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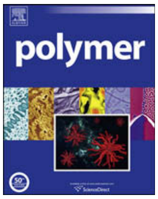

Effect of synthesis composition on the swelling pressure of polymeric hydrogels

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ABSTRACT

This paper focuses on the determination of the swelling pressure of polymeric hydrogels by variation of the composition of the monomer mixture used for synthesis via free radical polymerization. The method used is based on the principle of determining the swelling pressure at a given final volume of swelling. Data for different types of low swollen hydrogels based on weakly crosslinked poly(acrylic acid)/poly(sodium acrylate) copolymers are presented for swelling in deionised water. For polymer volume fractions ϕ_P between 0.03 and 0.30, swelling pressures p in the range of 0.20–4.23 MPa were obtained. No effect on the swelling pressure could be found by variation of monomer concentration and crosslinker content. In contrast, the content of sodium acrylate had an effect on the swelling pressure. The results are discussed based on the effect of counterion condensation.

1. Introduction

Some high molecular weight substances can form gels through absorption of liquids. Among those are highly swellable polymers on the basis of polyacrylates, which are also called Super Absorbing Polymers (SAP). The main field of application for SAP in the form of particles is the absorption and storage of liquids in hygienic products, such as diapers [1]. When coming in contact with aqueous liquids the SAP swells and forms a hydrogel. SAP can take up the 1000 fold of their dry weight, while storing the absorbed liquid even under pressure. In cosmetics such as creams, body lotions or powders, SAP provide the required humidity [2]. In agriculture, SAP serve for improving the humidity storage capacity of soils [3]. SAP are further used in controlled release applications, for example for pesticides, fertilizers, drugs or fragrances [4]. Electricity and communication cables are sealed with SAP against water penetration [5]. Recently, SAP systems were developed for self-repairing seals for tube connections in sewage systems and other applications in the field of civil engineering [6].

For the development of sealing materials based on SAP, information about the swelling pressure is of essential significance. Only few scientific studies had been concerned with the application of polymer hydrogels for sealing techniques. Such materials are used mostly empirically. Detailed analyses as well as conclusions regarding mechanisms and interrelations between polymer structure and amount, sealing volume and sealing performance are lacking.

Several different methods can be used for the determination of the swelling pressure of hydrogels. The analysis of the swelling pressure at a given pressure is the method which is described in most details [7–12]. Membrane osmometric determination of the swelling pressure is also suitable [13–15]. Other methods are investigations via ultra centrifuge [16] or the vapour pressure osmometry [17]. The analysis of the swelling pressure at a given final volume of swelling is the preferred method for investigations related to sealing techniques, and this method is also broadly used [18–21]. A new method and model for the analysis of gel blocking effects during the swelling of polymeric hydrogel particles with a fixed composition had been reported recently [22].

In this study the method for determining the swelling pressure of polymeric hydrogels relying on the analysis of the swelling pressure at a given final volume of swelling has been used for the investigation of hydrogels based on weakly crosslinked poly(acrylic acid)/poly(sodium acrylate) copolymers.

2. Experimental

2.1. Polymer synthesis

The polymer syntheses were performed by radical polymerisation of acrylic acid (AA) and sodium acrylate (SA) as functional monomers and *N*,*N*′-methylene bisacrylamide as crosslinker monomer (C) in solution. The redox system ammonium persulfate and sodium bisulfite was used as initiator. AA (99% purity; 0.02%

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hydroquinone monomethyl ether as stabilisator) was supplied by Sigma–Aldrich Chemie GmbH. *N*,*N*′-methylene bisacrylamide (>98% purity), sodium hydroxide (>98% purity), ammonium persulfate (>98% purity) und sodium bisulfite (97–100 % purity) were supplied by Merck KGaA.

AA was first dissolved in deionised water in an ice bath. Subsequently, the required amount of SA for co-polymerization was obtained through partial neutralization of AA with sodium hydroxide. Thereafter, the crosslinker was dissolved in this solution, which was then deaerated by bubbling with nitrogen for 10 min. Next, the solution was cooled down to 5 °C and stored for further 5 min. This monomer solution was then mixed with the initiator solution; the starter concentration amounts to 0.3%, relative to the total molar concentration of the functional monomers. Polymerization proceeded in closed glass tubes (height 110 mm, diameter 65 mm) for 240 min at 60 °C. Thereafter, the polymeric hydrogels were taken from the glass tubes and cut into small pieces. The hydrogel pieces were stored in deionised water at 20 °C for four days for washing out of the not reacted components, at daily exchange of the water. The fraction of extractables that were not incorporated into the network was determined based on analysis of the total organic carbon of the washing waters (TOC Analyzer 50–50; Shimadzu Germany GmbH). Then, the hydrogels were dried at 70 °C in vacuum. This drying method was chosen in order to prevent the formation of porosity in the polymer particles. The dry polymer particles were grinded in a ball mill type S1 (Retsch GmbH) and fractioned to different particles sizes in a sieving device type AS 200 control g (Retsch GmbH).

In the present study, polymers with monomer concentrations c_M of 1.3–2.6 mol l^{-1} have been used. The content of sodium acrylate κ_{SA} varied in the range of 0–100 mol% relative to the AA concentration and the content of crosslinker κ_C varied in the range of 0.6–2.4 mol% relative to the total concentration of monomer (AA + SA). The compositions of the polymeric hydrogels at the different levels of AA, SA and C are shown in Table 1.

The apparent densities shown in Table 1 have been determined via gas pycnometer (Pycnomatic ATC, Porotec GmbH). Particle sizes and span have been determined by an optical method with a scanner (Perfection 3200, Epson Germany GmbH). The particles were placed homogeneously on the glass plate of the scanner and were scanned afterwards. The volume-related grain size distributions have been analysed automatically by the Fraunhofer UMSICHT software tool "Optical Particle Analysis". The span is defined as:

$$\text{span} = \frac{d_{90} - d_{10}}{d_{50}}$$

with d_{90}: 90% of the particles are smaller or equal this diameter, d_{50}: 50% of the particles are smaller or equal this diameter, d_{10}: 10% of the particles are smaller or equal this diameter.

2.2. *Mean molecular weight of network chains*

The elastic moduli G' of the hydrogels were detected by oscillation rheology. Therefore, a reaction mixture was prepared as described in Section 2.1. The reaction mixture was transferred to a cylinder/gap system (heated to 60 °C; volume 13 ml) of a rotation rheometer (CS 10; Malvern Instruments Ltd.). After reaching the gelation point, the mixture was covered with a thin film of silicon oil to avoid evaporation of the reaction mixture during polymerisation. The reaction was monitored for 240 min by an oscillation experiment with a frequency of 1 Hz and a strain of 0.02. These parameters were in the range of the plateau moduli of the hydrogels, which was confirmed by frequency-sweep-experiments. For the calculation of the mean molecular weight of the network chains M_C (cf. Section 3.1.) the value of the elastic modulus at the end of the polymerisation was taken.

2.3. *Swelling pressure measurements*

For determination of the swelling pressure according to the principle of swelling at given volume, the device depicted in Fig. 1 was used. Details of the device are described elsewhere [22].

The measurements of the swelling pressure were done with a variation of the volume fraction of the polymer ϕ_P as defined below:

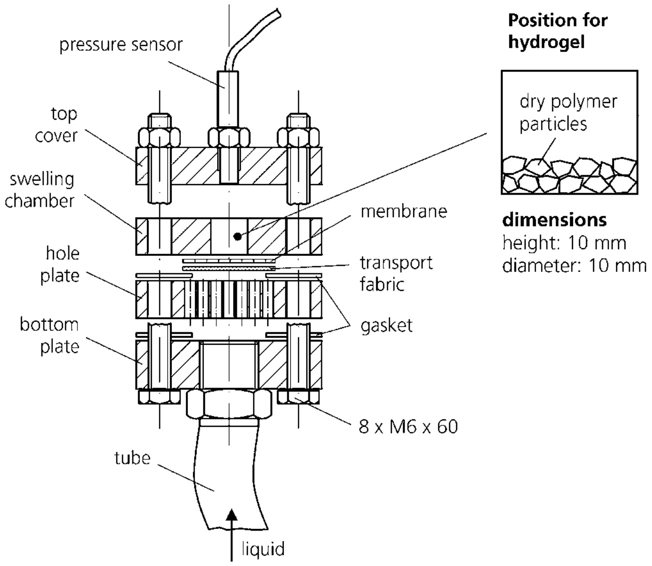

Fig. 1. Construction of the device for determining the swelling pressure according to the principle of swelling at a given volume.

Table 1
Compositions of the polymeric hydrogels.

Synthesis	c_M [mol l^{-1}]	κ_{SA} [mol%]	κ_C [mol%]	d_{50} [μm]	span [−]	Density ρ_P [g cm^{-3}]	M_C [g mol^{-1}]
AA2.6-C0.6-SA75	2.6	75	0.6	263	0.90	1.63	35579
AA2.6-C1.2-SA75	2.6	75	1.2	274	0.79	1.63	23346
AA2.6-C1.8-SA75	2.6	75	1.8	249	0.92	1.63	14828
AA2.6-C2.4-SA75	2.6	75	2.4	238	1.01	1.63	11454
AA2.6-C2.4-SA0	2.6	0	2.4	213	1.02	1.44	6159
AA2.6-C2.4-SA25	2.6	25	2.4	257	0.91	1.50	6341
AA2.6-C2.4-SA50	2.6	50	2.4	215	0.47	1.56	7811
AA2.6-C2.4-SA100	2.6	100	2.4	267	0.43	1.68	32192
AA1.3-C2.4-SA75	1.3	75	2.4	175	1.27	1.63	86600
AA1.9-C2.4-SA75	1.9	75	2.4	220	0.93	1.63	14326

$$\phi_P = \frac{V_P}{V_L + V_P} = \frac{1}{q_V}, \tag{1}$$

with: V_P: volume of polymer volume, V_L: volume of solvent and q_V: volume-related swelling degree.

A defined mass of dry polymer particles m_P was filled into the chamber. After closing the chamber the swelling solvent (deionised water) was supplied. The experiments were carried out at a temperature of 23 °C, and the swelling pressure was recorded over a period of two weeks.

From the chamber volume V_C and the polymer mass m_P, the volume fraction of the polymer ϕ_P was calculated using the apparent density ρ_P (V_p: volume of polymer):

$$\phi_P = \frac{V_P}{V_C} = \frac{m_P}{\rho_P V_C}. \tag{2}$$

3. Results and discussion

3.1. Calculation of the swelling pressure in equilibrium

The swelling pressure p in equilibrium can be described by combination of a mixing term (Flory–Huggins model), an elastic term (phantom-model) and an ionic term (Donnan potential) [23]:

$$p = p_{\text{mixing}} + p_{\text{elastic}} + p_{\text{ion}}. \tag{3}$$

The three terms in equation (3) yield the swelling pressure p as function of the volume fraction of the polymer ϕ_P:

$$p = -\frac{RT}{V_{\text{mL}}}\left(\ln(1-\phi_P) + \phi_P + \chi\phi_P^2\right) - RT\frac{\rho_P}{2M_c}\,\phi_P^{1/3}\phi_{P0}^{2/3} + RT\frac{\rho_p}{M_{\text{C-ion}}}\,\phi_P \tag{4}$$

with:

$$M_{\text{C-ion}} = \frac{(1-0,01\kappa_{SA})M_{AA} + 0,01\kappa_{SA}M_{SA}}{\kappa_{SA}} \tag{5}$$

and R: gas constant, T: temperature ($T = 296.15$ K), V_{mL}: molar volume of swelling liquid (deionised water, $V_{\text{mL}} = 18\ \text{ml mol}^{-1}$), ϕ_P: volume fraction of the polymer (cf. equation (2)), ϕ_{P0}: volume fraction of the polymer in synthesis state (cf. Table 1), χ: interaction parameter, ρ_P: density of the polymer, M_C: mean molecular weight of network chain, κ_{SA}: content of sodium acrylate (in mol%), M_{AA}: molecular weight of acrylic acid, M_{SA}: molecular weight of sodium acrylate, $M_{\text{C-ion}}$: molecular weight of polymer fraction containing counterions.

First, the mean molecular weight M_C of the network chains has been calculated from the experimentally obtained elastic modulus G' by using a phantom-model and a crosslinker functionality of 4 (see equation (6)); results are summarized in Table 1.

$$G' = RT\frac{\rho_P}{2M_C}\,\phi_P^{1/3}\phi_{P0}^{2/3} \tag{6}$$

With equations (4) and (5) the theoretical swelling pressure can be calculated. By adapting equation (4) to the measured swelling pressures one can obtain information about hydrogel structure and hydrogel inhomogeneities. A precondition is determination of the interaction parameter χ. This has been done by adopting equation (4) to describe the swelling pressure of the non ionic hydrogel (AA2.6-C2.4-SA0; $p_{\text{ion}} = 0$) as function of polymer volume fraction ϕ_P. Fitting of the experimental data (cf. Fig. 4, below) has been done using the software Microsoft Excel® and the method of minimum square deviation. An interaction parameter of $\chi = 0.58$ has been found and has been taken for all further calculations. This value of the interaction parameter is in good agreement with results of Yin [24], and Sohn and Dukjoon [25]. Yin had reported a value of $\chi = 0.56$, and Sohn and Dukjoon had determined values of $\chi = 0.59$–0.62, in both cases for hydrogels based on sodium polyacrylate in water. Because, due to the principle of swelling at a given volume (cf. Fig. 1), all the experiments were performed with hydrogels at low degree of swelling (cf. Sections 3.2 and 3.3), it was assumed that there is no significant dependency of the interaction parameter χ on the ionic term of the swelling pressure p_{ion}.

3.2. Effect of monomer concentration and crosslinker content on the swelling pressure in equilibrium

The swelling pressure as function of the volume fraction of polymer in the swelling chamber has been measured for hydrogels synthesized with varied monomer concentration (Fig. 2), and for hydrogels synthesized at varied crosslinker content (Fig. 3).

No significant effects of crosslinker content and monomer concentration could be found. This may be due to the relatively small mass related swelling degrees the polymers reach under the used conditions. The mass related swelling degree is defined as:

$$q_m = \frac{m_{\text{swollen}} - m_{\text{dry}}}{m_{\text{dry}}} \tag{7}$$

The range of volume fraction of polymer: $\phi_P = 0.03$–0.30 leads to mass related swelling degrees of q_m: 18.83–2.61.

Thus the entropic term and the elastic term are small in comparison to the ionic effects. The lines in Figs. 2 and 3 were obtained by fitting the experimental data to equation (4). Parameters as described in Section 3.1 were used. The data fitting was done by using the software Microsoft Excel® and the method of minimum square deviation. The ionic term was used as variation parameter and thus finally the concentrations of ions that contribute to producing the swelling pressure were calculated. We obtained effective ion ratios in the range of 0.2 up to 0.6 (cf. Section 3.3). As seen in Figs. 2 and 3 the theoretical data (lines) fit the experimental data very well.

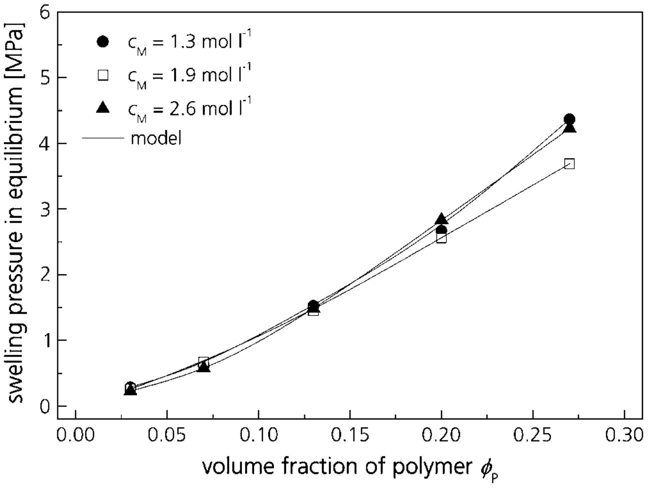

Fig. 2. Swelling pressure p in equilibrium state as function of volume fraction of polymer ϕ_P in hydrogels synthesized by variation of monomer concentration c_M ($\kappa_{SA} = 75$ mol%, $\kappa_C = 2.4$ mol%).

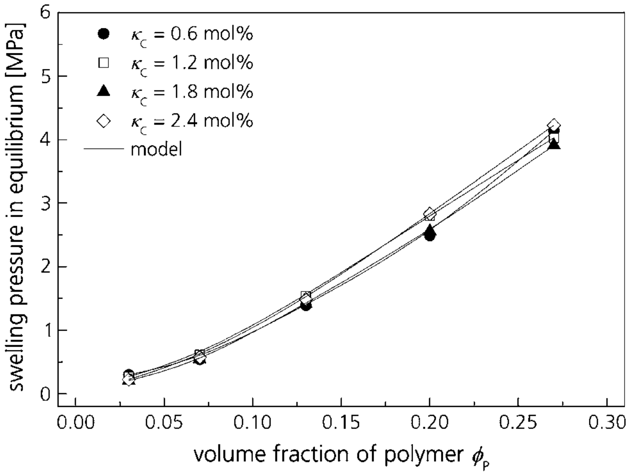

Fig. 3. Swelling pressure p in equilibrium state as function of volume fraction of polymer ϕ_P in hydrogels synthesized by variation of crosslinker content κ_C ($c_M = 2.6$ mol l^{-1}, $\kappa_{SA} = 75$ mol%).

3.3. *Effect of sodium acrylate content on the swelling pressure in equilibrium*

Fig. 4 shows the swelling pressure as function of the volume fraction of polymer in the swelling chamber for hydrogels synthesized by variation of the amount of sodium acrylate in the monomer mixture.

There is a significant influence of sodium acrylate content on the swelling pressure. The maximum value of swelling pressure is obtained for a content of sodium acrylate of $\kappa_{SA} = 75$ mol%. However, for $\kappa_{SA} = 100$ mol% there is no further increase of swelling pressure. Up to a value of volume fraction of polymer of $\phi_P = 0.12$ the values of swelling pressure are nearly identical for $\kappa_{SA} = 75$ mol% and $\kappa_{SA} = 100$ mol%. For $\phi_P = 0.12$ the hydrogels with $\kappa_{SA} = 100$ mol% have an even lower swelling pressure, and absolute values reach only about 2.5 MPa at the highest polymer volume fractions ϕ_P.

There are two reasons for this unexpected behaviour of hydrogels with $\kappa_{SA} = 100$ mol%. First, these are the only hydrogels which show a tendency to be pressed out through the stainless steel membrane of the swelling chamber (cf. Fig. 1) under the influence of the swelling pressure. This has been observed in experiments at high polymer volume fraction. The hydrogel itself is nearly incompressible; thus a small fraction of hydrogel that is pressed out of the chamber can lead to a relatively large drop of swelling pressure. Second, the only identical swelling pressure of hydrogels with $\kappa_{SA} = 100$ mol% and $\kappa_{SA} = 75$ mol% at low volume fractions of polymer is presumably due to inhomogeneities that occur during polymerisation of the hydrogels at $\kappa_{SA} = 100$ mol%. Because of the high content of ionic groups there are strong repulsive interactions between the growing polymer chains and the monomer. Thus not all functional monomers may have been incorporated into the network, and a fraction could have been washed out during the washing process after polymerization. In fact, Yin [24] reported a content of extractables in the range of 13 wt.% for weak cross-linked hydrogels with $\kappa_{SA} = 80$ mol%. In this work we obtained a fraction of extractables of 31.8 wt.% for the hydrogel of $\kappa_{SA} = 100$ mol%, of 8.2 wt.% for the hydrogel of $\kappa_{SA} = 75$ mol%, and less than 4 wt.% for the hydrogels of $\kappa_{SA} = 0$–50 mol%. The effect of monomer concentration onto resulting swelling pressure had been negligible (cf. Fig. 2); however, a lower fraction of ionic monomer incorporated into the hydrogel as compared to synthesis composition would lead to lower swelling pressure than expected. This can also be the case for the hydrogels synthesized at $\kappa_{SA} = 100$ mol%. In addition, gel inhomogeneities such as spatial fluctuations of composition and cross-linking density or even phase-separated domains, can lead to “osmotically passive” counterions [26,27], also leading to lower than expected swelling pressure.

Assuming that all ions that were present in the reaction mixture during synthesis contribute to the swelling pressure of the hydrogel the theoretical swelling pressure in equilibrium state could be calculated by equation (4). The results of these calculations compared with the experimental data are shown in Fig. 5. The hydrogel with $\kappa_{SA} = 0$ mol% has been used for the calculation of the interaction parameter χ (cf. Section 3.1), so this comparison would not have yielded additional information because the values are the same. The hydrogel with nominal $\kappa_{SA} = 100$ mol% did not show consistent values over the whole range of ϕ_P (cf. Fig. 4) for reasons discussed above. Therefore, only hydrogels with sodium acrylate content from $\kappa_{SA} = 25$ mol% to $\kappa_{SA} = 75$ mol% are used for this investigation. The concentrations of ions were obtained from the

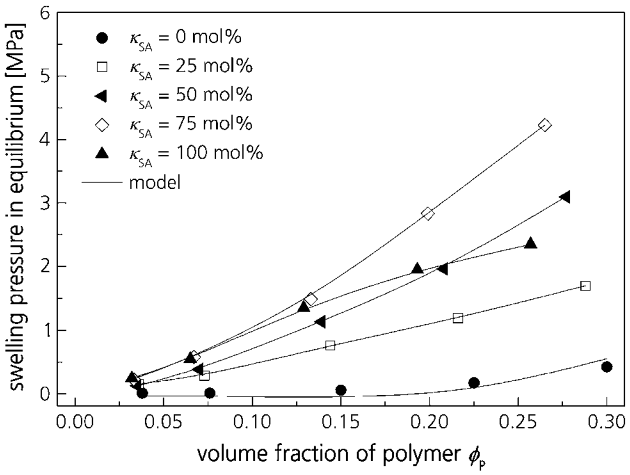

Fig. 4. Swelling pressure p in equilibrium state as function of volume fraction of polymer ϕ_P in hydrogels synthesized by variation of the content of sodium acrylate κ_{SA} ($c_M = 2.6$ mol l^{-1}, $\kappa_C = 2.4$ mol%).

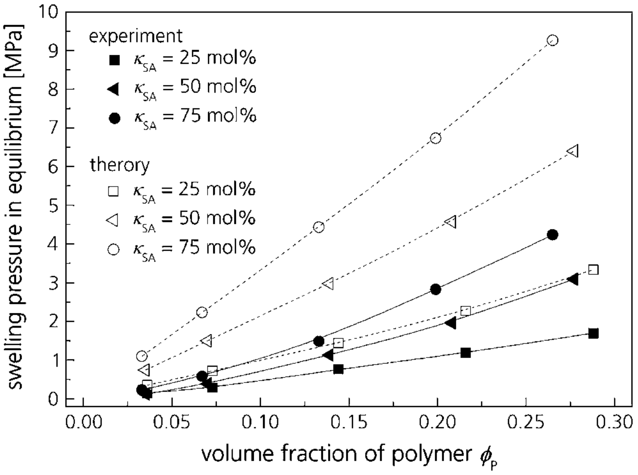

Fig. 5. Theoretical (open symbols) and experimental (filled symbols) values of swelling pressure p in equilibrium state as function of volume fraction of polymer ϕ_P for hydrogels synthesized by variation of the content of sodium acrylate κ_{SA}.

experiments by fitting the experimental data to equation (4) by using the ionic term as variation parameter (cf. Sections 3.1 and 3.2).

All values of swelling pressure that have been obtained by equation (4) are higher than the values that have been obtained by the experiments. From the differences, the contents of ions not contributing to the swelling pressure can be estimated. The reason could be counterion condensation within the polyelectrolyte hydrogel [28]. Fig. 6 shows the effective ion ratio which is the concentration of ions obtained by analysis of the experimental data in relation to the concentration of ions that were present in the reaction mixture during synthesis. As mentioned above, equation (4) has been used by assuming that all ions in the reaction mixture are incorporated stoichiometrically into the hydrogel and that all ionic groups are completely dissociated.

For the hydrogel with $\kappa_{SA} = 25$ mol% the effective ion ratio is nearly constant over the investigated range of polymer volume fraction ϕ_P. For the other hydrogels the value increases slowly from low to high values of ϕ_P but is always smaller than for the hydrogel with $\kappa_{SA} = 25$ mol%. From all values in Fig. 6 it appears that even at maximum only 50% of the ions are effective and contribute to the swelling pressure. Similar results had also been obtained for PAA-based hydrogels from the analysis of swelling data (e.g., [29]).

Hence, very clear differences in the degree of apparent counterion condensation between the different hydrogels have been found (highest for $\kappa_{SA} = 75$ mol%, lowest for $\kappa_{SA} = 25$ mol%). A quantification can be made by using the charge parameter [28,30]. The charge parameter can be calculated by using equation (8).

$$\xi = \frac{l_B}{b_P} \tag{8}$$

with l_B Bjerrum length, and b_P distance between the charges on the polymer chain. Using values of $l_B = 7.2$ Å [30] and $b_P = 16.8$ Å (calculated assuming a statistical monomer distribution and a C–C-distance of 1.4 Å), the following values of the charge parameter were obtained: $\kappa_{SA} = 25$ mol%: $\zeta = 0.43$, $\kappa_{SA} = 50$ mol%: $\zeta = 0.85$, $\kappa_{SA} = 75$ mol%: $\zeta = 1.13$.

The results that have been obtained could now be interpreted by using this charge parameter. Counterion condensation should occur for values of the charge parameter larger than 1 [28,30]. So counterion condensation should be more likely for $\kappa_{SA} = 50$ mol% and $\kappa_{SA} = 75$ mol% hydrogel, which is also shown by the results. Due to the smaller distance of charges counterion condensation occurs for these gels even below a value of 1.

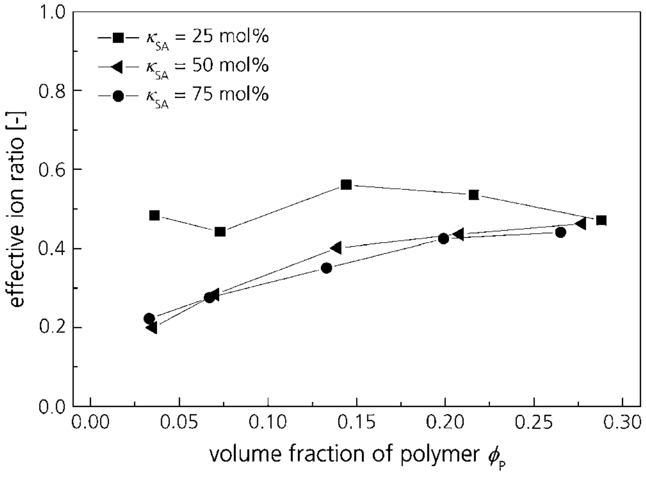

Fig. 6. Effective ion ratio as function of volume fraction of polymer ϕ_P for hydrogels synthesized by variation of the content of sodium acrylate κ_{SA}.

According to the Manning theory, there should be no counterion condensation for these polymeric hydrogels in this range for degree of ionisation. However, it should be kept in mind that the Manning theory is only valid for dilute solutions. In fact, also in other experimental studies it had been found that with increasing degree of ionisation the free swelling capacity of PAA-based hydrogels is increasing until a plateau is reached which depends on the degree of cross-linking. Even for weakly crosslinked materials, that plateau can be reached already at $\kappa_{SA} = 35$ mol% [15].

For high polymer fraction ϕ_P all hydrogels show almost identical values of the effective ion ratio (cf. Fig. 6). By constraining the hydrogel in a limited volume, relatively low degrees of swelling have been obtained in this study (cf. Section 3.1) The mass related swelling degrees are only in the range of 2.5 for these high values of ϕ_P. The polymer chains of the hydrogels are very close to each other at this ϕ_P. Therefore, fixed ion density is much higher than for the same hydrogels at free swelling equilibrium. Thus the mobility of ions is restricted due to the small liquid content. Hence, the low effective ion ratios can be understood as caused by the limited swelling due to the constraints of the given final volume.

However, the even lower effective ion ratios at low polymer volume fraction for two of the three hydrogels must still be explained. Theoretical studies had shown an effect of the chain ends on the distribution of charges [31]. At the chain ends there is a smaller electrostatic potential than in the middle of the chains. In the extreme case of very short oligomers this can result in a reduction of counterion condensation [31], and this would correspond to an increasing effective ion ratio. Transferred to the results obtained in this work, the cross-linking points could be considered as chain ends. Through their close distance (here due to highly constraint swelling), a reduction of counterion condensation could be possible, and this would result in the behaviour observed: increasing effective ion ratio with increasing volume fraction of polymer. Going to small polymer volume fraction ϕ_P and therefore high mass related swelling degrees q_m, the effective ion ratio decreases because of the effects of the relatively large charge parameter; this can be seen for $\kappa_{SA} = 50$ mol% and $\kappa_{SA} = 75$ mol% (cf. Fig. 6). Because the charge parameter is much smaller for $\kappa_{SA} = 25$ mol%, the effective ion ratio remains constant (cf. Fig. 6).

4. Conclusions

This study presents a method to determine the swelling pressure p of polymeric hydrogels which is based on the principle of determining the swelling pressure at a given final volume of swelling. Data for polymer particles made with different compositions of crosslinker, acrylic acid and sodium acrylate are presented. The investigation has been done for low swollen hydrogels with mass related swelling degrees q_m in the range of 18.83–2.61 for volume fractions of polymer ϕ_P in the range of 0.03–0.30.

No significant effect of crosslinker content κ_C and monomer concentration c_M on the swelling pressure was found. In contrast, a significant effect of sodium acrylate content κ_{SA} on the swelling pressure was found for volume fractions of polymer ϕ_P between 0.03 and 0.30, swelling pressures in the range of 0.30–4.23 MPa were obtained after times of up to 100 h for all polymeric hydrogels.

The experimental data were analysed by a theoretical model based on the Flory–Huggins theory. A good correlation between experimental data and theory was obtained. It could be shown that counterion condensation occurs in the hydrogels as function of sodium acrylate content and polymer volume fraction. The extent of counterion condensation increases with increasing sodium acrylate content from $\kappa_{SA} = 25$ mol% to $\kappa_{SA} = 50$ mol% for volume fractions of polymer ϕ_P up to 0.2. For the hydrogels with $\kappa_{SA} = 50$ and 75 mol%, extent of counterion condensation decreases with increasing polymer volume fraction.

The results obtained may be used for the design of improved sealing concepts on the basis of swellable materials. Especially the development of water swellable composite materials based on thermoplastics and super absorbing polymers will be focused on. The effects of polymer particle size on the kinetics of swelling pressure development and the water distribution in such swollen composite materials based on super absorbing polymers will be studied.

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