for this reaction found by Kershaw and Prue,[12] i.e., a cation is incorporated into the activated complex. The increase of the size of the activated complex by the introduced cation might have some bearing on the positive activation volume. The volume of the activation, $\Delta V^{\ddagger}$, was increased by the addition of macroions, similar to the increase observed for the U^{4+}–Tl^{3+} reaction. This increase of $\Delta V^{\ddagger}$ again shows the important contribution of the "dehydration effect" of the activated complex by the macroions, if the specific cation effect remains unaffected by the presence of the macroions.

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Role of Solvent in Polymer "Catalysis". Polyelectrolyte Catalysis on the Esterolysis of Neutral and Ionic Esters in Hexanol–Water Mixtures

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ABSTRACT: The catalytic activities of three kinds of poly(ethylenimines) quaternized with *n*-octyl bromide, *n*-lauryl bromide, and *n*-cetyl bromide (C8PEI, C12PEI, and C16PEI) on the alkaline hydrolysis of *p*-nitrophenyl acetate (PNPA), 3-nitro-4-acetoxybenzoic acid (NABA), and 3-acetoxy-*N*-(trimethylanilinium) iodide (ANTI) were studied in 1-hexanol–water mixtures. The reactivity of OH^- was found to be enhanced in the mixtures with decreasing water content. Furthermore, the remarkable role of the solvation effect of the polymers was shown; the polymers absorbed water molecules strongly and selectively from the mixture of 1-hexanol–water. These solvation and desolvation effects were also studied by fluorescence and light-scattering measurements.

The gigantic rate enhancement and retardation effects of macroions on chemical reactions, in particular on interionic reactions, were intensively investigated,[1–5] and the main cause for the catalysis was ascribed to strong electrostatic and hydrophobic interactions between the reactant species and the macroions.

For comparatively simple reaction systems, the theoretical interpretation by the Brönsted–Bjerrum–Manning theory was fairly successful, suggesting that electrostatic stabilization of the activated complex is responsible for the acceleration and that of the reactant is a cause of the deceleration.[6–8]

Recent studies of high-pressure influence of the polyelectrolyte catalysis revealed that the solvation and desolvation effects of reactant ions and/or activated complex are playing a key role in addition to the electrostatic stabilization mentioned above.[9] These solvent effects in polymer "catalysis" are certainly expected to manifest themselves clearly for reactions in organic solvents. Some studies have been reported on catalytic influences of polymers in organic solvent–water mixtures.[10–18] However, the hydration or dehydration effects of polymers were not investigated in detail. In organic solvents, ions are often reported to be dehydrated.[19,20] Furthermore, recent studies of catalytic effects of reversed micelles and liquid crystals have clearly demonstrated the important role of solvent molecules.[21–23]

Thus it was thought interesting to examine the catalytic action of polyelectrolytes in organic solvents. In the present paper, we studied the influence of polyelectrolytes on the alkaline hydrolysis of various esters in 1-hexanol containing small amounts of water.

Experimental Section

Materials. Poly(*N*-octylethylenimine bromide) (C8PEI), poly(*N*-laurylethylenimine bromide) (C12PEI), and poly(*N*-cetylethylenimine bromide) (C16PEI) were prepared by quaternization of poly(ethylenimine) with octyl bromide, lauryl bromide, and cetyl bromide, respectively. The poly(ethylenimine) was donated from Nippon Shokubai Co., Tokyo, and its degree of polymerization was 100. The quaternization was carried out in a nitromethane and nitroethane mixture (1:1) at 50 °C for 4 days. The degrees of quaternization of C8PEI, C12PEI, and C16PEI were 55, 58, and 59%, with respect to the total amount of nitrogen atoms in the polymer, respectively. The purification was carried out by reprecipitation with ethyl acetate. These polymers were soluble in 1-hexanol but insoluble in water. Cetyltrimethylammonium bromide (CTABr) and Brij35 [$C_{12}H_{25}(OCH_2CH_2)_{23}OH$] were commercially available and were used without further purification.

p-Nitrophenyl acetate (PNPA) was commercially available and further purified twice by crystallization from chloroform. 3-Acetoxy-*N*-(trimethylanilinium) iodide (ANTI) was synthesized by the method of Overberger et al.[24] and was purified by recrystallization in nitromethane. 3-Nitro-4-acetoxybenzoic acid (NABA) was prepared by the method of Overberger et al.[25] and was crystallized from benzene.

8-Anilino-1-naphthalenesulfonic acid ammonium salt (ANS) was purchased from the Wako Pure Chemical Co., Osaka, and purified by repeated crystallization from water.

1-Hexanol was of a spectral grade and was further distilled before use. For solution preparation, water was deionized and then distilled.

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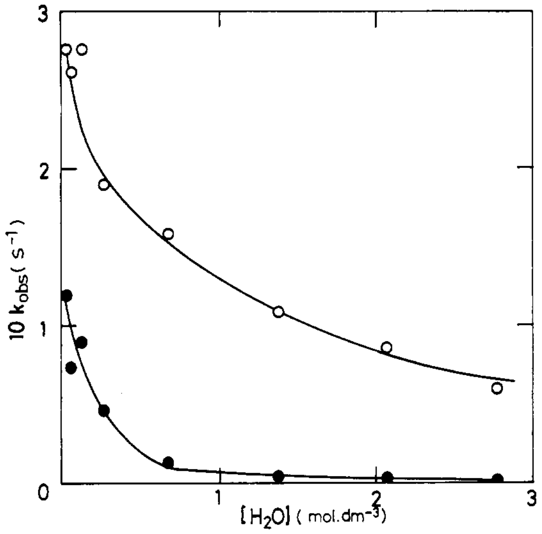

Figure 1. Influence of H_2O on alkaline hydrolysis of PNPA in 1-hexanol at 25 °C: [PNPA] = 2.5×10^{-5} mol dm^{-3}; $[OH^-]$ = 1.00×10^{-3} mol dm^{-3}; [C12PEI] = 0 (○), 5.51×10^{-3} (●) mol dm^{-3}.

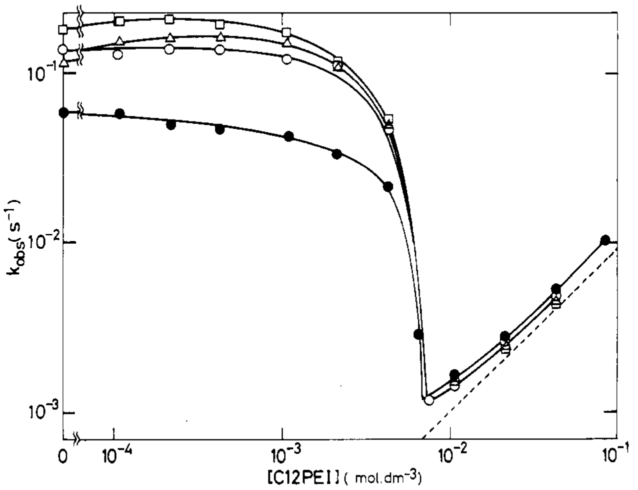

Figure 2. Influence of C12PEI on the alkaline hydrolysis of PNPA in 1-hexanol at 25 °C: [PNPA] = 2.5×10^{-5} mol dm^{-3}; $[OH^-]$ = 1.00×10^{-3} mol dm^{-3}; $[H_2O]$ = 5.56×10^{-2} (□), 2.78×10^{-1} (△), 5.56×10^{-1} (○), 2.78 (●) mol dm^{-3}

Kinetic Measurement. The reaction was initiated by adding 20 μL of a 1-hexanol solution of the esters to 3 mL of the polymer solution. The polymer solution was prepared by mixing the desired amounts of the polymers, sodium hydroxide solution, and water with 1-hexanol. The reaction rates were determined from the absorption changes at 400 nm for PNPA, 416 nm for NABA, and 293 nm for ANTI, respectively, using a high-sensitivity spectrophotometer equipped with a thermostated cell holder (SM-401, Union Engineering Co., Hirakata, Osaka-fu).

Fluorescence Measurement. The fluorescence measurements were carried out using ANS as a hydrophobic probe with a fluorescence spectrophotometer (FS-401, Union Engineering) at 25 °C.

Light-Scattering Measurement. The low-angle light-scattering measurements of the polymer solution were done with a KMX-6 photometer (Chromatix Co., Mountain View, Calif.) at room temperature. The measurement angle was fixed at 5.9°.

Results and Discussion

The influence of the water content on the hydrolysis rate constant, k_{obs}, of PNPA in 1-hexanol–water mixtures is shown in Figure 1. Clearly, the k_{obs} sharply increased with decreasing water content. This indicates that the hydroxide ions are dehydrated in 1-hexanol and the nucleophilicity of the ions is enhanced as compared with that of the hydrated ions in aqueous solution. Similar observations on the enhanced reactivity of the dehydrated nucleophiles have been reported in organic solvents.[19,20]

Figure 2 demonstrates the influence of C12PEI on the hydrolysis of PNPA in 1-hexanol. First, the k_{obs} slightly increased by addition of a tiny amount of C12PEI ([C12PEI] < 10^{-3} mol dm^{-3}) at low concentrations of water. Then, the rate constants decreased sharply ([C12PEI] = 10^{-3}–10^{-2} mol dm^{-3}) and again turned to increase at high concentrations ([C12PEI] > 10^{-2} mol dm^{-3}). The dotted line in this figure shows the rate constant of the hydrolysis carried out without addition of OH^-.

In the absence of the polymer, the weakly hydrated hydroxide ions react with the PNPA molecule as is schematically shown in Figure 3-1. The first increase in k_{obs} by the addition of C12PEI may be due to the dehydration effects on OH^- by C12PEI (Figure 3-2). Thus, the concentration of water in the bulk phase decreases as a result of preferential absorption by the polymers, which would favor dehydration and enhanced reactivity of OH^-. The enhancement of the nucleophilicity of water molecules by the polymer in the organic solvent is improbable because reaction was not observed in the absence of OH^-. It should be mentioned here that OH^- was also accumulated around the cationic polymer by the electrostatic forces. Therefore, it will be easily speculated that both OH^- and water molecules are absorbed by C12PEI, and the esterolysis in the bulk phase is retarded. This factor will be one of the reasons why k_{obs} decreased in the second region. The other reason is the decrease of the reactivity of OH^- absorbed in the polymer domain, because OH^- in this region is surrounded by a large amount of absorbed water molecules and subsequently is strongly hydrated (Figure 3-3). The third observation, i.e., the increase in k_{obs} at the higher concentration of C12PEI, is due to the nucleophilic attack of the free imino groups of C12PEI upon the esters (Figure 3-4). This conclusion is derived because the k_{obs} values in the presence of OH^- and in their absence (dotted line) were very close to each other.

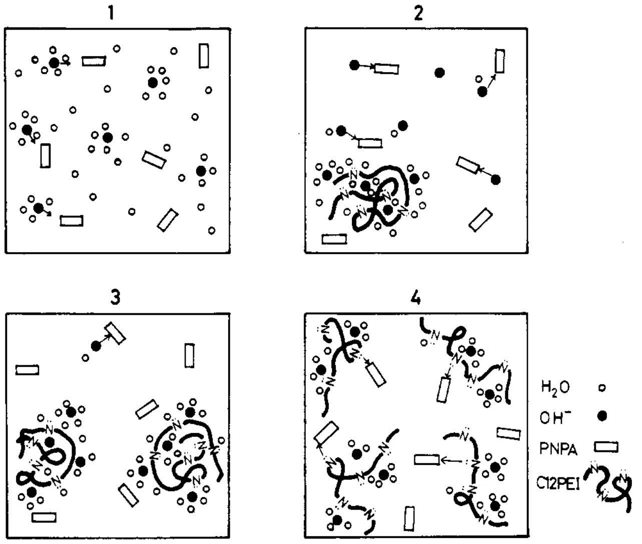

Figure 3. Schematic description of the hydrolysis of PNPA in the presence of C12PEI in 1-hexanol containing small amounts of water.

Figure 4 shows the influence of a cationic surfactant, CTABr, and a nonionic one, Brij35, upon the alkaline hydrolysis of PNPA. The data of C12PEI were reproduced by the broken line for comparison. The effect of CTABr was small compared with those of C12PEI and Brij35. Under the condition employed by us, the formation of the

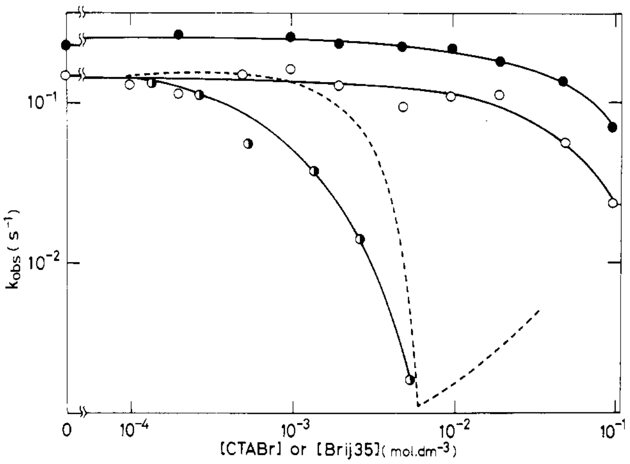

Figure 4. Influence of CTABr or Brij35 on the alkaline hydrolysis of PNPA in 1-hexanol at 25 °C: (●, ○) CTABr, (◑) Brij35, (---) C12PEI; [PNPA] = 2.50×10^{-5} mol dm^{-3}; [OH$^-$] = 1.00×10^{-3} mol dm^{-3}; [H$_2$O] = 5.56×10^{-2} mol dm^{-3} (●), 5.56×10^{-1} mol dm^{-3} (○, ◑, ---).

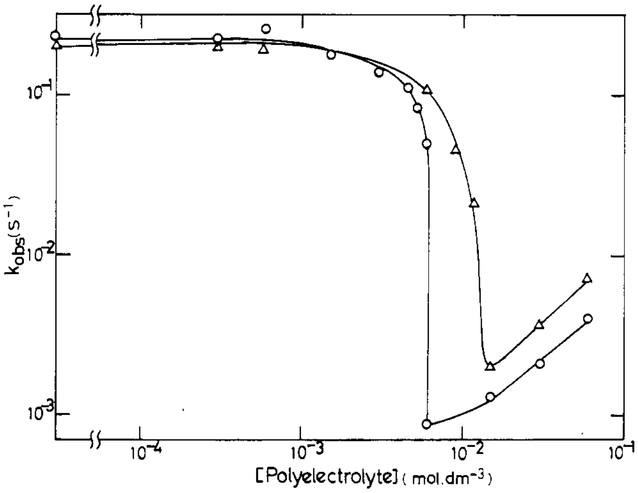

Figure 5. Influences of C8PEI and C16PEI on the alkaline hydrolysis of PNPA in 1-hexanol at 25 °C: (△) C16PEI; (○) C8PEI; [PNPA] = 2.50×10^{-5} mol dm^{-3}; [OH$^-$] = 1.00×10^{-3} mol dm^{-3}; [H$_2$O] = 5.56×10^{-2} mol dm^{-3}.

reversed micelles is highly plausible. The results show that the so-called "water pools" located in the center of the micelle are not as effective for the rate-retarding effects. This may be partly due to the factor that the reversed micelle of CTABr is not as stable as that of the polymer because CTABr is of low molecular weight. The strong inhibition by Brij35 is attributable to the oxyethylene groups of the surfactant, which would absorb water molecules effectively. It is interesting that both CTABr and Brij35 retarded the reaction, similarly to C12PEI.

The influences of C16PEI and C8PEI on the rate constants for the hydrolysis of PNPA are shown in Figure 5. The rate-retarding effect in the second concentration region of C8PEI was more remarkable than that of C16PEI, and the strength of the inhibition was in the order C8PEI > C12PEI > C16PEI. This may be due to the higher affinity to water molecules of the less hydrophobic polymer.

The thermodynamic parameters for the alkaline hydrolysis of PNPA with and without C12PEI are listed in Table I.[26] The enthalpy of activation, $\Delta H^{\ddagger}$, in hexanol–water is slightly smaller than that in water. This is consistent with the high reactivity of the dehydrated hydroxide ions in the concentration of 9.18×10^{-4} mol dm^{-3}, corresponding to the first region mentioned above, in which OH$^-$ was inferred to be dehydrated by the addition of the macroions.

Table I
Thermodynamic Parameters for the Hydrolysis of PNPA at 25 °C^a

[C12PEI], mol dm^{-3}	10^3k_{obs}, s^{-1}	$\Delta G^{\ddagger}$, kJ mol^{-1}	$\Delta H^{\ddagger}$, kJ mol^{-1}	$10^{-2}\Delta S^{\ddagger}$, JK^{-1} mol^{-1}
0^b	8.78	84.5 ± 2.0	23 ± 2	−2.1 ± 0.1
0^c	145	77.8 ± 2.6	20 ± 2	−1.9 ± 0.1
9.18×10^{-4} ^{c}	138	77.8 ± 2.5	10 ± 1	−2.3 ± 0.1
9.18×10^{-3} ^{c}	1.22	89.5 ± 6.9	16 ± 2	−2.4 ± 0.2
2.14×10^{-2} ^{c}	2.32	87.9 ± 5.9	26 ± 3	−2.1 ± 0.3

^{a} [PNPA] = 2.50×10^{-5} mol dm^{-3}, [OH$^-$] = 1.00×10^{-3} mol dm^{-3}. ^{b} In aqueous solution. ^{c} In mixed solvent (hexanol-water), [H$_2$O] = 5.56×10^{-1} mol dm^{-3}.

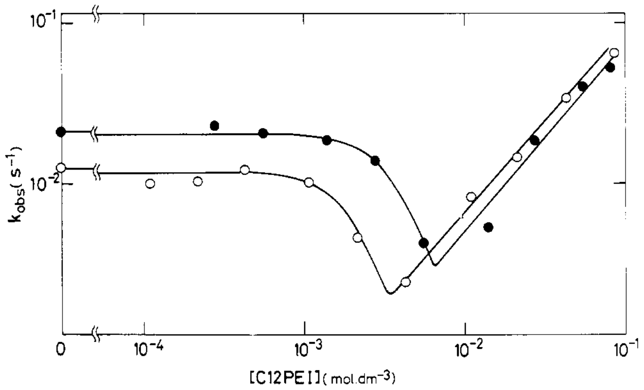

Figure 6. Influence of C12PEI on the alkaline hydrolysis of NABA in 1-hexanol at 25 °C: [NABA] = 2.50×10^{-5} mol dm^{-3}; [OH$^-$] = 1.00×10^{-3} mol dm^{-3}; [H$_2$O] = 1.39×10^{-1} mol dm^{-3} (●), 5.56×10^{-1} mol dm^{-3} (○).

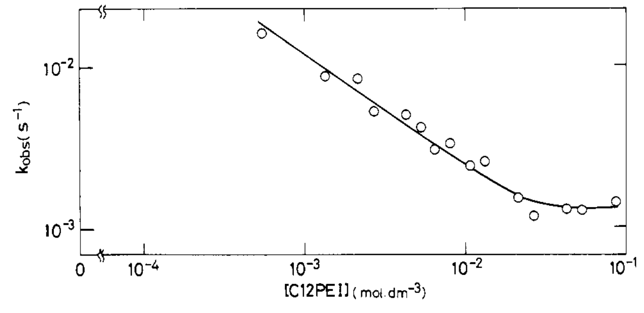

Figure 7. Influence of C12PEI on the alkaline hydrolysis of ANTI in 1-hexanol at 25 °C: [ANTI] = 2.50×10^{-5} mol dm^{-3}; [OH$^-$] = 1.00×10^{-3} mol dm^{-3}; [H$_2$O] = 5.56×10^{-1} mol dm^{-3}.

The influence of C12PEI upon the hydrolysis of an anionic ester, i.e., NABA, was examined (Figure 6). The magnitude of k_{obs} was about one order of magnitude smaller than that for PNPA. This is in part due to the electrostatic repulsion between similarly charged reactants, namely anionic ester NABA and OH$^-$. The k_{obs} values in the concentration region of C12PEI higher than 5×10^{-3} mol dm^{-3}, which corresponds to the third region, are much larger than those for PNPA. This is certainly due to an electrostatic interaction between the cationic polymer and the anionic ester. However, the polymer concentration dependence of the reaction rates was similar for PNPA and NABA.

Figure 7 shows the influence of C12PEI upon the hydrolysis rate of the cationic ester ANTI. The k_{obs} values at low polymer concentrations (in the first region) could not be determined because the reaction was too fast to follow with our spectrophotometer. The very rapid alkaline hydrolysis is due to the strong electrostatic forces

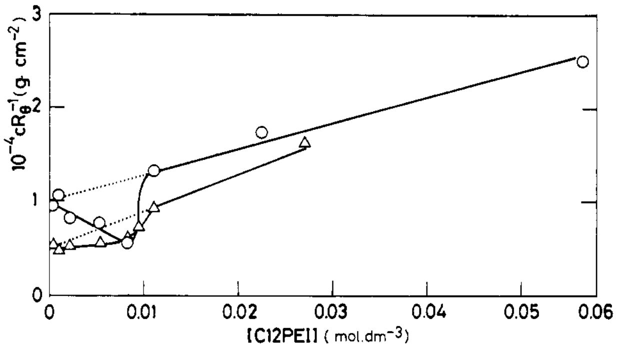

Figure 8. Light scattering of C12PEI in 1-hexanol containing small amounts of water at θ = 5.9°: [OH^-] = 1.00 × 10^{-3} mol dm^{-3}; [H_2O] = 5.56 × 10^{-2} mol dm^{-3} (○), 1.11 × 10^{-1} mol dm^{-3} (△).

between the cationic ester and the hydroxide anions. When the polymer concentration was raised, k_{obs} was decreased, though not so clearly as was the case for PNPA. The sharp increase of k_{obs} at higher polymer concentration was not observed, because the nucleophilic attack of the cationic C12PEI on the cationic ester ANTI is made difficult by strong electrostatic repulsion forces.

In order to confirm that preferential sharp bends of the curves observed in Figure 2 are not a result of aggregation of C12PEI, light-scattering measurements of the polymer solutions were conducted. Figure 8 shows the c/R_θ vs. c plots of C12PEI in 1-hexanol containing small amounts of water, where R is the Rayleigh ratio at a fixed angle (θ = 5.9°), and c is the concentration of C12PEI in g cm^{-3}. First, the slopes of the c/R_θ vs. c plots in the low concentration region of C12PEI are small (or even negative). At [C12PEI] $\simeq$ 10^{-2} mol dm^{-3}, the c/R_θ value increased sharply and then was followed by a gradual increase at the higher concentrations. It is notable that the drastic jump in this figure and the sharp bends of the curves in Figure 2 were observed at the same concentration. The first small slope of the c/R_θ vs. c plot may be attributed to a compact conformation of C12PEI because there exists OH^- in excess over the amount equivalent to C12PEI. Thus, it may be suggested that when [C12PEI] increases conformational change of C12PEI occurs at [C12PEI] $\simeq$ 10^{-2} mol dm^{-3} by a shortage of OH^-. However, it must be noted that the intercept of the c/R_θ vs. c plots at the low concentrations of C12PEI coincided well with the extrapolated ones of the data at the higher concentration region, as is shown by dotted lines. This agreement might indicate that the molecular weight of C12PEI in the solution does not change. Thus, we claim that aggregation of C12PEI does not occur with an increase in its concentration. A more quantitative light-scattering measurement is now in progress.

In order to confirm the prefrential hydration of C12PEI suggested above from the kinetic measurements, the fluorescence spectra of ANS were measured. Figure 9 shows the fluorescence spectra of ANS in 1-hexanol containing various amounts of water. The fluorescence intensity decreased by the addition of water with concomitant red shift of the position of the fluorescence maximum. This shows that ANS is effective as a hydrophobic probe, as was often reported.[27-29] As is shown in Figure 10, with the addition of C12PEI, first the fluorescence intensity slightly increased (curves 1, 2, and 3) and then turned to decrease drastically (curves 4, 5, and 6). Curve 1 indicates the fluorescence spectrum of ANS without C12PEI. The initial increase may reflect the strong hydrophobicity of the C12PEI polymer and the concentration of ANS around the polymer. The subsequent decrease suggests that the water molecules are accumulated around C12PEI (hydration effect), and the fluorescence intensity of the hydrophobic probe was rapidly weakened.

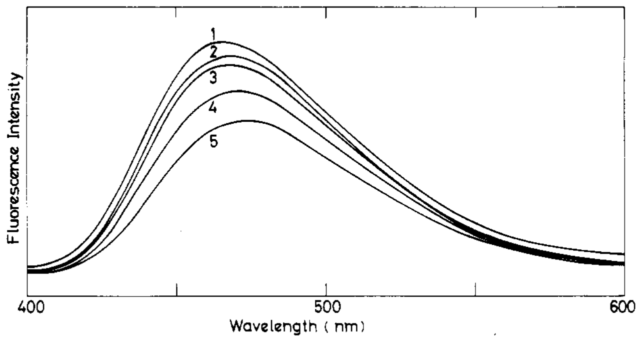

Figure 9. Effect of H_2O on the fluorescence spectrum of ANS in H_2O–1-hexanol solutions: [ANS] = 2.50 × 10^{-5} mol dm^{-3}; [H_2O] = 0 mol dm^{-3} (1), 6.94 × 10^{-2} mol dm^{-3} (2), 2.78 × 10^{-1} mol dm^{-3} (3), 6.94 × 10^{-1} mol dm^{-3} (4), 1.39 mol dm^{-3} (5); excitation wavelength 380 nm.

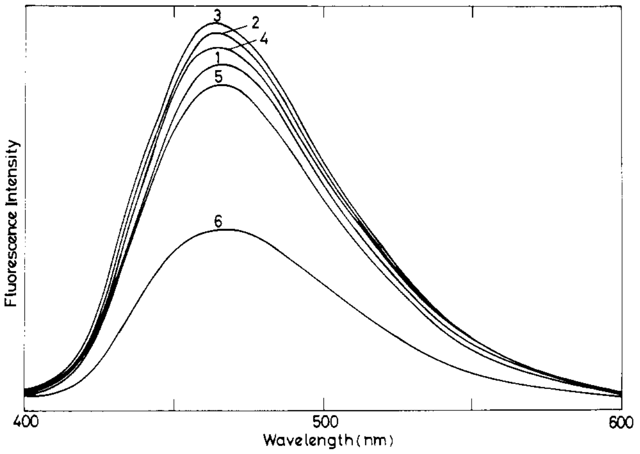

Figure 10. Effect of C12PEI on the ANS fluorescence spectrum in H_2O–1-hexanol–C12PEI solutions: [ANS] = 2.50 × 10^{-5} mol dm^{-3}; [H_2O] = 1.39 × 10^{-1} mol dm^{-3}; [C12PEI] = 0 (1), 1.38 × 10^{-3} (2), 2.75 × 10^{-3} (3), 1.38 × 10^{-2} (4), 2.75 × 10^{-2} (5), 9.61 × 10^{-1} (6) mol dm^{-3}; excitation wavelength 380 nm.

Summarizing the above results, we state as follows: the hydroxide ions are dehydrated in 1-hexanol and the nucleophilicity of the ions becomes high as compared with that in aqueous solution. With the addition of the hydrophobic cationic polymer, the reactivity is largely lowered, which is due to the "hydration" effect in the water-rich region around the polyion chain. The hydration effect is consistent with the measurements of fluorescence and light scattering.

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Conformation of Polyelectrolyte in Aqueous Solution

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ABSTRACT: The polyelectrolyte conformation in aqueous solution in the presence of an added neutral salt is studied by light scattering, using a poly(sodium acrylate) with a narrow molecular weight distribution. Comparing the experimental particle scattering function $P(\theta)$ with the theories for various conformations, it is confirmed that at the Θ state the conformation of polyelectrolyte is a Gaussian chain and at the non-Θ states the experimental $P(\theta)$ can be interpreted by the theory taking into account the excluded volume effect of segments rather than by the theory for the wormlike chain model.

It was clearly shown that the conformation of nonionic linear polymers is Gaussian at the Θ state and that, as the solvent becomes better, polymer chains expand into non-Gaussian ones on account of the so-called excluded volume effect.[2,3] It is also well-known that the conformation of the polymers having stiff backbones, for example, DNA,[4] polyisocyanate,[5] and polycrotonate,[6] deviates from the Gaussian chain and behaves like the wormlike chains. There is a clear difference between the molecular weight dependence of the expansions due to the excluded volume effect and those due to the stiffness of backbones. As the molecular weight increases, the conformation of linear flexible polymers more markedly deviates from the Gaussian chain if the expansion is due to the excluded volume effect. If the polymer is extended by the stiffness of the backbone, however, the polymer approaches the Gaussian chain as the molecular weight increases.

At low charge densities or at high ionic strengths, polyelectrolytes have more or less coiled conformations. As the ionic strength is decreased, the polyelectrolyte coil is expanded due to the electrostatic repulsion, which can be regarded as a kind of excluded volume effect. Consequently, the polyelectrolyte chains may become highly non-Gaussian ones. On the other hand, if there is no added salt, polyions are often assumed to be rods parallel to each other. If the concentration of added salt is finite but low, the polyelectrolytes are highly extended by the electrostatic interaction, and the bending force constant of polyelectrolyte chains must be much higher than that of the corresponding nonionic polymers. Therefore, it is understandable to assume that polyelectrolytes can be regarded as wormlike chains.

The polymer conformation, in general, can be observed in the overall behavior of polymers, for example, in the molecular weight dependence of the mean square radius of gyration $\langle s^2 \rangle$, frictional coefficient f, intrinsic viscosity $[\eta]$, etc. However, the conformation can be more directly studied by measurement of the particle scattering function $P(\theta)$ in light scattering, which reflects the local conformation as well as the overall conformation of polymers, that is by direct comparison of the experimental $P(\theta)$ with the values calculated for various conformations of the polymer such as a random coil, semiflexible chain, rod, etc.

In light scattering, however, it is important to use polymer samples having narrow molecular weight distributions, since $P(\theta)$ depends on the molecular weight distributions too. It is now possible to use poly(acrylic acid) having narrow molecular weight distributions and also a molecular weight high enough for light-scattering measurements.[7]

Deviation of the conformation from the Gaussian chain due to the excluded volume effect should be observed for nonionic polymers in good solvents too. However, the deviation is minor if the samples are nonionic polymers in organic solvents. The radius of gyration of polyelectrolytes can be changed to a much larger extent by the effect of charges than by the use of nonionic polymers.[8] It is interesting to investigate how the polyelectrolyte conformation does change with variation of the charge density of polyions or added salt concentrations.

Of course, the separation between short-range interaction and long-range interaction or between the effect of solvent on the stiffness of the backbone and the excluded volume of segments is merely practical. The extension of the polyelectrolyte chain by electrostatic repulsion must be caused more or less through both effects simultaneously. In this paper we simply discuss which effect is more predominant in the expansion of polyelectrolyte chains.

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