CHAPTER - 2

SILICA GEL STRUCTURE AND PROPERTIES

2.1 GEL PREPARATION AND PROPERTIES:

Although it is true that good quality crystals can occasionally be grown in substances which are not normally known as gels, the general observation is that gels, i.e. particularly silica gels are the best and most versatile growth media. We can not distinguish between gels, sols, collodial suspensions and pastes clearly, 'Gels are neither liquids not solids'. A gel has been defined as a 'two component system of a semisolid nature, rich in liquid(1)'. Gels are formed from suspensions or solutions by the establishment of a three dimensional system of cross linkages between the molecules of one component and the second component permeates this system as a continuous phase. Thus a gel can be regarded as 'a losely inter linked polymer'.

The materials which are generally called gels include not only silica gel but also agar, gelatin, soft soaps, a variety of oleates and stearates, various hydroxides in water, clay etc. Sols have structure similar to gels. Also there are hybrid media, which consists of small jelly-like particles seperated by relatively large tracts of liqid phase, known as "coagels".

The gelling process can be brought about in a number of ways. Gels can be produced by the coling of a sol, by chemical reaction or by the addition of precipitating agents or incompatible solvents. For example, gelatin can be gelled by cooling provided that the concentration exceeds about 10%. The non aqueous gels can be prepared by cooling sols of aluminium stearate, oleate or nepthenate in hydrocarbons on the other hand Alexander and Johnson(1) quote some substances (e.g. certain cellulose nitrates in alcohol and methyl celluloses in water) which show the opposite behaviour : they form gel on being warmed. Gel can also be formed by the action of two reagents in concentrated solution. This type of process gives rise to silica gel which is the most important. Detailed procedure for the preparation of a whole series of silica-alumina gels of varying pore size have been described by Plank and Drake(3,4).

Most of the gels are mechanically and optically except under strain. Transparent gels have complicated ionic adsorption properties and are ordinarily used are creking catalyst.

The gelling process itself takes an amount of time which can vary widely from minutes to many days, depending on the nature of material, it's temperature and history. For silica gel this has been studied by Treadwell and wieland(5). Since gelling is a matter of degree, quoted gelling times are always very approximate. The mechanical properties of fully developed gels can vary widely depending on the density and on the precise conditions during gelling(6).

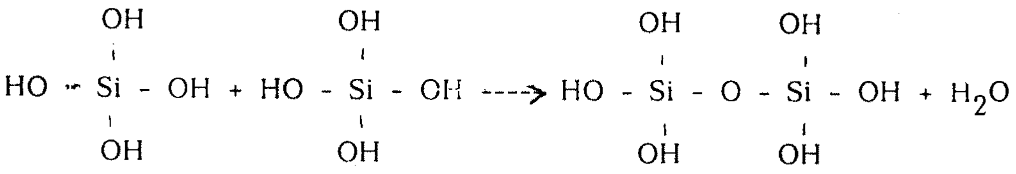
It is often said that reagents diffuse as rapidly through water but it is true only for electrolytes and very dilute gels. It is certainly not true for large molecules, not for colloids. One operative parameter is the size of the diffusing particles relative to the pore size in the gel. The study of chemisorption of alkali ions by koppen(7) is of some important considering that such gels ordinarily made from sodium meta-silicate.

2.2 GELLING MECHANISM AND STRUCTURE OF SILICA HYDROGELS

When sodium metasilicate goes into solution, monosilicic acid is produced in accordance with the dynamic equilibrium.

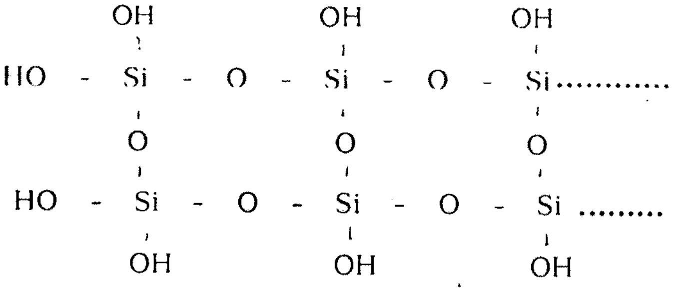
$$\mathrm{Na_2\ SiO_3 + 3H_2O} \dashrightarrow \mathrm{H_4SiO_4 + 2NaOH}$$

And it is accepted that monosilicic acid can be polymerized with the liberation of water.



$$\mathrm{HO-\underset{OH}{\overset{OH}{Si}}-OH + HO-\underset{OH}{\overset{OH}{Si}}-OH} \dashrightarrow \mathrm{HO-\underset{OH}{\overset{OH}{Si}}-O-\underset{OH}{\overset{OH}{Si}}-OH + H_2O}$$

This procedure can be repeated again and again until a three - dimensional network of Si-O links is established as in silica.



$$\begin{array}{ccccccccc} & & \mathrm{OH} & & & & \mathrm{OH} & & \mathrm{OH} \\ & & | & & & & | & & | \\ \mathrm{HO} & - & \mathrm{Si} & - & \mathrm{O} & - & \mathrm{Si} & - \mathrm{O} - & \mathrm{Si}\ldots\ldots\ldots\ldots \\ & & | & & & & | & & | \\ & & \mathrm{O} & & & & \mathrm{O} & & \mathrm{O} \\ & & | & & & & | & & | \\ \mathrm{HO} & - & \mathrm{Si} & - & \mathrm{O} & - & \mathrm{Si} & - \mathrm{O} - & \mathrm{Si}\ \ldots\ldots\ldots \\ & & | & & & & | & & | \\ & & \mathrm{OH} & & & & \mathrm{OH} & & \mathrm{OH} \end{array}$$

As the polymerization process continues, water accumulates on the top of gel surface. This phenomenon is known as 'syneresis' : Much of the water is due to condensation process and a small amount of gel shrinkage. The time required for gelatin is very sensitive to pH. Because gelatin is a gradual process, there is no unique definition of gelatin time. The results suggest convincingly that the reaction is ionic in character (Contrary to the impression conveyed by the simplified representation used above). There is much, that is still unclear about the mechanism, but it is known that two types of ions are produced : $H_3SiO_4^-$ and $H_2SiO_4^{2-}$, in relative amounts depending on the hydrogen ion concentration. . $H_2SiO_4^{2-}$ has high pH values, it is more reactive but as the charges are higher, there is a greater degree of mutual repulsion. $H_3SiO_4^-$ is favoured by moderately low pH values and is responsible for the initial formation of long chain polymerization products. In due course, cross-linkages are formed between these chains and contribute to the sharp increase of viscosity that gives indication for the onset of gelation. It is assumed that very long chains will cross-link more slowly than short chains because of their lower mobility. At very low pH values the tendency towards polymerization is diminished, and chain formation is slowed. As the pH increases the gel structure consisting of loosely bound platelets in which there is a lack of cross-linkages, the cellular nature becomes less distinct. Thus, there is a complicated interplay of reactions which, at any rate in the absence of other reagents, leads to a minimum gelling time at a pH of 8. But a really precise interpretation of this minimum is not yet available. Gelling time appears to be strongly temperature dependent Alexander(8) report that at 1.9°C, gelling is almost instantaneous at pH 6. There is also some evidence that different mechanism predominate below and above pH 3.2. In the presence of water ions, the pH changes can be very different(9). The pH of initially neutral gel increases during syneresis, as result of progressive and stabilizing hydroxyl.

Substitution for oxygen in the polymerized structure :

$- Si - O^- + H_2O \dashrightarrow Si - OH + OH^-$

Stability of silicon-oxygen bonds is responsible for the fact that the above polymerization is largely irreversible. Exceptional case is of dilute silica hydrogel made with water - glass and acetic acid. While gelling, most of the system become some-what opaque.

The gel is evidently not a simple three diamensional silica network. It actually consists of sheet like structure of varying degrees of surface roughness and porosity forming interconnected cells. The cell walls are ordinarily curved. The difference between old and new gels are too small but the differences between dense and light gels are observable. We can observe pore sizes, cell dimensions and cell wall thickness. The structural network in a silica hydrogel usually has no uniform pores. It shows only their size. There is a distribution of pore sizes within each gel. According to the nature of this distribution, one gel can be distinguished from the other. Hydrogels are characterized by two types of pores, 'primary' pores of nearly molecular dimensions and 'secondary' pores which behave as normal capillaries (using SEM the various pres sizes have been a studied). In dense gels, cell walls have pores from less than 0.1 μ to 0.5 μ and in lower density gels, pore sizes are from 0.1 μ to 4 μ that is dense gels have lower pore sizes and gels with lower density have greater pore sizes. The cell walls are thicker for the dense gels but size does not depend at all on gel density. Cell to cell diffusion is limited by pores of smaller size encountered along the diffusion path. Detailed studies regarding pore sizes of various types of gels and about the formation of air bubbles in gels are given by Henisch.

It is difficult to seperate the liquid phase by mechanical means but water can be extracted by means of drying agents. Drying has a small effect on volume. Dried silica gels can be more readily subjected to x-ray analysis. More information is known about dried gels than hydrogels from which they are made. Measurements on dried gels can give results which are also useful to hydrogels because the fractional volume change on gentle drying is small. But changes which occur during extensive drying are irreversible. Thus we can say that syneresis has effect on the average pore size i.e. On drying pore size gets reduced because of gel shrinkage.

Thus we can say that the basic gel structure affects the crystal growth characteristics, including growth rate and ultimate crystal size. Gel pore size will also affect the nucleation density.

2.2.1 TYPES OF GEL

Various types of gels can be prepared using a wide variety of techniques and materials. There are some advantages and disadvantages of these various types of gels.

1) SILICA GEL:

Mix aqueos solution of sodium silicate or sodium metasilicate (Sp.gr.1.03 to 1.06) and acid (1N to 4N of mineral or organic) form a gel. Better crystals can be grown. The disadvantage is that in some crystals there may be inclusion of SiO_2.

2) GELATIN GEL:

Dissolve 5 to 6 gm, of gelatin powder in water by stirring at a constant temperature of 5o°C for one hour and cool to room temperature. In order to strengthen the gel addition of 0.1 ml to 1.0 ml of formal dehyde is necessary.

It has great stability over large pH range (3 to 10.5). There is lack of interfering ions. There is a high optical clarity. Disadvantages are that it can be attacked by molds and it support more nucleation sites.

3) SILICA ALUMINA GEL:

The aluminium salt is dissolved in some acid before mixing with waterglass. Then acid and an aqeous solution of sodium metasilicate forms the gel. The gels are transparent. They have attractive flexibility but even though they are not used to grow crystals because crystals tend to be contaminated with aluminium.

The formation of cross linkages (during gelling) can be increased by partial substitution of Al for Si. Because of difference in valency cross links form more easily. Gelling time is reduced and the resulting gels have a higher density and a smaller pore size than those without aluminium(3). The gels can also be used for growing zeolites (Silicates).

2.3 GROWTH MECHANISM

2.3.1 FUNCTIONS OF GELS:

Gels are obviously not impermeable. But convection currents are suppressed above certain magnitude at any rate can be easily demonstrated. It is verified that particles have streaming and brownian motions in the ungelled solution but are at rest after gelling.

If the convection is absent, diffusion is the only mechanism available for the supply of solute to the growing crystal. Once the new solute is brought to the surface by diffusion, growth takes place either via screw dislocations after initial stages of growth at any rate or via two dimensional surface nucleation. The process of getting solute molecules to the active growth point is governed by surface diffusion. The surface diffusion coefficient increases with increasing temperature leading to the greater perfection and to fewer etch pits.

The gel medium prevents turbulence & remains chemically inert. It provides a 3 dimensional structure which permits the reagents to diffuse at a desirable controlled rate. And the absence of turbulence is beneficial in growing good quality crystals. The establishment of a stable pattern of concentration gradients is one of the principle functions of gel. The gel acts as a three dimensional crucible. It supports the crystal and at the same time helps to grow crystals without exerting major forces upon it. Because of the freedom from constraint, we get high structural perfection. The softness of the gel and the uniform nature of forces which it exerts upon the growing crystal make it possible to overdope specimens until they are metastable because of internal strain.

The important function of gel is to suppress nucleation and there by reduce the competitive nature of the growth. The success of the gel method is in controlling nucleation. That is nucleation control is believed to be the key to the success of the method.

2.3.2 ULTIMATE CRYSTAL SIZE AND REIMPLANTATION:

In simple gel-growth systems the crystals reach a stable, ultimate size. Crystals of small size (i.e. few mm in length) are large enough but there is a demand for large cystals. And the problem of growing much larger crystals is equivalent to the problem of limiting nucleation with a continuous reagent supply and removal of the waste product. When such methods for growth are unavailable or inconvenient, re-implantation of crystals from an exhausted gel into a new gel is possible.

While transferring, crystals must be handled with great care to minimize surface damages. A crystals is placed on to the surface of a set gel -in a tube and it is covered with more silica gel solution and it is then allowed to set, Before adding the feed solution the temperature is raised temporarily to permit a crystal surface layer to dissolve. To reduce nucleation problem at the boundary between new and old gel, the old gel surface is protected from dust, with these precautions, crystals can be re-implanted repeatedly and can be increased in size during each stage.

2.3.3 CUSP FORMATION:

Cusps are nothing but visible cracks in gels. When crystals grow in primary gel media, they are often found associated with cusp like cavities i.e. the regions in which the gel has been split and seperated from the growing faces. The cusps in the immediate vicinity of crystals arise from the pressure of the advancing growth surfaces and are the outcome of gel displacement. Cusps are always present in one form or another. Cusps are filled with solution. Thus the crystals is almost entirely surrounded not by gel but by solution. Therefore, it is assumed that the crystals nucleate in the gel, but they grow increasingly from solution. The diffusion process supplies solute to the cusps and governs the growth rate.

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