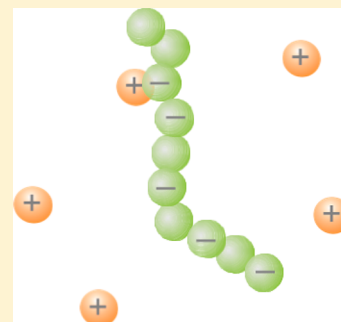


# Thermodynamic Model for Polyelectrolyte Hydrogels

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**ABSTRACT:** The composition and swelling behavior of hydrogels may be dramatically influenced by external stimuli. Polyelectrolyte hydrogels consisting of charged polymers are particularly well-known for a high sensitivity to the presence of ionic species. For a thermodynamic description of such systems, the polyelectrolyte Perturbed-Chain Statistical Association Fluid Theory (pePC-SAFT) equation of state was augmented and merged with an extension of the modeling of hydrogels. This combined approach allowed for two effects to be taken into account: first, charges along the polymer chain and their interaction with mobile ions of the same or opposite charge in aqueous solutions and, second, the elastic interactions of swellable networks and their effect on Helmholtz energy and pressure. Thus, predictions of the degree of counterion condensation on the polymer chains could be made both for vapor–liquid equilibria of aqueous polyelectrolyte solutions and for polyelectrolyte hydrogels in aqueous salt solutions. The influence of temperature and molecular weight thereon was predicted successfully, and the impact of the degree of neutralization and the effect of additional salts were examined in comparison to literature data. With the inclusion of the influence of the Donnan potential, our model gave good predictions of swellable polyelectrolyte hydrogel systems in salt solutions. Poly(acrylic acid) and poly(methacrylic acid) gels were studied along with their corresponding sodium salts. Their swelling behavior in aqueous NaCl and NaNO<sub>3</sub> solutions was examined.



## 1. INTRODUCTION

Hydrogels are polymer networks, which are capable of storing significant amounts of hydrophilic solvents. In the case of strong hydrogels, the mass of physically bound water may exceed the polymer dry weight by 1000-fold. Industrial applications and research interest not only is limited to these superabsorbent capabilities but also includes substance separation and purification processes, biomedical applications (such as wound moisture regulation or even implantable drug depots), and incorporation as sensors and actuators for microfluidic systems.<sup>1–4</sup> The latter applications in particular rely strongly on systems characterized as “smart” hydrogels in reference to the hydrogel sensitivity to external stimuli such as temperature, pH variation, and concentration changes. For years, hydrogel systems and similarly tunable polymers have been in the focus of experimental and modeling analyses.<sup>5–8</sup>

In our previous work, we focused extensively on the characterization and thermodynamic modeling of various influences on the swelling and gel compositions of systems of nonionic poly(*N*-isopropylacrylamide) (PNIPAAm) combined with aqueous mixtures of organic solvents, other polymers, and salts.<sup>9,10</sup> In the present work, we demonstrate that our model can be extended to all polyelectrolyte hydrogel systems and their physical peculiarities.

Polyelectrolytes are polymers carrying multiple positive or negative charges along their chain, with each such fixed charge theoretically having electrostatically attached counterions. This results in an overall-neutral molecular complex. In solution, however, counterions have the ability to dissociate, and by this release of ions, a charged polyion with unusual physical characteristics and unique properties is formed. These proper-

ties are highly relevant for industrial applications such as purification, in which, for example, semipermeable, negatively charged, polyelectrolyte membranes employ electrostatic repulsion to produce an anion-impenetrable membrane that remains penetrable by cations.<sup>11</sup> It is obvious that, by carrying net charges along the polymeric chain, molecules obtain a significantly higher hydrophilicity and dissolve much more easily in aqueous solutions or, in the case of hydrogel systems, are capable of much higher degrees of swelling and water uptake.

The experimental and theoretical description of polyelectrolytes has long been the focus of research<sup>12–14</sup> and with early modeling approaches employing Gibbs energy models.<sup>15</sup> An important contribution was the Gibbs model by Maurer and Prausnitz,<sup>16</sup> which was further developed by Orlov et al. for special hydrogel systems.<sup>17</sup> In extensive research on both the gel phase and the structural behavior of the polymer, molecular dynamics<sup>18,19</sup> and Monte Carlo<sup>20,21</sup> methods have been successfully employed. More recently, Naeem and Sadowski<sup>22,23</sup> proposed an approach for the thermodynamic description of polyelectrolyte solutions based on an equation of state and derived the polyelectrolyte Perturbed-Chain Statistical Association Fluid Theory (pePC-SAFT).

In our present work, we further develop this latter approach and contribute a new thermodynamic model for polyelectrolyte hydrogel systems, which has not, to our knowledge, been previously reported using equations of state. For the

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thermodynamic description and behavioral prediction of polyelectrolyte hydrogels, particular attention was paid to each of two augmentations: (a) the effect of fixed charges at the polymer chains, with their impact on the polymer structure, ion pairing, ionic interactions, and the Donnan potential and (b) the cross-linkages constituting the gel and immobilizing the polymer.

## 2. THERMODYNAMIC MODEL

The fundamental model applied for the thermodynamic description in our work is the Perturbed-Chain Statistical Association Fluid Theory (PC-SAFT). This branch of the SAFT family was developed by Groß and Sadowski<sup>24–26</sup> more than a decade ago and is founded on the equation of state proposed by Chapman et al.<sup>27</sup> SAFT is based on statistical thermodynamics and can precisely predict the intensive residual Helmholtz energy ( $a^{\text{residual}}$ ) of a system, i.e., the difference between the Helmholtz energies of an ideal gas and a real system. In PC-SAFT, molecules are represented as chains of spherical segments upon which energetic contributions are superimposed. These may account for repulsive forces (hard chain contribution) and attractive forces (dispersive and associative contributions). Several other extensions can be applied, such as the Debye–Hückel term given by Held et al.,<sup>28</sup> which is used in the present publication for the representation of the electrostatic forces of dilute ions in aqueous solutions. Another example is our previously described procedure for the thermodynamic description and behavioral prediction of swellable hydrogels, taking further elastic contributions to energy and pressure into account.<sup>9</sup> Thus, for PC-SAFT in this work,  $a^{\text{residual}}$  results in the sum of the hard chain, dispersion, association, electrostatic, and elastic Helmholtz energies, as given in eq 1.

$$a^{\text{residual}} = a^{\text{hard chain}} + a^{\text{dispersion}} + a^{\text{association}} + a^{\text{electrostatic}} + a^{\text{elastic}} \quad (1)$$

**2.1. Polyelectrolyte Peculiarity.** To account for the unusual physical attributes of polyelectrolytes, however, the PC-SAFT must be further augmented. Here, the model developed by Naeem and Sadowski<sup>22</sup> is used and augmented. The idea proposed by Manning<sup>29</sup> is the foundation of the theory, that polyions with completely dissociated counterions may develop excessively high local charge densities, and at the cost of lowering the entropy over the length of the chain, counterions may condense at regular intervals along the polymer chain. Due to such ion pair formation along the chain, the average distance  $b$  between two net charges increases and the Manning parameter  $\xi$ , which is related to the charge density, is diminished.

In eq 2,  $l_B$  is the Bjerrum length for 1:1 electrolytes according to eq 3, with  $e$  being the elementary charge,  $\epsilon$  the dielectric constant of the medium,  $k_B$  the Boltzmann constant, and  $T$  the temperature.

$$\xi = \frac{l_B}{b} \quad (2)$$

$$l_B = \frac{e^2}{4\pi\epsilon k_B T} \quad (3)$$

With values of  $\xi$  being larger than unity in the case of univalent counterions, Manning predicts a condensation of the free counterions to form ion pairs with the charged polymer segments. However, the remaining fixed polyion charges may still cause a significant increase in chain stiffness due to

repulsive electrostatics, resulting in a non-negligible influence on the hard chain reference fluid of pePC-SAFT. Thus, the equilibrium constant  $K$ , given in eq 4, is required for knowledge of the extent of counterion condensation.

$$K = \exp \frac{e^2}{4\pi\epsilon k_B T b} \quad (4)$$

The maximum distance of charges on the chain  $b$  in  $K$  reads as follows:

$$b = \frac{d_p m_p^{\text{seg}}}{c_p^{\text{seg}}} \quad (5)$$

Here, the pure-component parameter  $m_p^{\text{seg}}$  represents the number of segments of a polymer chain, while  $c_p^{\text{seg}}$  represents the number of charged monomeric units of the “naked” chain with all counterions dissociated. The temperature-dependent segment diameter of the polymer  $d_p$  is obtained according to the general eq 6, with the segment diameter parameter  $\sigma_i$  and dispersion energy parameter  $u_i/k_B$ .

$$d_i = \sigma_i \left( 1 - 0.12 \times \exp \left( \frac{-3u_i}{k_B T} \right) \right) \quad (6)$$

In the case of univalent conventional ions,  $c_i^{\text{seg}}$  equals  $m_i^{\text{seg}}$  in our model. For a given species of polyelectrolyte,  $c_i^{\text{seg}}$ , the number of charged units per chain, results from eq 7. Here,  $n_i$  is the number of monomeric units per polyelectrolyte chain. The degree of neutralization  $\alpha$  is an experimentally determined property, describing the molar extent at which, for example, the electrostatically neutral acid groups of an organic poly acid are chemically neutralized by a base, such as NaOH. The counterions, and thus the chain charges, are introduced by such neutralization reactions, yielding the polyelectrolyte.

$$c_i^{\text{seg}} = \alpha n_i \quad (7)$$

Calculations involving binary interactions in pePC-SAFT, e.g., the calculation of intermolecular energies, use simple combining rules, as in eqs 8 and 9. Here, the interaction parameter  $k_{ij}$  is introduced, the only binary component parameter used in the model. Notably, in our approach, the original energy-combining rule is modified insofar as, due to the electrostatic repulsion of equivalently charged segments of the polyion and free ions, the dispersion energy is reduced by the factor  $1 - \psi$  (eq 10). The fraction of actually charged monomers,  $\psi$ , is calculated from the degree of neutralization,  $\alpha$ , and the degree of counterion condensation,  $\beta$ . By the same reasoning, in the case of equivalently charged, mobile ionic species  $i$  and  $j$ ,  $\psi$  is set to unity, which is also valid explicitly for the case of  $i = j$ .  $\psi$  equals zero for all other component combinations, in accordance with the standard PC-SAFT procedure.

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \quad (8)$$

$$u_{ij} = \sqrt{u_i u_j} (1 - k_{ij}) (1 - \psi) \quad (9)$$

$$\psi = \alpha (1 - \beta) \quad (10)$$

Analogously, eq 6 may be used to calculate the respective binary variable  $d_{ij}$ , using the binary quantities  $\sigma_{ij}$  and  $u_{ij}$ . Consequently, as the dispersive cross interactions  $u_{ij}$  can be

Table 1. Pure-Component Parameters

	$m_i^{\text{seg}}/M_i$ segments per molecular weight mol g <sup>-1</sup>	$\sigma_i$ segment diameter Å	$u_i/k_B$ dispersion-energy parameter K	$N_i^{\text{assoc}}$ number of association sites	$\epsilon^{\text{AiBi}}/k_B$ association-energy parameter K	$\kappa^{\text{AiBi}}$ association-volume parameter	ref.
water	0.06687	$f(T)^a$	353.95	2	2425.67	0.04509	28
PAA/PA <sup>-</sup>	0.01600	4.2000	249.50	see eq 15	2035.00	0.33584	32
PMAA/PMA <sup>-</sup>	0.02600	3.7000	249.50	see eq 15	2610.00	0.07189	32
Na <sup>+</sup>	0.04350	2.8232	230.00	0			31
Cl <sup>-</sup>	0.02821	2.7599	170.00	0			31
NO <sub>3</sub> <sup>-</sup>	0.01613	3.2445	130.00	0			31

$$^a \sigma_{\text{water}} = 2.7927 \text{ Å} + 10.11 \text{ Å} \times \exp(-0.01775 \times T/\text{K}) - 1.1417 \times \exp(-0.01146 \times T/\text{K}).$$

neglected for small mobile ions  $i$  and  $j$  that are equivalently charged, the calculation of  $d_{ij}$  can be simplified to eq 11.

$$d_{ij} = \sigma_{ij}(1 - 0.12) \quad (11)$$

Another alternative to eq 4 for representation of the condensation and dissociation equilibrium constant  $K$  is the law of mass action (LMA), given in eq 12 for the case of an anionic polyelectrolyte monomeric unit  $A$  with cation  $B$  forming the ion pair  $BA$ .

$$K = \frac{\phi_{BA}}{\phi_B \phi_A} \quad (12)$$

Here,  $\phi_i$  are the volume fractions of charged segments of the anionic polymer and its counterions or added ions, calculated from the mole fractions  $x_i$  according to eq 13. For calculation of the volume fractions of other, uncharged components,  $c_i^{\text{seg}}$  is to be replaced by the segment number  $m_i^{\text{seg}}$ .

$$\phi_i = \frac{x_i c_i^{\text{seg}} d_i^3}{\sum_j x_j m_j^{\text{seg}} d_j^3} \quad (13)$$

From the LMA, the degree of counterion condensation,  $\beta$ , i.e., the fraction of charged monomeric units that form ion pairs, is calculable (eq 14).  $\beta$  thus represents a fraction of the potentially charged monomer units  $\phi_{\text{ch}}$ . Consequently, the volume fractions in the LMA (eq 12) can be written as  $\phi_{BA} = \beta \phi_{\text{ch}}$ ,  $\phi_A = (1 - \beta)\phi_{\text{ch}}$ , and  $\phi_B = (1 - \beta)\phi_C + \phi_{\hat{C}}$ . Here,  $\hat{C}$  represents an additional cation, which may be introduced into the system with an extra salt and is of the same type as the inherited polymer's counterion  $C$ .

By solving the LMA as in eq 14,  $\beta$  is obtained as the moles of ionic monomer/counterion ion pairs in relation to moles of charged monomers when all counterions are dissociated from the chain.

$$\beta = 1 + \frac{K\phi_{\hat{C}} + 1}{2K\phi_C} - \sqrt{\frac{1}{4} \left( \frac{-2K\phi_C - K\phi_{\hat{C}} - 1}{K\phi_C} \right)^2 - \frac{\phi_C + \phi_{\hat{C}}}{\phi_C}} \quad (14)$$

Our methodology differs from that of Naeem<sup>22</sup> or Kramarenko et al.<sup>30</sup> in that, first, we do not simplify the volume fraction of effectively charged monomeric units  $\phi_A$  being equal to the volume fraction of free counterions  $\phi_C$  and, second, with  $\hat{C}$ , we explicitly account for an additional salt which may contribute to the counterion species.

The value of  $\beta$  strongly influences the calculations within the pePC-SAFT energy contributions, viz., the hard chain and electrostatic interactions, given in detail in the Appendix. The contributions of dispersion and association are not modified but heavily influenced both by the reduction of dispersive

energy, as stated in eqs 9 and 10, and by the correction for the number of association sites  $N_i^{\text{assoc}}$  along the polyion component. The latter correction, eq 15, is newly proposed and originates in the assumption that only those acrylic acid or acrylate groups not occupied by condensed counterions can participate in hydrogen bonding.

$$N_i^{\text{assoc}} = n_{\text{monomer}}(1 - \alpha\beta) \quad (15)$$

The elastic contribution equation for the case of hydrogel systems is untouched, as the conformational influence of charge–charge repulsion within the polymer chain is corrected in the charged hard chain term. Details regarding the employed model expressions are given in the Appendix.

**2.2. pePC-SAFT Parameters.** For calculation via pePC-SAFT, each molecular species in a mixture has to be defined using a set of pure-component parameters. Elementary input quantities for the chain model of PC-SAFT and basic short-range attractive interactions are used for the segment number  $m_i^{\text{seg}}$ , the segment diameter  $\sigma_i$ , and dispersion-energy parameter  $u_i/k_B$ . The number of hydrogen bonding sites  $N_i^{\text{assoc}}$  is defined, and the association-energy parameter  $\epsilon^{\text{AiBi}}/k_B$  and association-volume parameter  $\kappa^{\text{AiBi}}$  are adjusted in accordance with the molecular structure. For the optional swelling contribution, the network functionality parameter  $\Phi$  can be set to values different from the ideal value of 4 in tetrahedral network structures. For our qualitative and predictive swelling calculations of polyelectrolytes, however, we did not alter the  $\Phi$  parameter from its ideal value.

Because the electrostatic contribution and the charged chain augmentation do not require any adjustable parameters, there is a maximum of only five pure-component parameters per chemical species, which are summarized in Table 1. Notably, the segment diameter parameter for water is adjusted with respect to the density anomaly and is thus not simply a scalar. Table 2 presents the nonzero binary adjustments. The  $k_{ij}$  parameters of the ions were adjusted with respect to the osmotic coefficients and solution density.<sup>31</sup>

### 3. RESULTS

When thermodynamically describing and predicting the behavior of polyelectrolyte hydrogel systems, particular attention must be paid to both the effect of fixed charges and the cross-linkage constituting the gel character, along with the implications of the latter on the elastic energy and pressure in the gel. The systems evaluated in the present work address aqueous solutions of charged polyions with their counterions, with and without additional salts. Both cross-linked and non-cross-linked systems are evaluated, as well as the influence of

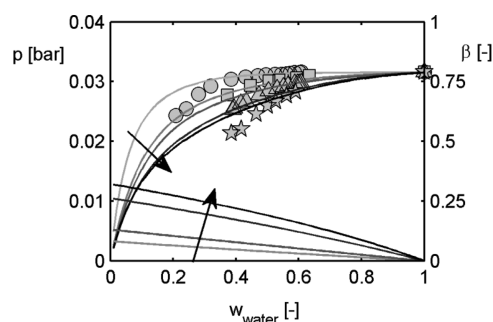
Table 2. Binary Interaction Parameters Used in This Work<sup>a</sup>

component <i>i</i>	component <i>j</i>	$k_{ij}$	ref.
PAA/PA <sup>−</sup>	water	−0.12	this work
PMAA/PMA <sup>−</sup>	water	−0.11	this work
Na <sup>+</sup>	water	0.000477	31
Cl <sup>−</sup>	water	−0.25	31
NO <sub>3</sub> <sup>−</sup>	water	−0.3	31
Cl <sup>−</sup>	Na <sup>+</sup>	0.3166	31
NO <sub>3</sub> <sup>−</sup>	Na <sup>+</sup>	−0.1350	31

<sup>a</sup>All other  $k_{ij}$  values are set to zero.

the degree of neutralization  $\alpha$ , which largely dictates the polyelectrolyte properties.

**3.1. Aqueous Polyelectrolyte Solutions.** The impact of  $\alpha$  is distinctly shown in Figure 1. In the given system of water

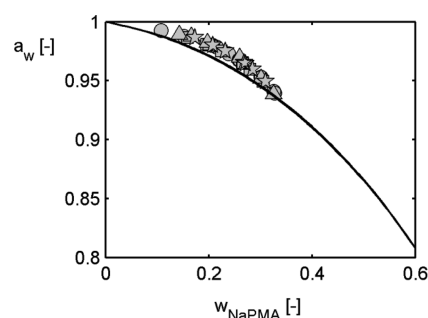


**Figure 1.** Vapor pressure of the the water/NaPA (4310 g mol<sup>−1</sup>) mixture and the corresponding counterion-condensation fraction  $\beta$  at 298.15 K and different degrees of neutralization  $\alpha$ , depending on the water weight fraction. Lines represent the model; symbols give the experimental vapor pressure data as used by Naeem and Sadowski<sup>22</sup> for  $\alpha = [0.00, 0.35, 0.50, 0.85]$ ; the arrows and five shades of gray indicate increasing  $\alpha$  values 0.00, 0.35, 0.50, 0.85, and 1.00.

and sodium poly acrylate (NaPA), pePC-SAFT pure-component parameters of non-cross-linked poly(acrylic acid) PAA, as taken from the literature,<sup>32</sup> were used to fit the binary  $k_{ij}$  to the mixture with water. The water activity, and thus the vapor–liquid equilibrium (VLE), are described well over a large concentration range. Notably, in highly concentrated polymer systems, both experiments and the model have their limitations. In applying the modifications to the model discussed above, i.e., introducing  $\alpha$  values greater than zero, PAA monomers are successively replaced with sodium poly acrylate (NaPA) in which the same parameters are used for PA<sup>−</sup> and PAA (except the change in molecular weight due to hydrogen loss). Na<sup>+</sup> pePC-SAFT parameters were taken from the literature.<sup>31</sup> With increasing  $\alpha$  values, the vapor pressure dropped significantly in the PA<sup>−</sup> system, in comparison to the uncharged PAA system, which is correctly predicted by the model.

In the same figure on the second axis, the corresponding calculated values of the counterion-condensation fraction  $\beta$  are given. Three main observations can be made. First, at very low polymer concentrations, nearly all counterions are dissociated from the chains, so that  $\beta$  is near zero. Second, increasing polymer concentrations, and thus increasing counterion concentrations, result in a nearly linearly increasing degree of counterion condensations. Third, the introduction of more charges at the polymer chains leads to an increasing charge density and, consequently, more ion pairs are formed at the chain to reduce the local net charge density.

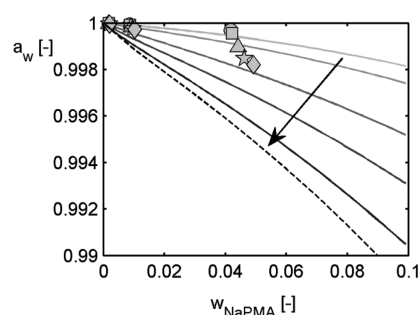
For substituting the polyelectrolyte NaPA with sodium polymethacrylate (NaPMA), we applied the pePC-SAFT pure-component parameters from poly(methacrylic acid) (PMAA) from the literature.<sup>32</sup> As shown in Figure 2, with  $k_{ij} = -0.11$



**Figure 2.** Dependence of the water activity in the water/NaPMA ( $\alpha = 1$ ) mixture on the weight fraction of the polyelectrolyte. Symbols represent experimental data<sup>33</sup> (circle: 10 000 g mol<sup>−1</sup>, 298.15 K; squares: 10 000 g mol<sup>−1</sup>, 323.15 K; triangles: 20 500 g mol<sup>−1</sup>, 298.15 K; stars: 20 500 g mol<sup>−1</sup>, 323.15 K), and congruent lines show the four corresponding pePC-SAFT calculations.

between PMA<sup>−</sup> and water at the fully neutralized polymer, i.e.,  $\alpha = 1$ , the model quantitatively describes the water activity and correctly predicts the negligible influence of temperature and molecular weight.

In contrast to the NaPA hydrogels, in the NaPMA system, the predicted influence of the degree of neutralization  $\alpha$  is slightly overestimated. As Figure 3 demonstrates, the comparison with experimental data displays qualitative agreement and accurate trends.



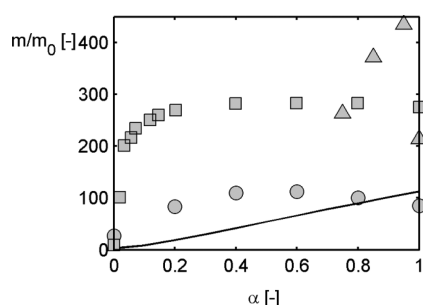
**Figure 3.** Dependence of the water activity in the water/NaPMA mixture on the polyelectrolyte weight fraction for different degrees of neutralization at 298.15 K. Experiments are represented by symbols<sup>34</sup> (circles:  $\alpha = 0.05$ ; squares:  $\alpha = 0.10$ ; triangles:  $\alpha = 0.30$ ; stars:  $\alpha = 0.50$ ; diamonds:  $\alpha = 0.80$ ). The lines represent the corresponding pePC-SAFT calculations, with shades of gray darkening to the dashed line of  $\alpha = 1$ .

**3.2. Polyelectrolyte Hydrogels in Water.** By using the obtained binary  $k_{ij}$  values in the swelling calculations, i.e., incorporating the elastic contributions to account for the swelling effects, polyelectrolyte hydrogel systems can be modeled. Theoretical assessments of the influence of  $\alpha$  suggest an increasing degree of swelling (DoS) in water with increasing neutralization. With the introduction of more charges at the polymer chain, the polyelectrolyte becomes more hydrophilic and can therefore store more water in the gel. Furthermore, the free counterions in the gel attract additional water but cannot



leave the gel phase without violation of the electroneutrality condition.

Figure 4 makes it obvious that our model prediction is correct, with the DoS (i.e., the mass of the swollen gel  $m$  over

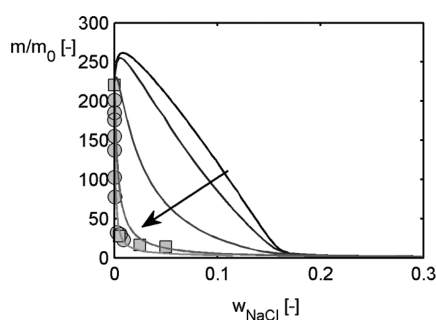


**Figure 4.** Degree of swelling  $m/m_0$  depending on the degree of neutralization  $\alpha$  in the water/NaPA system at 298.15 K. Symbols represent experimental data (circles;<sup>35</sup> squares;<sup>36</sup> triangles<sup>37</sup>). The line illustrates the model prediction.

the mass of the dry polymer  $m_0$ ) increasing to many times its original value with increasing  $\alpha$ . Literature data supports our postulation that charged gels are far greater absorbers than uncharged gels.

A comparison of the development of the experimental degree of swelling found by different researchers is not quantitatively reasonable, due to different gel production procedures. Moreover, even the expected qualitative similarity is inconsistent, suggesting significant difficulties in the accurate characterization and measurement of the gel swelling. Whereas Buchanan et al.<sup>35</sup> observe a maximum in the swelling at 50% neutralized gels after a relatively moderate increase, Philippova et al.<sup>36</sup> find a large plateau region at  $\alpha > 0.2$  after a very intense increase, while Lee and Huang<sup>37</sup> repeatedly observe a steep increase in the swelling until, at  $\alpha = 1$ , another sharp swelling decrease is observed. These inconsistencies strongly suggest caution regarding the experimental swelling data of polyelectrolyte gels.

**3.3. Polyelectrolyte Hydrogels in Salt Solutions.** So as to assess the ability of the model to predict the behavior of systems of higher complexity, we also examined the above-presented systems of water and polyelectrolyte with the addition of a supplemental salt, thereby adding another two mobile species to the system. Figure 5 shows the NaCl



**Figure 5.** Degree of swelling of the NaPA hydrogels with respect to the weight fraction of NaCl added to the aqueous solution at 298.15 K. Symbols represent akin related experimental data for the swelling systems (circles;<sup>37</sup> squares<sup>39</sup>); lines give the model prediction without the Donnan potential and with increasing Donnan potential strength along the arrow ( $\Delta\omega = 0, -0.0001, -0.001, -0.01, -0.1$  V).

influence on the swelling of the completely neutralized, aqueous NaPA system. As this figure shows, the experimental data suggest a very extreme shrinkage of the hydrogel for very small amounts of the additional salt in solution. Although the model also predicts a strong influence on the swelling, it takes the form of a rather delayed gel collapse at higher salt concentrations.

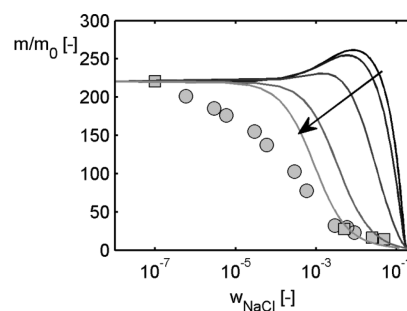
The physical cause of the decreased swelling is obvious once the influence of the charged chains is understood: the higher activity of counterions inside the gel, according to the law of mass action, causes an increase in ion pair formation. Consequently, electrostatic effects are screened and the hydrophilicity of the polyion decreases, resulting in lower water storage capacity: the gel shrinks. The discrepancy in Figure 5 between the experimental results and the model prediction is clearly unsatisfying, however, suggesting that some physical effect may have been overlooked.

The solving approach holds that, between two phases containing mobile cations and anions (e.g.,  $\text{Na}^+$  and  $\text{Cl}^-$ ) and immobile polyanions (e.g.,  $\text{PA}^-$ ), an electrical Donnan potential difference may exist.<sup>38</sup> The Donnan potential difference  $\Delta\omega = \omega^{\text{II}} - \omega^{\text{I}}$  arises from the greater number of  $\text{Na}^+$  ions present inside the gel than in the solution phase, and vice versa for the  $\text{Cl}^-$  ions, required for electroneutrality. A possible objective function (OF) for the solver algorithms (eq 17) can be obtained from the equilibrium conditions for the electrochemical potential, as given in eq 16, for the component  $i$  in phase A, with  $F$  being the Faraday constant and  $\mu_{0,i}^+$  being the reference standard potential of the pure component. This form can be achieved by equating  $\mu_i^A$  to  $\mu_i^B$  while using the relation  $f_i = x_i \gamma_i f_{0i}$  to replace the bracketed expression, where the fugacity  $f_i$  is defined as the product of mole fraction  $x_i$ , activity coefficient  $\gamma_i$ , and pure-component fugacity  $f_{0i}$ .

$$\mu_i^A = \mu_{0,i}^+ + RT \times \ln(x_i^A \gamma_i^A) + z_i F \omega^A \quad (16)$$

$$\text{OF} = \frac{f_i^{\text{I}}}{f_i^{\text{II}} \times \exp\left(\frac{\Delta\omega z_i F}{RT}\right)} - 1 = 0 \quad (17)$$

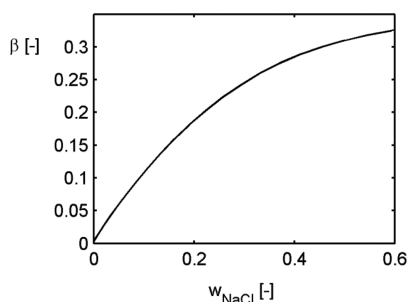
Thus, Figure 5 shows not only the previously described prediction neglecting the Donnan potential but also the influence of nonzero potentials on polyelectrolyte hydrogel swelling with additional salt. Values of  $\Delta\omega$  in the region from  $-0.01$  to  $-0.1$  V, known as common values in, for example, membrane technology, are able to quantitatively illustrate the strong influence of NaCl. Furthermore, in considering Figure 6, which focuses on the very small salt concentration range, the



**Figure 6.** Water/NaPA/NaCl system presented in Figure 5, with a focus on the effect of  $\Delta\omega$  at low NaCl concentrations with a semilog scale.

reversal of the trend produced by the Donnan influence at small salt concentrations becomes obvious. The impact of the interplay between fixed and mobile charges at low concentrations is apparently underestimated by the model for  $\Delta\omega = 0$ , which produces excessively high polymer fugacities, thus suggesting the necessity of specifying the Donnan potential.

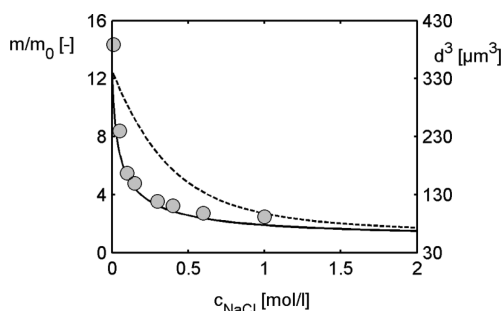
The influence of salt on the ion pair formation is evaluated via the counterion-condensation fraction  $\beta$  presented in Figure 7. In the highly swollen gel without additional salt, hardly any



**Figure 7.** Influence of added NaCl on the fraction of counterion condensation  $\beta$  in the NaPA hydrogel system with  $\Delta\omega = -0.01$  V at 298.15 K.

ion pairs are present. With increasing salt concentration, however, the condensation significantly increases, at first rapidly, with a slowly decelerated gain at salt mass fraction  $>0.2$ .

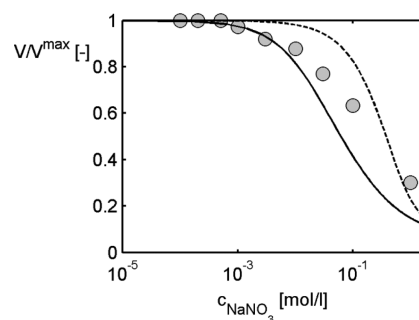
Specifying the Donnan potential in the modeling of another polymer system gives very good prediction results, as shown in Figure 8. Here, an averaged Donnan potential of  $-0.06$  V is



**Figure 8.** Influence of NaCl on PMAA swelling at 298.15 K. Symbols represent the experimentally observed swelling of the cubic diameter  $d$  of hollow microgels;<sup>41</sup> the lines give the model predictions of  $m/m_0$  with  $\Delta\omega = 0$  V (dashed line) and  $\Delta\omega = -0.06$  V (solid line).

used, in accordance with the experimental results of Safronov et al.,<sup>40</sup> who measured Donnan potentials of about  $-0.04$  to  $-0.08$  V in PMAA hydrogels. The experimental swelling results reported by Kozlovskaya et al.<sup>41</sup> for the water/PMAA/NaCl system demonstrate a strong agreement with our model predictions. Notably, they measured the diameter of hollow hydrogel capsules, resulting in observance of a much larger minimum swelling, which allowed for only a qualitative comparison with our model. These data do, however, display a very reasonable degree of influence of the Donnan potential on the impact of the NaCl on the polyelectrolyte swelling.

If one also exchanges the added salt, the experimental data of Zhang et al.<sup>42</sup> for the system water/PMAA/NaNO<sub>3</sub> correspond well to the model for prediction of the swelling with  $\Delta\omega = -0.06$  V; see Figure 9. Because only the thickness  $d$  of a planar



**Figure 9.** Influence of NaNO<sub>3</sub> on the swelling of PMAA hydrogels in water at 298.15 K. Symbols represent the experimental change in volume<sup>42</sup> of swelling brushes ( $d/d^{\max}$ );<sup>3</sup> the lines give the predicted volume transition  $V/V^{\max}$  with  $\Delta\omega = -0.06$  V (solid line) and without a Donnan potential (dashed line).

PMAA brush surface was measured, the model allows only for qualitative comparisons to investigate the influence of the salt on swelling transitions. Our prediction resulting from the inclusion of the Donnan potential gives a reasonably early transition change, in comparison to that resulting from the neglect of  $\Delta\omega$ .

#### 4. CONCLUSION

In the present work, we propose a model based on pePC-SAFT for swellable hydrogels built of polyelectrolytes. The charges of the polymer chains have a very strong influence on the thermodynamic behavior, as demonstrated through the vapor–liquid equilibria of non-cross-linked polymers as well as for the swelling equilibria of the cross-linked hydrogel polymers. The influence of charges along the chain was specially considered through the augmentation of the hard chain term in pePC-SAFT and the degree of counterion condensation, i.e., the formation of ion pairs between polymer charges and counterions, for the sake of enlarging the average distance between repulsive net charges along the polymer chain. The latter impacts pePC-SAFT terms in several ways and is influenced heavily by the degree of neutralization of the polyelectrolyte chain, as well as by ionic species originating from other salts added to the system.

For the binary systems PAA/NaPA and PMAA/NaPMA in water, we adjusted  $k_{ij}$  values to match VLE experimental data and satisfyingly predicted the influence of the degree of neutralization, the temperature, and the molecular weight of the polymer and could show the degree of counterion condensation accordingly. Notably, no additional fitted parameter was used for any further calculations. For transition to a model capable of the description of polyelectrolyte hydrogels, we coupled the approach for polyelectrolytes to the PC-SAFT extension for the modeling of hydrogels from our previous work. Here, the elastic contributions of the swelling polymer network to Helmholtz energy and gel pressure are explicitly taken into account. The effect of the degree of neutralization could be predicted and was compared with experimental data.

In complex systems, due to the immobilization of the charged polymer segments in the hydrogel phase network and the mobility of counterions and additional electrolytes, a Donnan potential is established. For such systems, we show that there exists an extraordinary influence by the latter on swelling equilibria. By factoring the Donnan potential into the applied isofugacity criteria, our new model is able to predict the swelling behavior of polyelectrolyte hydrogels using exper-

imentally dictated potentials. Our predictions are in good accordance with literature data for several polyelectrolyte hydrogel systems and exchangeable additional salts.

## 5. APPENDIX

### 5.1. Charged-Hard Chain Contribution

The Helmholtz energy of the hard chain,  $a^{\text{hard chain}}$ , is computed from the hard-sphere contribution,  $a^{\text{hs}}$ , as developed by Boublík<sup>43</sup> and Mansoori et al.<sup>44</sup> and used by Groß and Sadowski,<sup>24</sup> for the combination with the uncharged hard chain perturbation with the radial distribution function of the hard-sphere fluid  $g_i^{\text{hs}}$ .

$$\frac{a^{\text{hard chain}}}{k_B T} = \frac{a^{\text{hs}}}{k_B T} \sum_i x_i m_i^{\text{seg}} + \sum_i x_i (1 - m_i^{\text{seg}}) \times \ln[g_i^{\text{hs}}] \quad (18)$$

For the conversion of the *hard chain* to the *charged hard chain* model for polyelectrolyte calculations,  $g_{ii}^{\text{hs}}$  is extended by combination of the known equation for the uncharged chain  $y_{00}$  with the cavity correlation function  $y_{cc}$  for charged segments, and weighted with  $cc_i^{\text{seg}}$ , so that the term reduces to the standard PC-SAFT equation for  $cc_i^{\text{seg}} = 0$ .<sup>22</sup>

$$\ln[g_i^{\text{hs}}] = (1 - cc_i^{\text{seg}}) \times \ln[y_{00}(i, i)] + cc_i^{\text{seg}} \times \ln[y_{cc}(i, i)] \quad (19)$$

In eq 19,  $cc_i^{\text{seg}}$  denotes the fraction of effectively charged segments over all segments of the polymer and equals zero for all non-polyelectrolyte components.

$$cc^{\text{seg}} = \frac{c^{\text{seg}}}{m^{\text{seg}}} (1 - \beta) \quad (20)$$

The radial distribution function obtained from standard PC-SAFT is given in eq 21.

$$y_{00}(i, j) = \frac{1}{(1 - \zeta_3)} + \frac{d_i d_j}{d_i + d_j} \frac{3\zeta_2}{(1 - \zeta_3)^2} + \left( \frac{d_i d_j}{d_i + d_j} \right)^2 \frac{2\zeta_2^2}{(1 - \zeta_3)^3} \quad (21)$$

with  $\zeta_n$  defined as in eq 22 and  $\rho$  being the number density.

$$\zeta_n = \frac{\pi}{6} N_A \rho \sum_i x_i m_i^{\text{seg}} d_i^n \quad (22)$$

$y_{cc}$ , the modifying extension of the hard chain model for charged polyelectrolytes, was deduced by Naeem and Sadowski<sup>22</sup> via an approach using the mean spherical approximation theory for the electrostatics resulting from the polyelectrolyte influence on the hard chain, as proposed by Jiang et al.<sup>45</sup>

$$y_{cc}(i, i) = y_{00}(d_i) \exp \left( -z_i^2 \frac{l_B}{d_i} \left( 1 + \frac{1}{(1 + \Gamma d_i)^2} \right) \right) \quad (23)$$

The scaling parameter  $\Gamma$ , representing the electrostatic inverse screening length, in Jiang's publication is defined according to the implicit equation in eq 24.

$$\Gamma^2 = \pi l_B \sum_i^{\text{ncomp}} \rho_i \left( \frac{1}{1 + \Gamma d_i} \right)^2 \left( z_i - \frac{\pi P_i d_i^2}{2\tau} \right) \quad (24)$$

$\rho_i$  denotes the number density of component  $i$ ;  $z_i$  denotes its valence.  $\tau$  is an abbreviation incorporating the reduced density.

$$P_n = \sum_i^{\text{ncomp}} \frac{\rho_i d_i z_i}{1 + \Gamma d_i} \left( 1 + \frac{\pi}{2\tau} \sum_j^{\text{ncomp}} \frac{\rho_j d_j^3}{1 + \Gamma d_j} \right) \quad (25)$$

$$\tau = 1 - \frac{\pi}{6} \zeta_3 \quad (26)$$

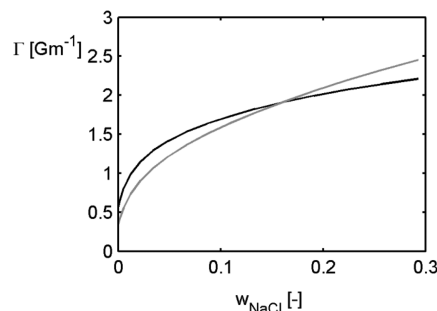
In the case of pePC-SAFT, with 1:1 electrolytes, the implicit equation reduces to eq 27.

$$\Gamma^2 = \frac{e^2 \rho}{4\epsilon k_B T} \sum_i^{\text{ncomp}} x_i c_i^{\text{seg}} \left( \frac{z_i}{1 + \Gamma d_i} \right)^2 \quad (27)$$

The calculation of 1:1 electrolytes in our polyelectrolyte model is adequate, as we consider only interactions with charged monomers and multiply the respective molar fraction by the number of charged segments per chain, thereby obtaining the quasi-molar fraction of charged monomers.

Interestingly, as shown in the comparative Figure 10,  $\Gamma$  can reasonably be replaced with a slim alternative used by Naeem (and later, by Jiang et al.<sup>46</sup>) for the polyion component  $p$ ; see eq 28.

$$\Gamma = \frac{\sqrt{1 + 2d_p \times \kappa} - 1}{2d_p} \quad (28)$$



**Figure 10.** Influence of salt on the electrostatic inverse screening length for the sodium poly acrylate (NaPA) hydrogel swelling calculation in aqueous NaCl. Gray denotes the computation with Jiang's implicit equation; black is the more elegant alternative.

Here,  $\kappa$  denotes a modified inverse Debye screening length, extended via the influence of charged polymers.

$$\kappa = \sqrt{\frac{e^2}{\epsilon k_B T} \rho \sum_i^{\text{ncomp}} x_i (1 - \beta_i) c_i^{\text{seg}} z_i^2} \quad (29)$$

### 5.2. Electrostatic Contribution

The electrostatic term for  $a^{\text{electrostatic}}$  was introduced by Cameretti and Sadowski,<sup>47</sup> with the proposal of the electrolyte PC-SAFT (ePC-SAFT) allowing for the thermodynamic description of ionic systems through a Debye-Hückel approach. In the modification for pePC-SAFT, the influence on polycharged polymers is implemented as in eq 30, where the abbreviation  $\chi_i$  in eq 31 contains the distance of the closest ionic approach equaling  $d_i$ .

$$\frac{a^{\text{electrostatic}}}{k_B T} = -\frac{e^2}{4\pi\epsilon k_B T} \sum_i \frac{x_i c_i^{\text{seg}} z_i^2 (1 - \beta_i)}{3} \kappa \chi_i \quad (30)$$

$$\chi_i = -\frac{3}{(\kappa d_i)^3} \left[ \frac{3}{2} + \ln(1 + \kappa d_i) - 2(1 + \kappa d_i) + \frac{1}{2}(1 + \kappa d_i)^2 \right] \quad (31)$$

### 5.3. Elastic Contribution

In case of hydrogel swelling calculations, free polymer chains are cross-linked to form a macromolecule with a reduced degree of freedom, and the stretching of the polymer network chains has to be taken into account. Solvent uptake by the gel, and the corresponding volume increase, provokes conformational changes in the network of cross-linked chains. As eq 32 shows, the quotients of gel volume,  $V$ , over the reference volume,  $V_0$ , and over the maximum volume,  $V_{\max}$ , strongly influence the counteracting elastic force expressed by the Helmholtz energy contribution.  $\Phi$  represents the network functionality parameter.

$$\frac{a^{\text{elastic}}}{k_B T} = x_p \frac{\Phi - 2}{\Phi} \left[ \frac{3}{2} \frac{\left(\frac{V}{V_0}\right)^{2/3} - 1}{1 - \left(\frac{V}{V_{\max}}\right)^{2/3}} - \ln\left(\frac{V}{V_0}\right) \right] \quad (32)$$

As deduced in previous publications,<sup>9,10</sup> phase equilibria of swelling hydrogels are calculable via the isofugacity criterion, balancing the products of  $x_i$ , fugacity coefficients  $\varphi_i$ , and pressure within the respective phases.

$$x_i^{\text{sol}} \varphi_i^{\text{sol}} p^{\text{sol}} = x_i^{\text{gel}} \varphi_i^{\text{gel}} p^{\text{gel}} \quad (33)$$

Due to the elastic force in the network,  $p^{\text{sol}}$  differs from  $p^{\text{gel}}$  by the swelling pressure  $p^{\text{elastic}}$ , obtained from the elastic Helmholtz energy, as in eq 34.

$$p^{\text{gel}} = - \left( \frac{\partial a^{\text{elastic}}}{\partial V} \right)_{T,x} \quad (34)$$

In the case of polyelectrolyte systems such as water/NaPA/NaCl, due to electroneutrality assumptions for the phases and the immobility of the cross-linked polyion, the combined isofugacity criteria for water and the mobile anion suffice the equilibrium requirements.

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### Notes

The authors declare no competing financial interest.

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## LIST OF SYMBOLS

$A$	anionic polyelectrolyte monomer
$a$	Helmholtz energy
$a_w$	water activity
$b$	charge–charge distance along the polymer
$B$	cation
$c$	molarity
$c^{\text{seg}}$	number of charged monomeric units
$cc^{\text{seg}}$	fraction of effectively charged segments

$C$	counterion
$d$	segment diameter, temperature dependent
$e$	elementary charge
$f$	fugacity
$F$	Faraday constant
$g$	radial distribution function
$k_B$	Boltzmann constant
$k_{ij}$	binary interaction parameter
$K$	counterion-condensation constant
$l_B$	Bjerrum length
$m$	gel mass
$m^{\text{seg}}$	segment-number parameter
$n$	number of monomers per chain
$N^{\text{assoc}}$	number of association sites
$N_A$	Avogadro constant
$p$	pressure
$R$	ideal gas constant
$T$	temperature
$u/k_B$	dispersion-energy parameter
$V$	volume
$w$	weight fraction
$x$	mole fraction
$y$	cavity correlation function
$z$	valence
$\alpha$	degree of neutralization
$\beta$	degree of counterion condensation
$\gamma$	activity coefficient
$\Gamma$	electrostatic inverse screening length
$\epsilon$	dielectric constant
$\epsilon^{\text{AiBi}}/k_B$	association-energy parameter
$\kappa$	inverse Debye screening length
$\kappa^{\text{AiBi}}$	association-volume parameter
$\mu$	chemical potential
$\xi$	Manning parameter
$\rho$	density
$\sigma$	segment diameter
$\tau$	abbreviation as in eq 26
$\varphi$	fugacity coefficient
$\phi$	volume fraction
$\Phi$	network functionality parameter
$\chi$	abbreviation as in eq 31
$\psi$	charge correction parameter
$\omega$	Donnan potential

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