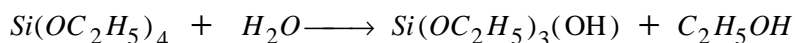


Experiment IX¹

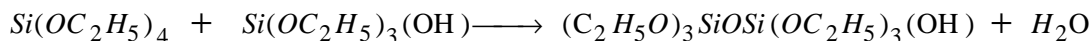
The Sol-Gel Preparation of Silica Gel Sensors

Sols are dispersions of colloidal particles (size 1 - 100 nm) in a liquid. A gel is an interconnected, rigid network with pores of submicrometer dimensions and polymeric chains whose average length is greater than a micron. The sol-gel process is a name given to the hydrolysis and polycondensation of inorganic compounds to form ceramic materials. One particular example is of a sol-gel process is the reaction of tetraethylorthosilicate, $\text{Si}(\text{OC}_2\text{H}_5)_4$, ethanol and water which you will explore today. These three reactants form a one phase solution that goes through a solution-to-gel transition to form a rigid, two-phase system comprised of solid silica (SiO_2) and solvent filled pores. In this experiment you will observe how cross-linking affects the physical properties of a silicate polymer containing an acid base indicator and other reagents useful for chemical sensing.

The fundamental reactions of the sol-gel process are polymerization. Hydrolysis occurs when $\text{Si}(\text{OC}_2\text{H}_5)_4$ and water are mixed in ethanol:



The intermediates that exist as a result of partial hydrolysis include molecules with Si-OH groups which are called silanols. Complete hydrolysis to form $\text{Si}(\text{OH})_4$ would yield silicic acid, but this does not generally occur. Instead condensation may occur between either two silanols or a silanol and an ethoxy group to form a bridging oxygen and a water or ethanol molecule. An example of a condensation reaction between two silanols with the elimination of water is shown below.



Then hydrolysis of $(\text{CH}_3\text{CH}_2\text{O})_3\text{SiOSi}(\text{OCH}_2\text{CH}_3)_3$ will produce for example, $(\text{CH}_3\text{CH}_2\text{O})_2\text{Si}(\text{OH})\text{OSi}(\text{OCH}_2\text{CH}_3)_3$ that can undergo further polymerization reactions.

The hydrolysis and polycondensation reactions are initiated at numerous sites and the kinetics of the reactions are therefore complex. When a sufficient number of interconnected Si-O-Si bonds are formed in a region, they interact cooperatively to form colloidal particles or a sol. With time, the colloidal particles link together to form a three

dimension network. At gelation, the viscosity of the solution increases dramatically and a solid object termed an alcogel results. A technologically important point is that alcogels can be formed in any shape or configuration desired.

A general observation which has emerged from many studies of SiO_2 alcogels is that the addition of acid or base catalyzes the process and lead to gels with vastly different structures and morphologies. Acid-catalysis forms linear polymers which are weakly cross-linked. These polymers entangle and form additional branches, resulting in gelation. Base-catalysis form more highly branched clusters due to more rapid hydrolysis. Gelation occurs by linking of the clusters. You can crudely think about the two cases as a plate of spaghetti (acid catalyzed) and a plate of tumbleweeds (base catalyzed). To gain more insight into the molecular level reaction responsible for these different structures consider that both hydrolysis and condensation may occur by acid- or base-catalyzed bimolecular nucleophilic substitution reactions. The acid catalyzed mechanisms are preceded by rapid protonation of the OR or OH substituents bonded directly to Si, whereas under basic conditions hydroxyl or silanolate anions attack Si directly.

Hazards

$\text{Si}(\text{OC}_2\text{H}_5)_4$ (CAS No. 11-04-1) Tetraethylorthosilicate is irritating to eyes, mucous membranes, and internal organs. Be sure to work in a fume hood and wear gloves when handling this volatile liquid.

Experimental Procedure.

A. Preparation of acid and base hydrolysis mixtures. Begin by placing 15.5 mL of absolute ethanol into two 100 mL Erlenmeyer flasks. In the hood, pour about 30 mL of tetraethylorthosilicate (TEOS) into a small beaker and immediately recap the stock bottle. Use this TEOS to measure out and add 15.0 mL of TEOS to each of the ethanol containing flasks.

Measure out 19.0 mL of distilled water and mix in 2-3 drops of concentrated HCl. Pour this aqueous solution into one of the TEOS-ethanol solutions and test the pH. The pH should be less than three. If it is too high, add a few more drops of HCl.

Measure out 19.0 mL of distilled water and mix in 8-10 drops of concentrated aqueous ammonia. Pour this aqueous solution into one of the TEOS-ethanol solutions and test the pH. The pH should be greater than 10. If it is too low, add a few more drops of base.

B. Sol-Gel Formation. Stir both solutions vigorously for one hour. If multiple layers are present in the solution after this time, add a few more drops of catalyst. Continue mixing until the two solutions are completely miscible.

Remove some of the sol from the acid catalyzed reaction flask and fill a Petri dish to a level of about 5 mm. Take the remainder of the sol and divide it among three test tubes. Add a few crystals of the sodium salt of bromothymol blue to the first test tube. Add a few crystals of potassium iodide to the second test tube and a few crystals of potassium thiocyanate to the third tube. Put the three labeled tubes in a drying oven at 60 C. Let the contents of the Petri dish slowly dry. Repeat this procedure for the base catalyzed materials.

After one week, take the tubes from the oven.

C. Indicator Tests. Place some of the acid catalyzed product that contains bromothymol blue in a covered beaker. Also place a small open container of aqueous ammonium hydroxide. Place the base catalyzed that contains bromothymol blue in a covered beaker. Also place a small open container of aqueous hydrochloric acid in the beaker.

Add some of the KI containing product to a Ag^+ or Pb^{2+} solution. Add some of a KSCN containing product to a Fe^{3+} or Cu^{2+} solution. Do the acid and base catalyzed materials do the same thing? Could this be useful as a chemical sensor?

Current Research Efforts

Sol-gel processing is a rapidly growing area of science.² The processing conditions allow the morphology of a wide variety of materials including semiconductors, insulators, ferroelectrics, and superconductors to be controlled. A significant advantage sol-gel science affords over more conventional materials processing routes is the mild conditions that one may employ. This allows thermally unstable inorganic compounds to be entrapped or covalently bonded within a sol-gel matrix. So mild are the processing conditions, that researchers have recently entrapped biologically active enzymes into SiO_2 .³ These new bio-materials and other novel hybrid structures hold many potential applications in chemical sensing, memory storage, linear and nonlinear optics, solar energy conversion, and microelectronics.

References

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