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an apparent discrepancy between the theoretical and the experimental salt concentration dependence of D_{eff}. We feel, however, that the assumptions underlying (6) cannot be primarily responsible for these discrepancies, as otherwise we would not have expected ϕ to be only slightly dependent on C irrespective the value of c_s.

It is also interesting to look at the salt concentration dependence of D_{eff} in the dilute regime. The hydrodynamic radius R_H of an isolated macromolecule can be obtained from D_{eff} at infinite dilution with respect to the macromolecular component

$$R_H = \lim_{C \to 0} \frac{k_B T}{6\pi\eta D_{\text{eff}}} \qquad (15)$$

and should be related to the root-mean-square radius of gyration $\langle S^2 \rangle^{1/2}$. The latter can be evaluated theoretically by using the theory of Odijk and Houwaart[5] in combination with the Fixman–Skolnick expression for the electrostatic excluded volume[6] (see part 1). As pointed out before, if not enough values are available at low concentrations to perform a proper extrapolation to $C = 0$, an approximate value for the hydrodynamic radius R_H' may be obtained by using D_{eff} at the lowest concentration at which measurements have been performed.

We have calculated the value of R_H' for the three salt concentrations 0.1, 0.025, and 0.01. This yields a ratio of 1:1.17:1.36, which may be compared to the ratio of the theoretical expression for $\langle S^2 \rangle^{1/2}$ under the same conditions. Using again three estimates for L_p, namely, 1×10^{-7}, 3×10^{-7}, and 5×10^{-7} cm, respectively, we find the following ratios: 1:1.34:1.70, 1:1.24:1.49, and 1:1.20:1.41. It is difficult to conclude anything definite at this stage about the theoretical salt concentration dependence of the root-mean-square radius of gyration although the comparison is not too unsatisfactory. This is in part due to the uncertainty about the value of L_p and to the known fact that R_H may differ from $\langle S^2 \rangle^{1/2}$.

Conclusions

It seems from the combination of the results presented here and in part 1 that the conclusions of scaling theory for polyelectrolyte–salt solutions are, at least qualitatively, justified by the experimental results obtained from quasi-elastic light scattering experiments on the NaPSS–NaCl system. There is still some doubt about the exact concentration power law for the correlation length in the semidilute regime in relation to the uncertainty about the exact value of the intrinsic persistence length of the poly(styrenesulfonate) chain. It is clear that the exponent is slightly larger than the theoretical value $^3/_4$ and may be even closer to $^4/_5$. The results obtained at different salt concentrations have revealed that the dependence of the effective diffusion coefficient in the semidilute regime is *not* fully accounted for by the theoretical expressions.

Registry No. NaPSS, 9080-79-9; NaCl, 7647-14-5.

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Scaling Relations for Aqueous Polyelectrolyte–Salt Solutions. 3. Osmotic Pressure as a Function of Molar Mass and Ionic Strength in the Semidilute Regime

Rudolf S. Koene, Taco Nicolai, and Michel Mandel*

Department of Physical and Macromolecular Chemistry, Gorlaeus Laboratories, University of Leiden, 2300 RA Leiden, The Netherlands. *Received May 25, 1982*

ABSTRACT: The osmotic pressure of aqueous solutions of sodium poly(styrenesulfonate) in NaCl of various concentrations c_s has been measured as a function of the macromolecular concentration C for three different molar masses. In the semidilute regime it has been found that at constant c_s the osmotic pressure increases with increasing C according to a power law with an exponent that is close to the value predicted by the scaling theory for polyelectrolyte solutions in the presence of excess salt. Also the theoretical requirement that in the semidilute regime osmotic pressure should be independent of molar mass has been found to be satisfied. The change of the osmotic pressure with salt concentration shows the same kind of discrepancy with respect to theory as observed with the effective diffusion coefficient in the semidilute regime measured with the help of quasi-elastic light scattering. These discrepancies may be understood if it is assumed that the effect of the low molar mass electrolyte not only is limited to screening of the electrostatic interactions in solution but also affects the quality of the polyelectrolyte solvent. With increasing salt concentration the water–salt mixture no longer acts as an athermal solvent.

Introduction

In two previous papers,[1,2] to be called parts 1 and 2 respectively, quasi-elastic light scattering experiments on aqueous solutions of sodium poly(styrenesulfonate) (NaPSS) of different molar masses and with different concentrations of added NaCl have been reported. In part 1 it has been shown that in the semidilute regime the measured diffusion coefficient D_{eff} of the charged macromolecule at constant salt concentration increases with macromolecular concentration according to a power law that is close to the predictions of scaling theory for polyelectrolytes[3] if D_{eff} is assumed to be inversely proportional to the correlation length ξ. Moreover, D_{eff} was found to be molar mass independent in the semidilute concentration region, in agreement with theoretical predictions. Experiments performed at different concentrations c_s of

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added salt (part 2) revealed that the ionic strength dependence of D_{eff} in the semidilute regime cannot be fully explained by the same theory, however.

In order to trace the origin of the latter discrepancy and, in particular, to verify whether or not it may be attributed to purely dynamic effects as can eventually be expected in quasi-elastic light scattering measurements, we have investigated the concentration dependence, both of the macromolecule and of the added salt, of a purely static property, i.e., the osmotic pressure Π_p, for the same systems. Only the semidilute regime has been considered, as measurements in the dilute regime for the molar masses investigated are very difficult because of the very small osmotic effect.[5,6]

For lower molar masses osmotic measurements on polyelectrolyte–salt solutions are commonly used for the determination of the (number-averaged) molar mass. So far to our knowledge no osmotic measurements have been reported for polyelectrolyte–salt solutions in the *semidilute regime*. For solutions of uncharged polymers the osmotic pressure has been intensively studied, recently also in the semidilute concentration region.[7-9] In general, Π_p of polymer–good solvent systems seems to follow the relation derived by des Cloizeaux[10] from scaling arguments, which will be briefly discussed in the next section.

Scaling Relations for the Osmotic Pressure

In the scaling approach to the osmotic pressure of a polymer in a good (athermal) solvent the osmotic pressure in the dilute regime is assumed to obey to a first approximation the van't Hoff relation.

$$\Pi_p \simeq RT(C/M) \tag{1}$$

Here, C is expressed in grams per unit volume and M is the molar mass of the polymer. This expression can be corrected for interactions in the dilute regime by the usual virial expansion.

$$\Pi_p/RT = C/M + A_2C^2 + A_3C^3 + ... \tag{2}$$

The second virial coefficient A_2 has the following molar mass dependence:[4]

$$A_2 \sim R_F{}^3M^{-2} \sim M^{-1/5} \tag{3}$$

where R_F stands for the Flory radius of the polymer.

$$R_F \simeq (\beta/L)^{1/5}M^{3/5} \tag{4}$$

Here, L is the persistence length of the macromolecular chain (which for large M is a measure of the Kuhn statistical segment length) and β is the excluded volume between segments.

In the semidilute regime the osmotic pressure should obey the following relation according to des Cloizeaux:[10]

$$\Pi_p/RT \sim (C/M)\Psi(C/C^*) \tag{5}$$

where Ψ represents a dimensionless function depending only on the ratio C/C^*. The critical concentration C^* stands for the concentration where the macromolecular chains start to overlap and is defined by

$$C^* \simeq M/R_F{}^3N_A \tag{6}$$

For large C ($C \gg C^*$) and in the limit of large M the thermodynamic properties should be independent of M, which implies that Ψ should scale like a simple power law $(C/C^*)^\nu$. Together with (4)–(6) this leads to the expression for the osmotic pressure in the semidilute regime.

$$\Pi_p/RT \sim (\beta/L)^{3/4}C^{9/4} \sim \xi^{-3} \quad (C \gg C^*) \tag{7}$$

The molar mass independent correlation length ξ is defined by the equation

$$\xi \simeq R_F(C^*/C)^\sigma \sim (\beta/L)^{-1/4}C^{-3/4} \tag{8}$$

According to (7), the osmotic pressure in the semidilute regime should increase with macromolecular concentration according to a $C^{9/4}$ power law (des Cloizeaux law of osmotic pressure) and should scale as ξ^{-3}.

It has been argued by Odijk[3] that for polyelectrolyte solutions with an excess of salt the same relations should apply, in both the dilute and the semidilute regimes, provided the influence of the electrostatic interactions between the fixed charges on the macromolecular chains is taken into account. Using a Debye–Hückel type of interaction potential between the fixed charges with a screening length κ^{-1}, defined by

$$\kappa^2 = 8\pi Q\mu \tag{9}$$

where μ is the ionic strength of the solution and $Q \equiv q^2/\epsilon k_BT$ is the Bjerrum length (with q the elementary charge, ϵ the relative permittivity of the solvent, and k_BT the mean thermal energy per molecule), Odijk gave the osmotic pressure in the semidilute regime by[3]

$$\Pi_p/RT \sim (L_t/\kappa)^{3/4}C^{9/4} \tag{10}$$

Here, β has been assumed to be proportional to κ^{-1} and L_t represents the total persistence length of the charged macromolecule. It has been shown[11] by Odijk and independently by Skolnick and Fixman that L_t may be approximated by a sum of two terms, an intrinsic persistence length L_p and an electrostatic term L_e, where the latter arises through the short-range electrostatic interactions between fixed charges.

$$L_t = L_p + L_e = L_p + (Q/4\kappa^2A^2)f \tag{11}$$

If the chain carries Z charges and has a contour length l, $A \equiv l/Z$ represents the average contour distance between two successive charges on the chain. The factor f, which should take into account a possible reduction of the real charge through the strong interactions with the counterions, is, according to simple condensation theory,[6,12] given by $f = 1$ for $A > Q$ and $f = A^2/Q^2$ for $A < Q$.

As shown by (10) the effect of the low molar mass electrolyte on the osmotic pressure in the semidilute concentration region is entirely expressed through the factor L_t/κ. According to theory, therefore, the quantity B_p, defined by

$$B_p \equiv \Pi_p(\kappa/L_t)^{3/4} \sim C^{9/4} \tag{12}$$

and which can be calculated for any polyelectrolyte solution in the semidilute regime if Π_p is measured and values of L_t and κ are determined, should be independent of molar mass and of the salt concentration but should increase with macromolecular concentration according to a $C^{9/4}$ power law.

Materials and Methods

The NaPSS samples were the same as used in parts 1 and 2. Three molar masses were used, with M respectively 4×10^5, 6.5×10^5, and 12×10^5 g mol^{-1}. For the first and last molar masses only aqueous solutions containing 0.01 M NaCl were measured. For the sample $M = 6.5 \times 10^5$ g mol^{-1} osmotic pressures were determined for four different salt concentrations $0.01 < c_s < 0.1$ mol L^{-1}. Polymer concentrations of the different solutions investigated were determined spectrophotometrically as in parts 1 and 2.

Osmotic pressures (expressed in heights of solvent h) were measured with a Knauer membrane osmometer with a temperature-stabilized cell using as membranes Sartorius ultrafilters (Type SM 117-33). For each solution (with given M, C, and c_s) at least three independent determinations of the osmotic pressure

Table I
Osmotic Pressure (cm of Water) as a Function of Concentration C (g L^{-1}) at $c_s = 0.01$ mol L^{-1} (NaCl) for Three Different Samples of NaPSS

$M = 4.0 \times 10^5$ g mol^{-1}		$M = 6.5 \times 10^5$ g mol^{-1}		$M = 12 \times 10^5$ g mol^{-1}	
C	Π_p	C	Π_p	C	Π_p
19.2	140	10.5	36.0	4.22	7.0
21.8	164	14.3	70.0	6.83	12.8
22.2	169	15.8	99.0	10.8	32.0
25.2	225	14.5	118	17.5	78.4
30.9	278	21.8	160	29.0	176
		29.1	205		

Table II
Osmotic Pressure (cm of Water) as a Function of Concentration C (g L^{-1}) at Different Concentrations c_s (mol L^{-1}) of NaCl ($M = 6.5 \times 10^5$ g mol^{-1})

$c_s = 0.005$		$c_s = 0.05$		$c_s = 0.01$		$c_s = 0.1$	
C	Π_p	C	Π_p	C	Π_p	C	Π_p
2.54	5.5	7.29	4.0	10.5	36.0	9.15	4.1
4.01	8.9	14.1	12.0	14.3	70.0	11.9	6.6
7.15	29.1	14.4	26.0	15.1	99.0	13.5	8.2
12.1	85.6	20.0	33.0	19.5	118	16.2	11.8
14.1	107	26.4	67.0	21.8	160	20.6	21.0
14.8	127	28.3	78.0	29.2	205	27.8	45.2
19.7	187						
26.1	205						

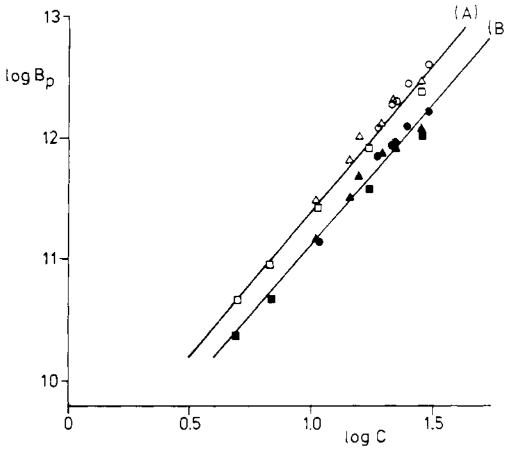

Figure 1. Variation of B_p (cm$^{-1/2}$) with macromolecular concentration C (g L^{-1}) for NaPSS in aqueous 0.01 M NaCl: M_w = 4×10^5 g mol^{-1} (circles), $M_w = 6.5 \times 10^5$ g mol^{-1} (triangles), and $M_w = 12 \times 10^5$ g mol^{-1} (squares). Open symbols correspond to B_p calculated with $L_p = 10^{-7}$ cm and filled symbols to $L = 5 \times 10^{-7}$ cm (see text).

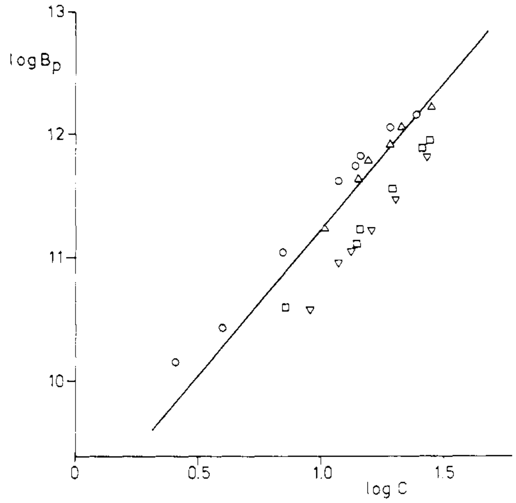

Figure 2. Variation of B_p (cm$^{-1/2}$) with macromolecular concentration C (g L^{-1}) for NaPSS in aqueous NaCl solutions; M_w = 6.5×10^5 g mol^{-1}. Salt concentrations: 0.005 (○), 0.01 (△), 0.05 (□), and 0.1 M (▽).

Table III
Least-Squares Parameters for the Linear Dependence of log B_p on log C: $\log B_p = W + \nu \log C$[a]

L_p, cm	W	ν	S[b]
10^{-7}	9.0 ± 0.1	2.43 ± 0.08	0.07
3×10^{-7}	8.9 ± 0.1	2.34 ± 0.08	0.07
5×10^{-7}	8.8 ± 0.1	2.29 ± 0.08	0.07

[a] All points for $c_s = 0.01$ M. [b] S is the standard deviation of the points with respect to the least-squares line.

were performed; the reproducibility was, in general, excellent ($\delta h \simeq 0.1$ cm). After each series of measurements the base line was checked for drift effects; if these seemed to have occurred, the measurements of that series were rejected and a new series was started. The accuracy in the osmotic pressure measurements is of the order of 1% (for $10 > h > 1$ cm) or better.

Experimental Results

Two sets of experiments have been performed: in the first, Π_p has been measured as function of C ($C > C^*$) at constant c_s but for the three different molar masses investigated; in the second, Π_p has been determined for a given M as a function of C at four different values of c_s. The systems investigated and the osmotic pressure results are summarized in Tables I and II, respectively.

In order to check the theory, we need to transform values of Π_p into B_p values according to (12). This transformation involves three difficulties as pointed out already in parts 1 and 2. The first refers to the value of L_p to be used, as for PSS no accurate value is available yet. It was found that for reasonable estimates, $10^{-7} \leq L_p \leq 5 \times 10^{-7}$ cm, the concentration power law of D_{eff} is slightly dependent on the choice of L_p. Therefore for the evaluation of B we shall use three values of L_p, i.e., 10^{-7}, 3×10^{-7}, and 5×10^{-7} cm. The second problem concerns the value of f that appears in the expression for L_e (see eq 11). As for NaPSS the condition $A < Q$ is satisfied, we shall use $f = A^2/Q^2$ based on the simple condensation approach although, strictly speaking, this expression is valid only in the limit of infinite dilution. The third difficulty is related to the evaluation of the ionic strength of the solutions, which enters the expression for κ. This is particularly the case for those systems where the concentration of the cations provided by the polyelectrolyte is of comparable magnitude to that of the added salt. We shall use, as done previously, an expression for μ in which a contribution of noncondensed counterions originating from the dissociation of the polyelectrolyte is added to that of the low molar mass salt (consistent with the estimate for f).

$$\mu = c_s\{1 + (A/Q)c_m/2c_s\} \tag{13}$$

Here, $c_m \equiv C/M_m$, with M_m the molar mass of a monomeric unit, represents the equivalent concentration, in mol L^{-1}, of the polyelectrolyte.

Values of log B_p thus calculated starting with the results of Table I are plotted against log C in Figure 1 for the two extreme values of L_p, only for the saake of clarity, and at constant $c_s = 0.01$. It is seen—and a least-squares analysis confirms—that in the semidilute region B_p is molar mass independent and that it obeys a simple concentration power law with an exponent that is only slightly larger than the theoretically predicted 2.25 (see Table III) but depends on the choice of L_p. It therefore can be concluded that in the semidilute regime B_p is molar mass independent, as required by scaling law and in good agreement with the quasi-elastic light scattering results of part 1.

Table IV
Least-Squares Parameters for the Linear Dependence of $\log B_p$ on $\log C$: $\log B_p = W + \nu \log C$[a]

c_s, mol L^{-1}	W	ν	S[b]
0.005	9.24 ± 0.04	2.14 ± 0.09	0.08
0.01	9.0 ± 0.3	2.2 ± 0.2	0.08
0.05	8.5 ± 0.2	2.33 ± 0.14	0.08
0.1	8.6 ± 0.2	2.18 ± 0.13	0.05

[a] All points for $M_w = 6.5 \times 10^5$ g mol^{-1} and $L_p = 3 \times 10^{-7}$ cm. [b] S is the standard deviation of the points with respect to the least-squares line.

Table V
Empirical Correction Factor $\bar{\phi}_p(c_s)$

c_s, mol L^{-1}	$10^{-5}M_w$, g mol^{-1}	$L_p = 10^{-7}$ cm $\nu = 2.434$	$L_p = 3 \times 10^{-3}$ cm $\nu = 2.34$	$L_p = 5 \times 10^{-7}$ cm $\nu = 2.24$
0.1	6.5	2.4 ± 0.3	3.8 ± 0.4	4.8 ± 0.4
0.05	6.5	2.1 ± 0.3	3.1 ± 0.5	3.8 ± 0.6
0.01	6.5	1.1 ± 0.2	1.3 ± 0.2	1.5 ± 0.2
0.005	6.5	0.8 ± 0.1	0.9 ± 0.1	1.0 ± 0.1
0.01	4.0	0.98 ± 0.08	1.2 ± 0.1	1.4 ± 0.1
0.01	12.0	1.3 ± 0.2	1.6 ± 0.2	1.9 ± 0.3

In Figure 2 values of $\log B_p$ vs. $\log C$ have been plotted for osmotic data in the semidilute regime at constant molar mass but at various values of c_s. Here again, as in part 2, it is obvious that contrary to the theoretical predictions, the data for different concentrations of added salt do not fall on the same line, which implies that the theoretical expressions do not fully account for the salt concentration dependence of the osmotic pressure. Least-squares analysis of these data show that the slopes of the different lines $\log B_p$ vs. $\log C$ are within experimental error identical (and again close to theoretical value 2.25) but that the intercepts decrease with increasing salt concentration. As an example the least-squares parameters are given in Table IV for $L_p = 3 \times 10^{-7}$ cm but the same trend is observed for the two other choices of L_p. We must therefore conclude that the osmotic pressure results confirm the observations made with the help of quasi-elastic light scattering and that the observed discrepancies are not to be related primarily to some special dynamic effect.

It is, of course, possible to introduce an additional salt concentration factor into the theoretical expression in the same empirical way as proposed for the light scattering experiments. Defining a quantity ϕ_p as the ratio between the theoretical and experimental value of Π_p

$$\phi_p = k_B T \left(\frac{a N_A}{10^3 M_m} \right)^{\nu} \left(\frac{C^{\nu}}{\Pi_p} \right) \left(\frac{L_t}{\kappa} \right)^{3/4} \qquad (14)$$

we find that for a given value of L_p and corresponding value of ν (taken from Table III) ϕ_p is fairly constant within a given series of solutions with constant c_s. With the average values $\bar{\phi}_p(c_s)$ (see Table V) as the correction factor mentioned, the quantities $J_p \equiv B_p \bar{\phi}_p(c_s)$ are found to be salt concentration independent and only to vary with C. This is shown in the log–log plot of Figure 3 for three estimates for L_p. The least-squares analysis of the lines $\log J_p$ vs. $\log C$ yields the parameters collected in Table VI. Here again the slope slightly depends on the choice of L_p and is of the correct magnitude although somewhat smaller than the theoretical value 2.25. The fit seems to be optimal with $L_p = 10^{-7}$ cm. No definite conclusion should be drawn from the latter statement because the procedure for evaluating J_p is rather rough. Note finally that the values of $\bar{\phi}_p$ are not expected to be comparable to those of $\bar{\phi}$ derived for the same series of solutions from light scattering results.

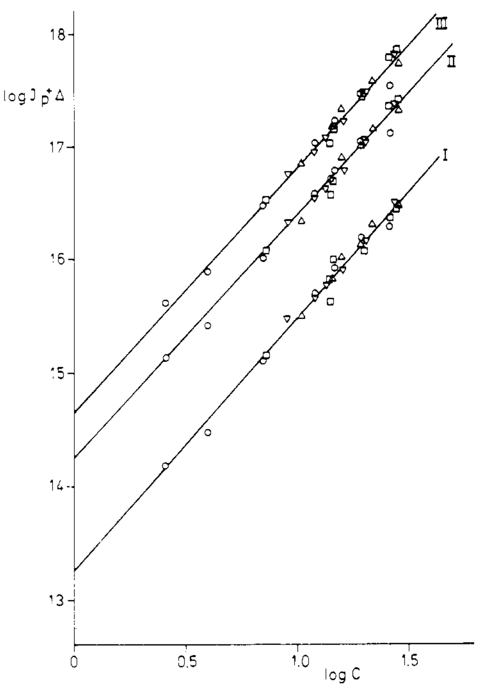

Figure 3. Variation of J_p (cm$^{-1/2}$) with macromolecular concentration for NaPSS in aqueous NaCl solutions; $M_w = 6.5 \times 10^5$ g mol^{-1}. Symbols as in Figure 2. $L_p = 10^{-7}$ (I), 3×10^{-7} (II), and 5×10^{-7} cm (III) (the lines are shifted along the ordinate with $\Delta_{I} = 0$, $\Delta_{II} = 1.0$, and $\Delta_{III} = 1.5$).

Table VI
Least-Squares Parameters of the Linear Dependence of $\log J_p$ on $\log C$: $\log J_p = W' + \nu \log C$[a]

L_p, cm	W'	ν	S[b]
10^{-7}	13.25 ± 0.05	2.24 ± 0.04	0.07
3×10^{-7}	13.24 ± 0.06	2.16 ± 0.05	0.06
5×10^{-7}	13.13 ± 0.13	2.17 ± 0.11	0.18

[a] All points independent of M_w and c_s included. [b] S is the standard deviation of the points with respect to the least-squares line.

Discussion

Both from the osmotic pressure and from the quasi-elastic light scattering measurements it can be concluded that the predictions of the theory for the semidilute regime are in reasonable agreement with the experimental results insofar as the molar mass and the macromolecular concentration are concerned but that there is a salt effect that cannot be explained by the existing scaling theory. Although in the handling of the experimental data a considerable number of assumptions have been introduced, some of which may be rather questionable, it is our feeling that these assumptions are *not* primarily responsible for the observed discrepancy between theory and experiment. Should that have been the case we would have expected that also other aspects of the theory would have been found inadequate to explain the observed results besides the c_s dependence of both ξ and Π_p in the semidilute regime. We think that the origin of the discrepancy should be traced to the neglect in the theory of the influence which increasing salt concentrations can have on the quality of the solvent. In the scaling theory for polyelectrolyte–salt systems[3] it has been assumed indeed that under all circumstances the macromolecule is in the presence of an athermal solvent.

In solutions of uncharged macromolecules the quality of the solvent in a given system can only be changed by a variation of the temperature. Unfortunately, no systematic experimental studies on the effect of the temperature on the osmotic pressure or quasi-elastic light scattering of such systems in the semidilute regime have been reported until now. To our knowledge the only result available so far that may be of relevance to this problem is the study of the osmotic pressure of a given polymer in two (good) solvents at the same temperature.[13] In that case the absolute value of Π_p in the dilute regime was found to be dependent on the nature of the solvent, which had no effect, however, on the exponent of the concentration power law.

In the case of polyelectrolytes the quality of the solvent may be affected at constant temperature by the nature and the amount of low molar mass electrolyte added. It is well-known for many polyelectrolytes in water that by increasing the concentration of added salt, Θ conditions may be reached. This follows from the steady decrease of A_2 with c_s down to zero or even negative values. In fact, for NaPSS it has been shown that at room temperature that Θ state is reached for 4.2 M NaCl.[14] Although the highest NaCl concentration used in the present investigation is still far from that at which Θ conditions should prevail, it may be large enough to invalidate one of the essential conditions on which the relations of the scaling theory used are based, namely, that the solvent may be considered to be athermal.

In the case of neutral polymers the influence of the quality of the solvent on the scaling relations for the semidilute regime has been considered by de Gennes.[15] The argument starts with a more general expression for the Flory radius than (4)

$$R_F \simeq v^{1/5}L^{2/5}N^{3/5} \sim v^{1/5}L^{-1/5}M^{3/5} \qquad (15)$$

where N represents the number of persistence lengths, which determines the contour length ($l = NL$), and v is the Flory excluded volume parameter.

$$v = \beta(1 - 2\,\chi) \qquad (16)$$

Here, χ is the dimensionless interaction parameter, which involves segment–segment, segment–solvent, and solvent–solvent interactions. It is generally positive and has a small value ($\chi < 0.5$) in a good solvent but increases with decreasing quality of the solvent such that at $\chi = 0.5$ the Θ conditions are reached. In an athermal solvent $\chi = 0$ and $v = \beta$ so that (15) reduces to (4). If $\chi > 0$ the expression for the critical concentration still holds provided (15) is used, which leads to the following expression for the correlation length in the semidilute regime:

$$\xi \sim (v/L)^{-1/4}C^{-3/4} = (1 - 2\chi)^{-1/4}(\beta/L)^{-1/4}C^{-3/4} \qquad (17)$$

As the osmotic pressure scales like ξ^{-3}, it follows that

$$\Pi_p/RT \sim (1 - 2\chi)^{3/4}(\beta/L)^{3/4}C^{9/4} \qquad (18)$$

This expression demonstrates that with increasing values of χ the osmotic pressure at given C and T will decrease. Of course, these expressions will no longer hold if Θ conditions are approached too closely.

In the case of polyelectrolyte solutions in the presence of low molar mass electrolyte the situation is more complicated. If Θ conditions are attained with increasing salt concentration, it may be assumed that also $\chi = \chi(c_s)$ will be an increasing function with c_s and that the osmotic pressure will decrease with increasing c_s at constant C and T. However, the excluded volume may also be affected by increasing c_s in a different way than assumed for the case of an athermal solvent. In the latter case $\beta/L \simeq L_t/\kappa$, because the excluded volume was considered to be primarily determined by electrostatic repulsions between segments such that $\beta \simeq L_t^2\kappa^{-1}$. If with increasing c_s the electrostatic interactions are more and more screened, a nonelectrostatic contribution (arising through van der Waals interactions) may no longer remain neligible. This means that a correction should be introduced such that $\beta/L \simeq (L_t/\kappa)g(c_s)$. It may be conjectured that g will be of order unity, however, up to $c_s \simeq 0.1$ mol L^{-1}, as L_t/κ is still of the order L_t^2. Therefore for nonathermal solvent conditions the osmotic pressure in the semidilute regime for polyelectrolyte–salt systems should obey the equation

$$\Pi_p/RT \sim (1 - 2\chi)^{3/4}g^{3/4}(L_t/\kappa)^{3/4}C^{9/4} \qquad (19)$$

Under the same circumstances the correlation length is expected to satisfy the relation

$$\xi \sim (1 - 2\chi)^{-1/4}g^{-1/4}(L_t/\kappa)^{-1/4}C^{-3/4} \qquad (20)$$

It then follows from (19) and (20) that according to the definitions of ϕ_p and ϕ, as given by (14) and by eq 7 of part 2, respectively, we have

$$\bar{\phi}_p \sim (1 - 2\chi)^{-3/4}g^{-3/4} \qquad (21)$$

$$\bar{\phi} \sim (1 - 2\chi)^{-1/4}g^{-1/4} \qquad (22)$$

If it is assumed that $g \simeq 1$ but that χ is expected to increase with increasing c_s, both correction factors will increase with increasing concentration c_s. This is in agreement with experimental results both for the osmotic pressure and for the effective diffusion coefficient in the semidilute regime, at least qualitatively. In a quantitative sense the agreement is less good. From (21) and (22) the ratio $\bar{\phi}_p/\bar{\phi}^3$ should be independent of c_s but this is not the case for the experimentally found correction factors. This quantitative comparison is, however, difficult to interpret in view of the fact that these factors have not been determined in a very accurate way from the experimental results. Furthermore, it is not to be excluded that there may also exist an additional dynamic correction for the value of ξ, which is derived from quasi-elastic light scattering experiments through an effective diffusion coefficient. The attempt we have made here to explain the discrepancies between theory and experiment insofar as salt effects are concerned is not meant to be more than of qualitative nature and more work, both experimental and theoretical, is needed to clarify these salt effects in a completely satisfactory way. We feel, however, that the influence of the additional salt on the solvent quality of polyelectrolyte solutions is a real effect that should be incorporated into the theory.

Conclusions

The osmotic pressure of aqueous NaPSS–NaCl solutions in the semidilute regime is in reasonably good agreement with the predictions of the scaling theory for polyelectrolyte–excess salt systems insofar as the molar mass independence and the macromolecular concentration dependence are concerned. The theory as presented so far cannot explain completely the influence of the concentration of added salt on the osmotic pressure as was also already concluded for the effective diffusion coefficient in the semidilute regime obtained from quasi-elastic light scattering experiments. Qualitatively, this discrepancy between theory and experiment may be thought to be due to the influence of the added salt on the quality of the solvent in these systems. If the salt concentration is increased, the low molar mass electrolyte–water mixture becomes a less good solvent and can no longer be considered as athermal. Therefore the important conclusion is reached that in polyelectrolyte–added salt systems the influence of the low molar mass electrolyte on the solution properties of the charged macromolecule is not only limited to a screening effect of the electrostatic interactions as generally assumed so far in most theoretical treatments.

Registry No. NaPSS, 9080-79-9; NaCl, 7647-14-5.

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Multiphase Equilibria in Solutions of Polydisperse Homopolymers. 2. Fundamentals of Three-Phase Separation in Quaternary Systems†

Karel Šolc

Michigan Molecular Institute, Midland, Michigan 48640. *Received July 22, 1982*

ABSTRACT: Conditions for three-phase separation are examined for quaternary systems consisting of a solvent and three polymeric homologues and obeying Flory–Huggins thermodynamics with concentration-independent parameter χ. The analysis is carried out in polymer composition space, with the advantage of being simple and easily applicable to systems with more components. The critical surface is topologically simple, either monotonous or containing fold(s) but no extrema nor saddle points. A family of coexistence curves can be drawn in the triangle of polymer compositions, with each curve being the locus of polymer compositions that, diluted with a solvent, can be at equilibrium. Heterogeneous double critical points arise at points where the critical surface displays a constrained extremum in the direction of the coexistence curve. The mechanism of three-phase separation is discussed in detail for the simplest case (three-phase region attached to one binary axis only). Such systems display at least one triple critical point located inside the composition triangle on the line of heterogeneous double critical points. At a given temperature, compositions of three coexisting phases depend on the solvent content and define a curve called the trinodal, anchored by its ends to the boundary of the three-phase region. The three-phase separation starts at the triple critical point; with decreasing temperature the trinodal grows and moves toward the above binary axis, until it exits out of the triangle and the three-phase region ceases to exist.

1. Introduction

The mechanism of three-phase separation in true ternary systems consisting of a solvent and two polymer homologues of chain lengths r_1 and r_2 is well established. Building on the pioneering work of Korteweg,[1] van der Waals and Kohnstamm,[2] and Schreinemakers,[3] Tompa has shown that the separation proceeds via the heterogeneous double-plait point mechanism[4] where, upon a change in temperature, a heterogeneous double critical point splits into a metastable and unstable critical point. Recently, his claim was reinforced by both analytical and numerical arguments.[5] Tompa's approach of analyzing the critical line, however, can be used only for true ternary systems and cannot be directly applied to quasi-ternary systems containing more than two polymeric components.[5,6] Yet any information in this respect would be appreciated since, in practice, all polymeric systems are polydisperse.

As the first step in this direction, we shall examine in this paper the principles of multiphase separation in quaternary systems consisting of a solvent (0) and three polymeric homologues (1, 2, 3) differing just by their chain lengths $r_3 > r_2 > r_1$. Graphical representation of such systems is still simple and helps greatly in understanding the phase separation process. In view of a recent misunderstanding concerning simple ternary systems,[6] such an exercise does not seem superfluous before proceeding to the general case, requiring a more abstract approach. It is assumed that the systems follow Flory–Huggins thermodynamics with concentration-independent parameter χ.[7]

First, let us review the essentials of three-phase separation in true ternary systems. The diagram best suited for this purpose seems to be a front view of the three-phase region of the binodal surface such as depicted in Figure 1. For various special lines, the interaction parameter χ is here plotted against the composition of the polymer mixture $w_2 = \phi_2/(\phi_1 + \phi_2)$, where ϕ_i is the volume fraction of polymer species i in the system. The binodal surface is literally caved in, with the S-shaped three-phase line DGHC (i.e., the locus of three-phase equilibrium compositions) arising as the line of intersection between the upper and lower stable parts of the surface. Both of these parts extend continuously beyond their line of intersection, plunging under the stable binodal surface, and are then "connected" by the unstable portion of the surface. The singular upper and lower cusp lines, DFAC and DBEC, mark the line of contact between the metastable extensions and the inner unstable portion of the surface. Each polymer mixture w_2 has its critical interaction parameter χ_c, and the locus of such points is called the critical line (–GBAH– in Figure 1). It is contained within the binodal surface and passes from the upper stable portion of the

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† Dedicated to Professor Dale J. Meier of the Michigan Molecular Institute on the occasion of his 60th birthday.

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