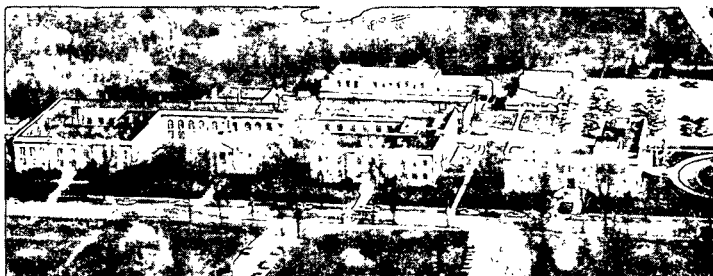


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THE ROLE OF POLYELECTROLYTE CHARGE DENSITY AND MOLECULAR
WEIGHT ON THE ADSORPTION AND FLOCCULATION OF COLLOIDAL
SILICA WITH POLYETHYLENIMINE

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on the Adsorption and Flocculation of Colloidal Silica with Polyethylenimine

G. Michael Lindquist and Robert A. Stratton

INTRODUCTION

The work discussed in this paper was taken from the thesis of G. Michael Lindquist presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy from The Institute of Paper Chemistry.

This study, the latest in a series of theses at the Institute dealing with the adsorption of various polymers on a variety of surfaces, including pulp fibers, demonstrates applications in mill effluent treatment. The results also are of importance to paper and board makers because similar mechanisms underlie the utility of polymers as retention and drainage aids. This extends the previous work by addressing the question: how does the adsorbed polymer promote flocculation? The mechanism of flocculation is found to be dependent on the relative degrees of electrostatic charge on the polymer and the surface which are functions of the pH of the system. This work suggests that, in the usual papermaking range of pH 4 to 6, flocculation (or retention) efficiency is independent of polymer chain length for a highly charged cationic macromolecule such as polyethylenimine. The dominant factor is the amount of charge per unit weight conveyed by the polymer.

This paper will be presented at the 49th ACS National Colloid Symposium in June, 1975 and will be submitted to the Journal of Colloid and Interface Science for publication.

The Role of Polyelectrolyte Charge Density and Molecular Weight
on the Adsorption and Flocculation of Colloidal Silica with Polyethylenimine

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ABSTRACT

The polyethylenimine (PEI)-water-Ludox AM colloidal silica system was used as a model system to investigate the relationship of charge density and molecular weight of the polyelectrolyte on the adsorption and subsequent flocculation of oppositely charged colloidal particles. Narrow molecular weight fractions of PEI ranging from 1,760 to 18,400 were prepared and characterized. Differences in polymer molecular weight, salt concentration, and pH were employed to vary the number of cationic charges per PEI molecule. At the concentrations of PEI required to initiate flocculation of Ludox AM, complete adsorption of PEI occurred regardless of molecular weight, pH, or ionic strength. However, at higher concentrations, adsorption increased with molecular weight, pH, and ionic strength. The flocculation results indicated that the relative importance between polymer bridging and electrostatic considerations is pH dependent. At pH 9 and greater, polymer bridging is the dominant mechanism of destabilization due to the low cationic charge of the PEI molecule. However, at pH less than 9, charge interaction between PEI and colloidal silica is the dominant consideration. An inverse linear relationship was found between the logarithm of the molar concentration of PEI required to initiate flocculation and the logarithm of the cationic charge on the PEI molecule.

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INTRODUCTION

There have been many studies undertaken in the past to determine the mode of action of polymers, both ionic and nonionic, on the stability of colloidal materials. The concept of polymer bridging between particles was offered by La Mer and coworkers (1,2). It is well established in nonionic polymer systems, and has also been applied in systems of particles and polymers of opposite sign (2-5). However, in the latter systems, charge neutralization, i.e., coulombic interactions between particle and polymer may play a significant or even a dominant role (6-9). Other investigators (10-13) have found that the mechanism of action of polyelectrolytes is a combination of polymer bridging and charge neutralization.

Analysis of the data cited above is complicated by the fact that a thorough evaluation of the size of the molecule in solution and the degree of charge on the polyelectrolyte and particle were not correlated with the ability of the polyelectrolyte to initiate destabilization of the colloidal dispersion. Cationic polyelectrolytes, for example, are subject to changes in charge and size in solution upon alteration of pH and ionic strength. Furthermore, the adsorbability of the polyelectrolyte on an oppositely charged surface may change with these solution properties. Therefore, because the influence of polyelectrolyte charge and particle charge on aggregation has not been evaluated, the information given has never been sufficiently complete to allow a satisfactory physical interpretation of the results.

The present study was designed to investigate a carefully characterized system of cationic polymer and colloidal particles. It was conducted with polyethylenimine (PEI) and colloidal silica in order to evaluate the role which polymer molecular weight and charge density play in the adsorption on, and

flocculation of an anionic material with a cationic polymer. By characterizing the changes in configuration and charge of PEI and colloidal silica induced by alteration in pH and ionic strength the relative importance of polymer bridging and charge neutralization can be evaluated. Furthermore, the use of narrow molecular weight fractions enables polymolecularity effects on adsorption to be minimized, and enables the conversion of concentration from weight to molar units.

EXPERIMENTAL

Silica Suspension

Ludox AM, generously supplied by E. I. du Pont de Nemours and Company, was chosen for this study because of its stability over a wide pH range, and because its aggregation properties and charge development have been previously characterized (14). According to the manufacturer this sol consists of nonporous, amorphous silica particles. The sol differs from other silica sols in that the surface is modified by the incorporation of about one aluminum atom per twenty silicon atoms on the surface. This substitution of aluminum results in the formation of a negative surface charge in addition to that due to the ionization of silanol groups on the surface.

To minimize the influences of undesirable impurities in the dispersion on the flocculation phenomena, the sol was dialyzed against distilled deionized water for five days with the dialyzate changed every 24 hours. A stock solution containing 0.5 g silica/100 ml was prepared by dilution of the dialyzed sample with distilled water. This solution was further diluted during the experiments to 0.3 g silica/100 ml, at which concentration all adsorption and flocculation measurements were carried out.

The particle size and specific surface area of Ludox AM were determined from an electron micrograph. The particle diameters of 490 particles were measured very accurately with a microcomparator. From these measurements the average particle diameter was found to be 140 Å and the specific surface area 190 sq m/g in excellent agreement with Allen and Matijević (14).

The surface charge density of Ludox AM was determined by the pH titration procedure described elsewhere (14). The method involves the determination of protons released from surface silanol groups upon addition of base.

Polymer

Polyethylenimine (PEI) from Dow Chemical Company (control number SA 1117-633974) was fractionated by gel permeation chromatography to limit effects of polymolecularity. The polymer was eluted through a bed of Bio-Gel P10 in an aqueous solvent containing 0.10N NaCl.

After fractionation the salt was removed from the fractions of PEI by diafiltration against distilled deionized water. An Amicon Model 202 ultrafiltration cell (Amicon Corporation, Lexington, Mass.), utilizing a UM2 membrane, was found to remove 99.9+% of sodium chloride after six sample volumes of filtrate were collected. Only negligible amounts of PEI were found in the filtrates indicating the high rejection ability of the membrane to these fractions of PEI.

Weight average molecular weights $\langle M \rangle_w$ of various fractions were determined by the sedimentation equilibrium method by the use of a Beckman Spinco Model E ultracentrifuge. All runs were made in an aqueous solvent of 0.10N sodium chloride to suppress charge effects. The diffusion coefficients of the fractions were measured by means of a free diffusion technique (15).

From these measurements the molecular sizes in 0.10N NaCl were calculated by using the Stokes equation.

$$\underline{R_e} = \frac{kT}{6\pi\eta_s \underline{D_o}}$$

Here $\underline{R_e}$ is the equivalent hydrodynamic radius, η_s is the solvent viscosity, $\underline{D_o}$ is the limiting diffusion coefficient, k is Boltzmann's constant, and T is the absolute temperature.

Intrinsic viscosities $[\eta]$ were measured in aqueous solvent having either no added sodium chloride or 0.10N sodium chloride as a function of pH in order to determine the extent of expansion of PEI. Throughout this study pH adjustments were made with either HCl or NaOH. Cannon No. 50 semimicroviscometers with solvent efflux times greater than 210 sec were used in the viscosity measurements. In the presence of 0.10N NaCl $[\eta]$ was determined as the reduced specific viscosity at infinite dilution from a plot of reduced specific viscosity versus concentration. For the case of no added NaCl, however, increasing negative slopes upon dilution prevented a least squares extrapolation to obtain a reliable value for $[\eta]$. This is typical polyelectrolyte behavior for salt-free systems (16,17). For this case the Fuoss and Strauss (18) procedure yielded linear plots from which $[\eta]$ was obtained. From the $\langle \underline{M} \rangle_w$ and $[\eta]$ data the molecular size of PEI was calculated using the Einstein-Stokes equation.

$$[\eta] = 2.5 \left(\frac{\underline{N_a}}{\underline{M}} \right) (4/3) \pi \underline{R_e}^3$$

Here $\underline{N_a}$ is Avogadro's number, \underline{M} is the polymer molecular weight, and $\underline{R_e}$ is the radius of the equivalent hydrodynamic sphere.

The degree of protonation, electrophoretic mobility, apparent diffusion coefficient, and extent of chloride binding of the PEI molecule as a function of solution pH were determined. The molecular charge was calculated from hydrogen

binding determinations as described by Kenchington (19) in both salt-free and 0.10N NaCl. The electrophoretic mobility and apparent diffusion coefficient of PEI were determined on a Beckman/Spinco Model H electrophoresis-diffusion instrument equipped with Tiselius cell and schlieren optics. Determination of the mobility in aqueous solvent containing less than 0.10N NaCl was unsuccessful. The ultra-filtration apparatus was used to determine the extent of chloride binding to PEI in 0.10N NaCl as a function of pH. The procedure is described elsewhere (20-22).

Flocculation Experiments

In each flocculation run a set of 50-ml screw cap centrifuge tubes was filled with 15 ml of 0.50 g/100 ml stock solution of Ludox AM. To the first tube, 10 ml of polymer solution at the desired concentration and the same pH and ionic strength as the sol was added with a pipette. Similarly another PEI solution differing only in polymer concentration from the previous solution was added to the next tube, etc. In this manner a series of suspensions of total volume 25 ml and 0.30 g/100 ml Ludox AM was prepared with varying polymer dosages.

The addition of the polymer with a pipette was performed in a manner such that the jet caused sufficient agitation and mixing. Since there is evidence that polymer adsorption is irreversible, the polymer was added to the sol so as to avoid exposing a small number of particles to very high polymer concentrations. The ionic strength and pH of both the Ludox AM solution and polymer solutions were adjusted separately to the same values to prevent or minimize changes in charge and configuration of the polymer upon mixing.

The centrifuge tubes were sealed and then agitated in a water bath at a constant agitation rate of 4.5 rpm. The tubes were rotated by placing them at the periphery of two 12-inch notched wheels mounted on a common axis. The notches of one wheel were advanced 15° relative to the second to ensure floc movement throughout the rotating tube. These conditions provided very little agitation within each tube but allowed no settling of flocs.

After sufficient agitation the turbidity and pH of the suspension in each tube was measured. The suspension turbidity was followed with a Brice-Phoenix light scattering photometer utilizing green light of wavelength 546 nm. The turbidity and polymer adsorption measurements were made after one hour of agitation since little or no change at longer times was found in preliminary analyses.

From the behavior of the turbidity versus the logarithm of the initial polymer dosage, the concentration of polymer required to initiate aggregation (CFC) was obtained. The settling concentration (SC) was defined as the minimum PEI dosage required to produce rapidly settling flocs (less than 15 min for complete settling). The restabilization concentration (RC) is the minimum PEI dosage required to induce restabilization of Ludox AM. Both SC and RC are estimates because of the wider spacing of data points at the higher PEI dosages.

The amount of PEI adsorbed was determined as the difference between the initial polymer dosage and that remaining unadsorbed. The suspension in each tube was centrifuged for 10-20 min at 10,000 rpm on a Sorvall Model RC2-B centrifuge to obtain a clear supernatant. A spectrophotometric method (15), based on a complex formed between PEI and the cupric ion (23) was used to determine the supernatant concentration of PEI.

RESULTS AND DISCUSSION

Charge Density of Ludox AM

Figure 1 is a plot of the surface charge density of Ludox AM as a function of pH. The charge density on the left ordinate is the sum of charges due to ionization of silanol protons and to the isomorphous lattice substitution of alumina on the particle surface. The contribution of the latter is 0.41 charge sites per 100 Å² assuming that each substituted aluminum atom results in the formation of a negatively charged site which is independent of pH at least in the pH range studied. Examination of titration curves (24) of modified and unmodified Ludox suggests the negative charge produced by the isomorphous lattice substitution is constant above pH 3; only at pH less than 3 did titration curves of Ludox AM indicate the uptake of protons. For unmodified Ludox, no such uptake apparently occurred.

The right-hand ordinate is the charge on the silica particle due to the ionization of silanol protons. Note that the contribution of the isomorphous lattice substitution to the total charge density of Ludox AM is significant. For example, at pH 8.5, 50% of the charge on the particle surface is due to the substitution of aluminum for silicon on the surface. At pH less than this, the contribution is even greater.

Polyethylenimine Characterization

Polyethylenimine is a polybase containing primary, secondary, and tertiary amine groups in the ratio of 1:2:1 (25). This ratio results from a structure of monomer units, $-\text{CH}_2-\text{CH}_2-\text{NH}-$, which is highly branched with branch points at every 3 to 3.5 monomer units (25). The three dimensional branched molecule assumes a spherically symmetric compact molecule in solution (26,27).

Table I shows the $\langle M \rangle_w$ and the limiting (concentration approaching zero and time approaching infinity) diffusion coefficient D_0 for select PEI fractions determined in 0.10N NaCl. The equivalent hydrodynamic diameters were calculated from D_0 utilizing the Stokes equation. The Stokes diameter has previously been shown (26) to yield the same approximate solution diameter for PEI as the Stokes-Einstein calculation under similar solution conditions.

Since PEI is a polybase, addition of protons (reduction in pH) will result in protonation of the amine groups and subsequent expansion of the polyion due to mutual charge repulsion. Figures 2 and 3 show the increase in cationic charge and $[\eta]$ of PEI as the pH is lowered in 0.10N NaCl and in the absence of added NaCl. The decrease in $[\eta]$ at less than pH 5 in the absence of NaCl is due to the ionic strength effect of chloride ion introduced in reducing pH. The small dependency of $[\eta]$ on pH in the presence of 0.10N NaCl is due to considerable counterion binding and to shielding of the cationic charges on the PEI molecule.

Table II indicates the Einstein-Stokes diameter and percentage expansion of the PEI molecule, $\langle M \rangle_w = 7,200$, as a function of pH. The maximum size of the PEI molecule is about 65% greater than its uncharged size in the absence of added NaCl. However, in the presence of 0.10N NaCl the expansion is only ca. 10%. That little expansion occurs in 0.10N NaCl is supported by the relative independence of diffusion coefficient on pH.

Figure 4 shows that the mobility of PEI in 0.10N NaCl increases rapidly between pH 11 and 8 but only slightly with further decrease in pH down to 3. The shape and magnitude of the curve is in agreement with that obtained earlier (26) for PEI of $\langle M \rangle_w = 10,400$. The mobility and viscosity data suggest that the point

of zero charge on the PEI molecule is approximately 10.8, which has been found previously (26). From the experimental mobility, the effective cationic charge on the PEI molecule was calculated according to the relationship developed by Henry (28) and modified by Gorin (29). Figure 2 shows the results of this calculation in comparison to the cationic charge obtained by titration. Although the electrokinetic charge determined by electrophoresis is of the same order of magnitude as that determined by acid-base titration, the effective charge determined from mobility data is lower. The increased extent of counterion binding apparently causes a reduction in charge from that determined by acid-base titration in high salt solutions (16). The extent of chloride binding on PEI in 0.10N NaCl as a function of pH is depicted in Figure 5. Subsequent discussion will show that in the absence of added NaCl, acid-base titration of PEI will yield reasonable values for the charge on the PEI molecule; however, in 0.10N NaCl the charge density calculated from electrophoresis data utilizing the Gorin relationship is a better procedure for determining the cationic character of the PEI molecule than is acid-base titration.

A more complete discussion of the characterization results, etc., of PEI is given elsewhere (22).

Adsorption of PEI on Ludox AM

Preliminary adsorption equilibrium studies utilizing dialyzed unfract ionated PEI (DUPEI) as the adsorbate showed the adsorption to be almost complete within 15 min of contact time. The adsorption was followed up to 12 hours and found to be the same as 60 min. Rapid attainment of adsorption equilibrium has also been found by others (4,6) for systems of polymers and oppositely charged nonporous particles. The adsorption data reported here are for two hours contact time.

Figures 6 and 7 show typical results obtained for the adsorption of PEI on Ludox AM for different pH and ionic strength conditions. Virtually complete adsorption of PEI occurs regardless of $\langle M \rangle_w$, pH, and ionic strength for initial PEI dosages less than 40 mg/liter. Later discussion will indicate that initiation of flocculation of colloidal silica under the conditions studied occurs at dosages considerably less than 40 mg/liter. Therefore, the extent of PEI adsorption on silica is not influenced by changes in $\langle M \rangle_w$, pH, and ionic strength at the concentration required for flocculation.

At higher concentrations, however, all of these factors affect the extent of adsorption. The decrease in adsorption with decreasing pH is attributed to the increase in cationic charge of the PEI molecule, the consequent increase in molecular size, and the lower surface charge density of silica. The high charge density of PEI leads to an increased size and increased electrostatic repulsion between highly charged PEI molecules adsorbed and those approaching the surface. The increased extent of adsorption with ionic strength can be attributed to the decreased intermolecular electrostatic interactions, reduced molecular size, and, perhaps, reduced solvent power.

Figure 7 is an equilibrium adsorption isotherm of PEI, $\langle M \rangle_w = 7,200$, on colloidal silica at five pH conditions. All of the isotherms are of the high affinity type and can be described by an equation of the Langmuir form (30) given as:

$$\frac{C_e}{C_*} = (1/C_M K) + \frac{C_e}{C_M} \quad (1)$$

where C_e is the equilibrium solution concentration, C_* is the loss in solution concentration due to adsorption, C_M is the loss in solution concentration when the surface is saturated with adsorbate, and K is the Langmuir constant.

According to Equation (1), a plot of $\frac{C_e}{C_*}$ versus C_e will be linear if the adsorption behavior is of the Langmuir type. The curves in the lower part of Figure 7 show that the adsorption behavior can be described by means of the Langmuir equation and that the adsorption data can be interpreted in terms of a "monolayer" of polymer. All of the equilibrium isotherms measured exhibited a good fit to the Langmuir equation. Values of $\frac{C_M}{C_e}$ were determined from the slope of the Langmuir plots and are presented in Table III. In all cases, the maximum amount of PEI adsorbed decreases with pH and ionic strength. Furthermore, the maximum amount increases somewhat with molecular weight at constant pH.

The following empirical equation has frequently been used (31) in relating the molecular weight to the limiting amount of polymer absorbed:

$$\frac{C_M}{C_e} = K \left(\frac{M}{w} \right)^n \quad (2)$$

In Equation (2) K and n are constants. The values of n lie in the range $0 < n < 1$ if $\frac{C_M}{C_e}$ is expressed on a weight per unit area basis. The size of n can be used as an indication of the configuration of the polymer on the surface for conditions in which all available surface sites are occupied.

If a polymer were to lie flat on the surface and remain so until a monolayer were formed, then the number of polymer molecules adsorbed would decrease as $\left(\frac{M}{w} \right)^n$ increased. However, the amount adsorbed on a weight basis would be independent of $\left(\frac{M}{w} \right)^n$ (i.e., $n=0$). If, in the other extreme, the polymer were attached to the surface at one point only, then the number of polymer molecules adsorbed should be independent of $\left(\frac{M}{w} \right)^n$, and the weight adsorbed would be in direct proportion to $\left(\frac{M}{w} \right)^n$ (i.e., $n=1$). Therefore, for all conceivable configurations of the polymer molecule on the surface, the exponent will have values ranging between the extremes of zero and one.

The value of \bar{n} in this study was found to be ~ 0.1 which is close to the limit of $\bar{n}=0$. This indicates that the PEI molecule lies in a relatively flattened configuration on the surface with more than one segment attached but nevertheless having some extension into the solution.

A low value of \bar{n} is normally found both experimentally (6) and theoretically (32,33) for systems of high interaction energies between polymer and surface. For example, the adsorption energy of polyions adsorbing onto an oppositely charged surface is $2 kT$ or greater per segment (6) indicating strong attractive forces and relatively flat configurations. According to Silberberg (32,33) more than 70 percent of the segments are in contact with the surface at interaction energies of only about kT .

For the nonporous colloidal silica, the adsorption of PEI on a weight basis increases only slightly with increasing $\langle \bar{M} \rangle_w$; however, the number of PEI molecules decreases. The number of PEI molecules per particle at adsorption saturation capacity (ASC) was calculated by considering that the PEI fractions employed have narrow molecular weight distributions. Since Hostetler and Swanson (26) obtain $\langle \bar{M} \rangle_w / \langle \bar{M} \rangle_n$ ratios of less than 1.03 for similar PEI fractions prepared following the same fraction procedure, the assumption is reasonable. The results of this calculation are included in Table IV. They indicate that the number of adsorbed PEI molecules per particle at ASC decreases as the size of the molecule increases, either by increasing $\langle \bar{M} \rangle_w$ or decreasing ionic strength and/or pH. Thus, the maximum number adsorbed per particle is determined by the space requirement of the PEI molecule. The decrease in number adsorbed with pH can also be attributed to increased electrostatic repulsion between juxtapositional adsorbed molecules.

The number of PEI molecules of known solution size which could geometrically be placed around a spherical silica particle of given diameter was calculated (22) and found to agree reasonably well with the ASC coverage in some cases of $\langle \underline{M} \rangle_w$ and pH; however, in other cases, e.g., at low pH, the agreement was not good.

In summary, the adsorption data indicate the following facts: (1) at the concentration of PEI required to initiate flocculation, there is no effect of $\langle \underline{M} \rangle_w$, pH, and ionic strength on the extent of adsorption, (2) the isotherm of PEI on Ludox AM obeys a high affinity type Langmuir isotherm, (3) PEI adsorbs with close contact with the particle surface, and (4) the maximum amount of PEI adsorbed is influenced by the space requirements of the PEI molecule and by the extent of electrostatic interactions between the macromolecules.

Flocculation

Figure 8 illustrates the dependence of the turbidity of Ludox AM sol (0.3 g/100 ml) on the initial dosage of PEI for five solution pH conditions. The turbidity of stable sols is low because of the small size of the Ludox particles. High turbidity values denote systems which have undergone flocculation; however, the aggregates are still small enough not to settle out completely. The critical flocculation concentration (CFC) was obtained by extrapolation of the dispersion turbidities to that of the unflocculated sol. Figure 8 illustrates that less PEI is required to initiate flocculation as the pH is lowered.

The flocculation boundaries for all the conditions of PEI molecular weight, pH, and ionic strength studied are given in Figure 9. Note that the units of the CFC have been converted from logarithmic units. These data points

indicate the PEI dosage required to just initiate flocculation. In all cases the CFC decreases with decreasing pH, less so in the presence of 0.10N NaCl.

To better illustrate the effect of polymer molecular weight on flocculation the smoothed curves in Figure 9 have been crossplotted as CFC versus the logarithm of the PEI molecular weight at integer values of pH in Figure 10. Figure 10a illustrates that for the case of no added NaCl at pH values less than 9, the CFC of PEI is independent of polymer molecular weight; at pH values of 9 and greater, the CFC decreases with increasing molecular weight.

Figures 9 and 10b show that in the presence of 0.10N NaCl, the CFC of PEI is reduced only slightly with a pH change from 9 to 3. The CFC is also independent of polymer molecular weight in this pH region. These experimental results are in good qualitative agreement with those of Dixon, et al. (12).

Because of the wide range of polymer dosage studied, both flocculation and restabilization of Ludox AM were observed. Stability domains of 0.3% Ludox AM toward PEI as a function of solution pH are shown in Figure 11. The hatched area on each plot is the flocculation region. The open area at low PEI dosage is the region in which flocculation does not occur while the upper open area is the restabilization region. The line through the hatch area is the minimum PEI dosage required to give rapidly settling flocs of aggregated Ludox AM, i.e., the settling concentration (SC). Flocs formed at PEI dosages below the SC line settle very slowly, while those found at higher dosages settle well within 15 minutes.

The use of narrow molecular weight fractions of PEI in this study, along with the carefully characterized silica particles, permits the calculation of the number of PEI molecules per silica particle at the CFC, SC, and

restabilization concentration (RC). Also the percent, θ , of the adsorption saturation capacity was calculated for these various polymer dosages. The results are presented in Table IV.

According to Figures 9 and 10, at pH 11 the CFC of PEI is strongly dependent upon $\langle \underline{M} \rangle_w$ of the polymer; the CFC decreases with increasing $\langle \underline{M} \rangle_w$ for both ionic strengths. Since the PEI molecule is unchanged as indicated in Figures 2-5 at this pH, the mode of aggregation must be of a bridging nature. The La Mer theory (1) predicts an improved efficiency in flocculation of colloidal materials with increasing polymer molecular weight. Thus, the results at pH 11 for both NaCl conditions are in accord with this theory. The strong molecular weight dependency at this pH is a result of a larger polymer being able to more effectively bridge between particles than a smaller polymer molecule. Bridging may also occur in destabilizing Ludox AM at pH 9 in conditions of no added NaCl because the nonzero slope in Figure 10a for pH 9 indicates that chain length is a significant factor in affecting the CFC.

At pH 11, the thickness of the diffuse electrical double layer as approximated by the reciprocal of the Debye-Hückel parameter κ is about 100 Å for the case of no added NaCl. In the presence of 0.10N NaCl, the thickness is 10 Å. Since the solution size of the smallest PEI molecule studied is about 25 Å, it is interesting that flocculation occurs at pH 11 when the diffuse electrical double layer extends beyond the extension of the PEI molecule. The concept of the necessity of the polymer segments to extend beyond the thickness of the double layer in order for flocculation to occur has been offered by Fleer (34). Apparently for the PEI-colloidal silica system this requirement is not necessary. The relatively high segment density of uncharged PEI on the particle surface, and the hydrophilic nature of silica, are factors which may contribute toward the $1/\kappa$ approximation becoming inapplicable.

In the presence of 0.10N NaCl, the CFC of PEI decreases with increasing PEI molecular weight at pH 11 although not to the same degree as that for the case of no added NaCl. The highly compressed diffuse layer at the higher ionic strength allows a closer average distance of approach. Furthermore, the PEI molecular diameter is in all cases greater than $1/\kappa$, allowing the polymer segments to flocculate the silica particles by extending beyond the double layer.

The decrease of the CFC of PEI in Figures 9 and 10 with pH might be attributed to several factors: (1) the greater cationic charge on the PEI molecule, causing greater compression of the diffuse electrical double layer and reduction of charge on the particle by an adsorbed PEI molecule, (2) improved bridging ability of the polymer due to increased solution size caused by intramolecular repulsion of the positively charged amino groups on the polymer chains, (3) reduction of surface charge density of silica per se.

However, the relative constancy of the solution size of the PEI molecule in the pH region of 7-3, as indicated by the viscosity data in Figure 2 and in Table II, indicates that the decrease in CFC from pH 7 to 3 can not be explained by an increase in solution size of the PEI molecule. Furthermore, it was shown (22) that if two PEI molecules have the same solution size but differing degree of cationic charge, the CFC of the PEI molecule with the greater degree of cationic charge was significantly lower than the other PEI molecule. This indicates solution size itself is not a significant parameter influencing flocculation at pH less than 9. This is further pointed out in Figure 12 where it is seen that two PEI molecules having the same number of cationic charges but differing $\langle M \rangle_w$ (and, therefore, differing solution size), have about the same flocculating ability.

The changing extent of silanol ionization with pH does not correlate with the changes in the CFC of PEI. For example, the number of negative charges per 100 Å² on Ludox AM at pH 3 is only about 50% of that which the surface possessed at pH 9. If the changing negative surface charge were the dominant factor for the decrease in CFC with pH, then one would expect about a twofold reduction in CFC in this pH range. However, the CFC of PEI in the absence of added NaCl decreased by about sixfold. Therefore, the changing negative surface charge density of silica per se is not responsible for the decrease in the CFC of PEI. Other evidence in the literature also suggests that there is no univocal relation between surface charge and stability (14,35-37).

The lack of correlation of the CFC of PEI with changes in solution size and particle charge, and the fact that the CFC becomes independent of polymer molecular weight at pH less than 9 suggests that under these conditions, the number of protonated amine groups (cationic charges) in the system is the important parameter influencing the efficiency of flocculation. This follows because the degree of protonation and, therefore, the number of protonated amines in the system, is independent of polymer molecular weight (17).

The greater the number of cationic charges per PEI molecule, the greater will be its ability to destabilize the dispersion. With increasing cationic charge, the PEI molecule will cause greater compression of the diffuse double layer and reversal of charge in localized areas on the particle surface. Figure 12 indicates the relationship between the molar CFC of PEI (that is, number of molecules of PEI per liter divided by Avogadro's number at CFC) and the number of cationic charges per PEI molecule z can be expressed as:

$$(\text{CFC})_{\text{molar}} = \frac{k}{z^2} \quad (3)$$

where $\underline{a} = 0.94$ in absence of added NaCl, and 0.71 in the presence of 0.10N NaCl. For the latter case \underline{z} was calculated from the electrophoretic mobility results in Figure 2. Equation (3) should be viewed empirically for absorbable polymeric ions and only as a distant parallel to the well-known Schulze-Hardy rule. It does point out that differences in flocculating ability between PEI molecules of differing $\langle \underline{M} \rangle_{\underline{w}}$ or under differing pH conditions are not due to size or chain length, but rather to the number of cationic charges carried per PEI molecule.

The molar CFC was also found (22) to fit the relationship $(\text{CFC})_{\text{molar}} = 10^{\underline{bz}}$; however, the value of \underline{b} decreased with increasing $\langle \underline{M} \rangle_{\underline{w}}$.

The importance of charge considerations in destabilization of colloidal silica by PEI can be further evaluated by considering the resulting net charge of the region in which a PEI molecule adsorbs on the particle surface. This concept of an adsorbed "patch" on the surface is plausible since the rate of polyelectrolyte adsorption on an oppositely charged surface is relatively fast compared to the rate of particle collision, i.e., adsorption is essentially complete before particle aggregation commences (4,6). We assume the patch charge to be the algebraic sum of the number of cationic charges on the PEI molecule and the number of negative charges in the area covered by the PEI molecule. By further assuming that the PEI molecule adsorbs in an area of diameter equal to its solution diameter (26) and that the surface charges on the particle are immobile, the calculation showed that for the salt-free case the patch charge reversed signs at pH 8.4. At pH greater than 8.4, the patch resulting from the adsorption of a PEI molecule still retains a net negative charge. At pH less than 8.4, a positive patch is formed on the particle surface which becomes more strongly cationic with decreasing pH. For the case of 0.10N NaCl present, the pH of similar charge reversal of the patch was at 9.3.

The patch charge calculation is completely harmonious with the experimental observations. For example, at pH 9 the patch charge for the case of no added NaCl is still negatively charged, although less so than the surrounding PEI-free area. Therefore, at this pH, particle aggregation must be of a bridging nature as further indicated by the dependency of the CFC on $\langle M \rangle_w$ (Figure 10a).

At pH less than 8.4, the patch becomes more strongly cationic with reduction in pH. The patch, therefore, has the capability to attract another silica particle via coulombic attraction. Furthermore, the presence of the positively charged patch disrupts the distribution of counterions about the silica particle. This disruption will distort and reduce the repulsive forces between oppositely charged silica particles. Hence, the greater the magnitude of the cationic patch charge and/or the greater the number of cationic patches on the surface, the more probable will be an interaction between particles leading to aggregation. The molar CFC of PEI decreases with increasing cationic charge brought about by either increasing molecular weight or reducing the pH.

Since the degree of ionization of polyelectrolytes is independent of molecular weight (17), the independence of CFC (when expressed in weight units) on molecular weight implies that the condition leading to colloidal instability depends only on the total number of positive charges and not their detailed distribution over the particle surface. For this statement to be strictly true, the exponent a in Equation (3) should be unity. This is a good approximation for the case of no added salt.

In the presence of 0.10N NaCl, the same flocculation phenomena occur except that less polymer is required to initiate aggregation because of the highly compressed double layer and reduced repulsive forces between like

charged particles. The reduced pH dependency of the CFC in 0.10N NaCl can probably be attributed to the reduced dependency of the PEI charge on pH. Under these conditions Figure 3 indicates that the effective charge on PEI only increased from 0.12 to 0.19 in a pH shift of 9 to 3.

The patch model is in agreement with all the experimental observations and appears to provide a reasonable explanation of the flocculation behavior.

Table IV shows the result of calculating the number of PEI molecules per particle at the CFC, settling concentration (SC), restabilization concentration (RC), and the theoretical dosage per particle required to neutralize all of the negative charges on a silica particle, $\underline{C_Q}$. The latter quantity was determined by dividing the number of negative charges on a silica particle by the number of cationic charges per PEI molecule under given pH conditions. The optimum dosage of PEI was not discernible in this study but it does lie between SC and RC.

The $\underline{C_Q}$ values in Table IV fall in general between the SC and RC for the pH range in which charge interactions between PEI and silica are dominant, i.e., at pH less than 9 for the salt-free case. This calculation suggests that for this polymer-colloid system the optimum flocculation dosage lies near that necessary for charge neutralization.

La Mer and coworkers (1,2) predict the optimum concentration of polymer required for flocculation is that which results in 50% of the adsorption saturation capacity. Despite the fact that the value of θ at $\underline{C_Q}$ is in the vicinity of 50%, this study has established that polymer bridging is not a significant mechanism in aggregating colloidal silica in the pH region of 3 to 7. Therefore, obtaining a value of θ ca. 50% for the optimum polymer dosage in systems of a polyelectrolyte

with an oppositely charged sol is not sufficient proof that bridging is a dominant mechanism.

Since C_Q is the concentration of PEI required to neutralize all the charges on the silica particle, it also will correspond to the concentration of polymer required to achieve zero electrophoretic mobility. Unfortunately due to the nature of Ludox AM these data are unavailable. For silica of larger particle size, however, Dixon, et al. (12) showed that the optimum PEI concentration corresponded to the concentration required for zero mobility. The C_Q values indicate that the CFC would occur when the dispersion has a mobility which is still negative despite the fact that the mechanism of flocculation involves electrostatic interactions.

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TABLE I

Polyethylenimine Characterization

Fraction	$\langle M \rangle_w$	$\frac{D}{D_0} \times 10^6, ^b$ cm ² /sec	Stokes Molecular Diameter, A ^b
2	18,400	0.73	71
3	14,000	0.85	62
5	7,200	0.95	45
7	4,400	1.30	35
9	2,200	1.85	25
11	1,760	2.54	22
DUPEI ^a	6,160	0.85	--

^aDialyzed unfractionated PEI whole sample.

^bpH ~ 10, 0.10N NaCl.

TABLE II

Effect of pH on Einstein-Stokes Diameter of
PEI Molecular Weight 7,200

Ionic Strength: No Added NaCl				In 0.10N NaCl			
pH	Degree of Proton- ation	Einstein- Stokes Diameter, A	Percent Expansion	pH	Einstein- Stokes Diameter, A	Percent Expansion	Apparent Diffusion Coeff. ^a
10.8	0.00	47	0	11.0	--	--	1.00
10.0	0.04	49	4	10.8	46	0	--
9.0	0.10	61	30	9.0	46	0	--
8.0	0.20	72	53	8.2	--	--	0.99
7.0	0.34	76	62	8.0	46	0	--
5.0	0.55	77	65	7.0	48	4	--
3.0	0.73	74	57	5.7	--	--	0.98
				5.0	51	10	--
				3.0	51	10	1.00

^a0.2% Concentration of PEI; $\underline{D} \times 10^6$, cm²/sec.

TABLE III
Saturation Adsorption Values for PEI
on 0.30% Ludox AM

$\langle M \rangle_w$	pH	C_M , mg/liter	Γ_s , mg/m ²
Salt Condition: No Added NaCl			
1,760	9.5	203	0.354
	7.8	166	0.290
	4.9	72	0.126
	3.1	52	0.091
7,200	11.1	377	0.656
	9.1	239	0.416
	7.1	138	0.241
	4.9	93	0.162
	3.0	49	0.085
18,400	7.2	151	0.263
	5.0	112	0.195
	3.1	89	0.155
Salt Condition: In the Presence of 0.10N NaCl			
1,760	10.95	324	0.565
	9.15	191	0.333
	7.0	150	0.261
	5.5	103	0.179
	3.1	56	0.098
7,200	11.0	277	0.483
	9.3	276	0.482
	6.8	231	0.402
	5.5	142	0.247
	2.9	100	0.174
18,400	3.1	175	0.305

TABLE IV.

Number of PEI Molecules per Particle and Percent of Saturation Adsorption Under Different Conditions

No Added NaCl		CFC		SC		RC		$\frac{C_M}{No.}$	$\frac{C_Q^a}{No.}$	
$\langle M \rangle_w$	pH	No.	$\theta, \%$	No.	$\theta, \%$	No.	$\theta, \%$	No.	No.	$\theta, \%$
1,760	11	24.8	--	--	--	--	--	--	--	--
	9	2.7	3.6	27.	36	63.	85	74.3	131.	--
	7	1.04	2.1	10.6	21	33.	66	49.6	30.	60
	5	0.40	1.4	5.3	19	15.5	55	28.2	14.2	50
	3	0.25	1.3	3.7	19	19.6	100	19.6	8.6	44
7,200	11	1.75	5.0	20.5	59	--	--	34.6	--	--
	9	0.52	2.5	11.	53	16.5	80	20.7	32.	--
	7	0.24	1.9	3.7	30	7.7	62	12.5	7.4	59
	5	0.11	1.3	2.1	25	5.2	63	8.3	3.5	42
	3	0.07	1.3	2.0	36	5.2	95	5.5	2.1	38
18,400	11	0.28	--	--	--	5.7	--	--	--	--
	9	0.17	--	1.45	--	3.1	--	--	12.5	--
	7	0.11	2.0	1.45	27	2.6	48	5.4	2.9	54
	5	0.07	1.7	1.45	36	2.2	55	4.0	1.3	32
	3	0.04	1.3	1.45	45	2.0	63	3.2	0.8	25

With 0.10N NaCl Present

$\langle M \rangle_w$	pH	CFC		SC		RC		$\frac{C_M}{No.}$	$\frac{C_Q}{No.}$
		No.	$\theta, \%$	No.	$\theta, \%$	No.	$\theta, \%$	No.	No.
1,760	11	2.22	1.8	21.	17	122.	100	122.	--
	9	0.22	0.24	9.5	11	90.	100	90.	123.
	7	0.22	0.39	5.0	9	57.	100	57.	60.
	5	0.20	0.59	3.7	11	34.	100	34.	42.
	3	0.15	0.71	3.7	18	21.	100	21.	33.
7,200	11	0.24	0.94	2.9	11	25.	98	25.6	--
	9	0.08	0.31	2.6	10	9.0	35	25.5	30.
	7	0.07	0.30	2.0	9	5.7	25	23.	15.
	5	0.06	0.50	1.4	12	8.6	72	12.	10.
	3	0.05	0.54	0.9	10	9.0	98	9.2	8.2
18,400	11	0.06	--	1.45	--	5.1	--	--	--
	9	0.04	--	1.45	--	5.1	--	--	12.
	7	0.04	--	1.0	--	5.1	--	--	5.8
	5	0.03	--	1.0	--	5.1	--	--	4.1
	3	0.03	0.38	1.0	16	5.2	83	6.3	3.2

^aDosage required to give a total overall balance of cationic charges due to PEI and anionic charges due to silica.

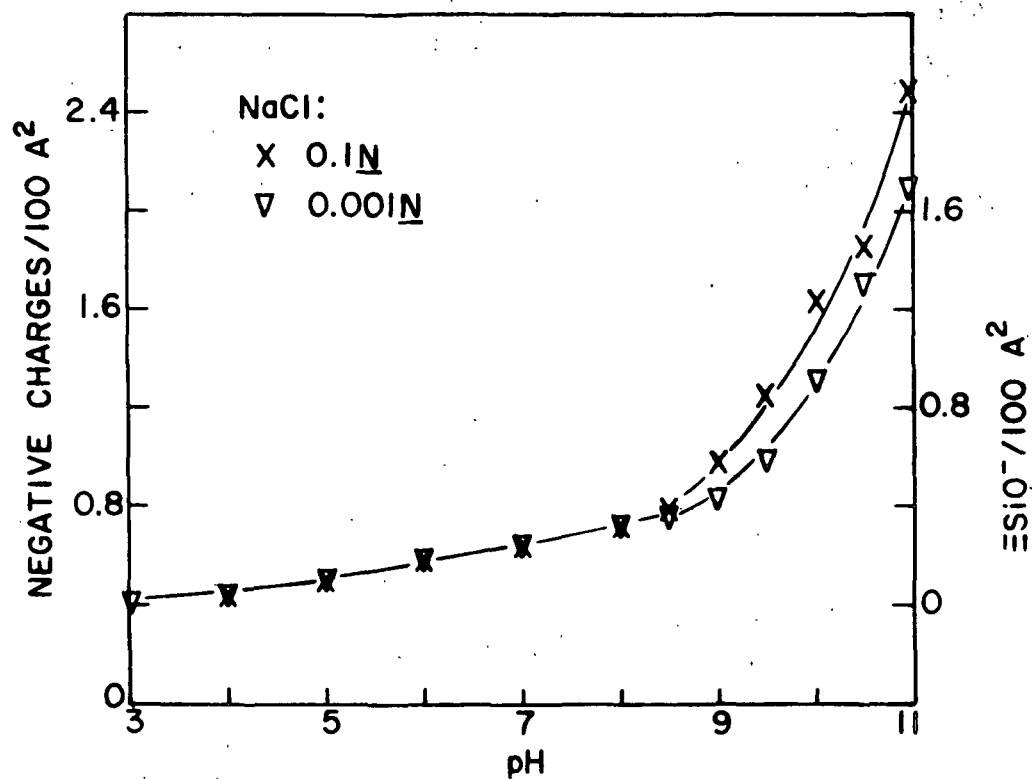


Fig. 1. Surface charge density of Ludox AM as a function of pH and ionic strength.

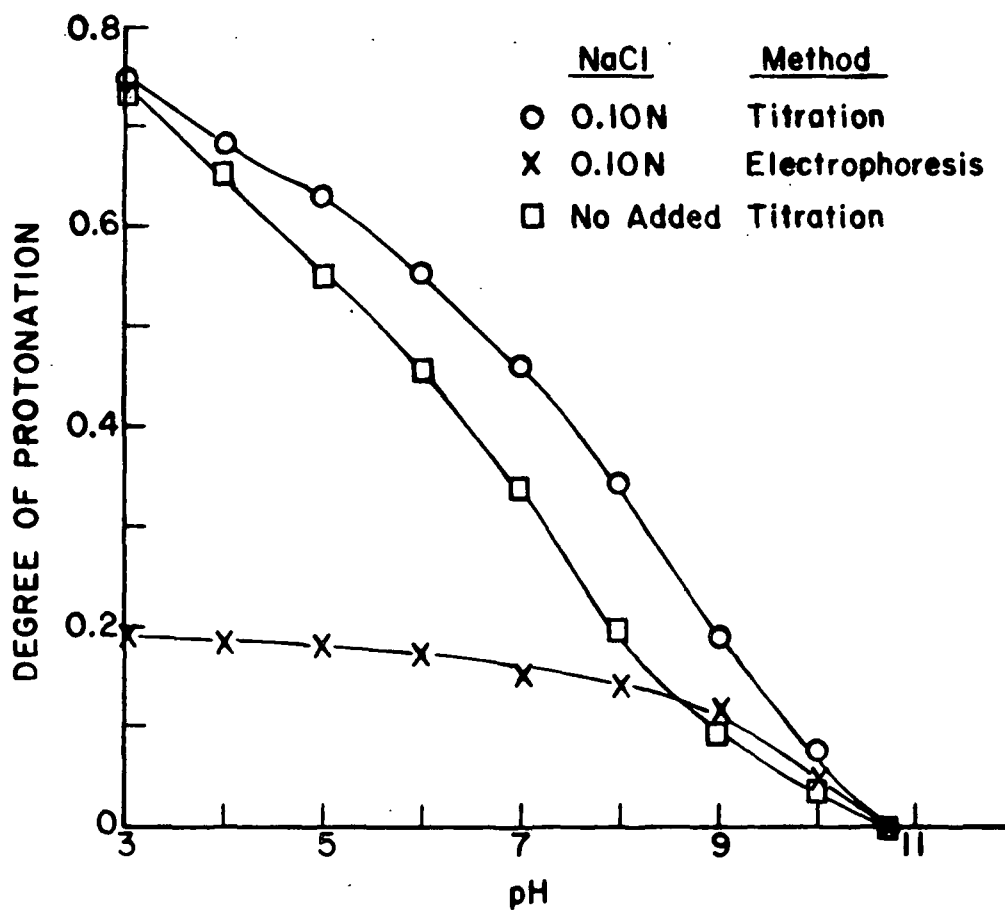


Fig. 2. Decimal fraction of amine groups protonated as a function of pH.

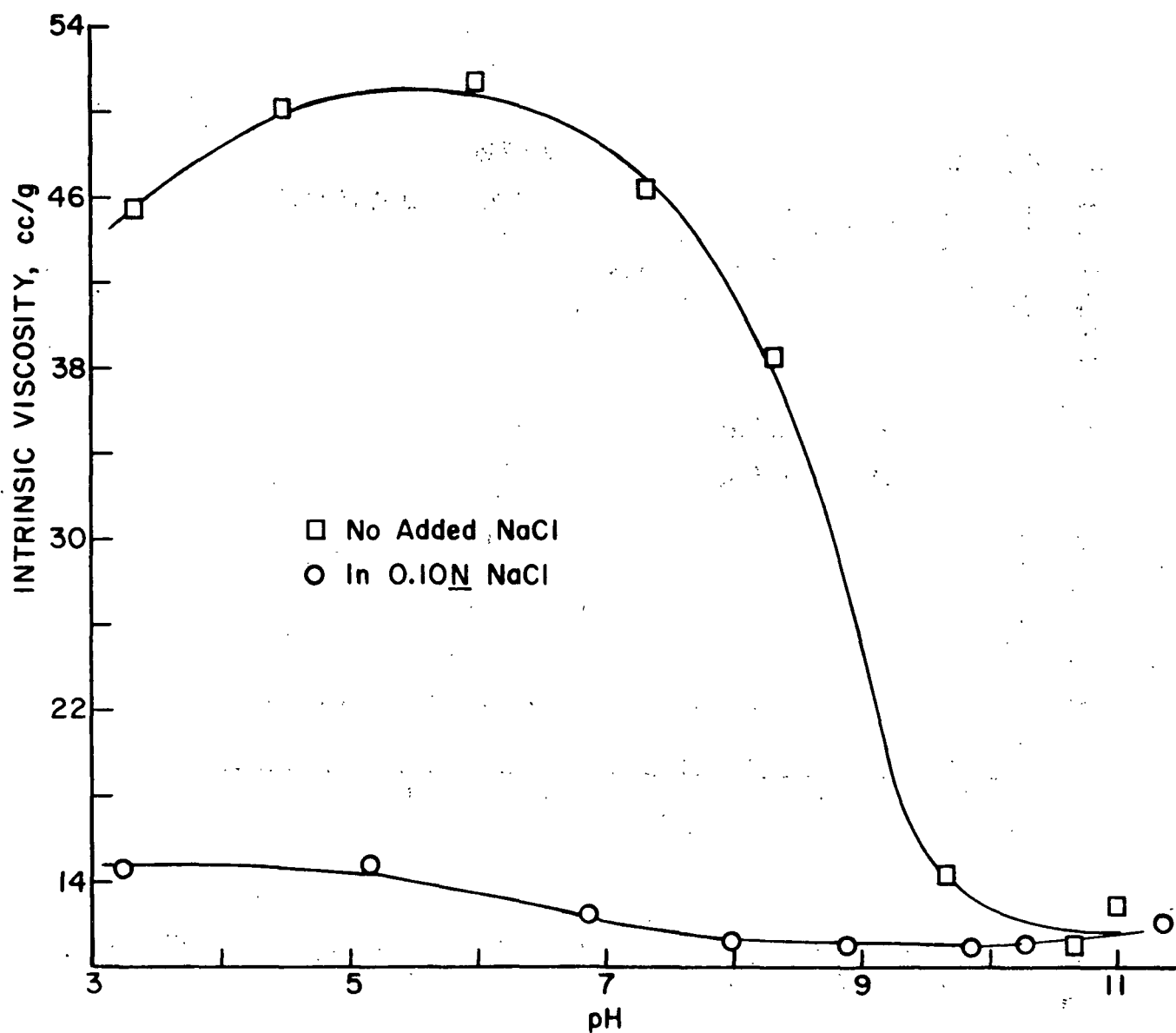


Fig. 3. Intrinsic viscosity of PEI as a function of pH and ionic strength.
 $\langle M \rangle_w = 7,200$.

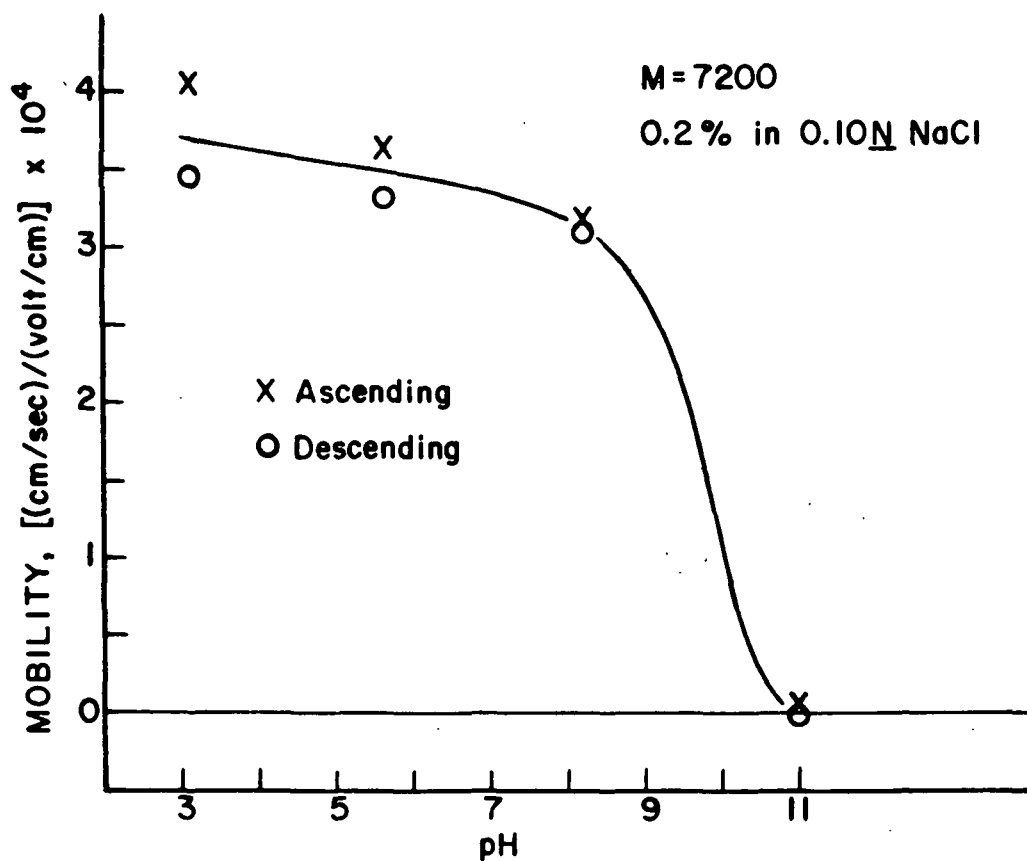


Fig. 4. Electrophoretic mobility of PEI F-5 ($\langle M \rangle_w = 7,200$) in 0.10N NaCl as a function of pH.

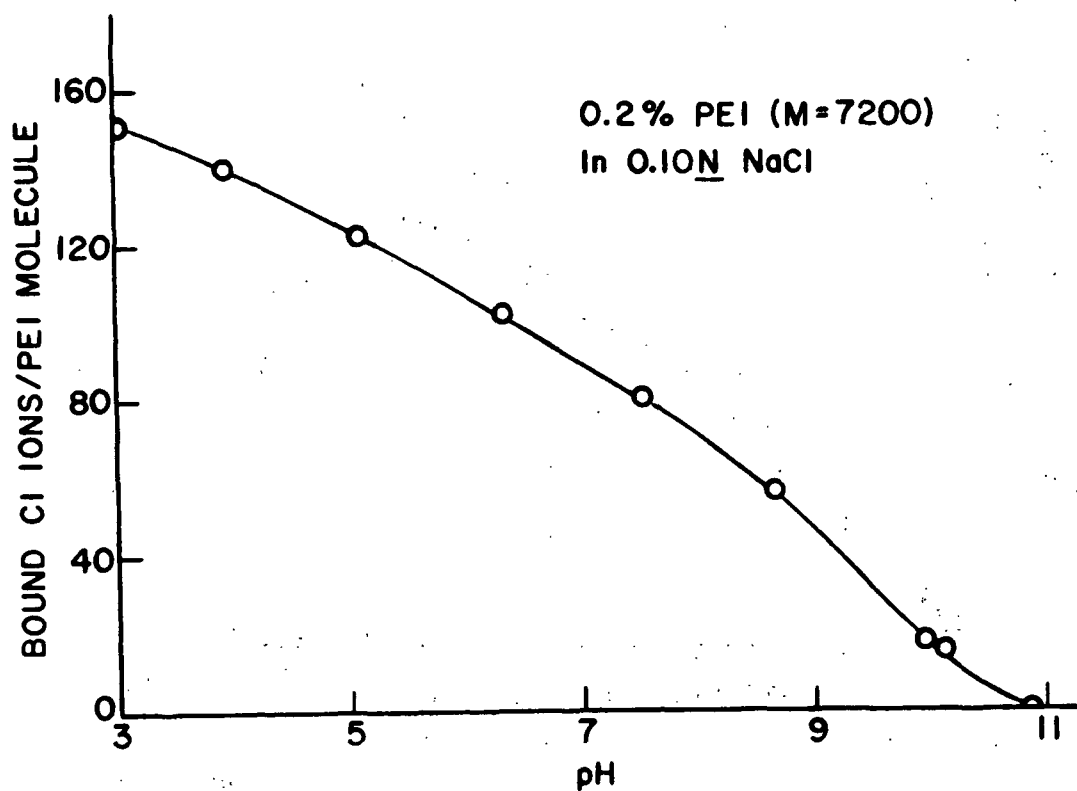


Fig. 5. Chloride binding on PEI.

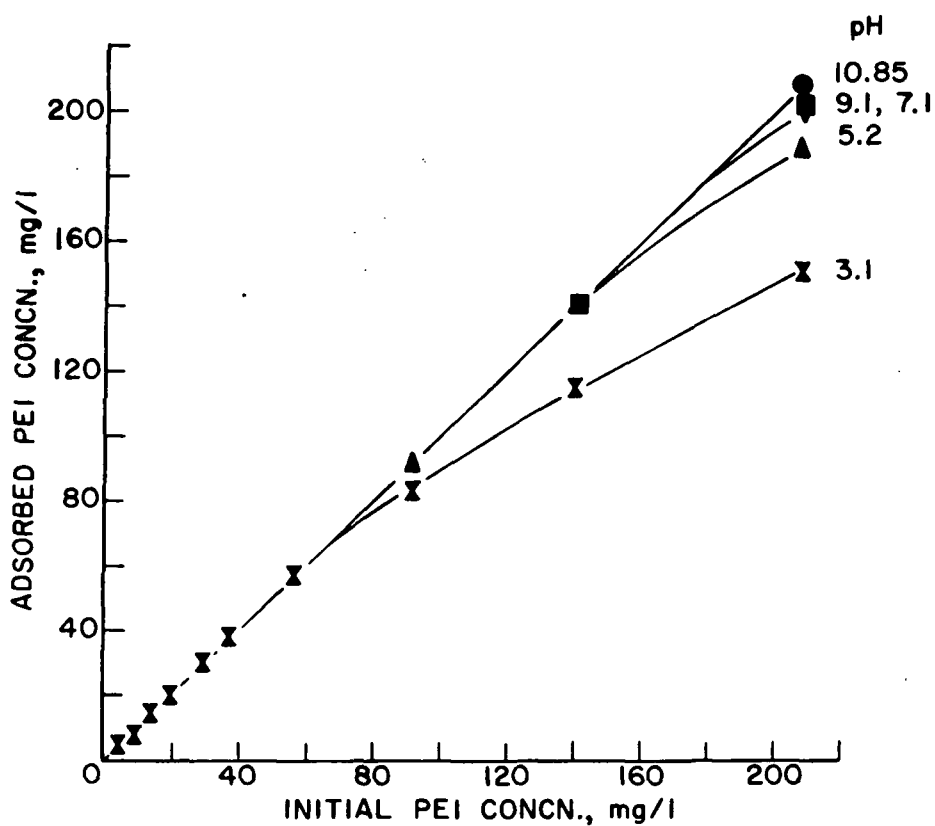
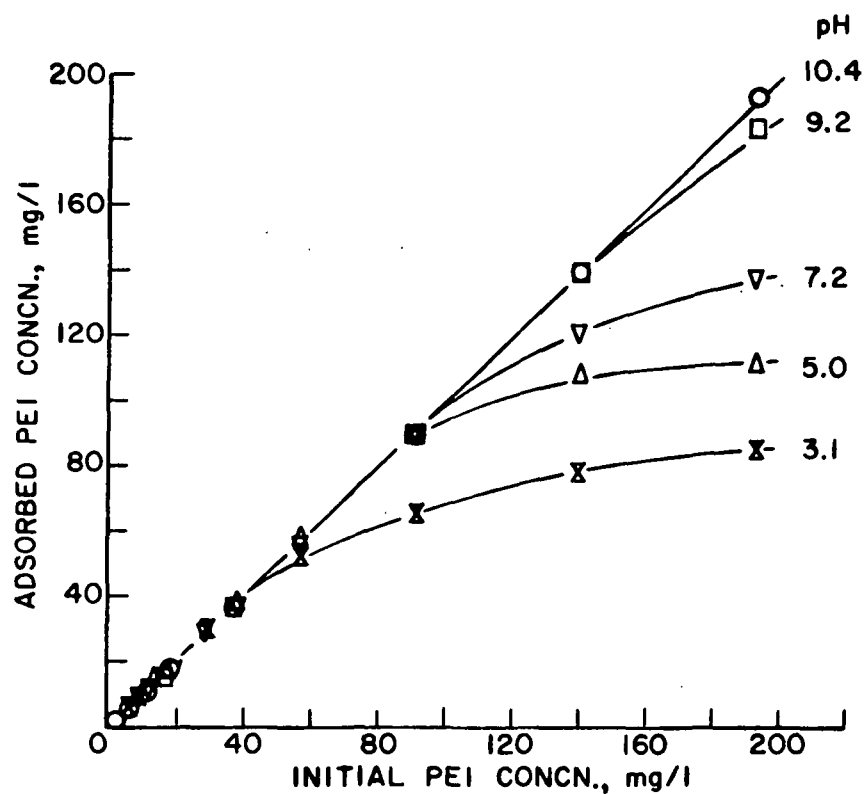


Fig. 6. Adsorption of PEI ($\bar{M}_w = 18,400$) on Ludox AM; open symbols for no added NaCl; shaded symbols in presence of 0.10N NaCl.

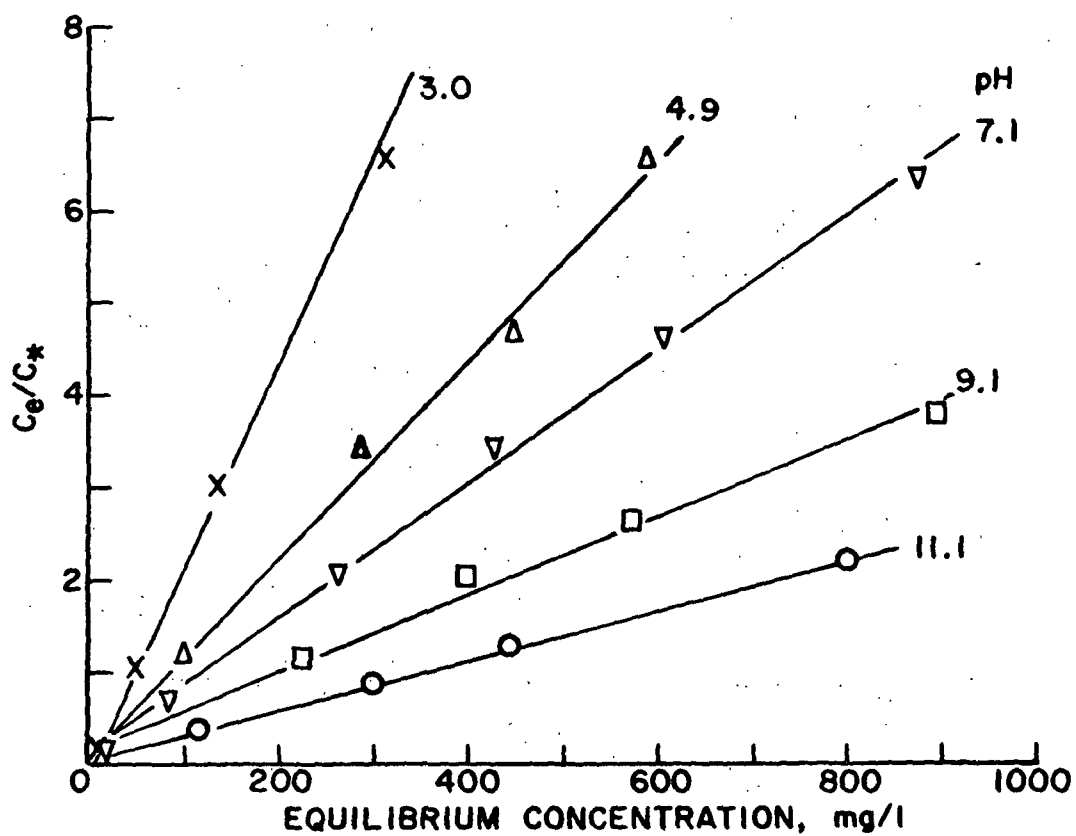
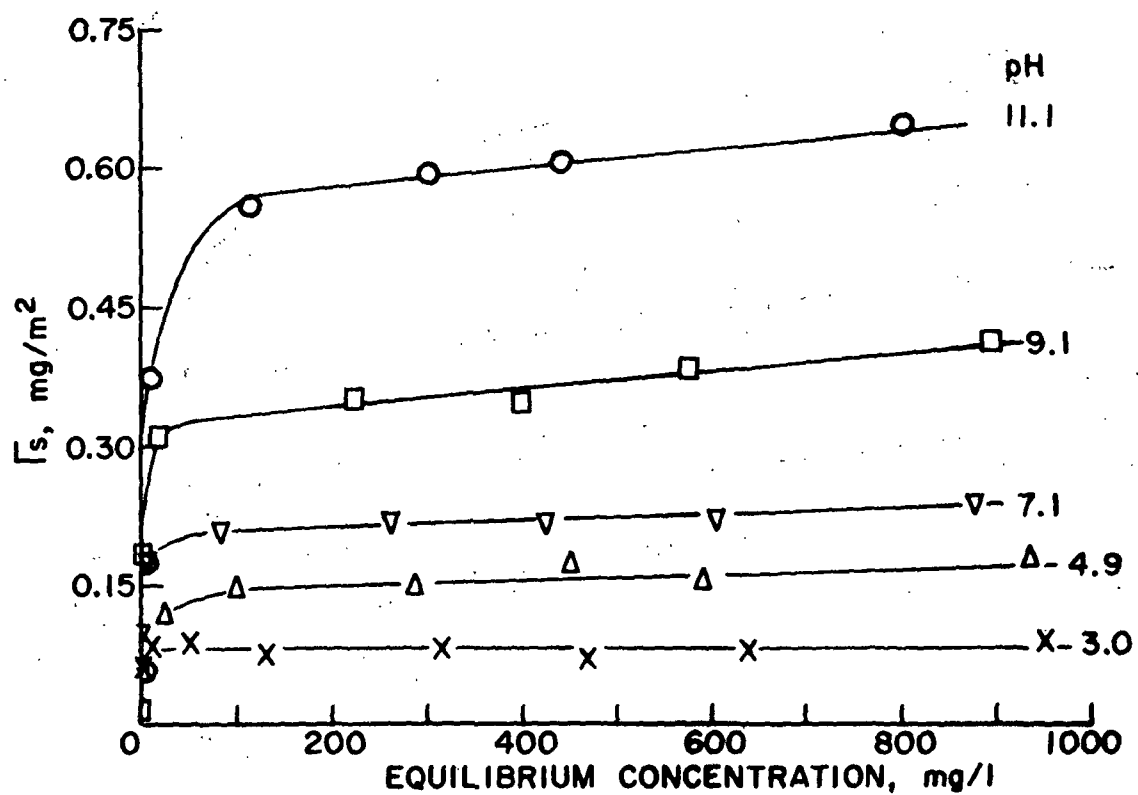


Fig. 7. Equilibrium adsorption isotherms - effect of pH. $\langle M \rangle_w = 7,200$, no added NaCl.

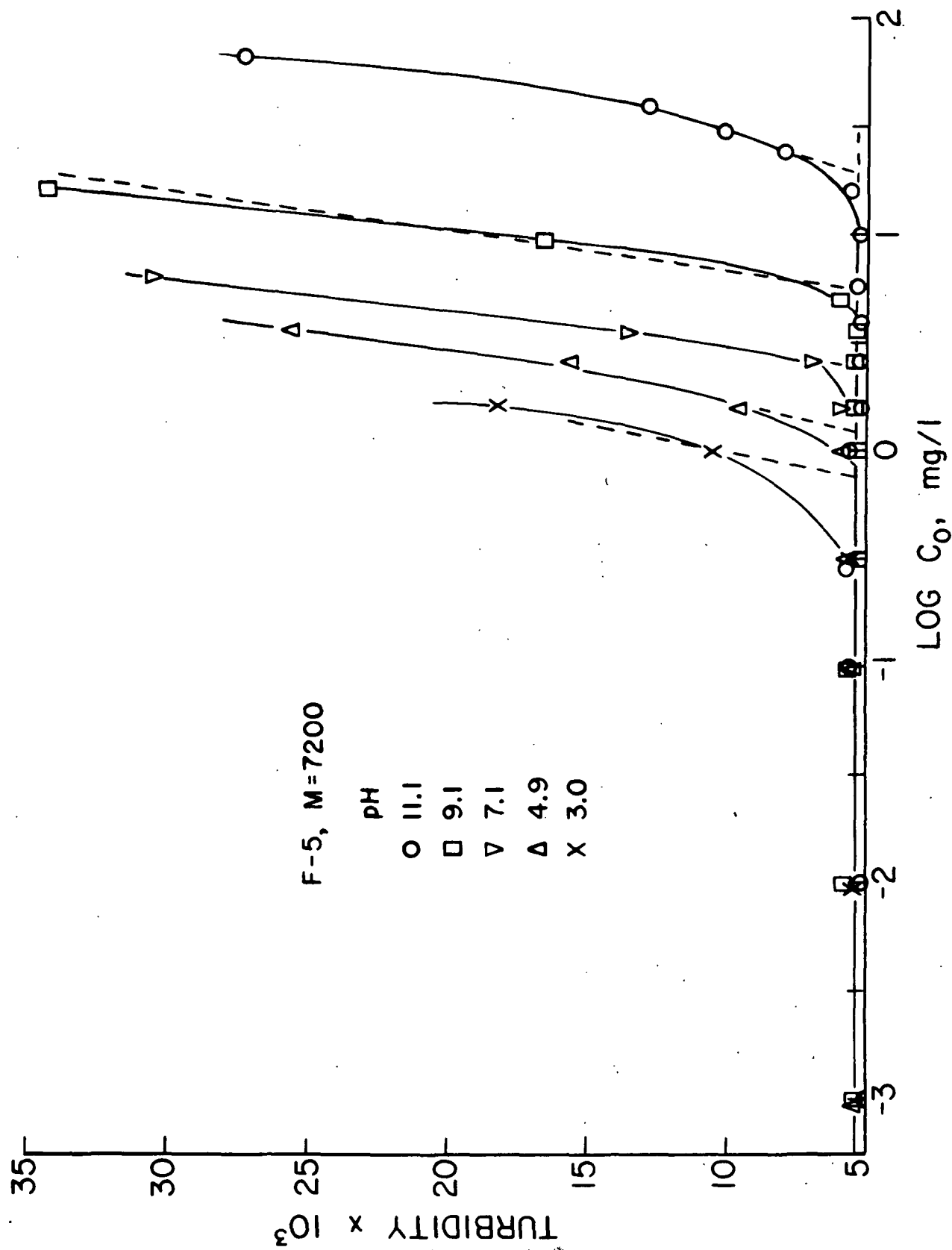


Fig. 8. Turbidity versus log. Initial PEI concentration.

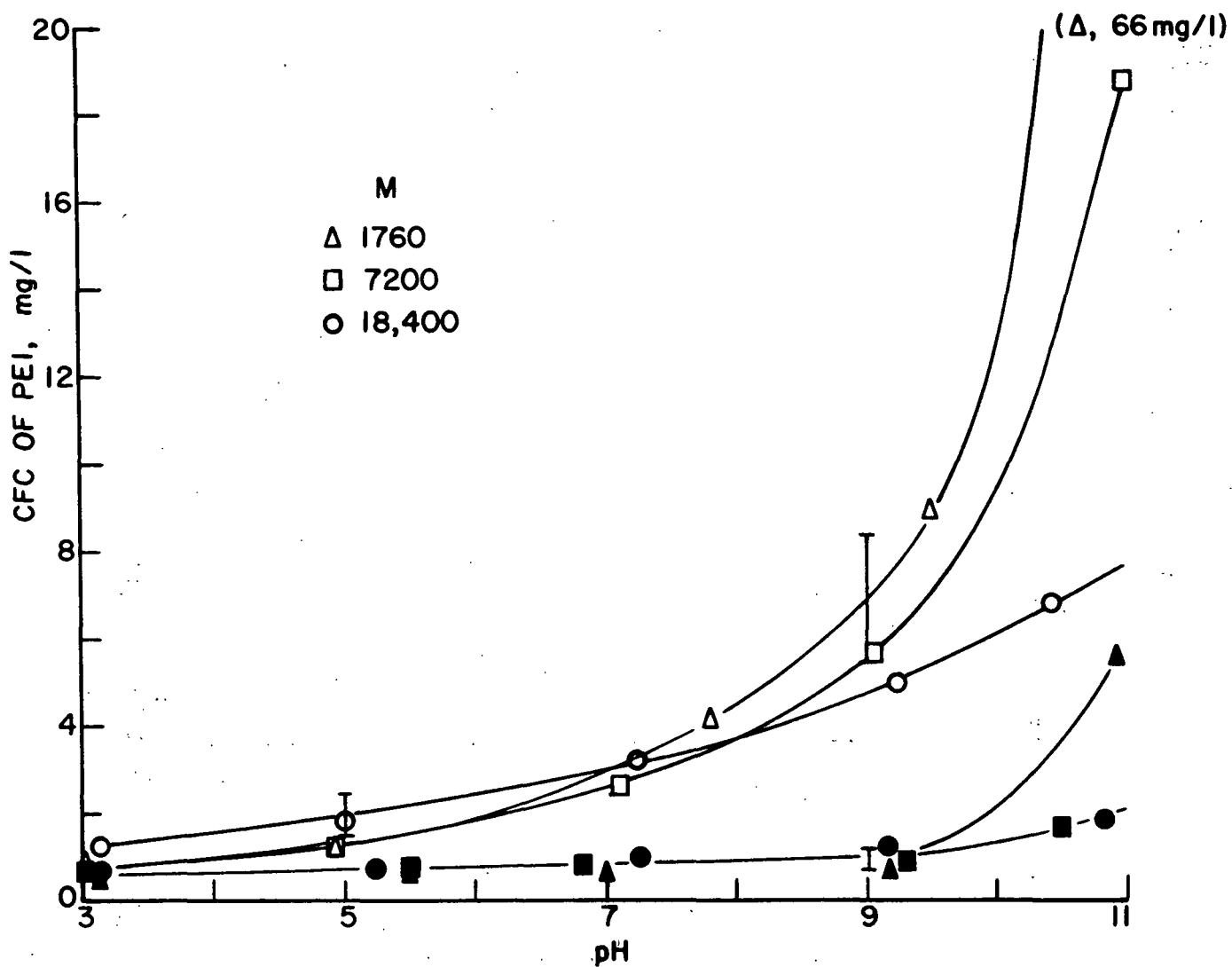


Fig. 9. Effect of pH and ionic strength on CFC; open symbols denote no added NaCl; shaded symbols denote presence of 0.10N NaCl. Vertical bars indicate error limits in estimation of CFC.

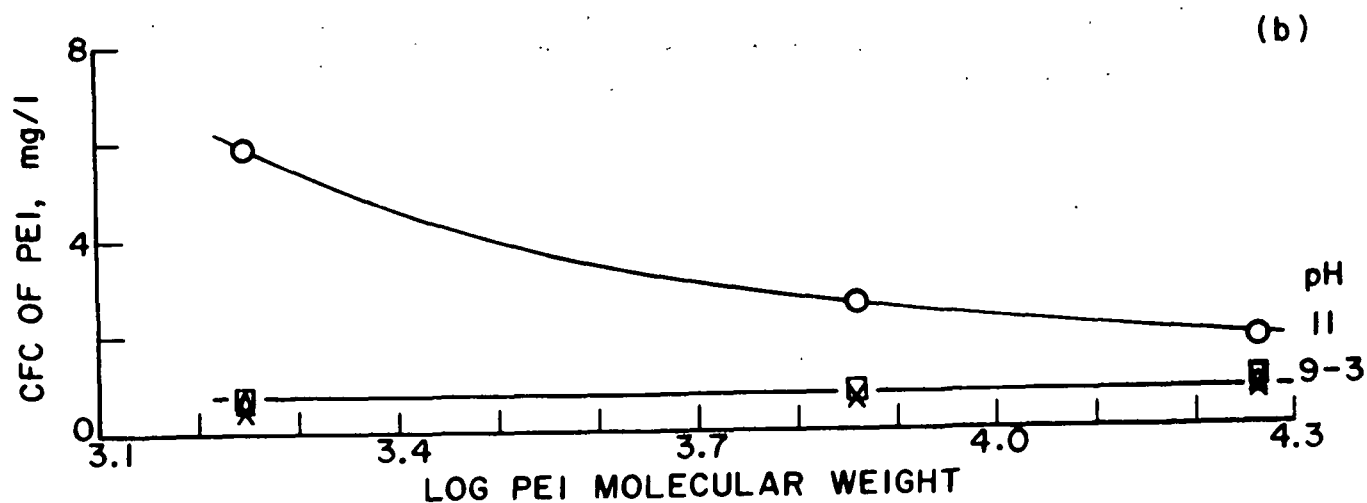
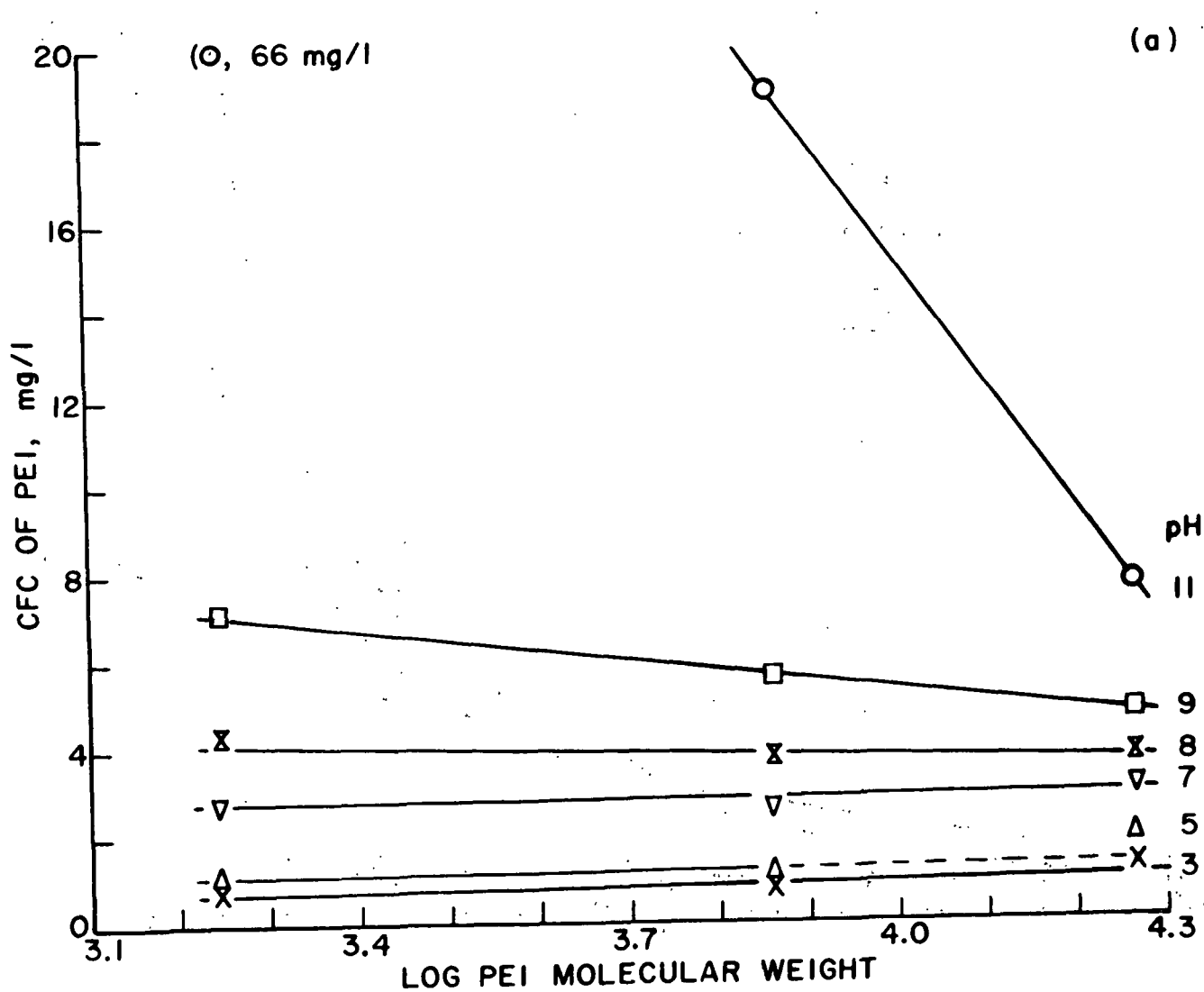


Fig. 10. Effect of PEI molecular weight on CFC (weight basis) of PEI at various pH values. Figure 10a: no added NaCl; Figure 10b: in presence of 0.10N NaCl.

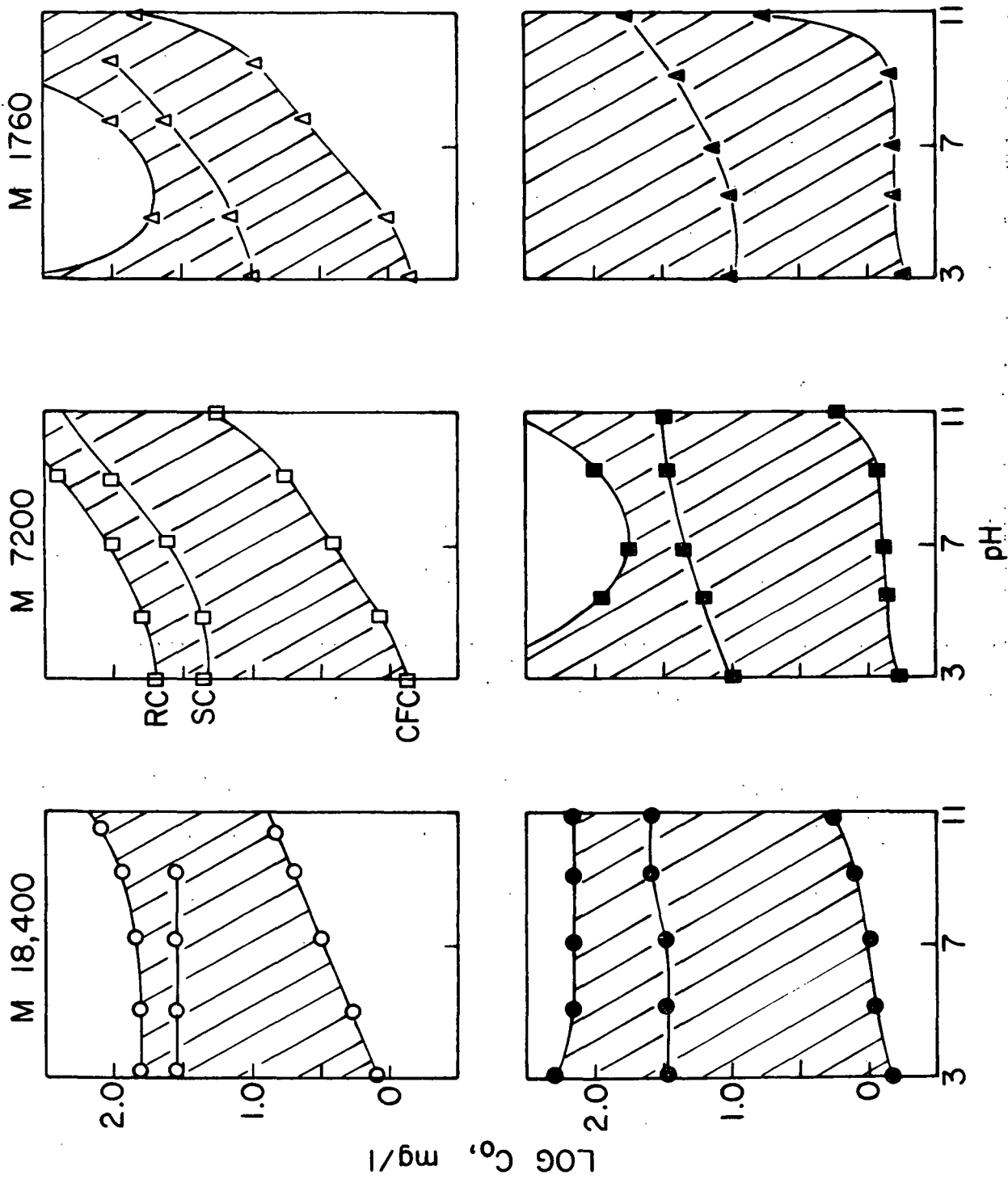


Fig. 11. Flocculation domains of 0.30% Ludox AM toward PEI for conditions studied. Top three plots are in no added NaCl; bottom three are in presence of 0.10N NaCl; hatched area is the flocculation region.

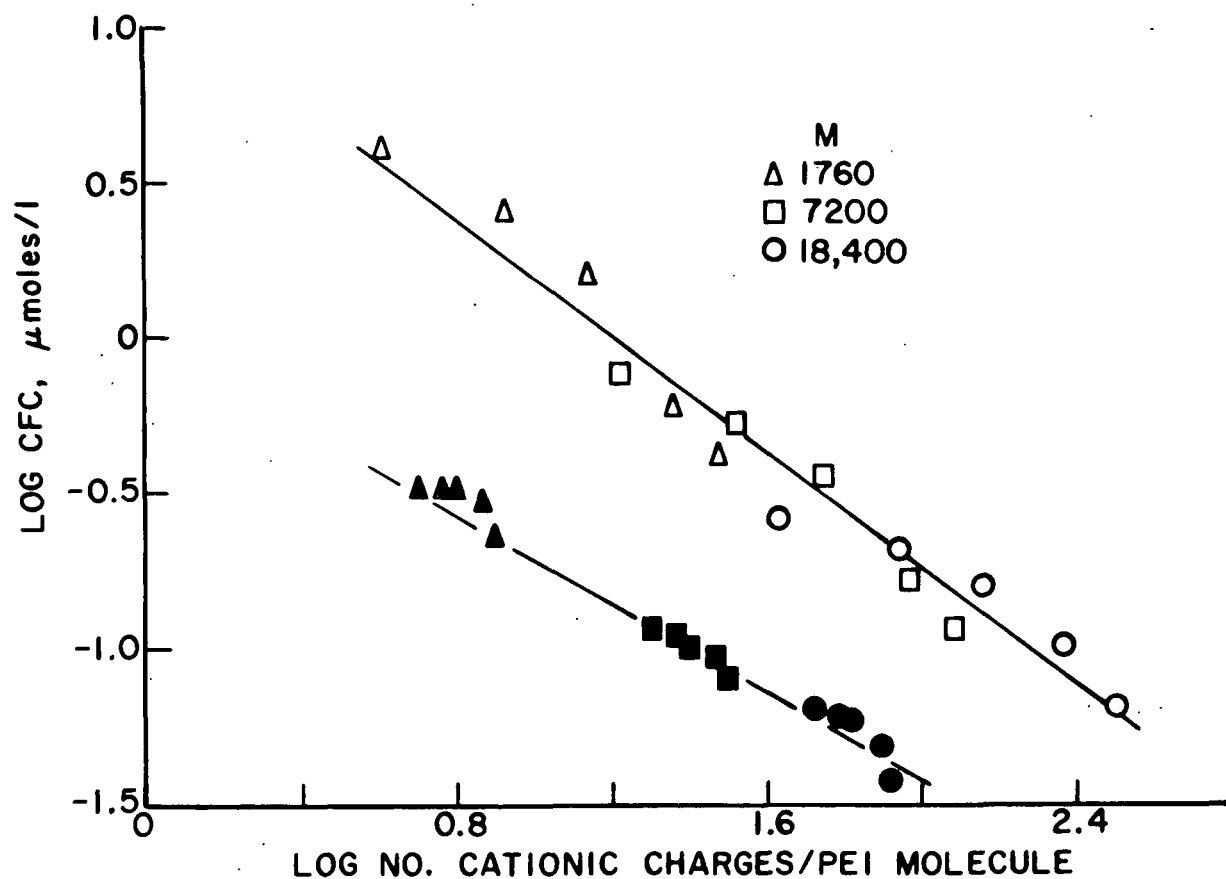


Fig. 12. Log cationic charge of the PEI molecule versus the log CFC of PEI (expressed as moles of polymer/liter); open symbols denote no added NaCl; shaded symbols denote presence of 0.10N NaCl.