Effect of Polyelectrolytes upon the Kinetics of Ionic Reactions

Part 6.—Some General Aspects

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The rate constant changes of ionic reactions due to the electrostatic polyelectrolyte effect can be described in some detail. For second-order reactions between ions of equal charge sign, it is shown that the inhomogeneous distribution of reactive ions is equivalent to a primary salt effect; the primary salt effect cannot explain the results at high macroion concentration. An expression is derived for this case taking into account the probability of site occupancy by both reactive partners. For first-order reactions, the overall change in rate constant with polymer concentration may be explained in terms of the theories of polyelectrolyte solutions, even when the electrostatic effect may be coupled with more specific interactions.

The study of the effect of macroions on the kinetics of reactions is an active area in polyelectrolyte physical chemistry.[1, 2] When the substrate is an ion, the inhomogeneity introduced by the macroions on the ionic distribution may couple with more specific substrate–macroion interactions, *e.g.* dipolar attraction, hydrogen bonding, hydrophobic interactions, *etc.*, to produce important modifications in the rate of reaction of the ionic substrate. Furthermore, when the substrate ions are drawn to the vicinity of an oppositely charged macromolecule by the large polyionic electric field, the reaction between the substrate and any reactive group forming part of the macroion, will be strongly favoured. Interactions in polyelectrolyte solutions may produce remarkable effects on the kinetics of ionic reactions.[2] Morawetz and Vogel [3] reported that the rate of aquation of $Co(NH_3)_5Cl^{2+}$ induced by Hg^{2+} ions is enhanced 176 000 times when poly-(vinylsulphonic acid) is present in a concentration of 5×10^{-5} equivalent dm^{-3}.

In the case of macromolecules having no significant electrostatic interactions with the substrate, synergetic effects can also be observed. Klotz *et al.*[4] found that the hydrolysis of phenolic esters could be increased by factors similar to those found for enzymes, when the solution contained poly(ethyleneimine) (PEI) modified by the inclusion of reactive groups and non-polar chains into the macroion. In this case hydrophobic interactions between the substrate and the non-polar groups in the macromolecule draw the substrate close to the polyion which subsequently is attacked by the specifically reactive groups of substituted PEI producing a large overall kinetic effect.

In spite of the variety of detailed mechanisms responsible for the observed modifications in the rates of reaction of ionic substrates in polyionic solutions, it is possible to visualize some general trends which may be accounted for by electrostatic interactions. Even when the direct electrostatic contribution to the observed changes in reaction rates is quantitatively small, in many instances it is the causative factor of the overall rate modifications,[5-8] *i.e.* when the (electrostatic) polyelectrolyte effect is suppressed

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by salt addition or by neutralization of the polyionic charge, in the case of weak polyelectrolytes, no modification in the rate constants is observed.

Mita *et al.*[9] have recently analysed the influence of the polyelectrolyte effect upon various types of reactions. They successfully interpreted the results in terms of a type of primary salt effect using polyelectrolyte theories; they used this interpretation to oppose the view that the effects arise from an increased concentration of reactant ions in the vicinity of the polyionic chain.

In this work the features of the electrostatic interactions for first and second order reactions are discussed and the general behaviour to be expected is described, thus allowing rationalization of the observations in different systems. It is demonstrated that the primary salt effect approach is identical to that considering local distribution of ions.

SECOND ORDER REACTIONS

In general the rates of reactions involving oppositely charged mobile ions are inhibited by macroions,[10, 11] while the rate of reaction between two ions of equal charge is increased by polyelectrolytes having charge opposite to that of the reactant ions.[3, 12-14]

It has been proposed [10] that the experimental results can be explained in terms of the modified local concentration of reactant ions due to the large electrostatic potential near the macroionic chain. If k_2 and k_2° denote the second-order rate constants in the presence and absence of polyelectrolyte respectively, the argument above leads to the following expression for the rate of reaction v_2,

$$v_2 = k_2\langle m_A\rangle \cdot \langle m_B\rangle = k_2^\circ\langle m_A \cdot m_B\rangle. \tag{1}$$

The angular brackets indicate averages taken over the polyionic domains into which the solution volume is divided.[2] Hence $\langle m_i\rangle = m_i^\circ$, the stoichiometric concentration of ion i. The local concentration of species i is related to the reduced electrostatic potential, $\Delta\Phi$, by the Boltzmann relation

$$m_i = m_i^* \cdot \exp(-z_i\Delta\Phi) \tag{2}$$

$\Delta\Phi$ being the difference in reduced electrostatic potential referred to the domain boundary, hence at the boundary $\Delta\Phi = 0$ and $m_i = m_i^*$. Eqn (2) may be replaced in eqn (1), and the rate constant ratio becomes,

$$\frac{k_2}{k_2^\circ} = \frac{\langle \exp(-z_A + z_B)\Delta\Phi\rangle}{\langle \exp(-z_A\Delta\Phi)\rangle \cdot \langle \exp(-z_B\Delta\Phi)\rangle}. \tag{3}$$

If z_A and z_B have the same sign, k_2/k_2° will be larger than unity. If they have opposite signs the rate constant ratio will be smaller than unity. Eqn (3) is then capable of explaining qualitatively the experimental observations. When both reactant partners are concentrated in the same element of volume near the polyion, the rate of collision increases and the reaction will proceed at a higher rate than in the absence of polyion. In contrast, when the reactants have opposite charge they will be separated by the macroion which attracts ions of opposite charge to the chain and repels the reactants having the same charge sign.

Using new experimental evidence, Morawetz *et al.*[3, 12] suggested that eqn (3) was not adequate to represent the results. The medium near the chain may be different from that in the bulk of the solution and consequently it would not be adequate to identify k_2° with the rate constant in polyelectrolyte solution by eqn (3). Furthermore the electrostatic interaction may not be the only contributing factor in fixing the local

distribution of ions. An outstanding example of this is the reaction between the cationic species of crystal violet with OH^- ions;[15] when polyanions are added the reaction is inhibited but when polycations are present the rate of reaction of both ions is increased. This is attributed to strong non-electrostatic interactions between the crystal violet cation and the positive macroion.

In principle, $\Delta\Phi$ in eqn (2) may be replaced by $\Delta\bar{\mu}_i/kT$, where $\Delta\bar{\mu}_i$ denotes the change in electrochemical potential of species i when it approaches the polyion. In this way non-electrostatic interactions can be included as well.

In spite of the fact that specific interactions are responsible for the observed differences in the accelerating power of polyelectrolytes for different reactive ions of equal charge, for many ionic reactions in polyelectrolyte solutions which have no added salt, $\Delta\bar{\mu}_i$, will be dominated by electrostatic interactions. These have been shown [5, 7-9] to be in many cases the causative factor in the observed changes in reaction rate in polyelectrolyte solutions. A simple verification of this fact being the almost complete suppression of rate enhancement when sufficient salt is added to the polyelectrolyte solution.

An apparently different way of explaining the polyelectrolyte effect on reaction rates is currently employed by Ise and coworkers [9] using an approach analogous to that of Brönsted for ionic reactions in electrolyte solutions (primary-salt effect). They assume that,

$$\frac{k_2}{k_2^\circ} = \frac{\gamma_A\gamma_B}{\gamma_{AB}^{\ddagger}} \tag{4}$$

where γ_i is the activity coefficient of reactant i in the polyelectrolyte solution and the superscript ‡ denotes the activated complex. Ise and Okubo [11] employed eqn (4) to explain quantitatively the observed inhibition in urea synthesis by polyelectrolytes. The activity coefficients of reactants in eqn (4) are experimental quantities and $\gamma_{AB}^{\ddagger}$ was assumed to be unity for the cyanate–ammonium reaction because the activated complex is in this case electrically neutral. They were able to account for the experimental kinetic results and also for the change in inhibition produced when polyanion salts with different monovalent counterions were employed. The activity coefficients may also be expressed in terms of polyelectrolyte theory, thus obtaining expressions for k_2/k_2° which enable the theoretical prediction of the rate constant ratio. Mita *et al.*[9] have used these expressions to explain experimental results.

Eqn (3) and (4) have been considered to correspond to different models of reactant ion–polyelectrolyte interactions, it may be shown however that they are completely equivalent. This stems from the fact that the activity coefficients of mobile ions in polyelectrolyte solutions are related to the electrostatic potential in the polyionic domain.

Marcus [16] derived a simplified expression for γ_i from the ratio of the concentration in the domain boundary, where the electrostatic force vanishes, to the average concentration in the solution. Thus,

$$\gamma_i = m_i^*/m_i^\circ \tag{5}$$

and taking domain averages in eqn (2),

$$m_i^\circ = m_i^*\langle\exp(-z_i\Delta\Phi)\rangle. \tag{6}$$

Hence,

$$\gamma_i = 1/\langle\exp(-z_i\Delta\Phi)\rangle. \tag{7}$$

If eqn (7) is now replaced in eqn (2), we have

$$\frac{\gamma_A \cdot \gamma_B}{\gamma_{AB}^{\ddagger}} = \frac{\langle \exp\left[-(z_A + z_B)\Delta\Phi\right]\rangle}{\langle \exp\left(-z_A\Delta\Phi\right)\rangle \cdot \langle \exp\left(-z_B\Delta\Phi\right)\rangle} \tag{8}$$

which demonstrates the equivalence of eqn (3) and (4).

If the γ_i terms in eqn (4) are expressed in terms of electrostatic interactions as described by the theory of polyelectrolyte solutions, eqn (8) is strictly valid. On the other hand, if the experimental activity coefficient data are employed to obtain the γ_i terms, existing non-electrostatic effects will contribute to γ_i and the factor $z_i\Delta\Phi$ should be replaced by $\Delta\bar{\mu}_i$ to maintain the validity of eqn (8).

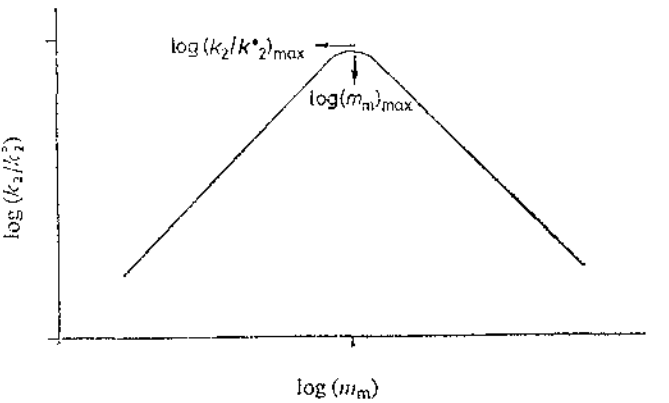

FIG. 1.—Effect of polyelectrolyte concentration on the rate constant of reactions involving two reactive counterions.

The effect of the presence of polyelectrolytes on the value of the rate constant ratio for reactions between two mobile counterions increases with the polyelectrolyte concentration, m_m (expressed in monomoles dm^{-3}) whenever m_m is small compared with the concentrations of reactive counterions. This is illustrated in fig. 1. However k_2/k_2° is observed to pass through a maximum at $m_m = (m_m)_{max}$, and then to decrease with m_m because when there are too many macroions the reacting counterions will be concentrated in different polyionic domains.

Mita *et al.*[9] have derived expressions based on Manning's theory [17] for the quotient $\gamma_A\cdot\gamma_B/\gamma_{AB}^{\ddagger}$. They dealt with the situation corresponding to m_m smaller than m_A or m_B, *i.e.* to the ascending limb of the curve in fig. 1. For $z_A = z_B$ their expression leads to negative values of k_2/k_2° when $m_m \geqslant (2m_m)_{max}$ and the maximum of the ratio of rate constants is an artifact of their assumption that reaction only proceeds between condensed ions of one species and uncondensed ions of the other. Eqn (4) is basically unable to explain the descending limb of the experimental curve of k_2/k_2° against m_m; this will be discussed below.

According to eqn (3), k_2/k_2° would be expected to increase with m_m as the fraction of condensed [17] reactant counterions increases. When the polyelectrolyte becomes saturated with counterions, *i.e.* $m_m = (m_m)_{max}$, a further addition of macroions would not be expected to affect the value of k_2/k_2° because it does not essentially alter the counterion distribution. Consequently the situation as described by eqn (3), as was the case for eqn (4), corresponds to an increasing value of k_2/k_2° at low m_m, with a plateau then being attained at $m_m > (m_m)_{max}$, as observed for first order reactions (see next section).

In order that eqn (3) may account for the experimental situation depicted in fig. 1, it is assumed that $(k_2)_{max}$ occurs when the degree of condensation of both reactants is a maximum on the same polyionic site (these polyionic sites will consist in general of more than one monomeric unit). Hence in eqn (1) the averages indicated should not be considered domain averages over all the solution, but rather the excess concentration of reactant averaged over those domains corresponding to sites occupied by both reactant ions.

When an excess of macroion relative to the concentration of reactive partners A and B exists, the reaction of these in the vicinity of the chain will be constant, however there is a probability (increasing with m_m) that some counterions A condense onto different polyionic sites from counterions B, producing a decrease in the rate of reaction compared with k_2/k_2° at $(m_m)_{max}$. In other words, if the polyelectrolyte concentration is increased above $(m_m)_{max}$, the fraction of sites containing only one reactive partner, either A or B, will increase. Under these conditions k_2/k_2° will decrease as m_m increases.

According to this picture, the polyelectrolyte effect of rate enhancement is fundamentally due to those reactant counterions A and B condensed onto the same polyionic site. This implies that the averaged concentrations appearing in eqn (1) should be taken on occupied polyionic sites; that is, that they will equal the domain average over all the solution multiplied by the probability that a site be occupied by both reactant ions. Let us assume that the polyelectrolyte is first saturated by condensed B counterions and as m_m increases further, reactant A reaches saturation. This situation arises whenever $|z_A| < |z_B|$ and $m_A > m_B$, or when $|z_A| > |z_B|$ and $m_A \gg m_B$.† Under these circumstances the number of polyionic sites per unit volume will be given by,

$$m_L = \frac{m_m}{K} \tag{9}$$

where K is the number of monomers per site. If m_m increases, a situation is attained where all B and a fraction of A are condensed onto macroionic sites. When m_m increases more, a point is reached where all A is condensed (if $|z_A| \geqslant |z_{counterion}|$, if not a constant maximum fraction of A).[17] At this point (k_2/k_2°) is maximum, and this is taken as the reference state to describe the polyelectrolyte effect on the rate of reaction. A further addition of polyelectrolyte will increase the fraction of sites having condensed B and no condensed A, thus leading to no enhancement of the rate of reaction. If the probability that A occupies a site already occupied by B is denoted by P_A^B, eqn (3) may be transformed into

$$\frac{k_2}{k_2^\circ} = \frac{\langle \exp\left[-(z_A+z_B)\Delta\Phi\right]\rangle \cdot P_A^B}{\langle \exp\left(-z_A\Delta\Phi\right)\rangle \cdot \langle \exp\left(-z_B\Delta\Phi\right)\rangle} \tag{10}$$

P_A^B will be given by,

$$P_A^B = 1, \qquad \text{for } m_A > m_L$$
$$P_A^B = m_A^\circ \cdot K/m_m, \qquad \text{for } m_A < m_L$$

eqn (10) becomes for $m_A < m_L$,

$$\log(k_2/k_2^\circ) = \log(k_2/k_2^\circ)_{max} - \log(m_m/m_A^\circ \cdot K)$$
$$= \log(k_2/k_2^\circ)_{max} - \log(R/K) \tag{11}$$

† Many experimental results were obtained for $|z_A| > |z_B|$ and $m_A \gg m_B$. In this case the relevant reactant concentration variable is m_A, because as soon as all A becomes condensed a further addition of polyelectrolyte (considered in the log m_m scale) will suffice to produce maximum condensation of B counterions.

where $R = m_m/m_s$ is the concentration ratio between polyelectrolyte (expressed as monomer units) and added mobile ions (either inert salt or reactant ions), in the present case $m_S = m_A$; $(k_2/k_2^0)_{max}$ is the value corresponding to $m_A = m_L$. Eqn (11) reflects the fact that for high polymer concentrations, $\log (k_2/k_2^0)$ decreases linearly with $\log m_m$ and the slope is (-1), a fact previously noted by Morawetz and Vogel.[3] According to eqn (1), at $(m_m)_{max}$, $R_{max} = K$ and the size of the site may be calculated from the experimental data. Eqn (11) explains in a simple fashion that different values of $(m_m)_{max}$ will be found for a given macroion whenever different initial concentrations of reactants are employed, because the maximum really depends on the ratio m_m/m_A and consequently there is no need to find other causes [13] to explain the change in $(m_m)_{max}$.

TABLE 1.—EFFECT OF POLYELECTROLYTES ON THE RATE OF REACTIONS INVOLVING TWO REACTIVE COUNTERIONS

poly-electrolyte	ref.	reactant A	reactant B	m_A	$m_{1/2}$	$(m_m)_{max}$	K	descending slope
PVS						1.9×10^{-3}	9.5	−1.0
PP	14	$Co(Phen)_3^{3+}$	$Co(Phen)_3^{2+}$	2×10^{-4}	2×10^{-5}	1.9×10^{-3}	9.5	−0.8
PSS						$<10^{-5}$	—	−1.2
PVS	3	Hg^{2+}	$Co(NH_3)_5Cl^{2+}$	5×10^{-5}	5×10^{-6}	1.2×10^{-4}	2.4	−0.8
PMES						2.1×10^{-4}	4.2	−1.0
			$Co(NH_3)_5Cl^{2+}$			1.0×10^{-4}	2.0	−1.0
PVS	12	Fe^{2+}	*cis*-$Co(NH_3)_4(N_3)_2^+$	5×10^{-5}	5×10^{-6}	3.8×10^{-4}	7.6	−0.9$_3$
			trans-$Co(NH_3)_4(N_3)_2^+$			5.9×10^{-4}	12	−1.3
		cis-$Co(en)_2Cl_2^+$		9×10^{-4}	$<10^{-4}$	3.2×10^{-2}	35.5	—
		trans-$Co(en)_2Cl_2^+$		4×10^{-4}		2.3×10^{-2}	57	—
PMES	13	*cis*-$Co(en)_2PyCl^{2+}$	$Ru(NH_3)_6^{2+}$			5.3×10^{-3}	10.6	−0.6
		cis-$Co(en)_2NH_3^{2+}$		5×10^{-4}	$<6\times10^{-5}$	5.3×10^{-3}	10.6	−0.7
		cis-$Co(en)_2PyCl^{2+}$	V[c]			5.5×10^{-3}	11	−0.6
			$Co(NH_3)_5X^{z+}$					
			X = 2-aminopyridine, 3-carboxylate ($z = 3$)		2×10^{-5}	$<10^{-3}$	—	−0.6
			X = *p*-dimethylamino-benzoate ($z = 3$)			$<10^{-3}$	—	−0.7
PVS	18	$Cr(II)^{2+}$	X = *o*-methylbenzoate ($z = 2$)	$>10^{-4}$		1.3×10^{-3}	—	−0.9
			X = *p*-sulphobenzoate ($z = 1$)		4×10^{-5}	2.6×10^{-3}	—	−0.9
			X = *o*-sulphobenzoate ($z = 1$)			4.8×10^{-3}	—	−0.8

Since eqn (4) is a relation between thermodynamic quantities it is not possible to introduce into it the probability of simultaneous site occupancy. According to polyelectrolyte theory,[16, 17] the activity coefficient of mobile ions depends very little on m_m, consequently eqn (11) can only predict a monotonous increase in k_2/k_2^0 with polyelectrolyte concentration until a maximum value is attained, thereon remaining constant.

Table 1 summarizes the available data on bimolecular reactions in polyelectrolyte solutions. These data had to be interpolated from the reported graphs and this procedure will thus introduce some uncertainty into the analysis. On the other hand, very few studies have been undertaken to define the details of the $\log (k_2/k_2)$ against $\log (m_m)$ curves.

The results in table 1 show that the predictions of eqn (11) are largely confirmed. Except for the results in ref. (13), the descending limbs of the curves have slopes close to (-1.0) as predicted. With regard to the calculated number of monomers per site, K, it is between 2 and 12 for $|z_A| > 1$; for $|z_A| = 1$, the values of K are 35.5 and 57.

It must be remembered that all the polyelectrolytes in table 1 have the same value for the distance between two adjacent ionogenic groups, 0.255 nm, which is the distance corresponding to monomers in poly-(vinylic) and poly-(phosphate) macroions. The observed range of K values suggests that specific interactions between counterions of equal charge play an important role in determining the value of $(m_m)_{max}$, *i.e.* the counterion–polyion interaction.

FIRST ORDER PROCESSES

For ionic substrates which undergo reaction by a unimolecular mechanism, the electrostatic polyelectrolyte effect would not be expected to influence the rate of reaction. The unimolecular hydrolysis of doubly charged phenyl phosphates however, is accelerated by polycations,[5, 8, 19] the rate constant ratio k/k° becoming >20. We shall describe some general features which characterize phenomenologically the observed effect of the polyelectrolytes on this type of reactions.

The value of k/k° in polyelectrolyte solutions is found to depend on the concentration ratio, $R = (m_m/m_s)$, which is the fundamental concentration variable in polyelectrolyte theories. In general m_s denotes the concentration of added mobile ions, but for solutions without added salts, m_s = concentration of ionic substrate. The rate constant ratio increases with R until a maximum acceleration is observed for $R = R_{max}$; from then on k/k° becomes independent of R. The rate enhancement by macroions is completely inhibited if enough electrolyte is added to the solution; this is strong evidence that the effect depends on the existence of an electrostatic field around the polymer chains. Moreover, the fact that k/k° depends on R rather than on m_m,[5] is a typical feature of phenomena governed by the polyelectrolyte effect, as described by the domain models of polyelectrolyte solutions.[16, 17] The maximum value of k/k° increases as the polyelectrolyte–substrate interaction becomes more intense,[8, 19] R_{max} is the concentration ratio corresponding to the maximum interaction between polyion and reactant ions. Consequently the value of R_{max} should depend on the charge density of the polymer and on the charge of the substrate. For weak polyions the charge density of the chain also depends on the degree of neutralization of the macroion i.

The same dependence of k/k° on R will be found for bimolecular reactions involving other ions and species having a constant concentration in the polymer domain. This is the case when the other reactive partner is H_2O, a reactive group attached to the polymeric chain, or, at constant pH, OH^- and H_3O^+ ions.

We shall define the polyelectrolyte interaction parameter, $\%A$, by the expression,

$$\%A = \frac{|Y - Y_s|}{|Y_p - Y_s|} \times 100 \qquad (12)$$

where Y is some intensive property of the solution for a given value of R and the subindices s and p denote its value in the electrolyte solution (no polyelectrolyte present, $R = 0$), and in polyelectrolyte solutions having no added salt ($R = \infty$), respectively. The kinetic $\%A$ is obtained if Y is made equal to the rate constant.

Fig. 2 is a plot of the kinetic $\%A$ against R for a number of reactions in solutions of two polycations. Fig. 2 contains the kinetic data corresponding to the unimolecular hydrolysis of *p*-nitro- and 2,4-dinitro-phenyl phosphates in poly-(vinylbenzyltrimethylammonium chloride) (PVBA-Cl) solutions,[5, 8] a non-reactive strong polycation. Also in fig. 2, the kinetic interaction parameter is plotted for the same substrates reacting with the amino groups in PEI of various degrees of neutralization, as well as that for the reaction of acetylsalicylic acid with PEI.[7] The predictions of

the electrostatic model are fully supported in all these systems. For bivalent substrate anions $R_{max} \sim 8$ in PVBA–Cl solutions and $iR_{max} \sim 10$ in PEI solutions; for univalent acetylsalicylate ion in PEI, $iR_{max} \sim 28$.

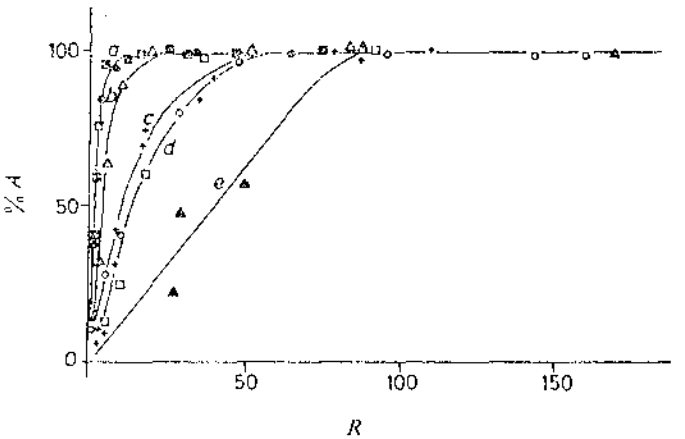

FIG. 2.—$\%A$ (kinetic) against R for the following reacting systems: (*a*) ●: DNPP/PVBA-Cl, ▨: NPP/PVBA-Cl. (*b*) △: NPP/PEI ($i = 0.47$). (*c*) +: DNPP/PEI ($i = 0.39$). (*d*) ○: NPP/PEI ($i = 0.25$), □: DNPP/PEI ($i = 0.24$). (*e*) ▲: AAS/PEI ($i = 0.39$). (NPP: *p*-nitrophenyl phosphate, DNPP: 2,4-dinitrophenyl phosphate, AAS: acetylsalicylic acid).

The electrostatic nature of the kinetic $\%A$ is even more clear if the curves illustrated in fig. 2 are compared to those in fig. 3, where the osmotic interaction parameter, corresponding to poly-(methacrylic acid) of various degrees of neutralization with added NaBr,[20] is plotted against $R = m_m/m_{NaBr}$ for different values of the degree of neutralization. The curves of fig. 3 correspond approximately to $iR_{max} \sim 30$.

According to Manning's theory of counterion condensation,[17] the local distribution of mobile ions depends on the charge parameter, ξ, defined by,

$$\xi = i\xi_{st} = i\frac{e^2}{\varepsilon kTb} \tag{13}$$

where b is the distance between two adjacent ionogenic groups and ξ_{st} is the charge parameter when all the ionogenic groups are ionized. When ξ exceeds a critical value (ξ_{crit}), Manning's theory assumes that the counterions condense onto the polymer chain to such an extent that the charge parameter is maintained equal to ξ_{crit}.

It is interesting to try applying Manning's model of counterion condensation to explain the kinetic effects for two reasons. First, it is a simple model having a clear physical meaning and secondly because it has proved quite successful in reproducing thermodynamic and transport properties of polyelectrolyte solutions.[2, 17]

According to Manning's theory, for monovalent ionogenic groups, $\xi_{crit} = 1/z$, where z is the counterion charge number. A consequence of this model is that polyvalent counterions condense preferentially to monovalent ones. Thus the case of bivalent substrate ions appears particularly amenable to description by this model. As iR increases, complete condensation of bivalent counterions occurs when the substrate concentration m_s is sufficientiy small compared to im_m. This condition is expressed by

$$m_s = \frac{im_m}{z}(1-\alpha) = \left(1 - \frac{1}{z \,.\, \xi_{st}}\right)\frac{im_m}{z} \tag{14}$$

where α is the fraction of uncondensed counterions. That is,

$$iR_{max} = z \Big/ \left(1 - \frac{1}{z \cdot \xi_{st}}\right). \tag{15}$$

This expression agrees with the observation that iR_{max} depends only on the charge density and the substrate ion charge number.

For PVBA–Cl and PEI solutions, iR_{max} is predicted to be 2.4 and 2.7, respectively. These values are some 3.5 times smaller than observed.

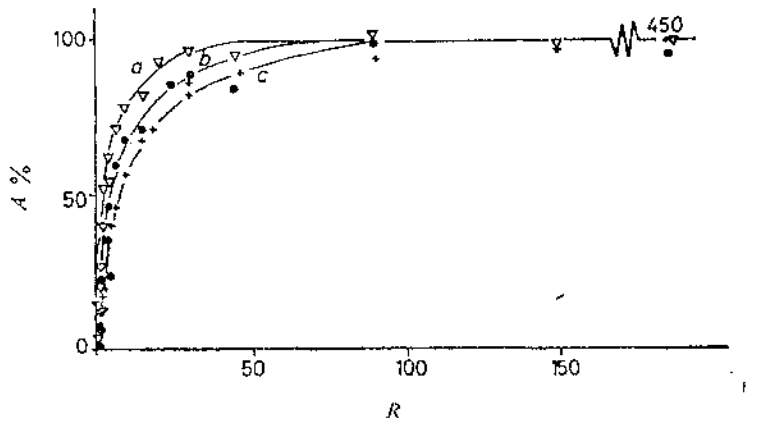

FIG. 3.—% A (osmotic) against R for poly-(methacrylic acid) with added NaBr.[20] (*a*) ▽ : $i = 0.8$, (*b*) ● : $i = 0.5$, (*c*) + : $i = 0.3$.

This discrepancy between observed and calculated values of iR_{max} may be attributed to the simplifications inherent in Manning's model. The model is successfully applied to the calculation of those properties which depend mainly on the free-counterions (*e.g.*, counterion activity coefficient, counterion diffusion coefficient, osmotic coefficient, *etc.*). On the other hand, the observed effect of polyelectrolytes on the rate of reaction is governed mainly by the condensed counterions, and the hypothesis of counterion condensation similar to a phase transition, does not adequately represent the detailed phenomenon. This is probably also the reason why Holtzer and Manning[21] found that the condensation model did not explain correctly the titration of weak polyions, which is also strongly dependent on the state of the condensed counterions.

CONCLUSIONS

(1) The inhibition of the rate of reaction produced by macroions on ionic reactions between mobile ions with charges of opposite sign, and the enhancement of the rates of reaction between two ions having the same charge sign caused by oppositely charged macroions (for low R values), can be explained either by the primary salt effect, as applied to polyelectrolyte solutions, or by the local distribution of ionic reactant. Both approaches are shown to be identical in these cases.

(2) The primary salt effect is basically unable to explain the decrease in k_2/k_2^0 for large m_m values. If the probability of simultaneous occupancy of macroionic sites by both reactant partners is taken into account, an expression based on local distribution of ions can be derived which agrees with experiment yielding a descending slope of (−1.0) and allowing calculation of the number of monomers per site.

(3) For first order reactions, the electrostatic effect explains qualitatively the k/k° curve which is similar to that for $\%A$ for the osmotic coefficients.

(4) The observation that R_{max} is only a function of polyion charge density and substrate charge is demonstrated theoretically. The theory of counter-ion condensation is, however, inadequate to predict quantitatively the value of R_{max}. This is attributed to the fact that processes dealing with the condensed counterions, like the polyelectrolyte effect on the rates of reaction and the titration of weak polyions, cannot be dealt with by the simple model of counterion condensation.

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