quantum yields $\varphi(\mathrm{IIIH^+}) \approx 30\varphi(\mathrm{IH^+})$, is the reason for the high conversion rate of 60%. However, 5,6-benzazulenium cation ($\mathrm{IVH^+}$) fluoresces as strongly as $\mathrm{IIIH^+}$ while only 15% of it is converted to the free base IV after the flash. Presumably differing quantum yields of side reactions and differing rates of the deprotonation reaction in the excited state determine also the conversion rates.

Both 5,6-benzazulene (IV) and guaiazulene (II) have only been investigated qualitatively. The change in optical density due to one of the transients agrees again with the corresponding absorption spectra of the free hydrocarbons IV and II. However, side reactions are much more predominant. Therefore, the calculation of accurate rate constants was not possible.

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The Primary Salt Effect on Rate of Reaction between Likely Charged Ionic Species by Polyelectrolytes

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Abstract: The rate constants were measured in the presence of various polyelectrolytes for the following two types of reactions between likely charged ionic species, namely bromoacetate–thiosulfate ion reaction and bromopentaamminecobaltic ion–mercuric ion reaction. Cationic polyelectrolytes such as polyethylenimine hydrochloride considerably enhanced the anion–anion reaction, whereas polystyrenesulfonate and other anionic polyelectrolytes also showed large accelerating effects on the cation–cation reaction. This primary salt effect by polyelectrolytes was markedly larger than that by simple electrolytes and was shown to be due to a lowering of the enthalpy and entropy of activation in contrast to the simple electrolyte cases in which these thermodynamic quantities were increased. The entropy loss by the addition of polyelectrolytes was in conformity to the enhanced regularity of ionic distribution in the polyelectrolyte solutions, which was previously concluded from the mean activity coefficient measurements.

We know that high molecular weight compounds exhibit various characteristic properties, which are not encountered for those of low molecular weight. Catalytic efficiency is not an exception. In this laboratory for example, intensive studies were carried out on the catalytic actions of various types of polysulfonic acids mainly in hydrolysis reactions.[1] The results showed that the reactions could be enhanced considerably more by polymer catalysts than by low molecular weight ones. It was concluded that the rate enhancement was due to nonspecific hydrophobic and electrostatic interactions which gave rise to an abnormally high accumulation of reactant molecules and ions around macroions. Though these investigations covered important aspects of the problem, there is still something to be further explored: no work was published on the catalytic influence of polyelectrolytes on reactions between rather simple ionic species.[2] The previous studies mentioned above indicate that this type of reaction might also be influenced by polyelectrolytes.

In previous papers from this laboratory, the mean activity coefficients of polyelectrolytes[3] were determined by emf measurements of a concentration cell with transference[4] and isopiestic vapor pressure measurements.[5] The results have revealed that the mean activity coefficients decrease linearly with the cube root of concentration, suggesting the existence of an interionic linkage in the polyelectrolyte solutions. Such thermodynamic behavior was not, however, newly found, but had earlier been pointed out for simple electrolyte solutions.[6] Nonetheless, it is important to point out that the cube-root rule holds in a much wider range of concentration for polyelectrolytes than for simple electrolytes. For example, the rule is valid between 10^{-3} and 10^{-1} M for sodium chloride, whereas the upper limit lies at about 1 equiv/1000 g of water for sodium polyacrylate.[7] Since the cube-root relation can be attributed to a more or less regular ionic lattice in the solutions,[6] it is feasible that strong electrostatic attractive forces between macroions and gegenions give rise to linkages between macroions and between gegenions through the intermediary of gegenions and macroions, respectively. Accordingly, the regular ionic

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(1) I. Sakurada, Y. Sakaguchi, *et al.*, *Kobunshi Kagaku*, **22**, 696, 701, 706, 711, 804, 808 (1965); **23**, 735, 741, 748, 849, 853 (1966); **24**, 87, 341, 570, 618 (1967); *Makromol. Chem.*, **91**, 243 (1966). For a comprehensive review, see the plenary lecture by I. Sakurada at the International Symposium on Macromolecular Chemistry, 1967, Brussels; *J. Pure Appl. Chem.*, in press.

(2) The catalytic actions of polyelectrolytes on a few reactions between fairly complicated ionic species have been studied; see H. Morawetz, "Macromolecules in Solution," Interscience Publishers, New York, N. Y., 1965, Chapter 9. See also NOTE ADDED IN PROOF.

(3) The mean activity coefficients should be correctly distinguished from the single-ion activity coefficients having no sound physical basis. For related problems peculiar to the polyelectrolyte solutions, see N. Ise and T. Okubo, *J. Phys. Chem.*, 70, 3025 (1966).

(4) See, for example, N. Ise and T. Okubo, *ibid.*, **69**, 4102 (1965).

(5) See, for example, T. Okubo, N. Ise, and F. Matsui, *J. Amer. Chem. Soc.*, **89**, 3697 (1967).

(6) N. Bjerrum, *Z. Anorg. Chem.*, **109**, 275 (1920); H. S. Frank and P. T. Thompson, *J. Chem. Phys.*, **31**, 1086 (1959); J. E. Desnoyers and B. E. Conway, *J. Phys. Chem.*, **68**, 2305 (1964).

(7) N. Ise and T. Okubo, *ibid.*, **71**, 1287 (1967).

lattice can be formed with greater ease than in simple electrolyte solutions. In other words, macroions act as rallying points for gegenions, pulling the latter to the vicinity of the polymer domain. It was supposed, therefore, that the rates of reactions between anions (or cations) would be larger in the presence of polycations (or polyanions) than in their absence.

Independently of such reasoning, extensive studies on reaction velocity in the 1920's disclosed that the velocity constants of reactions between ions changed markedly with concentrations of reactant electrolytes or of coexisting electrolytes. The kinetic anomaly demonstrated by the added electrolytes, *i.e.*, the primary salt effect, was accounted for by the Brønsted theory[8] with the aid of the interionic interaction theory of electrolytes.[9] Shortly thereafter, it was demonstrated that the presence of tri- or bivalent cations considerably enhanced the reaction between bromoacetate and thiosulfate ions, appreciable deviations from the ideal Brønsted–Debye behavior having been found.[10] To our knowledge, no reports have been published on the supposedly enormous accelerating effect of electrolytes of much higher valency, for example, synthetic and naturally occurring polyelectrolytes.[11]

Thus it was thought interesting to measure the catalytic influence of polyelectrolytes on ionic reactions. In the present paper, we have chosen two ionic reactions, namely the bromoacetate–thiosulfate reaction

$$CH_2BrCOO^- + S_2O_3^{2-} \longrightarrow CH_2(S_2O_3)COO^{2-} + Br^-$$

and the reaction between bromopentaamminecobaltic ions and mercuric ions

$$2[Co(NH_3)_5Br]^{2+} + Hg^{2+} + 2H_2O \longrightarrow 2[Co(NH_3)_5H_2O]^{3+} + HgBr_2$$

The bromoacetate–thiosulfate reaction is almost completely free from the interfering side reactions, and the kinetics can be followed precisely by iodine titration. Therefore, for this reaction we can expect to develop a detailed discussion on the catalytic influence by polycations, which may be compared with that by low molecular weight high valence cations thoroughly studied by LaMer and his associates.[10,12,13] The second type of reaction is one between cations,[14] the precise rate determination being possible by the use of a spectrophotometer.[15] Comparison of the primary salt effect by high molecular weight polyions and simple electrolyte ions in these two types of ionic reactions is the aim of the present paper.

Experimental Section

Materials. Commercially available bromoacetic acid (analytical grade) was dissolved in water and neutralized with sodium hydroxide solution using phenolphthalein as an indicator. The concentration of the stock solution of sodium bromoacetate was 0.05 *M*. The water used in the present work had a conductivity of 5×10^{-6} mho cm^{-1} or below. Aqueous solutions of sodium thiosulfate and iodine were prepared by the Nakarai Chemicals Co., Kyoto, and used within 1 week after preparation.

Bromopentaamminecobaltic nitrate $[Co(NH_3)_5Br](NO_3)_2$ was prepared by nitration of bromopentaamminecobaltic bromide by the method of Jörgensen,[16] the latter being prepared by the method of Willard and Hall,[17] as follows. Cobalt carbonate (25 g) was added slowly to 65 ml of 47% HBr, in which it dissolved; the solution was then filtered. To the filtrate were added 50 g of ammonium bromide and then 250 ml of concentrated ammonia solution. Further, 40 ml of 30% H_2O_2 was added dropwise with stirring and then a vigorous stream of nitrogen was blown through the solution for 4 hr to remove excess ammonia. By neutralization of the resulting solution with concentrated HBr solution, a red precipitate of aquopentaamminecobaltic bromide was obtained. Further addition of 50 ml of the HBr solution with heating over a water bath changed the color of the precipitate to violet ($[Co(NH_3)_5Br]Br_2$). After filtration, decantation with 250 ml of water, refiltration, and washing with ethanol, the precipitate was dried at 110°. The dried precipitate was dissolved in dilute sulfuric acid at 50° and then filtered; the filtrate was poured into ice-cooled concentrated nitric acid. A bright violet precipitate was formed which was washed repeatedly by decantation with dilute nitric acid until an SO_4^{2-} test became negative; the solution was filtered and the solid was washed with 45% ethanol aqueous solution and dried at 110°. The precipitate was purified by recrystallization from hot water, washed with ethanol, and dried at 110°.

Anal. Calcd for $[Co(NH_3)_5Br](NO_3)_2$: H, 4.3; N, 28.2; Br, 23.0; Co, 19.9. Found: H, 4.7; N, 28.1; Br, 22.9; Co, 19.5.

The bromopentaamminecobaltic nitrate was stored in a refrigerator. Its solution was prepared just before use by weighing out the nitrate.

A stock solution of mercuric nitrate was prepared by dissolving mercuric nitrate (reagent grade) in nitric acid. The presence of nitric acid may repress the hydrolysis of the nitrate and prevent undesired reactions. The mercuric ion solution was titrated with 0.1 *N* potassium thiocyanate solution with ferric ammonium sulfate as an indicator.[18] The concentration of nitric acid was determined in the presence of a large excess of sodium bromide by titration with 0.02 *N* sodium hydroxide with the aid of mixed indicators of bromothymol blue and phenol red. The concentration of mercuric nitrate in the stock solution was found to be 0.0134 *M* and that of nitric acid 0.0021 *M*. The stock solution was stored in a dark place. The kinetic measurements done at a 2-month interval show that this solution was stable. Just before use, the stock solution was dilluted by 2×10^{-3} *M* HNO_3 in order to adjust the concentration of mercuric ions.

The hydrochloride of polyethylenimine (PEI·HCl) was obtained by neutralization of polyethylenimine furnished from the Sumitomo Chemical Co., Osaka, and was used earlier for the mean activity measurements.[19]

Dimethyldiallylammonium chloride-SO_2 copolymer (DACS) was obtained from the Nitto Spinning Co., Fukushima, by courtesy of S. Harada. For the details of the preparation method and the properties of this cationic polyelectrolyte, see an earlier reference.[20] DACS was used without further purification and its solution was prepared by weighing out a dried sample. The degree of polymerization was 730 by osmometry.[21]

Sodium polyacrylate (NaPAA) was a gift from the Toa Gosei Chemicals Co., Nagoya. Its degree of polymerization was 640 by viscometry. A dilute solution of NaPAA was purified by cation- and anion-exchange resins and neutralized with sodium hydroxide.

Ethylenediamine (ED), diethylenetriamine (DT), and tetraethylenepentamine (TP) were commercially available. After purification by distillation under reduced pressure of nitrogen, the imines were converted into hydrochlorides. The hydrochloride

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[8] J. N. Bronsted, *Z. Physik. Chem.*, **102**, 169 (1922); **115**, 337 (1925).

[9] P. J. W. Debye and E. Hückel, *Physik. Z.*, **24**, 185 (1923).

[10] V. K. LaMer and R. W. Fessenden, *J. Amer. Chem. Soc.*, **54**, 2351 (1932).

[11] It has preliminarily been reported that for cationic surfactants the onset of micelle formation is accompanied by an increased catalytic activity for the bromoacetate–thiosulfate reaction if the micelle is positively charged. No detailed description has been published, however, and the system is too complicated to allow quantitative treatment of the data; see F. Sebba and J. H. Wiggill, *J. Colloid Sci.*, **21**, 115 (1966).

[12] V. K. LaMer, *J. Amer. Chem. Soc.*, **51**, 3341 (1929).

[13] V. K. LaMer and M. E. Kamner, *ibid.*, **57**, 2662, 2669 (1935).

[14] J. N. Brønsted and R. Livingston, *ibid.*, **49**, 435 (1927).

[15] A. R. Olson and T. R. Simonson, *J. Chem. Phys.*, **17**, 1167 (1949).

[16] S. M. Jörgensen, *J. Prakt. Chem.*, **18**, 216 (1878).

[17] H. H. Willard and D. Hall, *J. Amer. Chem. Soc.*, **44**, 2220 (1922).

[18] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1943, pp 480, 575.

[19] N. Ise and T. Okubo, *J. Phys. Chem.*, **70**, 2400 (1966).

[20] S. Harada and A. Arai, *Makromol. Chem.*, **107**, 64 (1967).

[21] N. Ise and T. Okubo, unpublished results.

of ethylamine [EA(HCl)] (reagent grade) was commercially available. It was used without further purification.

Sodium polystyrenesulfonate (NaPSt) was given by the Dow Chemical Co., Midland, Mich. The degree of polymerization was 2500.

Sodium polyethylenesulfonate (NaPES) was kindly furnished from the Hercules Powder Co., Wilmington, Del. The degree of polymerization was 770. Purification of NaPSt and NaPES was carried out by using cation- and anion-exchange resins. The concentration was determined by potentiometric titration.

In this work, fractionation of polyelectrolytes was not effected, since it was thought that, like many other solution properties, the catalytic activity would be insensitive toward the degree of polymerization unless the latter is smaller than about 100.

Anhydrous sodium sulfate (reagent grade) was used without further purification.

Kinetic Measurements

(a) The Bromoacetate–Thiosulfate Reaction. The solution of sodium thiosulfate and that of sodium bromoacetate containing a polyelectrolyte were placed in a thermostat. Most of the experiment was carried out at 25 ± 0.02°, unless otherwise specified. When the solutions had reached the bath temperature, a portion of the sodium bromoacetate solution was pipetted into the thiosulfate solution. At suitable intervals aliquots of the mixture were withdrawn and brought into starch-containing iodine solution. The amount of the iodine solution was just insufficient to react with all the thiosulfate present. The iodine titration was then completed by adding the iodine solution quickly. Thus the time error in stopping the reaction was minimized.

When PEI·HCl at higher concentrations was mixed with thiosulfate, the resulting mixture became slightly turbid. By subsequent addition of bromoacetate, however, the mixture again became transparent. It was confirmed by iodine titration that the thiosulfate ions did not react with coexisting polyelectrolytes.

The velocity constants were calculated by the formula $k = x/ta(a - x)$, where k is the velocity constant, a is the initial concentration of the two reactants in moles per liter, and x is the amount changed in time t. Usually the velocity constant was calculated from seven to nine measurements, for which the kinetic equation mentioned above was shown to be valid. The average deviation of the k values was at the highest 2%.

(b) The Cobaltammine–Mercuric Ion Reaction. The reaction velocity was precisely measured by taking advantage of the large difference between the extinction coefficients for two (reactant and product) cobaltammine compounds in the ultraviolet region. Using a uv spectrophotometer (Hitachi Manufacturing Co., Tokyo, Model EPS-3T), the absorption spectrum of bromopentaamminecobaltic ion at 254 mμ was measured as a function of time. The molar extinction coefficient was 1.72×10^4. The absorption of nitrate ion in the uv region was fortunately negligible at 254 mμ. The temperature of solution in the cell was believed to be kept constant within 0.02° by means of a thermostatically controlled cell holder. Except for the activation energy determination, the measurements were carried out at 15°.

The solutions of bromopentaamminecobaltic nitrate, mercuric nitrate, and electrolyte to be added were placed in a thermostat bath. The reaction was started by the addition of a mercuric nitrate solution to a solution containing bromopentaamminecobaltic nitrate and the electrolyte. A portion of the solution was transferred to an optical cell. In order to minimize temperature and time errors, the mixing was accomplished as rapidly as possible at the room temperature maintained within a maximum deviation of 1° from the measuring temperature. Into a reference cell, an electrolyte solution of the same concentration as in the reaction system was introduced. For sodium chloride, sodium sulfate, and sodium polyethylenesulfonate which showed no absorption at 254 mμ, however, pure water was used as a reference.

The spontaneous aquation of the bromopentaamminecobaltic ions was neglected under the present experimental conditions, since it proceeds much more slowly than the reaction in question,[14] and the present experiments were conducted using freshly prepared solutions.

Control experiments show that the polyelectrolytes used were inert to the bromopentaamminecobaltic ions.

The velocity constant k was calculated by the formula

$$k = [2/(2b - a)(t_2 - t_1)] \ln (a - x_1) \times (b - x_2/2)/(a - x_2)(b - x_1/2)$$

where a and b are the initial concentrations of bromopentaamminecobaltic nitrate and mercuric nitrate, respectively, and x_1 and x_2 are the amounts of the cobaltic nitrate consumed in time intervals 0 to t_1 and 0 to t_2, respectively. When no polyelectrolyte was present in the reaction system, the velocity constant was calculated at conversions ranging from 10 to 30% (based on the mole number of cobaltic nitrate). When polyelectrolyte was added, the calculation was performed at slightly higher conversions because of the large accelerating effects. In these conversion ranges, the k values obtained were constant with time within experimental error, which was at the highest 9% when the accelerating effects were large, and usually 3% or less.

Results and Discussion

Figure 1 contains the data of the velocity constant for the bromoacetate–thiosulfate ion reaction at 25°. The results clearly indicate that the presence of polyvalent cations from PEI·HCl and DACS strikingly accelerates the reaction. For example, the k value is 0.390 at an initial concentration of reactants of 0.01 M when no electrolyte is added, whereas it increases to 9.36 in the presence of a small quantity of PEI·HCl (1.2×10^{-2} equiv/l.).

Specifically, our first finding is that the cationic polyelectrolytes can accelerate the reaction, whereas NaPAA, an anionic polyelectrolyte, slightly deccelerates it in a low concentration region. This indicates that the regular ionic lattice does not spread over the entire solution at the polymer concentrations used, since otherwise the polyanion should also have an accelerating effect comparable to that by the polycations.

The second finding is that the k value decreases with increasing initial concentrations of the reactants at a given concentration of PEI·HCl. This implies that the Brønsted–Debye theory does not apply to the present system bromoacetate–thiosulfate–PEI·HCl. The theory can be written as

$$\log k = \log k_0 + 2AZ_AZ_B\sqrt{\mu} \qquad (1)$$

where μ is the ionic strength, k_0 the velocity constant at $\mu = 0$, A a constant, and Z the valency of the reactant indicated by the subscript. If the ionic strength should be taken as equal to one-half the summation of the products of the concentration of every ion in the solution, multiplied by the square of its respective electric charge, then k would become larger as the reactant concentration increases. This contradicts the observation. It would appear that the conventional concept of ionic strength cannot be used for polyelectrolyte-containing solutions, in which the Debye–Hückel theory[9] is no longer valid. Thus we are led back to the Brønsted theory,[8] which goes into the equation

$$k = k_0 f_A f_B / f_X \qquad (2)$$

where f denotes the single-ion activity coefficient, A and B are reactants, and X is the critical complex produced from the reactants. LaMer and Fessenden[10] asserted that the presence of high-valence ions lowers f_A and f_B and even more appreciably f_X, because X has a higher valency than the reactants in the case of reactions between likely charged ions. As a matter of fact, the mean activity coefficient measurements carried out previously on a ternary system H_2O–NaPAA–NaCl[5] show that in general $|\beta_{33}| << |\beta_{32}|$ $(= |\beta_{23}|) << |\beta_{22}|$, where $\beta_{33} = 2\partial \ln \gamma_3/\partial m_3$, $\beta_{32} = 2\partial \ln \gamma_3/\partial(m_2/Z_2)$, and $\beta_{22} = (1 + \alpha)\partial \ln \gamma_2/\partial(m_2/Z_2)$, γ is the mean activity coefficient, m is the concentration, Z_2 and α are stoichiometric and apparent valencies of a macroion, respectively, and the subscripts 2 and 3 denote NaPAA and NaCl, respectively. The inequality indicates that the higher the valency of an ion, the more markedly it affects coexisting ions. Since the mean activity coefficient is the geometric mean of the single-ion activity coefficient, f_X in the present study can be much more drastically lowered (by polyelectrolytes) than in LaMer–Fessenden's case, in which Ba^{2+} and La^{3+} were used. Consequently, k may be considerably large in the polyelectrolyte-containing solutions. Furthermore, the previous measurements[5] show that γ_3 generally increases with increasing m_3 (Figure 5 in ref 5). Since it is expected that this trend holds also for other simple electrolytes having higher valences, f_X in the present system should increase with increasing concentration of the complex (and hence the reactants) so that k becomes smaller, as is shown in Figure 1.

It is then interesting to investigate how closely the large accelerating effect observed is connected to the macromolecularity of the added electrolytes. Figure 1 also gives the velocity constant values obtained for low molecular weight analogs of PEI·HCl, *i.e.*, hydrochlorides of EA, ED, DT, and TP, which are mono-, di-, tri-, and pentavalent, respectively. It is seen that at a given hydrochloride concentration the k values of these analogs increase with rising valency, but are still small compared to those observed for approximately 100-valent PEI·HCl. It is thus possible to attribute the enormous accelerating effects to the plain fact that the ionized groups of macroions are linked together by polymer chain.

Figure 1 shows furthermore that two different kinds of 1:1-type electrolyte, *i.e.*, NaCl and EA(HCl), have about the same magnitude of k. This agreement implies that the accelerating effect observed for cationic polyelectrolytes may not be associated with the nonelectrostatic affinity of the nitrogen atom in the polycations with the reactant ions under consideration. Furthermore, the agreement may rule out a possibility that the difference in the hydrogen ion concentration gives rise to the observed difference in the k value, since the sodium chloride solution is neutral, whereas the EA(HCl) solution is acid.

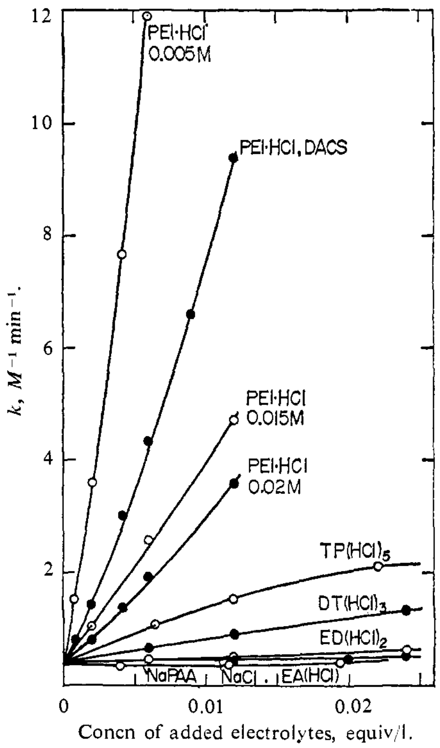

Figure 1. The primary salt effects by polyelectrolytes and simple electrolytes on the bromoacetate–thiosulfate ion reaction at 25°. The concentration of the reactants was 0.01 M unless otherwise indicated in the figure.

The rate constants were furthermore determined at 30 and 20°. Combining these values with those obtained at 25°, it is possible to calculate the activation energy, from which the enthalpy ($\Delta H^{\ddagger}$), entropy ($\Delta S^{\ddagger}$), and free energy ($\Delta G^{\ddagger}$) of activation are derivable. The results obtained are shown in Table I. For comparison, the thermodynamic quantities were also calculated for simple electrolyte-containing systems by using LaMer and Kamner's data.[13] It is most interesting to note that by the addition of PEI·HCl, $\Delta H^{\ddagger}$ decreases and $\Delta S^{\ddagger}$ also decreases. On the other hand, the addition of simple electrolyte increases $\Delta H^{\ddagger}$ (except for NaCl) and also $\Delta S^{\ddagger}$. For example, in the presence of 0.12 equiv/l. of barium chloride, $\Delta H^{\ddagger}$ increases by 190 cal/mol and $\Delta S^{\ddagger}$ increases by 2.41 cal/(deg mol). The reason for the $\Delta H^{\ddagger}$ decrease due to the NaCl addition is not clear. It should be mentioned, however, that the decrease was observed only at one concentration of NaCl between 12.5 and 37.5°, whereas at the same concentration and 0° $\Delta H^{\ddagger}$ increased. Thus we consider the decrease exceptional.

The essentially different feature of catalytic actions by polyelectrolytes and simple electrolytes should therefore be attributed to the mechanism. The large negative entropy of activation usually observed in the reactions between likely charged ions has its origin in the so-called "electrostriction" of solvent molecules

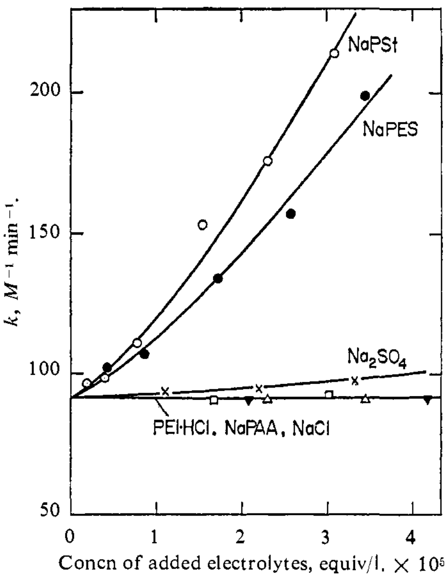

Figure 2. The primary salt effects by polyelectrolytes and simple electrolytes on the bromopentaamminecobaltic ion–mercuric ion reaction at 15°. Concentrat ions: bromopentaamminecobaltic nitrate, 8.00×10^{-5} *M*; mercuric nitrate, 2.67×10^{-4} *M*; HNO_3, 8.02×10^{-4} *M*. ○, NaPSt; ●, NaPES; ×, Na_2SO_4; ▼, PEI·HCl; △, NaPAA; □, NaCl.

by ions.[22] The increase in $\Delta S^{\ddagger}$ by the addition of simple electrolytes, therefore, is due to the liberation of bound solvent molecules, which is caused by the formation of a critical complex of a lower valence than the reactant ions. LaMer and Fessenden suggest that in the bromoacetate–thiosulfate–lanthanum chloride case, $(LaS_2O_3)^+$ and $(LaCH_2BrCOO)^{2+}$ can be formed, which may further react with bromoacetate ion and thiosulfate ion, respectively, to form critical complexes. On the other hand, the decrease in $\Delta S^{\ddagger}$ in the PEI·HCl case, indicating a minor contribution of the liberation of the solvent molecules, can be interpreted as implying that the regularity in the distribution of simple electrolyte ions was largely enhanced by the polyelectrolyte addition. It should be recalled that this interpretation is in line with the above-mentioned conclusion derived from the cube-root dependence of the mean activity coefficient. Thus, the presence of polycations gives rise to a highly abnormal local accumulation of reactant anions, but it does not provide an enhanced opportunity for collisions between the reactants, as reflected in the decrease in $\Delta S^{\ddagger}$. This is due to macroions exerting much stronger influence on the reactant ions than simple electrolyte ions of high valences (such as La^{3+} and Ba^{2+}).

Table I. Thermodynamic Quantities for the Bromoacetate–Thiosulfate Reaction in Aqueous Solution with and without Added Electrolytes[a]

Added electrolyte	Concn, equiv/l. × 10^2	$\Delta H^{\ddagger}$, cal/mol	$\Delta S^{\ddagger}$, cal/(deg mol)	$\Delta G^{\ddagger}$, cal/mol
		A. Polyelectrolyte[b]		
None		15,700	−15.4	20,300
PEI·HCl	0.600	13,200	−19.3	19,000
	1.20	12,100	−21.5	18,500
		B. Simple Electrolytes[c]		
None		15,360	−16.90	20,400
NaCl	18	15,090	−16.57	20,030
$BaCl_2$	12	15,550	−14.49	19,870
$LaCl_3$	9	17,460	−6.15	19,290

[a] 25°. [b] Obtained from the present study; reactant concentrations, 0.01 *M*. [c] Calculated from data reported by V. K. LaMer and M. E. Kamner, *J. Amer. Chem. Soc.*, **57**, 2662 (1935); reactant concentrations, 0.005 *M*.

In that case, one would be tempted to predict that the reaction rate would be decreased by the polyelectrolyte addition. This is evidently not the case, however. The factor accelerating the reaction is certainly the decrease in $\Delta H^{\ddagger}$, or in the activation energy (E_{act}). In this respect, it might be useful to recall that the clustering of the reactant anions around a simple electrolyte ion of a high valence operates to increase the heat of dilution for the activation process ($\Delta\bar{L}_{act}$), so that the activation energy increases, since $E_{act} = E°_{act} + \Delta\bar{L}_{act}$, where $\Delta\bar{L}_{act}$ is the difference between the relative partial molal heat content ($\bar{L}$) of the critical complex and the sum of $\bar{L}$'s of the reactants.[13] The heat-content data for polyelectrolyte-containing solutions, however, are so meager that we are unable to give even a qualitative discussion on the $\Delta H^{\ddagger}$ change which can be expected in the present case. At the moment, we can only say on the basis of this $\Delta H^{\ddagger}$ change that the concentration dependence of the heat content of simple electrolyte solutions would be sensitively influenced by the presence of polyelectrolytes. The detailed discussion on this problem will be given after the thermal data of the polyelectrolyte solutions being obtained in this laboratory has been accumulated.

The important conclusions obtained for the bromoacetate–thiosulfate–cationic polyelectrolyte system are further substantiated by experimental results obtained for the bromopentaamminecobaltic ion and mercuric ion reaction, which are presented in Figure 2. In this case, enormous accelerating effects were found for sodium salts of polystyrenesulfonic acid (NaPSt) and of polyethylenesulfonic acid (NaPES). The *k* value is 91.4 M^{-1} min^{-1} at 15° with no added electrolyte, and increases to about 200 M^{-1} min^{-1} by the addition of NaPSt or NaPES. We note that these macroions have charges of sign opposite to the reactant ions. It is also seen that PEI·HCl has practically no influence. This situation is qualitatively the same as shown by NaPAA in the bromoacetate–thiosulfate reaction. Figure 2 further shows the indifferent nature of NaPAA in the present reaction. This is probably due to largely depressed dissociation of PAA ions in the acid medium, in which the reaction under consideration was carried out.

It should be noted that the accelerating effect by the polymeric sulfonate was so large that the concentrations employed were as low as $\sim 10^{-5}$–10^{-6} equiv/l. Considering that the electrolyte concentration used for the bromoacetate–thiosulfate reaction was of the order of $\sim 10^{-2}$–10^{-4}, the accelerating effect of the polyelectrolytes in the bromopentaamminecobaltic ion–mercuric ion reaction is much larger than that for the bromoacetate–thiosulfate reaction. This is understandable because the former is a reaction between divalent ions only, and the latter is a reaction between

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[22] K. J. Laidler, "Reaction Kinetics," Vol. II, "Reactions in Solution," Pergamon Press, New York, N. Y., 1963, Chapter 1.

monovalent and divalent ions. The presence of polyelectrolytes naturally gives rise to a larger influence on the former than on the latter reaction.

From the measurements at 10, 15, and 20°, the thermodynamic quantities were determined and are shown in Table II. In this reaction system, also, the addition of the polyelectrolytes decreased $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. In the cases of Na_2SO_4 and NaCl, on the other hand, these quantities remained practically constant. This is probably due to the low concentration used in the present work, and it is expected that the further addition of these simple electrolytes would increase $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$.

Table II. Thermodynamic Quantities for the Bromopentaamminecobaltic Ion–Mercuric Ion Reaction in Aqueous Solution with and without Added Electrolytes[a]

Added electro- lyte	Concn, equiv/l. $\times 10^5$	$\Delta H^{\ddagger}$, cal/mol	$\Delta S^{\ddagger}$, cal/(deg mol)	$\Delta G^{\ddagger}$, cal/mol
None		11,900	−16.2	16,700
NaPSt	0.772	9,800	−23.2	16,500
	2.31	6,200	−34.9	16,200
NaPES	0.860	10,900	−19.6	16,600
	2.58	7,400	−30.8	16,200
NaCl	3.00	11,900	−16.2	16,700
Na_2SO_4	3.31	11,900	−16.0	16,500

[a] At 15° and the same concentrations of reactants as shown in Figure 2.

We note here that both cationic and anionic polyelectrolytes showed large rate-accelerating effects, though on different types of ionic reactions. This fact strongly excludes the specific role of nitrogen or sulfur atoms contained in the polyelectrolytes, which may be supposed to be a potential factor of the rate acceleration. This interpretation is further substantiated by our experiments on the (positively charged) bromopentaamminecobaltic ion–(negatively charged) hydroxide ion reaction.[23] According to the Brønsted–Debye theory, this type of reaction can be depressed by the addition of neutral salts.[14,15] Our preliminary studies, the details of which will be published at a later date, show that large rate-depressing effects are caused by the addition of anionic polyelectrolytes such as NaPES, NaPSt, NaPAA, and sodium polymethacrylate, whereas PEI·HCl was practically indifferent in the concentration range studied ($\sim 10^{-4}$–10^{-5} equiv/l.). This is acceptable since the reaction was performed in an alkali medium, in which the dissociation of PEI·HCl was depressed.

From the foregoing discussion, it is clear that the rate enhancement in the presence of polyelectrolytes is a result of the macromolecular character of the catalysts and is governed by the general coulombic law at least to the first approximation, though the quantitative theoretical treatment and the elucidation of the nature and structure of the critical complexes appear to be formidable tasks at present and will be studied in future work.[24]

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(23) N. Ise and F. Matsui, manuscript in preparation.

(24) Note Added in Proof. In the process of printing of this article, a short communication on the chloropentaamminecobaltic ion–mercuric ion reaction was brought to our attention by the courtesy of Professor H. Morawetz: B. Vogel and H. Morawetz, *J. Amer. Chem. Soc.*, **90**, 1368 (1968). He also drew our attention to his investigation on the bromopentaamminecobaltic ion–mercuric ion reaction published in a journal which is not easily accessible to us: H. Morawetz, *Svensk Kem. Tidskr.*, **79**, 309 (1967).