Catalysis of Ionic Reactions by Polyelectrolytes. Reaction of $Co(NH_3)_5Cl^{2+}$ and $Co(NH_3)_5Br^{2+}$ with Hg^{2+} in Poly(sulfonic acid) Solution[1,2]

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Abstract: The Hg^{2+}-induced aquation of $Co(NH_3)_5Cl^{2+}$ and $Co(NH_3)_5Br^{2+}$ is powerfully catalyzed by poly(vinylsulfonate) (PVS) and poly(methacryloxyethylsulfonate) (PMES). In the absence of added electrolyte, the $Co(NH_3)_5Cl^{2+}$ reaction was accelerated by a factor of 176,000 by 5×10^{-5} *N* PVS and by a factor of 24,700 by a similar concentration of PMES. Increasing polymer concentration at constant Hg^{2+}, or increasing Hg^{2+} concentrations at constant concentration of polyions, leads first to an increase and later to a sharp reduction of the reaction rate. These observations can be interpreted in terms of a model in which the catalytic efficiency of the polyion is characterized in terms of an effective concentration of binding sites in the polymer domain and dissociation constants of the polyion–reagent ion complexes. Dissociation constants calculated from the catalytic efficiency of the polyions are in good agreement with dialysis equilibrium of the reagent ions with PVS and PMES. The affinity of various inert cations for the polyanions may be estimated from their efficiency in reducing the catalytic power of the polyion. The activation energy of the $Co(NH_3)_5Cl^{2+}$ reaction with Hg^{2+} is substantially reduced under conditions where only a small fraction of the reagent ions are bound to the polyion.

In dilute solutions of polyelectrolytes containing little or no added salts, the domains occupied by the polyions contain very high densities of ionized groups, while the space between the macromolecules has only a very low concentration of ionic species. This situation results in large fluctuations of the electrostatic potential Ψ, and it is one of the central problems of the physical chemistry of polyelectrolytes to find experimental methods for the characterization of the magnitude of these fluctuations. Some years ago, one of us suggested[3–5] that the distribution of Ψ could be studied, in principle, by following the effect of a polyelectrolyte on the rate of a reaction involving two small ionic species carrying charges *m* and *n*, respectively. Qualitatively, if the sign of both *m* and *n* is opposite to that of the polyion, the reagents will tend to be concentrated in the polyion domains resulting in a higher collision frequency, so that the polyelectrolyte will act as a catalyst. Conversely, if *m* and *n* carry opposite signs, one of the reagents will be attracted to the polyion while the other one is being repelled and the polyelectrolyte will act as an inhibitor.

Let us assume that (a) the reaction rate in all small volume elements is governed by the same second-order rate constant k_2^0 (*i.e.*, that we may neglect effects such as would result, *e.g.*, from fluctuations of the local dielectric constant) and (b) the distribution of the ionic reagents is governed entirely by Coulombic forces. It can then be shown that the rate constant k_2 observed in polyelectrolyte solutions is related to k_2^0, the rate constant observed in the absence of polyelectrolyte, by[4,5]

$$k_2/k_2^0 = \langle X^{m+n}\rangle/\langle X^m\rangle\langle X^n\rangle$$
$$X = \exp(-e\Psi/kT) \qquad (1)$$

where *e* is the electronic charge, *kT* has the usual significance, and the angle brackets indicate averaging over the volume of the system.

In accordance with the principles outlined above, the hydroxide ion catalyzed hydrolysis of a cationic ester was strongly inhibited in solutions containing salts of polymeric acids[5] while the benzidine rearrangement, in which the rate-determining step is the hydrogen ion catalyzed conversion of the conjugate acid of hydrazobenzene to benzidine, was found to be much faster in solutions of a poly(sulfonic acid) than in benzenesulfonic acid of the same acidity.[6] Similar results were reported on a variety of other ionic reactions.[7–10]

In all these cases, one of the reagents is a relatively bulky organic species, which may be attracted to the polyion by other than Coulombic interactions, which invalidates the simple interpretation of the data as represented by eq 1. We have, therefore, chosen for the present investigation the reaction of two compact inorganic ions, *i.e.*

$$Co(NH_3)_5X^{2+} + H_2O + Hg^{2+} \longrightarrow Co(NH_3)_5H_2O^{3+} + HgX^+ \qquad (2)$$

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[2] For preliminary communications, see H. Morawetz, *Svensk Kem. Tidskr.*, **79**, 309 (1967); B. Vogel and H. Morawetz, *J. Am. Chem. Soc.*, **90**, 1368 (1968).

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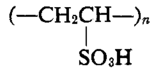
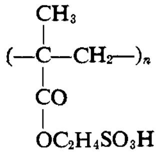
[10] I. Sakurada, Y. Sakaguchi, T. Ono, and T. Ueda, *Macromol. Chem.*, **91**, 243 (1966).

with X = Cl or Br, in solutions of poly(vinylsulfonic acid) (PVS) or poly(methacryloxyethylsulfonic acid) (PMES). This reaction has several advantages. (a) It may be followed spectrophotometrically at extreme dilution of the reagents. (b) It has been studied extensively by Brønsted and Livingston[11] and by Olson and Simonson,[12] who were concerned with kinetic salt effects in simple electrolyte solutions. (c) A series of similar reactions involving reagents of different charge are available (*i.e.*, $Co(NH_3)_5X^+ + OH^-$; $Co(NH_3)_4X_2^+ + Ag^+$; $Co(NH_3)_4X_2^+ + Hg^{2+}$, etc.), which should yield, by use of eq 1, a number of parameters for the detailed description of the distribution function of the electrostatic potential. In the present study, we have attempted to characterize the dependence of the polyion catalysis on the concentration of the reagents, the concentration and the nature of the polyion, the concentration and nature of added salts, and the reaction temperature.



$(-CH_2CH-)_n$ with SO_3H

PVS



$(-C(CH_3)(CO\,OC_2H_4SO_3H)-CH_2-)_n$

PMES

Experimental Section

Polymers. The sodium salt of PMES was obtained from Dr. D. Sheetz of the Dow Chemical Co. The intrinsic viscosity in 1 *M* $NaClO_4$ at 25° was 1.43 dl/g; C/S ratio 2.26 (calcd 2.25). The sodium salt of PVS was obtained from the monomer (purchased from the Columbia Organic Chemicals Co.) using the procedure of Breslow and Kutner.[13] The specific viscosity of 0.66 dl/g obtained for a 1% aqueous solution at 25° corresponds[13] to a weight-average molecular weight slightly above 40.000; C/S ratio 0.746 (calcd 0.749).

Inorganic Reagents. Bromopentaamminecobalt(III) perchlorate was prepared as described by Diehl, *et al.*[14] It has, in agreement with the literature, ϵ_{max} 1.76×10^4 at 253 mμ. Chloropentaamminecobalt(III) perchlorate, prepared according to Hynes, *et al.*,[15] had ϵ_{max} 1.88×10^4 at 229 mμ.

Aquopentaamminecobalt(III) perchlorate was prepared by heating a solution of 3 g of the bromo complex in 100 ml of 2 *M* aqueous perchloric acid at 100° for 2 hr. The aquo complex crystallized on cooling the solution to 5°. The precipitate was filtered, washed with cold water and ethanol, and dried. The procedure was repeated and complete conversion was confirmed by the disappearance of the 253-mμ absorption band. Analytical reagent grade mercuric perchlorate (City Chemical Co.) was used to adjust the mercury concentration.

Rate Measurements. Rate measurements were carried out in a 10-cm long water-jacketed stirred cylindrical cell with quartz windows. All reactions were carried out in solutions acidified with 0.001 *M* $HClO_4$. Unless otherwise specified, 5×10^{-6} *M* $Co(NH_3)_5X^{2+}$, 5×10^{-5} *M* Hg^{2+}, and a temperature of 5° were used. The reaction was started by addition of the cobalt complex to a solution containing all the other desired constituents. The progress of the reaction was followed with the use of a Beckman DU-2 spectrophotometer by the decrease in the absorbance at 230 mμ for the chloro complex and at 253 mμ for the bromo complex. "Infinity" readings were obtained after 10 half-lives; with very slow runs, the system was heated and readings were taken until constant optical densities were obtained. In most of the cases studied, the reaction followed the relation

$$\frac{1}{b-a}\ln\left[\frac{b-a}{b}\,\frac{D_0-D_\infty}{D-D_\infty}+\frac{a}{b}\right]=k_2t \qquad (3)$$

where b and a are the initial concentrations of Hg^{2+} and cobalt complex, respectively, and D_0, D, and D_∞ are the optical densities at the beginning of the reaction, at time t, and when the reaction is complete. Wherever the second-order plots were not linear, k_2 was obtained from the initial slope. The rate of the spontaneous aquation of $Co(NH_3)_5X^{2+}$ estimated from published data[16] was negligible compared to the rate of the Hg^{2+}-induced reaction. Experimental results are listed as $k_1 = bk_2$ in sec^{-1}.

Dialysis Equilibrium. PVS and PMES samples were exhaustively dialyzed before use in dialysis equilibrium determinations. Two Lucite blocks with a cylindrical depression of 10-ml volume (Rubber Chemical Co.) were used as dialysis cells. The two chambers were separated by a regenerated cellulose membrane extending 1 cm beyond the end of the liquid chambers, and the two blocks were tightly screwed together. Two inlets were provided through which the solutions could be introduced by a hypodermic syringe, and the inlets were closed by Nylon screw plugs. The cells were kept at 5° and shaken at least twice a day. A minimum of 3 days was allowed for equilibrium. The $Co(NH_3)_5Cl^{2+}$ concentration was determined by uv absorption at 229 mμ. The determination in the presence of polymer was carried out after addition of 1 *M* $HClO_4$ and with the use of a polymer solution as a blank. Material balance indicated negligible binding of the cobalt complex to the membrane. Mercuric ion was determined as the dithizone complex in the polymer-free solution by the method of Sandell.[17] The dissociation constant K_M of species M with the polyion was obtained from $K_M = C_M^0C_p/(C_M^i - C_M^0)$ where C_M^0 and C_M^i are the concentrations of M in the polymer-free and the polymer-containing solutions, respectively, and C_p is the polymer concentration in terms of the molarity of the monomeric residues. The dialysis equilibria were studied under conditions of a large excess of polymer over bound cation to obtain limiting values of K_M corresponding to negligible interactions between the bound cations.

Results and Discussion

Dependence of Catalytic Effect on Concentration of Polyelectrolyte and Simple Electrolyte. As expected, the catalytic effect produced by the two polysulfonic acids was enormous. However, the uv spectrum at the completion of the polyelectrolyte-catalyzed reaction was identical with that obtained in a solution prepared from corresponding concentrations of aquopentaamminecobalt(III) perchlorate and polymer, indicating that the polyelectrolyte did not alter the nature of the reaction. Typical data obtained with $Co(NH_3)_5Cl^{2+}$ listed in Table I show that, in the absence of simple salts, as little as 5×10^{-5} *N* polyanion produced an acceleration by a factor of 24,700 with PMES and by a factor of 176,000 with PVS. The higher effectiveness of the poly(vinylsulfonate) may be ascribed to the higher electrostatic potential on the polyanion carrying its charged groups closer to the chain backbone. With the closer spacing of the charged groups of the polyanion, cooperative interactions of two fixed anionic groups with a divalent cation may also contribute to the efficiency with which both Hg^{2+} and the cobalt complex are bound. It should also be noted that the catalytic effect of the polyanion decreases rapidly on addition of sodium perchlorate. This may be accounted for by the sharp reduction in the electrostatic potential of the polyanion as increasing counterion concentrations shield the field of its fixed charges. The kinetic effects

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Table I. Effect of 5×10^{-5} *N* PMES and PVS on the Hg^{2+}-Induced Aquation of $Co(NH_3)_5Cl^{2+}$ at Various Concentrations of $NaClO_4$

($NaClO_4$)	Acceleration factor, k_1/k_1^0 [a] PMES-catalyzed	 PVS-catalyzed
0	24,000	176,000
0.01	5,290	58,400
0.03	1,240	13,000
0.05		4,050
0.09		940

[a] The acceleration factor is based on $k_1^0 = 2.38 \times 10^{-7}$ measured in the absence of polymer with 5×10^{-5} *M* Hg^{2+} and in the presence of 0.01 *M* $NaClO_4$. The effect of varying salt concentration on k_1^0 was neglected. With $Co(NH_3)_5Br^{2+}$, the rate of the Hg^{2+}-induced reaction in the absence of polymer was found to increase by a factor of 2.26, when the $NaClO_4$ concentration was increased from 0.01 to 0.1. Thus, the acceleration factors would decrease somewhat faster with increasing ($NaClO_4$), if they were based on k_1^0 values determined at the same salt concentration.

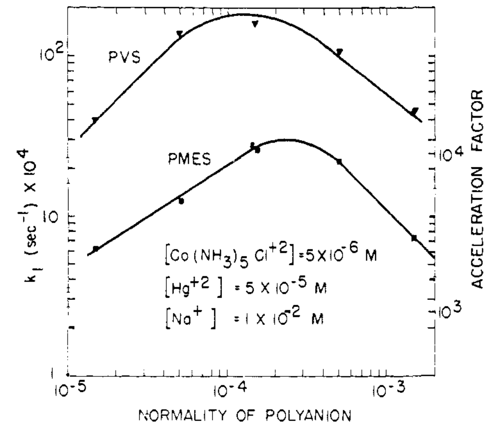

Figure 1. Polyanion catalysis of the reaction of $Co(NH_3)_5Cl^{2+}$ with Hg^{2+}. Dependence of catalytic effect on polyion concentration.

produced by polyelectrolytes are analogous to the well-known Brønsted kinetic salt effects in that reactions of like-charged reagents are accelerated. However, three points must be emphasized. (a) The effects produced by polyanions are incomparably larger than those produced by simple electrolytes. (b) Polyanions catalyze powerfully reactions of two counterions, while the interaction of two by-ions would be scarcely affected. (c) The two effects are not superimposable; while simple salts accelerate the reaction of $Co(NH_3)_5X^{2+}$ with Hg^{2+} in the absence of polyions,[11,12] they inhibit polyion catalysis.

The dependence of the catalytic effect on polymer concentration is illustrated in Figure 1. With both polymeric acids the rate increases with polyanion concentration only when this concentration is very low; at higher polyanion concentrations the rate passes through a maximum and then decreases sharply. This result may be interpreted as follows. As long as the sum of the concentrations of the two reagents is in large excess over the ionized sites of the polymer, only a small fraction of the reagent ions is held in the polyion domains, and the distribution of the counterions in any one of these domains may be considered to be independent of polyion concentration. The increase of the catalytic effect on polyion addition in the dilute concentration range reflects then the increasing fraction of bound $Co(NH_3)_5X^{2+}$. However, in more concentrated polymer solution the binding of both reagents is essentially complete, and further polymer addition distributes the reagents over more polymer domains, reducing the probability of their mutual collisions.

With very low polyanion concentrations, we observed pronounced deviations from second-order kinetics. This effect may be easily accounted for by preferential binding of the triply charged reaction product $Co(NH_3)_5H_2O^{3+}$ to the polyanion, so that the reagent ions are displaced from the polyion domain. Addition of $Co(NH_3)_5H_2O^{3+}$ at the outset of the reaction produced, in fact, kinetic effects in agreement with this interpretation.[18]

It was of interest to determine also the effect of the polyelectrolyte on the spontaneous aquation, since this reaction involves only one charged species. It was found that the rate constant for the aquation of $Co(NH_3)_5Br^{2+}$ at 45° decreased slightly from 7.6×10^{-5} to 7.2×10^{-5} and 7.1×10^{-5} on addition of 5×10^{-4} and 2.5×10^{-3} *N* PMES, respectively. On the other hand, addition of 5×10^{-4} and 2.5×10^{-3} *N* PVS raised k_1 to 2.05×10^{-4} and 2.55×10^{-4}. These results show that relatively small effects due to differences in the nature of the medium in the polyion domains, as compared to the bulk-average properties of the system, are superimposed on the large effects observed when two counterions react with each other.

We compared also the relative catalytic efficiency of the polymer in the Hg^{2+}-induced reaction of $Co(NH_3)_5Br^{2+}$ and $Co(NH_3)_5Cl^{2+}$. The data listed on Table II show that under the experimental conditions used (in which the polyion produced approximately a 1000-fold acceleration of the reaction rate) the k_{Br}/k_{Cl} ratio was about 20% lower in the presence of polymer than in its absence. This would seem to suggest that, even in the case of the two very similar cobalt complexes, specific interactions superimposed on electrostatic interactions produce significant effects.

Table II. Relative Susceptibility of the Hg^{2+}-Induced Reaction of $Co(NH_3)_5Br^{2+}$ and $Co(NH_3)_5Cl^{2+}$ to Polyanion Catalysis

Polyanion	($NaClO_4$)	k_{Br}	k_{Cl}	k_{Br}/k_{Cl}
None	0.01	540×10^{-7}	2.38×10^{-7}	227
5×10^{-5} *N* PVS	0.09	397×10^{-4}	2.23×10^{-4}	178
5×10^{-5} *N* PMES	0.03	498×10^{-4}	2.95×10^{-4}	169

Dependence of Reaction Rates on Hg^{2+} Concentration. Figure 2 illustrates the dependence of the first-order rate constant of the $Co(NH_3)_5Cl^{2+}$ reaction on the concentration of mercuric ion at two fixed PMES concentrations. It was found that the reaction rate first increases, but later decreases as the Hg^{2+} concentration is gradually increased. This behavior is interpreted as follows. At relatively low concentrations, an increase in the stoichiometric concentration of Hg^{2+} leads to a corresponding increase of its concentration

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(18) In a study similar to ours, N. Ise and F. Matusi (*J. Am. Chem. Soc.*, **90**, 4242 (1968)) employed polyelectrolyte solutions in the concentration range of 0.2–3 $\times 10^{-5}$ *N*, while the $Co(NH_3)_5Br^{2+}$ concentration was 8×10^{-5} *M*. Under these conditions, product inhibition of the reaction would be very severe. Since these authors did not appreciate this effect, they reported acceleration factors very much smaller than those found in our work and only partial conversion of $Co(NH_3)_5Br^{2+}$ to the aquo complex.

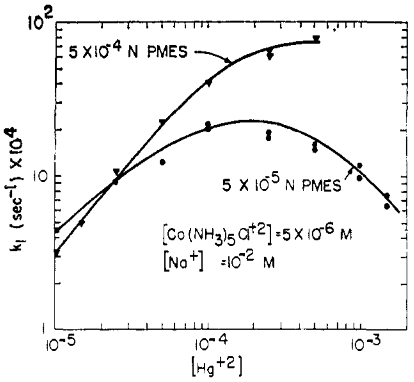

Figure 2. Dependence of the PMES-catalyzed aquation of $Co(NH_3)_5Cl^{2+}$ on Hg^{2+} concentration.

in the polyion domains, while the concentration of bound cobalt complex remains relatively unaffected. However, as the polyanion approaches saturation with the reagent ions, increasing concentrations of mercuric ion tend to displace the cobalt complex leading to reduced reactivity. As would be expected, the rate reaches a maximum at lower Hg^{2+} concentration as the polymer concentration is reduced.

Retardation of Polyanion-Catalyzed Reaction by Various Added Salts. The decrease in the efficiency of the polyelectrolyte to catalyze the reaction of $Co(NH_3)_5X^{2+}$ with Hg^{2+} when various salts are added to the system may be used as a measure of the interaction of the added counterion with the polyion. Studies of this type are exemplified in Table III, which shows that ions of the same charge may vary considerably in their inhibitory efficiency. With the alkali ions, the effectiveness of reducing the catalytic power of the polyion increases in the order $Li^+ < Na^+ < Cs^+$, *i.e.*, with decreasing radius of the solvated ion.[18a] PMES catalysis is reduced more sharply than catalysis by PVS, which signifies probably that the divalent reagent ions are more difficult to displace by monovalent ions if they are bound to the polyion with the higher density of anionic groups, favoring the formation of chelate complexes.[19] The data on the retardation of the $Co(NH_3)_5Cl^{2+}$ reaction by the addition of alkaline earth cations are more difficult to interpret. Their effectiveness increases, with both polyanions, in the order $Mg^{2+} < Sr^{2+} < Ba^{2+}$, but the retardation is much more dependent on the nature of the cation with PVS than with PMES. There is a striking reversal in the relative retarding efficiency of a given ion in reactions catalyzed by the two polyanions, Mg^{2+} being 40% more effective with PMES, while Ba^{2+} is 2.5 times more effective with PVS. We may note that in this case the inhibitor ions bear the same charge as the reagent ions, and their competition for binding sites on the polyion would be expected to reflect differences in ionic radius and ability to form chelate complexes.

Table III. Retardation by Inert Cations of the Hg^{2+}-Induced Aquation of $Co(NH_3)_5Cl^{2+}$ Catalyzed by 5×10^{-5} *N* Polyanions

	PMES catalysis		PVS catalysis	
Retarding ion	10^4k_1	Retardation factor	10^4k_1	Retardation factor
None	58.9		412	
0.01 *M* Li^+	20.1	2.9	204	2.0
0.01 *M* Na^+	12.6	4.7	139	3.0
0.01 *M* Cs^+	10.4	5.7	114	3.6
10^{-4} *M* Mg^{2+}	20.1	2.8	209	2.0
10^{-4} *M* Sr^{2+}	17.0	3.3	104	4.0
10^{-4} *M* Ba^{2+}	15.4	3.6	46	9.0

Model for the Interpretation of Polyion Catalysis. We have attempted to interpret the kinetic data in terms of a simplified model in which the effective local concentrations of the reagent ions are characterized by two discrete values inside and outside the polymer domains, respectively. Since the catalytic effect of the polyions is very large, we may assume that only the cobalt complex bound to the polymer domains makes a significant contribution to the observed first-order rate constant k_1. Denoting by k_2^0 the second-order constant observed in 0.01 *M* $NaClO_4$ solution in the absence of polymer, by C_{eff} the effective Hg^{2+} concentration in the polymer domains,[20] and by $(Co)_b$ and (Co) the concentrations of bound and stoichiometric cobalt complex, respectively

$$k_1 = k_2^0C_{eff}(Co)_b/(Co) \qquad (4)$$

The local concentration C_{eff} may be represented by $C_{eff}^{max}\alpha_{Hg}$, where C_{eff}^{max} corresponds to occupancy of all polymer binding sites by Hg^{2+} and $\alpha_{Hg} = 2(Hg)_b/C_p$ is the fraction of binding sites (corresponding to two anionic groups) associated with mercuric ions. The polymer concentration C_p is here expressed as a molarity of monomeric residues. Relation 4 becomes then

$$k_1 = 2k_2^0C_{eff}^{max}[(Hg)_b/C_p][(Co)_b/(Co)] \qquad (5)$$

We shall be specifically interested in two limiting cases. (1) If virtually all reagent ions are bound to the polymer, $(Co)_b = (Co)$ and $(Hg)_b = (Hg)$, so that

$$k_1 = 2k_2^0C_{eff}^{max}(Hg)/C_p \quad \text{(all reagent ions bound)} \qquad (6)$$

which allows us to estimate C_{eff}^{max} from k_1 values obtained at high polymer concentration. (2) When $(Co)_b \ll (Hg)$ and only a small fraction of the polymer binding sites are occupied by reagent ions, the dissociations of the polyion–reagent ion complexes are given by $(Hg)C_p/(Hg)_b = K_{Hg}$ and $(Co)C_p/(Co)_b = K_{Co}$ so that

$$k_1 = 2k_2^0(Hg)C_{eff}^{max}C_p/(\bar{K})^2$$

$$(Hg)_b \ll (Hg); \ (Co)_b \ll (Co);$$

$$2[(Hg)_b + (Co)_b] \ll C_p \qquad (7)$$

(18a) Note Added in Proof. An analogous observation was made by L. R. Romsted, R. B. Dunlap, and E. H. Cordes (*J. Phys. Chem.*, 71, 4581 (1967)), who studied the acid-catalyzed hydrolysis of methyl orthobenzoate in solutions of anionic micelles containing various alkali metal salts.

(19) Analogous observations have been frequently noted in ion-exchange equilibrium studies, where the preference for divalent over univalent ions tends to increase with decreasing swelling of the cross-linked ion exchanger particle. In the displacement of a univalent cation M^+ by divalent cations M^{2+}, the quantity $(m_{M^{2+}}/m_{M^+}{}^2)(a_{M^+}{}^2/a_{M^{2+}})$ where *m*'s are molarities in the resin phase and *a*'s are activities in the water solution, remains independent of the internal molality M_R of the resin phase (T. R. E. Kressman and J. A. Kitchener, *J. Chem. Soc.*, 1201 (1949); H. P. Gregor, O. R. Abolafia, and M. H. Gottlieb, *J. Phys. Chem.*, 58, 984 (1954)). In terms of the mole fractions $X_{M^{2+}}$ and X_{M^+} in the resin phase, we find then $X_{M^{2+}}/M_RX_{M^+}{}^2$ constant for any given values of a_{M^+} and $a_{M^{2+}}$, *i.e.*, $X_{M^{2+}}$ increases with M_R.

(20) The significance of such "effective local concentrations" is discussed in detail in H. Morawetz, "Macromolecules in Solution," Interscience Publishers, New York, N. Y., 1965, pp 432–434.

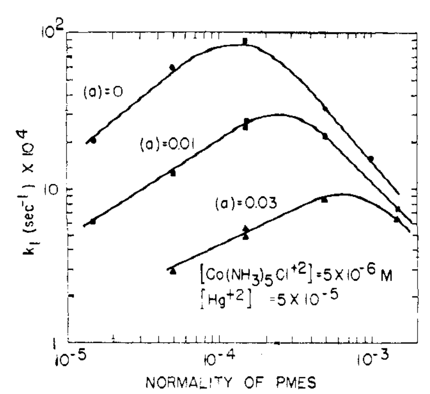

Figure 3. Effect of added $NaClO_4$ (a) on the PMES-catalyzed reaction of $Co(NH_3)_5Cl^{2+}$ with Hg^{2+}.

where $(\bar{K})^2 = K_{Hg}K_{Co}$. Thus, with the knowledge of C_{eff}^{max} from data obtained at high polymer concentration, we should be able to utilize data obtained at low polymer concentration to estimate the geometric mean of the dissociation constants characterizing the two reagent ions.

Qualitatively, the appearance of plots of the rate constant on polyion concentration (Figure 1) is in satisfactory agreement with the characteristics outlined above. At low polymer concentration, the rate increases almost in proportion to the polymer concentration, while at high concentrations of the polyion the rate is inversely proportional to C_p. Since the addition of inert salts should reduce the affinity of the reagent ions for the polyion (*i.e.*, increase K_{Hg} and K_{Co}), the catalytic power of the polyion will be reduced by inert salt addition under conditions where only a small fraction of the binding sites are associated with reagent ions. On the other hand, under conditions where all reagent ions are bound, k_1, for any polymer concentration, depends only on C_{eff}^{max}, which is determined by the geometry of the polyion. We should then expect that in the limit of high polymer concentrations k_1 will tend to be independent of the concentration of added salts. Figure 3 shows that this behavior is, in fact, observed.

Some values of C_{eff}^{max} and $(\bar{K})^2$ calculated from the kinetic data are listed in Table IV and are compared to K_{Co} and K_{Hg} obtained by dialysis equilibrium. The extremely large C_{eff}^{max} values should be specifically noted; they compare with C_{eff}^{max} of the order of 1 *M* estimated from chelate formation equilibria involving polymers in which each monomer residue carries a ligand group.[20,21] This difference in C_{eff}^{max} is not surprising, since ligand groups spaced rather closely to one another along the chain backbone cannot interact with one another in chelate formation because of prohibitive ring strain. By contrast, reagent ions bound to the polyanion cannot be considered as rigidly localized and the reaction involving ions attached to closely spaced binding sites would be expected to make a large contribution to C_{eff}^{max}.

Table IV. Analysis of Kinetic Data and Comparison with Dialysis Equilibrium

				$10^8(\bar{K})^2$		
Polymer	($NaClO_4$)	10^5K_{Co}	10^5K_{Hg}	Dial.	Kin.	C_{eff}^{max}
PMES	0.01	5.0	29	1.5	2.7	2.3
PMES	0.03	31	97	30	17	2.0
PVS	0.01	0.95	19	0.18	2.6	14.1
PVS	0.03	8.4	67	5.6	8.1	11.7

In comparing the behavior of PVS and PMES in the presence of 0.01 *M* $NaClO_4$, it is seen that the higher catalytic power of PVS is due to a sixfold higher value of C_{eff}^{max} while $\bar{K}$, as estimated from kinetic data, remains essentially unchanged. In 0.03 *M* $NaClO_4$, tighter binding of the reagent ions to the polyion also contributes to the higher catalytic efficiency of PVS. The $(\bar{K})^2$ values obtained from kinetic data lie, in three of the four systems investigated, within a factor of 2 of the values obtained by dialysis equilibration. This suggests that the simple model outlined above is a reasonable approximation to the physical situation. On the other hand, it should be noted that the dialysis data show large differences in the binding characteristics of the two ions. For instance, in the presence of 0.01 *M* $NaClO_4$, PMES binds the cobalt complex six times more tightly than Hg^{2+} and in the presence of 0.03 *M* $NaClO_4$, comparable Hg^{2+} binding to PVS and PMES is observed, while the cobalt complex is held four times more tightly by PVS. We must conclude that the assumption on which eq 1 is based, *i.e.*, that only long-range Coulombic forces need be considered in interpreting the effect of polyions on ionic reactions, is quite inadequate.[22]

The retarding effect of the alkaline earth ions may be interpreted in terms of a competition of inhibitory ions I and reagent ions R for the polyanion binding sites. Neglecting the difference of the affinity of the two reagent ions for the polyion as discussed above, the displacement of reagent ions by inhibitory ions is characterized by the equilibrium constant

$$K_i = \frac{(R_f)(I_b)}{(R_b)(I_f)} \tag{8}$$

Under the experimental conditions of the experiments listed in Table II, *i.e.*, a large excess of divalent counterions over polyion binding sites, all these sites may be considered occupied by either R or I. Defining f_R as the fraction of sites occupied by reagent ions, we may rewrite (8) as

$$K_i = \frac{1 - f_R}{f_R}\,\frac{2(R) - C_pf_R}{2(I) - C_p(1 - f_R)} \tag{9}$$

But $f_R = 2[(Co) + (Hg)]\alpha_b/C_p$, where α_b, the fraction of reagent ions bound, may be obtained from (5) as the geometric mean of $(Hg)_b/(Hg)$ and $(Co)_b/(Co)$ to yield

$$f_R = [(Co) + (Hg)]\sqrt{2k_1/k_2^0(Hg)C_pC_{eff}^{max}} \tag{10}$$

Under the conditions specified in Table II, and using C_{eff}^{max} values of 2.3 and 14 *M* for PMES and PVS, respectively (*cf.* Table III), this treatment leads to K_i values of 0.15, 0.27, and 0.30 for Mg^{2+}, Sr^{2+}, and Ba^{2+}

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(21) H. Morawetz and E. Sammak, *J. Phys. Chem.*, **61**, 1357 (1957).

(22) It should be noted that a complication may arise in the interpretation of the data of this study as a consequence of the partial hydrolysis of the Hg^{2+} ion. According to G. Mattock (*Acta Chem. Scand.*, **8**, 777 (1954)), this hydrolysis is characterized by $pK = 3.7$, so that at pH 3 about one-sixth of the stoichiometric Hg^{2+} is present as $HgOH^+$.

in the presence of PMES, while the corresponding values in the presence of PVS are 0.08, 0.30, and 0.66, respectively. It appears then that the reagent ions are in all cases more strongly bound than the alkaline earth ions.

Temperature Dependence of Polyion-Catalyzed Reaction. The analysis outlined in the previous section shows that, under conditions where all reagent ions are bound to the polymer domain, the catalytic effect depends on the high values of $C_{\mathrm{eff}}^{\max}$, which would be expected to be practically independent of temperature. We should then expect that at high polyion concentrations the activation energy is very similar to that characterizing the reaction in the absence of the polyion. On the other hand, at low polyion concentration the fraction of reagent ions bound would be expected to be temperature dependent and the activation energy may be significantly affected by the polyion. Specifically, using the formulation of eq 7

$$\Delta E^*_{\mathrm{cat}} = \Delta E^*_0 - 2\Delta H_{\mathrm{d}} \qquad (11)$$

where $\Delta E^*_{\mathrm{cat}}$ and ΔE^*_0 are the activation energies in the presence and the absence of catalytic polyion and ΔH_{d} is the enthalpy of dissociation of the polyion–reagent ion complex. It was expected that this dissociation would be endothermic, so that $\Delta E^*_{\mathrm{cat}} < \Delta E^*_0$ at low polyion concentrations. Table V is in agreement with these expectations in that the ΔE^* tend to increase with polymer concentrations. With PMES catalysis, the ΔE^* values come, at $C_{\mathrm{p}} = 1.5 \times 10^{-3}$ N, to within 1.4 kcal/mole of the value characterizing the reaction in the absence of polymer. With PVS, on the other hand, the activation energy remains low even at very high polymer concentrations, suggesting perhaps that the change in the nature of the reaction medium, when the reagent ions enter the polyion domain, produces significant changes in the activation process.

Table V. Temperature Dependence of the Reaction of $Co(NH_3)_5Cl^{2+}$ with Hg^{2+} in the Presence and Absence of Polymer

Polymer	Temp, °C	10^5C_{p}	10^5 (Hg^{2+})	$(NaClO_4)$	10^4k_1	ΔE^*, kcal/mole
None	35	0	50	0.01	0.78	
	48	0	50	0.01	3.06	
	55	0	50	0.01	5.85	
	62	0	50	0.01	10.3	19.6
PMES	5	5	50	0.03	5.95	
	25	5	50	0.03	25.6	12.0
	5	5	5	0.01	12.6	
	25	5	5	0.01	62.5	13.2
	5	50	5	0.01	22.2	
	25	50	5	0.01	149	16.0
	5	150	5	0.01	7.3	
	25	150	5	0.01	65.7	18.1
PVS	5	5	5	0.03	30.9	
	25	5	5	0.03	155	13.3
	5	300	5	0.03	18.6	
	25	300	5	0.03	129	15.7

Kinetics of Structural Interconversions. I. Cobalt(II) Chloride–Pyridine–Nitromethane

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Abstract: A kinetic examination of the $^{\mathrm{oct}}Co(py)_4Cl_2$ = $^{\mathrm{tet}}Co(py)_2Cl_2$ + 2py equilibrium in nitromethane and pyridine (py) has been carried out. The experimental data appear to fit the mechanism, $Co(py)_4Cl_4 \rightleftharpoons Co(py)_3Cl_2 + py$ (3) and $Co(py)_3Cl_2 \rightleftharpoons Co(py)_2Cl_2 + py$ (k_4, k_{-4}) (4), where reaction 3 equilibrates rapidly compared to reaction 4. The rate constant k_{-4} in nitromethane at $\mu = 0.1$ (Et_4NClO_4) and 25.0° is $(7.2 \pm 0.5) \times 10^4$ M^{-1} sec^{-1}, and $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are 5.4 ± 0.8 kcal/mole and −18 ± 3 eu, respectively. The corresponding rate constant in pyridine is $(3.1 \pm 0.3) \times 10^3$ M^{-1} sec^{-1}, and the activation parameters are 2.6 ± 1.0 kcal/mole and −34 ± 4 eu. Factors affecting the kinetics in the two solvents are discussed.

Equilibria between structural isomers of inorganic complexes in nonaqueous solvents are well known, and the subject has been recently reviewed by Katzin.[1] Configurational equilibria between octahedral and tetrahedral or square-planar cobalt(II) complexes have been reported.[1,2] Specifically, thermodynamic and spectral data have been obtained for a number of octahedral (oct)–tetrahedral (tet) equilibria of the type

$$^{\mathrm{oct}}CoL_4X_2 = {}^{\mathrm{tet}}CoL_2X_2 + 2L \qquad (1)$$

where L = pyridine or 2-methylpyridine and X^- = Cl^-, Br^-, I^-, OCN^-, SCN^-, and $SeCN^-$. In the case where L = pyridine (py) and X^- = Cl^-, data have been obtained in a number of organic solvents.[3-5] However, to our knowledge no kinetic studies have been made on these systems. The large enthalpy and spectral changes accompanying the octahedral–tetrahedral interconversion make these systems feasible for temperature-jump relaxation studies. In the present work we have investigated the kinetics of the octahedral–tetrahedral interconversion

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(2) G. W. Everett, Jr., and R. H. Holm, *J. Am. Chem. Soc.*, **87**, 5266 (1965), and references therein.

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