The present work embraces the colloid chemical studies of a highly active synthetic aluminosilicate hydrosol. Though the solid product of this system is well known since long time literature regarding the characteristics of the liquid hydrosol is extremely meagre. The synthetic colloid is a silicate based system and some of the properties are similar in nature to that of silicic acid hydrosol. No systematic study has yet been made with this system. Thus the literature as reviewed here belongs to those of the general characteristics of this type of colloid. As the synthetic hydrogel and hydrosol did not differ structurally and some of the important characteristics are similar in nature, important studies relating the solid product have also been incorporated. Literature regarding the general inorganic polymers whose properties have got some similarities with the present system has also been presented.

Liquid ion exchangers are not a recent invention. About half a century ago, Beutner\textsuperscript{3} studied 'oil membranes', which were, in principle, liquid ion exchangers. Experimental evidence on equilibria and ion exchange rates is still insufficient for serving as a basis for quantitative theories.
Conventional ion-exchangers are insoluble solids. However, ion exchange can also occur between two immiscible liquid phases. In recent years, liquids with ion-exchange properties have attracted considerable attention. These liquid ion-exchangers are prepared by dissolving compounds with ionogenic groups in organic solvents such as kerosene, trichloroethylene, chloroform and xylene which are immiscible with water. The ionogenic compounds must have hydrophobic groups in order to remain in the organic phase when the latter is contracted with aqueous solutions. Long chain aliphatic amines have been used for making liquid anion exchangers and fatty acids and dialkyl phosphates for cation exchangers. Liquid ion exchangers are used for ion exchange with aqueous electrolytes and for liquid-liquid extraction for electrolytes from aqueous solutions.

Liquid ion exchangers have several advantages. They are easily prepared, the concentration of the functional groups in the ion exchanger phase is readily adjusted, high ion-exchange rates can be attained by efficient dispersion of the organic phase in the aqueous phase, and continuous counter-current operation is much simpler with liquid than with solid ion exchangers. Disadvantages are that phase separation is somewhat more difficult and that losses of ion-exchange material can hardly be avoided, especially if the components of the organic phase are not completely insoluble in water.

Liquid ion exchangers differ from their solid counterparts in several respects. They absorb very little water from aqueous...
solutions, their dielectric constants are rather low, and the functional groups are not attached to a solid framework. Because of the low dielectric constant one must expect considerable association between the functional groups and the counterions. The molecules carrying the functional groups are free to diffuse within the ion exchanger phase, and when ionized, are subject to electric forces which may arise in the course of ion exchange.

The pioneer in the synthesis of inorganic exchanger was Gans\(^1\), a German Chemist, who actually synthesized alumino silicates of zeolitic type possessing cation exchange capacity greater than that of the natural one. Gans\(^1\) showed that ion active material would result from the action of an alkali aluminate on silicic acid but the action of alkali silicate on aluminium hydroxide gave an inert substance. Again the fact that molecular ratio of Al : alkali metal is always unity whatever be the composition of sodium alumino silicate lends further support to the belief that the alkali metal ion (the exchanging ion) is united through an oxygen atom to aluminium and not to silicon atom. Accordingly he gave the structural formula of the synthetic zeolite as shown below\(^{14}\).
Unlike the natural zeolites, these types of synthetic products are all amorphous and translucent. But afterwards siliceous zeolites with regular crystals have been synthesized by hydrothermal process from solution containing silica, alumina and alkali.

Aluminosilicate hydrogel or synthetic zeolites are characterised by relatively 'open' aluminosilicate framework in which each aluminium ion is bonded to four oxygen anions in tetrahedral coordination, and these tetrahedra are interlinked through the bridging oxygens to form tectosilicates.

Structural cavities are formed by such arrangement, which are occupied by non-framework cations and water molecules. The oxygen ions common to an aluminium and silicon tetrahedra are then reached by bonds of total strength $7/4$, and require a bond of strength $1/4$ for saturation. Such a bond is not provided by cations with large charge and small radius. It is therefore necessary that large univalent and bivalent cations, viz, alkali or alkaline earth ions, be present to the extent of an alkali ion or $1/2$ alkaline earth ion for every quadricovalent aluminium ion.

The structural chemistry of zeolites has enormously advanced in the past twenty years by the close collaboration of W.L. Bragg's School of crystallographers with mineralogists of the British Museum. Meier and Olson gave stereopairs of 27 well established structures.
Baur's work\textsuperscript{22}, in 1964, on location of a part of the non-framework cations and some water molecules in single crystals of natural faujasite has paved the way in this new direction. Consequently upon synthesis of NaX single crystals, around 1969, some very precise work has been done on the location of some of the non-framework cations and water molecules in it and its exchanged and dehydrated forms. Even then it has not been possible to obtain unequivocal data regarding crystallographic sitting of some of the non-framework cations and most of the water molecules. Apart from the limitations of X-ray methods in this regard, which have been very aptly pointed out by Smith\textsuperscript{23} in his review, this uncertainty in locating majority of the water molecules and some of the non-framework cations may be an inherent characteristic of zeolitic materials. In zeolites, the water molecules in the supercages and some non-framework exchangeable cations in hydration complexes with them form continuous filaments of zeolitic fluid\textsuperscript{24}, and behave like an electrolyte solution, and are highly mobile\textsuperscript{22}. It would therefore be difficult to pinpoint all the water molecules at definite crystallographic sites\textsuperscript{25}, at least for monovalent non-framework exchangeable cations at locations well within the supercages, since X-ray diffraction theory is applicable to crystalline periodic structures and not to a fluid continuum. Thus, for potassium-exchanged zeolite X, Mortier and Bosmans\textsuperscript{26} could only visualize random distribution of the water molecules in spherical volumes inside the sodalite cages. Moreover, the potassium ions in the supercages could not be located, and they were supposed to be distributed uniformly on the surface of
a sphere concentric with the supercage water sphere.

According to Costenoble and Mortier exchangeable cations can be located on various sites in zeolitic lattice. Some of these sites, in the large cages (α-cage), are easily accessible, while others are located in the dense (β) cages. The limited dimensions of the apertures which control access to these small cavities are frequently given as a factor limiting the ion exchange. Starting from Na\(^+\) loaded Y-zeolites it is not always possible to obtain a complete exchange with other cations at room temperature, higher exchange levels are obtained by increasing the exchange temperature. However, the diameter of some of these incompletely exchanged cations (e.g., Ca\(^{+2}\)) is smaller than the free aperture of the sodalite six rings. Ca\(^{+2}\) ions have a tightly bonded water sphere.

Maes and Cremers discussed the exchange of transition metal ions in NaX and NaY zeolites. They suggested that Ni and alkaline earth metal ions behaved similarly but other transition metal ions behaved differently. This was thought to be due exclusively to steric effect but Costenoble, Mortier and Uytterhoeven proposed the existence of a stable structure which was formed with Na\(^+\) ions and water molecules inside the sodalite cages as the reason for the incomplete exchange of Na-Y. This effect is kinetic rather than thermodynamic.

Because of the relatively large size and polarizability of the Ag\(^+\) ion a considerable amount of covalent interaction with the...
anionic framework and a consequently lowering of the interaction with water would be expected. Considering the monovalent exchanged samples the heats are seen to decrease in the order:

Li > Na > K > Rb > Cs

which is also the order of decreasing water content of the samples and the opposite order to the cationic radii. The available free space in the zeolite channels will increase when K⁺ is replaced by smaller Li⁺ and Na⁺ ions and this must account in part for the increase in water content and also for greater heats.

Studies of the thermodynamics of ion exchange of transition metals in zeolites have been few. This is in part because transition metal ions are prone to precipitate from solution under alkaline or even weakly acid conditions, and because many transition metal salt solutions are sufficiently acidic to dealuminate or decompose a zeolite. Both bivalent and tervalent chromium have been placed into zeolites by aqueous ion exchange, the former under the oxygen free conditions needed to prevent oxidation of Cr⁴⁺ to Cr⁶⁺. Fully hydrated bivalent chromium ion exchanged zeolite has an electronic spectrum which is similar to the electronic spectrum of hexaaquo \([\text{Cr}^{4+}(\text{H}_2\text{O})_6]\) ion. The chromium (III) ion-exchanged zeolites have electronic spectra characteristic of the \([\text{Cr}^{3+}(\text{H}_2\text{O})_6]\) ion when fully hydrated. The location and environment of Mn⁺² in hydrated and anhydrous zeolite have been investigated by X-ray crystallography. In the hydrated material the Mn⁺² ions have
trigonal-bipyramidal coordination provided by three equatorial oxygen atoms derived from six ring and two axial water molecules. It is interesting that the Mn$^{+2}$ ion becomes coordinated to the zeolite framework and assumes a trigonal bipyramidal coordination sphere, whereas Cu$^{+2}$, Ni$^{+2}$ and Co$^{+2}$ have an octahedral coordination sphere in fully hydrated zeolite A. There is no obvious reason for the preference shown by Mn$^{+2}$ for five coordination, particularly since non-intrazeolitic five coordinate complexes of Cu$^{+2}$, Ni$^{+2}$ and Co$^{+2}$ are well known. It may be assumed that a part of the zeolitic water remains coordinated to, and under direct influence of, the exchange cations, whereas the remaining part is held rather loosely in the structural channels and cavities by secondary forces. Zeolitic water is known to have anomalous properties with respect to normal water and to be more structured. Rabo et al have proposed that the strong electrostatic field associated with the cation polarizes the adsorbed hydrocarbon molecules to cause catalytic activity through the carbonium ion intermediates. Dempsey has evaluated the strength of this electrostatic field by assuming a full ionic model of zeolites. On the other hand, Hilschler has suggested that the polarizing action of the field due to the cation makes the proton of an adsorbed water molecule on the cation, acidic. It has been proposed for a rare earth zeolite by Venuto et al and for a magnesium zeolite by Hall that the proton released from an adsorbed water is transferred to the zeolite lattice so as to form an acidic hydroxyl group. Ward has performed IR studies on the basis of this thought and clarified
the acidic properties of zeolites. He concluded that the electrostatic potential or field due to the divalent cation dissociates an adsorbed water to produce an ion of the MOH$^+$ type.

The theoretical background for the light scattering method applied to silicate solutions or in colloidal silicate suspensions is given by the fundamental investigations of P. Debye, first with R.V. Nauman\textsuperscript{57} and then with E.W. Anacker\textsuperscript{58}. In the first series of experiments, carefully purified (filtered through sintered stainless steel and/or platinum filters) sodium silicate solutions (with the ratio SiO$_2$/Na$_2$O ranging from 0.5 to 3.75) were measured for their light diffusivity by determining the turbidity at an angle of 90° to the incident beam, then the angular scattering pattern, and the viscosity, as functions of the concentration. The turbidity is expressed here by

\[ \tau = \frac{32 \pi^3}{\lambda^4} \left( \frac{n_o}{n} \right)^2 \left( \frac{\mu - \mu_o}{\mu} \right)^2 \]

in which \( n (= N \cdot V) \) is the number of particles per cm$^3$, \( \mu_o \) is the refractive index of the solvent (H$_2$O), and \( \mu \) is that of the solution. It is most important to know that up to SiO$_2$/Na$_2$O = 2.0 the solutions of sodium silicates do not give any indication of an aggregation into colloidal particles, the solutions being similar to those of sugar. Above 2.0 the turbidities are higher than in sugar solutions, with perhaps some aggregation, but in every case very large particles are entirely absent. For SiO$_2$/Na$_2$O = 3.75, the
solutions show increasing molecular weights up to 5,000 or 10,000. The viscosity curves show a similar relation, and at high concentrations the viscosity rapidly increases because the molecules are very near to each other, although even then no flocculation of large colloidal particles occurs.

S.A. Greenberg and D. Sinclair applied Debye's theories of light scattering to the polymerization process of silicic acid suspensions using a photometer constructed by B.A. Brice, M. Halwer, and R.J. Speiser for the determination of molecular weights of polymers. The suspensions were prepared by mixing highly purified sodium metasilicate and ammonium acetate solutions. The measurement of the polymerization by the determination of turbidity and dissymmetry was also combined with measurement of the degree of depolarization, using horizontally (h), vertically (v), or unpolarized (u) incident light with the depolarization parameters.

\[
Q_v = \frac{H_v}{V_v} \quad Q_h = \frac{V_h}{H_h} \quad Q_u = \frac{(H_v + H_h)}{(V_v + V_h)} = \frac{H_u}{V_u}
\]

H and V referring to the intensities of the horizontal and vertical components.

The hydration theory of stability has been popular in colloid chemistry for a long time. In this theory, the repulsion between particles is attributed to the orientation of water dipoles in the electric field around the charged particle. In such a "solvation shell", the degree of orientation of the dipoles would
gradually decrease with increasing distance from the charged surface. When these diffuse hydration shells begin to interfere when the particles approach each other, the mutual repulsion of the oppositely oriented water dipoles around the colliding particles would account for particle repulsion.

The electric double layer of colloidal sol is consisting of a surface charge and a compensating counter ion charge, which is accumulated in the liquid in the neighbourhood of the surface of the particles. The counter ions are electrostatically attracted by the oppositely charged surface. At the same time, however, these ions have a tendency to diffuse away from the surface towards the bulk of the solution, where their concentration is lower. This situation is analogous to that in the earth's atmosphere, in which the gas molecules are subject to the competition between gravitation and diffusion. The action of the two competitive tendencies results in an equilibrium distribution of gas molecules in which their concentration gradually decreases with increasing distance from the earth's surface. Such a distribution is described as an "atmospheric" distribution. The same type of distribution is obtained in the double layer. The contribution of the counter ions near the particle surface is high, and it decreases with increasing distance from the surface. This diffuse character of the counterion "atmosphere" was recognised by Gouy\textsuperscript{62,63} in 1910 and by Chapman\textsuperscript{64} in 1913, who were the first to present a theoretical treatment of the counter ion distribution. The counterion atmosphere is often referred to as the diffuse or Gouy layer.
Clear, highly dispersed sols of silicic acid may be prepared by mixing sodium silicate solution with dilute acids or solutions of ammonium salts. According to Brintzing and Brintzinger, micromolecular solutions of silicic acid are first formed. In time, however, the small molecules combine to larger aggregates which are retained by semipermeable membranes. If the concentration of the components is high, silicic acid gels are formed.

Investigation of the highly purified and concentrated sols by electrochemical methods revealed that the colloidal particles had a very low charge density. For example, the purified sols of silicic acid contained particles with only one electron per 700 or even per 5000 SiO$_2$ molecules.

According to Kruyt, the flocculation value is the minimum salt concentration which is able to cause visible aggregation 18 hours after addition of the electrolyte. This time may be too long for unstable, rapidly ageing sols. Instead of stating just detectable aggregation, some authors have defined the flocculation value as the minimum concentration which is able to cause complete flocculation. These values, of course, are larger than those determined by turbidity measurements. The complete sedimentation, moreover, is the least characteristic final phase of the flocculation. In originally clear sols the appearance of turbidity is the sign that flocculation has occurred. The most reasonable definition of the flocculation value seems to be the following. The flocculation value is the minimum concentration of an electrolyte which is
able to decrease in the degree of dispersion, if the sol is observed two hours after addition of the electrolyte.

Flocculation and charge reversal of inorganic colloidal particles by organic polymers has been studied by numerous investigators, the literature has been reviewed and theories formulated by La Mer and Healy. Steric stabilization of colloidal solutions by adsorption of polymers has also been described by Heller. However, little experimental work has been done with well characterized colloidal particles so that the amount of flocculating polymer could be quantitatively related to the particle size and surface area of the particles being flocculated. In the case of polyelectrolytic flocculants, it has been pointed out by Heller that the charge on the colloidal particles need not be fully neutralized by the opposite ionic charges of the polyelectrolyte to cause flocculation if the polymer forms bridges between particles. Gregory concluded that in the flocculation process the lower molecular weight polymer was effective mainly by charge neutralization, whereas the high molecular weight polymer flocculated by bridging mechanism.

Zsigmondy, Kruyt, Tuorila and others have investigated the course of coagulation by means of ultramicroscope. The electron microscope and X-ray instruments can be used for the same purpose. Coagulation can also be investigated by the ultracentrifuge and by light scattering. Paine (1912) proposed to separate the coarse components by filtration or centrifugation, and to determine the amount of the separated substance by chemical methods. The course
of coagulation has also often been followed by simple turbidity measurement. Wannow and Hoffmann determined the flocculation point by measurement of the intensity of transmitted light.

Allen and Matijevic found that for a given particle size of silica and pH, aggregation occurred at a critical coagulation concentration (c.c.c.) of calcium ion when a certain number of calcium ions were exchanged for hydrogen on the surface of the particles. In this paper, it is shown for the first time that the true c.c.c., defined as the concentration of coagulating ions remaining in solution in equilibrium with the coagulate, increases with decreasing particle size. Thus, in a mixture of different particle sizes, larger particles can be preferentially coagulated and separated from smaller ones.

Previous investigators have reported particle size effects due to adsorption of coagulating ions on the coagulate. Thus O'Melia and Stumm reported that with a given concentration of silica, smaller particles require more iron (III) for coagulation, i.e., a higher apparent c.c.c., but this was only because more silica surface was present and more iron was adsorbed on the coagulate. The same effect was observed merely by increasing the concentration of silica of a given particle size. For the positive ferric hydroxide and aluminium hydroxide sols the polyvalent anions are much more effective than the univalent anions. Coagulation of sols is caused by the ions with charges opposite in sign to the charges on the sol particles, the flocculating power of bivalent ions is about 20 to 80
times greater than that of univalent ions, and the flocculating power of trivalent ions is many times greater than that of bivalent ions. This statement is known as Schultze Hardy rule.

Mukherjee (1919), Kruyt (1919), Burton and Bishop (1920) and many other colloid chemists found that the flocculation values depend on the degree of dilution of sols. If the hydrophobic sols are flocculated with univalent ions (e.g., NaCl) the flocculation value increases with increasing dilution of the sol; if, however, the coagulation is carried out with polyvalent ions the flocculation values decrease with increasing dilution. This is Burton's rule. The rule can also be formulated as follows. The more concentrated a sol the closer are the flocculation values of ions with different valencies. Exceptions to the rule are known, for example, the sols of Prussian Blue, if very dilute, become less stable towards all kinds of electrolytes. Concentrated emulsions of aniline in water on the contrary, are less stable towards all kinds of electrolytes than are dilute emulsions.

A clear understanding of the mechanism of coagulation were made by Hamaker, Deryagin, Verwey and Overbeek. These authors tried to calculate the forces and energies of repulsion and attraction between two particles, surrounded by ionic atmospheres, as they approach each other. The attractive forces are the well-known Van der Waals forces acting at surfaces. They originate in the unsaturated valency fields at the surface, for instance, of silver iodide particles, and they are the same forces which cause adsorption.
The first calculations of a general character were made by London; Hamaker extended these calculations to colloidal particles. The Van der Waals-London attraction decreases very strongly as the distance between the approaching particles increases, but it does not depend on the composition of the diluted aqueous medium. This attraction is opposed by the electrostatic forces of repulsion, whose intensity is determined by the structure of the ionic layer surrounding the particles. This is in turn determined by the electrolyte composition of the dispersion medium. Whether the approaching particles agglomerate or not is determined by the balance of the attractive Van der Waals-London and the repulsive coulomb forces. Verwey calculated the stability conditions in the presence of various electrolytes, and it is interesting to note that the theory was successful in partly explaining the Schultze-Hardy rule.

The original theory of Smoluchowski was further developed and extended to cover polydisperse systems by Mueller. The equations of Mueller were experimentally tested on gold sols by Wiegner and Tuorila, who found that the experimental results agreed quite well with calculation. In the simplest case when only two kinds of particles are present, the flocculation rate depends on the ratio $r_1/r_2$ of the particle radii, and also on the ratio of the number $n_1/n_2$ of the units participating in the aggregation. Generally it is found that aggregation is faster in a polydisperse system than in a monodisperse one. The coarse grains act as centres of aggregation, and on their surfaces the smaller units tend to stick.
Stabilisation of unstable lyophobic sols by means of hydrophilic substances is in practice a very important procedure. Stabilisation can be achieved when the hydrophilic substances is added in excess. Meidinger found that the ability of polyvinyl pyrrolidone to protect silver colloid against coagulation is nearly the same as that of gelatin.

Williams and Chang compared different hydrophilic colloids as protective substances for different sols and found that various hydrophilic colloids protect the different sols differently.

According to Carman, the coagulation of silica sols is caused by the building of interparticle chemical bonds; during the encounter between particles, siloxane bonds are formed from surface silanol groups according to the reaction:

\[
\begin{align*}
\text{Si—OH} + \text{OH—Si—} & \rightarrow \text{Si—O—Si—} + \text{H}_2\text{O}
\end{align*}
\]

Iler has shown that such a mechanism can be catalyzed by hydroxyl ions. In his model, the stability is related to lack of catalyst and/or to the presence of electrical charges on the particle.

On the other hand, in view of the compact structure of silica particles, dispersion forces could be operative. It is interesting to check whether the phenomenological behaviour of silica can be fully explained either by the Carman-Iler theory or on the basis of Van der Waals forces. Allen and Matijevic carried out
work on the stability of Ludox silica sols. Although the experimental conditions were different, coagulation and electrophoresis experiments performed by these authors and by Depasse and Watillon presented, except, for one case, the same general trend.

Ghosh and his collaborators\(^92\) studied the polymerisation process of silicic acid with the help of a light scattering apparatus in terms of the change in optical properties i.e., dissymmetry, depolarisation and turbidity. The shape of the particles has been found to be spherical. Freundlich and Gilling\(^93\) observed thixotropy in silica hydrosols at pH 8.5 to 9.5. Trippi and Schaller\(^94\) studied the rheological relations of silica suspensions at various concentrations and also the effect of temperature.

Although the gelation from a low molecular weight silicic acid has been studied in considerable details under various conditions of concentrations, temperature, pH of the system, often gelation rates, changes in molecular weights and particle size\(^95-97\) but the literature regarding the quantitative aspect of thixotropy is scarce.

Mitra and Mazumdar\(^98\) produced thixotropy in polysilicic acid suspensoid by controlled addition of electrolytes. The rheological nature of the suspensoid at the point of thixotropy has been characterised by the "breakdown with time curve" and "thixotropic co-efficient". They observed that thixotropic co-efficient was related to the reforming tendency of the suspensoid containing the flocculating
ions and amongst the alkaline earth cations the following relation was observed:

\[ \text{Ba}^{+2} > \text{Sr}^{+2} > \text{Ca}^{+2} > \text{Be}^{+2} \]

A clear understanding of the gelation of silicic acid by coagulation can be made by potential energy curves representing the attraction and repulsion forces and the zeta potential. Colloidal silica particles also form stable sols in aqueous medium because of two properties. Silica surfaces are assumed to be covered by silanol, SiOH groups unless silica has been dehydrated to produce a siloxane surface.

Mitra and Mazumdar studied the polymerisation characteristics of silicic acid sol under various experimental conditions. They observed that during the course of polymerisation there was always an "incubation period" which was assumed to be the induction period where a temporary equilibrium was established for proper orientation of the kinetic units of the silicic acid sol particles after which the entrapment of the dispersion medium in the formed network occurs. This induction period was again found to be dependent on the concentration, pH and nature of the electrolyte.

Nearly 55 years ago Freundlich reported that silica hydrosols were stable in spite of minimal surface charge (i.e., at pH values between 2 and 3) and that they coagulated in the presence of certain specific salts at high pH values (i.e., at high surface charge). This behaviour is not in agreement with the principle of
charge stabilization. According to this principle the stability modifications through electrolyte addition should correlate with electrokinetic zeta potential of the particles and should obey in ideal cases the Schultze-Hardy rule. The stability behaviour of hydrophilic sols on the other hand shows a very notable dependence upon the type of counterions. A connection between the lyotropic series (Hofmeister series) and the hydration characteristics is generally accepted nowadays. The occurrence of similar lyotropic series for hydrophobic colloids indicates that hydration is also an important feature governing the stability of many so-called hydrophobic colloid systems. Freundlich was the first to recognize this problem and he concluded that silica hydrosols were to be looked upon as hydrophilic rather than hydrophobic. Indeed, investigations of surface chemistry of the common types of silica show that their surface bears, depending on pretreatment, mainly isolated, geminal, and vicinal silanol groups (hydrophilic regions) and relatively inert siloxane groups (hydrophobic regions).

Among the confusing variety of different explanations for the extraordinary high stability of these sols, the following phenomena are considered nowadays:

1. The negative charge of silica particles, due to the dissociation of the silanol groups or the adsorption of hydroxyl and hydronium ions, and the resulting electrical double layer.

2. The hydration of the particle surface, leading to a protective layer of structural water molecules which are bound to the.
silanol groups via hydrogen bridges\textsuperscript{115}.

(3) A protective layer of polysilicic acid, which is of particular significance in aged systems.

Different models are suggested\textsuperscript{116} for the basic mechanism of destabilisation, depending on the type of silica, on the type of electrolyte system, and on the pH value. For flame hydrolised silica (cabosil) Harding\textsuperscript{112} reports departures from the classical principle of charge stabilization only for very small primary particles. Aggregates having primary particles of a diameter larger than 50 nm, however, show the classical behaviour for hydrophobic colloids.

Beside the investigations of coagulation, the silica/electrolyte interface itself has in recent years been a matter of intensive research, more so, in fact, than any other oxide/electrolyte interface. This research together with investigations of the surface chemistry of silica shows that this interface holds a very extraordinary position.\textsuperscript{117}

Although the dependence of the electrokinetic zeta potential on the pH value, with an isoelectric point at pH values between 2 and 3, is similar to other oxides, the surface charge and total capacity of double layer show a very different dependence on the pH value\textsuperscript{118}.

Generally, colloidal dispersions in the presence of polymers exhibit three basic phenomena; charge stabilisation, steric stabilisation or flocculation. Flocculation may occur even when polymar...
is added to an intrinsically stable (charged stabilized) dispersion (bridging flocculation).

Of all the water-soluble cellulose ethers, the sodium salt of carboxy methyl cellulose has come to occupy a unique position in industry as a challenging substitute for natural gums. The diverse uses to which this single substance can be put have been summarised by Caldwell and Watters\textsuperscript{119}, these cover almost the whole field from detergents to medicine via the paper, ceramic and textile industries. As with all other commercially important high molecular weight substances, practice has far surpassed theory in this case. The only recorded data on the physico-chemical properties of sodium carboxy methyl cellulose solution are those of Brown and Haughton. These data are very meagre and the explanation advanced to account certain characteristic features of the solution requires reconsideration in view of the recent theoretical development of the physical chemistry of polyelectrolytes\textsuperscript{121,122,123}.

The reduced viscosity of polyelectrolytes in solutions containing no added salts has been found in a number of cases to increase markedly with increasing dilution, but it appears that no confirmative information has yet been obtained as to whether such an increase of reduced viscosity persists up to the limit of infinite dilution, or whether, even if this is the case, the curve can be extrapolated to give a finite intrinsic viscosity. If we consider the fact that most of the reported data on the reduced viscosity of polyelectrolyte solutions in the absence of added salts can be
satisfactorily filled, at least to the lowest concentrations used in the particular experiments, by the so-called Fuoss viscosity equation\textsuperscript{122}, it appears reasonable to expect that the rising trend of the curve may actually be maintained to zero concentration in accordance with the Fuoss equation.

Suspensions of silica have been reported to exhibit Newtonian, thixotropic, and dilatant properties\textsuperscript{125,126}. In spite of various meanings attached to the words thixotropic\textsuperscript{127} and dilatant\textsuperscript{128} it has been amply demonstrated that silica suspensions may exhibit various Newtonian and non-Newtonian flow behaviours.

The viscosities of dilute solutions of spherical particles have been shown by Einstein\textsuperscript{129} to obey the equation

\[ \eta = \eta_0 (1 + 2.5\phi) \] ... (1)

where \(\eta\) is the viscosity of the suspension, \(\eta_0\) is the viscosity of the solvent, and \(\phi\) is the volume fraction of solute particles.

In the investigations of colloidal silica sols\textsuperscript{130} it was shown that the system was Newtonian but deviated from Einsteinian behaviour because of the electroviscous effects. Electroviscous effects can be determined by increasing ionic strength of the aqueous phase. Even when the electroviscous effects were destroyed, the silica sols did not appear to obey equation (1) due to the adsorption of a multilayer of water.
Although a great deal has been written about thixotropic systems\textsuperscript{32,131,132} and much is understood about the fundamental nature of the problem, very few systems have been examined in detail\textsuperscript{133,134}. The flow properties of colloidal silicas were studied with coaxial cylinder and capillary viscometer as a function of pH, electrolyte additions and the nature of the solvent\textsuperscript{135}. Pyrogenic or flame hydrolised silica is produced by hydrolysis of silicon halides in a hydrogen/oxygen flame. Despite proliferating industrial usage and frequent occurrence in natural systems, the importance of the stability of silica hydrosols was not sufficiently appreciated until recently\textsuperscript{136}.

Optical (light-scattering) methods for the study of the polymerisation in mixtures of sodium metasilicate and ammonium acetate solutions were applied by S.A. Greenberg and D. Sinclair\textsuperscript{137}, chiefly by turbidimetry, dissymmetry and depolarisation measurements, with the remarkable result that the silica particles behaved like isotropic spheres.

Great progress has been made in modern instrumentation in the field of light-scattering in the low angle range (down to 0.05°) and up to 140°, as seen in the high resolution scattering and recording photometer developed by W.H. Aughey and F.J. Baum\textsuperscript{138} for particles in the size of large molecules, up to colloid particles near 1\(\mu\), and even larger heterogeneities with a radius range up to 100\(\mu\) for the lowest angles and high resolutions. The instrument must therefore also be furnished with the possibility of variations in the...
intensity of the light in wide limits (ranging in the instrument mentioned here by a factor of $10^8$). Especially for solutions of high polymers another instrument of these general characteristics was described by D. McIntyre and G. C. Doderer, with automatic recording and determination of the ratio of the intensities of the scattered and the incident light.

According to R. K. Iler and R. L. Dalton, the viscosity of silica hydrosols is a sensitive indicator of the degree of hydration of its (spherical) particles — of the water bound on their surface. The calculations were based on an equation of M. Mooney.

A most elaborate calculation of the equilibria of silica polycondensation was given by W. Stober, starting from the molybdate reactive silicic acids as the limit condensates which reach a constant concentration of reversible establishment for relatively low amounts dissolved. If there is a true thermodynamic equilibrium possible between the single condensation steps, a formula can be developed, for pH below 12, for the total solubility of silicic acid, which is in reasonable agreement with the experimental data. The rather complicated equation makes evident that the influence of pH is restricted to the low molecular range, with the upper limit of molecular dispersity. In acidic or neutral media the influence of pH is very low for the total solubility. Another equation was derived which was valid for pH below 7. In alkaline media with pH above 9, a strong increase in monosilicic acid is noted which changes the concentrations with increasing pH by more than one order of
magnitude. However, both equations given by Stober are inadequate for calculation of the solubility because the maximum condensation step cannot be experimentally fixed with sufficient accuracy. An estimate and comparison with the data given by H. Baumann show that a satisfactory approximation is possible in the calculation.

The kinetics of exchange of several alkaline earth and transition metal ions in a synthetic sodium aluminosilicate hydrogel were studied by Mitra et al., under different conditions of temperature, exchange ion concentration, nature of co-ions, and the particle size of the hydrogel. The kinetics were controlled by particle diffusion and the law operated up to about 60-70% of exchange. The activation energy for diffusion decreases with an increase in the exchange cation radius in the alkaline earth series, while for the transition metal ions the activation energies showed no appreciable variation. For a fixed entering counterion, the activation energy for a series of co-ions increased with increasing association of the co-ion with counterion. Reduction in particle size of the hydrogel caused an increase in the relative exchange rates, and a decrease in the diffusion coefficients as well as in the activation energies for diffusion.

The course of formation of sodium alumino-silicate hydrogel in aqueous medium has been studied by Mitra and Roy with the help of light scattering apparatus. From their work it was concluded that:

1. A critical instability is necessary but is not a sufficient condition for gel formation. In addition, there must be a sufficient
concentration of the dispersed phase, depending upon the particle size, shape, the aggregation habits of the dispersed materials and the amount of the dispersion medium. During gelation with increasing dilutions, a point is normally reached beyond which the coagulated phase fails to immobilise the entire liquid and a gelatinous precipitate settles out.

(2) The turbidity of this type of gel is due to the appreciable difference in refractive indices of the alumino-silicate and water, and also to an appreciable increase in the particle size due to molecular growth.

(3) The nature of the gelation rate curves revealed that this type of interaction is a consecutive type of reaction. Introduction of alumina tetrahedra into the silicate network causes a reduction of the net charge and this leads to polymerisation into a gel and attachment of the alkali ion through hydration layers for balancing the deficient lattice charge.

(4) The $I_{90}/I_0$ ratio is directly related to the molecular growth of the gel and the effect of experimental variables has been clearly reflected through this study.

(5) Concentration of ingredients has a direct effect on the growth and there was a sudden jump in the growth rate from 25 to 30 dilution indicating the presence of a critical point.

(6) A similar effect was observed with changing concentration of alkali, the growth rate being the maximum at the $\text{Al}_2\text{O}_3:\text{SiO}_2$ ratio of 2.
Ion exchange in the alumino silicate hydrogel structure is a diffusion process involving distribution of the counter ions by diffusion. Whether the extent of exchange is partial or complete depends on the nature and concentration of electrolyte. Under the accelerated condition of exchange, such as boiling, the extent of exchange has been found to be independent of the volume, the electrolyte content remaining fixed. This leads to a diagonal relationship between the volume and concentration. The most economic condition of realising the full exchange capacity of the exchanger with minimum content of electrolyte is the repeated batchwise process which may be compared to an open system for the stepwise removal of exchanged counter ions. Titien in his study of ion exchange between alkali metal cations and Na-alumino-silicate gel at 276°, 298° and 319°K showed that except in the case of Na-Li exchange all other reactions are endothermic. The selectivity coefficient rises with increase in temperature. Variation of composition with optical properties of zeolites is not easily defined because of variation due to other causes. The electrical conductance of zeolite was studied by Schulze and Wiegel who showed that zeolite readily conducted electricity and the specific conductance was dependent on the exchangeable cations in the zeolite. The base exchange capacity of the natural siliceous ion exchangers is about 1.5 to 2 kilograins per cu ft while that of the artificial zeolite is about 10 kilograins per cu ft. Walton used the volume per structural oxygen atom as a measure of the molecular property and correlated this with the
cation exchange capacity.

Sufficiently large volume of work has been done on the properties of natural zeolites\textsuperscript{153-154} but systematic data with respect to the synthetic hydrosol is meagre.