Kinetic Analyses of Gegenion Binding in Polyelectrolyte Solution. Cationic Phosphorescence Probe and Poly(styrenesulfonate) Anion System

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The kinetics of binding between sodium poly(styrenesulfonate) (NaPSS) and cationic phosphorescence probes have been studied by phosphorescence decay methods. The probes (Scheme I) are *n*-(4-bromo-1-naphthoyl)methyl- (or pentyl, decyl) trimethylammonium bromide (BNK-1$^+$, BNK-5$^+$, and BNK-10$^+$ for *n* = 1, 5, and 10, respectively). From a method involving phosphorescent quenching for the BNK-1$^+$ and NaPSS systems, the association (k_f) and dissociation rates (k_b) are evaluated as 6.8×10^9 M^{-1} s^{-1} and 3.7×10^4 s^{-1}. The magnitude of k_f is close to the limit for diffusion-controlled quenching, which demonstrates that the probes are not bound via "site binding", but rather via "atmospheric binding". The magnitudes of k_f and the equilibrium association constant, K, decrease with NaCl addition or with increasing polymer concentration, whereas k_b increases. The results of these kinetics are consistent with Manning's theory of polyelectrolyte systems.

Introduction

Synthetic polyelectrolytes such as sodium poly(styrenesulfonate) are highly simplified analogues of biologically important macromolecules. Thus, the thermodynamic and kinetic study of synthetic polyelectrolytes may provide important information which can be applied to an understanding of the physicochemical properties of biological macromolecules. One of the most characteristic properties of polyelectrolytes in solution is the gegenion binding of macroions, which is mainly due to the high electrostatic potentials of the macroions. Many investigations, both experimental and theoretical, of the binding for various polyelectrolytes have been reported with emphasis on their static properties.[2] Kinetic studies have been less intensive probably as a result of the restrictions imposed by available experimental techniques. The main techniques employed to study the kinetics of aqueous polyelectrolyte systems have been temperature-jump,[3] electric-field-jump,[4] and ultrasonic-relaxation methods.[5] Other methods[6] have

Scheme I

BNK - 1$^\oplus$ BNK - 5$^\oplus$ BNK - 10$^\oplus$
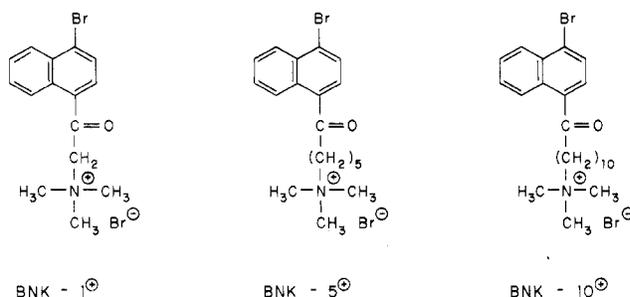
played only a minor role in obtaining kinetic information.

Experimental data on the gegenion binding can be classified according to two main types of association kinetics, i.e., (1) fast associations whose kinetics are characteristic of *diffusion-controlled* association reactions and (2) slow associations whose kinetics are characteristic of *comparatively slow* reactions.[7] Class 1 includes proton transfer reactions of polybases and dye–polyelectrolyte binding. In these cases, the binding of gegenions does not occur on a specific site of macroions and is termed atmospheric binding. On the other hand, most metal ion bindings to a great variety of macroion ligands are examples of class 2 and have typical rate constants of about 10^4–10^8 M^{-1} s^{-1}, i.e., values well below that for diffusion of simple ions in an aqueous medium. The rate-determining step of these relatively slow reactions is believed to be the exchange of water molecules bound to the gegenions or macroion ligands at specific sites.[9] Recently a theoretical discussion of the kinetic aspects of gegenion binding has been given by Schwartz et al.[10]

In this report, we apply photochemical techniques to determine the kinetic parameters for the gegenion binding between the cationic phosphorescence probes BNK-1$^+$, BNK-5$^+$, and BNK-10$^+$ (see Scheme I) and poly(styrenesulfonate) anions. These probes emit a strong phosphorescence in N$_2$-purged aqueous solution and are quenched efficiently with ionic quenchers such as nitrite

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(2) See, for example: (a) Huizenga, J. R.; Grieger, P. F.; Wall, F. T. *J. Am. Chem. Soc.* **1950**, *72*, 2636, 4228. (b) Wall, F. T.; Dremus, R. H. *Ibid.* **1954**, *76*, 868. (c) Wall, F. T.; Hill, W. B. *Ibid.* **1960**, *82*, 5599. (d) Buckner, P.; Cooper, R. E.; Wasserman, A. *J. Chem. Soc.* **1961**, 3974. (e) Rice, S. A.; Nagasawa, M. "Polyelectrolyte Solutions"; Academic Press: New York, 1961. (f) Kotin, L.; Nagasawa, M. *J. Chem. Phys.* **1962**, *36*, 873. (g) Okubo, T.; Nishizaki, Y.; Ise, N. *J. Phys. Chem.* **1965**, *69*, 3690. (h) Darskus, R. L.; Jordon, D. O.; Kurucsev, T. *Trans. Faraday Soc.* **1966**, *62*, 2876. (i) Dolar, D.; Span, J.; Pretner, A. *J. Polym. Sci., Part C* **1968**, *16*, 3557. (j) Baumgartner, E.; Liberman, S.; Lagos, A. E. *Z. Phys. Chem.* **1968**, *61*, 211. (k) Okubo, T.; Ise, N. *Macromolecules* **1969**, *2*, 407. (l) Manning, G. *J. Chem. Phys.* **1969**, *51*, 934. (m) Oosawa, F. "Polyelectrolytes"; Marcel Dekker: New York, 1971. (n) Paoletti, S.; Delben, F.; Crescenzi, V. *J. Phys. Chem.* **1976**, *80*, 2564. (o) Mita, K.; Okubo, T.; Ise, N. *J. Chem. Soc., Faraday Trans. I* **1976**, *72*, 1627. (p) Iwasa, K. *J. Phys. Chem.* **1977**, *81*, 1829.
(3) (a) Schwartz, G.; Balthasar, W. *Eur. J. Biochem.* **1970**, *12*, 461. (b) Nishikawa, H.; Tsuchida, E. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1545.
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(6) For fluorescence temperature-jump method, see: (a) Jovin, T. J.; Striker, G. "Chemical Relaxation in Molecular Biology"; Pecht, I., Rigler, R., Eds.; Springer-Verlag: West Berlin, 1977. For UV-stopped-flow method, see: (b) Nishikawa, H.; Tsuchida, E. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 1557. For conductance stopped-flow method, see: (c) Enokida, A.; Okubo, T.; Ise, N., publication in preparation.

(7) The other types of binding such as structure-enforced binding and charge-transfer binding were also proposed (see ref 8).
(8) See, for example: Boyd, G. E.; Bunzl, K. *J. Am. Chem. Soc.* **1974**, *96*, 2054.
(9) Some researchers call the former "primary" associations, and the latter "secondary" associations.
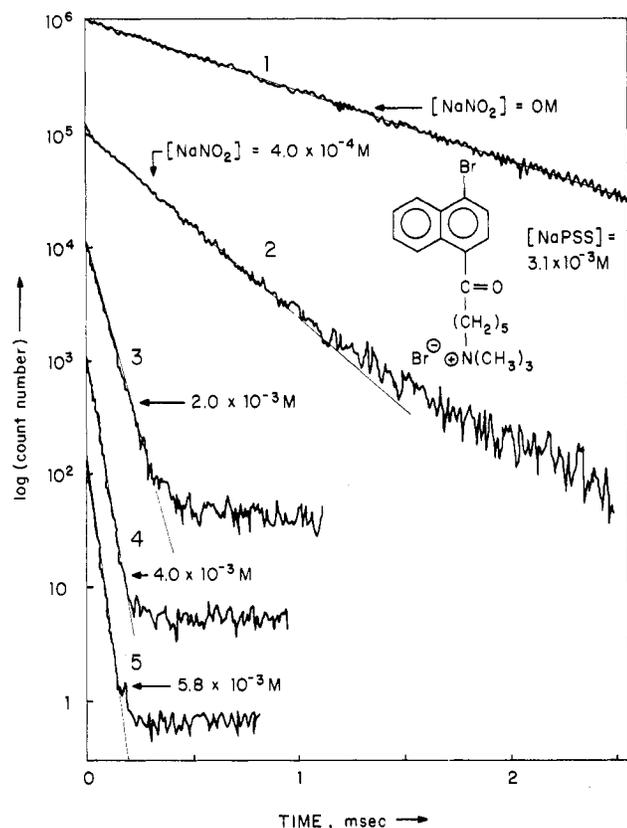(10) (a) Schwartz, G. *Eur. J. Biochem.* **1970**, *12*, 442. (b) Schwartz, G. *Ber. Bunsenges. Phys. Chem.* **1972**, *76*, 373.

Figure 1. Typical traces of decay of BNK-5$^+$'s phosphorescence in the presence of NaPSS and NaNO$_2$ quencher at 25 °C. [BNK-5$^+$] = 4 × 10^{-5} M; [NaPSS] = 3.10 × 10^{-3} M; [NaNO$_2$] = (1) 0, (2) 4 × 10^{-4}, (3) 2 × 10^{-3}, (4) 4 × 10^{-3}, and (5) 5.8 × 10^{-3} M.

ions. In the systems studied, both the probes and the macroions are highly hydrophobic. Thus, "atmospheric" binding is expected and will be strongly influenced by the electrostatic and hydrophobic interactions between macroions and their gegenions.

Experimental Section

Materials. The anionic polyelectrolyte, sodium poly-(styrenesulfonate) (NaPSS) was a gift of Dr. H. Gregor, Columbia University. The sample was purified by dialysis against pure water for 2 weeks, followed by ion exchange with cation- and anion-exchange resins. Equivalent concentrations of hydrogen poly(styrenesulfonate) (HPSS) were determined by acid titration. The molar extinction coefficient at 262 nm was 403 ([NaPSS] = 3 × 10^{-5} M) and decreased slightly with increasing polymer concentration. The phosphorescence probes employed (Scheme I) were BNK-1$^+$, BNK-5$^+$, and BNK-10$^+$. The syntheses and purifications of these samples are described elsewhere.[11,12] Sodium chloride was ultrapure grade (Alfa Products). Spectral-grade acetonitrile was used without further purification. Deionized water was obtained with ion-exchange resins and further distilled. Nitrogen (Linde, oxygen-free grade) was used as received.

Phosphorescence Measurements. Phosphorescence spectra were obtained by using a SPEX Fluorog fluorimeter. Lifetimes were measured by using the photon-counting technique as described earlier.[13,14] All solutions were nitrogen purged for 5–7 min just before measurement.
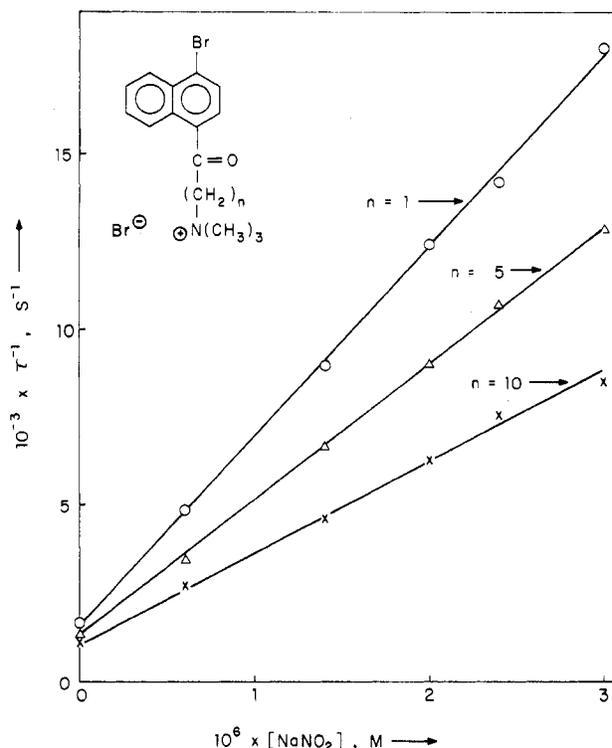

Figure 2. τ^{-1} vs. [NaNO$_2$] plots for BNK-1$^+$ (O), BNK-5$^+$ (‡), and BNK-10$^+$ (X). [BNK-n^+] = 4 × 10^{-5} M, at 21 °C for BNK-10$^+$ and at 25 °C for BNK-1$^+$ and BNK-5$^+$.

Results

Determination of Kinetic Parameters. Phosphorescence decay curves of the probes were found to fit first-order relaxation in both the presence and the absence of quencher (NaNO$_2$). A typical example of the phosphorescence decay in the presence of NaPSS and NaNO$_2$ quencher is given in Figure 1. A single first-order relaxation was observed up to a 99% decrease in the value of the initial intensity. From the slopes the lifetimes (τ) were derived. Figure 2 shows some plots of reciprocal phosphorescence lifetimes vs. quencher concentration. Excellent linearity is obtained, so that quenching rates could be determined from the slopes of the plots. The quenching rate constants obtained in this manner (k_q) were 5.30 × 10^9, 3.9 × 10^9, and 2.62 × 10^9 M^{-1} s^{-1} for BNK-1$^+$ (at 25 °C), BNK-5$^+$ (at 25 °C), and BNK-10$^+$ (at 21 °C), respectively. The increase in rate with decreasing size of the probe is attributed to the decrease in the strength of the electrostatic attraction between the probe cations and the anionic quencher.

The reaction rates between probes and macroanions were estimated from the reaction scheme[15] shown in eq 1.

$$T + P \underset{k_b}{\overset{k_f}{\rightleftharpoons}} T \cdot P \qquad (1)$$

no T $\qquad$ no T
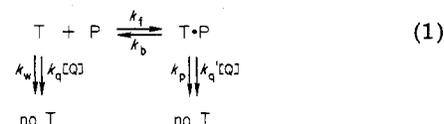
From this scheme, eq 2 may be derived.[15] In eq 2, k_f and

$$\tau^{-1} = k_b + k_p + k_q'[Q] - k_f k_b[P]/(k_f[P] + k_w + k_q(Q)) \qquad (2)$$

(11) Turro, N. J.; Bolt, J. D., *Photochem. Photobiol.* In press.
(12) Turro, N. J.; Okubo, T. *J. Phys. Chem.* Submitted for publication.
(13) Turro, N. J.; Liu, K.-C.; Chow, M.-F.; Lee, P. *Photochem. Photobiol.* **1978**, *27*, 523.
(14) Turro, N. J.; Aikawa, M. *J. Am. Chem. Soc.* **1980**, *102*, 4866.

(15) The basic mechanism of this paper is just the same as that reported for the micellar binding with its gegenion by Thomas et al. (see ref 16).
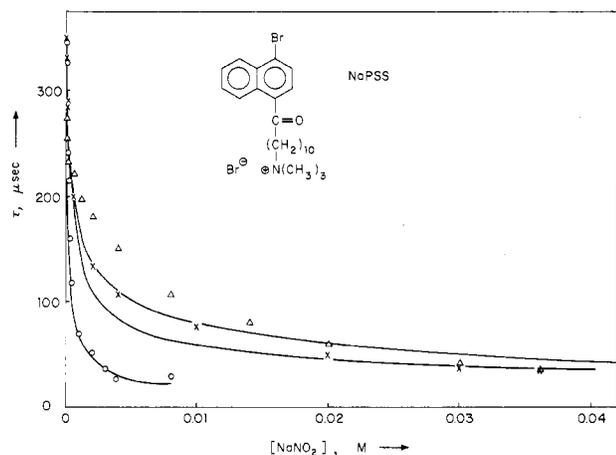(16) Almgren, M.; Grieser, F.; Thomas, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 279.

Figure 3. τ vs. [NaNO$_2$] plots for the BNK-10$^+$ + NaPSS + NaNO$_2$ + NaCl + H$_2$O systems at 21 °C. NaCl concentration dependence: [NaCl] = (O) 0, (X) 0.001, (□) 0.003, and (Δ) 0.01 M. [BNK-10$^+$] = 4 × 10^{-5} M; [NaPSS] = 3.10 × 10^{-3} M.

k_b are association and dissociation rates between macroions and their probe gegenions. k_w and k_p represent the triplet deactivation rate constants in the water phase and in complexes to the polymer, respectively. Since anionic quenchers, i.e., nitrite, are repelled from the macroanions by electrostatic forces, the k_q'[Q] term in eq 2 is expected to be negligibly small compared with the k_q[Q] term. It is plausible that the cooperative binding of the probes themselves occurs on the macroanion sites, especially for the strongly hydrophobic probe, BNK-10$^+$. However, we do not consider explicitly this factor in our treatment.

The various parameters of eq 2 were determined by computer simulation of experimental data. In addition, the rough value of K ($=k_f/k_b$) was obtained independently from the equation $K = k_q/k_q^*$[P] at low concentrations of quencher, where k_q^* is the apparent quenching rate constant in the presence of polymer and is obtained from the slope of the plot of τ^{-1} against quencher concentration. Typical examples of such plots are given in Figures 3 and 4. Solid curves show the calculated values from eq 2. The kinetic parameters thus obtained are compiled in Table I. Except for experiments 8–10 in Table I (the plots for experiments 9 and 10 are given in Figure 4), the experimental values of lifetimes gave an excellent fit to eq 2.

The k_f values are between 8.8 × 10^8 and 2 × 10^{10} M^{-1} s^{-1}, and the binding reaction of the present systems seems to be close to the diffusion-controlled reaction. When the largest probe (BNK-10$^+$) was used, the k_f and K values were small (experiments 2–4 in Table I). This is due to the fact that the effective charge numbers on the probe decrease with increasing size of the probe and the electrostatic attraction forces become weaker between the probes and the macroions.

Dependence of Rate Constants on Foreign Salt Concentration. Table I (experiments 4 and 11–13) indicates that, at a given polymer concentration, k_f and K decrease significantly with increasing concentration of sodium chloride. On the other hand, k_b increases. The electrostatic attraction between macroions and gegenions affords an explanation of this phenomenon; i.e., sodium chloride shields the electrostatic attraction between macroanions and probe cations. Therefore, the association process will be retarded with the salt. The dissociation process, on the other hand, is dependent on the extent of the attraction and is enhanced by the shielding effect. A theoretical discussion of these points will be given later.

The water quenching term, k_w, was insensitive to salt addition, but k_p increased sharply with addition of salt.

TABLE I: Kinetic Parameters of Binding of BNK-1$^+$, BNK-5$^+$, and BNK-10$^+$ to Poly(styrenesulfonate) Anions[a]

expt	probe	temp, °C	10^3 [NaPSS], M	10^3 [NaCl], M	[CH$_3$CN], vol %	10$^9 k_f$, M^{-1} s^{-1}	10$^{-4} k_b$, s^{-1}	10$^{-4} K$, M^{-1}	10$^{-9} k_g$, M^{-1} s^{-1}	10$^{-6} k_g'$, M^{-1} s^{-1}	10$^{-3} k_w$, s^{-1}	10$^{-3} k_p$, s^{-1}
1	BNK-1$^+$	7	2.94	0	0	1.6	2.7	6.1	2.37	2	1.00	2.2
2	BNK-1$^+$	25	3.10	0	0	6.8	3.7	18	5.30	1	1.61	1.6
3	BNK-5$^+$	25	3.10	0	0	7.6	3.8	20	3.90	1	1.34	1.4
4	BNK-10$^+$	21	2.94	0	0	2.3	3.9	5.9	2.62	2	1.08	2.9
5	BNK-10$^+$	32	2.94	0	10	2.6	4.7	5.4	2.79	2	1.15	3.4
6	BNK-10$^+$	21	2.94	0	20	1.3	4.5	2.8	1.96	2	1.18	2.1
7	BNK-10$^+$	21	2.94	0	0	0.88	5.5	1.6	1.27		1.46	3.1
8	BNK-10$^+$	21	0.118	0	0	20	0.5	400	2.62	0.5	1.08	5.5
9	BNK-10$^+$	21	0.294	0	0	20	0.7	300	2.62	0.3	1.08	3.9
10	BNK-10$^+$	21	0.98	0	0	7	1.5	50	2.62	0.3	1.08	2.9
11	BNK-10$^+$	21	2.94	1.00	0	2.0	4.3	4.7	2.62	2	1.08	3.7
12	BNK-10$^+$	21	2.94	3.00	0	1.7	5.0	3.4	2.60	1	1.08	7.3
13	BNK-10$^+$	21	2.94	10.0	0	1.5	5.7	2.6	2.58	1	0.95	10.8

[a] [BNK-n$^+$] = 4 × 10^{-5} M.
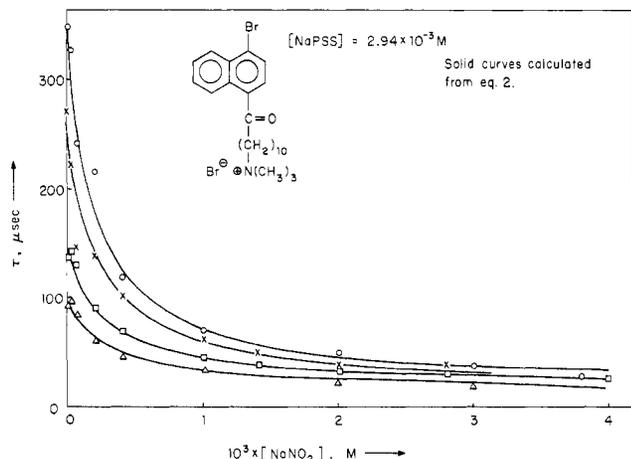
Figure 4. τ vs. [NaNO$_2$] plots for the BNK-10$^+$ + NaPSS + NaNO$_2$ + H$_2$O systems at 21 °C. Polymer concentration dependence: [NaPSS] = (O) 2.94×10^{-3}, (X) 9.8×10^{-4}, and ($\triangle$) = 2.94×10^{-4} M.

TABLE II: Thermodynamic Quantities for Binding of BNK-10$^+$ to NaPSS at 20 °C[a]

$\Delta G_f^{\ddagger} = 4.61$	$\Delta G_b^{\ddagger} = 11.0$	$\Delta G = -6.39$
$\Delta H_f^{\ddagger} = 3.20$	$\Delta H_b^{\ddagger} = 3.81$	$\Delta H = -0.61$
$\Delta S_f^{\ddagger} = -5$	$\Delta S_b^{\ddagger} = -25$	$\Delta S = 20$

[a] [BNK-10$^+$] = 4×10^{-5} M; [NaPSS] = 2.94×10^{-3} M. The units of free energies and enthalpies are kcal/mol, and entropies are in eu. The experimental uncertainty is believed to be ±0.1 for the free energies, ±0.5 for the enthalpies, and ±3 for the entropies.

Influence of Acetonitrile. The k_f and K values decreased with acetonitrile addition, whereas k_b increased slightly (see experiments 4, 6, and 7). This result is consistent with the expectation that organic molecules will weaken the hydrophobic attraction between PSS anions and BNK cations. k_w and k_p were found to be insensitive to addition of acetonitrile.

Polymer Concentration Dependence. As was described before, at low polymer concentration, reliable data on k_f, k_b, and K were not obtained (Figure 4). This result is ascribed to the specific concentration dependence of the activity of polyelectrolyte and is discussed in more detail in the Discussion section.[17] As is clear from Table I, k_f and K decreased very significantly with decreasing polymer concentration, whereas k_b increased. This trend may appear to be peculiar at first glance, but it is readily interpreted by the increase in the thermodynamic activity of polymer with dilution.
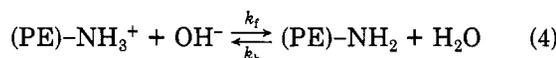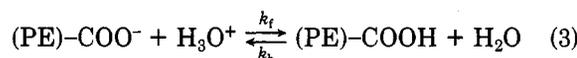
Temperature Dependence. From experiments 1, 4, and 5 in Table I, it is clear that all rate constants (k_f, k_b, k_q, k_w, and k_p) increased with rising temperature and K decreased. The temperature dependence of k_f, k_b, and K allows an evaluation of the free energies, enthalpies, and entropies of the binding equilibrium (ΔG, ΔH, and ΔS) and of the activation parameters for the association ($\Delta G_f^{\ddagger}$, $\Delta H_f^{\ddagger}$, and $\Delta S_f^{\ddagger}$) and for the dissociation ($\Delta G_b^{\ddagger}$, $\Delta H_b^{\ddagger}$, and $\Delta S_b^{\ddagger}$). The resulting thermodynamic and kinetic parameters are listed in Table II. The negative values of ΔG and ΔH show that the binding is a favorable process. The large positive value of ΔS, i.e., +20 eu, suggests that significant "dehydration" occurs in the course of association, which point is discussed later.

Scheme II
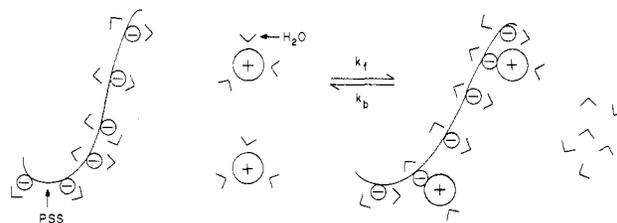
Discussion

The k_f values obtained are of the order of 10^9–10^{10} M^{-1} s^{-1}. Therefore, the bimolecular binding reaction occurs with a rate close to that expected for diffusion-controlled reaction. Our values are close to those reported for the association of Mg^{2+} with polyadenylic acid and polycytidilic acid (2×10^{10} and 1×10^{10} M^{-1} s^{-1}, respectively) and to rates of proton transfer reactions (i.e., eq 3 and 4) of

$$(PE)-COO^- + H_3O^+ \underset{k_b}{\overset{k_f}{\rightleftharpoons}} (PE)-COOH + H_2O \quad (3)$$

$$(PE)-NH_3^+ + OH^- \underset{k_b}{\overset{k_f}{\rightleftharpoons}} (PE)-NH_2 + H_2O \quad (4)$$

synthetic and biological polyelectrolytes (PEs): 2×10^{10}–3×10^{10} M^{-1} s^{-4} for polyethylenimine hydrochloride,[5g] 7.4×10^9 or 1×10^{10}–4×10^{10} M^{-1} s^{-1} for poly(L-lysine)[5a,f] and 1×10^{10}–5×10^{10} M^{-1} s^{-1} for human hemoglobin.[5b] Our binding systems do not need the attachment of the gegenions to specific sites of the macroions. In other words, the probe cations are not bound in the mode of "site binding", but "atmospheric binding". This is due to the fact that the probes are too large for specific site-binding. We must recall here that the rates of some kinds of metal ion–macroion ligand binding reactions are lower than a diffusion-controlled rate (about 10^5 M^{-1} s^{-1} for Mg^{2+} binding, for example).[3b,4,6b,c] In these reactions, the exchange of water molecules coordinated to the metal ions is the rate-determining step.

A large positive value was observed for the entropy of association (Table II). This supports the idea that the dehydration of water molecules, which were bound originally to the macroions and gegenions with electrostrictional forces, certainly occurs in the course of the gegenion binding. A schematic picture of the dehydration is shown in Scheme II. This sort of dehydration becomes very significant compared with the dehydration of simple electrolytes, as was discussed previously.[18]

Now we shall discuss the theoretical influence of salt and polymer concentration on the kinetic parameters. From the Bronsted–Bjerrum activated-complex theory and the thermodynamical relations, k_f or K is given by the mean activity coefficient (γ_2) of macroions and their gegenions[17b] as follows:

$$\ln (K/K^*) = \ln (k_f/k_f^*) = \ln (\gamma_2/\gamma_2^*) \quad (5)$$

The asterisk signifies an arbitrary reference state. If we use the Manning theory of polyelectrolytes in order to estimate the γ_2 values, eq 6 is obtained. In eq 6, ξ (= $e_0^2/(DkTb)$) is the charge density parameter of an infinite linear charge and a single nonadjustable parameter of Manning's theory. b is the distance between neighboring

(17) See, for example: (a) Manning, G. S. "Polyelectrolytes"; Selengny, E., Ed.; D. Reidel: Dordrecht, Holland, 1974. (b) Ise, N.; Okubo, T. *Macromolecules* **1978**, *11*, 439.

(18) See, for example: (a) Laidler, K. J.; Bunting, P. S. "The Chemical Kinetics and Enzyme Action", 2nd ed.; Clarendon Press: Oxford, 1973. (b) Ise, N. Maruno, T.; Okubo, T. *Proc. R. Soc. London, Ser. A* **1980**, *370*, 485. (c) Okubo, T. Maruno, T.; Ise, N. *Ibid.* **1980**, *370*, 501.

$$\ln \gamma_2 = -\tfrac{1}{2}\xi^{-1} \ln \left(\xi^{-1}n_e + 2n_0 + 2n_s\right) +$$

$$\xi^{-1}\ln\left[\frac{\xi^{-1}n_e + n_0 + n_s}{n_e + n_0 + n_s}\right] -$$

$$\tfrac{1}{2}\xi^{-2}\left[\frac{n_e}{\xi^{-1}n_e + 2n_0 + 2n_s}\right] + \text{constant} \quad (6)$$

charges on the macroion. D and e_0 are the dielectric constant and the electronic charge, and n_e, n_0, and n_s denote the concentrations of macroion, probe, and foreign salt, respectively. The influence of foreign salt on K or k_f is, therefore, given[19] by eq 7. In eq 7, K^* and k_f^* are

$$\ln (K/K^*) = \ln (k_f/k_f^*) =$$

$$-\ln\left(\frac{n_e + n_0 + n_s}{n_e + n_0}\right) + \xi^{-1}\ln\left[\frac{\xi^{-1}n_e + n_0 + n_s}{\xi^{-1}n_e + n_0} \times \right.$$

$$\left.\frac{(\xi^{-1}n_e + 2n_0)^{1/2}}{\xi^{-1}n_e + 2n_0 + 2n_s}\right] + \frac{\xi^{-2}n_e n_s}{(\xi^{-1}n_e + 2n_0 + 2n_s)(\xi^{-1}n_e + 2n_0)}$$

$$(7)$$

the association constant and the rate constant in the absence of sodium chloride. As is seen in Figure 5, except for one point, quantitative agreement was obtained between the observed and calculated values. The significant decrease in K and k_f is, therefore, explainable with the electrostatic interactions between macroions and gegenions. The increase in k_b in the presence of NaCl is not predicted directly with our theoretical treatment. However, a qualitative explanation is possible as described below.

Further discussion is now made on the polymer concentration dependence of the kinetic parameters. The changes in K and k_f as a function of polymer concentration follow from eq 7 and are shown in eq 8. Asterisks in eq

$$\ln (K/K^*) = \ln (k_f/k_f^*) =$$

$$-\tfrac{1}{2}\xi^{-1}\ln\left(\frac{\xi^{-1}n_e + 2n_0 + 2n_s}{\xi^{-1}n_e^* + 2n_0 + 2n_s}\right) +$$

$$\xi^{-1}\ln\left[\frac{\xi^{-1}n_e + n_0 + n_s)(n_e^* + n_0 + n_s)}{(\xi^{-1}n_e^* + n_0 + n_s)(n_e + n_0 + n_s)}\right] -$$

$$\frac{\xi^{-2}(n_e - n_e^*)(n_0 + n_s)}{(\xi^{-1}n_e + 2n_0 + 2n_s)(\xi^{-1}n_e^* + 2n_0 + 2n_s)} \quad (8)$$

8 denote the values at arbitrary polymer concentration. As is seen in Table III, the theory predicts the decreases in K and k_f. However, the agreement between the observed and the calculated values is not excellent. This is probably
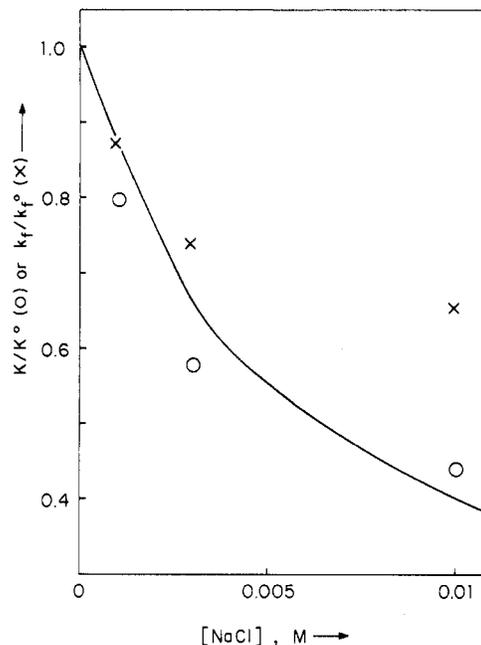
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(19) Ishiwatari, T.; Okubo, T.; Ise, N. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 3393.

Figure 5. NaCl effect on the K and k_f values: (O) observed for K/K^*; (X) observed for k_f/k_f^*; (—) calculated for K/K^* and k_f/k_f^* from eq 7.

TABLE III: Comparison of the Polymer Concentration Dependence of the Observed Values of K and k_f with Theory

[NaPSS], M	$(K/K^*)_{obsd}$	$(k_f/k_f^*)_{obsd}$	$(k/k^*$ or $k_f/k_f^*)_{theory}$
1.18×10^{-4}	1.00	1.00	1.00
2.94×10^{-4}	0.75	1.00	0.84
9.80×10^{-4}	0.13	0.35	0.66
2.94×10^{-3}	0.02	0.12	0.53

due to the defect of the theory; i.e., the present theory cannot predict the increase in k_b with increasing concentration.

These significant dependence of K, k_f, and k_b upon the salt and polymer concentrations may appear to be peculiar at first glance. However, it is clear now that these results are brought about with strong electrostatic interaction between probe and PSS anion. Of course, the hydrophobic interaction and the microenvironmental viscosities around the ions should be important also in determining the absolute values of the kinetic parameters. However, it is interesting that the electrostatic forces are certainly predominantly important even for fast reactions which occur near the diffusion-controlled rate.