

Recent Advances in Macroion "Catalysis": Role of Solvation and Desolvation Studied in Binary Solvent Systems and under High Pressures

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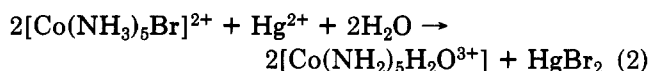
The catalytic influence of synthetic macromolecules has been studied on a variety of chemical reactions and has been a subject of numerous reviews.¹⁻²² Although intensive effort has been made in this field, the main interest appears to have been in increasing the acceleration of reaction rates. Indeed, only a few papers have been published on the rate-retarding effect of macromolecules,^{23,24} although this kind of study is believed to furnish a useful clue for the mechanism of macromolecular "catalysis". Furthermore, in most of the previous studies, attention has been paid exclusively to the overall rate or rate constant and the macromolecular influence thereupon. The principle of microscopic reversibility indicates that both a forward and a reverse step are involved in chemical reactions. When a chemical reaction is claimed to be accelerated by macromolecules, it is not at all clear which of the forward or reverse steps has been influenced. In addition, most of the previous studies have been carried out in water media; the role of solvent has not been considered properly. Obviously, these situations are most unsatisfactory if an in-depth survey is to be conducted to find a true cause or causes of the macromolecular "catalysis".

This Account is concerned with our experimental studies carried out to improve this situation. The studies have shown that the observed macroion influence on reaction rates cannot generally be accounted for in terms of the usually accepted explanation, namely, accumulation of reactants around the macroions followed by enhanced collision. In our own effort, relatively well-understood, simple, interionic reactions were studied in the presence of ionic macromolecules, namely, polyelectrolytes. This combination simplifies the interpretation of our results.

Previous Studies

In order to facilitate understanding of this account, we summarize five important facts from previous work.

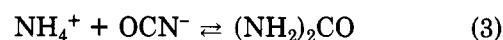
First, the reaction between similarly charged ionic species can be accelerated by addition of oppositely charged macroions. Two examples are taken from our earlier work²⁵ (eq 1 and 2) with hydrochloride of poly- $\text{CH}_2\text{BrCOO}^- + \text{S}_2\text{O}_3^{2-} \rightarrow \text{CH}_2(\text{S}_2\text{O}_3)\text{COO}^{2-} + \text{Br}^-$ (1)



Norio Ise and Tsuneo Okubo are authors of a paper entitled "Ordered Distribution of Electrically Charged Solutes in Dilute Solutions".⁷⁷ The present paper is based on lectures given at the Institut für Organische Chemie, Johannes-Gutenberg Universität, Mainz, Germany, where N.I. was a guest professor in the spring of 1981. T.O. was recently at Columbia University as a research associate with Professor N. J. Turro. S.K. was born in Kyoto in 1949 and received his B.S., M.S., and Ph.D. degrees from Kyoto University, where he is now an instructor.

ethylenimine (PEI) and with polystyrenesulfonate (PSS) or polyethylenesulfonate (PES) as the catalyst.

Second, the reaction between oppositely charged ionic species can be decelerated by addition of both cationic and anionic macroions. For example, Wöhler's synthesis of urea (reaction 3) was retarded by addition of



ionic macromolecules, e.g., polyacrylate (PAA) or a copolymer of diethyldiallylammonium chloride and sulfur dioxide (DECS).^{24,26}

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- (26) Addition of neutral polymers such as polyethylene glycol or polyvinylpyrrolidone did not cause retardation, ruling out that the deceleration observed with NaPAA and DECS was due to a viscosity effect.

A third fact is that the magnitude of the acceleration and deceleration by macroions, which is often denoted by k/k^* (k and k^* are the rate constants in the presence and absence of the macroions, respectively), depends on the valency of the reactants, the concentrations of reactants, macroions, and coexisting salts, the temperature, the dielectric constant, and so on. Generally speaking, the higher the valencies of the reactant are, the larger the polyelectrolyte influence. It is not difficult to observe 10^5 for the acceleration factor when the reactants are highly charged, e.g., for the $\text{Fe}(\text{CN})_6^{4-}-\text{S}_2\text{O}_8^{2-}$ reaction in the presence of polybrene, poly[(dimethylimino)-1,3-propanediyl(dimethylimino)-1,6-hexanediyl dibromide, a cationic polymer.²⁷

Fourth, whether it was acceleration or deceleration, macroions caused a larger effect than low molecular weight substances. At a reactant concentration of 0.01 M and at a polyelectrolyte concentration of 0.01 equiv L^{-1} , the k/k^* values for reactoin 1 were about 20, 3, and 1.8 for hydrochlorides of PEI (degree of polymerization of about 100), tetraethylenpentamine (TP), and diethylenetriamine (DT), respectively (TP and DT being low molecular weight analogues of PEI). Like many other solution properties of polymers, the k/k^* value appeared to level off with a further increase in the degree of polymerization above 100. In the case of deceleration, the k/k^* values of reaction 3 were 0.33 and 0.72 at a concentration of 0.0444 equiv L^{-1} for NaPAA and NaCl at a reactant concentration of 0.0205 M.²⁴

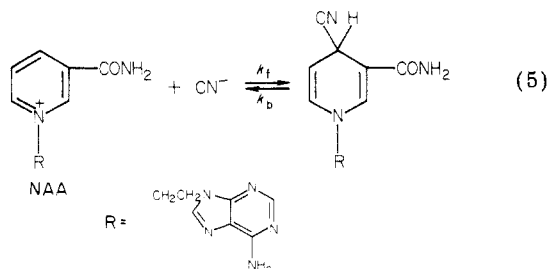
Finally, it is known that the observed acceleration and deceleration can be accounted for^{5,13,14,19} in terms of the Brønsted equation,²⁸ i.e., eq 4,²⁹ where for a re-

$$k/k_0 = f_A f_B / f_X (\approx k/k^*) \quad (4)$$

action $\text{A} + \text{B} \rightleftharpoons \text{X} \rightarrow \text{C} + \text{D}$, with X being the activated complex, the f 's are the activity coefficients, k is the rate constant, and the zero subscript implies zero ionic strength. In other words, the acceleration is due to the fact that f_X is decreased more than f_A and f_B by addition of macroions, i.e., stabilization of the activated complex. Deceleration, on the other hand, originates from stabilization of the reactants.

Influence of Macroions on the Rate Constants of Elementary Steps. Are They Really Catalysts?

The rate constant (k) and equilibrium constant (K) for an addition of CN^- to analogues of nicotinamide adenine dinucleotide, e.g., NAA (see eq 5), were studied



in the presence and absence of various macroions.³⁰ Since the forward process proceeds between a cation

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 (29) The influence of macroions is much more overwhelming than that of simple ions so that k/k_0 can be approximated by k/k^* .
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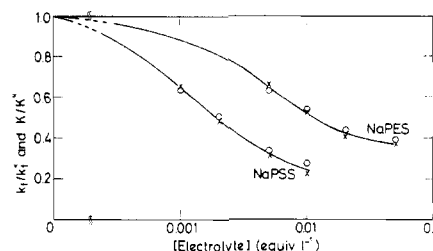


Figure 1. Polyelectrolyte influences on the forward rate constant (k_f) and the equilibrium constant (K) of the equilibrium reaction between NAA and CN^- at 25 °C: $[\text{NAA}] = 1.98 \times 10^{-4} \text{ M}$, $[\text{KCN}] = 4.0 \times 10^{-3} \text{ M}$, $[\text{KOH}] = 1.0 \times 10^{-3} \text{ M}$. Open circles represent k_f/k_f^* (k_f and k_f^* are the forward rate constants with and without polyelectrolytes) and the crosses represent K/K^* (K and K^* are the equilibrium constants in the presence of polyelectrolyte and in its absence). Data were taken from ref 30.

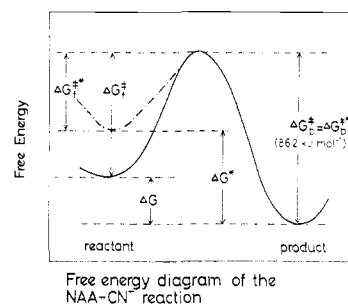


Figure 2. Free energy diagram of polyelectrolyte "catalysis" on an equilibrium reaction. In the case of the NAA- CN^- reaction, ΔG_b^* was 86.2 kJ mol^{-1} at 25 °C. Data were taken from ref 7 after modification.

(NAA) and an anion (CN^-), it should be decelerated by macroions. This was actually the case, as seen from Figure 1; k_f/k_f^* decreased from unity with increasing polymer concentration. Interestingly enough, the K/K^* values decreased also with the concentration to the same extent as k_f/k_f^* . In other words, $k_f/k_f^* = K/K^*$. This implies that the backward process was not influenced at all by the polyelectrolyte addition, since $K = k_f/k_b$. This is quite reasonable since the backward process is a decomposition process of an electrically neutral substance, which is hardly influenced by polyelectrolytes.

Thermodynamic and activation parameters of the NAA- CN^- reaction are consistent with the above observation. In the presence and absence of NaPSS and NaPES, the free energy of activation of the backward process (ΔG_b^*), which is equal to $\Delta G_f^* - \Delta G$ (ΔG_f^* and ΔG are the free energy of activation of the forward process and the free energy of the reaction, respectively), remained at 86.2 kJ mol^{-1} . In other words, it was the reactant state (not the activated or the product state) that was influenced by polyelectrolyte addition, as is depicted in Figure 2.

The quite independent influence of macroions upon the forward and backward processes was also observed for the nicotinamide adenine dinucleotide- CN^- reaction³¹ and the complexation of murexide with Ni^{2+} ^{32a} and with Cu^{2+} .^{32b}

It is pertinent to recall the definition of catalysts by Ostwald,³³ which says that catalysts are substances

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which affect the forward and backward processes in the same proportion. If we follow this definition, the synthetic polyelectrolytes should not be regarded as catalysts, since they affected the two processes in a different way; instead, they must be called "promoters" or "retarders". It is to be noted that this conclusion is contrary to the usually accepted view.³⁴

It should be remarked here that in such a basic aspect macromolecular "catalysis" contrasts with enzymatic catalysis.³⁸⁻⁴⁰ On the basis of the fact that synthetic macromolecules have remarkable rate-enhancing potential, their resemblance with enzymes is sometimes alluded to. In light of the basic difference mentioned above, however, this kind of argument is undoubtedly superficial.

Macroion "Catalysis" in Nonaqueous Media. Local Solvent Composition

Existing data support positively the idea that reaction rate is sensitively influenced by solvation of reactants and activated complex.⁴¹ In our earlier work,⁴² it was suggested that the hydration state of the reactant and activated complex might be perturbed by the electrostatic field of macroions, which would contribute to the observed rate enhancement. Soon afterward, Kabanov et al.⁴³ also pointed out the significance of solvation for hydrolyses of esters in ethanol-water mixtures. Also in the study of macromolecular and micellar "catalyses", the enhanced reactivity of dehydrated reactants has been noted by several authors.⁴⁴⁻⁴⁷ Recently, we studied polyelectrolyte "catalysis" in water-organic solvent mixtures in order to clarify the role of the solvation and desolvation in the "catalysis".

The first example was the cyanoethylation of an amino acid in aqueous dimethyl sulfoxide mixtures.⁴⁸ It is important to note here the large change in the reaction rate which was found for alkaline hydrolysis of esters with decreasing water concentration in the binary mixture of hexanol and small amounts of water.⁴⁹ For

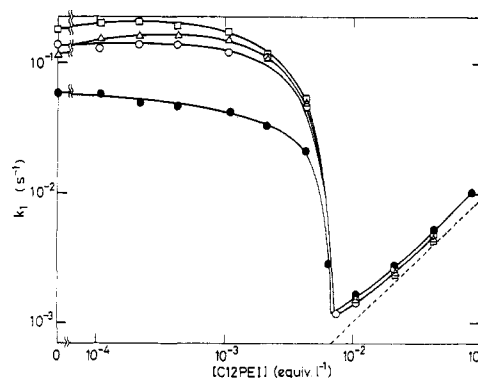


Figure 3. Influence of C12PEI on the alkaline hydrolysis of *p*-nitrophenyl acetate (PNPA) in water-hexanol at 25 °C: [PNPA] = 2.5×10^{-5} M, [OH⁻] = 10^{-3} M. [H₂O] in the binary solvent = 5.56×10^{-2} (□), 2.78×10^{-1} (Δ), 5.56×10^{-1} (○), and 2.78 M (●). C12PEI stands for polyethylenimine partially quaternized with lauryl bromide (degree of quaternization 58%). Data were taken from ref 49.

example, the first-order rate constants for *p*-nitrophenyl acetate (PNPA) at 25 °C were 8×10^{-2} , 1.1×10^{-1} , and 2.9×10^{-1} s⁻¹ at [H₂O] = 2.8, 1.4, and 0.1 M,⁵⁰ respectively. The observed increase in k_1 was suggested to be due to progressive dehydration of OH⁻ with decreasing water concentration for the esterolysis, since the rate change is too large to be ascribed to the dielectric constant factor.

Addition of cationic polymer, poly(ethylenimine) partially quaternized with lauryl bromide (C12PEI), to the esterolysis mixture under consideration gave a fairly complicated result, which is shown in Figure 3. Clearly, the rate constant dropped quite sharply at [C12PEI] = 10^{-2} equiv L⁻¹ and rose when the [C12PEI] was increased. The "negative" catalysis was accounted for as follows: in the absence of C12PEI, the reaction takes place between PNPA molecules and partially hydrated OH⁻. Addition of C12PEI causes concentration of water molecules around the macroions (because of the hydrophilicity of the polymer) and OH⁻ as a result of the electrostatic attraction. Thus, OH⁻ in the macroion domain is more strongly hydrated than in the bulk solvent so that the reaction is retarded. The rise in k_1 above [C12PEI] $\approx 10^{-2}$ equiv L⁻¹ is due to the nucleophilic attack of the free imino group of C12PEI, because the rate constant in the presence of OH⁻ and in the absence (dotted line in Figure 3) agreed to each other. Similar changes of the rate constant with polymer concentration were observed for other cationic macromolecules and for alkaline hydrolysis of an anionic ester, 3-nitro-4-acetoxybenzoic acid.⁴⁹

The explanation for the deceleration in the organic solvent-rich media was that polyethylenimine ions accumulated water to cause hydration of the reactants. The water enrichment in the macroion domain was strongly supported by an experimental result that the fluorescence intensity of 8-anilino-1-naphthalene-sulfonic acid ammonium salt (ANS), a hydrophobic probe, clearly decreased for the esterolysis reaction with increasing concentration of C12PEI. A similar but much more pronounced solvent effect was observed by

(50) These values were obtained for [PNPA] = 2.5×10^{-5} M and [OH⁻] = 10^{-3} M. Further lowering of the water concentration might give much larger rate constants, though such an expectation could not be experimentally substantiated because of the restricted performance of UV spectrophotometer.

(33) Ostwald, W. *Phys. Z.* 1902, 3, 313.

(34) The independent influences on the elementary processes have also been observed by addition of micelles,^{35,36} which are known to demonstrate powerful "catalytic" action as polyelectrolytes.³⁷

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(38) For a general account of catalysis, see: Jencks, W. P. "Catalysis in Chemistry and Enzymology"; McGraw-Hill: New York, 1969.

(39) Bender, M. L. "Mechanisms of Homogeneous Catalysis from Protons to Proteins"; Wiley-Interscience: New York, 1971.

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(47) Shinkai, S.; Kunitake, T. *Chem. Lett.* 1976, 109.

(48) Yamashita, K.; Kitano, H.; Ise, N. *Macromolecules* 1979, 12, 341.

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Table I
Activation Parameters for the Ag⁺-Induced Aquation of Co(NH₃)₅Br²⁺ in the Presence of NaPSS at 25 °C and at 1 bar

[NaPSS], equiv L ⁻¹	k ₂ /k ₂ [*]	ΔG [‡] , kJ mol ⁻¹	ΔH [‡] , kJ mol ⁻¹	ΔS [‡] , J K ⁻¹ mol ⁻¹	ΔV [‡] , mL mol ⁻¹
0	1	86.2 ± 0.3	32.6 ± 2.0	-180 ± 8	-5.3 ± 2
10 ⁻⁶	1.8	84.1	51.5	-109	-2.3
10 ⁻⁵	6	81.2	60.7	-71	16
5 × 10 ⁻⁵	91	74.9	81.6	21	30
10 ⁻⁴ ^a	407				76

^a Precipitation occurred above this concentration, but disappeared on application of high pressure.

us for a reaction of tris(oxalato)cobaltate in binary mixtures of water and organic solvents.⁵¹

In the preceding paragraphs, it was suggested that addition of macromolecules into reaction systems altered local solvent composition, which affected the "catalysis". Undoubtedly the concept of local solvent composition is vague. Effort toward quantitative treatment is desired.

Macroion "Catalysis" Studied with a High-Pressure Technique

The role of solvent in chemical reactions can be investigated conveniently by using a high-pressure technique.^{40,52} We applied this technique for a study of macromolecular "catalysis" with the special purpose of clarifying the significance of solvation and desolvation. According to the transition-state theory, the pressure dependence of the rate constant gives us the volume of activation (ΔV[‡]) by eq 6. Generally, ΔV[‡] is composed

$$[\partial \ln(\text{rate constant})/\partial P] = -\Delta V^{\ddagger}/RT \quad (6)$$

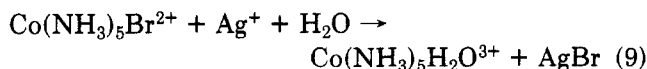
of two contributions as shown in eq 7, where ΔV₁[‡] is

$$\Delta V^{\ddagger} = \Delta V_1^{\ddagger} + \Delta V_2^{\ddagger} \quad (7)$$

the change of the reactant volume in the course of activation and ΔV₂[‡] is due to the change of state of electrostrictional solvation (or hydration) of reactants and activated complex. Most fortunately, as far as interionic reactions are concerned, previous studies^{52,53} show that

$$\Delta V^{\ddagger} = \Delta V_2^{\ddagger} \quad (8)$$

In other words, we can safely discuss the influence of solvation (hydration) in macroion "catalysis" on interionic reactions on the basis of ΔV[‡]. The pressure influence actually observed depended on the concentration of macroions. Experimental results⁵⁴ are shown in Figure 4 for the Ag⁺-induced aquation of Co(NH₃)₅Br²⁺ (eq 9). From the initial slope, ΔV[‡] at 1 bar is estimated



and shown in Table I, together with the free energy (ΔG[‡]), enthalpy (ΔH[‡]), and entropy (ΔS[‡]) of activation. The negative ΔV[‡] at [NaPSS] = 0 equiv L⁻¹ is reasonable, since the activated complex in this reaction may

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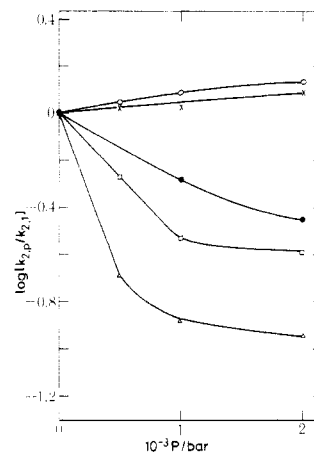
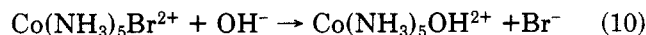


Figure 4. Pressure influence on the Ag⁺-induced aquation of Co(NH₃)₅Br²⁺ in the presence of sodium polystyrenesulfonate and in its absence at 25 °C: [Co(NH₃)₅Br²⁺] = 3.8 × 10⁻⁵ M, [HClO₄] = 1.17 × 10⁻⁴ M, [AgNO₃] = 10⁻³ M; ○, [NaPSS] = 0 equiv L⁻¹ (k_{2,1} = 5.3 × 10⁻³ M⁻¹ s⁻¹); ×, 10⁻⁶ equiv L⁻¹ (k_{2,1} = 9.5 × 10⁻³); ●, 10⁻⁵ equiv L⁻¹ (k_{2,1} = 3.2 × 10⁻²); □, 5 × 10⁻⁵ equiv L⁻¹ (k_{2,1} = 0.48); △, 10⁻⁴ equiv L⁻¹ (k_{2,1} = 2.16). Data were taken from ref 54.

be a triply charged one [Co(NH₃)₅Br²⁺...Ag⁺] according to Basolo and Pearson,⁵⁵ so that its hydration can be stronger than that of the reactant. Correspondingly, ΔS[‡] had a large negative value. Addition of polystyrenesulfonate, which accelerated the reaction between the similarly charged species, caused considerable increase in ΔV[‡] and ΔS[‡]. Recalling that ΔV[‡] reflects only the solvation term in this case, the drastic increase in ΔV[‡] can be interpreted as suggesting that the activated complex is more extensively dehydrated by the presence of the macroions than the reactants. The value of 76 mL mol⁻¹ is comparable with a volume change (52 mL mol⁻¹) observed for a polyphosphate-Mg²⁺ solution⁵⁶ and suggests that the dehydration took place not only from the activated complex but also from the macroions. Because a large amount of water was released from the activated complex, ΔS[‡] increased correspondingly. Obviously, the acceleration by PSS must be claimed to be entropic, because ΔH[‡] increased with PSS concentration. In other words, the f_X term (eq 4) was lowered by the ΔS[‡] increase.

In the case of reaction 10, a reaction between oppositely charged reactants,⁵⁷ the reaction is decelerated by macroions. The activated complex has a net positive charge⁵⁵ so that anionic macroions interact most



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Table II
Activation Parameters for the Alkaline Hydrolysis of $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ in the Presence of Sodium Polyethylenesulfonate at 25 °C and 1 bar

[NaPES], equiv L^{-1}	k/k^*	ΔG^\ddagger , kJ mol^{-1}	ΔH^\ddagger , kJ mol^{-1}	ΔS^\ddagger , $\text{J K}^{-1}\text{mol}^{-1}$	ΔV^\ddagger , mL mol^{-1}
0	1	68.4 ± 0.3	103.7 ± 2.0	118 ± 8	32 ± 2
10^{-5}	0.9	68.8	88.4	66	30
5×10^{-5}	0.3				23
10^{-4}	0.05	76.1	98.5	75	10

strongly with $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ and cationic ones with OH^- . Thus, stronger dehydration by added macroions takes place from the reactants. As a matter of fact, the ΔV^\ddagger (and hence ΔS^\ddagger) decreased with addition of an anionic polyelectrolyte, sodium polyethylenesulfonate (NaPES), as is seen from Table II. Needless to say, it must be $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ (not OH^-) that was dehydrated by PES. The dehydration of reactant caused stronger lowering of the f_A term through the ΔS^\ddagger decrease.

The study described above indicates that dehydration of activated complex or of reactants plays a key role in macromolecular "catalysis". When ΔV^\ddagger data were not available, as was the case for almost of all previous investigations, the observed increase in ΔS^\ddagger was sometimes taken as supporting the generally accepted view that macroions increased the local concentration of oppositely charged reactants and that, accordingly, the collision frequency was raised to cause acceleration. Our study shows that the situation is not so simple as previously and widely supposed; the desolvation factor cannot be overlooked when a correct interpretation of macroion "catalysis" is sought.

The ΔV^\ddagger values sensitively reflect the reaction mechanism. For example, the spontaneous aquations of $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ and $\text{Cr}(\text{NH}_3)_5\text{Br}^{2+}$ were found to have ΔV^\ddagger values of -8.7 and -9.3 mL mol^{-1} , respectively.⁵⁸ At an NaPES concentration of about 10^{-3} equiv L^{-1} , the ΔV^\ddagger values of the aquations were 12 mL mol^{-1} and -7.0 mL mol^{-1} for the Co complex and Cr complex, respectively. The difference in the polyelectrolyte influence in ΔV^\ddagger is consistent with the reaction mechanism; the aquation of the Co complex proceeds through the dissociative mechanism so that the valency of the activated complex is larger than that of the reactant, whereas the activated complex of the Cr complex is a doubly charged cation because the reaction goes through the associative mechanism.⁵⁹⁻⁶¹ Therefore, the anionic macroion interacts more strongly with the activated complex for the Co complex and dehydrates it, causing an increase in ΔV^\ddagger . On the other hand, for the Cr complex, the macroanions affect both the Cr complex and its activated complex practically to the same extent without a substantial change in ΔV^\ddagger .

Macroion "Catalysis" Involving Electrostatic and Hydrophobic Interactions under High Pressure

In reactions 9 and 10 studied under high pressure, only electrostatic interactions needed to be taken into account. Evidently, this is an ideal case. We took a further step toward more complicated cases by studying the high-pressure influence on the alkaline fading re-

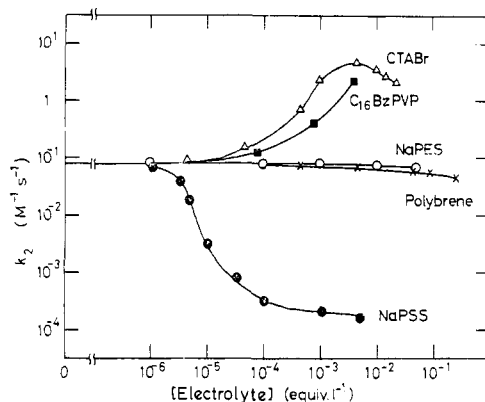
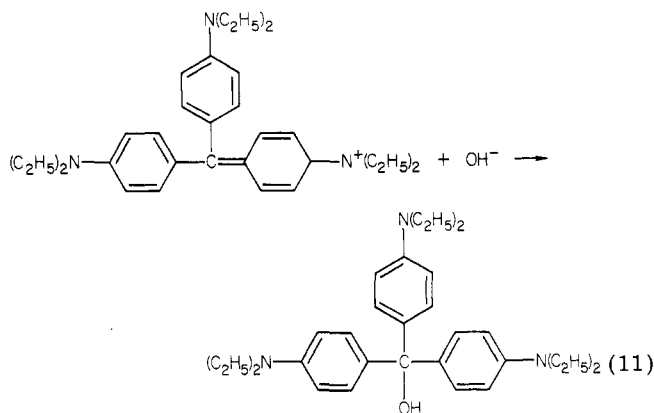


Figure 5. "Catalytic" action of polyelectrolytes on the fading reaction of ethyl violet at 25 °C: [dye] = 5×10^{-6} M, $[\text{OH}^-]$ = 2×10^{-2} M. Data were taken from ref 62.

actions of triphenylmethane dyes,⁶² e.g., ethyl violet. Since they are reactions between a cationic dye and OH^- (eq 11), addition of both cationic and anionic poly-



lectrolytes was expected to cause deceleration. However, what was observed were acceleration by hydrophobic cationic macroions and micelles (C16BzPVP, polyvinylpyridine quaternized with *n*-cetyl bromide and benzyl chloride; CTABr, cetyltrimethylammonium bromide), a small deceleration by less hydrophobic macroions (NaPES and polybrene), and a large deceleration by hydrophobic anionic macroions (NaPSS).^{62,63} This is shown in Figure 5. These observations are easily acceptable if due attention is paid to the electrostatic and hydrophobic interactions between the reactants and the macroions. In short, the acceleration by C16BzPVP can be accepted if the hydrophobic attraction of C16BzPVP toward the dye cations overwhelms the coulombic repulsion between them. The deceleration by NaPSS is also reasonable because the dye cations attracted to the PSS anions by the simul-

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Table III
Activation Parameters for the Fading Reaction of Ethyl Violet at 25 °C and 1 bar^a

polyelectrolyte	[polyelectrolyte], equiv L ⁻¹	k/k*	ΔG^\ddagger , kJ mol ⁻¹	ΔH^\ddagger , kJ mol ⁻¹	ΔS^\ddagger , J K ⁻¹ mol ⁻¹	ΔV^\ddagger , mL mol ⁻¹
none		1	79.5 ± 0.4	57.4 ± 2.0	-75 ± 8	-2.1 ± 1
C16BzPVP	7.7 × 10 ⁻⁵	1.2	79.1	49.4	-96	-3.2
	7.7 × 10 ⁻⁴	5.2	75.4	25.1	-167	-4.4
NaPSS	1.2 × 10 ⁻⁶	0.82	80.0	61.1	-63	-1.7
	1.2 × 10 ⁻⁵	0.064	86.3	151.6	218	8.5

^a [Ethyl violet] = 5 × 10⁻⁶ M, [NaOH] = 2 × 10⁻² M.

taneous action of hydrophobic and coulombic interactions are strongly separated from OH⁻, which is repelled by the macroanions.

The pressure influence on the fading reactions differed from that on the Co(NH₃)₅Br²⁺ reactions. Because of the presence of hydrophobic moiety, eq 7 must be extended to include the volume change (ΔV_3^\ddagger) of the "iceberg" structure⁶⁴ of water around hydrophobic groups. Thus,

$$\Delta V^\ddagger = \Delta V_1^\ddagger + \Delta V_2^\ddagger + \Delta V_3^\ddagger \quad (12)$$

The ΔV^\ddagger value in the absence of polyelectrolytes was negative (-2.1 mL mol⁻¹), as is shown in Table III. This would be justified as follows. The electrically neutral activated complex (Dye[‡]) would stabilize a larger iceberg structure than the cationic reactant dye (Dye⁺), because electric charge on solute species is generally expected to destroy, at least partly, an iceberg structure around the hydrophobic moiety of the solute.⁶⁵⁻⁶⁸ Furthermore, we know that the partial molal volumes of hydrophobic solutes such as methane, ethane, and propane in water are smaller by 20 mL mol⁻¹ than in nonpolar liquids.⁶⁹ This indicates that the hydrophobic solutes fill up part of the space that would be unoccupied in an ordinary ice cluster. A similar situation was found also for synthetic polyelectrolytes by dilatometric measurements.⁷⁰ Thus, ΔV_3^\ddagger is negative. On the other hand, ΔV_2^\ddagger may be positive for the present reaction between oppositely charged ionic species, but it would be negligible compared to ΔV_3^\ddagger for this reaction, because the electrostatic influence is of the secondary importance relative to the hydrophobic factor as can be judged from the kinetic data (Figure 5). Therefore, because ΔV_1^\ddagger can also be assumed to be negligible for the fading reaction,^{71,72} the observed value of -2.1 mL mol⁻¹ indicates that ΔV^\ddagger is largely determined by ΔV_3^\ddagger . The negative ΔS^\ddagger is consistent with the enhanced iceberg formation in the course of activation.

Addition of C16BzPVP gives rise to further stronger stabilization of the iceberg structure around Dye[‡] than that in the vicinity of Dye⁺, because no coulombic repulsion exists between the macrocations and Dye[‡]. Thus, ΔV_3^\ddagger (and ΔS_3^\ddagger) is understood to decrease with

addition of C16BzPVP. Since ΔV_2^\ddagger is negligible and ΔV_1^\ddagger is independent of the polymer, the overall effect is a decrease in ΔV^\ddagger , as observed. On the other hand, addition of NaPSS, a hydrophobic anionic polyelectrolyte, should cause stabilization of the iceberg structure around Dye[‡] (instead of Dye⁺), which would enhance incorporation of Dye⁺ into the iceberg structure. This gives rise to an increase in ΔV_3^\ddagger , and hence ΔV^\ddagger (from -2.1 to +8.5 mL mol⁻¹). Observed ΔS^\ddagger values are in line with the above reasoning.

The respective decrease and increase in ΔH^\ddagger by addition of C16BzPVP and NaPSS can be understood also in terms of the stronger stabilization of the iceberg structure around Dye[‡] and Dye⁺. We note that the acceleration, or lowering in the f_X term (eq 4), was brought about by the ΔH^\ddagger decrease whereas the deceleration is due to the ΔH^\ddagger increase. Essentially the same results were obtained for crystal violet.

Concluding Remarks

We have discussed "catalysis" by synthetic macroions in chemical reactions. Our effort has focused on interionic reactions in the presence of synthetic macroions and also on the role of solvent. It is ultimately clear that the most important factor in the "catalysis" is the large electrostatic potential of the macroions. This causes changes in the activities of the reactants and the activated complex by dehydration of these solutes, preferential accumulation of water, and so on. However, this behavior is not peculiar to macroions but is generally expected for systems in which a number of ionic charges are confined in a small space for some reason. Examples are ionic micelles and electrically charged polymer latex particles. The micelles can "catalyze" various reactions as mentioned above,³⁷ but they cannot be effective below the critical micelle concentration, as demonstrated before.¹³ Furthermore, they are always in dynamic equilibria with the monomeric form so that they cannot affect reactions much faster than their lifetime to the same extent as macroions. In this respect, the polymeric latex particles are stable and can be as efficient as macroions, as recent preliminary studies show.⁷³⁻⁷⁵

Finally, we have attempted to understand the changes of rate constants by addition of macromolecules. The study of macromolecular "catalysts" having reaction specificity and stereospecificity is a fascinating subject,^{22a,76} in which much more intensive efforts

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should be made. Finally, we note that there has been no successful observation of an allosteric effect with synthetic macromolecules.

One of our chief results is that the experimental value of ΔV^* is significant for the physical chemistry of polyelectrolyte solutions. Only one example is given here; our volumetric study as well as the previous one⁵⁶ cast strong suspicion on the point-charge approximation for counterions, which has been assumed in almost of all theoretical treatments of polyelectrolytes. If the approximation is right, ΔV^* could be negligibly small (~ 0). This was not the case, even at 10^{-5} – 10^{-4} equiv L⁻¹ of polyelectrolytes, as seen from Tables I and II and Figure 4.

The high-pressure study indicates that the rate enhancement by macroions is associated with substantial

dehydration of the activated complex, whereas the rate retardation is associated with dehydration of the reactants. The macroion "catalysis" in binary mixtures of water and organic solvent also demonstrates the significance of solvation and desolvation. This role of solvent is at least qualitatively in accord with the Brønsted-Bjerrum scheme, whereas it is not in accord with the usually accepted view of concentration of reactants followed by enhanced collision.

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