH_2CH_2OC(=O)C(CH_3)=CH_2$$

Scheme 1.

prepared by copolymerizing poly(ethylene oxide) (PEO) methacrylate bis-macromonomers with ‘small’ ionogenic monomers such as 2-acrylamido-2-methyl-1-propanesulfonic acid (APS), its potassium salt (APSP), and methacrylate of potassium (MAP). Contrary to usual ionic gels, which contain charged units randomly distributed within the network, in these gels, the ionogenic units are localized along the polymethacrylate chains within the network.

The aim of the present study is to investigate the osmotic properties of PEO gels with a different amount of locally distributed charged units. With this aim, the shear modulus and the swelling degree are measured for the gels equilibrated with the low-molecular-weight salt solutions. In addition, the osmotic deswelling experiments are performed. The obtained results are then used to evaluate the polymer and ionic osmotic-pressure contributions and analyze the osmotic efficiency of mobile ions.

2. Experimental

2.1. Materials

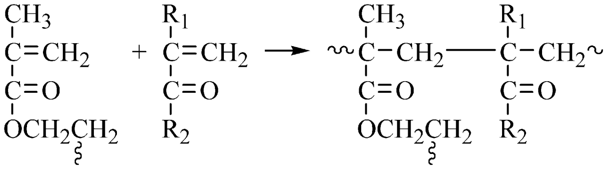
The PEO bis-macromonomers were synthesized by methacrylation of commercial poly(ethylene glycol) (PEG) samples (Loba Chemie, nominal molecular weight 4000 and 12000) as described in our earlier paper [20]. A simple Scheme 1 of this reaction is given above:

The macromonomers with molecular weights of 4000 and 12000 designated further as PEO1 and PEO2, respectively, had, on average, 1.5 and 1.3 terminal methacrylate groups per one PEO chain; the number of methacrylate groups was determined by UV spectrophotometry. MAP (Reakhim) was used as received. APSP was obtained by neutralization of APS (Fluka) with the stoichiometric amount of KOH and used directly in the form of solution.

2.2. Preparation of gels

Charged gels composed of PEO and polymethacrylate chains were prepared by radical copolymerization of the macromonomers and MAP or APSP in oxygen-free aqueous solution (see Scheme 2). The polymerization was initiated by the sodium persulfate-sodium thiosulfate system (0.5–1.0 g dm^{-3} of each component) and carried out at 30°C for 48 h. To prevent hydrolysis of ester bonds, phosphate buffer (1 mol m^{-3}, pH 7) was used as solvent for polymerization. The amount of unreacted MAP for very similar charged PEO gels was measured by us previously [19]; it is of the order of 1% of the amount of MAP in the starting mixture.

A series of PEO1–MAP gels was prepared as follows.



$R_1 = CH_3$; $R_2 = OK$ (**MAP**)

$R_1 = H$; $R_2 = NHC(CH_3)_2CH_2SO_3K$ (**APSP**)

Scheme 2.

The initial total mass fraction of comonomers in the reaction solution c_0 was held approximately constant while the ratio of MAP to the macromonomer PEO1 was varied in a wide range. In addition, a PEO2–MAP gel based on the macromonomer PEO2 and a PEO1–APSP gel were prepared. The values of c_0 for different gel samples as well as the initial concentration of macromonomer methacrylate groups c_M^0 and the initial concentration of ionogenic monomer c_{im}^0 are shown in Table 1.

The gel plates were prepared in a rectangular glass moulds of different thickness (4.7, 6.6, and 10 mm). When the gelation was completed, all the gel samples were thoroughly washed with phosphate buffer (1 mol m^{-3}, pH 7) and cut into smaller plates suitable for mechanical and osmotic deswelling measurements.

As MAP and APSP are strong electrolytes and should be fully ionized in aqueous solution, the fraction of charged units in the gel is given by $\beta = c_{im}^0/(c_{im}^0 + c_M^0 + c_{EO}^0)$, where c_{EO}^0 is the concentration of ethylene oxide units of macromonomer in the reaction solution. This implies that all negatively charged MAP and APSP monomers are incorporated into the network during synthesis and the gels stay fully ionized under the test conditions (when swelling in neutral salt solutions). The values of β are presented in Table 1. It is important to keep in mind that, in the gels under study, the charged units belongs only to the polymethacrylate chains, whereas the PEO chains contain no charged units at all, as shown in Fig. 1. Therefore, β characterizes an average charge density of the network. The fraction of charged units in the polymethacrylate chains is determined by $\beta_{loc} = c_{im}^0/(c_{im}^0 + c_M^0)$. This quantity, which characterizes the linear charge density of chains, is also given in Table 1.

2.3. Swelling and modulus measurements

The gels were swollen to equilibrium in distilled water or in aqueous NaCl solutions with the salt concentration c_s ranged from 10^{-4} to 1 mol dm^{-3}. Once equilibrium was attained, the gels were weighed and their moduli were measured. The swelling degree Q, i.e. the volume ratio of swollen gel to dry gel, was calculated from the weight of swollen gel m and the weight of initial gel m_0 as

$$Q = 1 + (\rho_p/\rho_s)[(m/m_0)/c_0 - 1] \quad (1)$$

Table 1
Conditions of preparation of the gels

Sample	Macromonomer	Ionogenic monomer	c_0 (g g^{-1})	c_M^0 (mol m^{-3})	c_{im}^0 (mol m^{-3})	β	β_{loc}
1	PEO1	MAP	0.17	60	33	0.009	0.36
2	PEO1	MAP	0.16	55	81	0.023	0.60
3	PEO1	MAP	0.18	57	260	0.067	0.82
4	PEO1	MAP	0.23	59	640	0.15	0.92
5	PEO1	APSP	0.19	63	79	0.020	0.56
6	PEO2	MAP	0.18	17	135	0.035	0.89

where ρ_p ($= 1.21$ g cm^{-3}) and ρ_s, respectively, are the densities of polymer and solvent, c_0 is the mass fraction of copolymer in the gel after preparation, which is taken to be equal to the initial total comonomer concentration (see Table 1).

The shear modulus G was determined by penetration technique as described elsewhere [11,21]. A steel sphere of radius $R = 1.9$ mm was forced down in steps into a gel plate. In each step, the penetration depth of the sphere h was measured after 30 s of relaxation as a function of applied force f (from 0.0001 to 0.01 N). All measurements were carried out at deformation $h \leq 0.2R$.

The general relation between h and f at small deformations is given by

$$h = h_0 + bf^{2/3} \tag{2}$$

where b is related to the modulus G as $b = [3/(16GR^{1/2})]^{2/3}$ [21]. As predicted by Eq. (2), reasonably straight lines are obtained for all gel samples when h is plotted against $f^{2/3}$. Shear moduli were calculated from the slopes of these lines. Standard deviation in modulus measured for several specimens of a gel was typically about 6%.

2.4. Measurements of swelling pressure

The swelling pressure was measured by the osmotic deswelling technique described elsewhere [22]. The gel samples placed in dialysis tubes were immersed in aqueous solutions of PEG (Merck, nominal molecular weight 40,000) of known osmotic pressure [23]. When equilibrium was attained, the samples were removed from the dialysis tubes and weighed. Thereafter, a predetermined amount of sodium chloride was added to each PEG solution to produce the desired salt concentration. The gels were placed back in the tubes and immersed in the solutions. Once the new equilibrium state was attained, the gels were weighed, new portions of NaCl were added, and the procedure was repeated. At the close of the experiment, the samples were dried and weighed. The dried gel weights were used to calculate the swelling degrees. In this way, the swelling pressure π, equal to the osmotic pressure of PEG solution, was determined as a function of the swelling degree and salt concentration ranged from 0.001 to 0.1 mol dm^{-3}. Although salts affect the properties of PEO solutions and gels, in case of NaCl, the salting-out of PEO chains is insignificant, especially at $c_s \leq 0.1$ mol dm^{-3} [19,24]. Thus, the osmotic pressure of PEG solutions was considered independent of c_s.

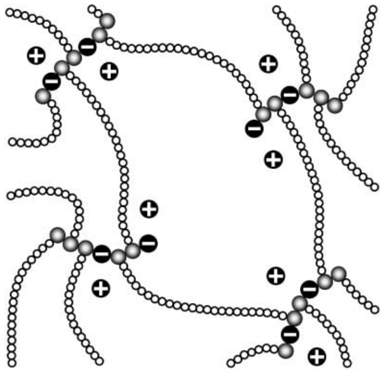


Fig. 1. Schematic illustration of a polyelectrolyte gel consisting of neutral PEO chains and negatively charged methacrylate chains. Open circles: ethylene oxide units. Grey circles: neutral units formed from the macromonomer methacrylate groups. Circles marked with minus and plus, respectively: anionic units and counterions formed from MAP or APSP.

3. Theoretical framework

The swelling pressure of a polymer gel π is a sum of the osmotic pressure π_{osm} and the elastic pressure π_{el} [3,25]

$$\pi = \pi_{osm} + \pi_{el} \tag{3}$$

This is consistent with the idea that the total free energy of the gel is split into two parts, the osmotic part leading to the gel swelling and the elastic part that restricts swelling. In turn, the osmotic pressure of a polyelectrolyte gel also consists of two contributions, the contribution from polymer–solvent mixing π_{pol} and the contribution from ion-solvent mixing and electrostatic effects π_{ion}

$$\pi_{osm} = \pi_{pol} + \pi_{ion} \tag{4}$$

The elastic pressure π_{el} is essentially the shear modulus G

$$\pi_{el} = -G \tag{5}$$

when π_{el} and G are power laws of polymer concentration with the exponent of 1/3 [25,26]. This is not the case when the network chains are strongly stretched, and the more general expressions for π_{el} were derived [25,27].

In the classical theory [3] and some recent models

[28,29], both π_{el} and π_{pol} are specified by the expressions derived for uncharged polymers, which do not include the network charge and salt content of the solution in the explicit form. The elastic pressure π_{el} is given [26,30] by

$$\pi_{\mathrm{el}} = -G_0(\phi/\phi_0)^{1/3} \tag{6}$$

where ϕ is the volume fraction of polymer, and ϕ_0 and G_0 are constants (the polymer volume fraction and the modulus for the gel in its preparation state). The polymer pressure π_{pol} can be expressed by a Flory–Huggins-type equation [3] or in the scaling form [31]

$$\pi_{\mathrm{pol}} = B\phi^{9/4} \tag{7}$$

where B is a constant (the coefficient of polymer–solvent interactions), the scaling exponent 9/4 is characteristic of a good-solvent solution. More advanced theories take into account the effects of electrostatic interactions on the chain conformation and predict G, π_{el} and π_{pol} to directly depend on the chain charge and salt concentration c_{s} [25,27]. In particular, the theory by Rubinstein et al. [25] predicts π_{pol} at high c_{s} to have the usual concentration dependence for uncharged polymers (cf. Eq. (7)) but a novel dependence on c_{s} and the ionization degree of chains β

$$\pi_{\mathrm{pol}} \sim \beta^n c_{\mathrm{s}}^{-3/4}\phi^{9/4} \tag{8}$$

where the exponent n is equal to 9/7, 3/2, and 3, respectively, for good, θ, and poor solvents.

The dominating contribution to π_{ion} is due to the translational entropy of free ions in the gel [3]. In the framework of the ideal Donnan equilibrium, it is

$$\pi_{\mathrm{ion}}^0 = \mathrm{R}T\beta c\kappa(K_{\mathrm{D}} + 1/K_{\mathrm{D}} - 2) \tag{9}$$

where R is the gas constant, T is temperature, c is the molar concentration of monomer units, $\kappa \equiv c_{\mathrm{s}}/(\beta c)$ is the reduced salt concentration, $K_{\mathrm{D}} = 1/(2\kappa) + (1 + 1/(2\kappa)^2)^{1/2}$. In the limit of low c_{s}, π_{ion}^0 is simply the pressure of an ideal gas of network counterions.

$$\pi_{\mathrm{ion}}^0 = \mathrm{R}T\beta c \tag{10}$$

In the opposite limit of high c_{s}, π_{ion}^0 has a quadratic concentration dependence.

$$\pi_{\mathrm{ion}}^0 = \mathrm{R}T(\beta c)^2/(4c_{\mathrm{s}}) \tag{11}$$

Another contribution to π_{ion} is due to electrostatic interactions between ions within the gel (both mobile and fixed). The effect of electrostatic interactions appears to be ambiguous. Indeed, the electrostatic repulsion of charges on the chains is suggested to result in a positive contribution to π_{ion} [4]. Such a contribution may be significant in strongly charged polyelectrolytes. At the same time, the fluctuations of charge density should lead to a negative osmotic-pressure contribution [14,15]. For example, for salt-free solvents, this contribution is expressed [14] as

$$\pi_{\mathrm{ion}}^c = [\mathrm{R}T\beta c/l_{\mathrm{B}} - (2l)], \qquad l_{\mathrm{B}} \ll l \tag{12}$$

where l is the distance between charged units along the chain, $l_{\mathrm{B}} = e^2/(\epsilon kT)$ the Bjerrum length, e the electron charge, ϵ the dielectric constant, k is the Boltzmann constant. The effect of fluctuations was calculated [6,28,29] using the conventional Debye–Huckel theory of simple electrolytes. It was shown that, in case of weakly charged networks, this effect is negligible. More advanced consideration of the electrostatic interactions in weakly charged polyelectrolyte solutions was made by Borue and Erukhimovich [15] using the correlation functions of the system. In their theory, the fluctuation contribution to π_{ion} may be much higher than that in the Debye–Huckel theory and comparable in value with the ideal gas term (Eq. (9)), especially in case of poor solvents.

The gels under study are composed of chains of two types: the neutral chains and the charged chains (see Fig. 1). The number of monomer units between junctions in a neutral chain coincides with the number of units in the macromonomer used. Typically, it is about 90. The average number of units between junctions (uncharged units) in a charged chain is evaluated as $1/(1 - \beta_{\mathrm{loc}})$. It ranges from 1.6 to 12.5 as β_{loc} increases from 0.36 to 0.92 (see Table 1). The charged network chains between junctions are consequently very short, much shorter than the neutral chains. They consist of not higher than two statistical segments (typically, one segment), and, hence, are very rigid as compared to the neutral chains. For this reason, we expect that the neutral chains (as weaker springs) will dominate the elasticity of the gels and π_{el} will not be affected by the electrostatic interactions. Some experimental evidences for this supposition will be shown later (see Fig. 4).

Therefore, we find π_{el} by Eq. (5) from the shear modulus G measured as a function of the swelling degree $Q = 1/\phi$. The swelling pressure π is obtained from the osmotic deswelling experiments or specified as equal to zero ($\pi = 0$) at free swelling. Using the data on π_{el} and π, the osmotic pressure is then evaluated by Eq. (3). We assume that the polymer contribution π_{pol} is dominated by the neutral network chains and, hence, independent of network charge and salt concentration. This approximation is justified because only a low fraction of monomer units of the network belongs to the charged chains; this fraction is given by the ratio $\beta/\beta_{\mathrm{loc}}$ and ranges from 0.025 to 0.16. According to this approximation and the fact that water is a good solvent for the neutral (PEO) chains, we use Eq. (7) to describe the concentration dependence of π_{pol}. The constant B is determined from the data on π_{osm} obtained at a large excess of salt. The ionic pressure π_{ion} for lower salt concentrations is then found by Eq. (4) and compared with the prediction of Eq. (9).

4. Results and discussion

4.1. Swelling of gels in salt solutions

A pronounced deswelling in low-molecular-weight salt

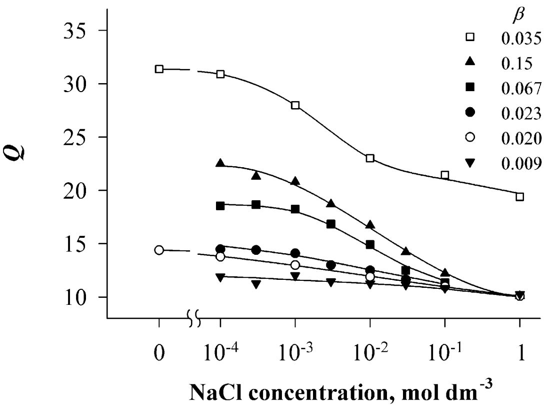


Fig. 2. Degree of swelling as a function of NaCl concentration for gels of different composition. Filled symbols: PEO1–MAP gels with varying fraction of charged units β; open circles and squares: PEO1–APSP and PEO2–MAP gels, respectively.

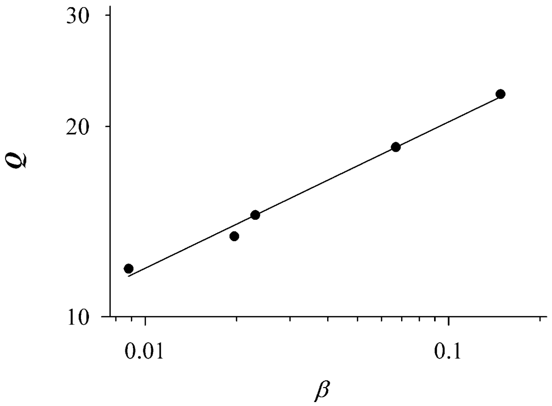


Fig. 3. Degree of swelling in 10^{-4} mol dm^{-3} NaCl as a function of fraction of charged monomer units in the gel. The best-fit line drawn through the data has a slope of 0.23 ± 0.01.

solutions is one of the basic properties of polyelectrolyte gels. When a swollen-in-water polyelectrolyte gel is immersed in a salt solution, it shrinks because the difference in the osmotic pressure inside and outside the gel decreases with increasing salt concentration [3].

Fig. 2 shows the equilibrium degree of swelling for charged PEO gels as a function of the salt concentration c_s. As expected, the swelling degree decreases with increasing salt concentration. As long as c_s is not too high, the incorporation of charged units into the network results in a gel swelling. The larger the fraction of charged units β, the higher the swelling degree. This is obviously a consequence of osmotic pressure exerted by counterions of the charged network chains. At large salt concentrations, the difference in the swelling degree of the gels disappears. This indicates that the ionic osmotic-pressure contribution becomes small as compared to the polymer one.

In Fig. 2 we compare the data for the PEO1–APSP gel and PEO1–MAP gels prepared using the same macromonomer. As is seen, the swelling curve for the PEO1–APSP gel complements well the family of curves for the PEO1–MAP gels considering the set of β values. This is consistent with the idea that the swelling degree of these gels depends only on the content of the charged units within the network but not on their chemical nature. This also supports that the PEO–MAP gels stay fully ionized under the swelling conditions as does the PEO1–APSP gel (contrary to MAP, APSP is 100% dissociated independently of pH in a very wide range).

In Fig. 3, the degree of swelling in the most dilute NaCl solution ($c_s = 10^{-4}$ mol dm^{-3}) is plotted in the log–log coordinates against the fraction of charged units in the gel. The experimental data are reasonably fitted by a straight line with the slope of 0.23 ± 0.01. The observed variation ($Q \sim \beta^{0.23}$) differs significantly from the theoretical predictions $Q \sim \beta^{3/2}$ and $Q \sim \beta^{6/5}$ [25] for salt-free polyelectrolyte gels in θ and good solvents, respectively. This can be attributed to the localization of charged units within the network as the theory assumes a homogeneous distribution of network charges. In addition, the exponent of the power law $Q(\beta)$ lower than the predicted one can indicate that the polymer and ionic parts of osmotic pressure are of the same order. The exponent of 0.6 lower than the expected one (3/2) was also observed by Silberberg-Bouhnik et al. [12] for weakly charged salt-free poly(acrylic acid) gels. This result was explained by the heterogeneous distribution of cross-links and, hence, charged units in the gel volume.

4.2. Elastic modulus of gels

The shear modulus was measured for the gels at the state of preparation and at swelling equilibrium in salt solutions of different concentration. Fig. 4 shows representative plots of the modulus as a function of swelling degree in log–log coordinates. The leftmost point of each plot (except for the filled squares) corresponds to the state of preparation, the other points, to the swelling equilibrium in salt solutions (see Fig. 2 for the dependence of swelling degree on salt

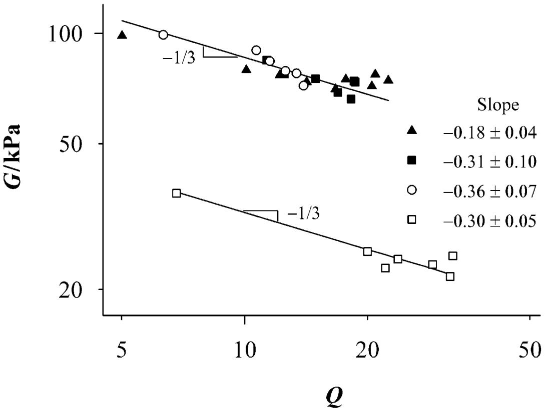


Fig. 4. Double logarithmic plot of shear modulus against swelling degree for PEO1–MAP gels with $\beta = 0.15$ (triangles) and $\beta = 0.067$ (filled squares), PEO2–MAP gel (open squares), and PEO1–APSP gel (circles). The straight lines drawn through the data show the expected slope of −1/3. More general fits to the data would lead to the slopes shown in the plot area.

concentration). The modulus decreases with increasing swelling degree, which accords with a lowering of the concentration of elastically active network chains. Within the experimental accuracy, the modulus variation is consistent with the prediction [3,30] $G \sim Q^{-1/3}$ (straight lines in Fig. 4) based on assumptions of Gaussian statistics and affine expansion of network chains. Small deviations from Gaussian elasticity (an upturn in the modulus) is only observed for the gel with the maximum charge density ($\beta = 0.15$) at high swelling degrees, which is probably caused by the strong stretching of network chains (cf. [11,32]).

As is seen from Fig. 4, the shear modulus is independent of the fraction of charged units β ranging from 0.02 to 0.15. At the same time, G correlates well with the number of neutral network chains. Indeed, this number is inversely proportional to the macromonomer molecular weight (see Table 1) because the neutral network chains are essentially the macromonomer chains and the gels were prepared with close weight concentrations of macromonomers. As the macromonomer molecular weight increases from 4000 to 12000, the number of neutral network chains decreases approximately by three times and G is lowered by a factor of ~2.6. This fact and independence of G on β support the idea stated in the theoretical section that the neutral network chains dominate the elasticity of the gels while the charged network chains are elastically inactive. In line with this idea, we suggest that the electrostatic interactions in the system do not affect the gel elasticity and the gel modulus is independent of salt concentration.

The results shown in Fig. 4 indicate that simple Eq. (6) derived for uncharged networks is valid for the charged PEO gels. The shear modulus for these gels can serve as a reasonable estimate of the elastic pressure π_{el} except, possibly, for the gel with $\beta = 0.15$ at high swelling degrees. In the latter case, the modulus will probably slightly overestimate the elastic pressure [11]. At free swelling, when the swelling pressure is $\pi = 0$, the modulus should also directly characterize the osmotic pressure π_{osm}.

4.3. Swelling pressure of gels

The swelling pressure for one of the PEO1–MAP gels was measured by the osmotic deswelling technique. The results are shown in Fig. 5 as functions of swelling degree for different salt concentrations. The free-swelling data for this gel (from Fig. 2), which refer to the zero swelling pressure, are also shown here. As expected, the swelling pressure π strongly depends on the swelling degree and salt concentration. Similar to the degree of free swelling, π decreases with increasing salt concentration, which can be attributed to a decrease in the ionic pressure π_{ion}. In the limit of high salt concentration ($c_s = 0.1$ mol dm^{-3}), the swelling pressure appears to become independent of π_{ion} small as compared to the polymer pressure π_{pol}. This is supported by the fact that, in this limit, the degree of free swelling is almost independent of the network charge density (see Fig. 2). Therefore, the swelling-pressure curve for $c_s = 0.1$ mol dm^{-3} reflects mainly the osmotic and elastic properties of the uncharged network ($\pi \approx \pi_{\mathrm{pol}} + \pi_{\mathrm{el}}$), while the difference $\pi(c_s) - \pi$ (0.1 mol dm^{-3}) approximately characterizes the ionic pressure π_{ion} at $c_s < 0.1$ mol dm^{-3}. This surely implies π_{pol} and π_{el} to be independent of salt concentration as discussed in the theoretical section. A more detailed analysis of the swelling-pressure data is given below.

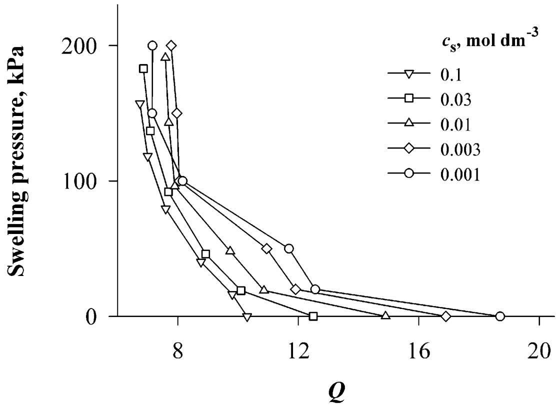


Fig. 5. Swelling pressure for the PEO1–MAP gel with $\beta = 0.067$ as a function of swelling degree at different salt concentrations.

4.4. Osmotic pressure in the high-salt limit

The osmotic pressure for $c_s = 0.1$ mol dm^{-3} found as $\pi_{\mathrm{osm}} = \pi + G$ is plotted against the swelling degree in log–log coordinates in Fig. 6. One data series is based on the osmotic deswelling results for the gel with $\beta = 0.067$ while the other series, on the free swelling experiments for gels with varying fraction of charged units β. The data related to constant β are well fit by the power law $\pi_{\mathrm{osm}} = B_{\mathrm{eff}} Q^{-9/4}$. This approximation is shown in Fig. 6 by a straight line with the slope of −9/4. A more general

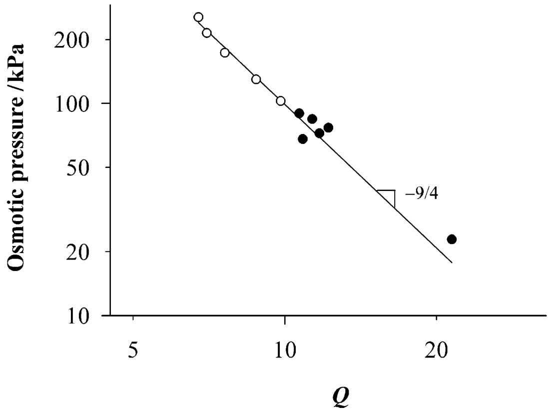


Fig. 6. Osmotic pressure of charged PEO gels at $c_s = 0.1$ mol dm^{-3}. Open circles: the gel with $\beta = 0.067$ at varying swelling pressure; filled circles: gels with different fractions of charged units at free swelling ($\pi = 0$). The straight line shows the expected slope of −9/4.

power fit to the data would yield a close scaling exponent of -2.33 ± 0.15. This is expected because the osmotic pressure at high salt concentrations should be dominated by the polymer pressure and expressed by Eq. (7). In the case of varying β, the agreement between the observed variation of π_{osm} and the $Q^{-9/4}$ expectation is not very good. The disagreement can be explained by the dependence of the 'effective' interaction coefficient B_{eff} on β and the swelling degree. Such dependence may exist because the ionic contribution to osmotic pressure is not fully negligible in the specified conditions.

The values of B_{eff} were calculated from the data shown in Fig. 6 using the least-squares fit (when possible) or simply as the ratio $\pi_{\mathrm{osm}}/Q^{-9/4}$. The osmotic deswelling measurements and the free swelling experiments is found to lead to the consistent estimates of B_{eff}. The effective interaction coefficient increases with increasing β. This corresponds to the rise in the ionic contribution to osmotic pressure. Indeed, using Eq. (4), one can write the effective interaction coefficient as $B_{\mathrm{eff}} = B + B_{\mathrm{ion}}$, where B is the 'true' interaction coefficient of Eq. (7), $B_{\mathrm{ion}} = \pi_{\mathrm{ion}}/Q^{-9/4}$ is an increasing function of β. At $\beta = 0$, the values of π_{ion} and B_{ion} should be equal to zero and, hence, the equality $B_{\mathrm{eff}} = B$ should be valid. On this basis, we found B by extrapolation of the B_{eff} data to $\beta = 0$. For PEO1-based gels, this gives $B = 16.5 \pm 1$ Mpa. The estimated value of B allows calculation of the polymer osmotic-pressure contribution by Eq. (7). In this calculation, B is assumed to be independent of salt concentration as discussed above.

The estimated polymer pressure π_{pol} is worth comparing with the osmotic pressure of semidilute aqueous solutions of PEO. With this aim, we analyzed the data of Roots et al. [23] on a high-molecular-weight PEO. The data were well fitted to Eq. (7) in the range of sufficiently high concentrations of polymer ($0.045 \leq \phi \leq 0.088$), which resulted in the interaction coefficient $B \approx 27.5$ MPa. This value is higher than the value of B found for the PEO-based gels. Hence, the osmotic pressure of PEO solutions is higher than the polymer pressure π_{pol} for the PEO gels at the same concentration. Similar results were obtained for several other polymer–solvent systems [33,34]. Furthermore, it was shown [34] that the polymer osmotic-pressure contribution of gels decreases as the network density increases. This obviously implies that B (and, hence, B_{eff}) depends on the network density being higher for looser networks. The network-density dependence of B_{eff} is probably revealed in the fact that the effective interaction coefficient for the PEO2–MAP gel is noticeably higher than that for PEO1-based gels with close β. Note that the former gel prepared from the longer PEO chains should have a looser network. For this gel, B is roughly estimated at 21.5 MPa.

4.5. Osmotic efficiency of counterions

The ionic part of osmotic pressure π_{ion} was determined (at $c_s < 0.1$ mol dm^{-3}) as the difference between π_{osm} and π_{pol}. The reduced ionic pressure was then calculated as the ratio of π_{ion} to the ideal-gas pressure of counterions RTc_{im}, where $c_{\mathrm{im}} = \beta c$ is the concentration of charged units in the gel. The reduced ionic pressure is presented as a function of the reduced salt concentration c_s/c_{im} because, within the ideal Donnan framework, this representation leads to a master curve defined by Eq. (9) and allows comparison of different data.

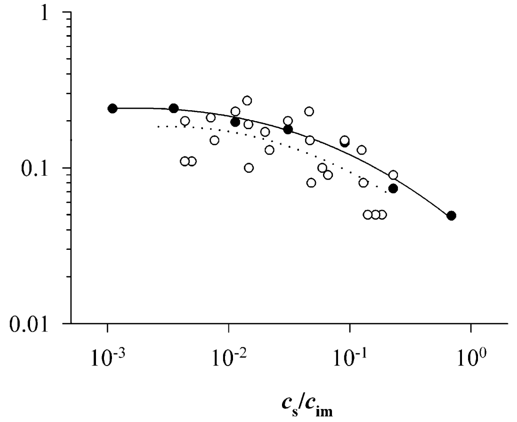


Fig. 7. Reduced ionic pressure as a function of reduced salt concentration for the PEO1–MAP gel with $\beta = 0.067$. Filled symbols: data based on the free swelling experiments; open circles: data based on the osmotic deswelling measurements. The solid and dotted regression lines are shown to help the comparison of different data.

In Fig. 7 we compare the data on π_{ion} obtained by two distinct ways for the PEO1–MAP gel with $\beta = 0.067$. As is seen, the free swelling experiments and the osmotic deswelling measurements lead to consistent results. Thus, both of these experimental methods give reliable information on π_{ion}, although the data based on osmotic deswelling have a rather large scattering.

Fig. 8 shows the reduced ionic pressure for gels with different fractions of charged units within the network. The Donnan master curve is also shown here. As is seen, the reduced ionic pressure is much less than that calculated

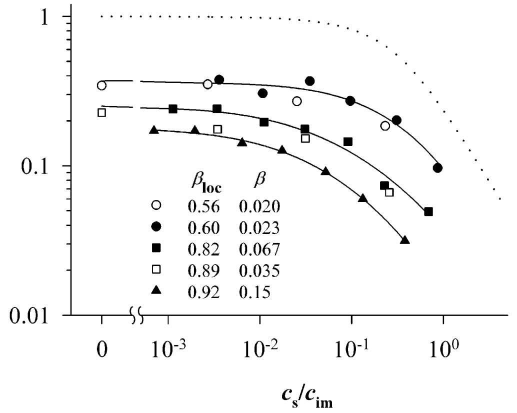


Fig. 8. Reduced ionic pressure as a function of reduced salt concentration for gels of different composition. The symbols have the same meaning as in Fig. 2. The values of β and β_{loc} are shown in the plot area. The dotted line represents the prediction of the Donnan theory.

by Eq. (9). Moreover, the reduced ionic pressure decreases with increasing network charge being controlled by the fraction of charged units in the charged chains β_{loc} rather than the average fraction of charged units in the network β. This is evident from the comparison of data for the PEO2–MAP gel and the PEO1-based gels. Close ratios $\pi_{\mathrm{ion}}/(RTc_{\mathrm{im}})$ (shown by open and filled squares) are observed for the PEO2–MAP gel and the PEO1-based gel, which have close values of β_{loc} and different β.

Low values and the β_{loc} dependence of the reduced ionic pressure can be partially explained by the condensation of counterion as the gels under study contain strongly charged chains. According to Manning's theory [16], the counterion condensation begins when the distance l between charged units along the chain becomes equal to the Bjerrum length l_{B}. In case of water at room temperature, the Bjerrum length is $l_{\mathrm{B}} \approx 0.7$ nm. The distance l is determined by the fraction of charged units in the chain, namely $l = b/\beta_{\mathrm{loc}}$, where $b \approx 0.25$ nm is the monomer unit size. The onset of counterion condensation then corresponds to the equality $\beta_{\mathrm{loc}} = \beta_{\mathrm{loc}}^{\mathrm{eff}}$, where $\beta_{\mathrm{loc}}^{\mathrm{eff}} \equiv b/l_{\mathrm{B}} \approx 0.35$. As shown in Table 1, the values of β_{loc} range from 0.36 to 0.92 being higher than $\beta_{\mathrm{loc}}^{\mathrm{eff}}$. Therefore, a part of counterions should be bound to the charged chains, i.e. osmotically passive. This part should increase with β_{loc}, in agreement with the experimental data.

In Fig. 9, we present the data of Fig. 8 corrected for the Manning condensation. To make this correction, we replace the nominal concentration of counterions c_{im} by the concentration of osmotically active counterions $c_{\mathrm{im}}^{\mathrm{eff}} = (\beta_{\mathrm{loc}}^{\mathrm{eff}}/\beta_{\mathrm{loc}})c_{\mathrm{im}}$. It is evident that the difference between the reduced ionic pressures for different gels almost disappears owing to this correction. Excepting the data on the gel with the highest β, all the data are superimposed on the same curve. This indicates that the corrected reduced ionic pressure weakly depends on the nominal network-charge density. At the same time, the data points in Fig. 9 are still far from the Donnan master curve though noticeably nearer than in Fig. 8. This means that the Manning condensation does not explain the whole magnitude of deviation between the calculated and observed values of π_{ion}. Thus, along with this type of condensation, there are some other reasons for low osmotic efficiency of mobile ions.

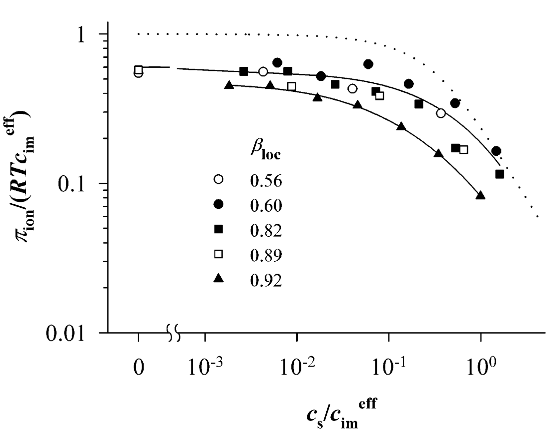


Fig. 9. Data of Fig. 8 corrected for the Manning condensation of counterions on highly charged network chains. The symbols and dotted line have the same meaning as in Fig. 8.

As shown from Fig. 9, the growth of salt concentration leads to an abrupt decrease in the reduced ionic pressure starting from $c_{\mathrm{s}} \sim 0.1c_{\mathrm{im}}^{\mathrm{eff}}$. At low c_{s}, the reduced ionic pressure is approximately constant and, hence, the ionic pressure is proportional to the ideal-gas pressure of counterions, i.e. $\pi_{\mathrm{ion}} = \phi_{\mathrm{p}}RTc_{\mathrm{im}}^{\mathrm{eff}}$, where ϕ_{p} is the osmotic coefficient. The osmotic coefficient is equal to about 0.45 for the gel with $\beta = 0.15$ and $\phi_{\mathrm{p}} \approx 0.6$ for the other samples. The observed osmotic coefficients are worth comparing with the theoretical predictions and data reported for the systems with more or less random distribution of charged units. Such a comparison allows getting a further insight into the reasons of low osmotic efficiency of counterions.

The osmotic coefficient can be estimated by Eq. (12). This equation is derived for the case when $l_{\mathrm{B}} \ll l$ but a rough estimate can be made for the onset of counterion condensation. At $l_{\mathrm{B}} = l$, Eq. (12) leads to $\pi_{\mathrm{ion}}^{\mathrm{c}} = -RT\beta c/2$. Using Eq. (10), the osmotic coefficient is then estimated as $\phi_{\mathrm{p}} = (\pi_{\mathrm{ion}}^{0} + \pi_{\mathrm{ion}}^{\mathrm{c}})/(RT\beta c) = 1/2$, which is close to the values of ϕ_{p} for the charged PEO gels. As shown by our calculations, the Borue–Erukhimovich theory [15] can also explain the differences between the calculated and observed values of reduced ionic pressure (Fig. 9). However, this theory is also developed for weakly charged chains and hardly applicable in our case. Anyhow, the comparison shows that direct electrostatic interactions between ions (both mobile and fixed) can significantly lower the ionic pressure of gels.

As to experimental data on the osmotic coefficients for the systems with approximately random distribution of network charge, one such system is semidilute solutions of weakly charged poly(acrylic acid) studied by Silberberg-Bouhnik at al. [12] using the osmotic deswelling. For this system, the osmotic coefficient was found to be equal to ~0.5 at ionization degree $\beta = 0.065$ and decreasing with increasing β. Another system is hydrolyzed polyacrylamide gels with a very low cross-link density. For the gels with $\beta \approx 0.15$, the osmotic coefficient of about 0.8 was obtained from the elastic modulus data [11]. This value seems overestimated because the non-Gaussian correction to π_{el} was not taken into account. Using this correction leads to a lower ϕ_{p} of about 0.3. The osmotic coefficients of the same order were found by Nisato et al. [35] for weakly ionized poly(acrylic acid) gels though the non-Gaussian corrections were also not used in that study. These gels however could be more heterogeneous due to their higher cross-link density.

Thus, the values of ϕ_{p} (corrected for the Manning condensation) for the PEO gels with locally distributed charges are close to those reported for some polymer solutions and gels with approximately random distribution of charged units. As indicated above, they are also close to the theoretically predicted osmotic coefficients resulting from the electrostatic interactions (fluctuations of charge density). Correspondingly, one can assume that the Manning condensation and charge density fluctuations are the main factors reducing the osmotic efficiency of counterions in the charged PEO gels. At the same time, it is not improbable that counterion condensation via mechanism proposed by Zeldovich et al. [17] plays a role in the osmotic properties of these gels.

5. Conclusions

We studied the osmotic properties of polyelectrolyte gels consisting of neutral PEO chains and strongly charged polymethacrylate chains. The fraction of charged monomer units in the network ranged from 0.009 to 0.15. The swelling degree Q and the shear modulus G of gels were measured at equilibrium in salt solutions of different concentration. The osmotic deswelling measurements of gels were also performed. On this basis, we find that the elastic properties of the gels are dominated by the neutral network chains, which have much more conformational degrees of freedom than the charged chains between junctions. We suggest that the polymer osmotic pressure π_{pol} is also dominated by the neutral network chains. Some experimental evidences for this suggestion are given. In particular, it is shown that π_{pol} and the osmotic pressure for semidilute aqueous solutions of PEO have the same concentration dependence. We show that localization of charges within the network is responsible for a lowering of the ionic osmotic-pressure contribution. This effect is caused by counterion condensation on strongly charged chains that appear in weakly (on average) charged gels. We also assume that the electrostatic interactions between ions (both free and fixed) additionally reduce the ionic pressure. Due to these two factors, the incorporation of charges into the network results in much less swelling that one can expect. However, it is difficult to synthesize a PEO network with more random distribution of charges, and the networks under study seem to be currently the only example of charged networks based on PEO.

Acknowledgements

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