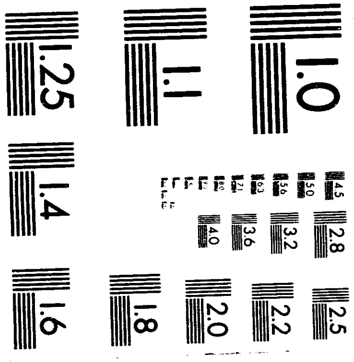
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UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

AN EQUILIBRIUM MODEL FOR LIGAND-MODIFIED MICELLAR-ENHANCED ULTRAFILTRATION

SELECTIVE SEPARATION OF METAL IONS USING IMINOACETIC SUBSTITUTED POLYAMINES

AND

A THEORETICAL MODEL FOR THE TITRATION BEHAVIOR OF POLYAMINES

A DISSERTATION
SUBMITTED TO THE GRADUATE FACULTY
in partial fulfillment of the requirements for the
degree of
DOCTOR OF PHILOSOPHY

BY
UDENI RAJARATNA DHARMAWARDANA
Norman, Oklahoma
1992

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ABSTRACT

This text consists mainly of three chapters, the first two chapters aiming at developing an economical and efficient method to remove metal ions selectively from an aqueous stream. Chapter 3 consists of some fundamental investigations carried out to model the titration behavior of polyelectrolytes.

Chapter 1

An equilibrium model for ligand-modified micellar enhanced ultrafiltration

In chapter 1, the Ligand-Modified Micellar Enhanced Ultrafiltration (LM-MEUF) method has been investigated using the semi-equilibrium-dialysis (SED) method, with N-n-dodecyl iminodiacetic acid as the ligand. A theoretical model has been formulated based on certain reasonable assumptions. The model fits quite well with the experimental results. The model predictions have been compared with the results of previous ultrafiltration studies. Using this model many important features of LM-MEUF, such as the ion-expulsion effect and salt effect, have been discussed. Additional theoretical and experimental studies have been described to investigate the possibility of recovering the ligands used in the separation. The results suggests that a cationic surfactant with a ligand such as N-n-dodecyl iminodiacetic acid will be ideal for the LM-MEUF process. This model can be used to make predictions about the performance of the system.

Chapter 2

Selective separation of metal ions using iminoacetic substituted polyamines

Polyamines with a substituted ligand group have been synthesized and used in investigating selective separation of copper ions from aqueous solution. Here, the investigations have been carried out using the equilibrium dialysis technique, in dialysis cells used for semi-equilibrium dialysis work. Although such ligand-substituted polymers in metal ion separations have been studied previously, most studies have been limited to investigating the types of possible ligands and carrying out ultrafiltration studies to test their applicability. None of the work relates to problems in obtaining selectivity. However, it has been observed that the expected selectivities are not obtained experimentally. In the present study the emphasis has been placed on obtaining better selectivity and solving the problems associated with it. In addition, a hyperbolic model for binding of metal to the ligand has been proposed and tested, and the limitations have been identified. This work also points out that the dialysis experiments carried out in small 5 mL cells can be used for fundamental investigation of metal binding to a polymer. The Donnan expulsion effect has been observed and modelled for an unbound metal ion, calcium. The osmotic dilution effect has been neglected.

The selectivity has been found to be hindered severely by the presence of salt in the system. An added reagent to enhance the expulsion effect or an additional ultrafiltration cycle to remove excess salt has been proposed. A few ultrafiltration experiments using the stirred cell have been carried out to relate the dialysis results to larger scale runs. The selectivities and separations obtained in these experiments were comparable.

Chapter 3

A theoretical model for the titration behavior of polyamines

A novel approach to explain the titration behavior of polymeric amines based on the binding behavior of counterions has been described. The counterion distribution has been modelled by using Oosawa's two phase theory and the thermodynamic equilibrium of each species between the two phases have been modelled. The model predicts experimental results very accurately within a certain range of concentration of the polymer. The initial charge parameter and the intrinsic dissociation constant of the protonated amine sites were kept constant.

CHAPTER 1

AN EQUILIBRIUM MODEL FOR LIGAND MODIFIED MICELLAR ENHANCED ULTRAFILTRATION

1.1 INTRODUCTION

1.1.1 Toxic metal pollutants in waste water

Ground and surface water pollution is a vital problem in almost every country. Large volumes of contaminated wastewater are produced daily by industry. Inexpensive and efficient methods of water purification are needed and improvements of existing methods have to be made to suit new requirements. The Environmental Protection Agency (EPA) of the United States has quite recently assessed(1) the hazards caused by the elements Sb, As, Be, Cd, Cr, Cu, Pb, Hg, Ni, Se, Ag, Tl and Zn as toxic pollutants, in addition to the radioactive elements. When these metal ions are present at excessive levels in an aqueous discharge, the stream remains unusable due to the adverse effects associated with consumption. Cd, Cu, Pb, Hg, Ni, Ag and Zn are the heavy metals in this group normally present in cationic form. The predominant anionic forms of metal pollutants are arsenate, chromate, complex cyanides, and selenate. A list of health effects associated with some of these toxic metals and the drinking water regulations are listed in table 1.1.1.

Table 1.1.1 List of some toxic metals, associated health effects and the drinking water regulation standards.

Metal	Drinking Water Regulation(mg/L)	Health effects
As	0.05	kidney, liver, bone dysfunction
Cd	0.01	kidney, liver, bone dysfunction carcinogen.
Cr	0.05	kidney damage, nausea, ulcers.
Cu	1.0	undesirable taste
Pb	0.05	brain damage on accumulation
Hg	0.002	liver damage and circulatory collapse
Se	0.01	same as Arsenic
Ag	0.05	tissue accumulation
Zn	5.0	undesirable taste

1.1.2 Separation of metal pollutants from aqueous solutions

One method to separate metal ions from solution is to use ion-exchange resins(2), where the target metal ion is bound to a specific resin, by passing the solution through a column packed with the resin. In a subsequent process a solution at a particular pH is passed through the column to recover the ligand. This recovery process is called elution and the pollutant metal ion is collected with the eluent. Such ion-exchange processes occur in a heterogenous medium and therefore the overall process can become inefficient and costly.

In addition to the ion-exchange processes, several membrane based separation techniques which are carried out in an homogeneous solution have been developed to remove undesired constituents from aqueous streams. Some of the commonly cited techniques are listed below.

1. Micellar-enhanced ultrafiltration (MEUF)(3,4,5)
2. Chelation in combination with ultrafiltration(2)
3. Reverse osmosis(6)
4. Charged membrane ultrafiltration(7)
5. Coupled membrane transport(8)

The work described in this text is mainly related to MEUF, which consists of a number of related methods where the separation is achieved by adding a surfactant to the stream prior to ultrafiltration.

1.1.3 Micellar-enhanced ultrafiltration (MEUF)

Micellar-enhanced ultrafiltration (MEUF) is a separation technique which has a great potential for application in various waste water treatment processes. In the MEUF process, a surfactant is added to the wastewater stream, at concentrations well above the critical micelle concentration (CMC) under conditions such that the surfactant remains mainly in the micellar form. The kind of surfactant being added is selected so that most of the organic pollutants or the multivalent ionic species in the waste water are solubilized by or bound to the surfactant micelles. The mechanism of solubilization greatly depends upon the surfactant structure and the structure of the solubilizate(9). In the subsequent ultrafiltration, performed with a membrane of appropriate pore size, the micelles together with the solubilized contaminants are separated from the main stream. The water coming out through the membrane, called the permeate, is almost free of contaminants, whereas the retained solution, called the retentate is concentrated with the contaminants and the surfactant.

Although theoretically MEUF is satisfactory for removing most contaminants from waste water streams, there exist some practical problems. For example, in MEUF there is the possibility that the surfactant monomers will pass through the membrane at high enough concentrations to pollute the water stream. To some extent this can be avoided by using non-toxic surfactants and surfactants having CMC values as low as possible. It is also possible to add suitable reagents such as polymers or salts which lower the CMC of surfactants. However, there are limitations to the effectiveness of such strategies.

Despite these problems MEUF has been applied for removal of organics and multivalent charged species from water, and these results have shown excellent separations(3,4,5). In addition to the MEUF applications, surfactant micelles have been used to expel ions of similar charge from the retentate solution to the permeate. In all of these ion separation processes the separation is based on the ionic charge and therefore little selectivity can be achieved among ions of the same charge. However, it is sometimes desirable to have one metal ion separated from the waste stream in preference to another having the same charge. By introducing such selectivity for separation one should be able to make the overall process more cost-efficient by not having to separate non-toxic ions from the stream. The Ligand-Modified Micellar-Enhanced Ultrafiltration method that has been developed(10,11) and investigated in present work is designed to achieve the selective separation of metal ions, so that only the targeted constituent is removed.

1.1.4 Ligand-modified micellar-enhanced ultrafiltration (LM-MEUF)

In LM-MEUF a surfactant is used as in MEUF, and a ligand is solubilized in the surfactant micelles. Therefore, these surfactant micelles now act as active centers for specific metal ion-binding. The type of ligand to be used can be varied depending upon the target metal ion of interest. Next, the system is subjected to ultrafiltration as usual. The metal ion bound to the micelles via the ligand remains in the retentate solution, while the unbound ions are free to pass through the membrane. One important feature of the LM-MEUF is the pH dependence of the separation, for ligands exhibiting pH-dependent metal binding behavior. This can be advantageous in the LM-MEUF process, enabling the recovery of used ligand or micelle-solubilized-ligand by lowering the pH. However, for optimum metal-complexation it is often desirable to work at a pH of 5 to 7, which may be easily achieved with natural wastewater streams. The operation of LM-MEUF is explained by the schematic diagram shown in figure 1.1.1.

To understand the LM-MEUF and related processes, it is necessary to have a clear understanding of the behavior of the surfactants used.

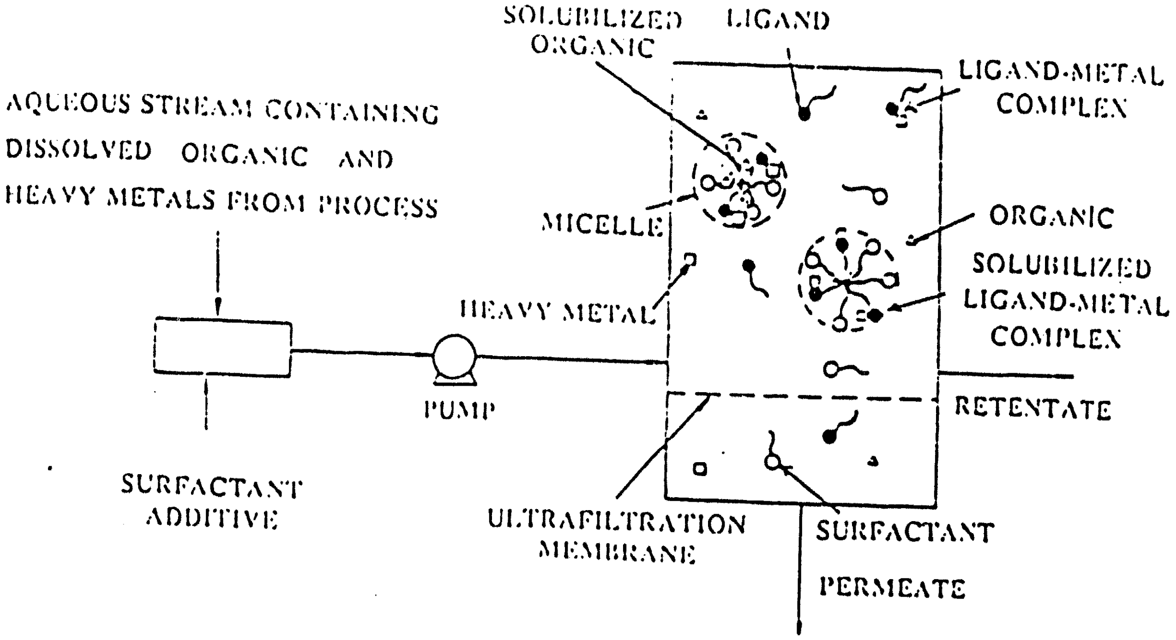


Figure 1.1.1 Schematic representation of LM-MEUF separation process(10)

1.1.5 Behavior of surfactants

The principal physical and chemical properties of surfactants are described in many articles and books(9,12). The surfactant molecules (called amphiphilic molecules) consist of a hydrophobic tail, and a hydrophobic head group, and are capable of forming aggregates called micelles, beyond a certain concentration called the critical micellar concentration or CMC. The effects of micelle formation can be observed by studying changes in properties of the surfactant solution, such as surface tension, electrical conductivity, density, viscosity, etc. These surfactant aggregates are more stable than the single molecules distributed in the solution, because in the aggregates, the hydrophobic tails are in a favorable organic environment, while the hydrophilic heads are exposed to the aqueous environment. Thus surfactant aggregation or micellization can be a thermodynamically favorable process. The head group-head group repulsion in the case of ionic micelles is one important force opposing micellization. The existence of a CMC may be a consequence of cancellation of these opposing forces.

In general micelles have an average radius of 12 to 30 Å and consist of 50 to 100 or more monomers. The hydrophobic tail groups form a hydrocarbon-like micellar interior, which can dissolve non-polar organic molecules, while the hydrophilic head groups and some of the counterions of the ionic micelle are located in a compact layer known as the Stern layer, extending a few Å from the shear surface of the micelle. However, many of the counterions are located outside the Stern layer, forming the Gouy-Chapman electrical double layer, where they are in rapid equilibrium with the ions in the bulk of the solution(13).

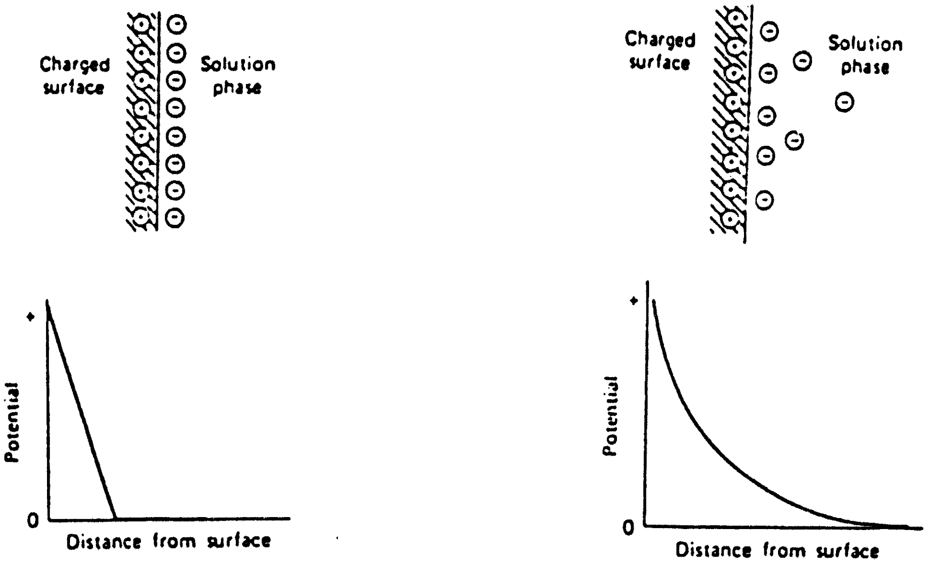
A surfactant molecule may be non-ionic, cationic, anionic, or zwitterionic. The most commonly used non-ionic surfactants contain polyoxyethylene or polyoxypropylene chains, often linked to alcohols or phenols containing long alkyl chain substituents. In nonionic surfactants, the absence of head group-head group repulsion makes the micellization process more favorable compared with the ionic surfactants. The most common anionic surfactants are the carboxylates, sulfates, or sulfonates of long chain alkyls, with alkali metal counterions. The cationic surfactants are usually long chain hydrocarbon quaternary amines or pyridines with halide counterions.

Solubilization of an organic compound or the hydrocarbon moiety of a compound is related to micellization. The solubilized compound or the hydrocarbon group interacts with the organic interior, and little or no solubilization is observed until the CMC is reached. Similarly, solubilization of organics with a hydrophilic moiety, which may otherwise be insoluble or sparingly soluble, may occur due to the interaction between charged groups of the micelles and the solubilizate. In most instances both the hydrophobic and the hydrophilic groups in the micelles may take part in solubilizing an organic compound(9,14). However, the nature of the solute as well as the surfactant, and the nature of the medium, the presence of electrolytes in the solution, and the temperature are some parameters which affect the solubilization.

The solubilization phenomenon is of practical importance in detergency, enhanced-oil recovery, catalysis, and in separation methods such as micellar enhanced ultrafiltration (MEUF). In Ligand Modified Micellar-Enhanced Ultrafiltration, which is investigated in this research, an important requirement for the process is solubilization of a ligand in surfactant micelles. General features of micellar solubilization have been described by McBain, Hutchinson, and Elworthy(15). As a result of solubilization the shape of the micelles may be changed. In general, a micelle at comparatively low surfactant concentrations takes a spherical shape(9) but by incorporation of the solubilizate it is possible to deform this spherical structure. To further understand the solubilization and the behavior of counterions, the electrical nature of the surfactant surface has to be clearly understood.

1.1.6 Electrical double layer(9,16)

At any interface there is always an unequal distribution of electrical charges between the two phases, causing one side of the interface to be charged positively and the other side negatively. This gives rise to a potential barrier across the interface, called the electrical double layer. Helmholtz viewed the counterions as being lined up parallel to the charged surface at a distance of about one molecular diameter. According to this theory the potential should fall off rapidly to zero at a very short distance from the charged surface. Helmholtz treated the electrical double layer as a parallel plate condenser. Some of the drawbacks of this model were overcome by the model proposed by Gouy and Chapman, in which the distribution of the counterions in a diffuse layer was considered instead of a fixed ionic layer. The Helmholtz and Gouy-Chapman model are shown schematically, in figure 1.1.2.



(a) (b)

Figure 1.1.2 Schematic representation of (a) Helmholtz and (b) Gouy-Chapman models of electrical layer[9].

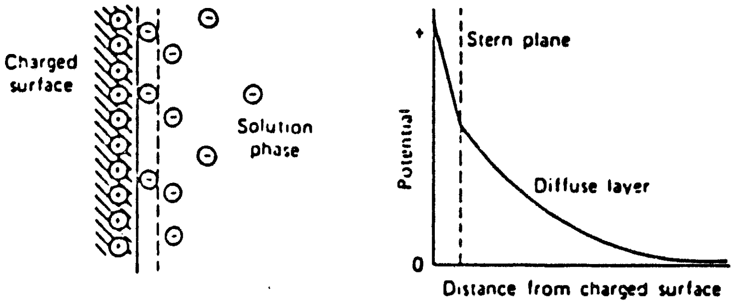


Figure 1.1.3 Schematic representation of Stern model of electrical layer[9]

The above model was further modified by Stern, who divided the solution side of the double layer into two parts.

1. A layer of strongly held counterions, adsorbed close to the charged surface in fixed sites.
2. A diffuse layer of counterions similar to that envisioned in the Gouy-Chapman model.

The Stern model can be understood schematically, as is shown in figure 1.1.3.

1.1.7 Debye length(9,16)

An important parameter derived from the mathematical treatment of the electrical double layer is the Debye length, which is the distance from the charged surface into the solution within which the major portion of electrical interactions with the surface can be considered to occur. The Debye length is inversely proportional to the valence of the ions in the solution phase, and inversely proportional to the square root of their concentration, in the solution. It is also directly proportional to the absolute temperature and the dielectric constant (permittivity) of the medium.

Therefore it is expected that in a solvent of high dielectric constant such as water, the electrical effects extend much further into the solution phase than in a solvent of low dielectric constant such as a hydrocarbon. On the other hand, in the presence of an electrolyte the electrical effects have shorter ranges than in its absence, so that the electrical double layer is compressed. For example, for a 1:1 electrolyte at room temperature in aqueous solution, the Debye lengths in Å, are 3 for 1M, 10 for

.01M, 100 for 0.001M and 300 for 0.0001M solutions.

1.1.8 Micellar structure and shape

Major types of micelles that are found in a surfactant solution are(9)

1. Relatively small spherical micelles with aggregation number less than 100
2. Elongated cylindrical rodlike micelles.
3. Large flat lamellar micelles.
4. Vesicles (spherical structures consisting of lamellar micelles arranged in one or more concentric spheres.

As the surfactant concentration increases, micelles tend to go from spherical micelles to cylindrical rodlike micelles or large flat lamellar micelles or sometimes vesicles.

1.1.9 Counterions around the micelles(9)

In ionic micelles, the aqueous solution-micelle interfacial region contains the ionic head groups, the Stern layer of the electrical double layer pertaining to these groups, more than half of the counterions associated with the micelle, and water. The remaining counterions are contained in the Gouy-Chapman portion of the double layer that extends further into the aqueous phase. In non-ionic surfactant micelles the structures are essentially the same except that the outer region contains no counter-ions, but includes coils of hydrated polyoxyethylene or similar chains(9).

The interior region of the micelle containing hydrophobic groups has a radius approximately equal to the length of the fully extended hydrophobic chain. The aqueous phase is believed to penetrate into the micelle beyond the hydrophilic head groups and the first few methylene groups of the hydrophobic chain adjacent to hydrophilic head are often considered to be in the hydration sphere. It is therefore useful to divide the interior region into an outer core that may be penetrated by water and an inner core from which water is virtually excluded.

1.1.10 Micellar aggregation numbers

Micellar aggregation numbers have been determined by light scattering(17), sedimentation rates(18), in the ultracentrifuge, and recently by NMR self-diffusion coefficients(19), small angle neutron scattering (SANS)(20), vapor pressure, and freezing point(21) methods.

Aggregation numbers in aqueous solution increase with increase in the length of the hydrophobic group and also increase with an increase in the extent of binding of counterions to the micelle in ionic surfactants. Addition of a neutral electrolyte to solutions of ionic surfactants in aqueous solution causes an increase in the aggregation number, owing to compression of the electrical double layer surrounding the ionic head groups. Solubilization of a small amount of hydrocarbons or long chain polar compounds generally causes an increase in the aggregation number of the micelle, until the solubilization limit is reached.

1.1.11 Critical micellar concentration

In an aqueous medium, ionic surfactants have much higher CMC's than nonionics containing equivalent hydrophobic groups. Quaternary cationics and pyridinium compounds have smaller CMC's than the corresponding trimethyl compounds, presumably because the packing of the planar pyridinium groups is more favorable than the packing of tetrahedral trimethyl ammonium groups in the micelle.

1.1.12 Counterion binding to the micelle and distribution of counterions

Increased counterion binding in aqueous systems causes a decrease in the CMC. The extent of counterion binding increases with the increase in the polarizability and valence of the counterion, and decreases with an increase in the hydrated radius(9). Therefore, in aqueous medium for anionic dodecyl sulfates, the CMC decreases in the order $Li^+ > Na^+ > K^+ > Cs^+ > Ca^{2+}, Mg^{2+}$. For cationic surfactants the order of decreasing CMC for counterions is $F^- > Cl^- > Br^- > I^-$, which shows that the iodide has the lowest CMC(9).

However, the CMC cannot be correlated with the degree of counterion binding to the micelle in the case of surfactants of different types. The degree of counterion binding to the micelle depends on the surface charge density of the micelle. The greater the surface charge density or the smaller the size of the head groups, the larger will be the extent of counterion binding. The surface area per head group has been shown to decrease with increase in the length of the alkyl chain.

Distribution of counterions around micelles has been treated both qualitatively and quantitatively, in the two phase theory presented by Oosawa(22). A basic assumption of the Oosawa model is that the ratio of concentration of a given counterion in the two regions, in the immediate vicinity of a polyion and in the bulk solution, is given by the Boltzmann equation. Therefore, if β is the degree of dissociation of the polyion (fraction of counterions free), $\delta\psi$ is the average potential difference between the two regions of counterion distribution, ϕ is the volume of the region close to the polymer chain as a fraction of total volume of solution, and k, and T are respectively the Boltzmann constant and absolute temperature, then

$$(\beta/\phi) \, / \, [(1-\beta)/(1-\phi)] = \exp\,[-(e_0\delta\psi)/\,kT]$$

where, e_0 is the electronic charge.

Therefore,

$$\beta/(1-\beta) = \phi/(1-\phi) \, . \, \exp\,[-(e_0\delta\psi)/\,kT]$$

$$\ln\,(1-\beta)/\beta = \ln\,(1-\phi)/\phi + (e_0\delta\psi)/\,kT$$

In Oosawa's equation the second term is further simplified for a spherical polyion such as a surfactant micelle, to give

$$\ln\,(1-\beta)/\beta = \ln\,(1-\phi)/\phi + \beta z P(1-\phi^{1/3})$$

where P is a dimensionless potential parameter and z is absolute value of the counterion charge.

This theory has been successfully applied to model the rejection of chromate ions in the presence of CPC micelles(23), in semiequilibrium dialysis experiments. In addition the effect of added NaCl on the parameter P has been determined and shown to obey the following relationship.

$$P = P^0 / \{ 1 + \alpha[\mathrm{NaCl}]^{1/2} \}$$

where an adjustable parameter α had an optimum value of 23.8 M^{-1} and the value of P in the absence of NaCl (P^0) was 55.1 ± 3.5.

1.1.13 Effect of an added electrolyte

The presence of an electrolyte causes a change in the CMC, the effect being more pronounced in the case of ionic surfactants than with zwitterionics or nonionics. The depression of the CMC merely reflects the compression of the double layer, in the presence of ionic electrolytes, which decreases the repulsion between head groups in the micelle(9).

1.1.14 Semi-equilibrium dialysis(24)(SED)

Semi-equilibrium dialysis experiments are carried out with surfactants, where the surfactants are included in the retentate compartment and pure water is in the permeate at the start. There is a slow transfer of surfactant monomers through the membrane, reflecting the difference in thermodynamic activity of the surfactant between the two compartments. After about 20 hours, the total surfactant concentration in the permeate usually exceeds the CMC by 10 to 30%, and each day after that there is an additional 5 to 10% increase in surfactant concentration in the permeate. But although equilibrium is not reached in the permeate within a reasonable time (weeks or months), small molecules or ions can reach equilibrium with the surfactant solutions on both sides of the membrane. This is the "semi-equilibrium" condition, and analysis of results requires accounting for the interactions of the small solute species with the micelles in both compartments. With careful analysis of SED results, the equilibrium binding of solutes to micelles can be inferred.

1.1.15 Ultrafiltration(UF)$^{(25)}$

Separation of macromolecular solution by filtration under an applied hydrostatic pressure is referred to as ultrafiltration. In general, the term ultrafiltration is used to describe separation involving solutes of molecular dimensions greater than 20 Å in diameter. Separation of particles larger than 1 micron is called filtration. Separation of particles whose molecular dimensions are of the same order of magnitude as those of the solvent is referred to as reverse osmosis. The various filtration processes are different in the applied hydrostatic pressure. In ordinary filtration the applied pressure is less than one atmosphere, in ultrafiltration 1 to 10 atmospheres, and in reverse osmosis, it is 10 to 100 atmospheres. Thus, ultrafiltration encompasses membrane-based, pressure-activated separations involving solutions of medium-molecular-weight (ca 1000 and up) solutes, macromolecules and colloids at hydrostatic pressure between 1 to 10 atmospheres.

The percentage rejection (R) of an ultrafiltration membrane for a certain solute is generally expressed as follows:

$$R = [\ 1 - (C_p/C_f)\ ] \times 100$$

where C_p and C_f are the concentrations of the solute in the product and in the feed solution, respectively.

For most ultrafiltration systems of practical importance, the rejection in ultrafiltration for a given solute, to a first approximation, has been shown to be independent of the applied pressure, whereas the solvent flux is directly proportional to the applied pressure. For economic reasons it is important to have the ultrafiltration rate as high as possible.

Applications of Ultrafiltration

Ultrafiltration can be used for concentration, purification, or separation of large molecules, whose chemical structure and biological activities are likely to be altered by common concentrative procedures such as precipitation, evaporation, or freeze drying. This process can also be used in quantitative analysis, to recover or concentrate specific compounds and to bring them into detectable ranges.

When the mixture to be purified is placed in a membrane cell, and water is forced through the membrane by an applied pressure, the purification is often governed by the relationship(25)

$$C_0 / C_f = \exp (V_f/V_0)$$

where C_0 is the initial impurity concentration, C_f is the final impurity concentration, V_0 is the volume of the initial mixture in the cell, and V_f is the volume of water used to wash.

Separation of two or more species differing in molecular weight can be effected by ultrafiltration if the molecular weight difference is fairly large (perhaps a factor of 10), and if a membrane exists with a proper molecular weight cutoff. As a rule the ultrafiltration membranes in use today have fairly diffuse molecular cutoffs, and therefore it is difficult to obtain a good separation if the molecular weights are close.

Operational problems in Ultrafiltration

A major factor limiting the speed and effectiveness is the buildup of a layer of solute molecules being retained, on the upstream surface of the membrane, during the course of ultrafiltration. This process is called concentration polarization. Since this layer reduces the rate of ultrafiltration, controlling this is very important, and the layer can be diminished to a certain extent by rapid stirring.

1.1.16 Investigation of micelle formation.

The formation of micelles is most widely detected by experimental determination of physical data such as surface tension, viscosity, electrical conductivity etc(9). A sharp break in such properties can be seen at the point of micelle formation. More sensitive methods such as measurement of surfactant ion activities by ion-selective electrodes(26) have been used to study micellar aggregation of surfactant molecules in solution. In addition, semi-equilibrium dialysis, a technique that has been widely used in the present work, can be used to indicate qualitatively the formation of micelles.

1.1.17 Investigation of solubilization of solutes in micelles(27)

The *mass action model* treats the solubilization process as the stepwise addition of the solute into micelles composed of surfactant and the solutes. Thus the mass action model assumes the existence of equilibria between the solute molecules and the surfactant molecules, and micelles containing both surfactant and solubilizate. The *pseudo-phase separation model*, in contrast, treats solubilization as an equilibrium of the solute between the micellar phase and the aqueous phase. Solubilization of a compound in micelles is quantitatively represented by the solubilization equilibrium constant.

Solubilization equilibrium constants

The solubilization equilibrium constants for organic solutes in surfactant solutions have been defined differently by various authors.

Method 1

In determining solubilization by vapor pressure method, the solubilization constant (K) has been defined as(39)

$$K = X_A / C_{A,U}$$

where,

$$X_A = C_{A,M} / (C_{S,M} + C_{A,M})$$

where, X_A is the mole fraction of organic solute in the micellar phase, $C_{A,U}$ is the concentration of unsolubilized organic solute in the aqueous phase, $C_{A,M}$ is the concentration of the solubilized solute in the micellar solution and $C_{S,M}$ is the concentration of surfactant in micellar form.

Method 2

Another way of determining solubilization equilibrium constant is by semi-equilibrium dialysis, using the equation(39)

$$K = (1 - X_A)\,[C_{A,ret} - C_{A,per}] \,/\, [\,C_{A,per}\,C_{S,ret} - C_{A,ret}\,C_{S,per}\,]$$

Here, $C_{S,ret}$ is the concentration of surfactant in micellar form in the retentate, usually almost equal to total concentration of surfactant in retentate, and $C_{S,per}$ is the concentration of surfactant in micellar form in the permeate, which is usually much smaller than the total surfactant concentration in the permeate. This $C_{S,per}$ term is usually calculated using a model for dependence of activity coefficients on intra-micellar mole fraction of organic solute and using the Gibbs-Duhem equation. Semi-equilibrium dialysis is a technique that has been successfully used to determine solubilization equilibrium constants of many compounds in micelles.

1.1.18 Metal-ligand complexes

The complexes of metal ions with a multidentate ligand which occupies two or more co-ordination sites, and in which rings are formed, are referred to as chelates(28). A ring may be formed with two electrovalent, one electrovalent and one covalent, or two covalent bonds with the metal. If the number of ligands bound to the metal is such that the charge on the metal is exactly neutralized, such chelate compounds are called inner complexes(28). The most stable rings formed are usually the five membered rings(28). Typical charged groups in a ligand are hydroxylic, carboxylic, sulfonic, oxime, imine, amine, thiol, and phosphate groups, and the electron-donating groups usually contain oxygen, nitrogen, or sulphur atoms.

The coordination sites on a metal may all be filled or some may remain unfilled. In case of unsaturated chelates the free coordination sites may be occupied with water molecules, to form hydrated chelates. Such hydrated chelates are only poorly extracted into organic phases, during organic extractions. In such organic extractions the chelate is preferentially dissolved in a suitable organic solvent, thereby achieving the separation.

The LM-MEUF process, mentioned previously, is somewhat similar to separation of metals by complexation followed by solvent extraction. In LM-MEUF, the surfactant micellar phase is used to solubilize the chelate, replacing the organic phase in solvent extraction. The organic phase can dissolve only hydrophobic ligands and their hydrophobic chelates. However, the surfactant micelles may be able to solubilize any kind of chelate, depending upon the operating solubilization mechanism.

In organic extractions, the extraction equilibrium can be represented in terms of the extraction equilibrium constant (K_{ex}), by taking the extraction process as

$$M^{n+} + n\,HA_{(org)} = MA_{n(org)} + n\,H^{+}$$

$$K_{ex} = [\,MA_{n(org)}]\,[H^{+}]^{n} \,/\, [M^{n+}]\,[HA_{(org)}]^{n}$$

Here, the ratio $[\,MA_{n(org)}] \,/\, [M^{n+}]$ is equal to the distribution coefficient (D). Therefore,

$$K_{ex} = D.(\,[H^{+}]^{n} \,/\, [HA_{(org)}]^{n})$$

Similar to the importance of distribution coefficient in an organic extraction process, the solubilization constant, for micellar solubilization of the chelate, is important in

LM-MEUF.

1.1.19 Investigation of metal complexation with a ligand

In investigating the binding of a metal ion to a ligand, it is necessary to determine both the stoichiometry of the binding equilibria and the equilibrium constants (or binding constants) of the metal-ligand binding equilibria.

Optical spectroscopy is the most widely applied experimental method of finding binding constants(29,30). One of the most characteristic effects of complex formation is the change in spectral properties. The excitation of electrons of both the metal ion and the ligand is affected by their interaction. The electrons of transition metal ions are easily excited and therefore these species absorb in the visible region, leading to colored compounds. The electron systems of non-transition metals are much more stable; excitation of their electrons requires greater energy so that the compounds absorb in the UV region. Owing to the interaction of the central metal and the ligand a charge transfer from the ligand to the metal ion or vice versa may occur, leading to intense spectral bands in the visible or near UV region. Complex formation also shifts the IR spectrum of ligands due to changes in vibrational-rotational characteristics of the ligand(29).

Beer's law

The relationship between the absorbance and the composition of a given solution is ordinarily consistent with Beer's law (sometimes called the Beer-Lambert law)(29,30). It is a common procedure to obtain absorbances at several different wavelengths, which can be used as a check for the reliability of the method. If unreliable results are obtained, possible reasons are the formation of more than one complex or interference due to other species. The absorbances may deviate from Beer's law due to formation of complexes with different stoichiometry, when one of the species exceeds a certain concentration. In such situations it is advisable to use at least two sets of calibration standards, one at low concentrations and the other at higher concentrations of the species. It may occur that the absorbances fit better to a quadratic equation than to a linear equation.

The error of spectrophotometric measurements will be determined by chemical and instrumental factors. In addition to deviations from Beer's law described above, errors may arise because of changes in the molar absorptivity caused by changes in the medium. Usually, the lower limit of the apparent complexation constant that can be obtained by absorbance methods(29) is on the order of 0.2 $L.Mol^{-1}$.

Two widely used methods using uv-visible absorbances, are (1) the continuous variation method(30) and (2) the mole ratio method(30), which are described below.

Continuous variation method

The metal-ligand complexation equilibrium for formation of only one type of complex is written as,

$$m\,M + n\,L = M_m L_n$$

Experimentally, a series of solutions is prepared with the sum of total concentrations of M and L constant, but their proportions varying continuously.

Therefore,

$$T_M + T_L = C$$

where T_M, T_L, and C represents the total metal, total ligand and the sum of both respectively.

Let

$$X = C. \{T_L / (T_M + T_L)\} \text{ and } 1 - X = C.\{T_M / (T_M + T_L)\}$$

Experimentally, X is varied while C is kept constant.

At equilibrium,

$$[M] = C(1\text{-}X) - m[M_mL_n]$$

$$[L] = CX - n[M_mL_n]$$

where $[M_mL_n] = \beta_{mn} [M]^m [L]^n$ by the definition of β_{mn}.

By differentiating an expression of $[M_mL_n]$ with respect to X, it is possible to determine the value of X corresponding to the maximum $[M_mL_n]$.

Therefore,

$$m\{ CX - n[M_mL_n] \} = n\{C(1\text{-}X) - m[M_mL_n]\}$$

$$n/m = X_{max} / (1 - X_{max})$$

Any property such as uv absorbance that varies linearly with M_mL_n is measured and plotted as a function of X, to obtain n/m. To keep the activity coefficient nearly the same in all systems, a fixed excess salt concentration may be used.

Mole ratio method

In this method the total concentration of one species is kept constant while the other is varied. More reliable information can be obtained by mole ratio methods than by the previous method, particularly when successive complex formation occurs. Plots of absorbance versus the concentration of the variable component give at low concentrations a nearly linear variation of absorbance followed by a curved region and eventually a constant absorbance region (plateau). If many different complexes are formed, it may be that several plateaus in the curve will be observed. In addition the sharpness of curvature is a measure of the stability of the complex formed. If the complex is highly stable the plot will look like two intersecting straight lines. According to Meyer and Ayres(31), the mole ratio of successive complexes can be determined if K_n is greater than or equal to 600 times the K_{n+1}. If the complex formation is favored by increased ionic strength, then the break points in the curve become more pronounced with the increased ionic strength. According to the Bent and French method(32), the logarithm of the complex concentration varies as

$$\log [M_mL_n] = m \log [M] + n \log [L] + \log b_{mn}$$

By this method it is possible to obtain m and n separately.

Potentiometry

Potentiometric titrations and pH titrations are widely used techniques(29,33) for investigating metal-ligand complexation. The activity of an ionic species undergoes a change as a consequence of a complexation equilibrium. If an electrode is available that is reversible with respect to its ion so that the Nernst equation, $E = E^0 + RT/nF \ln a_{ion}$ can be applied, then the measurement of the potential of that electrode in the solution can be used to study the complexation equilibria.

When pH titrations are used to study complexation equilibrium, the metal-ligand complexation is considered as a competitive reaction between the metal and proton. One problem encountered in pH titrations is the change in ionic strength, due to which the activity coefficient and the liquid junction potential of the pH electrode may change. Temperature is also an important parameter in potentiometric or pH titration experiments.

1.1.20 Aim of the research

LM-MEUF is one of a new class of colloid-enhanced ultrafiltration methods(20.21), all of which use an added soluble colloid (surfactant aggregate and/or polyelectrolyte), either to associate with or to repel target species that are to be removed from an aqueous solution(3-5,23,34-41). The solution is treated in an ultrafiltration (UF) unit so that the colloid is rejected, at the same time that the target species become concentrated, either in the permeate (solution passing through membrane) or in the retentate (solution not passing through membrane) stream.

In removing organic solutes with MEUF, either an anionic, cationic, or neutral surfactant is added to the feed stream, so that the micelles which form will solubilize the organic, either in the hydrophobic interior of the micelles or with the polar head groups of the solutes 'anchored' in the polar-ionic outer region of the micelles. For solutes that are solubilized effectively by the micelles, it is possible to produce a permeate having a very low concentration of organic solutes and a retentate that becomes highly concentrated in both the surfactant and solubilized species(3-5,34-41). One advantage of MEUF is that organics and heavy metal ions can be removed simultaneously, provided that the micelles have a charge opposite that of the target metal ions.

In MEUF, cationic metal ions adsorb or bind strongly to the micelles, so that the permeate will have a very low concentration of either the metal or the surfactant. In an alternative process called ion-expulsion ultrafiltration (IEUF), the added colloid comprises either positively charged micelles of a cationic surfactant or a positively charged polyelectrolyte(5,23).

Previously(10,11) it has been demonstrated that LM-MEUF can be used to concentrate Cu^{2+} in the retentate and Ca^{2+} in the permeate, by using N-dodecyl iminodiacetic acid (NIDA) as the ligand and N-hexadecylpyridinium chloride (referred to as cetylpyridinium chloride, or CPC) as the cationic surfactant. Stirred-cell UF results were obtained to show the feasibility of the process. In the present work, extensive semi-equilibrium dialysis (SED) experiments performed on the same system, are described.

The results of several types of ultrafiltration experiment and SED experiments taken together indicate that MEUF processes are *equilibrium-controlled*, as opposed to kinetically-controlled(5,23). However, IEUF processes are susceptible to diffusional effects that tend to diminish the concentration of the expelled ions in the permeate, as compared with equilibrium concentrations. Because LM-MEUF can involve both the binding of certain ions in the retentate and the expulsion of other ions into the permeate, it was thought that it would be worthwhile comparing the results of the previous stirred-cell LM-MEUF experiments(10) with equilibrium results obtained with SED; this comparison would indicate the extent of the discrepancy between equilibrium and UF process results under reasonable operating conditions. Moreover, it was intended to obtain extensive equilibrium results to provide the basis for developing models to predict optimum conditions for LM-MEUF separations.

1.2 EXPERIMENTAL SECTION

1.2.1 Materials

N-dodecyl iminodiacetic acid (NIDA), molecular weight 301 Da, and N-butyl iminodiacetic acid (BIDA), molecular weight 189 Da were synthesized elsewhere(10,47). Cetylpyridinium chloride (CPC) monohydrate with molecular weight 358 Da, was obtained from Hexcel Corp, and used without further purification. Analytical reagent grade $CuCl_2.2H_2O$ and $CaCl_2.2H_2O$ were used as the source of copper and calcium ions respectively. The sodium hydroxide and potassium hydrogen phthalate used in all titration experiments were of analytical reagent grade. The reagent PAR [4-(2-pyridylazo)resorcinol, monosodium salt monohydrate] was obtained from Aldrich Company. All aqueous solutions were prepared using double-distilled deionized water.

1.2.2 Methods

Spectrophotometric analyses were performed with an HP8452A diode-array spectrophotometer, using a 1 cm cell with 10 second signal-averaging and using 3 confirmation wavelengths. Atomic absorption (AA) analyses were carried out using Varian Spectr-AA-20 AA-analyzer.

For the analysis of copper by the PAR method(42), the following procedure was used. Approximately 0.1 mM PAR solution was prepared by dissolving 0.001 to 0.002 grams of reagent in 50 ml water. Buffer solution was prepared by dissolving 0.2 g of sodium acetate in 200 mL of water and adjusting the pH to 4.5 by acetic acid. To PAR solutions of 3.00 ml each, respectively 1, 5, 10, 15, and 20 drops of a standard

$CuCl_2$ solution (approximately 0.2 mM) were weighed and added, 2 mL portions of pH 4.5 buffer were added, and the solutions were diluted to total volume of 10 mL. The absorbances of all solutions were measured at 510 nm.

For AA analysis, samples were diluted to the optimum concentration range and, if necessary, compared against standards containing the appropriate concentrations of surfactant to minimize interferences. In analyzing copper and calcium in a mixture of the two cations, the standards were prepared with both metals in the same solution. For calcium analysis, potassium chloride was used as an ionization suppressor.

All potentiometric titrations were carried out using an Orion EA 940 expandable ionanalyzer, with a pH electrode (Orion Research, Sure-Flow Ross Combination Type). The solutions were kept in a nitrogen atmosphere throughout the titration experiments. Sodium hydroxide solutions were standardized with potassium hydrogen phthalate. NIDA and BIDA concentrations were determined by spectrophotometry of copper and ferric complexes. The procedure used was a slightly modified form of the method reported for the EDTA-Fe complex(43), as described below.

A pH 2.2 buffer solution was prepared by dissolving 2.0 g of chloroacetic acid in 200 mL of water and adjusting the pH by adding sodium hydroxide. A standard solution of 3.00 mM NIDA in 0.100 M CPC was prepared by weighing the required amount of NIDA accurately. An approximately 4.0 mM $FeCl_3$ solution was prepared in 0.01 M HCl. Solutions with 2 mL of the $FeCl_3$ solution, 2 mL of the buffer, and exactly measured amounts of the NIDA solutions (approximately 0.2, 0.3, 0.8, 1.0, 1.5, and 2.0 mL respectively) were mixed and the final volume of the solution was brought to 10 mL by adding 0.100 M CPC, using calibrated volumetric glassware to measure the volumes. Absorbances were measured at 328, 330, 334, and 340 nm respectively, with respect to a blank solution prepared the same way. In determining the concentrations of unknowns, samples were treated the same way as the blank and concentrations were inferred from the calibration curve.

1.2.3 Dialysis experiments

Semi-equilibrium dialysis experiments were carried out as described previously(14,34,36,38). Regenerated cellulose membranes (6,000 Da molecular weight cut-off) were soaked in the metal ion solutions (ca. 1 mM) for one day and soaked in water for one more day prior to use in order to minimize errors caused by adsorption of the metal ions by the membrane. The equilibration period was 24 hours, at which time semi-equilibrium is achieved, as reported previously(3). In all experiments, the initial CPC concentration in the retentate was 0.100 M.

Solutions of 1.00 mM NIDA or BIDA in 0.100 M CPC, containing different metal ion concentrations, were prepared by mixing required proportions of 3.00 mM NIDA in 0.100 M CPC and 3.00 mM copper in 0.100 M CPC. Adjustments of pH were made by adding sodium hydroxide or hydrochloric acid as necessary. To investigate the effect of sodium chloride, some experiments were performed with the same known concentrations of sodium chloride added to the retentate and permeate solutions.

The concentrations of Cu^{2+} and Ca^{2+} in the permeate and retentate, and the pH of the retentate solution were measured when equilibrium was attained. During the data analysis the concepts % Expulsion and % Retention were used as defined below.

% Expulsion = [1 - (Retentate/Permeate)] X 100

% Retention = [1 - (Permeate/Retentate)] X 100

1.2.4 Determination of ionization constants of NIDA in CPC solution

NIDA (1.00 mM) in 0.100 M CPC was titrated with a standard sodium hydroxide solution (approximately 40 mM, and the actual mM concentration known to 3 significant figures) and the pH versus volume of base data were fitted by the program PKAS(33,44) to obtain the step-wise ionization constants of the protonated ligand. Similar titrations were carried out in the presence of copper and calcium metal ions at varying concentrations (1.00 to 5.00 mM) and the data were fitted by the program BEST(33,44) to obtain the stability constants of the metal-ligand complexes.

1.2.5 Investigation of recovery of the ligand

Recovery of the used ligand was investigated by ultrafiltration experiments, in which the pH was lowered by adding concentrated HCl and the retentate copper was calculated using the experimentally determined copper in the permeate. The volumes of permeate collected were each 25 mL. Theoretically, it is possible to carry out the ligand recovery in two different ways,

(1) by acid treatment

(2) by base treatment.

Before experimental investigations were performed the recovery was investigated by theoretical species distributions derived from simple modelling of the system. In this derivation the stability constants related to metal complexation determined in section 1.2.4 experiments were used. In deriving equilibrium constants for the hydroxide complexes the solubility product constant of copper hydroxide (1.6 x 10^{-19} M^3) was used. For each calculation total metal, total ligand, and the pH were kept constant, while calculations were performed at several different pH values. The model equations were solved using the Simultaneous Equation Solver program (SEQS, CET Research Group, Norman, Oklahoma).

1.3 RESULTS AND DISCUSSION

1.3.1 Effect of micellar environment on pK

The titration plots of free NIDA, NIDA with Cu and NIDA with Ca are shown in figures 1.2.1 and 1.2.2. The differing binding behavior of the two metals can be distinctly seen by comparing these graphs. Interestingly, when the titration curves were quantitatively analyzed the behavior of the second ionization of the ligand was found to be affected significantly by the environment (type of surfactant used, whether cationic or anionic). Therefore to further investigate this behavior more titrations were carried out in the presence of CPC and SDS surfactants, and in just water, using BIDA and NIDA (note that with NIDA it is not possible to obtain the titration curve in just water). These results were plotted as shown in figures 1.2.3 and 1.2.4. For both ligands, the pK for the first ionization is independent of the micellar environment while for the second ionization the pK_a is higher in aqueous solution than in CPC micelles. However, in SDS micelles this pKa is found to be somewhat lower than in aqueous solution. This is a clear indication of the interaction of positively charged CPC head groups with the solubilized ligand to promote its ionization. In contrast the negative charge in SDS micelles acts to supress the ionization of the ligand. Therefore, in fitting of titration data by programs PKAS and BEST, the constants derived are expected to be significantly affected by this.

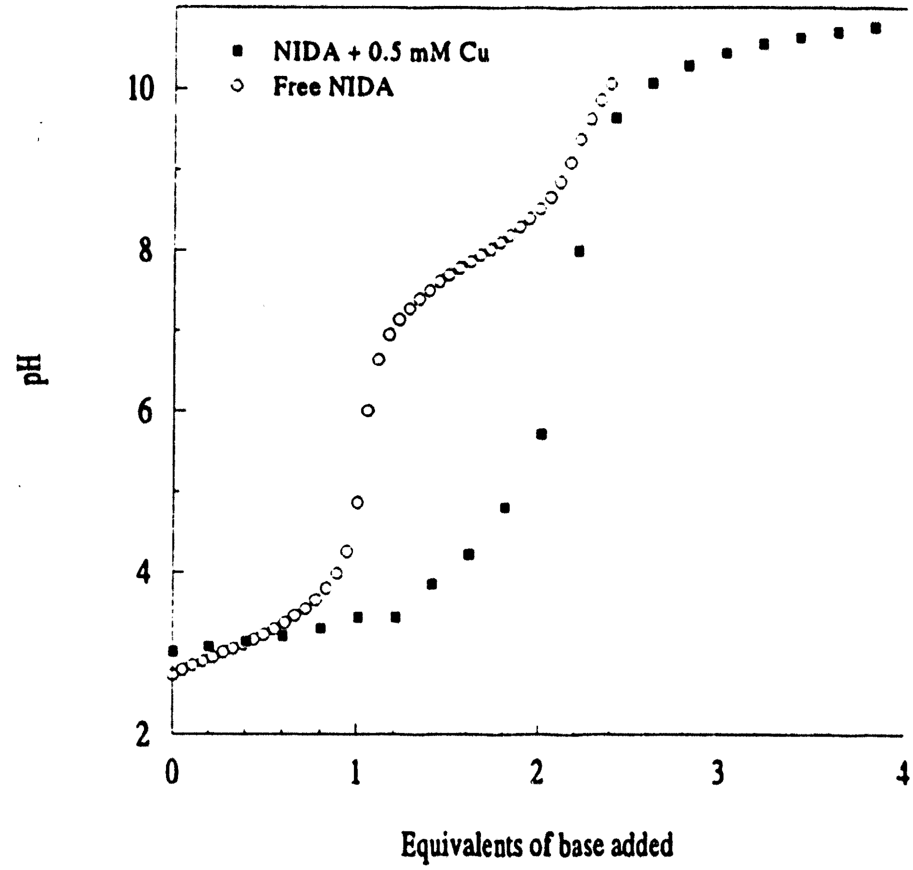


Figure 1.2.1 Titration behavior of NIDA in the presence and absence of Cu in 0.100 M CPC.

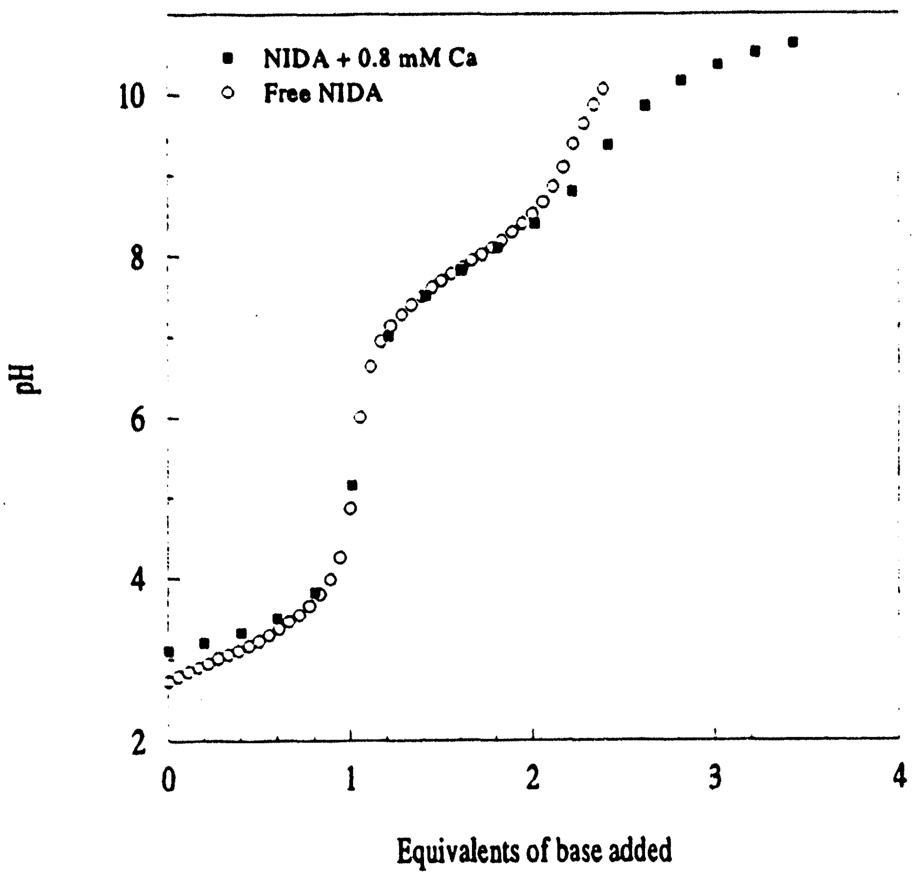


Figure 1.2.2 Titration behavior of NIDA in the presence and absence of Ca in 0.100 M CPC solution.

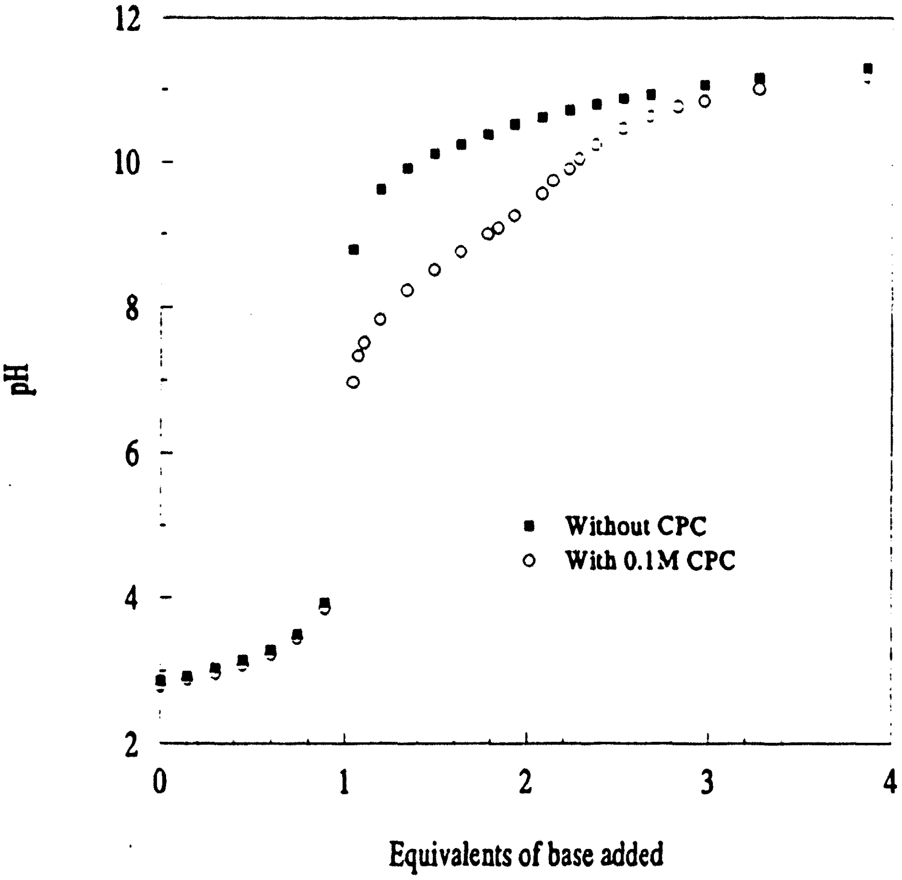


Figure 1.2.3 Titration of 20.00 mL of 2.989 mM BIDA in water and 0.100 M CPC solution with 17.75 mM NaOH.

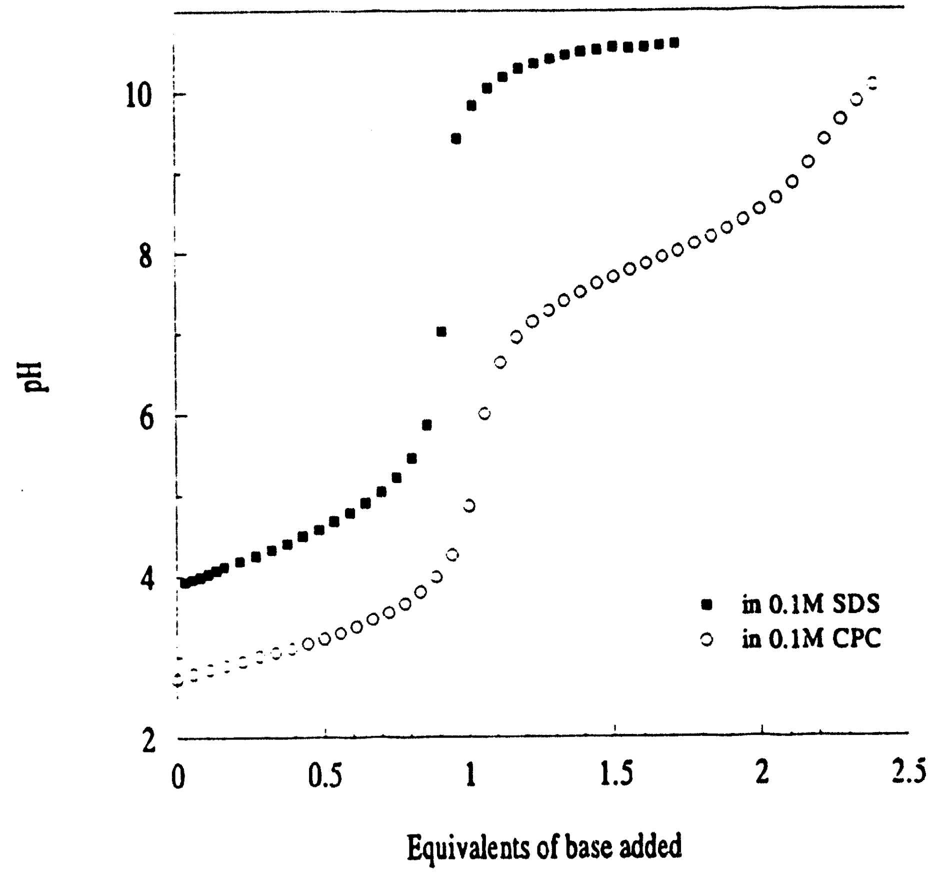


Figure 1.2.4 Titration behavior of NIDA dissolved in 0.100 M SDS and CPC solutions titrated with NaOH.

Analysis of NIDA by spectrophotometry, using complexation with ferric ions, was not very successful. This method gave reliable results for NIDA in the retentate, but the determination of BIDA by this method gave inconsistent results. Therefore, the BIDA was determined by spectrophotometry using the Cu-complex and NIDA was determined using the Fe-complex. The molar absorptivity of the ferric-NIDA complex was substantially greater (1974 M^{-1} at 330 nm) than that of the copper-NIDA complex.

1.3.2 SED results

Data obtained from SED experiments with BIDA are shown in table 1.2.1. The results indicate that a significant fraction of the BIDA passes into the permeate solution during the 24-hour period of equilibration, limiting its potential use as a ligand in LM-MEUF separations. Therefore, additional experiments were not performed with this compound.

The concentration of NIDA in the permeate was estimated to be less than 5×10^{-6} M (not accurately determined) when the initial retentate contained 1.00 mM NIDA, 0.100 M CPC, 0.1 to 1.5 mM Cu^{2+} and Ca^{2+}, and pH 6.0. Because the permeate NIDA concentration was not detectable (due to interference from CPC), this result was checked by a material balance on the retentate. Knowing the initial retentate NIDA concentrations, taking into account the water transferred from retentate to permeate during the experiment, and assuming that a negligible amount of NIDA transferred into the permeate, it was possible to calculate the final retentate NIDA concentrations shown in Table 1.2.2. The good agreement between this calculated value and the measured concentrations (which differed by less than 4%) confirms that a negligible amount of NIDA transfers into the permeate under these conditions.

Tables 1.2.3 to 1.2.11 show the permeate and retentate concentrations in SED experiments, performed with copper and calcium individually, and in the mixtures, under different experimental conditions. Figures 1.2.8 to 1.2.16 show the permeate versus retentate concentration curves corresponding to these tables. Note that the calculated values shown in tables 1.2.9 to 1.2.11 and the theoretical curves (shown by the connected curve) in figures 1.2.8 to 1.2.16 correspond to the values obtained using the model described later.

The results in tables 1.2.8 and 1.2.10 (or figures 1.2.11 and 1.2.13) and tables 1.2.9 and 1.2.11 (or figures 1.2.12 and 1.2.14) which show copper and calcium results, are each from single set of experiments carried out with both Ca and Cu together. The same results have been tabulated again respectively in tables 1.2.12 and 1.2.13, which were created in order to explain the percentage Cu retentions and Ca expulsions.

1.2.1 Results of SED experiments using BIDA in CPC micelles

Initial BIDA/mM	Retentate BIDA/mM	Permeate BIDA/mM
4.99	3.01	0.505
	2.96	0.564
3.89	2.33	0.302
	2.30	0.300
2.10	1.33	0.140
1.13	0.673	----
	0.651	----

Table 1.2.2. Comparison of analytical concentration of NIDA in retentate with values calculated from initial concentration and dilution factor inferred from CPC concentration

Initial NIDA/mM	Retentate NIDA/mM		Retentate CPC/M
	Actual	Calculated	
1.50	1.23	1.25	0.083
	1.20	1.08	0.072
1.19	0.957	0.981	0.082
	----	0.974	0.082
1.04	0.890	0.837	0.081
	0.830	0.860	0.083
0.475	0.402	0.387	0.082
	0.346	0.342	0.072

Table 1.2.3 NLLSQ analysis of data of SED experiments with Cu alone at pH 6.0 using 1.00 mM initial NIDA, without added salt.

pH = 6.0
B(0) = 2E-3
B(1) = 2E-8
B(2) = 3E4
B(3) = 3E7
B(4) = 7.78E-4 ± 1.293E-5
RMSD = 1.216E-4

Ret.Cu(mM)	Per Cu(mM)	NaOH added(mM)	Per.Cu(mM) calc.
0.3462	0.0239	1.35	0.0137
0.3424	0.0231	1.35	0.0134
0.5640	0.0738	1.73	0.0358
0.5514	0.0844	1.73	0.0332
0.7742	0.2527	1.80	0.2539
0.7473	0.2511	1.80	0.1765
0.8134	0.3689	1.90	0.4019
0.8621	0.3674	1.90	0.6322
0.8101	0.5044	1.90	0.3870
0.7849	0.4779	1.90	0.2824

Table 1.2.4 NLLSQ analysis of data of SED experiments with Cu alone at pH 6.0 using 1.50 mM initial NIDA without added salt

pH = 6.0
B(0) = 2E-3
B(1) = 2E-8
B(2) = 3E4
B(3) = 3E7
B(4) = 1.1233E-3 ± 1.202E-5
RMSD = 6.635E-5

Ret.Cu(mM)	Per Cu(mM)	NaOH added(mM)	Per.Cu(mM) calc.
0.6412	0.0140	2.00	0.0165
0.6530	0.0176	2.00	0.0172
0.9192	0.0661	2.80	0.0411
0.8891	0.0696	2.80	0.0350
0.9776	0.1130	2.85	0.0579
0.9617	0.1146	2.85	0.0522
1.0480	0.2186	2.85	0.1019
1.0600	0.2292	2.85	0.1144
1.2260	0.5250	2.85	0.5881
1.2240	0.5718	2.85	0.5805

Table 1.2.5 NLLSQ analysis of data of SED experiments with Cu alone at pH 5.2 using 1.00 mM NIDA without salt

pH = 5.2
B(0) = 2E-3
B(1) = 2E-8
B(2) = 3E4
B(3) = 3E7
B(4) = 8.8236E-4 ± 2.0999E-5
RMSD = 1.0300E-4

Ret.Cu(mM)	Per Cu(mM)	NaOH added(mM)	Per.Cu(mM) calc.
0.255	0.021	1.10	0.040
0.255	0.023	1.10	0.039
0.237	0.039	1.15	0.035
0.358	0.031	1.25	0.059
0.365	0.042	1.25	0.061
0.393	0.117	1.30	0.067
0.396	0.118	1.30	0.068
0.513	0.201	1.45	0.102
0.596	0.362	1.55	0.139
0.629	0.288	1.55	0.162
0.514	0.210	1.45	0.103
0.861	0.422	1.65	0.521
0.800	0.479	1.65	0.369
1.300	1.780	1.70	1.936
1.272	1.956	1.70	1.862

Table 1.2.6 NLLSQ analysis of data of SED experiments with Cu alone at pH 5.2 using 1.00 mM initial NIDA with 1.00 M NaCl

pH = 5.2
B(0) = 2E-3
B(1) = 2E-8
B(2) = 3E4
B(3) = 3E7
B(4) = 1.0388E-3 ± 1.4065E-5
RMSD = 2.6159E-5

Ret.Cu(mM)	Per Cu(mM)	NaOH added(mM)	Per.Cu(mM) calc.
0.353	0.008	1.15	0.005
0.347	0.008	1.15	0.005
0.679	0.008	1.40	0.016
0.661	0.014	1.40	0.015
0.592	0.012	1.40	0.012
0.581	0.010	1.40	0.011
1.068	0.053	1.70	0.119
1.040	0.063	1.70	0.101
1.040	0.118	1.70	0.101
1.050	0.123	1.70	0.107
1.340	0.385	1.70	0.372
1.335	0.397	1.70	0.367

Table 1.2.7 NLLSQ analysis of data of SED experiments with Ca alone at pH 6.0 using 1.00 mM NIDA with no added salt

pH = 6.0
B(0) = 2E-3
B(1) = 2E-8
B(2) = 0
B(3) = 4E5
B(4) = 8.00E-4
RMSD = 1.987E-4

Ret.Ca(mM)	Per Ca(mM)	NaOH added(mM)	Per.Ca(mM) calc.
0.091	1.256	1.00	1.019
0.152	1.598	1.00	1.434
0.124	1.189	1.00	1.257
0.145	1.676	1.00	1.392
0.081	1.267	1.00	0.935
0.099	1.264	1.00	1.082
0.092	0.920	1.00	1.028
0.058	0.944	1.00	0.731
0.017	0.408	1.00	0.258
0.023	0.404	1.00	0.347

Table 1.2.8 NLLSQ analysis of Cu data of SED experiments with Cu and Ca together at pH 6.0 using 1.00 mM NIDA with 5.00 mM added NaCl

pH = 6.0
B(0) = 2E-3
B(1) = 2E-8
B(2) = 3E4
B(3) = 3E7
B(4) = 9.745E-4 ± 9.715E-6
RMSD = 4.629E-5

Ret.Cu(mM)	Per Cu(mM)	NaOH added(mM)	Per.Cu(mM) calc.
1.108	0.424	1.90	0.490
1.080	0.398	1.90	0.408
0.927	0.201	1.90	0.077
0.996	0.240	1.90	0.181
0.910	0.054	1.90	0.064
0.895	0.057	1.90	0.055
0.750	0.022	1.85	0.019
0.739	0.026	1.85	0.018
0.520	0.000	1.75	0.007
0.437	0.000	1.75	0.005
0.124	0.038	1.20	0.001
0.138	0.012	1.20	0.001

Table 1.2.9 NLLSQ analysis of Ca data of SED experiments with Cu and Ca together at pH 6.0 using 1.00 mM NIDA with no added salt

pH = 6.0
B(0) = 2E-3
B(1) = 2E-8
B(2) = 0
B(3) = 4E5
B(4) = 9.79E-4
RMSD = 1.7274E-4

Ret.Ca(mM)	Per Ca(mM)	NaOH added(mM)	Per.Ca(mM) calc.
0.341	1.374	1.90	1.917
0.364	1.693	1.90	1.999
0.258	1.496	1.90	1.593
0.208	1.327	1.90	1.371
0.192	1.012	1.90	1.298
0.129	0.999	1.85	0.978
0.129	0.971	1.85	0.978
0.077	0.785	1.65	0.692
0.075	0.772	1.65	0.677
0.011	0.174	1.20	0.146
0.011	0.195	1.20	0.157
0.211	1.269	1.90	1.384
0.243	1.377	1.90	1.530
0.170	1.065	1.90	1.187
0.171	1.020	1.90	1.190
0.108	0.630	1.90	0.840
0.093	0.878	1.90	0.745
0.094	0.746	1.90	0.747
0.078	0.661	1.90	0.642
0.066	0.529	1.90	0.608
0.063	0.462	1.90	0.581
0.020	0.219	1.90	0.190
0.021	0.238	1.90	0.201

Table 1.2.10 NLLSQ analysis of Ca data of SED experiments with Cu and Ca together at pH 6.0 using 1.00 mM NIDA with 5.00 mM added NaCl

pH = 6.0
B(0) = 2E-3
B(1) = 2E-8
B(2) = 0
B(3) = 4E5
B(4) = 9.74E-4
RMSD = 2.413E-4

Ret.Ca(mM)	Per Ca(mM)	NaOH added(mM)	Per.Ca(mM) calc.
0.563	1.260	1.70	1.678
0.483	1.153	1.70	1.480
0.352	0.884	1.70	1.137
0.372	0.998	1.70	1.190
0.387	0.851	1.70	1.231
0.369	0.863	1.70	1.184
0.258	0.833	1.60	0.875
0.230	0.777	1.60	0.790
0.228	0.568	1.45	0.792
0.187	0.535	1.45	0.663
0.061	0.234	1.00	0.241
0.054	0.243	1.00	0.216

Table 1.2.11 NLLSQ analysis of Cu data of SED experiments with Cu and Ca together at pH 6.0 using 1.00 mM initial NIDA with no added salt

pH = 6
B(0) = 2E-3
B(1) = 2E-8
B(2) = 3E4
B(3) = 3E7
B(4) = 9.789E-4 ± 1.050E-5
RMSD = 6.635E-5

Ret.Cu(mM)	Per Cu(mM)	NaOH added(mM)	Per.Cu(mM) calc.
1.057	0.652	1.90	0.752
1.078	0.684	1.90	0.867
0.913	0.302	1.90	0.166
0.847	0.290	1.90	0.094
0.871	0.191	1.90	0.112
0.628	0.055	1.85	0.029
0.685	0.058	1.85	0.037
0.357	0.023	1.65	0.010
0.209	0.003	1.20	0.006
0.211	0.003	1.20	0.007
1.006	0.688	1.90	0.476
1.086	0.770	1.90	0.911
0.936	0.369	1.90	0.212
0.927	0.392	1.90	0.192
0.783	0.213	1.90	0.061
0.813	0.216	1.90	0.074
0.723	0.081	1.90	0.044
0.711	0.077	1.90	0.042
0.528	0.016	1.65	0.021
0.527	0.008	1.65	0.021
0.172	0.003	1.20	0.003
0.172	0.003	1.20	0.003

Table 1.2.12 Results of SED experiments with Cu and Ca, using 1.0 mM NIDA with no added salt
(plotted in figures 1.2.12 and 1.2.14)

Initial (mM)		Retentate (mM)		Permeate (mM)		%Ret	%Expul.
Cu	Ca	Cu	Ca	Cu	Ca	Cu	Ca
1.819	1.146	1.006	0.211	0.688	1.269	31.61	83.37
		1.086	0.243	0.770	1.377	29.10	82.35
1.478	0.944	0.936	0.170	0.369	1.065	60.58	84.04
		0.927	0.171	0.392	1.020	57.71	83.24
1.139	0.734	0.782	0.108	0.213	0.630	72.76	82.86
		0.813	0.093	0.216	0.878	73.43	89.41
0.954	0.618	0.723	0.094	0.081	0.746	88.80	87.40
		0.711	0.078	0.077	0.661	89.17	88.20
0.606	0.416	0.527	0.066	0.016	0.529	96.96	87.52
		0.527	0.062	0.008	0.461	98.48	86.55
0.159	0.098	0.172	0.020	0.003	0.218	98.26	90.83
		0.171	0.021	0.003	0.238	98.25	91.18

Table 1.2.13 Results of SED experiments with Cu and Ca, using 1.0 mM NIDA with 5 mM added salt (plotted in figures 1.2.11 and 1.2.13)

Initial (mM)		Retentate (mM)		Permeate (mM)		%Ret	%Expul.
Cu	Ca	Cu	Ca	Cu	Ca	Cu	Ca
1.586	1.669	1.108	0.563	0.424	1.260	61.73	55.32
		1.080	0.482	0.398	1.153	63.15	58.20
1.290	1.320	0.927	0.352	0.201	0.884	78.32	60.18
		0.995	0.327	0.240	0.998	75.88	62.73
1.058	1.031	0.910	0.387	0.054	0.851	94.07	54.52
		0.895	0.369	0.057	0.863	93.63	57.24
0.839	0.833	0.750	0.258	0.022	0.833	97.07	69.03
		0.739	0.230	0.026	0.777	96.48	70.40
0.571	0.569	0.520	0.227	0.004	0.569	99.23	60.11
		0.437	0.186	0.001	0.535	99.77	65.23
0.117	0.127	0.124	0.061	0.001	0.234	99.19	73.93
		0.138	0.054	0.001	0.243	99.28	77.78

1.3.3 A model for LM-MEUF process

Prior to applying any equilibrium thermodynamic relationships to this system, it was necessary to build up a qualitative model describing the nature of solubilization, and the metal binding behavior.

The solubility of NIDA in water at near-neutral pH was found to be very small (less than 5 x 10^{-6} M), primarily because of the presence of the highly hydrophobic dodecyl chain. Because the concentration of NIDA in the permeate is so small, it is not possible to determine a solubilization isotherm for that ligand in the CPC micelles. On the other hand, this result shows that it is justifiable to neglect the concentration of the ligand that is lost in SED experiments, and presumably in the analogous LM-MEUF process. With ligands like BIDA that are more soluble than NIDA (and presumably not totally bound to micelles in the retentate) it will be necessary to include information about the binding of these species to the surfactant micelles in order to model the LM-MEUF separation process.

Presumably the NIDA solubilizes in the CPC micelles with the dodecyl head groups localized in the micellar interior and the polar iminodiacetic groups in the outer polar/ionic region of the micelles. At the CPC concentration employed here (0.100 M) the micelles are approximately spherical in shape(9). Therefore, under these conditions the micellar solubilized ligand and the metal-ligand complex in the solution can be most conveniently represented as shown in the figure 1.2.5. Simple calculations show that on average only 1 or 2 molecules of NIDA are solubilized in a single micelle at the given experimental concentrations. Therefore, little interaction between ligands

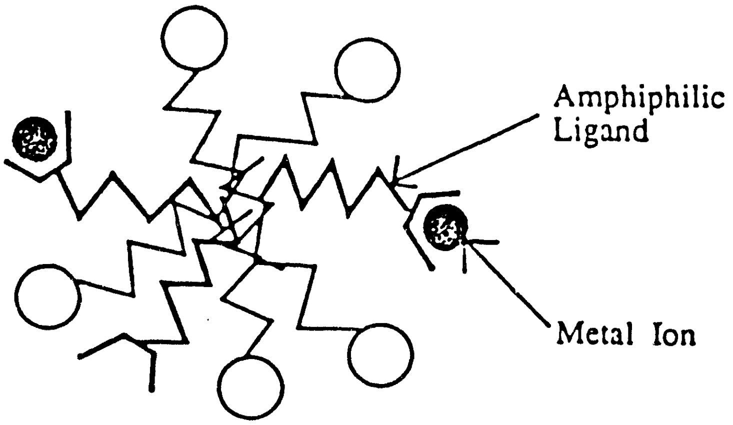


Figure 1.2.5 Representation of a surfactant micelle with solubilized amphiphilic ligands and ligand-metal complexes(11)

is expected to occur within the micelles. In modelling the SED results, we assume that all of the solubilized NIDA molecules have an equal chance to complex with metal ions or participate in the various acid-base equilibria; **i.e.**, the environment of the NIDA is assumed to be independent of the degree of solubilization in the micelles.

The stepwise ionization constants(29,30) in molar units (K_1 and K_2 as defined in model equations later) obtained for NIDA by fitting the experimental titration data were 2.0×10^{-3} and 2.0×10^{-8} respectively, in 0.100 M CPC solutions, with no added NaCl. Similarly, stability constants obtained for metal-NIDA complexes for copper and calcium (K_{m1}, K_{m2}, and K_{m3} as defined in model equations) are shown in table 1.1.2.

Table 1.2.14 Values of metal complexation constants with Cu and Ca for NIDA derived from analysis of titration data.

	copper (molar units)	calcium (molar units)
K_{m1}	3.0×10^{4}	- -
K_{m2}	3.0×10^{7}	- -
K_{m3}	- -	4.0×10^{5}

However, as expected it was not possible to fit the whole curve of any titration with a single set of constants. Therefore, in all the curves it was necessary omit at least a few points, to obtain the best fitting. The existence of a significant K_{m3} value with insignificant K_{m1} and K_{m2} values in case of calcium binding cannot be accepted and may be due to bad fitting of the results. However, it is important to note that under these experimental conditions, formation of a complex with 2 ligands attached to a single metal is highly unlikely both sterically and entropically, because both ligands have to be either in the same micelle making the resulting complex sterically unfavorable or in two different micelles making it entropically unfavorable. Therefore it is reasonable to consider the value of K_{m3} as zero in case of Cu and Ca both.

1.3.4 Model equations

Simple ionic equilibrium equations can be applied to relate the concentrations of free and bound NIDA and metal ions in either compartment. Equilibrium constants for these equations pertain both to the ionization of the uncomplexed ligand and the binding of metal ions to the ligand in the micelle. Mass and charge balance equations must also apply in the retentate and permeate solutions. Most importantly, the activity of neutral electrolytes must be the same on the two sides of the membrane at equilibrium. In the solutions containing no added sodium chloride, it is assumed that activity coefficients may be equated to unity in all solutions, so that ionic concentrations may be used in place of equilibrium ion activities. For solutions with added NaCl, activity coefficients are estimated using the Davies equation(45).

Ionization of the ligand

$H_2L = HL + H$

$HL = L + H$

(1). $K_1 = [HL][H]_r/[H_2L]$

(2). $K_2 = [H]_r[L]_r/[HL]$

Metal-ligand complexation

(3). $K_{m1} = [MHL]/[M]_r[HL]$

(4). $K_{m2} = [ML]/[M]_r[L]_r$

(5). $K_{m3} = [ML_2]/[M]_r[L]_r^2$

The mass balance equations for retentate

(6). $M_{total} = [M]_r + [MHL] + [ML] + [ML_2]$

(7). $L_{total} = [L]_r + [HL] + [H_2L] + [ML] + [MHL] + 2[ML_2]$

Activity balance for equilibrium between compartments

Replacing activities by concentrations,

(8). $[M]_r[Cl]_r^2 = [M]_p[Cl]_p^2$

(9). $[H]_r[Cl]_r = [H]_p[Cl]_p$

(10). $[Na]_r[Cl]_r = [Na]_p[Cl]_p$

Charge balance for the permeate

(11). $[Na]_p + 2[M]_p + [H]_p + [CP^+]_p = [OH]_p + [Cl]_p$

In all cases, the subscripts "p" and "r" denote permeate and retentate concentrations, respectively. The terms with no subscript also denotes retentate concentrations. The CP^+ concentration in the permeate was assumed to be equal to the CMC value of CPC$^{(46)}$ (9.0×10^{-4} in the absence of sodium chloride and 5.0×10^{-4} in 0.100 M NaCl), which represents the monomer concentration in the retentate solution. In addition to equations 1 to 11, the assumption was made that the sodium concentrations in retentate were constant and equal to the total of the concentration of sodium added as sodium hydroxide (in adjusting the pH) plus any added sodium chloride. The concentration of chloride in the retentate was also assumed to remain fixed and equal to the concentration of unbound chloride from CPC (assumed to be equal to 20% that of the total CPC$^{(23)}$), with the dilution factor taken into account, plus the concentration of any added sodium chloride. Chloride ion concentrations from other sources were considered to be negligible in comparison with $[Cl^-]$ contributed by CPC and added NaCl. Therefore, the equations

(12). $[Na]_r = [NaOH]_{added} + [NaCl]_{added}$

(13). $[Cl]_r = 0.02M \times 0.8 + [NaCl]_{added}$

were included in the model. However, when analyzing the system in detail it was found that the concentration of CP^+ in the permeate is not a critical parameter.

Solving the model equations

Simplification of equations (8) and (13) gives,

$$(a) \quad [Cl]_p^2 = [M]_r.(.02 \times 0.8 + [NaCl]_{added})^2 / [M]_p$$

Equations (9) and (13) give

$$(b) \quad [H]_p = [H]_r.(.02 \times 0.8 + [NaCl]_{added}) / [Cl]_p$$

Substituting Cl_p from equation (a) in (b),

$$(c) \quad [H]_p = [H]_r. ([M]_p/[M]_r)^{1/2}$$

Similarly, from equations (10) and (13),

$$(d) \quad [Na]_p = [Na]_r. ([M]_p/[M]_r)^{1/2}$$

Simplification of equations (d) and equation (11) gives,

$$(e) \quad 2. [M]_p + ([M]_p/[M]_r)^{1/2}.[Na]_r + [H]_r.([M]_p/[M]_r)^{1/2} + [CP^+]_p - ([M]_r/[M]_p)^{1/2}.(.02 \times .08 + [NaCl]_{added}) - K_w/[H]_r .([M]_r/[M]_p)^{1/2} = 0$$

The final equation (e) shows the relationship between the free metal concentration in the permeate (same as the total metal in the permeate) and the retentate. The relationship between total metal in the retentate and the free metal in the retentate is derived by solving following two equations (in terms of free ligand in the retentate) which are derived from equations (3) to (6) and equations (1), (2), and (7) respectively.

$$\text{(f)} \quad [M]_{total} = [M]_r[1 + (K_{m1}/K_2).[H]_r.[L]_r + K_{m2}.[L]_r + K_{m3}.[L]_r^2]$$

$$\text{(g)} \quad [L]_{total} - [M]_{total} = ([L]_r - [M]_r) + [H]_r.[L]_r(1/K_2)$$
$$+ [H]_r^2.[L]_r.[1 / (K_1.K_2)] + K_{m2}.[M]_r.[L]_r^2$$

Since it is quite difficult to obtain a single equation from equations (f) and (g), a reasonable approximation was made. With no loss of reality in the present system it is possible to omit the $[L]_r^2$ terms from above two equations because in case of copper the whole term become zero whereas in calcium the term is negligibly small at concentrations of metal and the ligand employed.

Therefore, the approximate equations give

$$\text{(h)} \quad [M]_{total} = [M]_r[1 + (K_{m1}/K_2).[H]_r.[L]_r + K_{m2}.[L]_r]$$

$$\text{(i)} \quad [L]_{total} - [M]_{total} = [L]_r + [H]_r.[L]_r(1/K_2) + [H]_r^2.[L]_r.[1 / (K_1.K_2)]$$
$$- [M]_{total} / [1 + (K_{m1}/K_2).[H]_r.[L]_r + K_{m2}.[L]_r]$$

Using the initial estimates of NIDA concentrations, and an equation (i) expressed in terms of the free ligand concentration [L] was obtained and solved, using a Newton-Raphson iterative procedure(48) included in the model-specific subroutine of a nonlinear least squares (NLLSQ) program(4c . Using this solution for [L], the concentration of free metal [M] in the retentate (M_r) was calculated using the equation (h). The permeate metal concentrations were then predicted, using the estimated values of the free retentate metal concentrations and solving equation (e) by a second Newton-Raphson routine.

The least squares program ultimately found the best values of the variable parameters that produced a minimum in the sum of squares of deviations between the predicted and experimental values of the permeate metal concentrations. The derived values of the total ligand concentrations in the retentate (for the systems containing Cu^{2+}) were in all cases quite close to the expected values, calculated from initial ligand concentrations, corrected for dilution. The NLLSQ results of all experiments are tabulated in tables 1.2.3 to 1.2.11. In these tables B(0), B(1), B(2), B(3), and B(4) are the parameters representing K_1, K_2, K_{m1}, K_{m2}, and $[L]_{total}$ respectively. The figures 1.2.6 to 1.2.14 have drawn using the data from these tables respectively.

In modelling data for all of the systems, a reasonable correlation could be obtained by using only equilibrium constants and other parameters determined independently of the SED experiments; that is, no adjustment of the parameters was required to fit the dialysis data with the model. An improved goodness of fit could be obtained, however, by treating the concentrations of NIDA in the retentate (in the series of experiments in which Cu^{2+} was present) as variable parameters. In the experiments with Ca^{2+} alone, the NIDA concentrations could not be inferred in this way from the model, because the derived values of the concentrations of NIDA are relatively insensitive to variations in the concentrations of Ca^{2+}. In addition, reasonably small root mean square deviation (RMSD) values (shown in tables) show the good agreement between experimental and the model results.

Examining all of the SED results, it was observed that the permeate concentration versus retentate concentration plots (figures 1.2.6 to 1.2.14) generally exhibit two identifiable regions:

1. The primary complexation region for the cation, where most of the metal ions remain in the retentate solution, bound to the solubilized ligand.

2. A region in which divalent cation concentrations increase rapidly in the permeate, owing to ion expulsion. The expulsion effect predominates when the ligand is nearly all complexed. Free metal ions are expelled from the retentate because of the excess positive charge of CPC micelles.

In the case of a non-complexed metal such as calcium, region 1 is not very important and is insignificant while region 2 predominates, as seen from figures 1.2.10, 1.2.12, and 1.2.13. With a complexed metal such as Cu both regions can always be identified and also the range of region 1 and the relative extent of region 1 depends

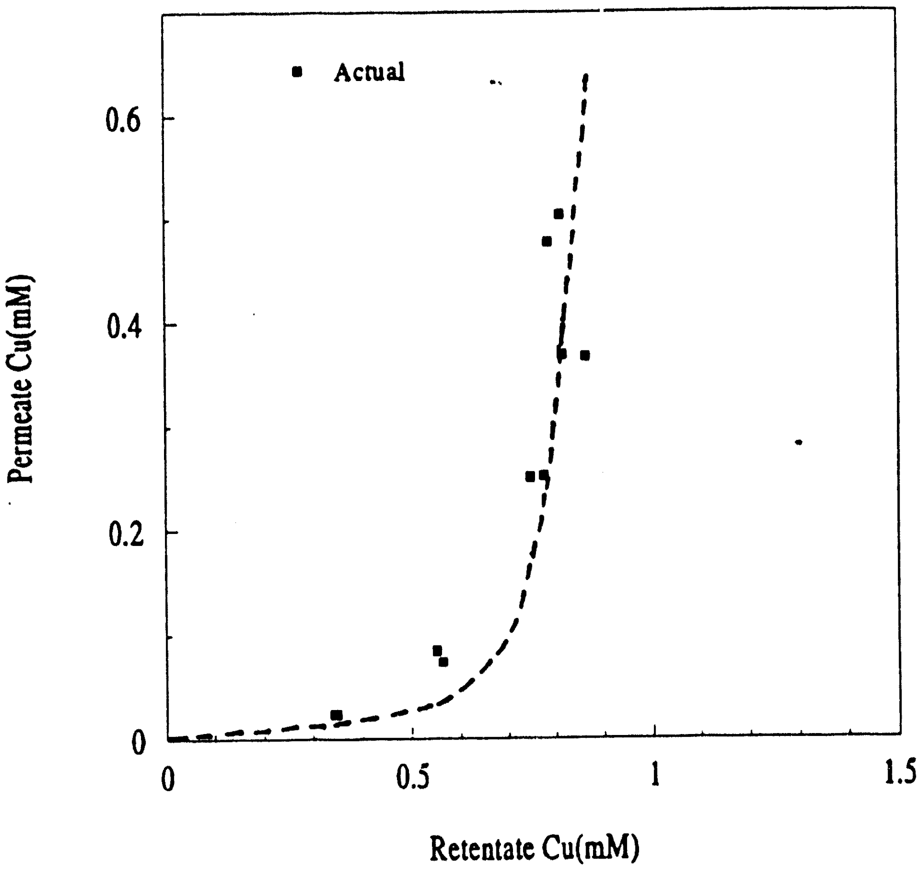


Figure 1.2.6 Actual and model results of SED experiments with Cu alone, at pH 6.0 using 1.00 mM NIDA with no added salt.

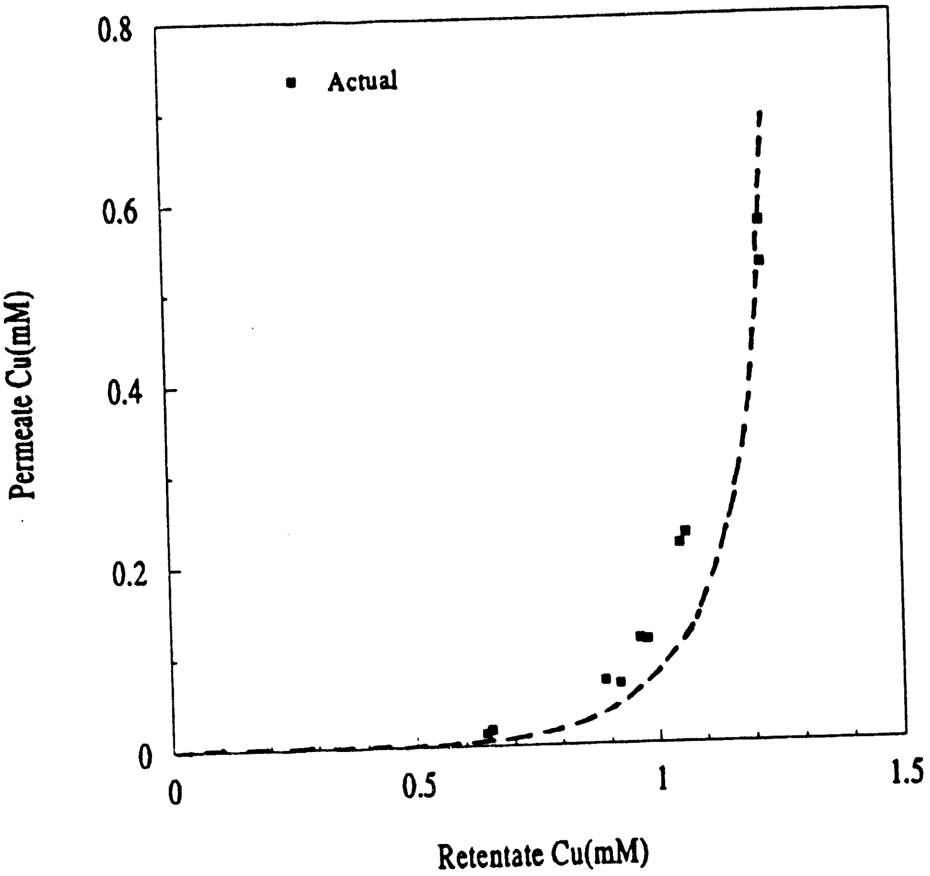


Figure 1.2.7 Actual and model results of SED experiments with Cu alone at pH 6.0 using 1.50 mM initial NIDA with no added salt.

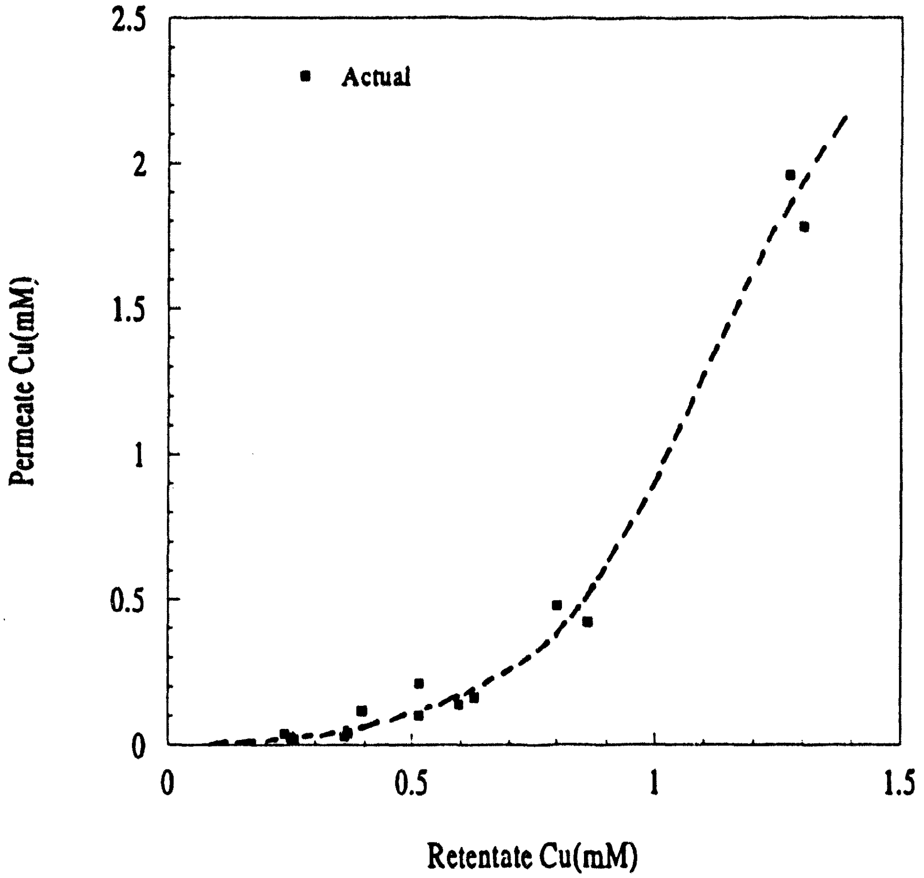
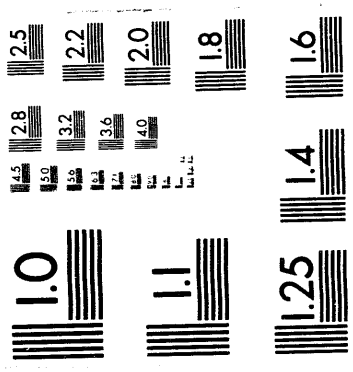


Figure 1.2.8 Actual and model results of SED experiments with Cu alone at pH 5.2 using 1.00 mM initial NIDA with no added salt.



2.5
2.2
2.0
1.8
1.6
2.8
3.2
3.6
4.0
1.4
4.5
5.0
5.6
6.3
7.1
8.0
1.0
1.1
1.25

2 of 3

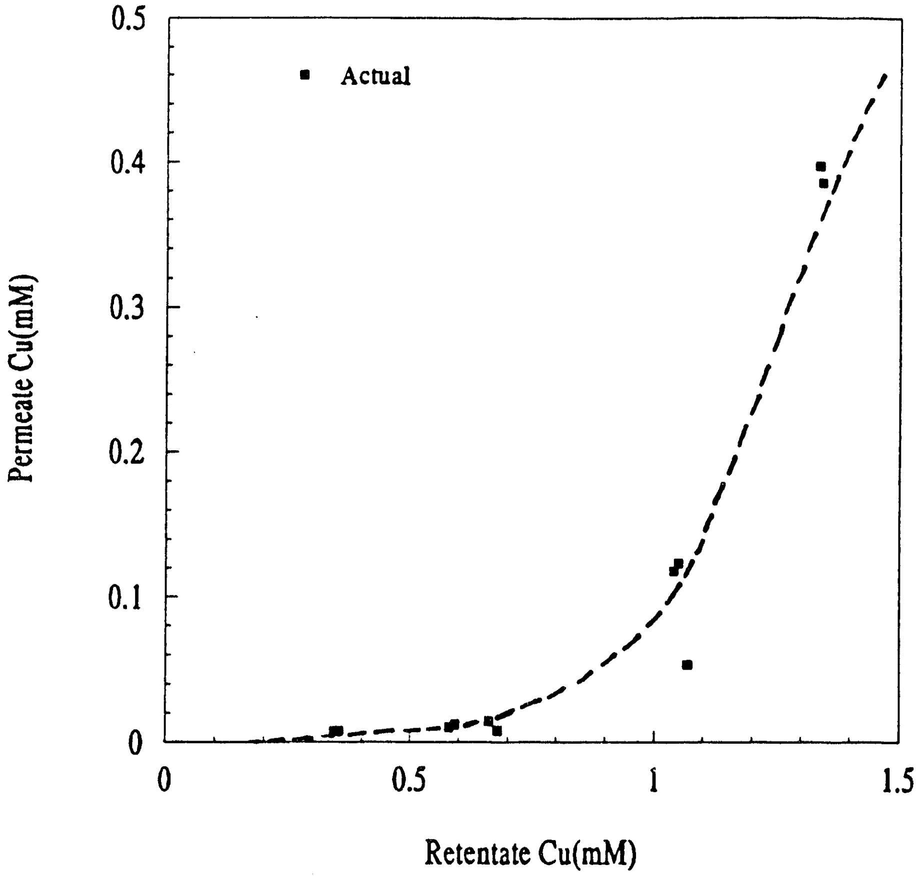


Figure 1.2.9 Actual and model results of SED experiments with Cu alone at pH 5.2 using 1.00 mM NIDA with 1.00M added NaCl

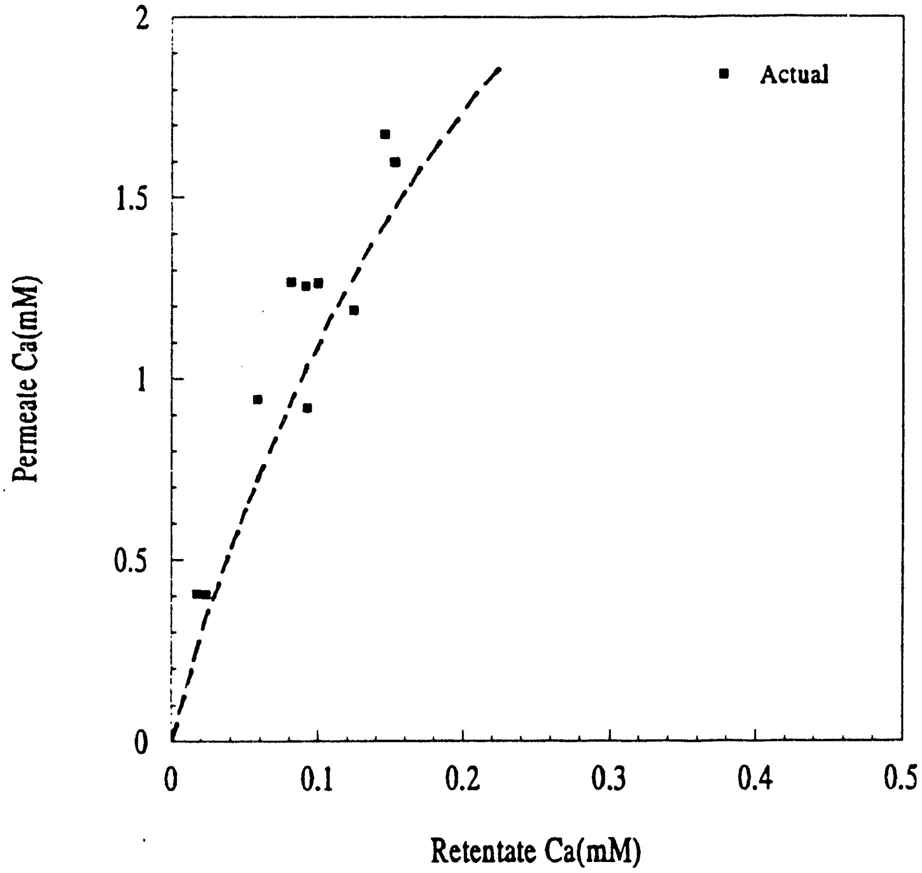


Figure 1.2.10 Actual and model results of SED experiments with Ca alone at pH 6.0 using 1.00 mM initial NIDA with no added salt.

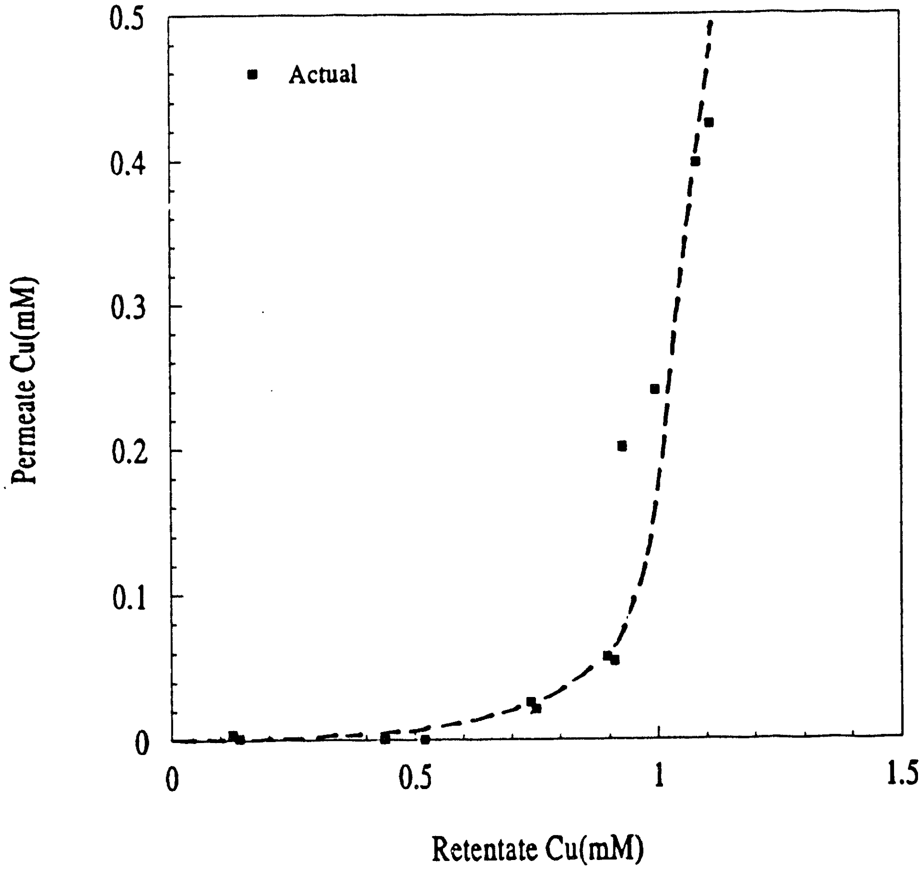


Figure 1.2.11 Actual and model results of Cu in SED experiments with both Ca and Cu together at pH 6.0 using 1.00 mM initial NIDA with 5.00 mM added NaCl.

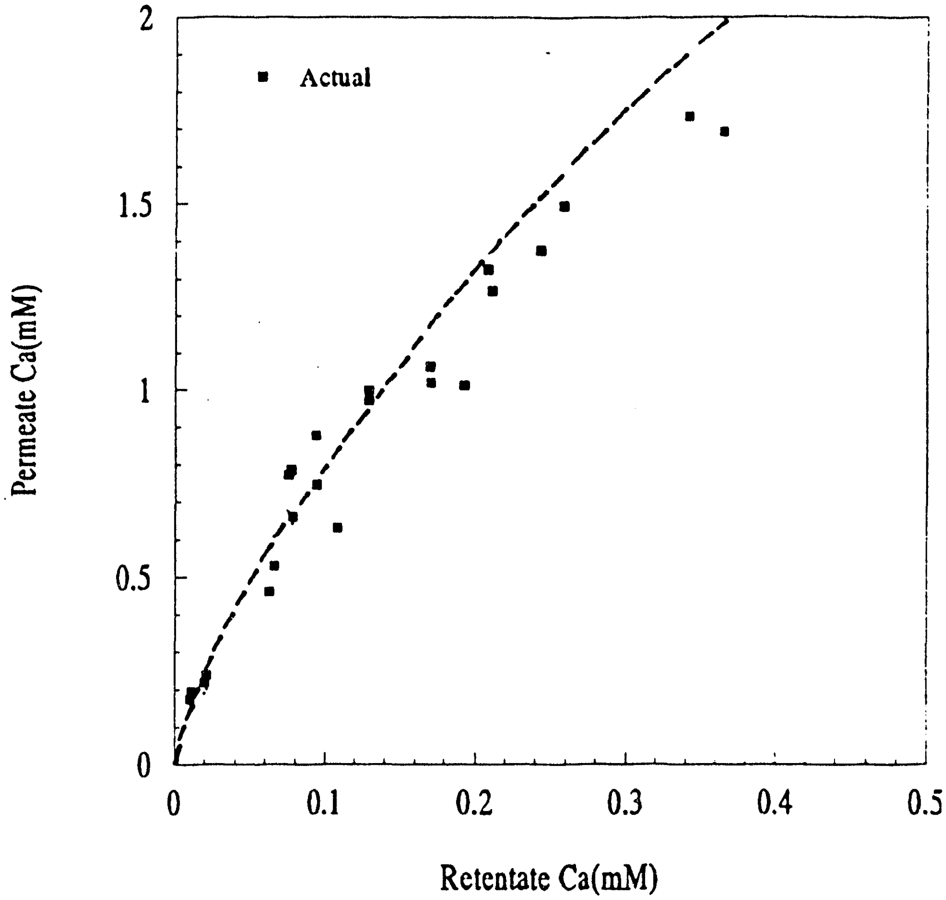


Figure 1.2.12 Actual and model results of Ca in SED experiments with both Cu and Ca together at pH 6.0 using 1.00 mM NIDA with no added salt.

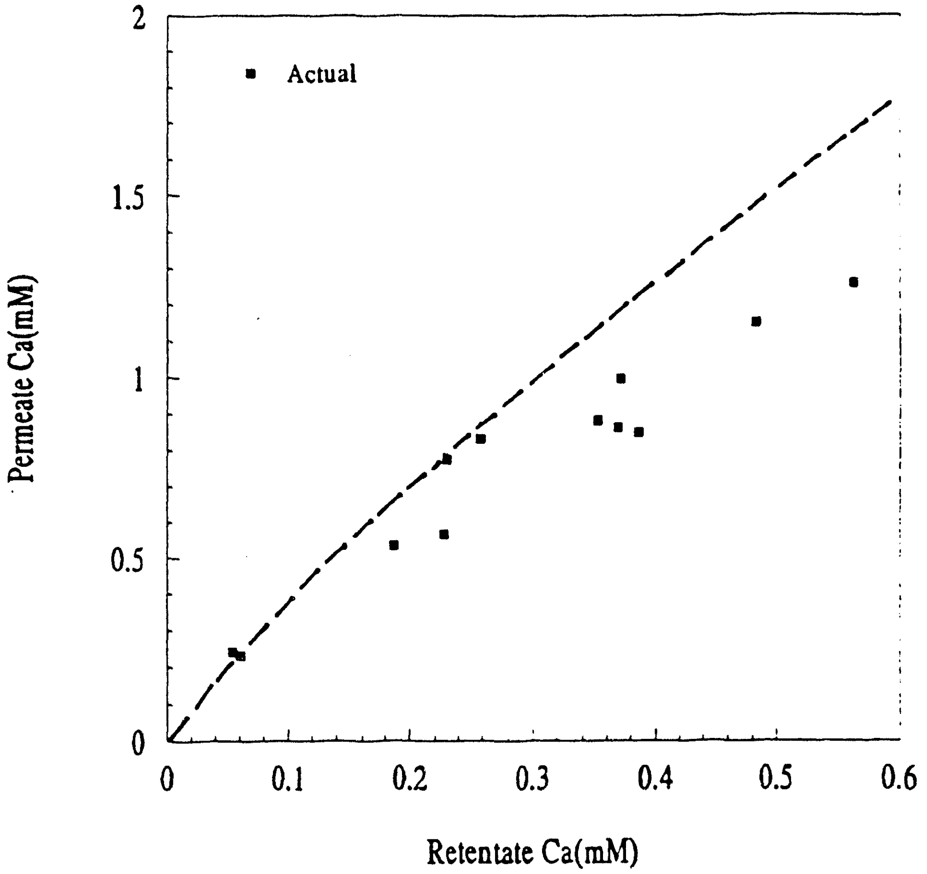


Figure 1.2.13 Actual and model results of Ca in SED experiments with both Cu and Ca together at pH 6.0 using 1.00 mM NIDA with 5.0 mM added NaCl.

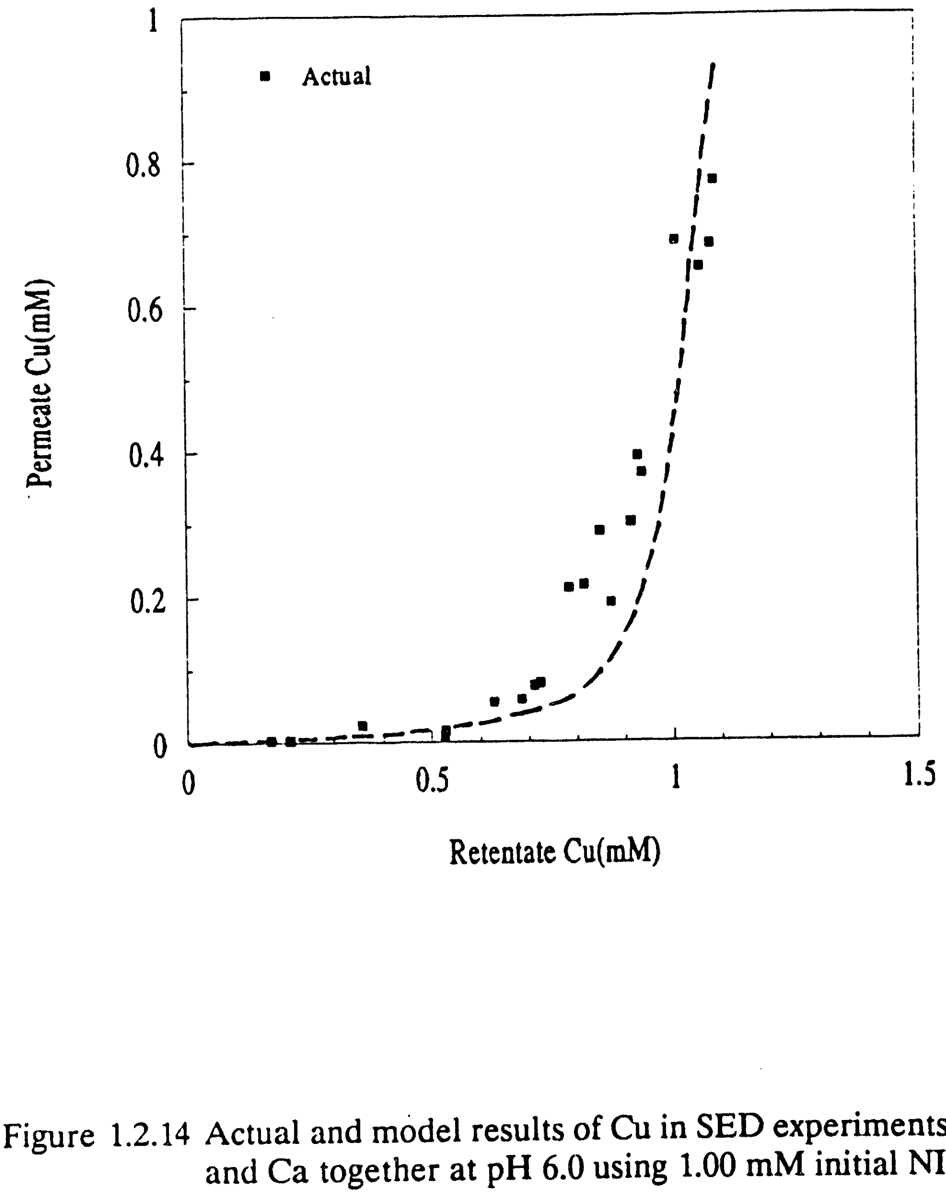


Figure 1.2.14 Actual and model results of Cu in SED experiments with Cu and Ca together at pH 6.0 using 1.00 mM initial NIDA with no added salt.

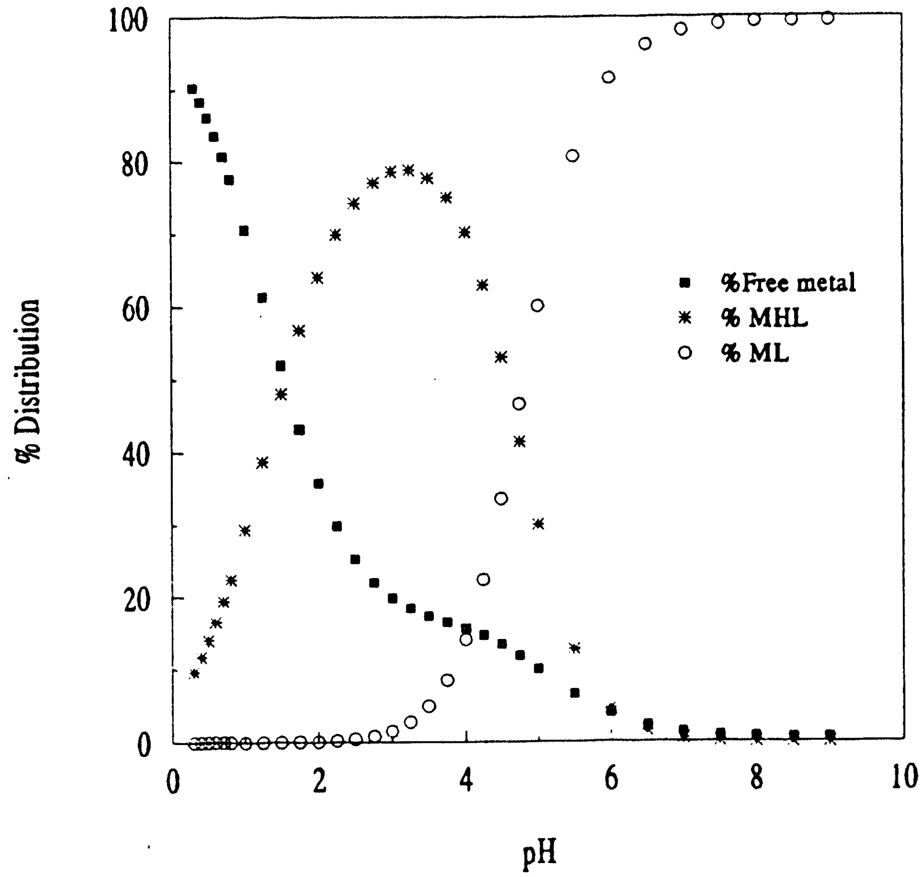


Figure 1.2.15 Distribution of Free metal and complexed metal species in Cu-NIDA system at different pH values.

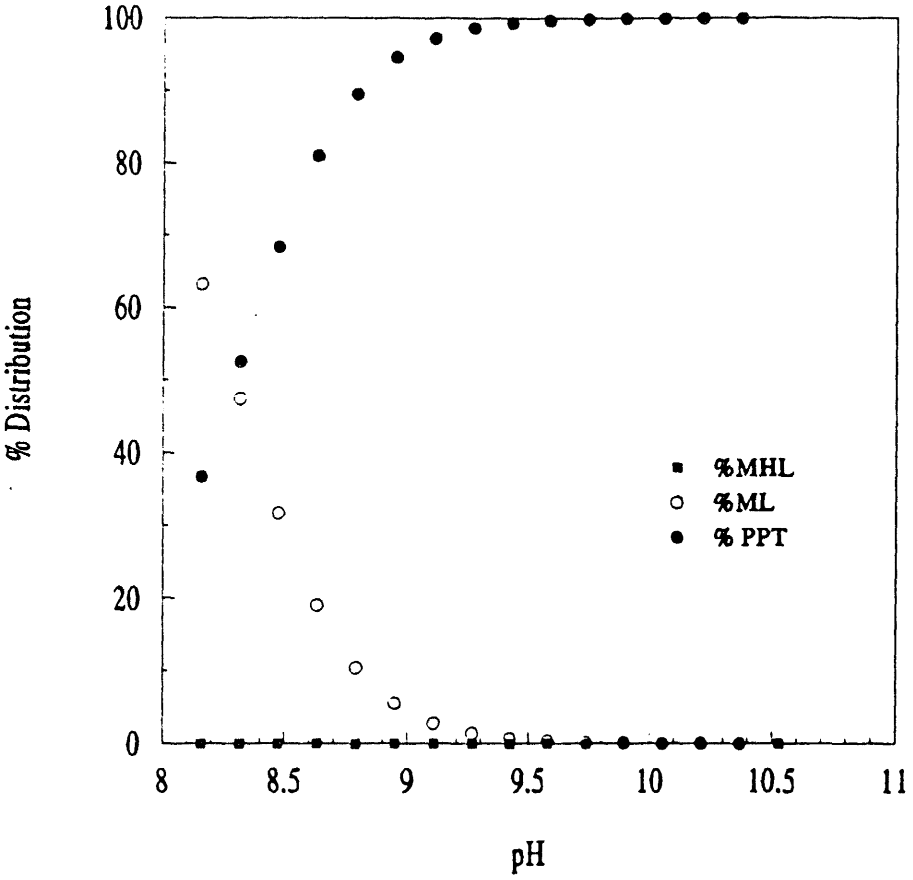


Figure 1.2.16 Distribution of metal hydroxide precipitate, and complexed metal in Cu-NIDA system at higher pH values.

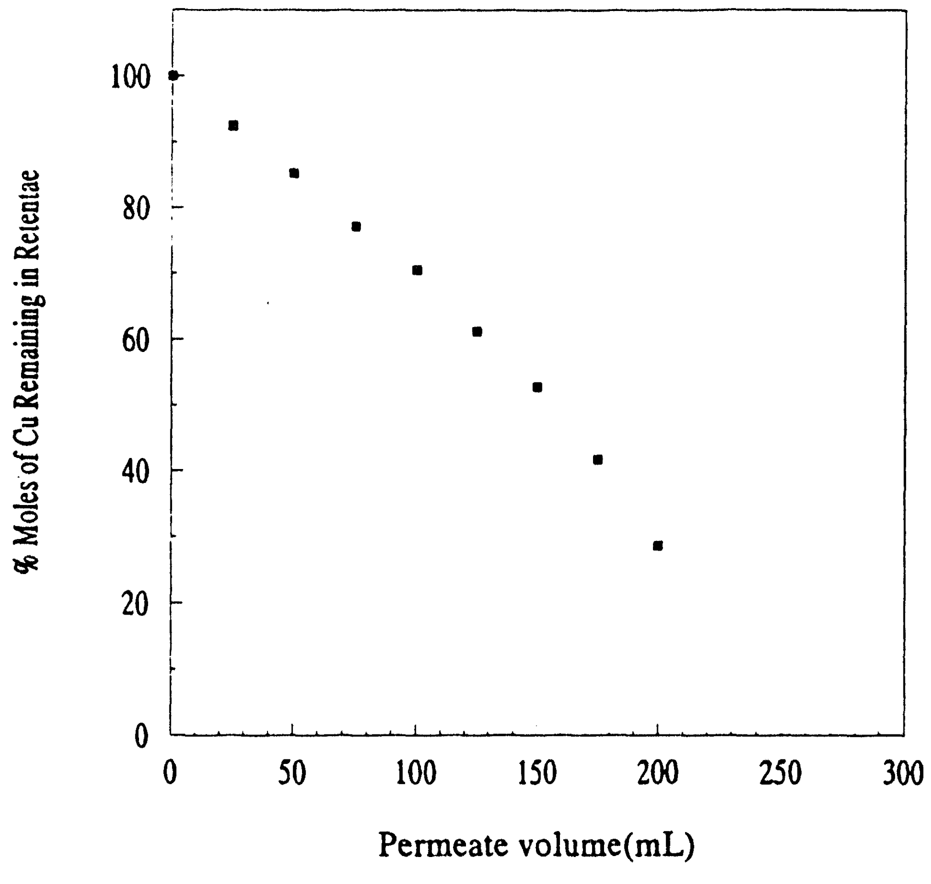


Figure 1.2.17 Results of an ultrafiltration experiment to recover NIDA at pH 0.8

on conditions such as the concentration of ligand, presence of salt and pH, as shown by figures 1.2.7, 1.2.8, 1.2.9, and 1.2.14. It is seen that region 1 which reflects the binding extends further as the ligand concentration is increased or as the pH is increased.

An important feature of this model is that it can quantitatively explain the considerable improvement in retention of target metal ions, especially around region 1, that is induced by the addition of sodium chloride to the retentate compartment as shown by comparison of figures 1.2.8 and 1.2.9 and also by comparison of the retentions tabulated in tables 1.2.12 and 1.2.13. This observation is the opposite of that noted in MEUF experiments performed previously(3,50,51), where addition of NaCl decreases the rejection of divalent cations. Qualitatively, the increased retention of metal ions in LM-MEUF separations can be attributed to electrolyte screening of the ion expulsion effect on the free target metal ions. Moreover, the transfer of sodium ions from the retentate into the permeate may be expected to diminish the expulsion of other metal ions. The present model does not incorporate the former effect directly, but considers the later. A net expulsion of sodium ions is predicted from the model (in solving the model equations the retentate sodium concentration was kept fixed, and the permeate concentration was allowed to change accordingly). The permeate sodium concentration predicted was higher than the retentate. Similarly, the model predicts that the addition of a divalent cation such as calcium will be more effective than sodium in preventing the ion expulsion of copper.

{Viz: From equation (d), $\{[Na]_p/[Na]_r\}^2 = [M]_p/[M]_r$. If Ca^{2+} is used instead of Na^+, then equation (d) becomes, $[Ca]_p/[Ca]_r = [M]_p/[M]_r$. Since, excess Ca^{2+} or Na^+ are present initially in the retentate in both cases, $[Na]_p/[Na]_r$ and $[Ca]_p/[Ca]_r$ ratios in the above equations are both less than unity. Therefore, the $[M]_p/[M]_r$ ratio in the presence of Na is much less than the same ratio in the presence of Ca}.

This effect can be seen in the present results, by comparing figures 1.2.6 where there is no Ca present and 1.2.14 where there is calcium as well as copper. Figure 1.2.14 shows that presence of only 0.5 to 1.0 mM calcium greatly improves the retention of copper, as compared with results for copper alone in Figure 1.2.6. The separations observed in Figure 1.2.14 are relatively close to those in Figure 1.2.11, where the sodium chloride concentration is 5.0 mM. Although it has not been tested experimentally, the model suggests that a 3+ metal cation would be even more effective in screening the ion expulsion effect.

Present experiments and modelling show that an increase in ionic strength, which causes Cu^{2+} to be more effectively rejected by the membrane, does not greatly change the values of the equilibrium constants in the model. One might have anticipated that added NaCl would modify the values of several of the binding constants; in particular, the repulsion between the positively charged micelles and the free Cu^{2+} ions should be diminished, permitting these cations to bind somewhat more strongly to the micelle-solubilized ligands. However, in modelling of the results, the binding constants determined for the ligand (with metal ions and protons) did not have to be modified significantly to account for changes in ionic strength. A small activity coefficient correction, calculated using the Davies equation(45), was applied in modelling the results for solutions containing added NaCl, and these changes did not make much of a difference in the final model results. It may be possible that the present SED experimental results are not very sensitive to detect such a change.

1.3.5 Effect of ion expulsion on the selectivity

Although ion expulsion can diminish the retention of individual cations, as clearly seen from tables 1.2.12 and 1.2.13, (the retention values in table 1.2.12 with no added salt are better than that of table 1.2.13 with added salt) this effect is very important in enhancing selectivity in the removal of cations in the mixed ion systems. When copper and calcium ions are both present in the feed solutions, the copper predominantly complexes with the ligand, leaving most of the calcium free. The cationic CPC expels free calcium from the retentate, without allowing a significant concentration of the copper to be removed. In the absence of ion expulsion, the calcium ions would distribute almost equally between the retentate and permeate solutions, removing any selectivity for this cation. Similar effects have been observed in the previous UF experiments(10). In order for ion expulsion to be effective, the charge of the surfactant micelles must be considerably greater than that of the small dissolved cations. Therefore, it will almost always be advantageous to use a cationic surfactant such as CPC in the LM-MEUF process for the relative separation of cations.

Calcium ions can affect the retention of copper ions, and the expulsion of calcium is also affected by the presence of free copper ions, as was observed in the previous LM-MEUF study⁽¹⁰⁾. The present work has not combined the model equations for calcium and copper in considering mixtures of the metal ions, so the model predictions do not include this effect. However, at the concentrations employed in present SED experiments, such deviations are not very significant.

These results show clearly that LM-MEUF under the conditions employed can be used to achieve good separation and good selectivity for copper and calcium. Selectivity ratios calculated from the plotted data were varying from 4:1 (Cu:Ca) to 8:1 for the retentate solutions, whereas for the permeate solutions the selectivities vary from 1:2 (Cu:Ca) to 1:90, without any added salt (calculated based on table 1.2.12). The presence of an added salt enhances the retention of copper, but it also reduces the selectivity, by hindering the expulsion of calcium. It is also clear that better separations are achieved at low metal ion concentrations. Reasonably accurate predictions of retention and selectivity can be made, although the model would require modification to account for the effect of ligands having significant solubility in water.

The same model equations can be used to make predictions about separation or the selectivity etc. by using the SEQS program to solve simultaneous equations, for given variable values.

1.3.6 The effect of pH and ligand concentration.

The effect of increased ligand concentration is to increase the retention without effecting the ion-expulsion. By lowering the pH the retention is reduced due to reduced complexation. A pH value of 6, would be a more suitable and a practical value to achieve desired separation.

1.3.7 Comparison with LM-MEUF results

The results of SED experiments and the model can be used to compare equilibrium concentrations with those obtained from LM-MEUF, although the concentrations of CPC, metal ions, and ligand employed were somewhat different in the LM-MEUF study than in the present SED experiments. The SED results provide information about equilibrium retentions and selectivities, whereas the separations achieved in the UF experiments are inherently non-equilibrium results. The model equations described above were applied to calculate permeate metal ion concentrations, for conditions corresponding to Table 1 in reference (10) by using the simultaneous equations solver (SEQS, CET Research Group, Norman, Oklahoma) program. Approximately equivalent results are predicted, although some of the retentions of Cu^{2+} were not as good as expected. Thus, for feed concentrations of CPC equal to 0.157 M, with ligand concentration of 0.785 mM and copper concentrations of 0.3 to 0.7 mM, the model predicts permeate Cu concentrations equal to 0.001 to 0.008 mM at pH 7. The observed copper concentrations in the LM-MEUF experiments varied from 0.008 to 0.040 mM under similar conditions.

1.3.8 Recovery of the ligand

The theoretical plots in figures 1.2.15 and 1.2.16 show the distribution of each type of species and their variation with pH. The figure 1.2.17 shows the results of a recovery experiment carried out by ultrafiltration at pH 0.8. An experimental recovery run was carried out at a pH of about 10 after base treatment, by ultrafiltration. Unexpectedly, in this experiment the ligand started to precipitate with the metal hydroxide from solution and the desired recovery could not be achieved.

The percentage of copper that exists as free copper at pH 0.8 is about 75% from the species distribution curves shown in figure 1.2.15. This shows that, only about 75% of the metal ions can be removed from the ligand by doing ultrafiltration at pH 0.8. This value agrees well with the recovery results shown in figure 1.2.17 where, about 25% of copper has remained in the retentate, bound to the ligand, after one ultrafiltration cycle. However, detailed modelling of the ultrafiltration process similar to the LM-MEUF modelling described above did not reproduce the experimental results. A possible reason is that the screening of ion-expulsion due to the presence of large excess of Cl^- ions in solution, which is not taken into account by the model. The species distribution diagram at basic conditions is shown in figure 1.2.16, which shows the possibility of recovering the used ligand by precipitating the bound metal as the metal hydroxide at pH values higher than 9.5. However, in an actual experiment that was done at pH 9.5, it was found that the metal tends to precipitate with the ligand possibly in the form of metal-ligand-hydroxide.

From the species distribution diagram (figure 1.2.15) it is evident that the pH values at which the MHL and the ML complexes become maximum are, 2.70 and 7.70 respectively. Thus it is the pKa_1 value that prohibit easy recovery of the ligand. Therefore, for better recovery of the ligand it is convenient to use a ligand with a higher pKa_1 value so that more metal ions will become free at lower pH values.

1.4 CONCLUSION

The applicability of LM-MEUF in water purification has been further confirmed by the present research and a detailed equilibrium model has been developed to predict the conditions required to achieve efficient water purification. Excellent rejection of copper and expulsion of calcium are simultaneously achieved. Added sodium chloride increases the rejection of copper ions, but reduces the extent of expulsion of the calcium.

Although the presence of many different metal ions may sometimes reduce the effectiveness of the overall separation, this problem can be largely avoided by choosing a ligand concentration that just exceeds that required to bind the target ion(s) in the retentate. Under these conditions the charge of the micelles will be little influenced by the presence of the ligand, the target ions, or the metal ions to be expelled into the permeate. For the screened ion-expulsion that may be observed due to the natural salt content in waste water, a simple procedure is removing the salt by an additional UF run. Recovery of the used ligand is possible at highly acidic pH values by ultrafiltration. However, further work is needed to explore the possibility of improving the recovery.

CHAPTER 2

SELECTIVE SEPARATION OF METAL IONS USING IMINOACETIC SUBSTITUTED POLYAMINES

2.1 INTRODUCTION

2.1.1 Behavior of charged polymers (polyelectrolytes)

Polyelectrolytes are polymers with multiple ionizable groups. In aqueous solutions, they are partially dissociated into polyvalent macroions and free counterions. When polyelectrolytes are dissociated the polymer molecule carries a high charge density, causing it to attract a large fraction of the counterions towards it. This feature of polyelectrolytes is important for their ion-binding and ion-expulsion behavior. Polyelectrolytes may be cationic, anionic, or zwitterionic. A polyelectrolyte may include amine, carboxylate, sulfonate and other organic functional groups, as well as an sp_3 hybridized carbon backbone. As with typical hydrocarbon chains there is freedom of rotation about the carbon-carbon bonds. The electrical field around the polymer may influence the conformation of the polymer chain. When the polymer chain is highly charged the mutual repulsion between charges ordinarily causes the polymer to extend to a more nearly linear conformation. Obviously, conformational changes occurring in the polymer may change the apparent volume of the molecule. According to Oosawa(22), the contracted form of the polyelectrolyte has four areas in which the counterions may be located: (1) the free ion region (2) the region within the influencing sphere of the whole molecule (i.e. bound but mobile) (3) the cylindrical region within the immediate vicinity of the polyion (bound but less mobile) (4) ion pair region (completely bound, potential hole).

2.1.2 Counterion binding to polyelectrolytes

Explanations of electrochemical or solution behavior of polyelectrolytes have long been a challenge in physical chemistry. Early experimental observation showed that many theories of simple electrolytes do not apply to high molecular weight electrolytes. None of the theories presented up to now have been completely satisfactory in explaining the most prominent features of polyelectrolytes.

Generally, the behavior of polyions has been explained based on one of two different models(22,52).

(1) Treating the polymer as a uniformly charged sphere

(2) Treating the polymer as an extended chain with distributed charges.

It can be seen that model 1 is an oversimplified case for a saturated carbon-chain polymer, but the chain model should often correspond more closely to the reality.

A topic of central importance with all polyelectrolytes is the manner in which the polyion interacts with its counterions. Conventionally(53), two modes of interactions, namely *field binding* resulting from purely electrostatic effects and *specific binding* due to more intimate contact between the two species, have been proposed. The theory of counterion binding has been significantly advanced during recent years due to work of many groups(22,54-58). Important concepts have been introduced, including *counterion condensation* and *critical linear charge density*. According to modern theories the polymer is viewed as an infinite line charge with linear charge density (β) given by:

$$\beta = z_p e/b$$

where z_p is the electrovalence of charges, e is the protonic charge, and b is the average distance (in cgs units) between charges for the fully extended chain (in the state of maximum extension without distortion of bond angles). The parameter b is given by the number of charges on the chain divided by the end-to-end length of the chain in the state of maximum extension. In a simple form of the theory, the inter-polymer interactions are neglected and the dielectric constant close to the chain is taken to be that of pure solvent (ϵ). In this theory, the parameter representing linear charge density (ξ) is defined by:

$$\xi = e^2 / \epsilon kTb$$

where k is the Boltzmann constant and T the absolute temperature.

It has been shown that(53), with monovalent charge groups throughout and with fully mobile counterions, the system is unstable if ξ is greater than 1. Therefore, sufficient counterions will condense to bring ξ equal to 1. Thus, in water at 25^{0}C, with ϵ = 78.5, the critical value $\xi = 1$ corresponds to the charge spacing b = 7.135 Å (0.713 nm). As an example, in the case of maximally charged vinyl or acrylic chains, b = 2.5 Å and the parameter ξ has a value 2.85, which requires the condensation of 65% of the counterions to give ξ = 1. Alternatively stated, for an ionizing electrolyte of this type, condensation will start to occur at 35% ionization(53). The remaining uncondensed counterions will still remain subjected to electrostatic interactions which can be treated by Debye-Huckel theory.

Despite the important information that can be derived from the more general condensation model, the two phase theory of counterion binding of polyelectrolytes introduced by Oosawa(22) remains as a simple and readily applicable theory of polyelectrolyte behavior in solution. The distribution of counterions is the main parameter that determines the thermodynamic properties of a system. The distribution of counterions around a cylindrical rodlike polyelectrolyte is given by Oosawa's theory as:

$$\ln[(1-\beta)/\beta] = \ln[\phi/(1-\phi)] + \beta qzQ\ln[1/\phi]$$

It should be noted that the parameter Q used here does not have the same value as the parameter used in case of spherical micelles described in section 2 of chapter 1. Here β and ϕ denote the fraction of free counterions and the volume fraction of the polymer, respectively.

2.1.3 Metal-polymer complexes

Metal polymer complexes are not only important for metal ion separation, but they have also been used to produce highly specific and efficient types of catalysts. In addition they have been used in designing conductive polymers in solid state chemistry(59).

In metalloenzymes such as hemoglobin, where a metal complex is the active site, the macromolecular protein part plays a significant role by controlling the reactivity of the metal complex.

2.1.4 Binding of polymers to metals

Consider a macromolecule P, which consists of several monomeric units, each of which has a single binding site for a certain metal ion M (1:1 complexation).

(1) $M + L = ML$

If the dissociation and association constants for the above reaction are K_d and K_a respectively, then,

(2) $K_d = [M]\,[L] / [ML] = 1 / K_a$

Let R be the average number of moles of metal bound per unit mole of the chelating unit of the polymer (referred to as *binding ratio*), then,

(3) $R = [M]_{bound} / [L]_{total} = [ML] / ([L] + [ML])$

Combining equations (2) and (3),

(4) $R = [M] / (K_d + [M])$ or $R = K_a [M] / (1 + K_a [M])$, which are equivalent to the equation of the Langmuir isotherm.

Binding isotherms$^{(53)}$

In general when a substrate binds to a polymer, one or more of the following isotherms may apply under different conditions.

(1) Linear binding isotherm (or partition binding mode)

This is the simplest possible type of binding isotherm. In this case the binding ratio (R) is directly proportional to the free solute concentration (here the concentration of metal ion, M).

Therefore,

$R = K[M]$

Generally this occurs when the polymer molecule is compact and a nonpolar or slightly-polar substrate partitions between the bulk solution and the relatively hydrophobic interior of the polymer molecule. In the case of synthetic polymers, such binding is likely with nonionized poly(methacrylic acid) and alkanes or aromatic hydrocarbons(61). However, it should also be noted that even more complicated isotherms will take this linear form at very low solute concentrations.

(2) Hyperbolic binding isotherm (Langmuir type isotherm)

The hyperbolic binding isotherm is actually the most commonly encountered isotherm, and it is analogous to the Langmuir adsorption isotherm. The binding equation as described above, takes the form,

$R = K[M] / (1 + K[M])$

However, in the binding of a metal ion to a polymer, commonly the binding does not go to completion. Since R is defined as the average number of moles of metal ions bound per one mole of ligand unit in the polymer, R should reach a value of 1 as [M] approaches fairly high values. However, in the case of ligands attached to the polymer the R calculated even at very high [M] may not be 1, but may be a fractional value less than 1. Clearly, this is an indication that out of the total ligand sites available in the polymer ligand only a fraction can be bound to metal ions. In a such situation the binding will takes a slightly different form(53)

$R = K n [M] / (1 + K[M])$

Clearly n is the limiting value of R when $K[M] >> 1$ or $[M] >> 1/K$. There exist many different ways of testing data, and these are described in the literature(29,53). All those methods are based on different forms of the same equation, but some methods may sometimes give a better representation of data in different regions of the graph. The forms of the equations in some of these methods are given in the following table.

Table 2.1.1 Different linearized forms of hyperbolic binding isotherm.

Type of plot	Form of the equation
Double-reciprocal plot	$1/R = 1 + 1/K[M]$
Scatchard plot	$R/[M] = K - KR$
Linearized Langmuir plot	$[M]/R = [M] + 1/K$

Since most of these representations may yield a very uneven distribution of points it may become difficult to draw the best line to determine parameters. Therefore, a more reliable method in testing the data for hyperbolic isotherm is to fit directly the data to the hyperbolic equation by a non-linear least square method(53,60).

(3) Isotherm for Heterogeneous site binding(53)

The previous binding model can be extended to a case where all the binding sites are not equivalent, in which case the equation takes the form,

$$R = n^{\alpha} K_a^{\alpha} [M] / (1 + K_a^{\alpha} [M]) + n^{\beta} K_a^{\beta} [M] / (1 + K_a^{\beta} [M]) + \ldots\ldots$$

where the binding constants and relevant n values for each binding step have been denoted with superscripts α, β, ... etc. In this case the linearized Langmuir plot or the Scatchard plot will be curved, representing the combination of all individual straight lines. Binding data of the biological macromolecules with metals, in biochemical work has been interpreted in most literature(29,53) by the Scatchard plot and by other slightly different forms under the conditions of heterogeneous site binding. Consequently, any heterogeneity in binding can be identified from the deviations of a linearized plot.

2.1.5 Investigation of metal ion binding to a polymer

The same methods applied in studying the binding of metal ions to monomeric ligand molecules can be used for studying metal binding to polymeric ligands as well. Such methods include equilibrium dialysis, ultrafiltration, potentiometry, spectroscopic studies and a few other methods(29,53). However the method of calculation is not as straightforward as in the case of monomeric species. Most of the older work used Bjerrum's method(30) to calculate complexation constants from the potentiometric titrations . Necessary modifications of these calculations to account for the electrostatic effect of the complexed polymer have been made recently by Gregor(61).

2.1.6 Use of coordinated polymers in metal ion separations

The use of coordinated polymers to remove metal ions from an aqueous phase was proposed many years ago(2,62-64). The synthesis of several different chelating polymer complexes, suitable for different metal ions has been discussed(63). The capability of iminodiacetic acid to form stable complexes with metal ions has also been known(64). Substitution of iminoacetic groups to a polymer backbone consisting of amine nitrogens was reported by Geckeler and co-workers(62). In their work, a ligand substituted polymer synthesized (with less than 50% substitution) starting from poly(vinylamine) have been investigated to separate metal ions: Fe, Ni, Cu, Cd, and Hg, at different pH conditions. These results showed reasonably good capacities for this polymer to bind Cu, Ni and Cd.

In addition to substituted polymers, poly(ethylenimine) or PEI with no substitution has shown(65) promising capacities for Cu, Ni, Hg, Cd, and Zn. Polyethylene-based quinol-8-ol (PEQ) has been synthesized and used for separation of Zr, Nb, W, Bi from other elements, very recently(66). Use of soluble polychelatogens for separation of actinide and transition and rare-earth ions have been studied using sixteen different polymers and derivatives based on PEI, poly(vinyl alcohol), poly(urethane) and poly(acrylic acid) in terms of their capacity and selectivity. All the previous investigations have been carried out using ultrafiltration.

2.1.7 Goals of the Research

The previous studies described in section 2.1.6 have explored both the synthesis of polymers substituted with different ligand groups and preliminary studies of their use in separation of certain metal ions from others. Most of this work has emphasized the effectiveness of separation and the significant capacity of the polymers for metal ions during the process(65-67). From the preliminary investigations of the present work it has been observed that it is impossible to obtain the required or expected selectivity in this separation process by just concentrating on the binding ability of the polymer-ligand to the metal. To achieve a good selectivity the polymer solution should have a fairly good ability to expel metal ions not bound to the polymer to the other side of the membrane. This has been explained in detail in part 1 (Chapter 1) of the present work.

Since this ion-expulsion ability of the polymer-ligand has been overlooked in all of the previous studies(62-67), the research remains incomplete, and further work is necessary to investigate this. In addition, the binding behavior of metals depends very much on the concentration and the nature of the polymer being used. Therefore, more information about the binding behavior of copper to polymers with different percentage substitutions will be of tremendous use in understanding the overall process.

The present work has the following goals, finally aiming at developing an efficient and economical metal ion separation process, to selectively separate target metal ions from others.

(1) Investigation of binding behavior of copper with polymers of varying degree of substitution to study any optimum degree of substitution for a practical water purification process.

(2) Quantitative interpretation of binding data by a suitable isotherm, so that modelling of the system in the future will be facilitated.

(3) Investigation of expulsion ability of the system for the uncomplexed metal ion and the methods of improving this ion expulsion ability.

(4) Preliminary investigation of recovery of the used polymer by acid treatment.

2.1.8 Experimental Approach

The experiments have been performed using a mixture of copper and calcium ions, with copper as the target ion. Poly(allylamine) polymers substituted with iminoacetic ligand groups have been used as the polymer-ligand. However, the results of this work may also be applicable to many other ligand substituted polymers. Equilibrium dialysis has been used to study the process.

The binding behavior of copper with polymers of varying degree of substitution has been studied, at different pH conditions. Expulsion of calcium ions by different polymers has been investigated. In quantitative modelling of binding data the non-linear least-squares data analysis technique has been used. The pH effect on ion expulsion ability has been investigated. Methods to enhance the calcium ion expulsion and their effect on copper retention have been studied. Finally, the recovery of used ligand has been investigated.

2.2 EXPERIMENTAL SECTION

2.2.1a Materials.

Poly(allylamine hydrochloride) (PAAH) of approximate molecular weight 60,000 was obtained from Polysciences Inc. and used as obtained. This material was kept in a tightly closed bottle because it tends to absorb moisture and it changes from pure white to slightly yellow on prolonged exposure to air. Poly(ethylenimine) (50% solution in water) and chloroacetic acid were obtained from Aldrich Company.

In several experiments, PAAH was purified by ultrafiltration, while in some experiments the unpurified PAAH was used intentionally. All molarity measurements in the case of polymers were based on the molecular weight of the monomer unit.

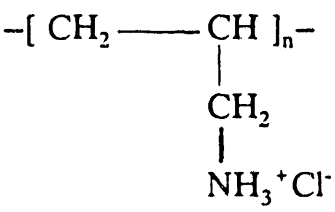
Poly(1-1-dimethyl-3-5-dimethylene-piperidinium chloride) or poly(dimethyl diallyl ammonium chloride) (PDDAC) was obtained from Aldrich Company, as a 20 weight % solution. All molarity calculations were based on this percentage composition.

Chloroacetic acid (CLAC) was obtained from Aldrich Company.

2.2.1b. Dialysis experiments

The dialysis experiments were carried out at 25^0 C, the same way as semi equilibrium dialysis reported earlier, except that in this case true equilibrium is attainable. In analyzing dialysis data the concepts percentage expulsion and percentage retention have been used as defined in section 3 of chapter 1.

Poly(allylamine hydrochloride)



$$-[\,CH_2 - \underset{\begin{array}{c}|\\CH_2\\|\\NH_3^+Cl^-\end{array}}{CH}\,]_n-$$

Poly(ethylenimine)

$-[\,CH_2 - NH\,]_n-$

poly(dimethyl diallyl ammonium chloride)

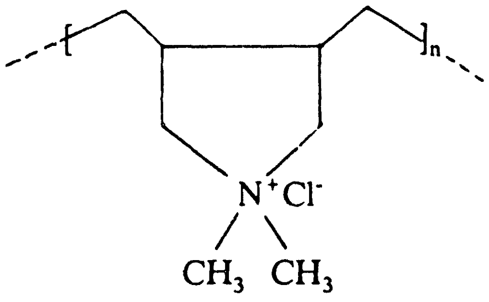


Figure 2.1.1 Chemical structures of different polymers used in investigations.

2.2.1c. Ultrafiltration experiments

All ultrafiltration experiments were carried out with 300 mL initial volume and under a pressure of 70 psi, at 25^0 C, with continuous stirring.

2.2.2 Substitution of iminoacetic groups to the polymer

The substitution reaction was carried out as reported previously(10,47), and the chemical reaction can be represented by two steps

Step 1 - monosubstitution

$RNH_2 + Cl.CH_2COOH$ ------------> $RNH(CH_2COOH) + HCl$

Step 2 - disubstitution

$RNH(CH_2COOH) + Cl.CH_2COOH$ -----> $RN(CH_2COOH)_2 + HCl$

Amounts of PAAH and the CLAC used were changed depending on the product desired. In general two different procedures were employed in synthesizing substituted polymer products.

Procedure 1

In this synthesis procedure, PAAH and chloroacetic acid were mixed in the required proportion by weight of the solids PAAH and CLAC, as received, and the reaction was carried out as follows.

A weighed amount of PAAH and a weighed amount of chloroacetic acid (CLAC) were mixed in a round bottom flask, bringing the total volume to about 50 mL by adding water. The solution was refluxed at 50^0 C for 6 to 8 hours while being stirred. The solution was maintained at about pH 9 throughout by initially adding 1 drop of a phenolphthalein solution to the solution, and frequently adding sodium hydroxide as necessary to keep the solution just pink colored.

Procedure 2

In this synthesis procedure, two solutions of PAAH and CLAC of known concentration were used as stock solutions. The stock solution of chloroacetic acid was standardized by titrating with sodium hydroxide. The concentration of PAAH solution was determined from the initial weight of PAAH used. Required proportions of these solutions were mixed and the reaction was carried out as described in procedure 1. For the products synthesized by this method, the extent of substitution can be approximately calculated knowing the initial quantities of PAAH and CLAC used in the reaction.

2.2.3 Separation of the synthesized product

The final product was recovered by two methods: (1) precipitation and (2) ultrafiltration. By precipitation it was possible to obtain the product in solid form, whereas by ultrafiltration the product obtained was a solution. However, the purification by ultrafiltration has the advantage that it can be carried out quantitatively(25).

Separation by precipitation

In this method, the product polymer was precipitated from solution by acidifying to reach the isoelectric pH (approximately pH 4). Then the supernatant solution was decanted off and this procedure was repeated 2 to 3 times. The final product was recrystallized with an ethanol or methanol and water mixture. The recrystallized product was washed with dry ethanol several times. Although the nature of the product varied according to extent of substitution, generally the product was pure white in color and hard and crystalline in nature. Also the products were found to be more stable in air than the original amine.

Separation by ultrafiltration

In this method, the product was washed with a large amount of water (about 1 to 1.5 L) in an UF cell until all the excess reagents and by products were removed. The wash solutions (permeates) were tested for chloride during each wash cycle.

The loss of polymer in this method is minimal compared to the previous method. Therefore, quite reasonable values for the extent of substitution may be obtained by calculations for products purified by this method, even though the synthesis has been carried out by method 1.

Table 2.1.2 Summary of compositions and the methods used in synthesis, purification and characterization of the substituted polymer products used in dialysis experiments

Product	Synthesis	Initial	Product	Composition		Method of
Number	Method	Polymer	Recovery	Actual	Expected	Determination
2.2.4a	Proced. 1	Unpurif.	Recryst.	135%	----	Elem. Anal.
2.2.4b	Proced. 1	Unpurif.	Recryst.	8.0 mM ligand	----	Fe-Complex
2.2.4c	Proced. 1	Unpurif.	Recryst.	117%	----	Elem. Anal.
2.2.4d	Proced. 1	Unpurif.	Ultrafil.	----	20%	Calculation
2.2.4e	Proced. 2	Unpurif.	Ultrafil.	----	8.4%	Calculation
2.2.4g	Proced. 2	Purified	Ultrafil.	----	20.7%	Calculation
2.2.4h	Proced. 2	Purified	Ultrafil.	----	41.5%	Calculation
2.2.4i	Proced. 2	Purified	Ultrafil.	----	83%	Calculation
2.2.4j	Proced. 2	Purified	Ultrafil.	----	100%	Calculation
2.2.4k	Proced. 2	Purified	Ultrafil.	100%	100%	Elem. Anal.
2.2.4l	Proced. 2	Purified	Ultrafil.	100%	92%	Elem. Anal.

2.2.4 Synthesis of substituted polymers with different extents of substitution

This section describes the synthesis different ligand substituted polymers in detail. However, the table 2.1.2 gives an outline of what has been described in this section.

Synthesis of polymers with maximum ligand substitution

In aiming at studying the separation using highly substituted polymers, the goal of the following synthesis was to obtain product with maximum possible substitution.

2.2.4a A synthesis was carried out using 5g PAAH and a large excess of (about 15g) CLAC, by refluxing for 8 to 10 hours, until no further reaction occurs. The product was separated by precipitation, purified by recrystallization, and elemental analysis was carried out. Several polymers with lower degree of substitution were synthesized to study their suitability in the desired separation process.

Synthesis of polymers with lower extents of substitution

Iminoacetic substituted products were synthesized by several different ways. Most of the initial syntheses were carried out by procedure 1 using unpurified polymer as described from section 2.2.4b to 2.2.4d. However, due to difficulty in estimating the percentage composition of the polymer without doing elemental analysis, most of the later syntheses were carried out using procedure 2.

Synthesis by procedure 1 using unpurified polymer

2.2.4b A synthesis reaction was carried out using 3.00 grams of solid PAAH and 3.00 grams of solid CLAC, as described in synthesis procedure 1. The substituted polymer was separated by precipitation and purified by recrystallization. A solution was prepared by dissolving all the solid product in 100 mL water. The percentage substitution of this product or the concentration of the prepared solution was not known.

2.2.4c A synthesis reaction was carried out using 10.4563 grams of solid PAAH and 5.1776 grams of solid CLAC, until it appeared that further reaction was not occurring. The product polymer was separated by precipitation and purified by recrystallization with 1:1 water/ethanol mixture. This product was dried by first rinsing several times with absolute ethanol and keeping it in a drying oven at 40 C^0. The elemental analysis for C and N were obtained for this product.

2.2.4d A substituted polymer was synthesized using 2.50 grams of PAAH and 0.50 grams of CLAC. The reaction mixture after completion of the reaction was washed by ultrafiltration with about 1 to 1.5 liters of water in an UF cell and the final retentate was brought to 100 mL.

Since the purification was carried out by UF the % substitution of this product could be calculated without making a large error. This solution was expected to be free of any impurities and approximately 265 mM in nitrogen neglecting the loss of polymer in the UF process. This solution was expected to be approximately 52.9 mM with respect to iminoacetic ligand groups (about 20% substituted).

Synthesis by procedure 2 using unpurified polymer

2.2.4e A stock solution of PAAH was prepared by dissolving 5.00 grams of PAAH in 100 mL of solution. A synthesis reaction was carried out using 20 ml of this solution and 2 mL of a 0.45 M chloroacetic acid solution until no further evidence of reaction was seen by observing the phenolphthalein color. The final reaction mixture was purified by washing with 1 to 1.5 liters of water in an UF cell. The retentate solution was transferred to a 100 mL flask and brought to 100 mL accurately.

Neglecting any loss of low molecular weight polymer in the purification process, this polymer solution was estimated to be 107.0 mM in polymer nitrogen and 9.0 mM in iminoacetic groups (about 8.4% substituted), assuming the reaction has gone to completion.

Synthesis by procedure 2 using UF purified polymer

In preparing purer products, for use in which low molecular weight polymer material being would not pass into the permeate, some syntheses were carried out using the UF purified PAAH. The extent of low molecular weight polymer in a polymer sample was determined as described below, during the purification process.

2.2.4f A 5.036 grams sample of PAAH polymer was washed with 450 mL of water in an UF cell. The permeate solutions were collected and brought to a final volume of 500 mL by adding water. Exactly 50 mL of this diluted permeate solution was evaporated to dryness in an open beaker and the residual solid weighed 0.0934 grams. From this result, the extent of low molecular weight polymer (less than 6K dalton) in the PAAH sample was estimated to be 1.85% by weight. It was assumed that most of the low molecular weight polymer has been washed into the permeate by about 450 mL of water. The retentate solution was taken and diluted to 200 mL and used in subsequent synthesis experiments. This solution was estimated to be 4.102 g per 100 mL (or 217 mM in polymer nitrogen).

Several polymers with different percentages of substitution were synthesized using this stock solution, aiming at carrying out dialysis experiments, to investigate the effect of substitution on the copper retention and calcium expulsion. It was speculated that the ion expulsion ability should increase as the percentage substitution decreases.

Synthesis of a polymer with 20.7% ligand substitution

2.2.4g A substitution reaction was carried out using a 10 mL of the UF purified 217 mM solution in section 2.2.4f and 1 mL of a 0.45 M chloroacetic solution. The final polymer product was purified by UF and the purified solution volume was brought to 100 mL. This product was estimated as 4.50 mM in ligand groups and 21.70 mM in polymer nitrogen (20.7% substituted).

Synthesis of a polymer with 41.5% ligand substitution

2.2.4h A synthesis reaction as described above (section 2.2.4g) was carried out using 10 mL of the 217 mM purified polymer solution and 2 mL of 0.45 M chloroacetate, to produce a product that is 9.00 mM in chloroacetate and 21.7 mM in polymer nitrogen (41.5% substituted).

Synthesis of a polymer with 83% ligand substitution

2.2.4i A synthesis similar to 2.24g was carried out using 10 mL of the purified polymer solution and 4.0 mL of the 0.45 M chloroacetic acid solution, to produce a polymer product that is 18.0 mM in iminoacetic groups and 21.7 mM in polymer nitrogen (83% substituted), assuming that the reaction has gone to completion.

Synthesis of a products with 100% substitution

2.2.4j 2.01 grams of polyallylamine hydrochloride was purified by UF with about 1.2 liter of water, and the final retentate solution was brought to exactly 200 mL. This solution was estimated as 0.1075 M in N, neglecting the amine lost during the washing. Based on 1.85% amine loss experimentally found earlier, this solution was estimated to be 0.1055 M.

Two syntheses were carried out as described in 2.2.4k and 2.2.4l using the same procedure and same amount of material, to investigate the quantitative reproducibility of the synthesis procedure.

2.2.4k A synthesis was carried out using 20.00 mL of the stock solution and exactly 2.00 mL of a 1.0155 M chloroacetic acid solution, until completion of the reaction. The product solution was purified by UF with 1 to 1.5 liter of water. The final retentate solution was brought to 100 mL and used as the stock solution for subsequent dialysis experiments. The concentration of this solution in polymer is 21.1 mM, which is accurate enough for dialysis experiments. The concentration of iminoacetic group is not exactly known, but can be calculated approximately as 20.3 mM. For proper characterization, a 10-15 mL fraction of this stock solution was freeze dried and dried in a vacuum desiccator for a few days and elemental analysis was carried out.

2.2.4l This synthesis reaction was carried out in exactly the same way as described in the previous section (section 2.2.4k) and the elemental analysis was done the same way.

2.2.5 Characterization of substituted polymers

The methods tried were,

(1) Titration of the product with a base.

(2) Spectrophotometric study of Cu-polymer complex and Fe-polymer complex(44).

(3) Determination of primary amine groups by reacting with salicylaldehyde(68).

(4) Based on the sodium hydroxide consumed and CLAC used initially, in the synthesis.

The most suitable method for characterization of the polymer substituted products was found to be elemental analysis, which was done at Midwest Microlab Ltd (Indianapolis, Indiana). However, it was not possible to carry out elemental analysis with many samples because the expense was too great. Therefore, only the most important samples were characterized by elemental analysis.

The method of determination of percentage substitution by calculations based on the initial quantities of amine and CLAC used in the reaction was found to be adequate for experiments where quantitative determinations were not required.

2.2.6 Characterization by spectrophotometric analysis of copper and ferric complexes.

2.2.6a Spectrophotometric titration of the substituted polymer with copper

<u>method 1</u>

The 135% substituted characterized polymer was used to test the possibility of determination of substituted polymers by spectrophotometric titration with copper. By weighing the required amount of polymer accurately, a 10 mM solution of 135%

substituted polymer was prepared. Exactly 3.00 mL of this solution was titrated with an exactly 10 mM copper solution measuring the absorbance at 650 nm. However, in this experiment the absorbance was increasing, even after addition of 23.0 mL of the copper solution.

The same titration was carried out by adding the polymer solution to a 3.000 mL sample of the 10.0 mM copper solution. The titration volumes were measured using a micro-pipet. This titration produced an end point which was accurately determined using a volume versus absorbance plot. It was found that 0.500 mL were exactly titrated with the 3.00 mL of 10.0 mM copper solution. This showed that the 10 mM solution of 135% substituted polymer has a maximum capacity of 60 millimoles of copper per liter. This is equivalent to a binding ratio of 6 copper atoms per ligand group, which is an unexpectedly high value.

method 2

This spectrophotometric titration was carried out according to a method that has been described elsewhere(69). A 5% solution of sodium acetate was prepared by dissolving a weighed amount of sodium acetate in water. The pH of this solution was brought to 5.5 by adding glacial acetic acid. This solution was used as a buffer solution for pH 5.5. A 2.0 mM copper acetate solution and a known solution of the polymer were prepared in pH 5.5 buffer solutions. Several 1 mL samples of the copper solution were exactly measured into 10 mL volumetric flasks and exactly measured different volumes of polymer solution were added to each flask. Then the total volumes of each were brought to 10 mL by adding a buffer solution. The absorbances of the solutions were measured at 300 nm. The end point was determined using a volume versus absorbance graph.

UV calibration of standard polymer solutions using 135% substituted polymer

In this analysis the use was made of the peak of Cu-polymer complex shown at about 246 nm. Although considerable interference arose because of the absorption of the Cu-Cl bond, care was taken to avoid this by using a proper reference or blank. A 5.00 mM solution of $CuCl_2$ was prepared and different amounts of a 1.995 mM solution of 135% substituted polymer were added to 1.00 mL portions of this copper solution. The final volumes were brought to 25.00 mL by adding water. No buffer was added but the pH values of the solutions were checked and found to be in the range 6.30 to 6.70. Absorbances were measured at 246, 256, 266, and 276 nm. However, in all samples to be analyzed, pH had to be maintained in this range. The calibration graph was drawn and the molar extinction at 246 nm was determined as 3324 M^{-1}.

2.2.6b Fe-polymer complex method to determine substituted polymers

UV calibration of standard polymer solutions using 135% substituted polymer

A chloroacetate/NaOH buffer solution at 2.2 was prepared as described in the experimental section of chapter 1. To 1 mL portions of 1.949 mM $FeCl_3$ solution prepared with a pH 2.2 buffer, in 10 mL volumetric flasks, different volumes of 7.815

mM 135% substituted polymer solutions were added and the final volume was brought to 10 mL by adding water. Absorbances were measured at 254, 260, 270, and 280 nm. A calibration graph was drawn to obtain a molar extinction of 1670 M^{-1} at 254 nm.

2.2.7 Characterization by the amount of NaOH used

A synthesis was carried out with 3.0g of polymer and 3.0 g of CLAC, both initially made just basic to phenolphthalein and the NaOH consumed was determined during the course of reaction. However, it was very difficult to obtain accurate measurements because the color changes at the end point were not sharp enough.

Table 2.1.7 Summary of all the dialysis experiments performed using different polymer products.

Table number	Polymer Conc.(mM)	Percent. Lig. Subst.	Initial pH	Polymer Used	Details
2.2.1	0.17	135%	5.0	2.2.4a	Cu only
2.2.2	0.17	135%	6.0	2.2.4a	Cu only
2.2.3	----	----	4.0	2.2.4b	Cu only
2.2.4	----	----	4.5	2.2.4b	Ca only
2.2.5	1.0	135%	3.0	2.2.4a	Ca only
2.2.6	1.0	135%	4.5-5.0	2.2.4a	Ca only
2.2.7	1.0	135%	3.0	2.2.4a	Cu only
2.2.8	1.0	135%	5.0	2.2.4a	Cu + Ca
2.2.9	26.5	20%	5.0	2.2.4d	Cu + Ca
2.2.10	53.5	8.4%	5..0	2.2.4e	Cu + Ca
2.2.11	0.75	117%	7.0	2.2.4c	Cu + Ca
2.2.12	1.7	117%	7.0	2.2.4C	Cu + Ca
2.2.13	4.8	117%	7.0	2.2.4c	Cu + Ca
2.2.14	1.0	Unsubst.	5.0	----	Cu + Ca
2.2.15	53.5	Unsubst.	5.0	----	Cu + Ca
2.2.16	4.34	20.7%	7.0	2.2.4g	Cu + Ca
2.2.17	4.34	41.5%	5.0	2.2.4g	Cu + Ca
2.2.18	4.34	41.5%	7.0	2.2.4g	Cu + Ca
2.2.19	4.34	83%	7.0	2.2.4g	Cu + Ca
2.2.20	2.0	100%	6.0	2.2.4K	Cu only
2.2.21	2.0	100%	6.0	2.2.4k	Cu + 1.0M KCl
2.2.22	2.0	92%	6.0	2.2.4l	Cu only

2.2.23	4.34	41.5%	7.0	2.2.4g	Cu+Ca+ 0.108M PAAH
2.2.24	1.63	117%	7.0	2.2.4c	Cu+Ca+CPC
2.2.25	----	----	----	----	Cu + Ca+ PDDAC
2.2.26	1.63	117%	7.0	2.2.4c	Cu + Ca + PDDAC
2.2.27	1.63	117%	7.0	2.2.4c	Cu + Ca + PAAH
2.2.28	----	----	7.0	----	Cu + Ca + PAAH
2.2.29	53.5	Unsubst.	----	----	Cu + Ca + PAAH
2.2.30	21.4	Unsubst.	----	----	Cu + Ca + PAAH
2.2.31	10.7	Unsubst.	----	----	Cu + Ca + PAAH
2.2.32	2.0	100%	6.0	2.2.4k	Cu + Ca + 0.0527M PAAH (pre-ultrafil.)

2.2.8 Equilibrium dialysis experiments with the synthesized polymers

Following sections describe details of dialysis experiments performed using the synthesized polymers. The characteristics of the products used in these dialysis experiments are provided in table 2.1.2 and the details of all the dialysis experiments performed using these products are summarized in table 2.1.7.

0.17 mM of 135% substituted characterized polymer

2.2.8a This experiment was carried out with 0.17 mM (very low concentration) of the 135% substituted polymer, as described below. A 10 mM solution of the 135% substituted polymer was prepared by dissolving 0.1521 grams of the polymer. This solution was diluted serially 3 times and 10 times respectively to obtain a 0.33 mM solution. This 0.33 mM solution was diluted again exactly by half during the process of making solutions by mixing with different volumes of copper and calcium solutions and water, for dialysis experiments. The results of dialysis experiments with this polymer solution at pH 5.0 and at pH 6.0 are shown in tables 2.2.1 and 2.2.2 respectively.

1.00 mM of 135% substituted characterized polymer with Ca at low pH values

Since the results of previous experiments showed satisfactory copper binding by the substituted polymers, in subsequent experiments it was intended to investigate any possibility of electrostatic binding of the dissociated carboxylic groups with calcium, by varying the pH of the solution. These experiments were carried out with only calcium in the system using 1.00 mM of 137% substituted polymer as described below.

2.2.8b A 1.995 mM stock solution of the polymer was prepared by accurately weighing a sample of solid polymer. Dialysis solutions were prepared by diluting this solution 2 times. The results of dialysis experiments carried out at initial pH ranges of 3.5 to 4, 4.5 to 5.0, and at 3.7 (±0.1) are shown in tables 2.2.5, 2.2.6, and 2.2.7 respectively.

1.00 mM of 135% substituted characterized polymer with Cu and Ca

2.2.8c An identical set of dialysis experiments as in section 2.2.8b was performed with copper and calcium at an initial retentate pH of 5. The final pH values in the retentate after the experiment were also measured, and found to vary from 5.9 to 6.5. The results of these experiments are shown in table 2.2.8.

Equilibrium dialysis using polymers with lesser extents of substitution

Uncharacterized polymer with approximately 1 mM in ligand groups

The following experiments were carried out with uncharacterized, partially-substituted polymer synthesized using equal quantities of PAAH and CLAC; the results show the feasibility of using less-substituted polymers to bind copper. However, these results do not give any quantitative information.

2.2.8d Dialysis experiments were carried out using the substituted polymer solution described in 2.2.4b. This solution was a partially substituted polymer with percentage substitution and concentration not exactly known. However, previous analysis of the stock solution by Fe-polymer complex method showed that dialysis solutions were approximately 1 mM in ligand groups. The dialysis experiments were carried out at pH 4.0 and 4.5 and the results are shown in tables 2.2.3 and 2.2.4 respectively.

Different concentrations of 117% substituted characterized polymer at pH 7.0

Although the 117% substituted polymer is close to the maximum (135%) attained in extent of substitution, the experimentation with this product was much easier owing to its better solubility. Also this product was expected to have a better complexing power for copper than the less-substituted products. Therefore, more experiments were carried out with this product, using a wide range of concentrations. Since the degree of substitution here is quite close to the maximum substitution obtained, these experimental investigations at different concentrations are fairly important.

2.2.8f Using the 117% substituted polymer synthesized in section 2.2.4c three different sets of dialysis experiments were carried out using 0.75 mM, 1.70 mM, and 4.80 mM concentrations of the polymer based on N, at pH 7.0. The results are shown in tables 2.2.11, 2.2.12, and 2.2.13 respectively.

The dialysis experiments described in sections 2.2.8g and 2.2.8h, have been carried out using the substituted polymers, synthesized from initially unpurified polymer. The aim of these experiments was to investigate the effect of percentage substitution on the final selectivity and separation. In these two experiments the ligand concentrations were nearly equal (5.3 mM in 2.2.8g and 4.5 mM in 2.2.8h) while the total polymer concentration was changed. Also the % substitutions are quite low (8.4% and 20%) so that a concentration of unsubstituted polymer which is critical for better ion expulsion, can be attained without having to much increase the total polymer concentration.

Approximately 20% substituted and 26.5 mM polymer at pH 5.0

2.2.8g The substituted polymer solution prepared in section 2.2.4d, diluted 10 times, was used to prepare the solution for this experiment. The dialysis solution was approximately 26.5 mM based on N with a 20% ligand substitution. Results of this experiment are shown in the table 2.2.9.

Approximately 8.4% substituted and 53.5 mM polymer at pH 5.0

2.2.8h The substituted polymer solution prepared in section 2.2.4e was used in this experiment after diluting by exactly a factor of 2. This dialysis solution therefore consists of approximately 53.5 mM polymer, substituted with 8.4% iminoacetic groups. The results of dialysis experiments are shown in table 2.2.10

Dialysis experiments using polymers purified by ultrafiltration

The following dialysis experiments (section 2.2.8g to section 2.2.8k) were carried out to investigate the effect of extent of substitution of the polymer on the separation as well as the selectivity of the final product. The total polymer concentrations used in these experiments are too low to observe a large calcium expulsion effect. However, the effect of concentration on copper binding can be conveniently studied by these experiments. Since these polymers have been synthesized using the purified polymer, no polymer material can pass through the membrane, thus avoiding complications in interpreting the experimental results.

4.34 mM of 20.7% substituted polymer at pH 7.0

2.2.8i The substituted polymer solution prepared in section 2.2.4g was diluted by a factor of 5 before use in dialysis experiments. Therefore, the dialysis solutions are 4.34 mM in polymer with 20.7% ligand substitution. These experiments were carried out at pH 7.0. The results are shown in table 2.2.16.

4.34 mM of 41.5% substituted polymer at pH 5.0 and 7.0

2.2.8j The substituted polymer solution prepared in section 2.2.4h was used in this experiment after 5 times dilution. Therefore, the dialysis solution is 4.34 mM in polymer with 41.5% ligand substitution. The two set of experiments carried out at pH 5.0 and 7.0 are shown in tables 2.2.17 and 2.2.18 respectively.

4.34 mM of 83% substituted polymer at pH 7.0

2.2.8k The substituted polymer solution prepared in section 2.2.4i was used in this experiment with a dilution factor of 5. Therefore, the dialysis solution is 4.34 mM in polymer with 41.5% ligand substitution. The experiments were carried out at an initial pH of 7.0, and the results are shown in table 2.2.19.

Dialysis with 100% and 92% substitution characterized polymers in the presence and absence of excess salt, pH 6.0

The main aim of these experiments was to investigate quantitatively the binding behavior of copper with this polymer in the absence and the presence of excess salt. The copper concentrations in these experiments were determined more accurately by the PAR method.

2.2.8l Dialysis experiments were carried out at pH 6.0, using 2 mM of the characterized 100% substituted polymer synthesized in section 2.2.4k, with no salt added to the system. The results are shown in table 2.2.20.

2.2.8m Dialysis experiments were carried out the same way as described above (section 2.2.8l), but with the addition of 1.0 M KCl to both sides of the dialysis cell. The results of dialysis experiments are shown in table 2.2.21

2.2.8n Dialysis experiments were carried out using 2 mM of 92% substituted polymer, at pH 6.0, without any added salt. The results are shown in table 2.2.22.

2.2.9 Equilibrium dialysis experiments to investigate Ca-expulsion

Experiments 2.2.9a and 2.2.9b were performed with unsubstituted PAAH at pH 5.0 to investigate the ion expulsion ability and the binding of Cu and Ca to PAAH at pH 5.0.

Dialysis experiments using PAAH at low concentration

2.2.9a Dialysis experiments were carried out with 1 mM concentration of the unpurified unsubstituted PAAH at pH 5.0 (adjusted by adding NaOH), to investigate the possibility of ion-binding to the free polymer at this pH. The results are shown in Table 2.2.14.

Dialysis experiments using PAAH at high concentration

2.2.9b Dialysis experiments were carried out with 53.5 mM unpurified unsubstituted PAAH, which is a much higher concentration than that used in the previous experiment. In this experiment also the initial pH was adjusted to 5.0 by adding NaOH. This experiment was aimed at investigating the expulsion effect of PAAH at pH 5.0. Results of the dialysis experiments are shown in table 2.2.15.

The results of this experiment can be compared with the results of the experiment described in section 2.2.8h, which also has been carried out with 53.5 mM polymer but with a 8.4% ligand substitution.

2.2.10 Dialysis experiments with added reagents to increase calcium expulsion

One method to induce expulsion effect to the system without reducing the binding ability of the ligand substituted polymer is by adding another reagent with good ion expulsion ability, in the system. Therefore, equilibrium dialysis experiments were performed with added reagents such as,

(1) CPC,

(2) PDDAC

(3) PAAH,

Dialysis experiments with added PAAH using 41.5% substituted polymer with Cu and Ca both and at pH 7.0

2.2.10a The solution used in these dialysis experiments was prepared by 5-fold dilution of the solution of substituted polymer synthesized using purified PAAH, described in section 2.2.4h, which was 41.5% ligand substituted and 21.7 mM in N. Therefore the diluted dialysis solution was 4.34 mM in 41.5% substituted polymer. The experiments were carried out at pH 7.0, after addition of 108.5 mM concentration of unsubstituted purified PAAH to this solution. The results of these experiment are shown in Table 2.2.23, which indicates the effect of added free PAAH on expulsion of calcium.

Dialysis experiments using 1.63 mM of 117% substituted polymer and added PAAH at pH 7.0

2.2.10b Dialysis experiments were carried out using different amounts of PAAH, in the presence of 1.63 mM of 117% substituted polymer at a pH of 7.0. The copper and calcium concentrations were kept almost fixed in all experiments. The aim of these experiments was to investigate the effect of the PAAH concentration on calcium ion expulsion, in a situation where most copper was bound to a polymer ligand. The results are shown in table 2.2.27.

Dialysis experiments using PAAH and Ca without any polymer ligand at pH 7.0

2.2.10c Dialysis experiments were carried out using different amounts of PAAH, in the absence of any substituted polymer at pH 7.0, using only calcium in the system. The calcium concentration was kept almost fixed in all experiments. The aim of these experiments was to investigate the effect of the PAAH concentration on calcium ion expulsion, in the absence of copper, or copper bound to a polymer ligand. The results are shown in table 2.2.28.

Dialysis experiments using 1.63 mM of 117% substituted polymer and added CPC at pH 7.0

2.2.10d Dialysis experiments were carried out with 1.63 mM of 117% substituted polymer at pH 7.0, using different amounts of CPC and fixed amounts of copper and calcium in each experiment. In all these experiments, the permeate CPC concentrations were determined by UV-spectrophotometry. This set of experiments was performed to determine the capability of CPC to enhance ion-expulsion. Results of these experiments are shown in table 2.2.24.

Dialysis experiments using 1.63 mM of 117% substituted polymer and added PDDAC at pH 7.0

2.2.10e In this set of dialysis experiments, different concentrations of PDDAC polymer were used with a 1.63 mM concentration of 117% substituted polymer, while copper and calcium concentrations were kept almost constant in all experiments, and the pH was brought to 7.0. The results are shown in table 2.2.26.

2.2.11 Dialysis experiments to investigate the ion-expulsion ability of purified PAAH without pH adjustment

Dialysis experiments were performed using the 0.1055 M, UF-purified PAAH solution prepared in section 2.2.4j, without pH adjustment. However, the pH of the solutions of these experiments were found to be in the range 4.0 to 5.0. These dialysis experiments were carried out at 3 different PAAH polymer concentrations, with varying copper concentrations. In these experiments copper was used to investigate expulsion instead of calcium, because Cu itself did not show any binding to PAAH, and it was much easier to determine Cu by UV spectrophotometry than Ca. Determination of copper was carried out by the PAR method(43). The results of these experiments carried out with 53.5 mM, 21.4 mM, and 10.7 mM concentrations of polymer are shown in tables 2.2.29, 2.2.30, and 2.2.31, respectively.

The main aim of these experiments was to obtain a general quantitative expression for ion expulsion behavior of PAAH, for comparison with predictions of Oosawa's theory. However, this attempt did not produce successful results. The actual data points showed less ion expulsion than predicted by the model, especially at higher copper concentrations, even after including a correction factor to account for the osmotic dilution effect.

2.2.12 Dialysis experiments to investigate the effect of salt content

The results from all experiments up to now, suggested the necessity of investigating the effect of salt content owing to the pH adjustment or any other factor. Therefore, the following experiment was carried out using a UF purified solution mixture after adding different amounts of calcium.

A solution was prepared by mixing 50 mL of 0.1055 M purified PAAH solution prepared in 2.2.4j, 10 mL of the solution of 100% substituted polymer prepared in section 2.2.4k, 20 mL of approximately 5 mM cupric chloride solution, and 20 mL of water. The pH of the solution was adjusted to 6.0 by adding about 1.3 mL of a 0.2454 M NaOH solution and the solution was purified by UF, with about 1L of water, to remove any excess salt added due to pH adjustment. Dialysis experiments were carried out using this purified solution after addition of varying amounts of calcium chloride. The results are shown in table 2.2.32.

2.2.13 Ultrafiltration Experiments

Ultrafiltration experiments described in the following sections were carried out to investigate the applicability of dialysis results to larger-scale ultrafiltrations. In all these experiments the initial solution volumes were 300 mL and the permeate samples collected were each 25 mL, except in case of recovery experiments. The solutions were stirred throughout the experiments. All pH adjustments were carried out by adding NaOH or HCl as necessary.

Ultrafiltration experiments with 117% substituted polymer

2.2.13a An ultrafiltration experiment was carried out at pH 7.0, using 1.96 mM concentration of 117% substituted polymer, and adding respectively, 0.0256 grams and 0.0331 grams of cupric chloride and calcium chloride to the solution.

The permeate samples were analyzed for Cu and Ca by atomic absorption spectrometry, and the retentate values were calculated using the permeate results and and mass balance equations. The results are shown in table 2.2.33.

Ultrafiltration with added PDDAC polymer

2.2.13b An ultrafiltration experiment was carried out at pH 7.0, using a 3.68 mM concentration of 117% substituted polymer, and an added concentration of 42 mM of PDDAC polymer, after addition of 0.0256 grams and 0.0220 grams of cupric chloride and calcium chloride respectively. The results of this experiment are shown in table 2.2.34.

2.2.14 Experiments to investigate recovery of used polymer

Preliminary investigations

In these preliminary recovery experiments, the recovery of the used polymer was investigated by three methods as described below.

1. By acid treatment to break the metal-polymer bond
2. By base treatment to precipitate the metal as hydroxide
3. By adjusting the pH to precipitate the polymer at its isoelectric point.

Addition of an acid has been a standard method to dissociate the metal-ligand bonds, as described in chapter 1.

Method 2

An attempt to recover the synthesized polymer by addition of a base was carried out in solution prior to ultrafiltration experiments. This was not successful due to precipitation of the polymer with the metal (possibly in the form of ML(OH)), as found analogous experiments in chapter 1.

A similar attempt with the PEI-Cu complex was also not successful because in this case the pH increase did not precipitate the copper at all.

Method 3

An experiment was carried out by using a concentrated solution of 117% substituted polymer with adequate copper to bind with it in solution. The pH of this solution was close to pH 7.0. The pH was lowered by adding 5M HCl slowly until the solution became cloudy (precipitation point). However, the exact value of the iso electric pH was not known in this case. A clear white precipitate of the polymer was observed initially in the experiment. However, eventually the white solid became bluish by absorbing copper from solution and therefore the experiment was not successful.

Method 1

Recovery by lowering the pH and subsequent UF runs

A 300 mL of 1.96 mM solution of 117% substituted polymer was prepared and 0.08 grams of cupric chloride was added to this solution and the pH was adjusted to 1.0 by adding about 4.0 mL of concentrated HCl. The copper concentration of this solution was determined by atomic absorption spectrometry and found to be 1.293 mM in copper. An ultrafiltration experiment was carried out using this solution. In this recovery experiment, the number of permeate samples collected was less than in previous UF experiments.

During the first UF cycle a volume of 187 mL of the permeate solution was collected and the concentration of copper in the permeate and the retentate were determined and the results are shown below.

Permeate copper concentration in first UF run = 1.208 mM.

Retentate copper concentration of first UF
after diluting to 300 ml = 0.592 mM

The diluted retentate solution from the first cycle was used in the second UF cycle after adjusting the pH to 1.0 again. The second UF cycle was carried out using this solution collecting a permeate volume of 235 mL. The copper concentration of the permeate and the retentate after dilution to 300 mL were determined.

Permeate copper concentration of second UF run = 0.575 mM

Retentate copper concentration of second UF

after diluting to 300 mL = 0.158 mM

A third UF cycle was carried out similarly, by bringing the retentate solution from the second UF cycle to 278 mL and pH of 1.0. In the third cycle, carried out with this solution, the permeate volume collected was 223 mL. The experimental determination of copper in permeate solution and the retentate diluted to 300 mL gave the following results.

Permeate copper concentration of third UF run = 0.161 mM

Retentate copper concentration of third UF

after diluting to 300 mL = 0.0252

It was possible to calculate the percentage recovery, which is defined as percentage of moles of copper removed from the starting number of moles of copper in the retentate in each cycle. This showed the percentage recovery values to be 54%, 73%, and 84% respectively for first, second, and third cycles.

Table 2.2.1 Results of equilibrium dialysis experiments using 0.17 mM of maximum substituted (135%) polymer at pH 6.0, with only Cu.

Initial Cu(mM)	Retentate Cu(mM)	Permeate Cu(mM)	% Cu Ret.
1.5(approx.)	1.312	0.0977	92.55
	1.278	0.1137	91.10
0.8	0.834	0.0058	99.30
	0.868	0.0044	99.49
0.5	0.813	0.0031	99.61
	0.811	0.0040	99.51

Table 2.2.2 Results of equilibrium dialysis experiments using 0.17 mM of maximum substituted (135%) polymer at pH 5.0, with only Cu.

Initial Cu(mM)	Retentate Cu(mM)	Permeate Cu(mM)	% Cu Ret.
0.5	0.553	0.011	98.01
	0.526	0.010	98.10
0.8	1.018	0.024	97.61
	0.785	0.004	99.49
1.5	1.424	0.105	99.63
	1.335	0.123	90.79
2.0	1.365	0.338	75.24
	1.536	0.333	78.32
3.0	2.082	0.767	63.16
	2.327	0.773	66.78

Table 2.2.3 Results of equilibrium dialysis experiments using partially substituted (about 1 mM in iminoacetic ligand) polymer at pH 4.0, with only Cu.

Initial Cu(mM)	Retentate Cu(mM)	Permeate Cu(mM)	% Cu Ret.
2.50	precipitated		
1.40	1.495	0.012	99.20
	1.602	0.014	99.13
1.10	1.235	0.008	99.35
	1.228	0.011	99.10
0.70	0.873	0.013	98.51
	0.911	0.006	99.34
0.36	0.507	0.004	99.21
	0.584	0.003	99.49

Table 2.2.4 Results of equilibrium dialysis experiments using partially substituted (about 1 mM in iminoacetic ligand) polymer at pH 4.5 with only Ca

Initial Ca(mM)	Retentate Ca(mM)	Permeate Ca(mM)	%Ca Expul.
2.50	0.828	0.891	07.10
	0.751	1.016	26.08
	0.730	0.937	22.09
1.40	0.437	0.543	19.52
	0.407	0.535	33.93
1.07	0.292	0.403	27.54
	0.268	0.378	29.10
0.71	0.144	0.242	40.50
0.36	0.064	0.096	33.33
	0.059	0.102	42.16

Table 2.2.5 Results of equilibrium dialysis experiments using 1.00 mM of maximum substituted (135%) polymer at pH 3.0, with only Ca

Initial Ca(mM)	Retentate Ca(mM)	Permeate Ca(mM)
0.861(measured)	0.455	0.468
	0.505	0.468
0.824	0.428	0.436
	0.440	0.446
0.532	0.287	0.285
	0.268	0.285
0.430	0.210	0.222
	0.209	0.220
0.258	0.140	0.142
	0.135	0.132

Table 2.2.6 Results of equilibrium dialysis experiments using 1.00 mM of maximum substituted (135%) polymer at pH 4.5-5.0, with only Ca

Initial Ca(mM)	Retentate Ca(mM)	Permeate Ca(mM)
0.827(measured)	0.595	0.423
	0.421	0.418
0.627	0.272	0.270
	0.291	0.292
0.496	0.180	0.180
	0.115	0.214
0.379	0.150	0.143
	0.153	0.154
0.257	0.104	0.108
	0.090	0.113

Table 2.2.7 Results of equilibrium dialysis experiments using 1.00 mM of maximum substituted (135%) polymer at pH 3.0, with only Cu

Initial Cu(mM)	Retentate Cu(mM)	Permeate Cu(mM)	% Cu Ret.
1.25	1.202	0.442	63.23
	1.056	0.379	64.11
1.00	0.858	0.512	40.33
	0.786	0.372	52.67
0.60	0.402	0.190	52.74
	0.598	0.204	65.89
0.36	0.348	0.094	72.99
	0.345	0.095	72.46

Table 2.2.8 Results of equilibrium dialysis experiments using 1.00 mM of maximum substituted (135%) polymer at pH 5.0, with Cu and Ca both

Initial (mM)		Retentate (mM)		Permeate (mM)		% Cu Ret.
Cu	Ca	Cu	Ca	Cu	Ca	
1.25	1.25(calc.)	0.677	0.641	0.411	0.574	39.29
		0.692	0.642	0.414	0.583	40.17
1.00	1.00	0.514	0.553	0.326	0.490	36.58
		0.630	0.534	0.301	0.453	52.22
0.80	0.80	0.402	0.423	0.185	0.362	53.98
		0.482	0.417	0.189	0.394	60.79
0.60	0.60	0.164	0.267	0.084	0.277	48.78
0.36	0.36	0.218	0.144	0.019	0.149	91.28
		0.233	0.152	0.016	0.154	93.13

Table 2.2.9 Results of equilibrium dialysis experiments using 26.50 mM of 20% substituted polymer at pH 5.0, with Cu and Ca both

Initial(mM)		Retentate (mM)		Permeate (mM)		%Ret	% Expul.
Cu	Ca	Cu	Ca	Cu	Ca	Cu	Ca
0.500	0.500	0.435	0.254	0.004	0.550	99.1	53.8
		0.504	0.254	0.003	0.507	99.4	49.9
0.667	0.667	0.581	0.347	0.006	0.658	99.0	47.3
		0.597	0.300	0.007	0.628	98.8	52.2
1.000	1.000	0.874	0.593	0.021	0.949	97.6	37.5
		0.882	0.620	0.022	0.960	97.5	35.4

Table 2.2.10 Results of equilibrium dialysis experiments using 53.50 mM of 8.4% substituted polymer at pH 5.0, with Cu and Ca both

Retentate (mM)		Permeate (mM)		%Ret	%Expul.
Cu	Ca	Cu	Ca	Cu	Ca
0.443	0.124	0.025	0.442	94.4	71.9
0.422	0.122	0.026	0.446	93.8	72.6
0.607	0.263	0.062	0.722	89.8	63.6
0.607	0.221	0.047	0.671	92.3	67.1
0.680	0.286	0.101	0.755	85.1	62.1
0.666	0.275	0.095	0.746	85.7	63.1
0.729	0.357	0.218	0.894	70.1	60.1
0.712	0.365	0.252	0.857	64.6	57.4

Table 2.2.11 Results of equilibrium dialysis experiments using 0.75 mM of 117% substituted polymer at pH 7.0, with Cu and Ca both

Initial (mM)		Retentate (mM)		Permeate (mM)		%Ret	%Expul.
Cu	Ca	Cu	Ca	Cu	Ca	Cu	Ca
0.141	0.246	0.143	0.135	0.002	0.188	98.60	28.19
		0.146	0.139	-----	-----	-----	
0.250	0.265	0.286	0.123	0.002	0.173	99.30	28.90
		0.293	0.118	0.002	0.169	99.32	30.18
0.410	0.256	0.385	0.128	0.005	0.178	98.70	28.09
		0.391	0.135	0.008	0.186	97.95	27.42
0.577	0.252	0.464	0.165	0.024	0.200	94.83	17.50
		0.470	0.144	0.023	0.199	95.11	27.64
0.620	0.254	0.600	0.152	0.045	0.205	92.50	25.85
		0.518	0.176	0.048	0.208	90.73	15.38
0.769	0.256	0.872	0.150	0.044	0.206	94.95	27.18
		0.894	0.147	0.044	0.201	95.08	26.87

Table 2.2.12 Results of equilibrium dialysis experiments using 1.70 mM of 117% substituted polymer at pH 7.0, with Cu and Ca both

Initial (mM)		Retentate (mM)		Permeate (mM)		%Ret.
Cu	Ca	Cu	Ca	Cu	Ca	Cu
0.212	0.601	0.188	0.309	0.001	0.276	99.47
		0.191	0.279	0.001	0.276	99.48
0.578	0.539	0.574	0.221	0.001	0.270	99.83
		0.594	0.252	0.001	0.246	99.83
1.049	0.576	0.897	0.264	0.019	0.268	97.88
		0.902	0.245	0.020	0.323	97.78
----	----	1.034	0.257	0.067	0.267	93.52
		0.989	0.263	0.074	0.251	92.52

Table 2.2.13 Results of equilibrium dialysis experiments using 4.80 mM of 117% substituted polymer at pH 7.0, with Cu and Ca both

Initial(mM)		Retentate(mM)		Permeate(mM)		%Ret.
Cu	Ca	Cu	Ca	Cu	Ca	Cu
0.424	0.598	0.392	0.253	0.001	0.297	99.74
		0.380	0.249	0.001	0.298	99.74
0.975	0.552	0.957	0.246	0.001	0.283	99.90
		0.947	0.233	0.001	0.290	99.89
1.321	0.532	1.332	0.253	0.001	0.294	99.92
		1.327	0.241	0.001	0.298	99.92
1.680	0.564	1.528	0.240	0.001	0.288	99.93
		1.517	0.242	0.001	0.301	99.93

Table 2.2.14 Results of equilibrium dialysis experiments using 1.00 mM of unpurified PAAH at pH 5.0, with Cu and Ca both

Initial(mM)		Retentate (mM)		Permeate (mM)	
Cu	Ca	Cu	Ca	Cu	Ca
0.500	0.500	0.167	0.268	0.186	0.272
		0.166	0.259	0.180	0.262
0.830	0.830	0.336	0.438	0.359	0.433
		0.331	0.420	0.350	0.424
1.000	1.000	0.436	0.544	0.455	0.536
		0.445	0.548	0.457	0.546
1.250	1.250	0.503	0.605	0.509	0.601
		0.564	0.653	0.571	0.646

Table 2.2.15 Results of equilibrium dialysis experiments using 53.50 mM of unpurified PAAH at pH 5.0, with Cu and Ca both

Retentate (mM)		Permeate (mM)		%Expulsions		Total%
Cu	Ca	Cu	Ca	Ca	Cu	(Cu+Ca)
0.183	0.238	0.219	0.362	34.3	16.4	50.7
0.163	0.219	0.213	0.349	37.2	23.5	60.7
0.231	0.341	0.337	0.520	34.4	31.5	65.9
0.264	0.341	0.329	0.527	35.3	19.8	55.1
0.407	0.638	0.519	0.919	30.6	21.6	52.2
0.394	0.629	0.519	0.924	31.9	24.1	56.0

Table 2.2.16 Results of equilibrium dialysis experiments using 4.34 mM of 20.7% substituted polymer at pH 7.0, with Cu and Ca both

Initial(mM)		Retentate(mM)		Permeate(mM)		% Ret.
Cu	Ca	Cu	Ca	Cu	Ca	Cu
0.144	0.089	0.140	0.019	0.008	0.032	94.3
		0.134	0.021	0.007	0.045	94.8
0.492	0.350	0.459	0.097	0.004	0.134	99.1
		0.449	0.091	0.006	0.141	98.7
0.649	0.476	0.568	0.144	0.007	0.210	98.8
		0.581	0.156	0.008	0.217	98.6
0.966	0.766	0.827	0.336	0.015	0.380	98.2
		0.853	0.344	0.017	0.389	98.0
1.372	1.025	1.154	0.501	0.034	0.551	97.1
		1.143	0.493	0.033	0.539	97.1

Table 2.2.17 Results of equilibrium dialysis experiments using 4.34 mM of 41.5% substituted polymer at pH 5.0, with Cu and Ca both

Initial(mM)		Retentate(mM)		Permeate(mM)		% Ret.
Cu	Ca	Cu	Ca	Cu	Ca	Cu
0.144	0.109	0.111	0.039	0	0.070	100
		0.111	0.031	0	0.069	100
0.480	0.362	0.333	0.121	0.052	0.254	84.4
		0.339	0.190	0.055	0.242	83.8
0.791	0.589	0.513	0.309	0.168	0.318	67.3
		0.524	0.303	0.177	0.326	66.2
0.949	0.735	0.584	0.353	0.248	0.399	57.5
		0.604	0.383	0.195	0.471	67.7
1.183	0.889	0.685	0.438	0.425	0.604	38.0
		0.706	0.442	0.381	0.601	46.0

Table 2.2.18 Results of equilibrium dialysis experiments using 4.34 mM of 41.5% substituted polymer at pH 7.0, with Cu and Ca both

Initial(mM)		Retentate(mM)		Permeate(mM)		%Ret
Cu	Ca	Cu	Ca	Cu	Ca	Cu
0.151	0.122	0.134	0.024	0	0.039	100
		0.138	0.025	0	0.045	100
0.470	0.349	0.422	0.086	0	0.156	100
		0.426	0.094	0	0.204	100
0.770	0.592	0.667	0.231	0.003	0.300	99.5
		0.666	0.223	0.006	0.334	99.1
0.895	0.759	0.714	0.272	0.008	0.344	98.9
		0.755	0.300	0.007	0.378	99.1
0.744	0.858	0.771	0.384	0.025	0.491	96.8
		0.778	0.381	0.018	0.457	97.7
0.825	0.956	0.895	0.603	0.019	0.623	97.9
		0.910	0.596	0.018	0.598	98.0
1.055	1.196	1.033	0.475	0.033	0.484	96.8
		1.088	0.492	0.032	0.491	97.1
1.110	1.159	1.044	0.597	0.032	0.602	96.9
		0.943	0.598	0.018	0.604	98.9

Table 2.2.19 Results of equilibrium dialysis experiments using 4.34 mM of 83% substituted polymer at pH 7.0, with Cu and Ca both

Initial(mM)		Retentate(mM)		Permeate(mM)		% Ret.
Cu	Ca	Cu	Ca	Cu	Ca	Cu
0.195	0.147	0.145	0.051	0.006	0.051	95.9
		0.139	0.045	0.006	0.052	95.7
0.488	0.367	0.441	0.100	0.003	0.113	99.3
		0.439	0.094	0.005	0.119	98.9
0.876	0.680	0.792	0.353	0.025	0.358	96.8
		0.793	0.353	0.021	0.364	97.4
0.986	0.971	0.858	0.529	0.063	0.503	92.7
		0.827	0.501	0.051	0.487	93.8
1.335	1.238	1.108	0.664	0.063	0.622	94.3
		1.095	0.657	0.064	0.638	94.2

Table 2.2.20 Results of equilibrium dialysis experiments using 2.00 mM of 100% substituted polymer at pH 6.0, with only Cu and no added salt

Initial Cu(mM)	Retentate Cu(mM)	Permeate Cu(mM)	%Cu Ret.
0.104(calc.)	0.104	0.0002	99.81
0.208	0.225	0.0006	99.73
0.312	0.272	0.0027	99.90
0.416	0.342	0.0220	93.57
0.624	0.386	0.1010	73.83
0.832	0.544	0.2140	60.66
1.040	0.657	0.3350	49.01
1.248	0.776	0.4530	41.62

Table 2.2.21 Results of equilibrium dialysis experiments using 2.00 mM of 100% substituted polymer at pH 6.0, with only Cu and 1.0 M added KCl

Initial Cu(mM)	Retentate Cu(mM)	Permeate Cu(mM)	% Cu Ret.
0.104(calc.)	0.111	0.002	98.20
0.208	0.213	0.003	98.83
0.312	0.311	0.005	98.39
0.416	0.380	0.041	89.21
0.624	0.499	0.150	69.94
0.832	0.570	0.245	57.02

Table 2.2.22 Results of equilibrium dialysis experiments using 2.00 mM of 92% substituted polymer at pH 6.0, with only Cu and no added salt.

Initial Cu(mM)	Retentate Cu(mM)	Permeate Cu(mM)	% Cu Ret.
0.104(calc.)	0.104	0.004	98.35
0.208	0.173	0.002	98.96
0.312	0.230	0.009	96.22
0.416	0.282	0.034	87.94
0.624	0.383	0.126	67.10
0.832	0.406	0.212	47.78
1.040	0.666	0.367	44.89
1.248	0.774	0.480	37.98

Table 2.2.23 Results of equilibrium dialysis experiments using 4.34 mM of 41.5% substituted polymer with 108.5 mM of added PAAH, at pH 7.0, with Cu and Ca both

Initial(mM)		Retentate(mM)		Permeate(mM)		%Ret	%Expul.
Cu	Ca	Cu	Ca	Cu	Ca	Cu	Ca
0.169	0.087	0.158	0.030	0.006	0.061	96.20	50.82
		0.154	0.032	0.001	0.062	99.40	48.39
0.338	0.205	0.307	0.058	0.003	0.128	99.00	54.69
		0.331	0.058	0.003	0.110	99.10	47.27
0.521	0.376	0.480	0.097	0.003	0.224	99.40	56.70
		0.487	0.094	0.006	0.219	98.80	57.08
0.669	0.480	0.598	0.132	0.006	0.293	99.00	54.95
		0.623	0.130	0.004	0.295	99.40	55.93
0.860	0.627	0.790	0.242	0.011	0.383	98.60	36.81
		0.762	0.202	0.019	0.394	97.50	48.73

Table 2.2.24 Results of equilibrium dialysis experiments using 1.63 mM of 117% substituted polymer with different amounts of added CPC, at pH 7.0, with Cu and Ca both

Initial(mM)			Retentate(mM)		Permeate(mM)			%Ret	%Exp.
Cu	Ca	CPC	Cu	Ca	CPC	Cu	Ca	Cu	Ca
0.500	0.263	6.67	0.454	0.111	0.437	0.036	0.280	92.1	60.4
			0.447	0.107	0.484	0.031	0.277	93.1	61.4
0.512	0.235	13.34	0.425	0.084	0.460	0.046	0.323	89.2	74.0
			0.480	0.085	0.450	0.049	0.336	89.8	74.7
0.508	0.242	26.68	0.469	0.074	0.425	0.038	0.356	91.9	79.2
			0.429	0.073	0.435	0.036	0.359	91.6	79.7
0.489	0.233	53.36	0.397	0.056	0.488	0.037	0.405	90.7	86.2
			0.396	0.059	0.493	0.043	0.409	89.1	85.6

Table 2.2.25 Results of equilibrium dialysis experiments using different concentrations of PDDAC polymer without pH control, with only Ca

Initial(mM) Ca	PDDAC (mM)	Retentate(mM) Ca	Permeate(mM) Ca	%Exp. Ca
0.574	20.0	0.154	0.461	66.59
		0.112	0.425	73.58
0.573	40.0	0.122	0.505	75.82
		0.135	0.505	73.20
----	100.0	0.141	0.552	74.52
		0.143	0.571	74.99
0.545	167.0	0.240	0.645	62.77
		0.230	0.648	64.50
----	500.0	0.253	0.827	69.43
		0.253	0.790	67.94

Table 2.2.26 Results of equilibrium dialysis experiments using 1.63 mM of 117% substituted polymer with different amounts of added PDDAC, at pH 7.0, with Cu and Ca both

Initial(mM)			Retentate(mM)		Permeate(mM)		%Expul
Cu	Ca	PDDAC(mM)	Cu	Ca	Cu	Ca	Ca
0.482	0.384	23.0	0.408	0.114	0.015	0.272	58.09
			0.409	0.118	0.019	0.266	55.64
0.483	0.366	34.0	0.389	0.069	0.023	0.363	80.99
0.472	0.363	46.0	0.378	0.088	0.032	0.360	75.56
			0.380	0.074	0.032	0.372	80.11

Table 2.2.27 Results of equilibrium dialysis experiments using 1.63 mM of 117% substituted polymer with different amounts of added PAAH, at pH 7.0, with Cu and Ca both

Initial(mM)		(mM)	Retentate(mM)		Permeate(mM)		%Ret	%Expul
Cu	Ca	PAAH	Cu	Ca	Cu	Ca	Cu	Ca
0.402	0.251	3.8	0.454	0.107	0.006	0.108	98.7	0.9
			0.453	0.105	0.006	0.129	98.7	18.6
		7.6	0.464	0.099	0.008	0.117	98.3	15.4
			0.471	0.109	0.008	0.127	98.3	14.2
		11.4	0.480	0.097	0.006	0.125	98.8	22.4
		15.2	0.479	0.101	0.006	0.114	98.7	11.4
			0.475	0.097	0.005	0.111	98.9	12.6

Table 2.2.28 Results of equilibrium dialysis experiments using different amounts of added PAAH, at pH 7.0, with only Ca

Initial(mM)	(mM)	Retentate(mM)	Permeate(mM)	%Expul.
Ca	PAAH	Ca	Ca	Ca
0.596	38.2	0.223	0.450	50.0
		0.238	0.460	48.3
0.626	114.6	0.234	0.514	54.5
		0.224	0.504	55.6
0.517	191	0.226	0.527	57.1
		0.232	0.539	57.0

Table 2.2.29 Dialysis with 53.5 mM of UF purified PAAH, no pH control.

Initial Cu(mM)	Retentate Cu(mM)	Permeate Cu(mM)	% Cu Expul.
0.124(calc.)	0.005	0.087	94.25
0.248	0.015	0.252	94.05
0.372	0.023	0.308	92.53
0.496	0.037	0.421	91.21
0.744	0.070	0.676	89.64
0.992	0.137	0.920	85.11
1.240	0.179	0.972	81.58

Table 2.2.30 Results of equilibrium dialysis experiments using 21.4 mM of purified PAAH, with only Cu, with no pH control

Initial Cu(mM)	Retentate Cu(mM)	Permeate Cu(mM)	% Cu Expul.
0.124(calc.)	0.006	0.073	91.78
0.248	0.025	0.205	87.80
0.372	-----	-----	-----
0.496	0.067	0.374	82.09
0.744	0.062	0.403	84.62
0.992	0.261	0.844	69.08

Table 2.2.31 Results of equilibrium dialysis experiments using 10.7 mM of purified PAAH, with only Cu, with no pH control

Initial Cu(mM)	Retentate Cu(mM)	Permeate Cu(mM)	% Cu Expul.
0.124(calc.)	0.012	0.059	79.66
0.248	0.025	0.135	81.48
0.372	0.114	0.344	66.86
0.744	0.173	0.453	61.81
0.992	0.251	0.572	56.12

Table 2.2.32 Results of equilibrium dialysis experiments using 2.0 mM of 100% substituted polymer and 52.7 mM of added purified PAAH, at pH 6.0, with Cu and Ca both, after purifying the total mixture by ultrafiltration

Retentate(mM)		Permeate(mM)		% Ret.	% Expul.
Cu	Ca	Cu	Ca	Cu	Ca
0.282	0.094	0.020	0.753	92.91	87.52
0.298	0.312	0.014	1.370	95.30	77.23
0.315	0.694	0.010	2.000	96.83	65.30
0.332	1.050	0.007	2.470	97.89	57.49
0.343	1.270	0.007	2.750	97.96	53.82
0.319	1.570	0.010	3.060	96.87	48.69

Table 2.2.33 Results of ultrafiltration experiment using 1.96 mM 117% substituted polymer, at pH 7.0, to selectively separate Cu and Ca

	Cu(mM)	Ca(mM)	% Cu Retention
Initial concentrations			
	0.459	0.541	
sample 1	0.003	0.295	99.40
2	0.002	0.359	
3	0.002	0.374	
4	0.001	0.390	
5	0.078	0.432	
6	0.030	0.437	
7	0.020	0.475	
8	0.030	0.535	
Final retentate (calculated for 100 mL))			
	1.335	0.799	

Table 2.2.34 Results of ultrafiltration experiment using 3.68 mM 117% substituted polymer, with 40 mM added PDDAC polymer at pH 7.0, to selectively separate Cu from Ca for selective separation of Cu and Ca

	Cu(mM)	Ca(mM)	% Cu Retention
Initial concentrations			
	0.424	0.424	
sample 1	0.001	0.385	99.78
2	0.001	0.405	
3	0.001	0.422	
4	0.001	0.405	
5	0.001	0.419	
6	0.001	0.578	
7	0.001	0.472	
8	0.001	0.464	
9	0.001	0.429	
Final retentate (calculated for 100 mL)			
	1.693	0.385	

2.3 RESULTS AND DISCUSSION

Results of the present work can be used to obtain valuable information about the binding behavior of copper to the polymers, and the ability of the polymers to expel calcium ions. In addition to application-oriented observations, several observations about the fundamental nature of binding and polymer behavior can be inferred from these results.

2.3.1 Binding behavior of metals to poly(allylamine) substituted with iminoacetic chelating groups

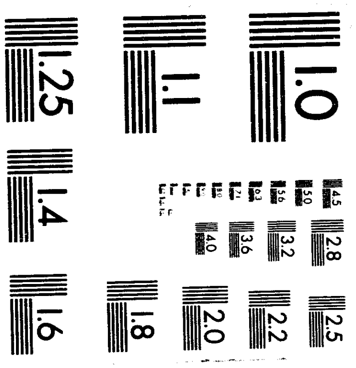
Poly(allylamine) itself is a neutral polymeric amine. In slightly acidic or less basic solutions it tends to form the cationic protonated amine. In aqueous solutions the protonated polymer chain should be in the extended form, due to the repulsive forces of positive charges, whereas, the amine at fairly high pH values will be neutral and tend to take a random coil conformation. Therefore, in the intermediate pH range a conformational transition probably occurs during an acid-base titration. In this case the transition occurs mainly due to the change in polymer charge. Similarly, it is possible to have a change in polymer configuration during metal complexation, if the reaction is accompanied by a change in the polymer charge. In addition however, conformational transitions in a polymer molecule may be possible due to cross-linking(59). In addition, a change in the solution ionic strength, which in turn changes the effective charge repulsion in the polymer chain, may account for a conformational transition in a polymer.

Conformational effects caused by acid-base titration have been demonstrated previously(70) by conductometric titration of polyvinylamine followed by viscosity measurements. The results indicate sharp breaks in conductivity and viscosity curves, attributed to conformational change in the polymer chain. Interestingly, this change occurs at a degree of neutralization of about 0.35 and these transitions have not been observed by potentiometric titrations. However, the same effect has been observed during complexation of polyvinylamine with copper. Calculation of degree of charge in the polymer during the reaction has shown that the transitions occur at the same degree of charge in both protonation and metal complexation(70), indicating the importance of polymer charge in conformational transitions.

The same behavior is expected with poly(allylamine) because this polymer is similar to poly(vinylamine) except in the length of side chain. However, the present work has concentrated more on the nature of binding of copper ions to the polymers and therefore such conformational transitions were not studied in detail except in cases where the metal binding was drastically affected by it. If the total charge is increased on the polymer due to metal binding, extension of the chain and enhanced binding of the metal (due to reduced hindrance), may be possible. However, the actual situation may become complicated due to the possibility of cross-linking and formation of inter-polymer and intra-polymer metal complexes(59,73).

As in the case of protonation, during metal-complexation if the reaction causes an increase of the charge in the polymer, the subsequent reaction becomes more and more difficult thermodynamically, due to repulsive forces and steric crowding. This effect can be seen by the gradual decrease in protonation or metal complexation (stability) constants. In this regard, it is expected that 100% reaction is impossible in most substitution reactions carried out on polymer chains, particularly if the reaction leads to a charge increase or if the substituent group is fairly large. However, if the driving force for the reaction is large enough to overcome any repulsive forces, then the reaction may proceed nearly to completion. In interpreting titration results of several polymeric tertiary amines, Hagi and co-workers(71) explain that the more densely a polymeric chain is charged by successive protonation, the more pronounced will be the decrease in the apparent pK_a values. Previous reports(72) indicate that with certain polyamines, only about 30% protonation can be achieved. Nonetheless, from the elemental analysis of the poly(allylamine hydrochloride) used in the present work, the moles of nitrogen and chlorine are found to be almost the same (section 2.2.5a), showing almost complete protonation of the polyamine. However, during the synthesis of iminoacetic substituted polymer (section 2.2.4a), the maximum substitution achieved was 135% of the nitrogen, which is 67.5% of the maximum possible substitution. The lack of complete substitution probably owes to steric repulsion rather than the charge effect.

In general the iminoacetic group behaves as a good chelating ligand for copper ions. The binding stoichiometry in case of monomeric ligands is reported to be either 1:1 or 1:2 metal to ligand ratio. In most cases, copper appears to bind to 2 chelating sites, making four-coordinated square-planar complexes. However, when the ligand groups are in a polymeric chain the binding behavior may change due to steric factors


1.0
1.1
1.25
1.4
1.6
1.8
2.0
2.2
2.5
2.8
3.2
3.6
4.0
4.5
5.0
5.6
6.3

3 of 3

and cross-linking.

2.3.2 Binding Models

By considering the simplest situation, binding of only one chelation site to one metal atom, the equation is

$$M + L = ML$$

If the simple and most common hyperbolic binding model applies, a plot of the fraction of metal bound per ligand (R) versus free metal concentration should have the typical hyperbolic shape. In dialysis experiments, if the ionic strength of both permeate and retentate solutions are kept fairly high by adding a salt, the Donnan expulsion effect can be avoided. In this case the metal ion concentration in the permeate is nearly equal to the free metal ion concentration in the retentate, making it possible to infer the total bound metal concentration from the difference of retentate and permeate concentrations.

By considering binding with more than one ligand molecule per metal a similar model can be formulated.

$$M + nL = ML_n$$

(1) $K_d = [M]\,[L]^n / [ML_n] \quad \text{or} \quad K_a = [ML_n] / ([M]\,[L]^n)$

(2) $R = [M]_{bound} / [L]_{total} = [ML_n] / ([L] + n.[ML_n])$

$= K_a\,[M].[L]^n / ([L] + n.K_a\,[M].[L]^n)$

(3) $1/R = (1/K_a). (1/[M]). (1/[L]^{n-1}) + n$

where [M] is equal to the concentration of free metal in the retentate and [L] is equal to the concentration of free ligand in the retentate.

Let,

m_r = total metal in the retentate determined experimentally,

m_p = total metal in the permeate determined experimentally.

By mass balance equations,

(4) $L_0 = [L] + n.[ML_n] = [L] + n(m_r - m_p)$.

Therefore,

(5) $[L] = L_0 - n(m_r - m_p)$

and a plot of 1/R versus $1/m_p\,[L_0 - n(m_r - m_p)]$ should be a straight line with slope 1/K and intercept n.

However, in this case,

$$[L_0 - n(m_r - m_p)] \text{ should be } > 0$$

Therefore,

$$n > L_0 / (m_r - m_p)$$

In order for n to attain large value, the metal retention should be low even with fairly high initial ligand concentration. As a special case when n = 2, the final equation becomes

(6) $$1/R = (1/K).[1/m_p\{L_0 - 2(m_r - m_p)\}] + 2$$

Attempts were made to fit the experimental dialysis results to this model, by assuming n = 2. These attempts were unsuccessful with most of the data sets, due to the fact that the expression $\{L_0 - n(m_r - m_p)\}$ became negative. This means that the metal is too strongly bound to fit this model with n=2. However, this does not mean that it is impossible to have more than one ligand site bound to a single metal ion.

Since what is observed here is an average result, it is possible that there may be some ligand sites which are not taking part in binding at all, while a few ligand sites are taking part in two ligand sites to one metal binding and most ligands are involved in binding exactly to one metal. If two different ligand sites bound to the same metal are far apart in the polymer, the situation is similar to cross-linking, which is perhaps the main process causing conformational changes in the polymer. In any event, it is impossible for a single iminoacetic ligand moiety to bind to two metal ions.

Under these condition it is possible to assume 1:1 binding of ligand to metal, as an approximate situation. At least under very dilute conditions and very low percentage ligand substitution, the above condition may be satisfied. However, since 100% saturation of ligand groups with metal is not expected, the results should fit the hyperbolic isotherm or the Langmuir type isotherm, with the parameter not equal to unity. Therefore, this isotherm was tested using the experimental data, by non-linear least-square regression analysis. A Langmuir type isotherm has been used previously by Tsuchida and Nishide(73) to interpret binding data of copper ions with polymeric resins.

2.3.3 Application of binding models to actual results

In quantitative interpretation of binding data, using the binding results of some experiments, the Langmuir plots (figures 2.2.1 to 2.2.9) and the linearized Langmuir plots (figures 2.2.1a to 2.2.9a) were drawn. Figures 2.2.1 to 2.2.9 were drawn using data from tables 2.2.2, 2.2.8, 2.2.12, 2.2.11, 2.2.16, 2.2.18, 2.2.17, 2.2.20, and 2.2.21 respectively. The best fit curves by NLLSQ analysis also were drawn in the same graphs for comparison. The NLLSQ parameters obtained from data fitting using the metal bound per ligand, R, as the dependent variable and the free metal concentration as the independent variable are listed in table 2.3.1.

Table 2.3.1 Results of non-linear least square fitting of binding data to a hyperbolic isotherm, as shown in figures 2.2.1 to 2.2.9

Figure	Binding constant(K)	n	RMSD in R
2.2.1	1.13E5	2.91	0.4769
2.2.2	2.09E5	0.27	0.0476
2.2.3	6.76E5	0.56	0.0953
2.2.4	3.24E5	0.92	0.1964
2.2.5	7.76E4	1.77	0.1443
2.2.6	6.61E5	0.54	0.0532
2.2.7	1.00E5	0.22	0.0224
2.2.8	1.43E6	0.16	0.0321
2.2.9	4.85E5	0.18	0.0227

When calculating the free metal concentration in the retentate, in experiments with both Ca and Cu, with no excess added salt, a correction was made to account for the copper ions expelled into the permeate due to Donnan expulsion, based on the ratio of Ca ions expelled from the retentate. Calcium ions are not bound to the polymer. In most of the preliminary dialysis experiments, a precise quantitative treatment was not possible because the concentrations of the polymer chelating groups were not known exactly and most of the values used have been only approximate. The polymer concentrations used were estimated using the initial polymer concentrations neglecting any osmotic dilution effects. However, the idea of analyzing the data was to obtain a reasonably accurate trend in fitting the data qualitatively or semi-quantitatively.

In all NLLSQ analysis the best value of the binding constants obtained varied between 7.00E4 and 7.00E5, whereas, the n values obtained from the data of figures 2.2.1 and 2.2.5 were quite large compared to that of other data. It is not possible to come to a conclusion regarding the n values obtained from analysis of data in figures 2.2.5, 2.2.6, and 2.2.7, because the extent of ligand substitution used in these analyses were only approximately known. However, the n value of 2.91 from figure 2.2.1 is unacceptable according to this simple model. In this experiment, a fairly low concentration of maximum-substituted polymer has been used. Under these conditions the polymer is more likely to be fully extended, since in addition to being very dilute, 35% of the nitrogen sites are attached with 2 ligand groups, of which one is possibly ionized giving a negative charge to the polymer. Therefore, it is not impossible to have all ligand groups bound to metals, giving an n value of unity. However, a much higher value such as 2.9 can only be explained as due to additional modes of binding probably due to electrostatic or non-specific binding forces.

The capacity of the ligand at 1.00 mM concentration of the chelating ligand groups, shown in figure 2.2.2, is much lower compared to the results at low concentration. This is again as expected, because at a higher concentration of the polymer the polymer conformation may change more towards a coiled form rather than a straight rod form. Therefore more cross linking is possible, causing a decrease in binding capacity. In addition, it is possible for the polymer-metal complex to precipitate under these conditions, leading to lowered binding capacity.

The binding curves in figures 2.2.3, and 2.2.4, drawn from results of tables 2.2.12 and 2.2.11 respectively, are from experiments carried out at pH 7.0, with 117% substituted polymer characterized by elemental analysis. Interestingly, in figure 2.2.4, the limiting R value is fairly close to unity, showing 1:1 average binding ratio as the saturation is reached. This is an indication of more effective binding as far as the ligand sites are concerned. The only difference between this experiment and the experiment which gave the results of figure 2.2.4 is the concentration of the polymer. This a clear indication that it is possible to achieve close to the theoretical binding capacities if low polymer concentrations are used, with a suitable % substitution such as 117%.

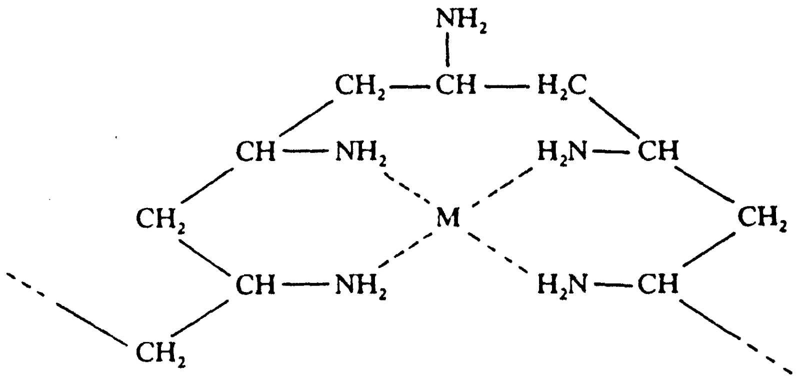
Figures 2.2.5, 2.2.6, and 2.2.7 are the results of dialysis experiments using different extents of substitution of the same polymer, taken from tables 2.2.16, 2.2.18, and 2.2.17, respectively. The extent of substitution has been calculated based on the initial quantities used in the synthesis reaction. Here again in the case of the 20.7%

mono substituted polymer, where the concentration of chelation groups is fairly dilute, the metal bound per ligand tends to rise above unity, similar to what is observed in figure 2.2.1. A large difference in the actual extent of substitution from the calculated value cannot be expected in this polymer, because much excess polymer has been used in the synthesis reaction(section 2.2.4g). However, in this case there exists another possibility, that some fraction of the polymeric amine groups which may be unprotonated at pH 7.0 may account for some additional binding of copper. Although similar binding of copper to free amine group in poly(ethylenimine) and poly(vinylamine) have been reported previously, the reported trend of binding ability decreases from poly(ethylenimine) to poly(vinylamine), and on this basis very low copper binding by the free allylic amines can be expected. However, from the experiments carried out at pH 5.0, in section 2.2.10a and 2.2.10b, no copper binding was observed. Although, in previous experiments shown in figures 2.2.3 and 2.2.4, carried out at pH 7.0, and in later experiments shown in figures 2.2.8 and 2.2.9, carried out at pH 6.0, no such binding has been observed, it is not possible to completely exclude the possibility of such binding at pH values close to 7.0, because these experiments have been carried out with almost 100% or more than 100% substituted polymers, which therefore contain insignificant fractions or none of the free amine groups.

Also, using the experimental results of section 2.2.8l, 2.2.8m, and 2.2.8n, the binding behavior with the characterized, 100% ligand substituted polymer can be shown clearly and more accurately. However, the experiment of section 2.2.8l (figure

2.2.8) did not have excess salt in the system and also the correction for ion expulsion could not be made because it was an experiment using only copper. Therefore the binding constant obtained may not be an accurate value. However, visual observation of results at higher copper concentrations showed no significant difference in permeate and retentate concentrations in the two experiments, which means that the screening effect in the absence and presence of 1.0 M KCl is almost identical. This is another indication of the presence of significantly high screening of charges in the polymer solution even in the absence of added excess salt. The metal complexation constants (stability constants) obtained from the NLLSQ analysis based on 1:1 complex formation are 1.43×10^6 and 4.85×10^5, in the absence and presence of excess salt, respectively. The higher binding constant observed in the absence of salt may arise from neglect of ion-expulsion effects in the experiment with no salt. However, there exists another possibility, since at sufficiently high salt concentration to overcome repulsion between polymer charges, the polymer tend to behave more coiled conformation, rather than a extended form. The better copper binding ability of the linear conformation compared to the coiled as speculated before, may lead to a better binding in the absence of salt. Both graphs give the same average number of ligands per metal ratio of approximately 6. Such a high ratio of ligand bound per metal means that a comparatively large fraction of ligands remains free. Copper in its most stable form tends to bind with maximum of 2 iminoacetic ligands in a four coordinated square planar complex. Such a situation has been observed previously with copper binding to poly(vinyl amine), where the ratio has been between 5 and 6, in which case, the structure of the metal-polymer complex has been proposed to be with highly shrunk polymer backbone having Cu ions 4-coordinated to amine groups in the polymer leaving 1 over 5 or 2 over 6 amine groups unchelated(70), as shown in figure 2.1.2. It is very likely that a similar situation may arise in case of substituted PAAH polymers also.

Figure 2.1.2. The proposed configuration of poly(vinylamine) polymer, complexed with copper(70).



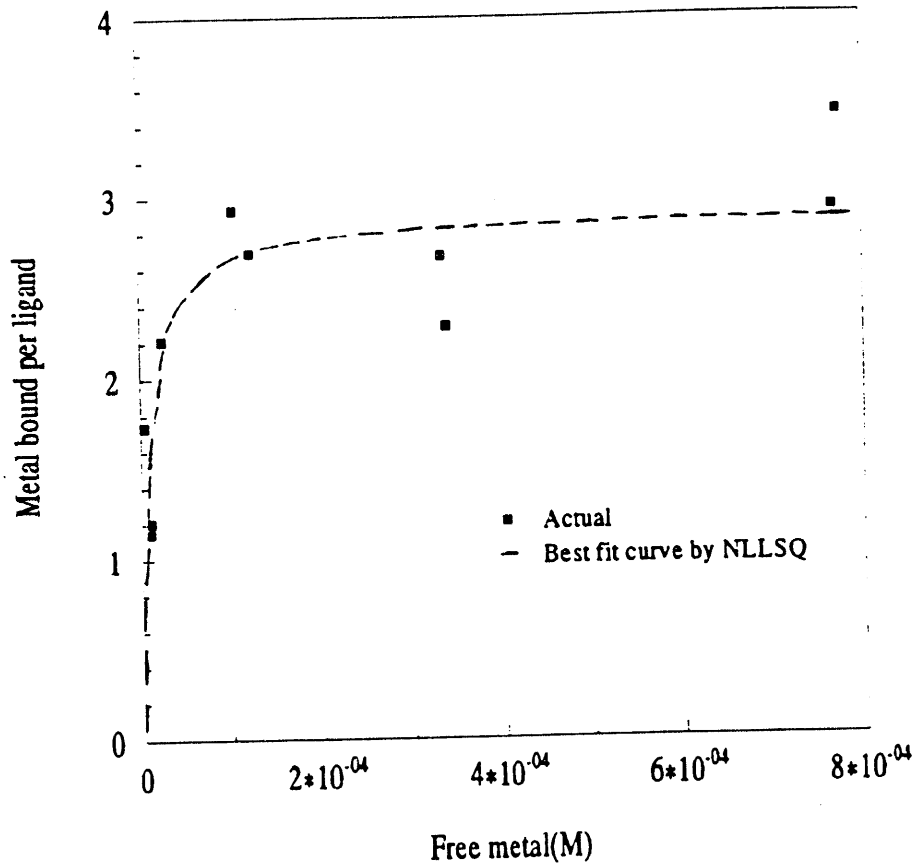


Figure 2.2.1 Binding isotherm of 0.17 mM of 135% substituted polymer with Cu, pH 5.0.

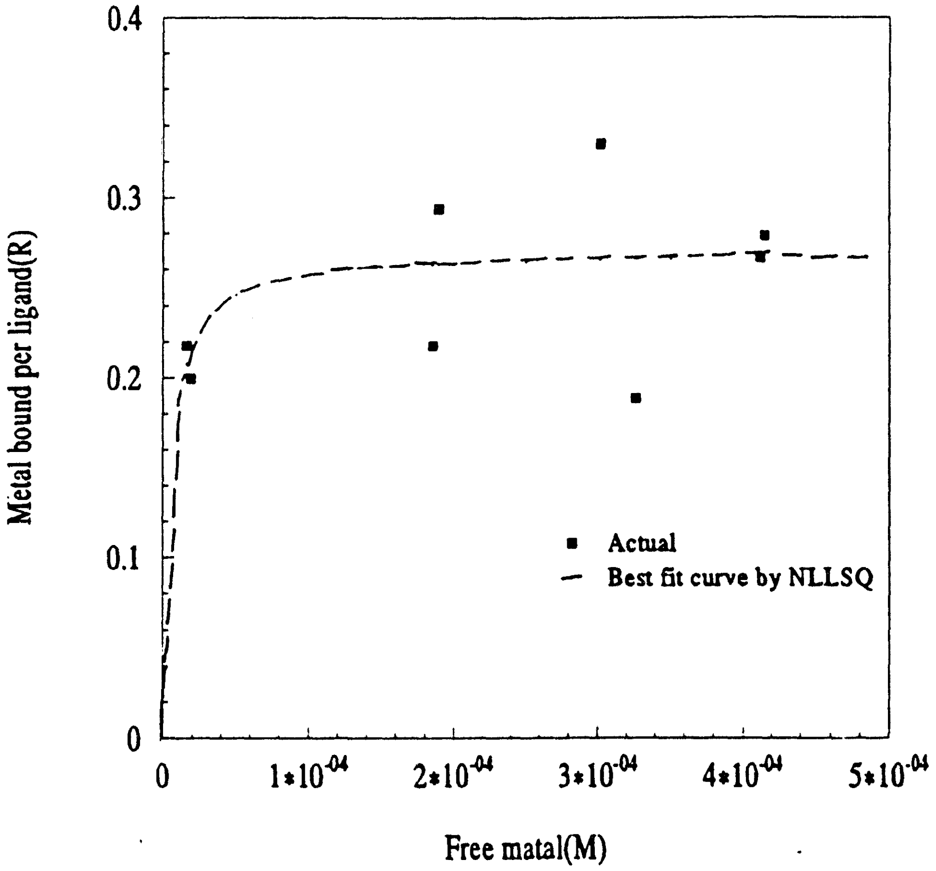


Figure 2.2.2 Binding isotherm of 1.0 mM 135% substituted polymer with Cu, pH 6.0.

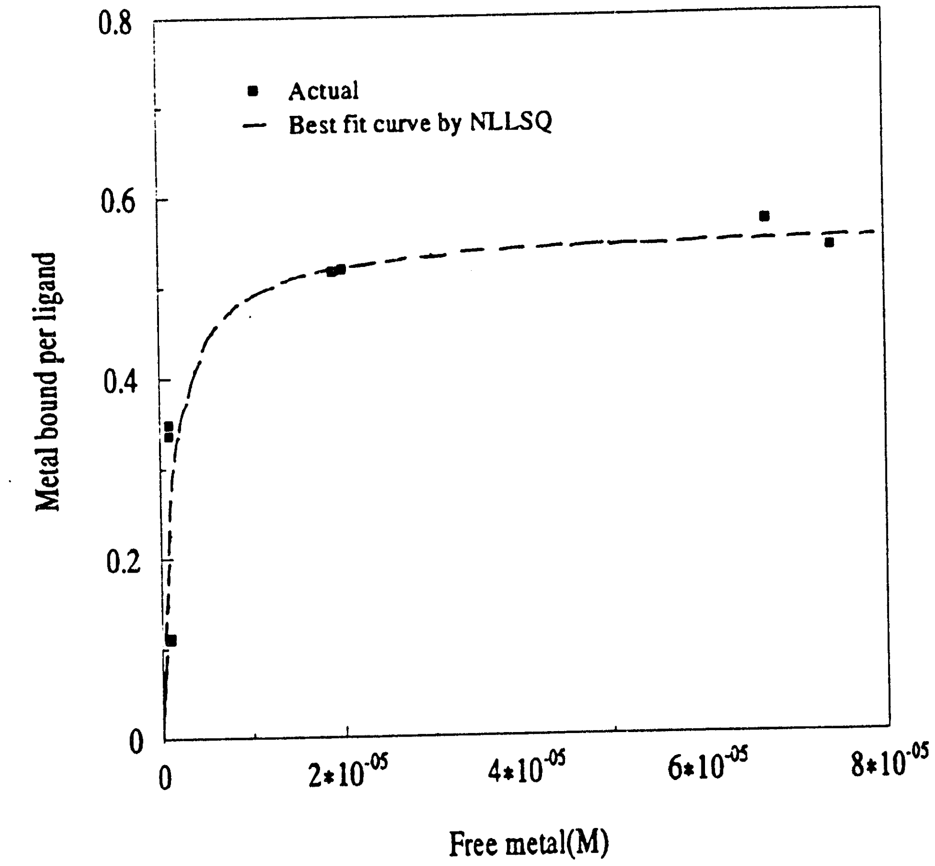


Figure 2.2.3 Binding isotherm of 1.7 mM 117% substituted polymer with Cu, pH 7.0.

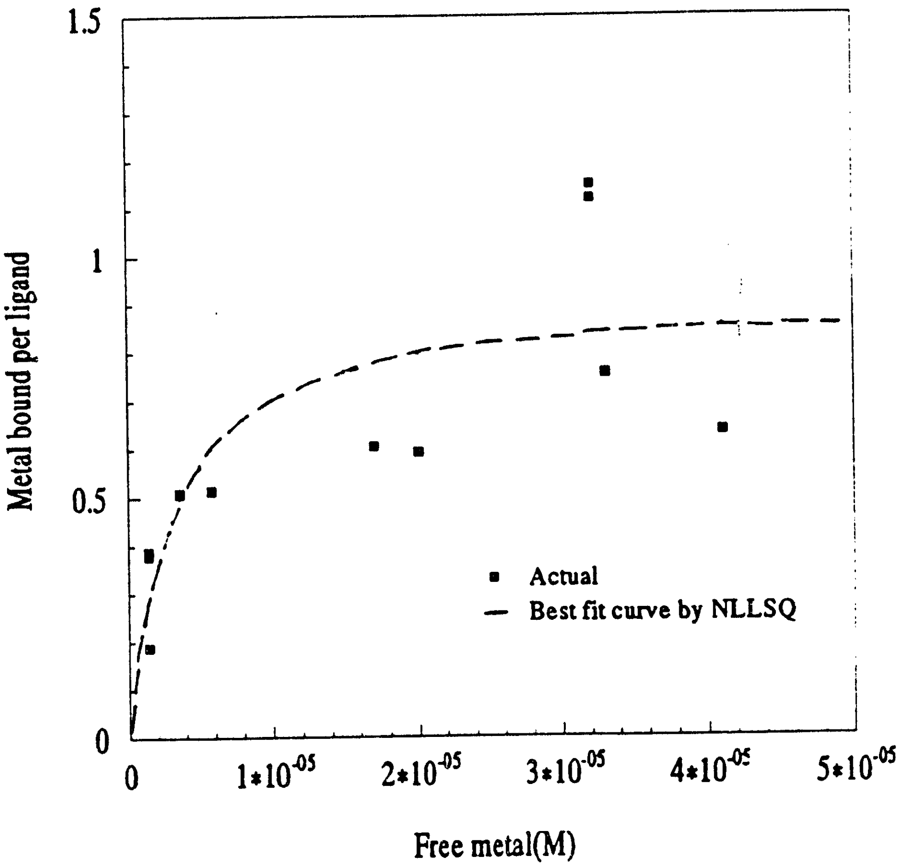


Figure 2.2.4 Binding isotherm of 0.75 mM 117% substituted polymer with Cu, pH 7.0.

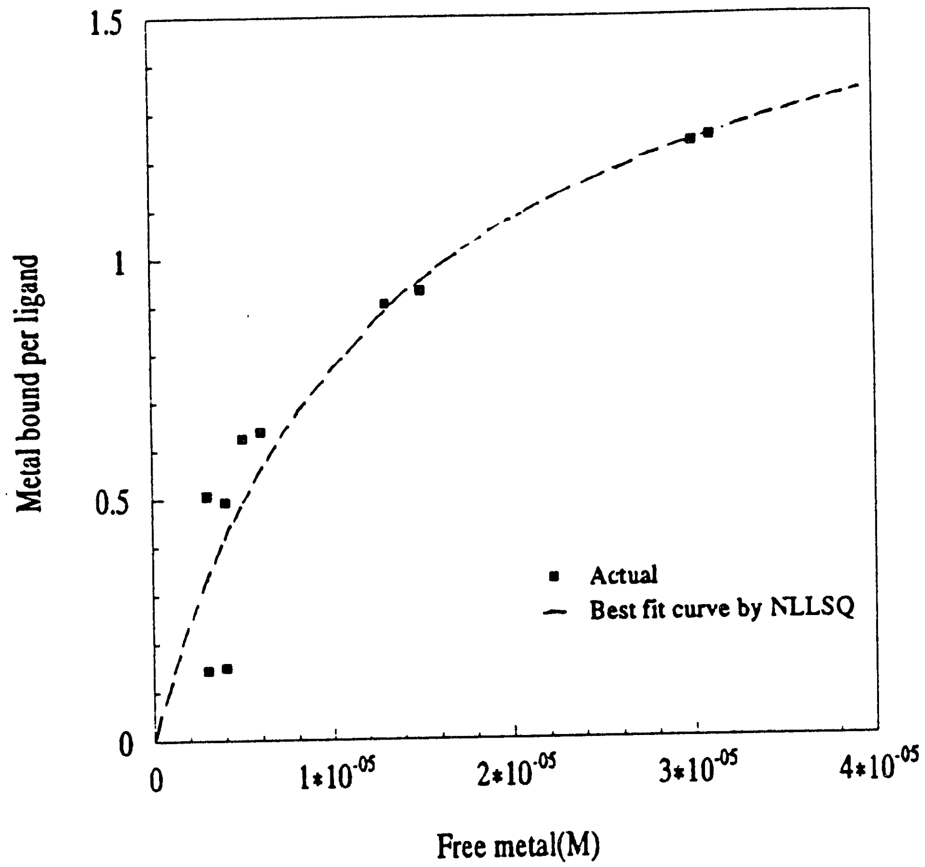


Figure 2.2.5 Binding isotherm of 4.24 mM 21% substituted polymer with Cu, pH 7.0.

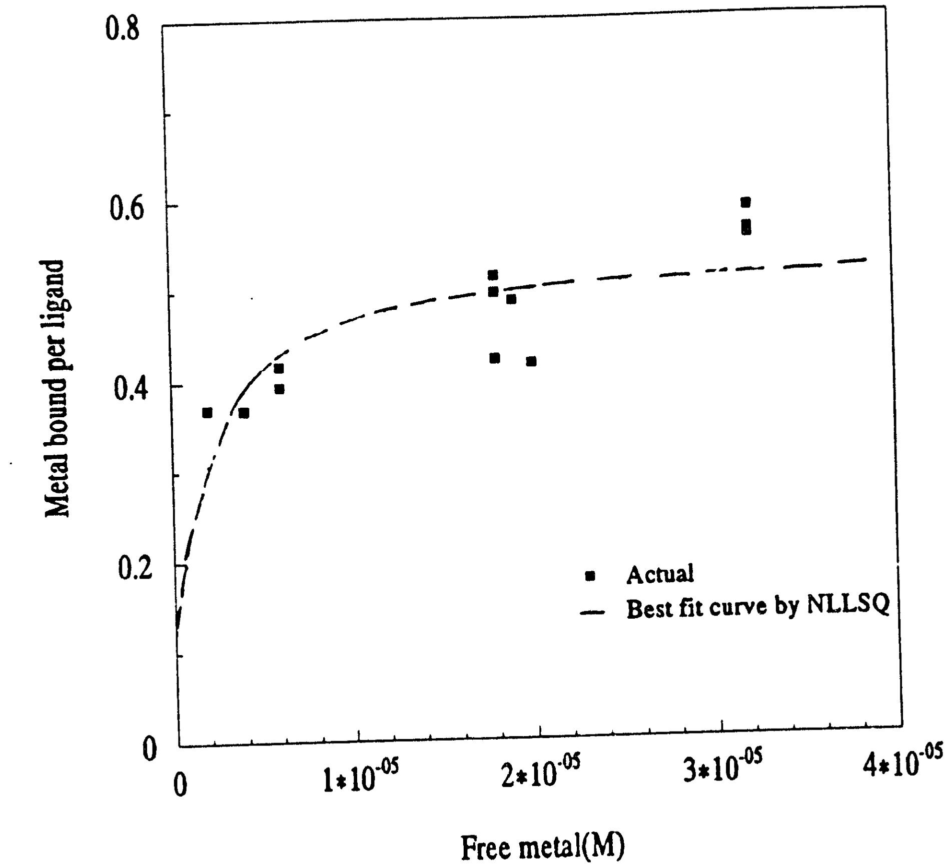


Figure 2.2.6 Binding isotherm of 4.24 mM 41.5% substituted polymer with Cu, pH 7.0.

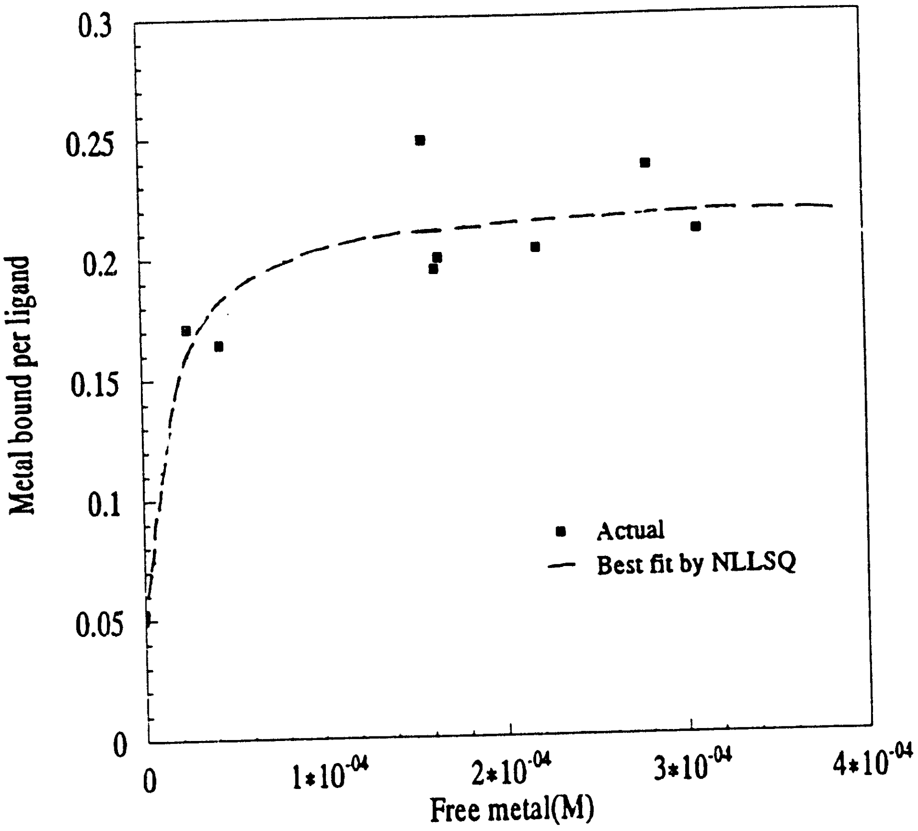


Figure 2.2.7 Binding isotherm of 4.24 mM 41.5% substituted polymer with Cu, pH 5.0.

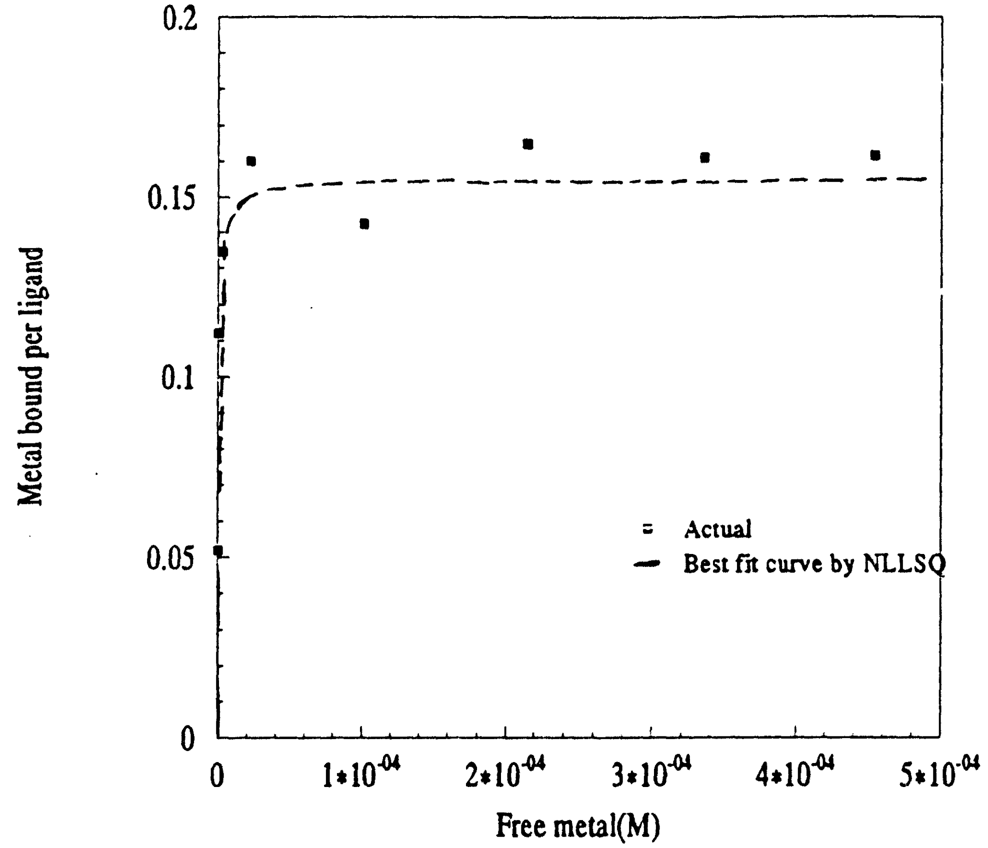


Figure 2.2.8 Binding isotherm of 2.0 mM 100% substituted polymer with Cu, pH 6.0 without added salt.

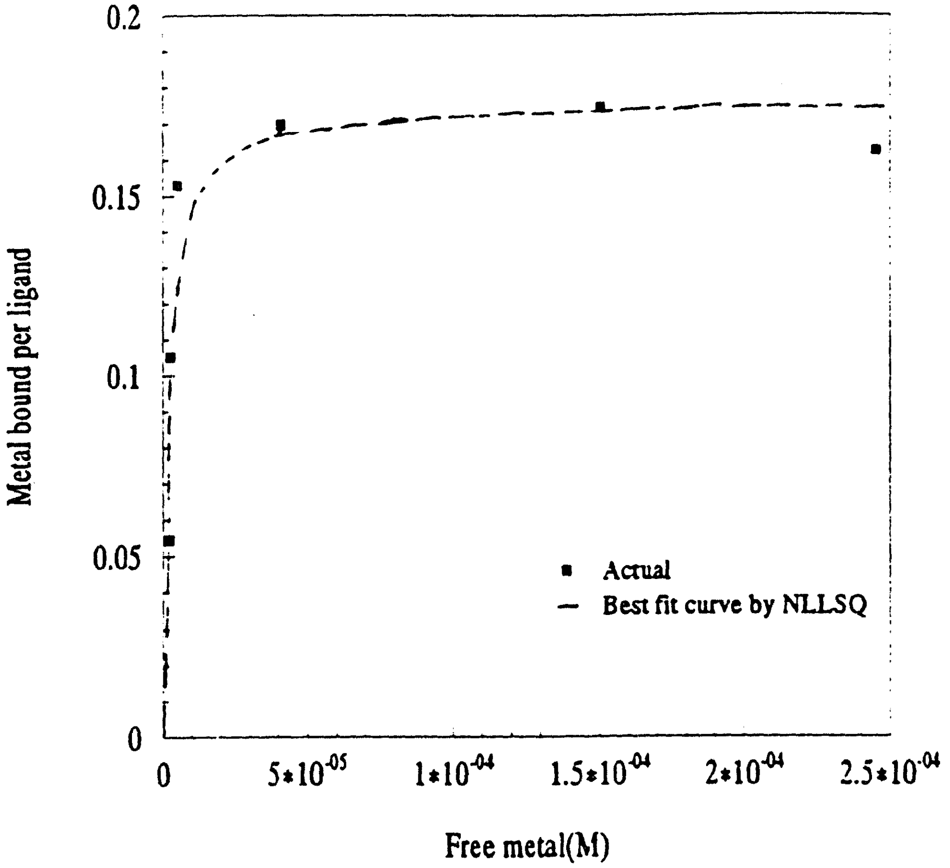


Figure 2.2.9 Binding isotherm of 2.0 mM 100% substituted polymer with Cu, pH 6.0, with) 1.0 M KCl.

2.3.4 Analysis of linearized Langmuir plots

One advantage of the linearized graphs is that it is possible to determine any deviation from the model from the graphs, provided that the points are fairly well distributed. Although in the previous modelling a fixed binding constant was assumed, in an ideal situation it cannot be expected to be constant.

In the figures 2.2.1a and 2.2.2a the distribution of points is so uneven that it is difficult to predict any trend in the actual behavior of the graph. By analyzing the graph very carefully, a slight curvature in the plot, from an initial large slope to a much flatter region can be noticed. If this is the case, this means that the binding constant does not remain constant throughout, but changes gradually from a very high value to a much lower value at higher metal saturation. This is what is really expected. However, by selecting the hyperbolic model with a fixed binding constant, what is determined is an average binding constant obtained as the reciprocal of slope of the best fit line.

In addition, the results at very low copper concentrations may be subject to large variation due to possible experimental errors, which may prohibit any precise conclusion in this concentration range. The detection limit of copper by atomic adsorption using the flame was in the micromolar range. However, by using the PAR reagent spectrophotometrically, more reliable data could be obtained at lower copper concentrations, provided no interfering ion is present.

The linear plots with 117% substituted polymers (i.e. 117% substituted) in figures 2.2.3a and 2.2.4a show that the points deviate from straight lines, in the low saturation region more than at higher saturation. However, fig 2.2.3a shows an excellent agreement of experimental data with the best fit data. Note that, curvature of the best fit line reflects the use of a logarithmic scale for the X-axis. In figure 2.2.4a, which has been carried out with more than twice the diluted polymer compared to that of figure 2.2.3a, the curvature of the actual data from a higher binding constant at low saturation to a lower binding constant at higher saturation can again be seen. Another similar case is the figure 2.2.5a (ignoring the last two points which are likely in error), in which the percentage substitution of the polymer is as low as 20%. Figure 2.2.6a and 2.2.7a, which have been carried out at 41.5% substituted polymer at pH 7.0 and 5 respectively, also show the same trend. Interestingly, none of the figures 2.2.8a, 2.2.9a or 2.2.3a show this trend, mainly because in all these cases the % substitution is 100% or close to 100%. Although the same 117% substituted polymer has been used in the experiments related to figure 2.2.3a and figure 2.2.4a, the polymer concentrations are different. The limiting value of the metal bound per ligand inferred from table 2.3.1, for figure 2.2.3a of 0.56 shows that in this case the polymer is not fully saturated with copper, whereas the same value of figure 2.2.4a of 0.92 shows a close to fully saturated ligand. Therefore, it possible that in the figure 2.2.3a such curvature is not seen because only a fraction of the ligand groups are bound to metal ions and in which region the binding constant may be remaining constant.

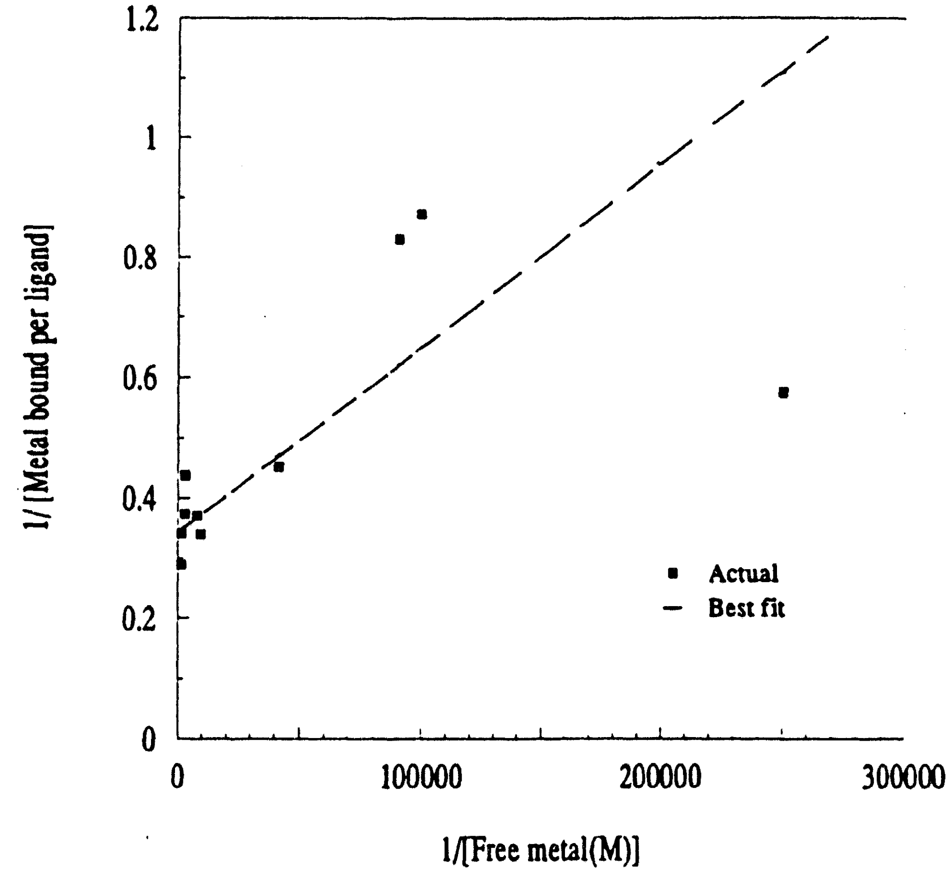


Figure 2.2.1a Linearized Langmuir plot of figure 2.2.1 results.

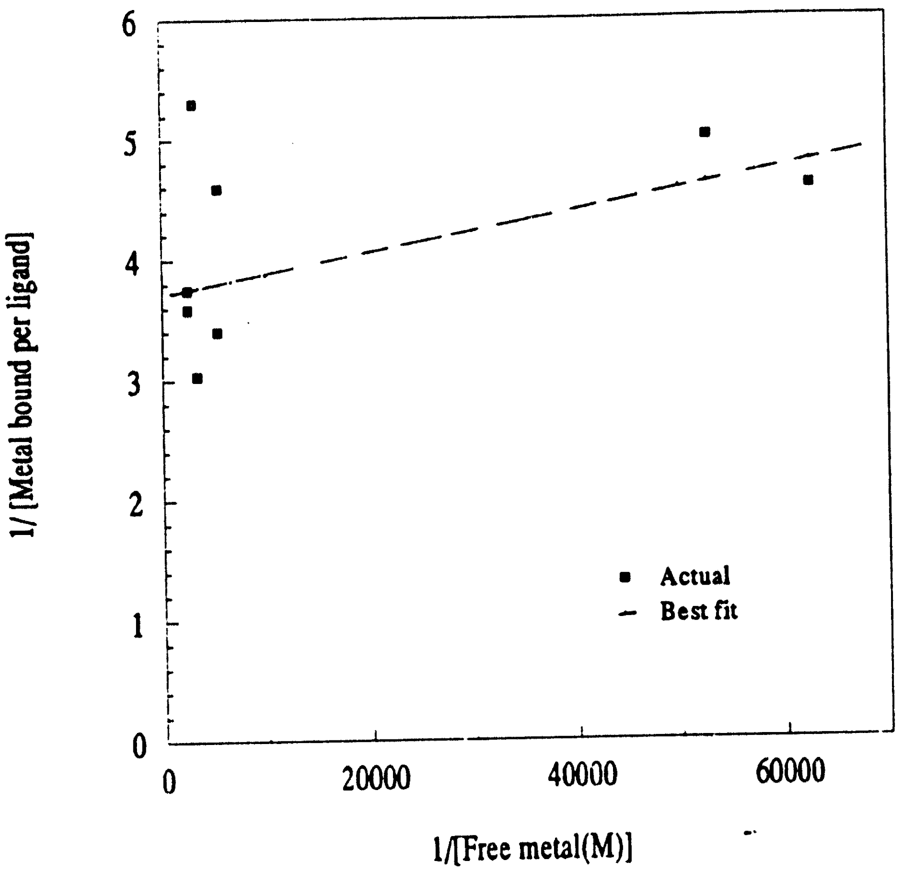


Figure 2.2.2a Linearized Langmuir plot of figure 2.2.2 results.

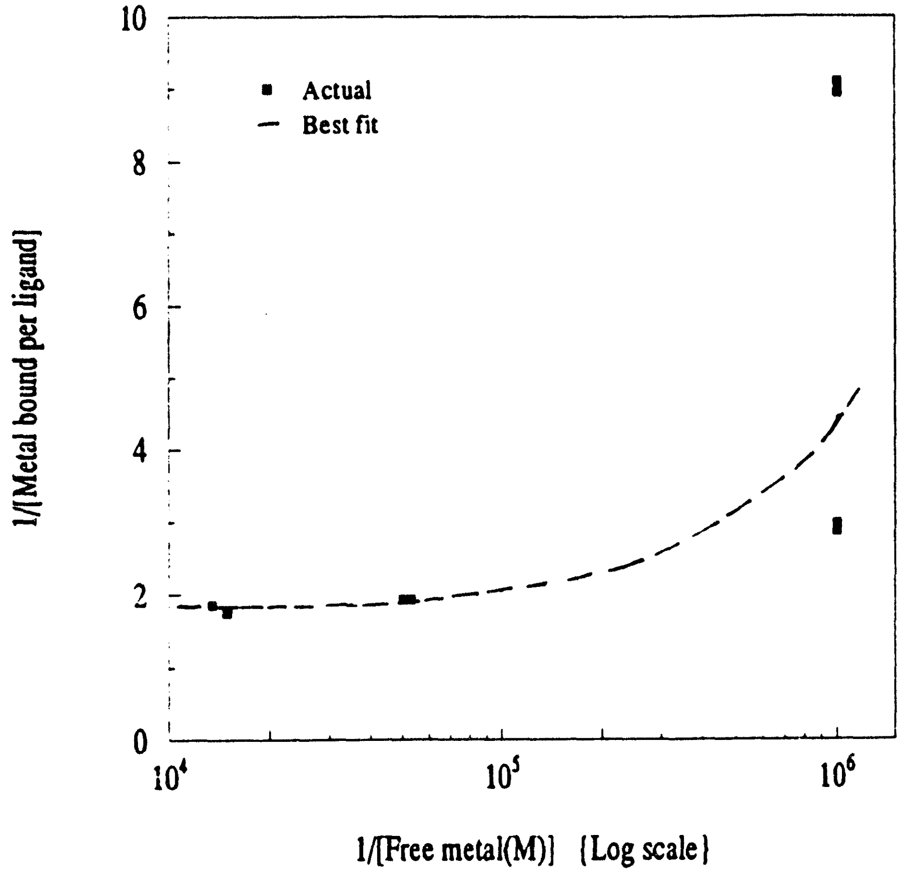


Figure 2.2.3a Linearized Langmuir plot of figure 2.2.3 results shown in semi-log scale.

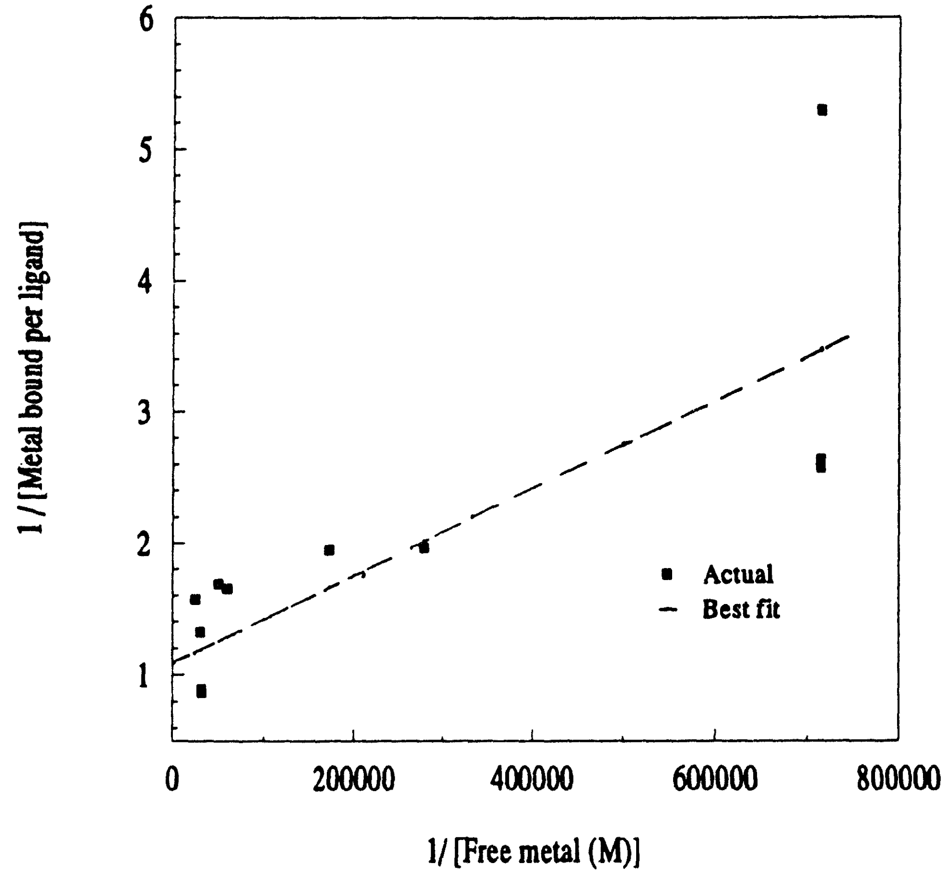


Figure 2.2.4a Linearized Langmuir plot of figure 2.2.4 results

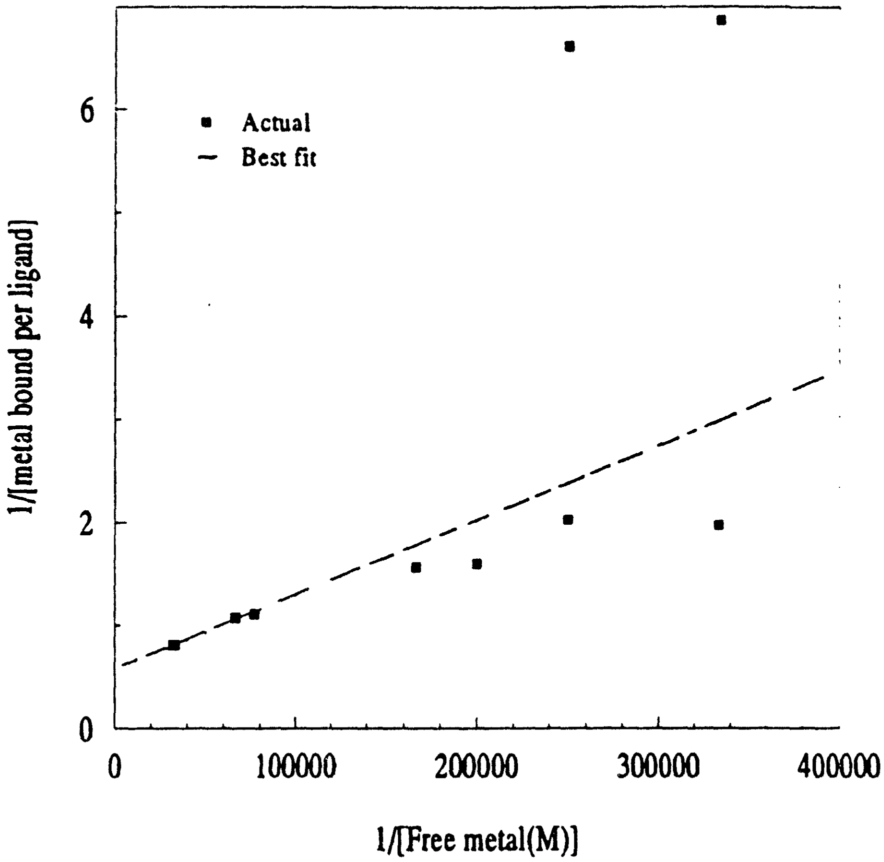


Figure 2.2.5a Linearized Langmuir plot of figure 2.2.5 results

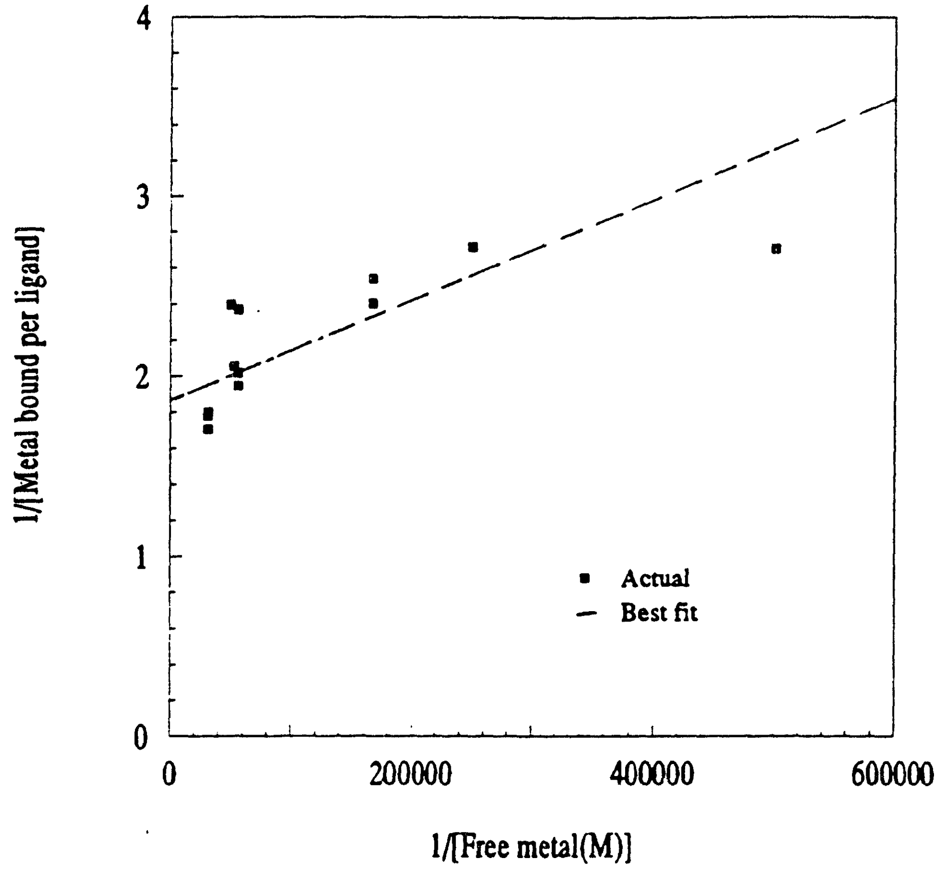


Figure 2.2.6a Linearized Langmuir plot of figure 2.2.6 results.

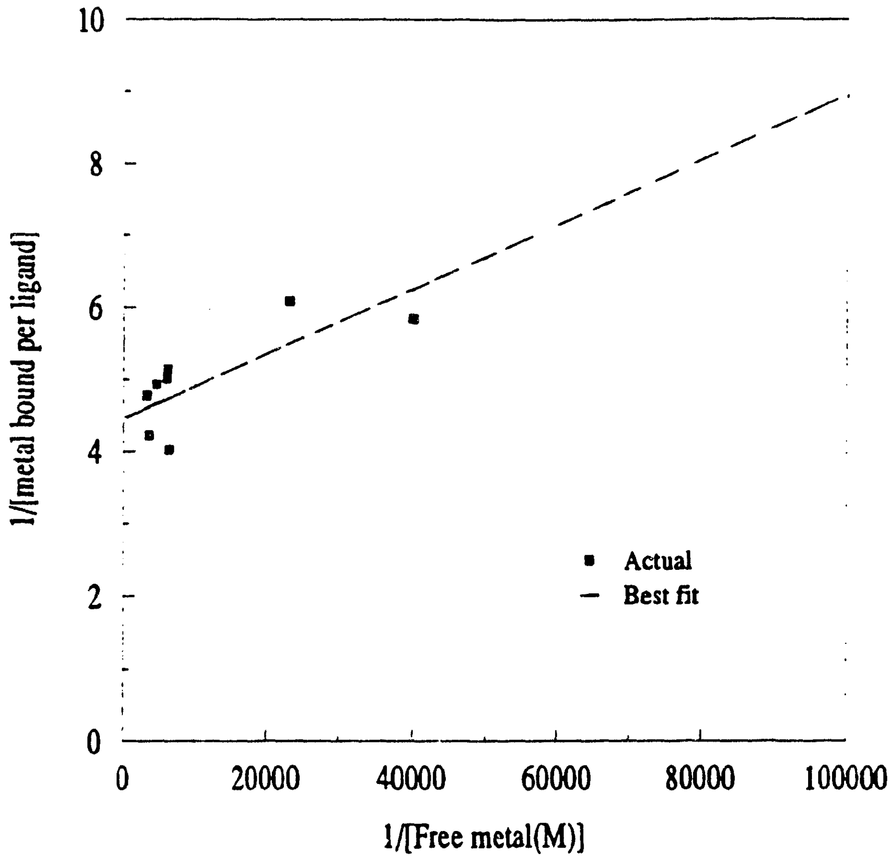


Figure 2.2.7a Linearized Langmuir plot of figure 2.2.7 results

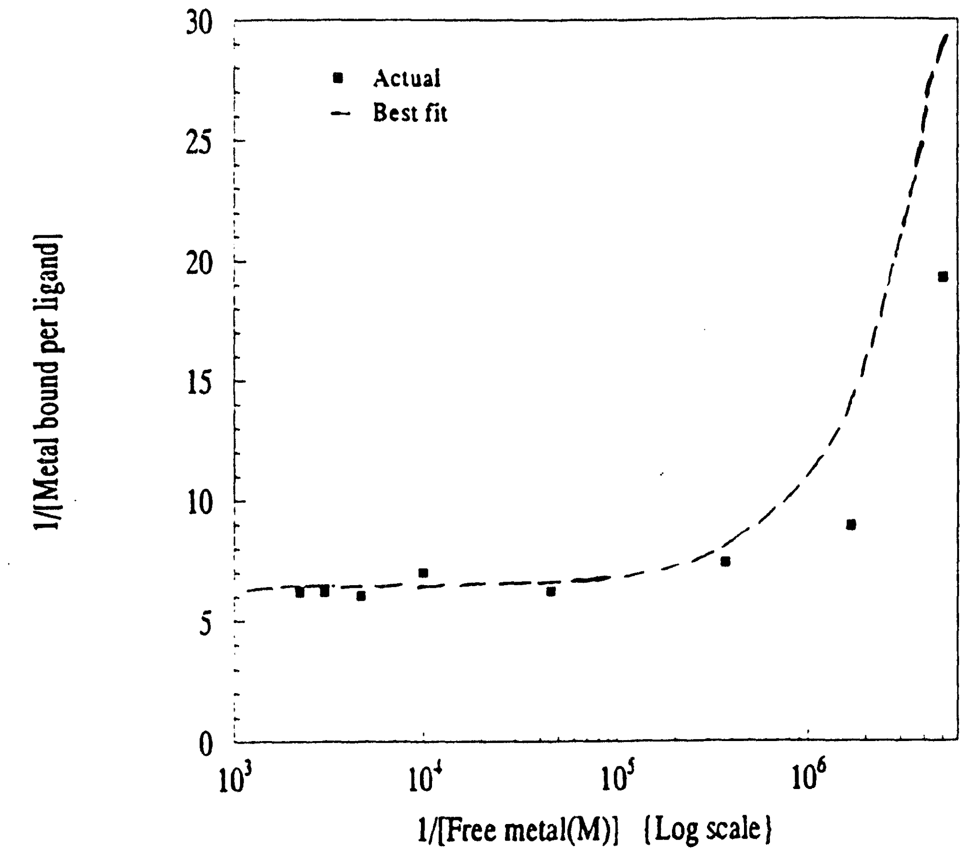


Figure 2.2.8a Linearized Langmuir plot of figure 2.2.8 results shown in semi-log scale.

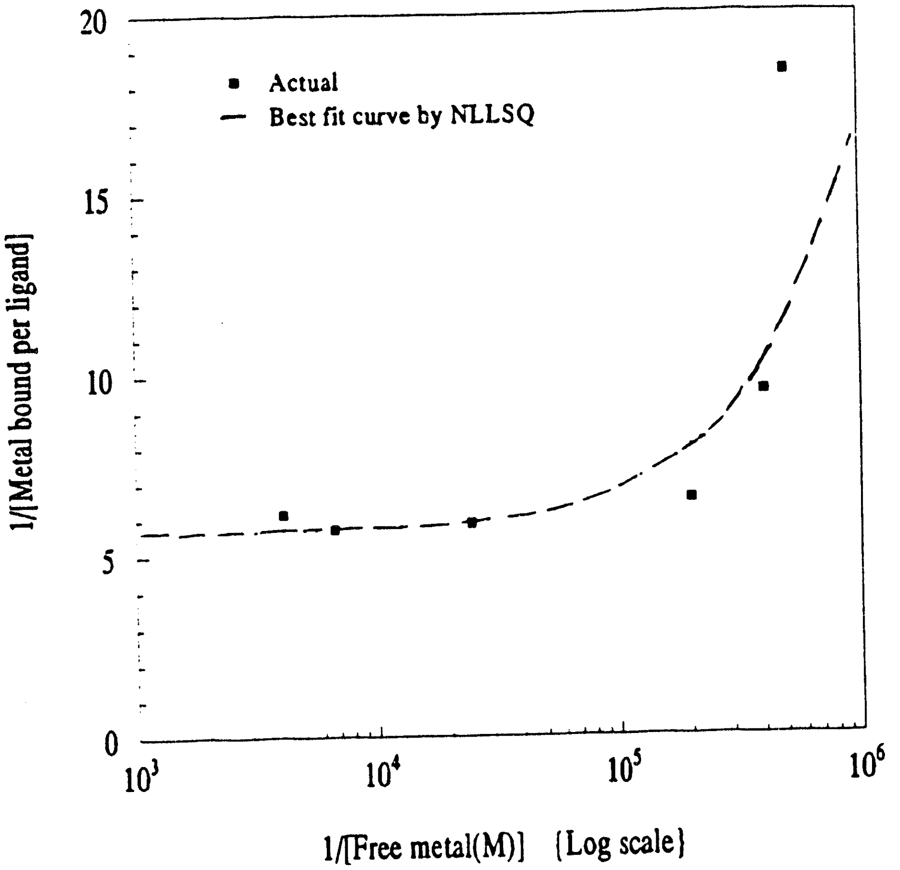


Figure 2.2.9a Linearized Langmuir plot of figure 2.2.9 results shown in semi-log scale.

Two possible explanations for the much lower stability constant at high copper saturation, compared to lower saturation, can be given.

(1) Initial copper binding may cause a conformational transition (from extended to coiled form) which diminishes the subsequent binding of copper.

(2) Metal ion binding to the polymer may produce an excess charge which is gradually introduced into the polymer making subsequent binding more difficult.

These results show that a better data fit may be obtained if heterogeneous binding isotherm is assumed.

2.3.5 Analytical characterization of the polymers

Characterization of ligand substituted polymers by elemental analysis

By elemental analysis it was possible to determine the extent of substitution quite accurately. In the case of maximum substituted polymer it was possible to determine the composition of mono- and di- substitution separately, in addition to the total percentage substitution. The results of elemental analysis carried out with unreacted PAAH and with some of the synthesized products described in section 2.2.4 are shown in table 2.1.3 as weight percentages.

Table 2.1.3 Results of elemental analyses of PAAH and substituted polymers.

Product	%C	%H	%N	%O	%Cl
1. PAAH	35.19	9.30	13.96	0	35.22
2. Maximum substituted (section 2.2.4a)	45.78	7.68	9.31	36.22	0
3. Partially substituted (section 2.2.4c)	39.20	7.85	11.39	19.71	13.88
4. Partially substituted (section 2.2.4k)	38.66	8.40	11.73	17.69	21.93
5. Partially substituted (section 2.2.4l)	38.21	8.28	10.29	----	---

Calculations based on results of elemental analysis

These results agree well with the formula of the starting PAAH. The number of moles of N is the same as the number of moles of Cl, within experimental accuracy, showing that the amine is almost 100% in the protonated form.

The analysis of above results for the product polymer gave an average formula of $C_{5.7}H_{11.46}N\ O_{3.37}$. There was no Cl found in the product showing that all the nitrogens have been substituted. However, it is seen that the total weight is about 1.00 less than 100, possibly due to experimental errors. The above formula shows that the

$C_{2.7}H_{2.46}O_{3.37}$ unit has been added to the total polymer. However, since this may include some moisture, the calculations were done strictly based on carbon atoms. Therefore the number of chloroacetic groups ($C_2H_2O_2$ units) added is 1.35, which is equivalent to 135% ligand substitution.

Calculation of extent of mono- and di- substitution

2-, 1-, and 0- substitutions lead to $C_7H_{12}NO_4$, $C_5H_{10}NO_2$, C_3H_9NCl groups in the chain respectively. However, from the analysis no Cl was found in the product. showing that no zero substituted (free amine units) exist in the polymer chain (the product has been separated under acidic conditions).

Taking the fraction of 2-substitution as x, from mass balance of carbon atoms

$$7.x + 5.(1-x) = 5.7$$

$$x = 0.35$$

The result is 35% 2-substitution and 65% 1-substitution leading to total substitution of 135%. Similar calculations were carried out with the other products to give percentage substitutions as shown in table 2.1.4.

The results of elemental analysis described showed 100% substitution for the product synthesized in 2.2.4k and 92% substitution for the product synthesized in section 2.2.4l. This shows that synthesis by method 2 can yield almost the expected substitution products. However, in the case of method 2 it has not been possible to obtain 50% substituted product as expected; and instead a 117% substitution has been obtained. This may be due to the lower solubility of the more highly-substituted polymers compared to the less substituted, causing them to precipitate preferentially from solution.

Table 2.1.4 Calculated percentage substitutions of synthesized polymers.

Product	% substitution
Partially substituted (section 2.2.4c)	117
Partially substituted (section 2.2.4k)	100
Partially substituted (section 2.2.4l)	92

Characterization by other methods

None of the analytical techniques described in section 2.2.6 and 2.2.7 could give reliable results with the polymer. It seems that the complexation of polymeric ligands does not follow a fixed stoichiometry at all polymer concentrations or at all solution conditions. In some cases the binding ratio was much higher than expected, for which no good explanation can be given. For example the results tabulated in section 2.2.6b indicate that the maximum substituted polymer at a concentration (with respect to imino nitrogen) of 0.33 mM gives an analytical concentration of 1.3 to 1.4 mM, about 4.5 times higher than expected. Similarly, in the dialysis results of table 2.2.1 and 2.2.2, for experiments performed using 0.17 mM concentration of 117% substituted polymer, 3 to 4 times higher binding ratios than the maximum expected are observed.

Similar observations were made in section 2.2.6a for experiments in titrations with copper, where the end point showed about 6 times more copper absorption by the maximum substituted ligand at about 1.5 mM concentration.

Although an excellent calibration curve was obtained with the Cu-polymer complex at 246 nm, the analytical results were not reliable, perhaps due to interference by the Cu-Cl bond. Therefore the analytical results using spectrophotometry of polymer metal complexes are not suitable for characterizing the different polymers. However, better results may be obtained with a polymer having the same characteristics as the polymer used in the standard.

Although spectrophotometric titration by method 2 described in section 2.2.6a, gave reasonably good results with a PEI sample, the results obtained with a 117% substituted polymer, contradicted other experimental results of present work. For example with PEI the binding ratio obtained by this method was 1:4.5 moles of copper to moles of amine units in the polymer, which is exactly the reported value from previous work(69). The ratio obtained for 117% substituted polymer was 1:10, which is too large a value and this does not agree with the results of a later experiment described in section 2.2.8a. However, the only difference between the experiment of section 2.2.8a and this experiment was the buffer strength. These results show that many difficulties arise in attempting to determine the polymer by these techniques. Although, these methods have been used in the past to characterize polymers, the validity of such results appear to be questionable.

Although the calibration graph obtained using Fe-complex method in section

2.2.6b was reasonably good for determination of the polymer, the polymer in the presence of copper could not be determined accurately because of interferences. The cause of the interference was also sought in the literature and was found to owe mainly to absorption by Fe- and Cu- bond with chlorides and to competitive formation of Cu-polymer complex$^{(69)}$. Some results of analysis of 135% substituted polymer samples, carried out using the Fe-complex method, are shown in table 2.1.5.

Table 2.1.5 Results of characterization of polymers by Fe-complex method.

Sample	Determined ligand concentrations (mM) (analysis at 4 wave lengths)	Actual/Exp. Ratio
A 0.33 mM solution of 135% substituted polymer	1.482, 1.466, 1.354	about 4.5
A 5.07 mM solution of 135% substituted polymer	4.286, 4.347, 4.414, 4.433	about 0.9
A 1.27 mM solution of 135% substituted polymer	1.034, 1.048, 1.070, 1.080	about 0.9
Solution synthesized in 2.2.4b of unknown concentration	8.684, 8.916, 8.725, 7.881	---------

With 0.9111M NaOH used in the synthesis described in section 2.2.7, the volumes consumed due to the reaction and the calculated percentage substitutions based on these volumes are shown in table 2.1.6.

Table 2.1.6 Percentage substitution with time during a synthesis of a substituted polymer.

Volume and Time	Percentage Substitution
16.5 mL in 3 hours	46.85
19.5 mL in 6 hours	55.37
21.5 mL in 9 hours	61.05
24.0 mL in 24 hours	68.15

Percentage substitutions have been calculated according to:

percentage substitution = moles NaOH consumed / moles of PAAH X 100

However, it was found that it is difficult to obtain a reliable value of extent of substitution, probably due to the error in determining the end point.

Acid-base titration data did not provide very good end points to determine concentrations of the amine. In case of the synthesized substituted amines it was not possible to find the initial fraction of dissociation in the solution. A computer model based on the NLLSQ program gave fairly good results in determining the end point in case of initial PAAH polymer. However, this model failed in the case of substituted polymer, due to the presence of more functional groups.

2.3.6 Retention of copper and expulsion of Ca by the synthesized polymers

One major aim of this work is to investigate the ion-expulsion behavior. Tables 2.2.1, 2.2.2, 2.2.7 and, 2.2.8 show the results of dialysis experiments carried out with maximum substituted (135% substituted) polymer and copper. It was difficult to work with fairly high concentrations of copper or the polymer in this situation, due to the tendency for precipitation of either the polymer itself or the polymer-metal complex. Very good retentions, close to 99.5% have been obtained with polymer concentrations of 0.2 to 0.25 of the copper concentrations, at dilute concentrations of the polymer (about 0.17 mM). Although this seems fairly economical, use of this polymer is not convenient due to precipitation problems. However, when the same polymer is used at higher concentrations (about 1 mM), the retention is drastically reduced to values in the range 40-60%, as is shown in table 2.2.8. This behavior may be due to the transition between extended and coiled polymer conformations as the concentration changes, or to precipitation of some of the polymer at higher concentration without absorbing enough copper at the working pH, which in turn may be reasonably close to the isoelectric point of the polymer. In some of the identical experiments shown in table 2.2.7 but performed at pH 3.0, better retention values have been observed, which is difficult to explain with the available information.

Another problem identified in working with the maximum substituted polymer was the lack of expulsion of calcium by the polymer, possibly because there is no large net positive charge on the polymer to cause expulsion. Instead, there may be additional negative charges contributed by the unbound ligand sites, as mentioned before. Therefore, the selectivity of the separation will be very poor. Results of dialysis experiments carried out with only calcium, and with copper and calcium both, at lower and higher pH, are tabulated in tables 2.2.5, 2.2.6, 2.2.8. Results show that lowering the pH does not enhance the expulsion ability of the maximum substituted polymer. This is because almost every amine nitrogen has been substituted either 1:1 or 1:2. The only factor capable of causing a slight improvement in Ca expulsion in the pH 3.0 experiment may be the removal of negative charges due to protonation of the unbound ligand sites.

For these reasons, it was thought that a much less substituted product would be more suitable for the desired separation process. Results given in tables 2.2.3 and 2.2.4 show that a partially substituted polymer can give excellent retentions (over 99%) and better Ca expulsions (20 to 40%), even at pH values close to 4.0. Although, in this situation the % substitution was not known exactly, it is expected to be less than 100%. The results of dialysis experiments performed using polymers with lower degree of substitution, with the goal of further increasing the Ca-expulsion ability without at the same time affecting the Cu retention, are shown in tables 2.2.9 and 2.2.10 (also plotted in figure 2.3.1). These results can be compared with the results shown in tables 2.2.15 and 2.2.29 which are from experiments using unsubstituted polymers with and without pH adjustment (for comparison see figure 2.3.1). In these experiments to reduce the % substitution, while at the same time keeping Cu binding ability the same, the total concentration of the polymer (with respect to nitrogens) had to be increased. At pH 5.0 with approximately 20% substituted polymer (table 2.2.9), the Ca expulsion has increased to values close to 50%, and with 8.4% substituted polymer (table 2.2.10) it rises to 70%, which is a dramatic increase. However, the retention ability has been reduced in the later case to a maximum value of 94%, which is a comparatively large decrease from the value of almost 99% in the former case. Therefore, this shows that it is not possible to reduce the extent of substitution without significantly decreasing the copper binding ability.

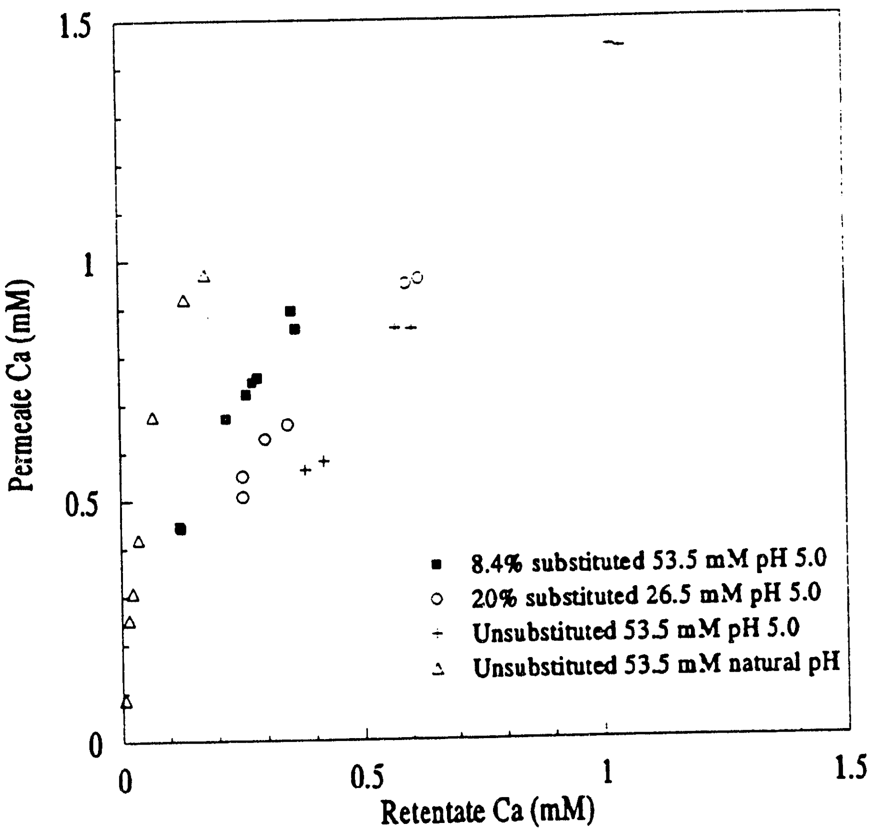


Figure 2.3.1 Calcium expulsion by polymers with different degree of substitution.

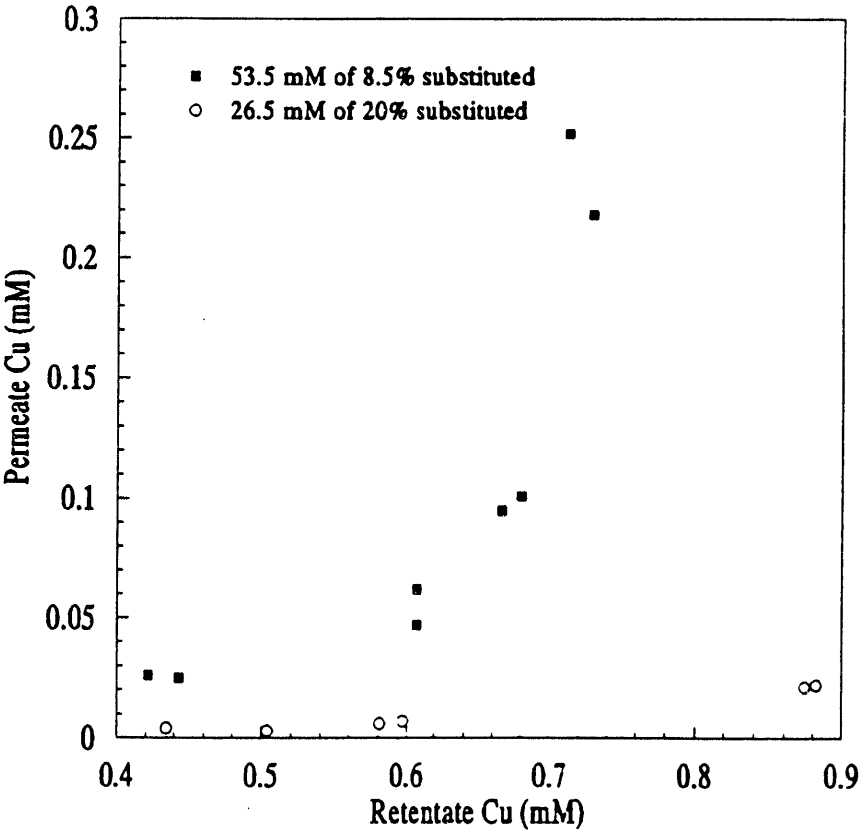


Figure 2.3.2 Copper binding at 8.5% and 20% ligand substitutions using same concentration of ligand sites

Another interesting observation made with 20% and 8.4% substituted polymers is that in these two polymers, even with approximately the same amount of ligand, the 20% substituted polymer produces a much higher copper binding ratio than the 8.4% substituted polymer, as shown by the graphs in figure 2.3.2. This may be due to the difference in total polymer concentrations of the two solutions; thus the 8.4% substituted polymer solution is about twice as concentrated in total polymer, as the 20% substituted polymer solution. The higher concentration may lead to lowered binding capacity due to steric hindrance which arises because of the more nearly random coil configuration of the polymer.

Further experiments were carried out with higher concentrations of the 117% substituted polymer (section 2.2.8f), at a higher pH (pH 7.0). The results are shown in tables, 2.2.11, 2.2.12, and 2.2.13. These data show that at pH 7.0, with 117% substituted (or 1:1.17 substituted) polymer, greater than 99% copper retentions can be achieved by using about twice the number of moles of ligand as the initial moles of copper. This does not really mean that the complexation is 1:2 moles of ligand to copper, since even beyond this concentration of copper the retentions are quite good. However, the calcium expulsions observed in these experiments were very poor because the concentration of unsubstituted polymer units in these experiments were fairly low compared to the calcium concentrations used. These experiments only show the trends in copper binding to 117% substituted polymer at different concentrations of the polymer. Very clearly, from the % retention values it is seen that the copper retentions get better as the polymer concentration is increased within fairly small concentration ranges, and this is due to increased number of binding sites.

From these preliminary experiments it was clearly seen that the expulsion of calcium ions is very low in almost all cases, while the copper retention is exceptionally good and does not need any further improvement. However, one major goals of the present work is to investigate ion expulsion during polymer based separation processes, so that a better selectivity can be obtained. With the goal of determining the ion expulsion capability of PAAH at pH 5.0, dialysis experiments were performed, giving the results tabulated in tables 2.2.14 and 2.2.15. From the experiments related to table 2.2.15, it was intended to determine whether it is possible to obtain a reasonably good calcium expulsion by using unsubstituted polymer, whereas, from the experiments related to table 2.2.14 it was planned to study whether there is any significant binding of copper or calcium to free PAAH at pH 5.0. Results in Table 2.2.15 show that the calcium ion expulsion obtained with unsubstituted PAAH at pH 5.0 is not good as it should be, even though its concentration is more than 50 times that of Cu or Ca. The % expulsions observed are between 30 and 40% for Ca and between 15 to 30% for Cu, (between 50% and 65% as a total) which is much lower than expected. Therefore, the ion expulsion ability of PAAH has been significantly hindered under these conditions. Almost insignificant copper or calcium binding observed from the results of table 2.2.14. This shows that the reduced expulsion is not arising as a consequence of copper or calcium binding to PAAH. The difference in individual percentage expulsions observed in the results of table 2.2.15 for copper and calcium is an unexpected result. The only possible reason may be significant hydrolysis of copper ions compared to calcium in solution at pH 5.0.

Another possible reason for hindered ion expulsion ability of PAAH may be the presence of low molecular weight species in PAAH, causing a significant fraction of the polymer to transfer into the permeate. To test this possibility subsequent dialysis experiments were carried out with the UF purified polymer at different extent of substitution and at same total polymer (based on N) concentrations. The results are shown in tables 2.2.16, 2.2.17, 2.2.18, 2.2.19. The calcium expulsions observed in these experiments were not better than in the previous experiments, and were almost independent of the degree of substitution mainly because of comparatively low polymer concentrations used.

2.3.7 Dialysis experiments with added reagents to enhance ion expulsion

From the results of previously discussed experimental results, it is evident that by having lower percentages of ligand substitution to the polymer, it is practically impossible to induce adequate ion expulsion capability. This is because there is always a lower limit to the % substitution that will give better Ca expulsion while preserving good Cu retention. Results of experiment described in section 2.2.8h (table 2.2.10) show that with 8.4% substituted polymer the expulsion obtained was better than in the other experiments. Another method to increase the unsubstituted polymer (which causes the ion expulsion), while keeping the concentration of the binding ligand fixed, is by the adding a reagent causing Ca ion expulsion to a known quantity of a ligand substituted polymer.

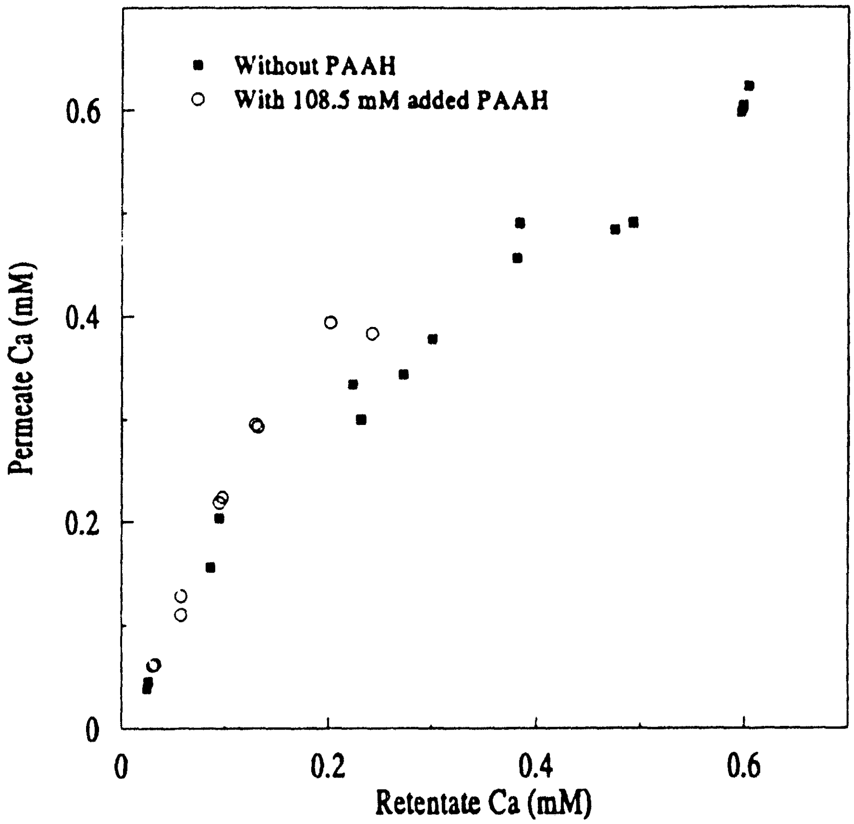


Figure 2.3.3 Calcium expulsion in the presence and absence of added PAAH using 4.34 mM of 41.5% substituted polymer at pH 7.0

Three reagents used in such experiments were: (1) PAAH (2) PDDAC (3) CPC. To infer the effectiveness of PAAH in inducing ion expulsion the results shown in table 2.2.23 can be compared with the results of an identical experiment with no added PAAH in table 2.2.18. The trend is clearly shown by the graphs in figure 2.3.3 which are drawn using the data of tables 2.2.18 and 2.2.23. Some results in table 2.2.23 show significant calcium expulsions compared to the results of table 2.2.18. However, the trend is more clearly seen from the graph in figure 2.3.3, where no significant increase in ion expulsion can be seen due to added PAAH. The results of Table 2.2.27 show the effects of different concentrations of PAAH polymer on Ca expulsion at about 0.25 mM initial Ca concentrations. The percentage expulsions in these experiments are not good, mainly because the PAAH concentrations used were too low compared to the metal ion concentrations. Usually, to induce any significant ion expulsion the polymer concentration should be much higher compared to the concentration of the metal ions. All these results indicate that PAAH does not induce sufficient expulsion ability to the system.

The experimental results with CPC, shown in table 2.2.24, indicate that CPC is more effective in enhancing the ion-expulsion ability compared to PAAH. The percentage Ca expulsion in this case has gone up to about 85% with approximately 20 times higher CPC, compared to Ca, and to 80% with approximately 10 times higher CPC. However, the use of CPC in this situation does not give a tremendous advantage owing to the fact that some CPC monomers leak through the membrane to the permeate solution. Interestingly, the concentration of CPC monomers found in the permeate was almost half of what is expected from the CMC (800 to 900 micromolar), which indicates some interaction between CPC and the polymeric ligand in the retentate. This interaction again is not unexpected because the 117% substituted polymer used in this experiment has many additional free unprotonated ligand sites which carry a negative charge.

The enhancement of expulsion obtained with the addition of PDDAC is quite comparable to that obtained with CPC. With PDDAC, as shown in table 2.2.26, about 80% Ca expulsion can be achieved with close to 100-fold higher concentration than Ca. However, from the results of table 2.2.25, it is seen that this may be the maximum percentage expulsion possible using PDDAC.

2.3.7 Investigation of expulsion ability of free PAAH

Since it was not possible to achieve the desired ion expulsion by PAAH solutions at pH 5.0, it was intended to investigate this by doing several dialysis experiments without adjusting the pH. Only copper was employed in this experiment because of convenience in analytical determination by UV spectrophotometry. Results shown in tables 2.2.29, 2.2.30, and 2.2.31 show percentage expulsions ranging from 80 to 95% at PAAH concentrations of about 50 to 500 times the copper concentrations, 70 to 92% expulsions at PAAH concentrations of about 20 to 200 times the copper concentrations, and 43 to 80% expulsions at PAAH concentrations of 10 to 100 times the copper concentrations respectively. These expulsion values are extremely good and are more or less the expected values. However, an attempt to fit these expulsion data with a model based on Oosawa's theory was not successful.

From these findings it is likely that the increase in salt content during the pH adjustment by addition of an acid or base is at least partially responsible for the reduced ion expulsion ability of the free polymer. This was further investigated by the next experiment carried out with the UF purification of the solution mixture after pH adjustment. The results of dialysis experiments carried out using this solution have been tabulated in table 2.2.32. The results show tremendous increases in expulsion ability even though this solution had only about 10 mM of free PAAH, which is little less than 100 times the total Ca concentration.

2.4 CONCLUSION

Selective separation of metal ions using substituted polymers is possible. There exist no major problems with achieving the desired retention of the binding metal. However, it will be more convenient to use partially substituted polymers (close to 1:1 or less) other than fully or maximum substituted polymers to avoid precipitation problems. The polymer with 117% ligand substitution produced very good results in terms of copper binding, and this polymer did not have any solubility problems. The binding ability of substituted polymers reduces if the polymer concentration is increased by large amounts, or if the salt content is increased. Any other factor that changes the polymer configuration to a more nearly random coiled structure will also reduce the binding ability of the polymer. However, at fairly small concentration ranges the increase of total polymer concentration may increase the binding due to increase of total ligand sites.

It is impossible to induce any significant calcium ion expulsion ability in the polymer by lowering the pH. To obtain any significant selectivity, it is necessary to add a polymer which does not affect the pH of the solution, such as PDDAC. Although CPC can induce a comparable expulsion ability, it introduces other problems such as the presence of excessive monomer which contaminates the purified stream. CPC will also bind with the free ligand sites in the polymer and the effect of this on metal binding have not been investigated. The addition of free PAAH does not induce much ion expulsion ability as expected, possibly owing to the presence of excess salt introduced in the pH adjustment. However, the expected selectivity can be achieved by removing any excess salt present in the system. In an ultrafiltration separation process this can be achieved by having a preliminary UF run prior to actual separation cycles. The PDDAC polymer is quite effective in inducing ion expulsion ability to the system.

Binding isotherms of copper with iminoacetic substituted polymers are quite closely of the Langmuir or hyperbolic type. However, present work reveals that it may be best represented by the heterogeneous binding isotherm.

In recovery of the used polymer, addition of acid does not completely break the ligand from the metal until a pH less than 1 is reached. Therefore, this may not be economical. Addition of base causes some ligand to precipitate with the metal. Further investigations are needed to establish a good economical method of recovery. There exists another possible method of recovery, changing the extent of substitution of the synthesized polymer so that its iso-electric pH is changed and it can be precipitated from a concentrated solution at that pH. This again needs further investigations, including synthesis of the desired ligand.

CHAPTER 3

A THEORETICAL MODEL FOR THE TITRATION BEHAVIOR OF POLYAMINES

3.1. INTRODUCTION

3.1.1 Titration behavior of polymers

The characteristics of pH titration curves of polymers having acidic or basic groups are much different from those of titration curves for small molecules. Ionization becomes more and more difficult due to the build up of charges on the polymer. Therefore, in contrast with systems of monomeric acids or bases, it may be difficult to determine a clear end point in a titration curve of a polyacid or a polybase. Moreover, it is generally not possible to model the titration curve based on an assumed single acid dissociation constant. In addition to this, since polymer configurations tend to change under different solution conditions, no single type of behavior may be observed throughout a wide range of polymer concentrations.

In a number of previous studies of the titration behavior of polymers various models have been used to fit data(74-79). However, in most of these studies, the equations employed have required using empirical constants, although subsequently the determined empirical constants have been given a physical meaning.

The Henderson-Hasselbalch equation, for a monobasic acid can be given by,

$$pH = pK - \log [(1 - \alpha) / \alpha]$$

where α is the degree of dissociation of the acid. The same equation has been applied(74) to polymeric systems by including empirical parameters pKav and n, which are dependent upon the system. This equation is written as

$$pH = pK_{av} - n. \log [(1 - \alpha) / \alpha]$$

Theoretical analysis of the behavior of polyelectrolytes has been developed by Katchalsky and Gillis(75) and Arnold and Overbeek(76). Their work has led to the following expression for the potentiometric behavior of polymeric bases.

$$pH = pK_0 - 0.434/kT (\partial G_{el}/\partial v) - \log \beta/(1-\beta)$$

where pK_0 is the intrinsic dissociation constant of the cationic acid conjugate, β is the degree of protonation, and G_{el} is the electrostatic free energy of the polyion having υ positively charged groups. Here $(\partial G_{el}/\partial \upsilon)$ can be expressed as

$$\partial G_{el}/\partial \upsilon = \epsilon \psi_0(\beta)$$

in terms of the electrostatic surface potential, $\psi_0(\beta)$ at degree of protonation, β, and the charge of a proton, ϵ. The constant 0.434 relates natural log and the log with base 10; $\log x = 0.434 \ln x$.

However, in general the modified Henderson-Hasselbalch equation, which is derived from the above equation, for a polybase takes the form,

$$pH = pK - \log [\beta/(1-\beta)] - 0.434 q\psi/kT$$

where q is the electrovalency of the polyion, ψ is the mean electrostatic potential at the degree of ionization, β, and k is the Boltzmann constant. Most theoretical treatments discussed in previous work are based on the above equation. In addition to these theoretical relationships several equations have been proposed as suitable empirical relations between the apparent dissociation constant K_{app}, pH and β.

The equation by Kern(77), predicts that pK should depend linearly on pH:

$$pK = pK_0 + B \, . \, pH$$

where B is an empirically derived constant. Kagawa and co-workers(78) used the relationship,

$$pK_{app} = pK + m \log [\beta / (1 - \beta)]$$

Mandell(79) used a quadratic relation between pK and α:

$$pK = pK_0 + P_1 . \beta + P_2 . \beta^2 + \ldots\ldots\ldots$$

where, all the parameters (pK_0, P_1,...) pertain to a particular titration. Bloys and Treslong(72), have used the same formula in determining the titration behavior of polyethylenimine; the same workers have later used a more complicated equation involving a parameter to account for nearest neighbor interactions to analyze the same polymer system(80).

Manning applied his counterion condensation model to explain the titration behavior of polyelectrolytes(90). Quite recently, Strauss, Barbieri and Wong(81), and then Strauss(82), and more recently Marcellet and Wozniak(83), have used a method treating potentiometric titration curves in terms of successive ionization constants applied to oligomeric subunits of the polymeric chain, thereby allowing the resolution of subunits into species differing in their state of deprotonation.

The effect of polyion charge can be seen not only in relation to the ionization of the polymer molecule itself but also that of any molecules bound to it. For example in case of micellar solubilized molecules, in which the micelle is considered to be a spherical polyion, the acid-base behavior has been observed to vary significantly. Quite a large amount of work has been carried out previously to investigate this phenomenon both qualitatively and quantitatively. According to a recent review(84) two approaches have been used by workers.

(1) Relating the pK_a in the presence of interface to that in the bulk water by taking into account the surface potential and the effect of transfer of a probe from bulk water to the interface.

(2) Determining pK_a values by using "effective pH" values calculated by considering the possible exchange equilibria between the ions present in the bulk phase and the surfactant counterions.

Investigation of the effect of polyion charge on acid-base behavior of micellar solubilized molecules has wide applications owing to the ability of the micelles to solubilize various kinds of water insoluble organic acid-base molecules. The theories developed for such micellar systems are applicable to polymers as well with the exception that most polymers in dilute solutions are more nearly cylindrical or rod-like in shape, rather than spherical.

In the case of an acid-base indicator the apparent pK of solutes in the presence of an aqueous micelle can be different from that in pure water owing to combination of medium and electrostatic effects. The Stern layer, which is the inner layer of bound ions at a charged surface, in general has the characteristics of lower polarity and permittivity and higher ionic strength compared to the bulk phase(84).

According to Gregor(85) it is possible to distinguish five different modes of ion-binding to a polyion, namely; (1) coulombic binding (2) Stern layer binding (3) hydrophobic binding or adsorption (4) hydrolytic binding (through H-bond formation) (5) ligand binding. The present work is mainly related to first two types of binding and the rest will not be discussed here.

In coulombic binding the attractive force is electrostatic and the annular region of bound counterions has been assigned the same dielectric constant as the bulk by Gregor and Kagawa(85). However, these workers have mentioned the importance of considering a local dielectric constant different from the bulk for the region of bound counterions. The ions bound to the polyion by coulombic binding remain in the Gouy- Chapman layer and this type of binding is supposed to occur where there is no specific interactions between fixed charges and counterions(85). For Stern layer binding to occur, the chain potential has to be quite large or the counterions have to be quite small(85).

3.1.2 Polyelectrolyte theories

The prevailing modern theory of polyelectrolyte solutions is based on analysis of the properties of an infinitely long cylinder with electric charge distributed uniformly along its surface. The cylindrical model for a single polyelectrolyte chain was introduced independently by Alfrey, Berg and Morawetz(56), and Fuoss, Katchalsky and Lifson(57). Most workers agree that the cylindrical model should be applicable to polyelectrolyte solutions at low concentration.

Poisson-Boltzman equation

Consider a positively-charged surface, with an electrical potential at the surface of ψ_0, which is in contact with a solution phase containing positive and negative ions. At any point far from the surface, where the potential is y, the potential energy of an ion in the electric field is given by $ze\psi$, where z is the valence of the ion and e is the electronic charge. The probability of finding an ion at some particular point will be proportional to the Boltzman factor exp $(-ze\psi/kT)$. The net charge density (ρ) at any point is given by the sum of total charges due to ions of both charges.

$$\rho = z\,e\,(\,n^+ + n^-\,)$$

$$= z\,n_0\,e\,(\,\exp(ze\psi/kT) + \exp(-ze\psi/kT)\,)$$

The Poisson equation relates potential gradient at a given point to the charge density at that point by:

$$\nabla^2\psi = -\,4\,\pi\,\rho\,/\,D$$

where D is the dielectric constant of the medium. By combining the Poisson and Boltzman equations the widely used Poisson-Boltzman (P.B) equation is obtained.

$$\nabla^2\psi = (\,4\,\pi\,n_0\,z\,e\,/\,D\,)\,[\,\exp(ze\psi/kT) + \exp(-ze\psi/kT)\,]$$

In the Debye-Hückel approximation to the P.B equation it is assumed that $Ze\psi << kT$ so that the exponential terms can be approximated by the first terms in their expansions, giving the following equation.

$$\nabla^2\psi = 8\,\pi\,n_0\,z^2\,e^2\,\psi\,/\,D\,K\,T$$

$$= \kappa^2\,\psi$$

where $\kappa^2 = 4\,\pi\,e^2\,/\,D\,k\,T\,\Sigma\,n_i\,z_i^2$ if many different ions (n_i) of different charges (z_i) are involved.

Lifson and Katchalsky(58) have described the analysis of the cylindrical version of the P.B. equation without using the Debye-Hückel approximation. In the cell model described by them the polyelectrolyte solution as a whole is divided into several sub volumes with a radius (R), Length (h), parallel to each other. If there are n polyelectrolyte molecules per unit volume then,

$$n \pi R^2 h = 1$$

The radius a, is introduced to represent the minimum distance of approach to the axis, so that the volume fraction ϕ occupied by the polyion is given by

$$\phi = N \pi a^2 / N \pi R^2 h = a^2 / R^2$$

Quite recently, Manning(54) has presented a more rigorous demonstration of counterion condensation in polyelectrolytes by analysis of the P. B. equation. However, as reported by Manning(54), the terminology counterion condensation was first introduced by Oosawa's group. The idea of counterion condensation is that there exists a critical charge density ϵ_{crit} on the cylinder, at which counterions will associate themselves with the surface of the cylinder so that the net charge density is maintained at the critical value. This phenomenon occurs if the solution is infinitely dilute. Oosawa has re-interpreted his two-phase theory using the counterion condensation concept(22).

3.1.3 Aim of the present work

In the work described here, a different approach is developed to describe the titration behavior of polyelectrolytes, by considering only the counterion distribution of the polyelectrolyte to produce the titration curve. This approach needs a clear understanding of the polyelectrolyte models and their counterion behavior. The two state model presented by Oosawa(22) is used as the basis for predicting the counterion distribution. This model is outstanding from the standpoint of its simplicity and general applicability. The Oosawa theory assumes distribution of counterions around a polymer surface within two distinct phases, governed by the Boltzmann distribution. A brief explanation of the Oosawa's theory is given in chapter 1 of this text, whereas a complete description is given elsewhere(22). Thermodynamic equilibrium of the species involved between the two phases is considered. The ultimate aim of this work is to obtain a better understanding of the titration behavior of polyacids and polybases.

Application of the mass action law to the equilibrium of site bound counterions with the counterions in the immediate vicinity of the surface has been reported by Guéron and Weisbuch(86). However, in the approach used in present work, such an equilibrium between counterions is not considered, but an equilibrium constant associated with counterion free amine and surface protons is introduced.

3.2 MODELLING AND EXPERIMENTAL SECTION

3.2.1 Detailed description of the model

The model described in the present work has been formulated to describe the titration behavior of polyallylamine with a standard hydrochloric acid solution. The polyamine is considered to be in a rodlike, extended conformation throughout the titration. This assumption should be valid at least at low concentrations of the polymer.

As the polymer becomes gradually protonated during a titration, the initially added polyamine groups will remain in solution in three different forms as, the free amine, the protonated amine with no counterions attached, and the protonated amine with the cationic charge neutralized by the bound counterions. The mass balance equation for the amine can be written as

$$(1) \qquad [\text{polyamine}] = [RNH_3^+] + [RNH_2] + [RNH_3^+.Cl^-]$$

in which case the counterion is chloride contributed by the added HCl and NaCl. The concentration of species represented by square bracketed terms in this work denote the concentration of those species, based on the total volume of the solution and not on the intrinsic volume fraction.

According to Oosawa's model, the counterions are distributed between two distinct phases, one the region occupied by macroions where most of the bound counterions exist and the other the bulk solution free of macroions. The fraction of free counterions, β, is defined as

$$(2) \qquad \beta = n_{Cl,bulk} / (n_{Cl,bulk} + n_{Cl,surface})$$

where n denotes the number of moles of species indicated by subscripts. By dividing both denominator and numerator by total solution volume, the following equation will be obtained.

(3) $\beta = [Cl_{bulk}] / \{ [Cl_{bulk}] + [Cl_{surface}] \}$

where the terms $[Cl_{bulk}]$ and $[Cl_{surface}]$ are not the actual concentration of chloride in each phase, but the concentration with respect to the total solution volume, as explained before. Such a definition is more convenient here in applying mass balance equations and the Oosawa equation.

The hydrogen ion concentrations in the surface and the bulk phases are also defined the same way with respect to total solution volume. Oosawa's equation for a polymer with a cylindrical shape can be written:

(4) $\ln \{ (1-\beta)/\beta \} = \ln \{ \phi/(1-\phi) \} + Q \ln (1/\phi)$

where ϕ denotes the fractional volume of the surface phase, and Q is the parameter related to charge density on the polymer. The parameter Q can be related to the value of this parameter in the fully dissociated state, Q_0 the extent of protonation, α, and the fraction of counterion dissociation in the polymer, b, as follows.

(5) $Q = Q_0.b.\alpha$

where $b = 1 - ([RNH_3^+.Cl^-] / [\text{polyamine}])$.

Therefore, the Oosawa's equation as applied to the present case takes the form

(6) $\ln \{ (1-\beta)/\beta \} = \ln \{ \phi/(1-\phi) \} + Q_0.b.\alpha \ln (1/\phi)$

It should be noted here that the factor ϕ is equal to the apparent volume of the surface phase per mole of the polymer unit, ϕ_0, times the molar concentration of the polymeric units, giving the equation

(7) $\phi = \phi_0 \cdot [\text{polyamine}]$

Equilibrium of species between the two phases

Activities of HCl in the surface phase and the bulk phase have to be equal. In these equations instead of the [H] and [Cl] with respect to total volumes, the actual concentrations have to be used. These actual concentrations are easily calculated using the volume fraction of the surface phase (ϕ) and the bulk phase ($1-\phi$), as follows.

Actual [H] in the surface phase = $[H_{surface}] / \phi$

Actual [H] in the bulk phase = $[H_{bulk}] / (1-\phi)$

Actual [Cl] in the surface phase = $[Cl_{surface}] / \phi$

Actual [Cl] in the bulk phase = $[Cl_{bulk}] / (1-\phi)$

Therefore the activity balance equation is

(8) $([H_{surface}] / \phi) . [Cl_{surface}] / \phi = ([H_{bulk}] / (1-\phi)).([Cl_{bulk}] / (1-\phi))$

Although it is possible to write analogous activity balance equations for distribution of NaCl between the two phases, such an equation may not be useful in analyzing a system without excess NaCl.

Mass balance equations

It is possible to write equations for the proton balance and the mass balance of chloride ions. All protons coming from the added acid are distributed between two phases as free protons or as protonated amine. The proton balance equation is

$$(9)\ [H_{bulk}] + [\text{polyamine}].\alpha + (1-\alpha)\ .\ [Cl_{surface}] + [H_{surface}] = [\text{Acid}]$$

where [Acid] denotes the added HCl concentration during the titration after taking the dilution factor into account. Similarly, the mass balance equation for chloride ions is

$$(10)\qquad [Cl_{surface}] + [Cl_{bulk}] = [\text{Acid}] + [\text{NaCl}]$$

where [NaCl] denotes the added NaCl concentration after taking the dilution factor into account.

Another important assumption made here is that all the counterions that exist in the phase in the vicinity of the polymer chain remain bound to the amine. Therefore

$$(11)\qquad [RNH_3^+.Cl^-] = [Cl_{surface}]$$

and using equation (1),

$$[\text{polyamine}] = [RNH_3^+] + [RNH_2] + [Cl_{surface}]$$

Mass action law for the equilibrium process

An equilibrium exists between the counterion-free protonated amine and the deprotonated amine and the protons in the surface phase. In the proposed model the intrinsic equilibrium constant for protonation of amine is considered to be a constant throughout, and denoted by K, given by

$$K = [RNH_3^+] / [RNH_2][H^+_{surface}]$$

It is important to note that the protonated amine bound to counterions is not included in the above equilibrium because it is assumed that only the counterion-free protonated amines take part in the equilibrium. The degree of protonation of the amine, α, is defined as

$$\alpha = [RNH_3^+] / \{ [RNH_2] + [RNH_3^+] \}$$

Therefore, intrinsic equilibrium constant, K is given by

(12) $$K = \alpha / \{(1-\alpha) . [H^+_{surface}] \}$$

Finally, including the dilution factor, the terms [NaCl] and [Acid] can be expressed as follows.

(13) $$[Acid] = [Acid_0] . \{ v/(v+v_0) \}$$

(14) $$[NaCl] = [NaCl_0] . \{ v_0/(v+v_0) \}$$

(15) $$[polyamine] = [polyamine_0] . \{ v_0/(v+v_0) \}$$

where the terms with subscript zero indicate the initial concentrations of the species in the beginning of titration, and v_0, v are the initial volume and the volume titrated respectively. Equations (1) to (15) are the only equations required to model the system. Finally, the equivalents of amine titrated can be determined using the titration volumes calculated. However, in addition, the following equations can be written to derive some useful parameters.

The protonation constants

The apparent protonation constant according to the definition of present work can be written as,

$$K_{app} = \alpha / \{(1-\alpha) . [H_{bulk}] \}$$

This constant is based on the polyamine units free of bound counterions. The amine units bound to counterions are assumed to be not taking part in the equilibrium:

$$RNH_3^+ \rightleftharpoons RNH_2 + H^+$$

Although, this seems to be the real protonation constant for the equilibrium, the protonation constant defined including the counterion bound amines also in the initial concentration of polyamine may be a useful parameter because, in most other work using different approaches the apparent K is defined this way. Therefore, the protonation constant defined as follows and denoted by Knormal will be very useful for comparison.

$$K_{normal} = \{ [RNH_3^+] + [RNH_3^+ Cl^-] \} / \{ [RNH_2] . [H_{bulk}] \}$$

which is same as

$$K_{normal} = K_{app} + \{ [Cl_{surface}] \} / \{ [RNH_2] . [H_{bulk}] \}$$

Solving the model equations

The equations described above were rearranged to obtain a single expression in terms of surface and bulk hydrogen concentrations, β, α, K, ϕ_0, and Q_0 substituted into the equation (6). This equation was solved numerically by a specific subroutine included in the usual NLLSQ program, using arbitrary values for K, Q_0, and ϕ_0. The main routine of the NLLSQ program$^{(49)}$ then determined the best values of these constants, to predict the experimental value of added volume of acid during the titration using the bulk pH as the independent variable. The titration data were fitted with the model by using the NLLSQ program. Finally the model equations were input in the Simultaneous Equation Solver Program (SEQS, CET Research Group, Norman Oklahoma) and solved for some titration results using the values derived by NLLSQ analysis to check the program accuracy. A sample output report is shown in figure 3.2.9.

3.2.2 Experimental section

Poly(allylamine hydrochloride) (PAAH) described in chapter 2 was used as the polyelectrolyte in this titration study. The sodium hydroxide used was carbonate free, obtained from Baker Co. Hydrochloric acid solutions for titrations were prepared accurately using a standardized stock solution of HCl. The titration set up was same as described in the work of chapter 1. Poly(allylamine) for the titration experiments was prepared using PAAH as follows.

A concentrated stock solution of PAAH was prepared by weighing an exact amount of solid PAAH. This solution was neutralized with a solution of carbonate free NaOH, and the volume of the final solution was adjusted to a known volume. Solutions for each titration experiments were prepared by diluting these solutions accurately. Even in the absence of any added salt to the titration solutions an amount of salt equal to concentration of the polymer will exists in each titration samples owing to the above procedure.

To test the titration model described above, several titration experiments were carried out using different concentrations of poly(allylamine) with different amounts of added NaCl as described below. Titrations were carried out with 0.2 M added NaCl and without any added NaCl. In all these titrations the volume increase of the solution was kept to a minimum by using a much stronger HCl solution than the amine solution. The concentrations of HCl solutions used in the present experiments were varied depending on the concentration of the polyamine solution. Details of the six titration experiments are described below.

Titrations with no added excess salt (low salt concentrations)

(1) 0.00950 M PAA with 0.0095M NaCl in 20.00 mL total initial volume titrated with 0.04838 M HCl.

(2) 0.04745 M PAA with 0.04745 M NaCl in 20.00 mL total initial volume titrated with 0.2409 M HCl.

(3) 0.09500 M PAA with 0.09500 M NaCl in 20.00 mL total initial volume titrated with 0.4820 M HCl.

Titrations with 0.2000 M added excess salt (high salt concentrations)

(4) 0.00950 M PAA with 0.2095M NaCl in 20.00 mL total initial volume titrated with 0.04838 M HCl.

(5) 0.04745 M PAA with 0.2475 M NaCl in 20.00 mL total initial volume titrated with 0.2409 M HCl.

(6) 0.09500 M PAA with 0.2950 M NaCl in 20.00 mL total initial volume titrated with 0.4820 M HCl.

3.3 RESULTS AND DISCUSSION

The ultimate least squares analysis curves obtained using the model and the actual titration curves are shown in figures 3.2.1 to 3.2.6 respectively for the titrations (1) to (6) described above. The actual titration curve agrees very well with the modelled curves at the concentration range 10 to 100 mM of the polymer, with a salt concentrations varying from 0 to 0.2 M. This can be seen clearly by comparing the individual titration curves and also the RMSD values generated by the NLLSQ program. The several approximations made in the present model do not seem to lead to large discrepancies between experimental and calculated results. It may be that a compensation of errors is partly responsible for the very good fit. Despite this possibility, the present model serves as a very good representation of the polymer titration system.

In NLLSQ data analysis the best fit values for parameters K, Q_0, and ϕ_0 were searched by first letting all parameters vary from system to system and then keeping some of them fixed. The results of NLLSQ analyses obtained by allowing all three parameters to vary in individual titrations are shown in table 3.2.1. In this analysis with some titration data it was not possible to obtain good results either because the program did not converge or the results indicated large errors in the parameter. This table shows that in addition to large errors in the fitted parameters, there is a significant variation in parameter values from one experiment to the other. To obtain better results from data fitting it was found desirable to have at least one more parameter value fixed globally.

Table 3.2.1 Results of NLLSQ analysis of titration data allowing parameters K, Q_0 and, ϕ_0 to vary.

Tit. No.	K	Q_0	ϕ_0	RMSD	Converged
1	6.3E9	0.452	1.8e-4	5.0E-5	No
2	1.36(±.15)E10	0.574±.130	4.3(±6.5)E-3	4.4E-5	Yes
3	1.89(±.21)E10	0.585±.130	4.6(±5.2)E-3	4.0E-5	Yes
4	1.5E10	0.38	2.4E-3	8.0E-5	No
5	2.30(±.92)E10	0.37±.23	2.92(±20)E-4	1.9E-5	Yes
6	2.5(±.70)E10	0.83±.20	17.9(±6.3)E-3	8.6E-5	Yes

The procedure for the theoretical calculation of the potential parameter value, Q_0 has been described by Oosawa(22). Based on the distance between the charged amine groups of 2.5 Å the value of Q_0 is calculated to be 2.83. Use of this value in the NLLSQ program while varying the K and ϕ_0 yielded a very large value for ϕ_0 and a much larger RMSD value, and also the model did not fit all titration data sets equally well. Therefore it was not possible to use this calculated value of the potential parameter in the model.

The next attempt was to find a suitable value for the parameter ϕ_0, in which case the definition of this may be not straightforward. According to Oosawa's theory this parameter is the volume fraction occupied by the polyion, which is same as the apparent molar volume of the monomer unit times the molar concentration of monomer units. Apparent molar volumes of monomer units of polymers have been determined by several previous workers(87,88) by experimental determination of partial molar volume of the monomer units at different concentrations of the polymer and then extrapolating this variable to zero concentration, to infer the limiting apparent molar volume. The apparent molar volume of poly(allylamine) has not been reported previously. Therefore instead of the actual value an estimated value had to be used. In addition, most previous work(87,88) showed that the apparent molar volume of a polyelectrolyte may change with its fraction of dissociation as well as the concentration. However, this variation in apparent molar volume was found to be so small that in this model a fixed average value can be used.

By analyzing the structure of the PAAH monomeric unit and the dimensions of polymer molecule, it was found reasonable to consider this molecule to have almost similar dimensions as poly(acrylic acid) polymer. The partial molar volume of this polymer was found to be of the order of 40 mL/mole(88). The NLLSQ analysis performed using this value for ϕ_0 did not fit all the titration data sufficiently well.

By considering all of these observations it can be concluded that the model equations are not valid if the volume fraction is specified by the apparent molar volume of the polyion, although this volume has been used in previous applications(23) of Oosawa's equation. However, a comment may be made regarding the value of the volume fraction which should be used in Oosawa's equation. Oosawa's equation has been derived using the Boltzman distribution, which is not restricted only to a particular volume region around the molecule. Therefore, if Oosawa's equation is applied without knowledge of the effective value of the potential parameter, it is always possible to select some value of ϕ for a given potential parameter value so that the equation is satisfied.

Table 3.2.2 Results of NLLSQ analysis of titration data allowing parameters only K and Q_0 to vary.

Titration	K	Q_0	RMSD
1	6.43(±.63)E9	0.58±.02	5.0E-5
2	1.34(±.11)E10	0.54±.02	4.2E-5
3	1.85(±.15)E10	0.54±.02	3.8E-5
4	1.48(±.19)E10	0.39±.02	7.7E-5
5	2.40(±.97)E10	0.48±.01	2.3E-5
6	1.90(±.32)E10	0.45±.41	9.7E-5

Further NLLSQ analysis showed that, when the ϕ_0 was kept fixed at quite small value in the range 1.0 mL to 4.0 mL while the other parameters were allowed to vary, a fairly good correlation with experimental data can be obtained. Therefore, for all the titrations the NLLSQ analysis was performed using a fixed average ϕ0 value of 3.0

mL while other parameters were allowed to vary. Under these conditions the NLLSQ results are shown in table 3.2.2.

The extremely low value of ϕ_0 seems to indicate that the counterion binding described by the model equations occurs only at the immediate vicinity of the polymer surface. It may perhaps be describing the Stern layer binding. The volume fraction represented by ϕ_0 can be interpreted as a site volume, excluding any volume occupied by the molecules or ions themselves. At such a close vicinity to the polymer surface the interaction may be so strong that most of the bound counterions remain attached at sites on the polymer, which is one of the assumption in the present model. The unexpectedly small value of the potential parameter, Q_0 (compared to the calculated value of 2.83) is due to very small thickness of the surface phase, which makes the difference between average potentials of the two phases fairly small. Clearly, the higher the ϕ_0 value is the higher the corresponding Q_0 value.

Even with the restrictions and reservations expressed above, it is clear that the present model provides a good correlation of the experimental results. Therefore, an effort was made to fit all the results by holding the intrinsic equilibrium constant (K) of the amine units at a constant value of 1.5e10, which was found to be a reasonable value for K from the previous least squares analyses. The value of ϕ_0 was kept fixed at 0.003 L as before. The graphs shown in figures 3.2.1 to 3.2.6 are the theoretical and experimental results for the titrations (1) to (6) respectively, obtained by using the parameters obtained from this NLLSQ analyses. The results of analyses are shown in table 3.2.3.

Table 3.2.3 Results of NLLSQ analysis of titration data allowing parameters only Q_0 to vary.

Titration	Q_0	RMSD
1	0.73±.02	1.2E-4
2	0.57±.01	4.4E-5
3	0.50±.01	4.7E-5
4	0.39±.01	7.5E-5
5	0.38±.01	7.7E-5
6	0.40±.01	1.0E-4

These results show that in the presence of added excess salt the charge parameter, Q_0, tends to remain almost fixed at approximately 0.40, whereas in the absence of excess salt it varies from 0.73 at low polymer concentration to 0.50 at higher polymer concentrations. The variation of the Q_0 value in the absence of excess salt may owe to a screening effect caused by the polymer molecules as the concentration increases. However, such a screening effect becomes insignificant compared to the screening caused by salt in the presence of excess salt. The screening caused by excess salt is fairly so high that the Q_0 value is reduced to almost 0.38 from 0.73.

At fairly low concentrations of the polymer, in the absence of excess salt, the polymer chain will tend to become more nearly linear than otherwise. Therefore, the Oosawa equation based on cylindrical polymer conformation will become more nearly valid for the results of titrations (1) and (2) rather than the others. However again, as the concentration increases the polymer may tend to achieve a coiled conformation. Despite the possible errors already mention and the neglect of the difference in dielectric constants between the bulk and the surface phases, and of the activity coefficients in both phases, the present model represents the titration behavior of polyamines quite well. Very broad concentration ranges were not used in testing this model because of the limitations, the applicability of the cylindrical model at higher concentrations, and the possibility of significantly large experimental errors at lower concentrations.

Finally, the pKapp and the pKnorm values calculated using the model for the titration experiment (1) were plotted against the fraction titrated and pH, and the graphs obtained are shown in figures 3.2.7 and 3.2.8 respectively. Figure 3.2.7 shows that the pK values vary linearly with the fraction titrated (X). The linear variation of pK with the fraction of titration can be inferred from the previous work(91) where an approximately linear relationship between {pH + log[X/(1-X)]} vs. X has been observed. It should be noted that the term {pH + log[X/(1-X)]} is equal to pK_{app}. Some workers have attempted to fit the titration behavior of polymers assuming linear variation of pK with the pH(77), and the approximate validity of this assumption can be inferred from the present model.

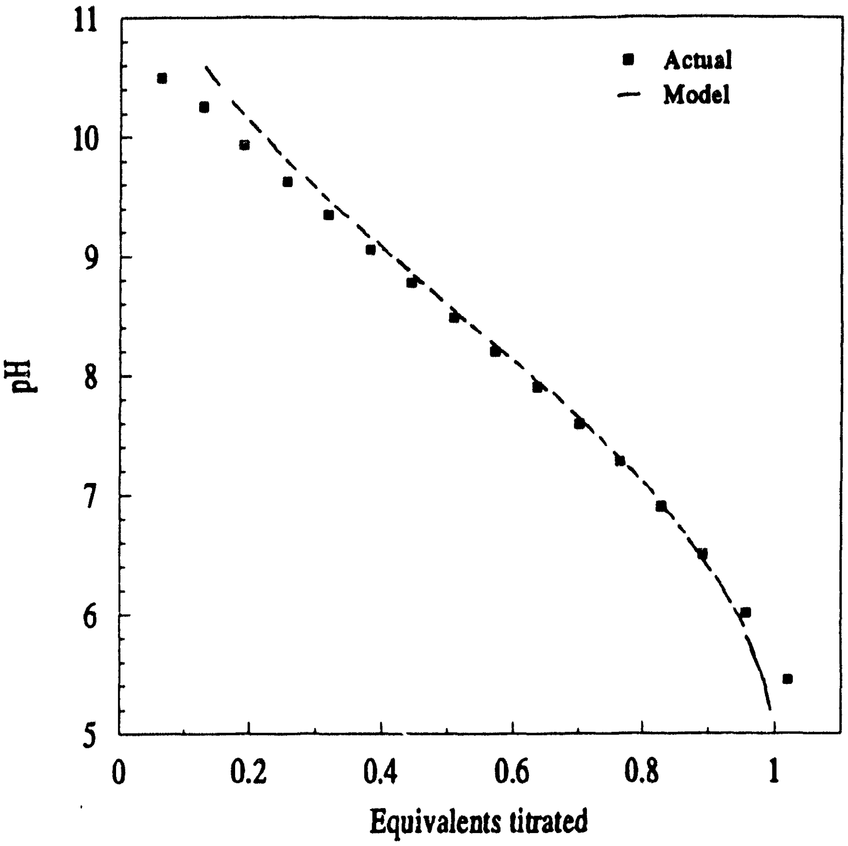


Figure 3.2.1 Titration of 0.0095 M PAA with 0.04838 M HCl in a 20.00 mL initial volume with 0.04745 M NaCl.

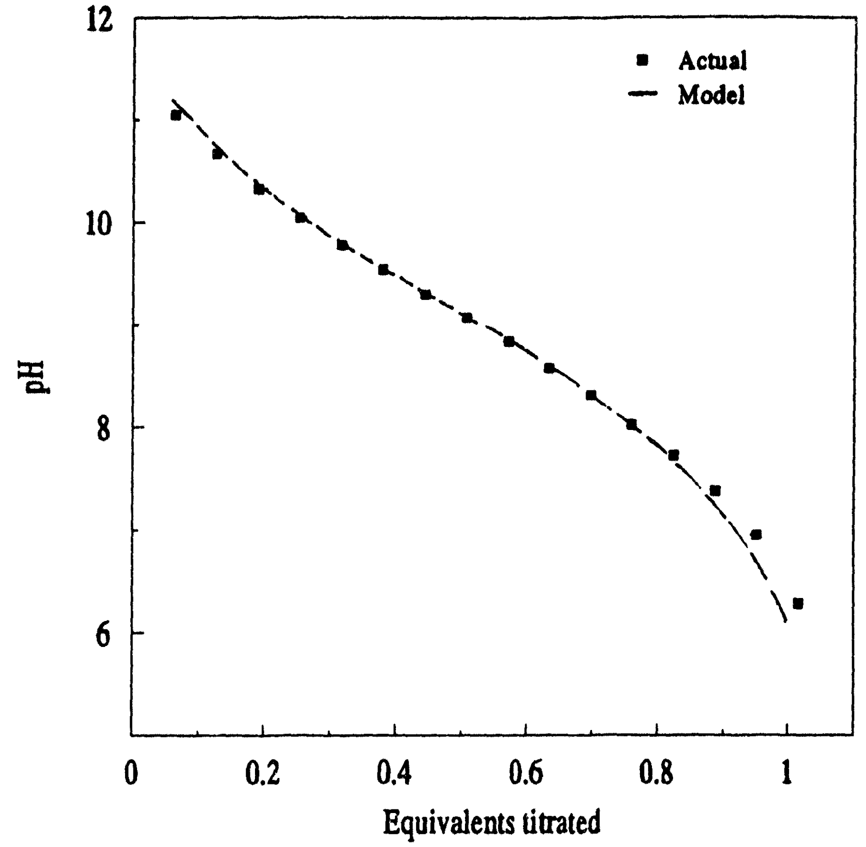


Figure 3.2.2 Titration of 0.04745 M PAA with 0.2409 M HCl in a 20.00 mL initial volume with 0.04745 M NaCl.

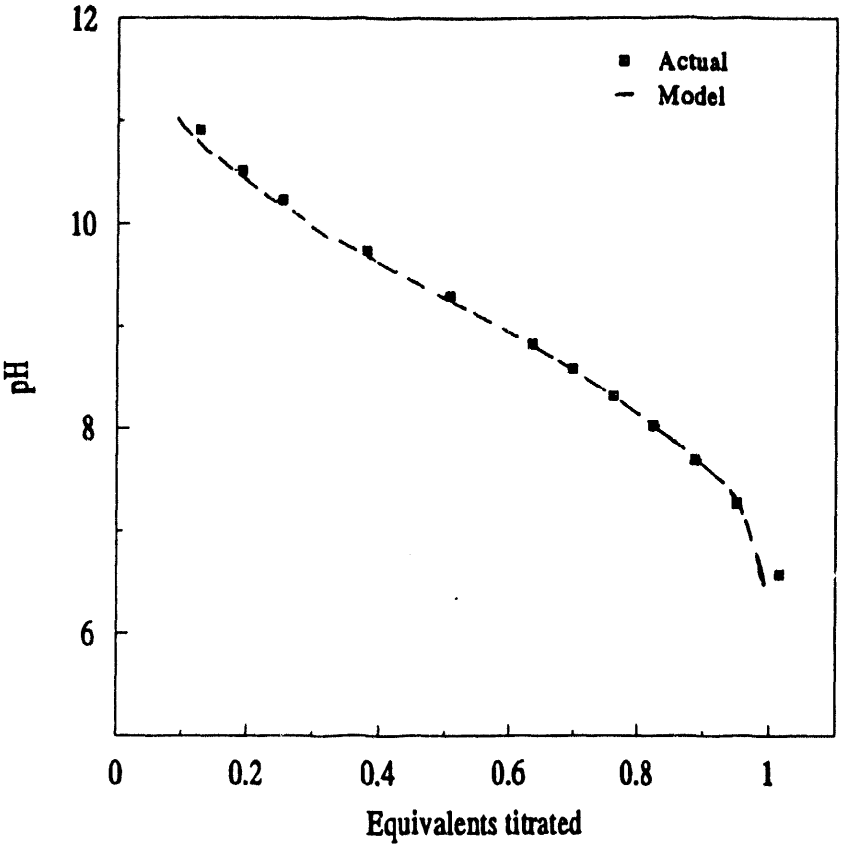


Figure 3.2.3 Titration of 0.095 M PAA with 0.482 M HCl in a 20.00 mL initial volume with 0.095 M NaCl.

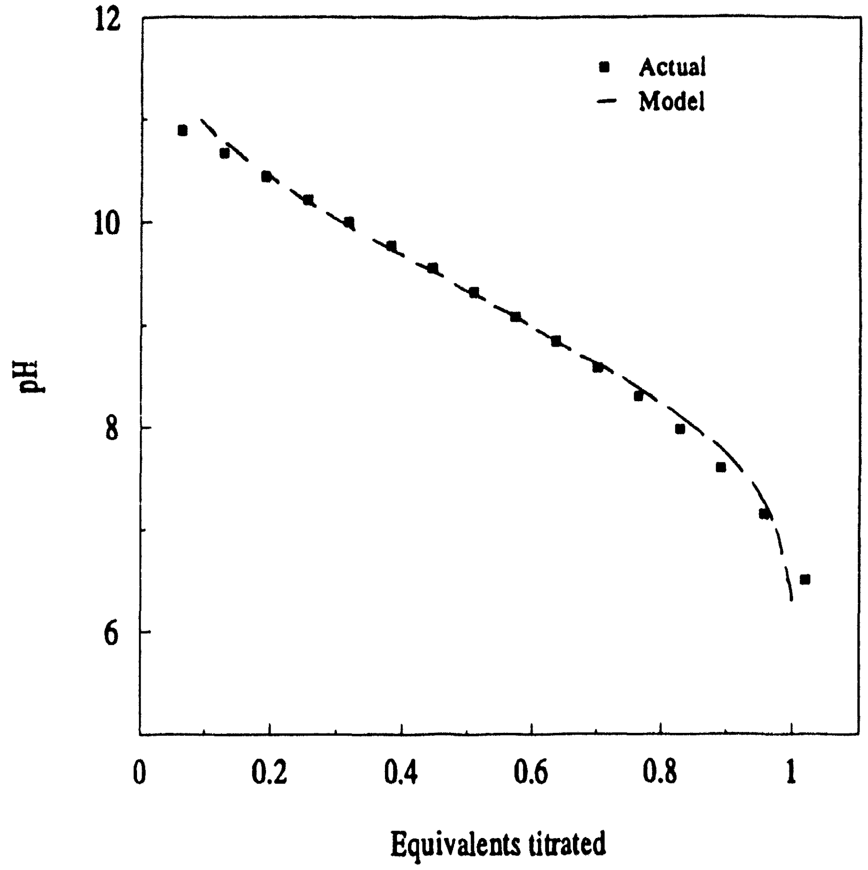


Figure 3.2.4 Titration of 0.0095 M PAA with 0.04838 M HCl in a 20.00 mL initial volume with 0.2095 M NaCl.

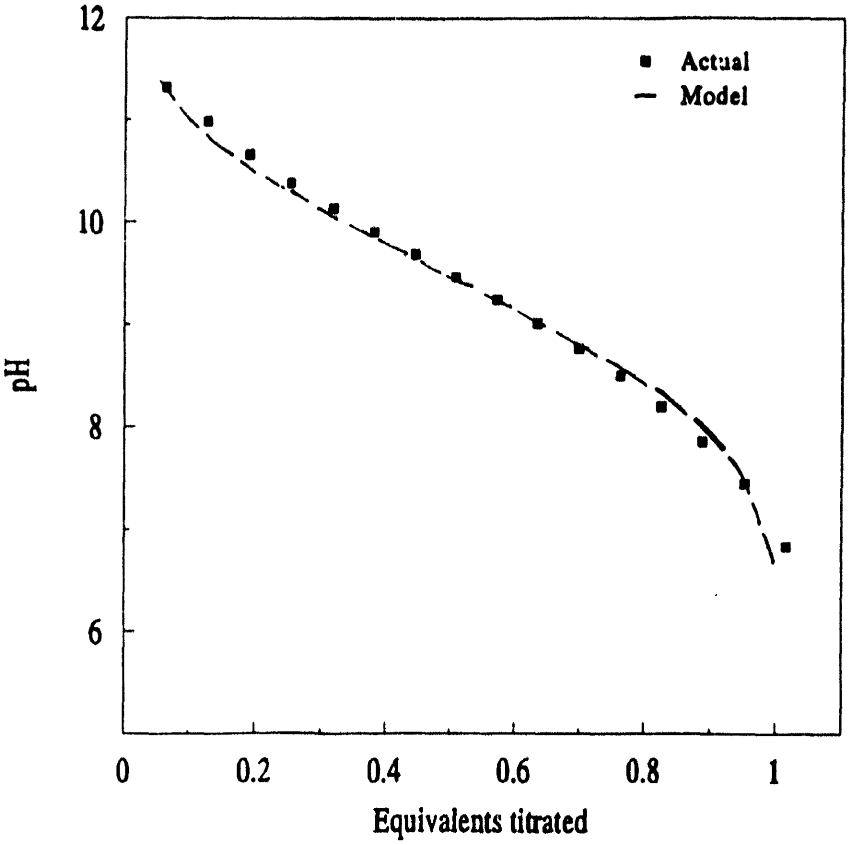


Figure 3.2.5 Titration of 0.04745 M PAA with 0.2409 M HCl in 20.00 mL initial volume with 0.2475 M NaCl.

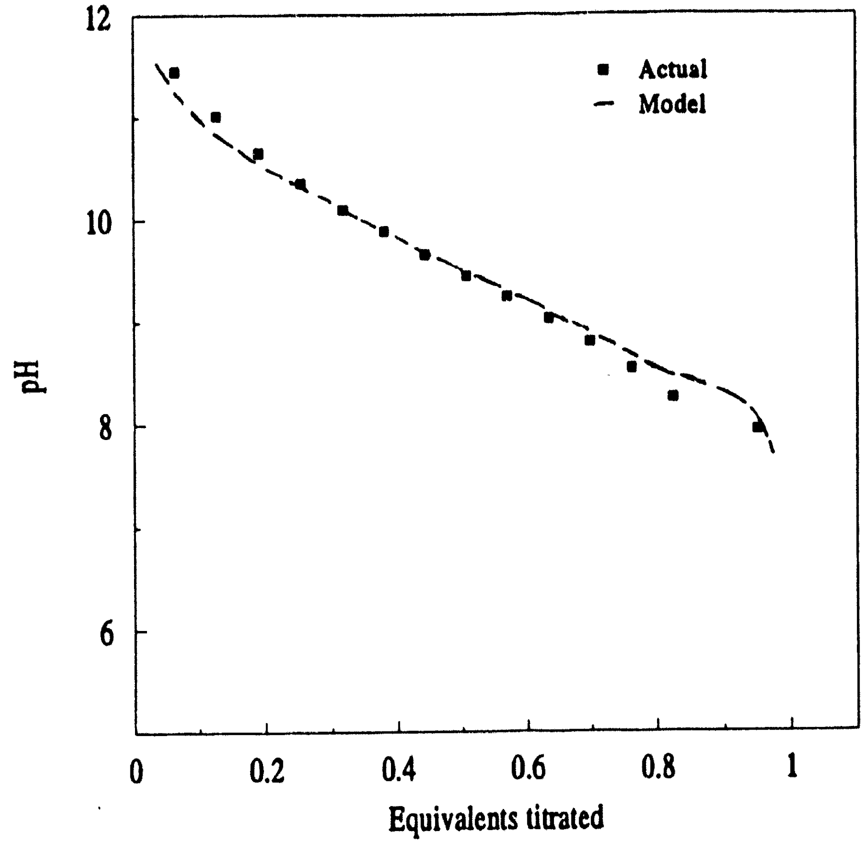


Figure 3.2.6 Titration of 0.095 M PAA with 0.4820 M HCl in 20.00 mL initial volume with 0.2950 M NaCl.

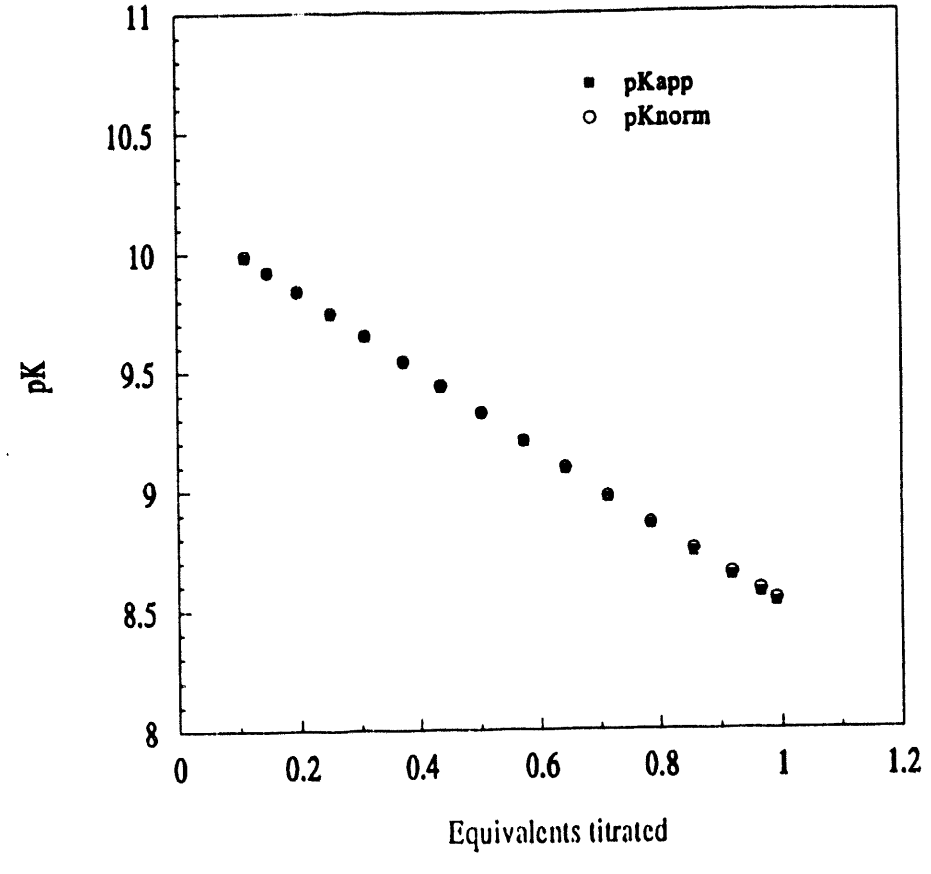


Figure 3.2.7 Variation of pKapp and pKnorm with fraction of titration

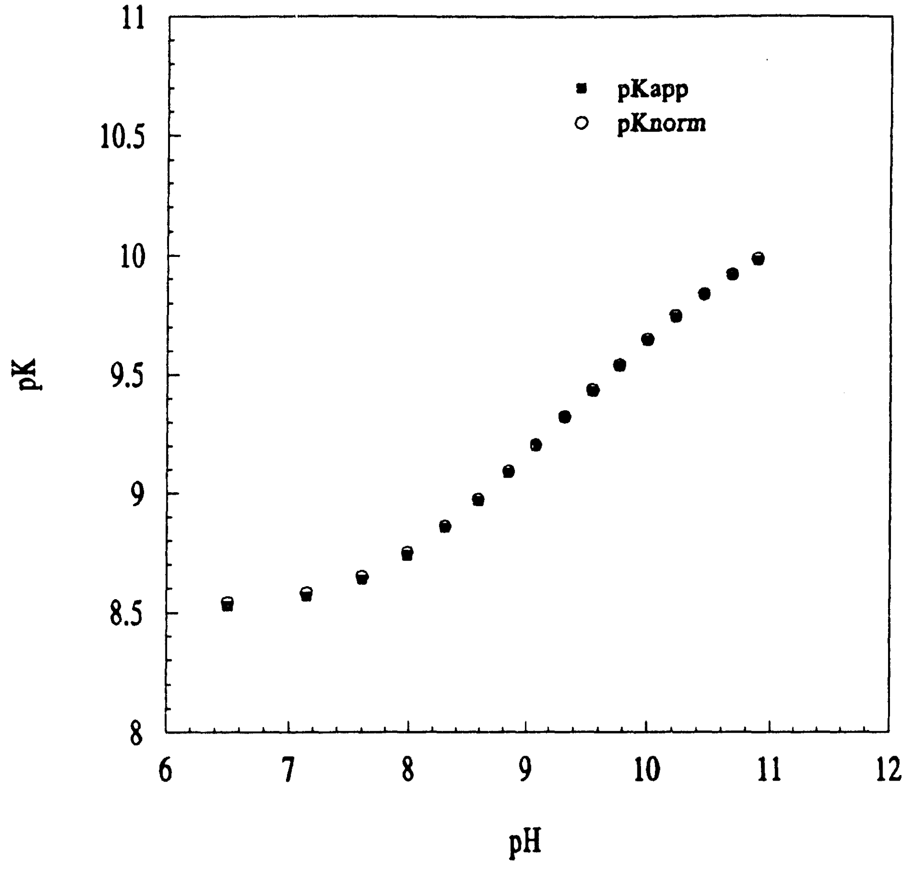


Figure 3.2.8 Variation of pKapp and pKnorm with pH

3.3 CONCLUSION

The titration behavior of polyamines is adequately explained by the present model. Applications of the model show the importance of equilibria involving the different ionic species and the distribution of species between the two potential regions. However, there may exist some ambiguity in selecting the actual phase boundary for the two phases at which the model is valid. However, from analyses done from the present work it is clear that the model equations are valid only if it is assumed that the inner phase has a small thickness, comparable with the Stern layer. This assumption is supported by a previous review by Stigter(89), where it is specifically stated that the Boltzmann distribution is applicable to distribution of counterions in the Stern layer. No comment about the applicability of the same law to counterions in the Gouy-Chapman layer has been made.

These findings can be clarified only by doing more titration experiments using different polymers, which have unbranched backbones as the PAAH used in this work, and testing the present model. An activity coefficient correction to concentration terms may be necessary to improve this model. An improved model for titration behavior of polymers will be very useful in characterizing polymers.

Figure 3.2.9 A sample output of the SEQS program using model equations for titration (1).

```
TITRATION 1 PH 10.00
Scaled Sum (Residuals)^2= 1.23628e-24
------EQUATIONS------
 1) ln((1-be)/be)=ln(phi/(1-phi))+b*Q*ln(1/phi)
 2) Q=X*Q0
 3) cib=1-be
 4)
[Hplus]+[polyamine]*X*V0/(V+V0)+(1-X)*[Clsurf]+[Hplussurf]=[acid]* (1-(V0/(V+V0)
))
 5) K=X/[Hplussurf]/(1-X)*phi
 6) [Clsurf]/[Cl]=cib/(1-cib)
 7) [Clsurf]+[Cl]=[acid]*V/(V+V0)+[NaCl]*V0/(V+V0)
 8) [Hplussurf]/phi/[Hplus]*(1-phi)=[Cl]/([Clsurf]/phi)/(1-phi)
 9) pH=-log([Hplus]/(1-phi))
10) Kapp=X/(1-X)/[Hplus]*(1-phi)
11) pKapp=log(Kapp)
12) x1=[acid]*V/[polyamine]/V0
13) phi=pi*[polyamine]
14) XX =( X*[polyamine] +( (1-X)*[Clsurf]) ) /[polyamine]
15) Knorm = XX/(1-XX)/[Hplus]/(1-phi)
16) b=1-([Clsurf]/[polyamine])
------VARIABLES------
 1)                          be  9.99872846408e-001*B Lower= 1.000e-05 Upper= 1.000e+00
 2)                         phi  3.80000000000e-005*P
 3)                           b  9.97319196291e-001*P
 4)                           Q  1.18997305919e-001*P
 5)                           X  3.06773152665e-001*P
 6)                          Q0  3.87900000000e-001*H
 7)                         cib  1.27153591602e-004*P
 8)                     [Hplus]  9.99962000000e-011*P
 9)                 [polyamine]  9.50000000000e-003*H
10)                          V0  2.00000000000e-002*H
11)                           V  1.21251353535e-003*P
12)                    [Clsurf]  2.54676352345e-005*P
13)                 [Hplussurf]  1.13553320762e-015*P
14)                      [acid]  4.83800000000e-002*H
15)                           K  1.48090000000e+010*H
16)                        [Cl]  2.00264865604e-001*P
17)                      [NaCl]  2.09500000000e-001*H
18)                          pH  1.00000000000e+001*H*R
19)                        Kapp  4.42529243991e+009*P
20)                       pKapp  9.64594197579e+000*P
21)                          x1  3.08744236000e-001*P
22)                          pi  4.00000000000e-003*H
23)                          XX  3.08631557769e-001*P
24)                       Knorm  4.46440705491e+009*P
------SCALED------RESIDUALS------
 1) -4.95159e-14
 2) -1.11022e-16
 3) -1.11078e-12
 4)  4.44089e-16
 5)  2.22045e-16
 6) -2.22045e-16
 7) -1.11022e-16
 8)  2.22045e-16
 9)  6.66134e-16
10) -2.22045e-16
11) -2.22045e-16
12)  2.22045e-16
13) -2.22045e-16
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