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Counterion Activity of Highly Charged Strong Polyelectrolytes

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ABSTRACT: Comprehensive counterion activity studies have revealed clear influence of the polyelectrolyte concentration and chain length on the polyion−counterion interaction, neither of which is evident from the existing theoretical models. The counterion activity coefficient (f_a) increases below the overlap concentration c^* as calculated from Odijk's scaling approach. At dilutions where the Debye length (l_D) exceeds the contour length (L), this increase is more pronounced. It is concluded that these changes in the ionic interactions are primarily responsible for the strong increase of the equivalent conductivity (Λ) below c^*. The findings are not restricted to oligomers but apply to all chain lengths of polyelectrolytes at concentrations less than c^*. The correlation of f_a and Λ with both c^* and the ratio l_D/L leads to a general description of polyelectrolyte behavior. Experiments were performed above and below c^* and over the range $0.1 \le l_D/L \le 10$ using a series of poly(vinylbenzyltrialkylammonium) model polyelectrolytes with contour lengths over a range 7 nm $\le L \le$ 102 nm and characterized by a charge density parameter $\xi = 2.85$.

Introduction

In polyelectrolyte solutions specific interactions between the polyion and its counterions are responsible for deviations from the solution behavior of both neutral polymers and simple electrolytes. The charge density along the polyelectrolyte chain has the most significant effect on the polyion−counterion interaction. In particular, if the charge distance (b) is less than the Bjerrum length ($l_B = 0.712$ nm in water at 20 °C), the electrical field around the polyion becomes so strong that some of the counterions become trapped within very short distances from the polyion[1−10] (counterion condensation). To model the onset of this condensation phenomenon, Manning has introduced and defined the charge density parameter $\xi = l_B/b$ with 1 as a critical value for monovalent counterions.[4] Since this pioneering effort, numerous extensive studies have been performed to verify ξ,[11,12] all which will not be discussed herein since they are well treated in monographs.[13−18] Only the key aspects of polyelectrolyte theory important for the model development and experimental data discussion will be summarized herein.

The ionic interaction between the polyion and the counterions may be quantified by various coefficients. These include (i) the activity coefficient of the counterions (f_a), (ii) the self-diffusion parameter (D_i/D_i^0), and (iii) the osmotic coefficient (f_o), where D_i is the self-diffusion coefficient of the counterions in solution and D_i^0 is the corresponding value in pure solvent.[19]

For $\xi > 1$ Manning has derived the following relation:[5]

$$f_o < f_a = 1.21 f_o < \frac{D_i}{D_i^0} = 1.74 f_o = 1.438 f_a \qquad (1)$$

Recently, the prediction that $f_a/f_o = 1.21$ has been confirmed.[20] Furthermore, on the basis of his theory and the derivations of Huzienga[21] and Kurucsev,[22] Manning has calculated the interaction parameter of the equivalent conductivity:[23]

$$f_c = D_i/D_i^0 = 0.87\xi^{-1} \quad \text{and later}^{17} \quad f_c = 0.866\xi^{-1} \qquad (2)$$

Table 1. Interaction Coefficients for Polyelectrolytes with Monovalent Counterions and $\xi > 1$ in Aqueous Solution

coeff	author	relationship	eq	ref
f_0	Manning	$1/(2\xi)$	3	4
	Lifson		3	
	Katchalsky		3	
f_a	Manning	$(1/\xi)\exp(-1/2)$	4	4
	Iwasa		4	25
	Gueron	$0.7\xi^{-1}$	5	26
$D_i/D_i^0 = f_c$	Manning	$0.87\xi^{-1}$	6	5
	Yoshida	$0.33 + 0.43\xi^{-1}$	7	27, 28

The values of the interaction coefficients f_a, f_c, and f_o in Manning's theory (eqs 1 and 2) do not have the same values due to different Debye−Hückel nonideal effects for the uncondensed counterions.[20] The theoretical relationships for the aforementioned interaction parameters from Manning's theory,[4,5,7−10,24] as well as from the models of Iwasa,[25] Gueron,[26] and Yoshida,[27,28] have been previously summarized.[18] Tables 1 and 2 provide summaries of the models for the case of monovalent counterions where $\xi > 1$. It is over these conditions that the present discussion will focus.

Iwasa's calculations[25] are based on cluster theory whereas Gueron and Weisbuch[26] have derived expressions for the activity coefficients from the Poisson−Boltzmann equation. Their model suggests that the polarizability of the counterion sheath may affect activity coefficients and, more generally, the ionic distributions themselves. In Yoshida's cell model[27,28] the contributions of the counterions to the activity coefficients are composed of the contribution from both the condensed counterions, with $^1/_3(1 - \xi^{-1})$, and the noncondensed counterions, with $0.76\xi^{-1}$.

In contrast to the charge density[29−35] and the type of the counterions,[30,35−44] the chemical structure and the

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Table 2. Interaction Coefficients for Polyelectrolytes with Monovalent Counterions and $\xi > 1$ in Aqueous Solution with Addition of Salt

coeff	author	relationship	eq	ref
f_0	Manning	$((X/2\xi) + 2)(X + 2)^{-1}$	8	4
f_a	Manning	$[((X/\xi) + 1)/(X + 1)] \exp[(- X/2\xi)/((X/\xi) + 2)]$	9	4
	Iwasa	$[((X/\xi) + 1)/(X + 1)] \exp\{(X/\xi)/((X/\xi) + 2)[- {}^1/_2 + 0.39((X/\xi)/((X/\xi) + 2) - 1)]\}$	10	25
	Gueron	$(0.7(X/\xi) + 1)(X + 1)^{-1}$	11	26
$D_i/D_i^0 = f_c$	Manning	$[((X/\xi) + 1)/(X + 1)]\{1 - (X/3\xi)[(X/\xi)(1 + \pi) + 2]^{-1}\}$	12	5

Table 3. Macromolecular Characteristics of the Poly(vinylbenzyltrialkylammonium) Chloride Model Compounds

	prepolymer						
parameter	I	II	III	IV	V	VI	VII
P_n	27	63	56	142	181	82	407
M_w/M_n	1.17	1.20	1.26	1.33	1.44	1.93	1.84
L (nm)	6.75	15.75	14	35.5	45.25	20.5	101.75
c^*(monomol L^{-1})	1.45×10^{-1}	2.68×10^{-2}	3.38×10^{-2}	5.27×10^{-3}	3.24×10^{-3}	1.58×10^{-2}	6.41×10^{-4}

chain length[30,41,45−53] of polyelectrolytes have been less extensively considered in the examination of the polyion−counterion interaction. In addition, most of experimental work has been carried out at concentrations too high to be considered highly diluted,[29,30,36,37,42,45,47,48] hence preventing rigorous model discrimination. Furthermore, the water quality often did not correspond to that required for salt-free conditions.[30,31,42,43,48,53] Polymer samples were also highly polydisperse[43] and, therefore, unsuitable for the elucidation of chain length influences.

Recently, Manning and Mohanty have published theoretical approaches *restricted to oligomers*.[54] They have also revisited the counterion condensation[20] considering the importance of the ratio of the Debye length to the contour length, l_D/L, with l_D defined as

$$l_D = [4\pi N_A l_B(\xi^{-1}c_p + 2c_s)]^{-1/2} \tag{13}$$

Here the quantities N_A, c_p, and c_s are Avogadro's number, the polyelectrolyte concentration in monomol m^{-3}, and the salt concentration in mol m^{-3}. The other symbols have been explained in the preceding paragraph. The significance of the ratio l_D/L has been derived theoretically[55] and is supported with conductivity measurements as well as a limited amount of counterion activity data.[56] However, *the validation of theoretical approaches was prevented by the lack of structurally defined highly pure strong polyelectrolytes having a narrow molar mass distribution over a sufficiently wide range of chain lengths*. A systematic study[53] with uniform poly(L-lysine), a nonpermanently charged polyelectrolyte, investigating the influence of the chain length on the electrolytic conductivity was performed at concentrations in the range 2.5×10^{-3}−6×10^{-2} monomol L^{-1}. These concentrations are in the semidilute regime, above the overlap concentration defined by the Odijk model.[57] Overall, no cationic polymer models have been synthesized to date which permit a systematic evaluation of the various polyelectrolyte theories. Recently, a family of poly(vinylbenzyltrialkylammonium) model compounds has been prepared by controlled radical polymerization[58] in order to study the influence of the chemical structure and the polymer chain length on both the polyion−counterion interaction and the electrolytic transport properties at various ionic strengths. Thus, it is intended in this experimental work to examine the influence of parameters such as the chain length, chemical structure, polyelectrolyte concentration (above and below the overlap concentration), and the ionic strength on the polyion−counterion interaction. The discussion and conclusions from it will point out the limitations of the existing theories and stimulate the development of refined models.

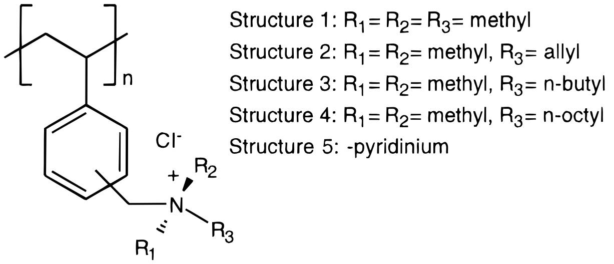

Figure 1. Structures of the various poly(vinylbenzyltrialkylammonium) chloride model compounds.

Experimental Section

Materials. Poly(vinylbenzyltrialkylammonium) model compounds have been synthesized, purified, and characterized as described previously.[58] Starting from seven precursor polymers with average contour lengths in the range 7−102 nm, 35 polymers possessing five different chemical structures were obtained. The structural variation is depictured in Figure 1.

Further details such as the degree of polymerization P_n, the molar mass distribution M_w/M_n, the contour length L, and the overlap concentration c^* resulting from the various precursors are summarized in Table 3.

Measurements. Activity measurements were performed with a model 692 pH/ion meter (Metrohm, Herisau, Switzerland) at 20 °C under an inert atmosphere. The temperature was adjusted by using a titration vessel (Metrohm) coupled with a glass jacket. The latter was connected to a thermostat in which the recirculating fluid was maintained within a temperature range of ±0.03 K. Additionally, a temperature sensor, PT 1000 (Metrohm), was applied in order to correct fluctuations and deviations of the temperature. A titration lid (Metrohm) equipped with an ion selective electrode, a double-junction reference electrode (Ag/AgCl/KNO$_3$) (Metrohm), temperature sensor, holes for inert gas inlet and outlet (capillaries), and a pipet sealed the titration vessel.

Calibration curves were measured before and after each data set with standard solutions of NaCl (Merck, Switzerland). Experiments were repeated at least in duplicate by adding the polymer or salt solution by means of an EDOS 5221 (Eppendorf, Germany). To avoid significant ionic impurities, the outflow of the reference electrode has been minimized and controlled by conductivity measurements as described previously.[18] The reproducibility of f_a was within ±5%.

Conductivity measurements were performed with a model 712 conductometer (Metrohm, Herisau, Switzerland).[56] The reproducibility of the data was within 5% for the lowest

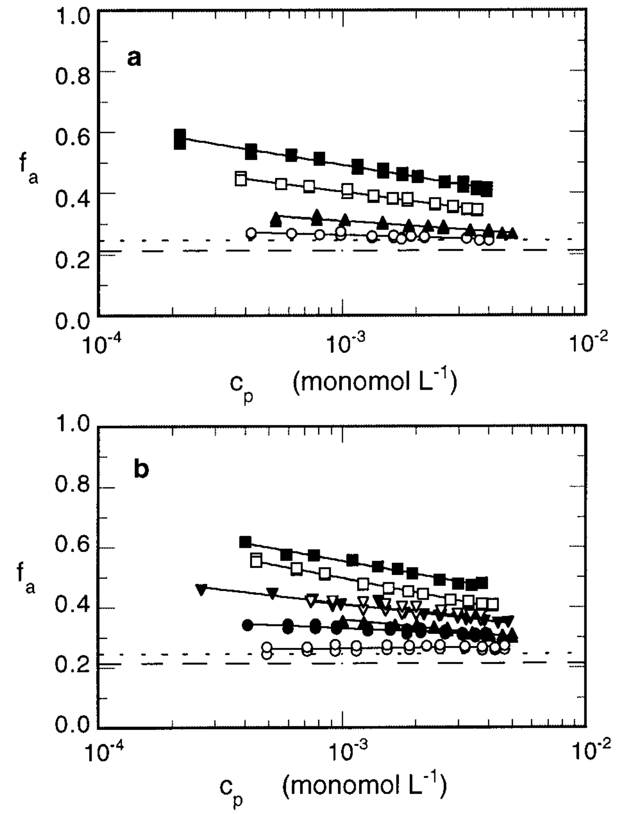

Figure 2. Concentration dependence of the counterion activity coefficient (f_a) for various chain lengths: (a) structure **2**, (b) structure **4**. P_n: ■, 27; □, 56; ▼, 63; ▽, 82; ▲, 142; ●, 181; ○, 407; - - - Manning/Iwasa; · · · Gueron.

concentrations ($c_p < 10^{-5}$ monomol L^{-1}) and better than 2% at higher concentrations ($c_p > 10^{-3}$ monomol L^{-1}). The concentrations of the polyelectrolyte stock solutions were determined by potentiometric titration (argentometric) of the chloride counterion using a 736 GP Titrino (Metrohm) to within ±1%.

Results

Activity Data. A plot of the counterion activity coefficient (f_a) as a function of the logarithm of the polyelectrolyte concentration was found to be most informative means to demonstrate the concentration-dependent changes. The activity coefficient of the counterions of a polyelectrolyte solution with known concentration (c_p in monomol L^{-1}) was calculated from the measured counterion activity (a_i) as

$$f_a = \frac{a_i}{c_p} \qquad (14)$$

Selected examples from the extensive experimental data will be presented in this section in order to indicate general trends. Figure 1 schematizes the polycations investigated herein. An example of these data is provided in Figure 2 where the concentration dependence of f_a is given.

The parameter f_a is reciprocally related to the chain length, as is shown for two structures: -dimethylallyl- (Figure 2a) and -dimethyl-*n*-octyl- (Figure 2b). The same trend was observed for all structures investigated (Figure 1, Table 3). It is also evident from Figure 2a,b that the concentration influence is stronger for shorter polymer chains. A comparison with theoretical predictions (eqs 4 and 5 in Table 1) shows that with the exception of the data for the highest contour length all experimental activity coefficients are above the theoretical values at this low polyelectrolyte concentrations ($2 \times 10^{-4} < c_p < 5 \times 10^{-3}$ monomol L^{-1}). In addition, the theoretical approaches predict neither an influence of the chain length nor the concentration dependence. Therefore, the presented data, if correct, reveal a previously unrecognized limitation in the polyelectrolyte models.

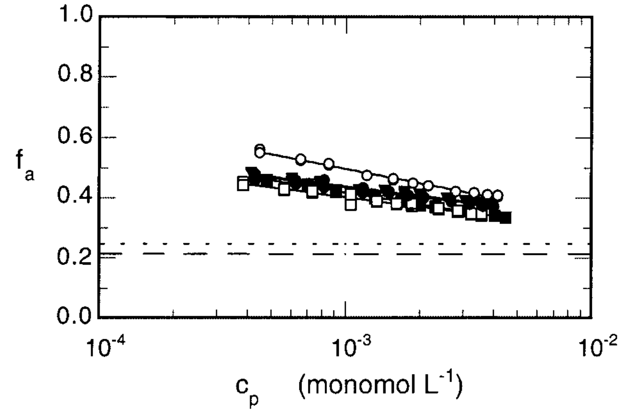

Figure 3. Concentration dependence of the counterion activity coefficient (f_a) for various structures of $P_n = 56$. Structure: ■, **1**; □, **2**; ●, **3**; ○, **4**; ▼, **5**.

The experimental activity coefficients for a constant degree of polymerization, $P_n = 56$, indicate only a slight differences as a function of chemical structure (Figure 3).

In all cases investigated and for all chain lengths structure **2** (-dimethylallyl-) consistently had the lowest activity whereas structure **4** (-dimethyl-*n*-octyl-) was always somewhat higher than the others. The increase of f_a for larger substituents at the ionic group is qualitatively in agreement with earlier findings for similar polymers.[59] The latter were, however, polydisperse and had much higher degrees of polymerization, revealing the need for new experiments with controlled polymers.

Since the ionic strength varies the extension of the ionic atmosphere (l_D), the counterion activity, as a function of the ionic strength, was also examined. For this purpose, three precise polymer concentrations, nominally 5×10^{-4}, 1×10^{-3}, and 5×10^{-3} monomol L^{-1}, have been titrated with NaCl solutions. The measurements were performed for different contour lengths of a given structure. The results show the influence of the polyelectrolyte concentration and the chain length, as is demonstrated in Figure 4 for the -dimethyl-*n*-butyl- polymer (structure **3**). Figure 4a presents the experimental data for the lowest degree of polymerization ($P_n = 27$, $L \approx 7$ nm) while Figure 4b corresponds to the longest chain ($P_n = 407$, $L \approx 102$ nm). Clearly, the deviations between the models and the data are more significant for oligomers (Figure 4a) than higher molar mass polymers (Figure 4b).

The experimental counterion activity coefficients (f_{exp}) plotted in Figure 4 have been corrected according to the relation $f_a^c = f_{exp}/f_s$.[25,60] This correction considers the interactions of the small ions, i.e., the activity coefficient (f_s) of the added low molar mass salt, in the absence of the polyelectrolyte. With increasing dilution there is less need for this correction. For the experimental conditions in this part, $5 \times 10^{-4} < c_p < 5 \times 10^{-3}$ monomol L^{-1} and $0.1 < c_p/c_s = X < 10$, the corrections were approximately

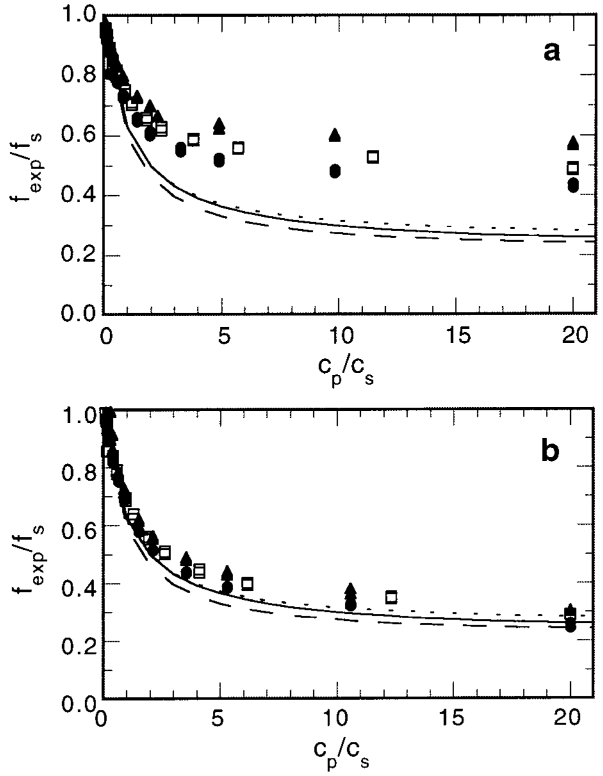

Figure 4. Corrected counterion activity coefficient vs the ratio ($c_p/c_s = X$) for structure **3**. (a) $P_n = 27$, c_p = (●) 3.93×10^{-3}, (□) 1.46×10^{-3}, and (▲) 3.78×10^{-4} monomol L^{-1}. (b) $P_n = 407$, c_p = (●) 4.23×10^{-3}, (□) 1.58×10^{-3}, and (▲) 4.07×10^{-4} monomol L^{-1}; (· · ·) Gueron, (—) Manning, (- - -) Iwasa.

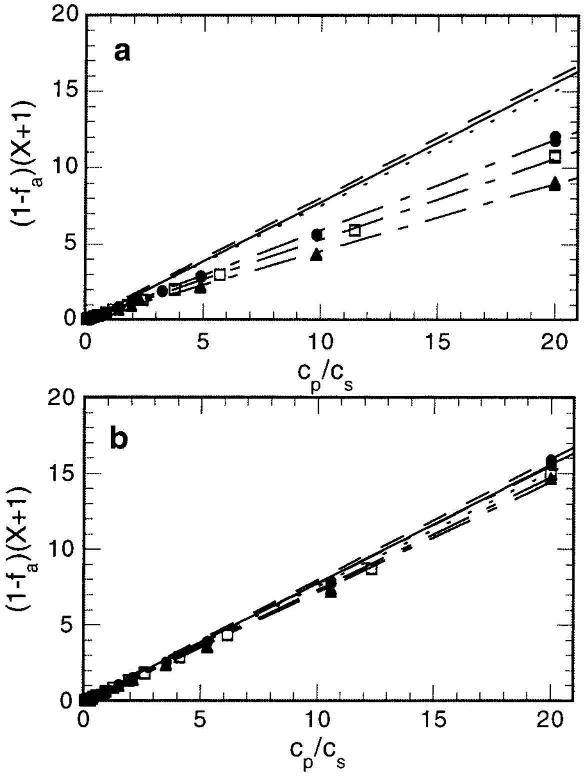

Figure 5. Data from Figure 4 plotted according to eq 15: (a) $P_n = 27$, (b) $P_n = 407$.

Table 4. Fraction of Bound Counterions $f_m{}^c$ from Linear Regression of Eq 15 for Structure 3

P_n	c_p (10^3 monomol L^{-1})	$f_m{}^c$	r
27	3.93	0.591	0.9997
	1.46	0.532	0.9997
	0.378	0.446	0.9988
56	4.21	0.667	0.9997
	1.57	0.638	0.9986
	0.404	0.564	0.9997
181	4.04	0.754	0.9997
	1.50	0.715	0.9998
	0.388	0.679	0.9997
407	4.23	0.779	0.9995
	1.58	0.741	0.9996
	0.407	0.730	0.9996
Gueron		*0.754*	1
Manning		*0.782*	1
Iwasa		*0.794*	1

15% for the highest salt and polymer concentrations and approximately 3% for the lowest polymer and salt concentrations. Again, the data confirm increasing deviation from the theories with decreasing chain length. The influence of the chain length becomes more clear if the data are plotted as $(1 - f_a)(X + 1)$ vs ($X = c_p/c_s$) corresponding to eq 15 and with f_a corrected as discussed previously (Figure 5).

The axes in Figure 5 are analogous to those derived by Ander et al.,[11,61,62] who described the diffusion process in salt containing polyelectrolyte solutions. By plotting $(1 - D_i/D_i^0)(X + 1)$ as a function of X, they were able to estimate using the slope ($f_m{}^c$), a parameter which is a measure for the fraction of condensed counterions. Considering $D_i/D_i^0 \sim f_a$, the Ander relationship has been modified as follows:[18]

$$(1 - f_a)(X + 1) \sim f_m{}^c X \qquad (15)$$

with $f_a = f_{exp}/f_s$ and $(1 - f_m{}^c) \sim \xi^{-1}$. For the comparison with the theories of Manning,[4] Iwasa,[25] and Gueron,[26] f_a in eq 15 was replaced by the theoretical value calculated using eqs 9–11 of Table 2. The slopes of the three model plots, $(1 - f_a)(X + 1)$ as a function of X, in Figure 5 had exactly the values as those calculated directly from eqs 4 and 5 for salt-free polyelectrolyte solutions. This linearity holds over the total experimental range, even for low values of c_p/c_s. Therefore, for further discussion the values $(1 - f_m{}^c)$ of eq 15 are considered as equivalent to f_a. Is has to be mentioned that the linearized theoretical curves of Manning and Iwasa do not exactly meet the origin whereas Gueron's does. As was the case for Figure 4, the data in Figure 5 reveal large discrepancies for the various theories in the oligomer range (Figure 5a), though not in the high molar mass domain (Figure 5b).

It is important to note that, even in the case where the replacement of the self-diffusion parameter D_i/D_i^0 by f_a would not be completely compensate for small ion interactions or not deliver absolute values, the strong dependence of the activity coefficient on concentration and chain length persists. Therefore, it can be concluded that the chain length and concentration effects observed are not anomalies attributed to recalculations. Table 4 summarizes all extrapolated data for different chain lengths of structure **3** (-dimethyl-*n*-butyl-) as well as the values from the theories. The lack of all theories' ability to predict a chain length and concentration dependence of the activity coefficient is obvious. Appropriate data were collected for three different polyelectrolyte concentrations of structures **1**–**5**. These extrapolation results are summarized in Table 5.

Conductivity Data. The equivalent conductivity (Λ) was calculated from the measured specific conductivities

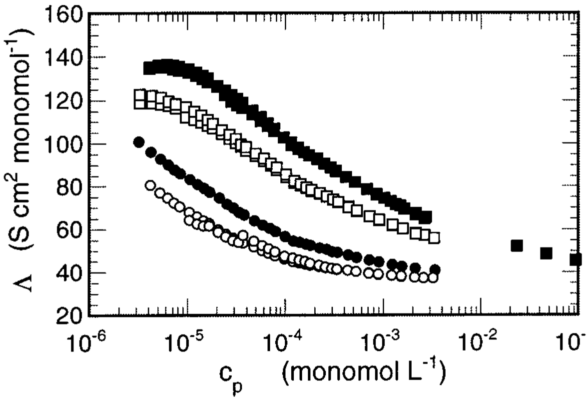

Figure 6. Concentration dependence of the equivalent conductivity (Λ) for various chain lengths of structure **3**. P_n: ■, 27; □, 56; ●, 181; ○, 407.

Table 5. Fraction of Bound Counterions $f_m{}^c$ from Linear Regression of Eq 15; $P_n = 56$

structure	c_p (10^3 monomol L^{-1})	$f_m{}^c$	r
1	3.66	0.725	0.9996
	1.36	0.660	0.9978
	0.352	0.579	0.9974
2	3.71	0.713	0.9995
	1.38	0.661	0.9997
	0.356	0.586	0.9994
3	4.21	0.667	0.9997
	1.57	0.638	0.9986
	0.404	0.564	0.9997
4	3.83	0.666	0.9997
	1.43	0.633	0.9995
	0.368	0.573	0.9987
5	0.361	0.666	0.9997
	1.40	0.643	0.9998
	0.425	0.575	0.9992

of the solution (κ) and the solvent (κ_0):

$$\Lambda = \frac{\kappa - \kappa_0}{c_p} \tag{16}$$

An influence of the chain length is clearly observed, as is presented, for example, for the -dimethyl-*n*-butyl-structure in Figure 6.

A significant influence of the substituent size on the equivalent conductivity has not been found. In general, the polymer with the longest substituent side chain (structure **4**) was slightly lower than that of the other structures (data not shown). If the ionic strength was increased by addition of low molar mass salt, the equivalent conductivity decreased for all chain lengths, with this effect being stronger in the highly diluted range ($c_p < c^*$). The conductivity results of this study confirm the general description of the electrolytic conductivity behavior of highly charged strong polyelectrolytes, which has been established for other chemical structures recently.[56] Therefore, the following discussion will focus more on the activity data, which are submitted the first time in such a comprehensive form for highly charged strong polyelectrolytes.

Discussion

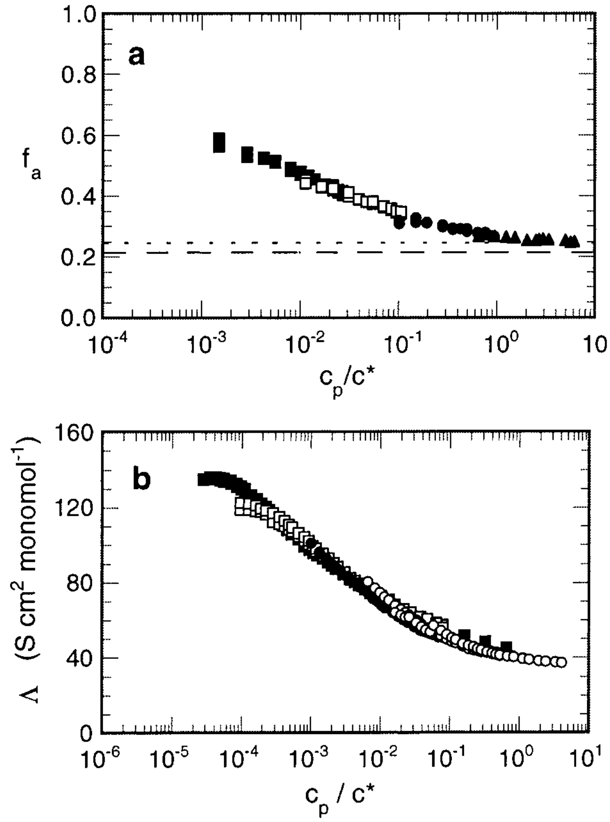

Figure 7. Counterion activity coefficient (f_a) and equivalent conductivity (Λ) vs the ratio c_p/c^* for various chain lengths of structure **2** (a) and structure **3** (b). P_n: ■, 27; □, 56; ▲, 142; ●, 181; ○, 407; (- - -) Manning/Iwasa; (· · ·) Gueron.

Salt-Free Polyelectrolyte Solutions. The strong increase of both the counterion activity coefficient and the equivalent conductivity is assigned to the range below the overlap concentration c^*, which was calculated from[37,63]

$$c^* = (N_A L^2 a)^{-1} \tag{17}$$

Here the symbols N_A, L, and a represent Avogadro's number, the contour length, and the length of one monomer unit. To demonstrate this correlation, the experimental data of Figures 2a and 6 are plotted vs the ratio of the polyelectrolyte to the overlap concentration, c_p/c^* in Figure 7.

Both f_a and Λ increase monotonically below c^*, i.e., $c_p/c^* = 1$. However, the beginning of the strong linear increase is located not at $c_p/c^* = 1$ but at a somewhat lower value, approximately one-tenth of c_p/c^*. Therefore, a further correlation was performed relative to the ratio l_D/L (Figure 8). Figure 8 shows clearly the strong linear increase of f_a and Λ above $l_D/L = 1$, although this increase starts moderately already at $0.282 = (4\pi)^{-1/2}$, the value for l_D/L at $c_p = c^*$. This value was calculated by combining eqs 13 and 17 and setting $c_s \rightarrow 0$, $\xi = l_B/b$, $a = b$. The transition range $0.282 \leq l_D/L \leq 1$ is marked by shading in Figure 8.

Theoretical dependencies for f_a and Λ are added to the experimental data in Figure 8. For $c_p > c^*$, i.e., $l_D/L < 0.282$, the agreement between the calculated and experimental f_a is sufficient. However, none of the theories explain the increase of f_a at high dilutions, which is a limitation.

The theoretical equivalent conductivity was calculated according to[21−23,64,65]

$$\Lambda = f_c(\lambda_c^0 + \lambda_p) \tag{18}$$

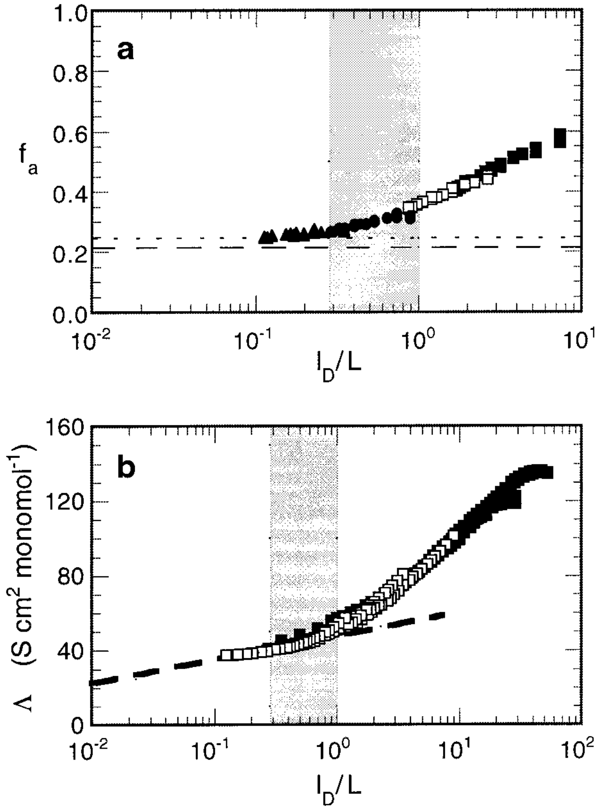

Figure 8. Counterion activity coefficient (f_a) and equivalent conductivity (Λ) vs the ratio l_D/L for various chain lengths of structure **2** (a) and structure **3** (b). P_n: ■, 27; □, 56; ▲, 142; ●, 181; ○, 407; (- - -) Manning/Iwasa; (• • •) Gueron; (- - -) theory with $L = 102$ nm. Shaded: transition range $0.282 \leq l_D/L \leq 1$.

with the equivalent conductivity of the polyion[19]

$$\lambda_p = \frac{0.866 H \left|\ln \frac{r}{l_D}\right|}{1 + (1 - 0.866)(\lambda_c^0)^{-1} H \left|\ln \frac{r}{l_D}\right|} \tag{19}$$

where $f_c = 0.866\xi^{-1}$, $\lambda_c^0 = 69$ S cm^2 monomol^{-1}, $H = 2.297 \times 10^{-3}$ s^3 A^2 mol^{-1} kg^{-1}, and $r = 1.2 \times 10^{-9}$ m.[18] In this model λ_p is determined by a temperature-dependent electrophoretic mobility factor $H = 4\epsilon\epsilon_0 RT/3\eta$,[64] which contains the viscosity of the solvent η as well as its relative permittivity $\epsilon\epsilon_0$, the equivalent conductivity of the counterion in an infinitely diluted solution in the absence of polyions λ_c^0, the radius of the polymer chain r, and the Debye screening length l_D. The parameter l_D is obtained from eq 13. The agreement between theory and experiment is excellent for $l_D/L < 1$, if the ratio is calculated with $L = 102$ nm, the value for the longest experimentally investigated polyelectrolyte chains. For this chain length practically no deviation from the theoretical behavior of f_a was indicated in Figure 2. The theoretical increase of the equivalent conductivity Λ in Figure 8b results from the increase of λ_p, from eq 19, with dilution.

It should be mentioned that the chemical structur has an opposing influence on f_a and Λ. On one hand, f_a increases for larger substituents at the ionic group. This is likely due to an increasing screening of the polyion charge by more voluminous hydrophobic substituents. On the other hand, the chain radius increases with the substituent size. This results in smaller λ_p values and reduced Λ. Therefore, the substituent influence is less pronounced for the conductivity than for the counterion activity data.

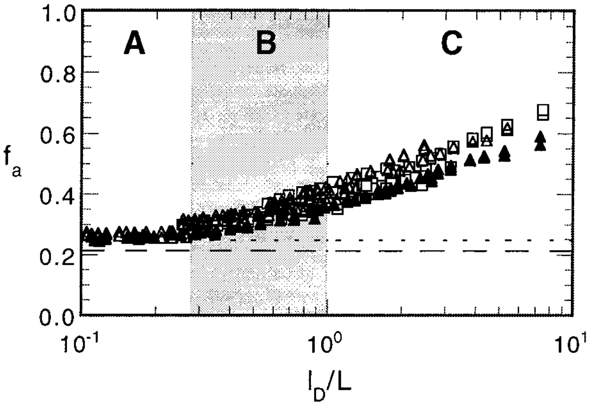

Figure 9. Counterion activity coefficient (f_a) vs the ratio l_D/L for various chain lengths and structures. Structure: ■, **1**; ▲, **2**; □, **3**; △, **4**; (- - -) Manning/Iwasa, (• • •) Gueron. A: Manning range; B (shaded): transition range; C: highly diluted range.

Figure 9 summarizes the counterion activity coefficients for four investigated structures.

All polymers can be fit by the general model which is characterized by a low and constant counterion activity coefficient above the overlap concentration and $l_D/L < (4\pi)^{-1/2}$ (range A in Figure 9).[56] In the transition range, between $l_D/L = (4\pi)^{-1/2}$ and $l_D = L$, f_a increases moderately (range B, shaded, in Figure 9). The strongest increase of f_a occurs in the highly diluted range where l_D exceeds L (range C in Figure 9). Here also the higher values of f_a for the polymers with larger substituents are most visible.

Polyelectrolyte Solutions with Addition of Salt. From Tables 4 and 5 the counterion activity coefficients have been calculated as $f_a = (1 - f_m{}^c)$ and plotted, in Figure 10, as a function of the polyelectrolyte concentration for both various chain lengths and structures.

The same activity coefficient dependencies are observed in salt-containing (Figure 10) and salt-free (Figure 2) solutions. The parameter f_a increases with dilution and with decreasing chain length (Figure 10a). A weak structural influence is visible in the range of higher polyelectrolyte concentrations. Since all measurements were performed in the same c_p/c_s range, the total ionic strength was higher for the higher polyelectrolyte concentrations. It is expected that the steric hindrance of chain coiling is more pronounced if the size of the substituents at the ionic group increases. The resulting differences of the coil dimensions at constant ionic strength, for polylectrolytes having the same chain length but various substituents, could be responsible for deviations of f_a.

To examine whether the contour length influence, for a given charge distance and similar chain radius, is universal, the data of this study have been compared with appropriate results from poly(sodium styrenesulfonate) standards (NaPSS).[18,66] For two degrees of polymerization, $P_n = 39$ and 890, and $c_p = 10^{-3}$ monomol L^{-1} f_a was determined as 0.432 and 0.129 in a comparable range of c_p/c_s. For a comparison at the same polyelectrolyte concentration, the f_a of structure **3** (-dimethyl-*n*-butyl-) was calculated for $c_p = 10^{-3}$ monomol L^{-1} from linear regressions of the plots in Figure 10a. Further, from the plots in Figure 10b, it can be concluded that the structural influence at this concen-

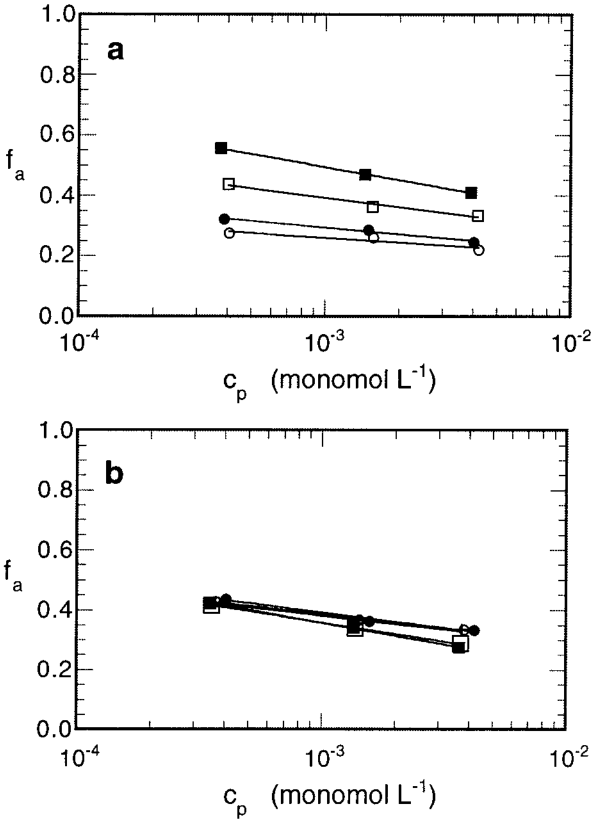

Figure 10. Concentration dependence of the counterion activity coefficient (f_a) for various chain lengths and structures with addition of salt: (a) structure **3** and P_n = (■) 27, (□) 56, (●) 181, and (○) 407. (b) P_n = 56 and structure (■) **1**, (□) **2**, (●) **3**, and (○) **4**.

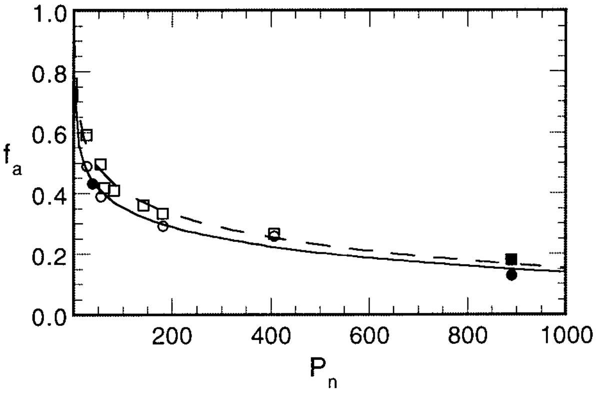

Figure 11. Counterion activity coefficient (f_a) vs degree of polymerization (P_n) for $c_p = 10^{-3}$ monomol L^{-1}: (- - -) in water, (□) structure **4**, (■) NaPSS; (—) with salt, (○) structure **3**, (●) NaPSS.

tration is negligible. In particular, for structures **1** and **2** (-trimethyl- and -dimethylallyl-), as well as for structures **3** and **4** (-dimethyl-*n*-buty-l and -dimethyl-*n*-octyl-), virtually no differences have been observed. Figure 11 confirms the general chain length dependence of f_a for both conditions, polyelectrolyte solution without and with added salt. The parameter f_a is somewhat higher in aqueous solution than in salt-containing media. However, the differences disappear with increasing chain length.

Interpretation. Recently, the electrolytic conductivity behavior of highly charged strong polyelectrolytes has been explained by hypothesizing that the interaction parameter of the equivalent conductivity, f_c in eq 18, increases below c^*.[18,56] With the present results, sufficient experimental data are available to support this explanation. Some details will be discussed generally in the following paragraph. Quantitative model calculations, on the basis of the theory of Ramanathan and Woodbury,[55] Manning and Mohanty's counterion condensation model for oligomers,[54] and the model proposals of Dobrynin, Colby, Rubinstein et al.,[53,67] are in progress and will be the topic of a subsequent publication.

At high dilutions the local counterion concentration around the polyion exceeds the applied experimental concentration by approximately 3−6 orders of magnitude. This results in a high diffusion potential of the "bound" counterions.[9] The strong electrical field around the polyion may also influence the water structure close to the polyelectrolyte backbone as has been reported for low molar mass ions. For example, it is known that the partial specific volumes of electrolytes decrease with dilution. The values of this parameter can only be explained by including a change of the water structure in the environment of the ions.[67] However, there is no quantitative information available about the order of magnitude of such a change in the environment of polyions. The majority of theoretical approaches for polyelectrolytes are based on a constancy of the solvent properties. This implies that a change of the water structure in the environment of the polyion has not been considered.

Manning and Mohanty have concluded that when the contour lengths (L) is of order as the Debye screening length (l_D), it influences neither the threshold charge density for condensation nor the number of condensed counterions, but instead appears as one of the parameters determining the structure of the condensed layer.[54] This is approximately in agreement with the experimental findings of this work. The counterion activity already increases moderately when c^* is passed. This point is characterized by $L \approx 3.6 l_D$, calculated from $l_D/L = 0.282$ at c^* for monovalent polyelectrolytes with $a = b$ investigated herein. Other theoretical studies have concluded that counterion inhomogeneities at the ends of the polyelectrolyte chain are on the order of a Debye length.[69,70] This would imply $L > 3 l_D$ as a threshold for the onset of a constant interaction parameter. At present, the critical value above which changes of the structure of the condensed layer will influence the counterion activity cannot be ascertained more precisely. However, activity and conductivity measurements show that when L approaches the value of l_D, a threshold occurs in the polyelectrolyte solution behavior.

Recently, experimental counterion activity and conductance results have been compared with theoretical models for other polyelectrolyte structures in order to clarify the departure from the theories.[71] Although the authors have focused on the effect of the charge density and the chain conformation, the conclusions from the presented work may also be helpful to explain their experimental findings.

Conclusions

Counterion activity studies reveal a general influence of concentration, chain length, and ionic strength on the polyion−counterion interaction for highly charged strong polyelectrolytes having charge distances less than the Bjerrum length. Different concentration regimes could be identified which are best characterized by the ratio of the Debye to the contour length. The activity data support the explanation of the electrolytical conductivity behavior of polyelectrolytes in dilute and semidilute aqueous solutions. The experimental data are used for model calculations, which are in progress and will include the comparison with various theoretical approaches.

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