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A thesis, presented to the Department of Chemistry of Union College, in partial fulfillment of the requirements for the Degree of Bachelor of Science in Chemistry, by

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ON THE VISCOSITY OF SILICIC ACID GEL MIXTURES

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Introduction

The phenomenon of gelation as exhibited by hydrated silica, the so-called silicic acid colloid, is one which has been found to be influenced by any one of seven or more variables. In the main the factors which determine the setting time are, as mentioned by Hurd and Carver (6) and Hurd and Hallstrom (9):

(1) The silica concentration
(2) The acid concentration
(3) pH
(4) Temperature
(5) Agitation
(6) Added soluble materials
(7) Type of silicate

Of the above factors, (4),and (6) were studied individually while the other factors were held constant. The method of study, as differentiated from the tilted rod method utilized by Hurd and Hallstrom (9), was with an Ostwald viscometer. Prasad. Mehta,and Desai (10) have already used this instrument with success. A study of the complete period of gelation can be made starting from the point of mix, through the formation of colloidal silicic acid from the chemical union of sodium silicate and acetic acid, through the growth of colloidal sized particles, and finally the coagulation or gelatinization of the hydrated colloidal particles.

This thesis contains the results of experiments which were formulated with a view to ascertain the applicability of the viscometer in studying the process of gelation and also the effect of electrolytes on the viscosity of gel-forming mixtures.

HISTORICAL:

Prakash and Dahr (20) have shown that viscosity measurements of solutions of sodium silicate and an acid are an indication of what they believe happens as a gel sets. Dahr and Chakravarty (2), as mentioned by Prasad, Mehta, and Desai, have noted the effect of salts on the viscosity of silicic acid sols and found that with increasing quantities of the electrolytes there first occurred a fall in the viscosity and then a rise. Dahr concluded that the increased viscosity was a measure of the degree of hydration of a particle. Prasad, Mehta, and Desai, using a modification of Scarpa's viscometer have obtained viscosity curves similar to those recorded in this thesis. They concluded that the increase in viscosity was due to the hydration of the colloidal particles. They also used Hatcheck's equation to find the amount of hydration.

PROCEDURE

Preparation of solutions:

A quantity of silicate solution was prepared by diluting E brand sodium silicate with recently boiled distilled water. This particular brand manufactured by the Philadelphia Quartz Company is represented as having a Na_2O/SiO_2 ratio by weight of 1/3.19. The normality of the resulting solution, as its equivalent in sodium hydroxide, was determined as 1.2425 N with a standard sulfuric acid solution using methyl orange as the indicator.

Acetic acid prepared by diluting 99.5% glacial acetic acid with recently boiled distilled water, was mixed with the silicate through the experimentation. The normality of the acid was found to be 2.008 N by titrating with a standard sodium hydroxide solution using phenolphthalein as the indicator.

The electrolyte solutions where required were made by dissolving predetermined amounts of the salts in recently boiled distilled water to give three molar concentrations in every instance. No difficulty was encountered in obtaining these concentrations.

Preparation of Gel Mixtures:

Now, it is exceedingly important that conditions attending the mixing of the gel-forming solutions be accurately controlled and recorded if the consequent viscosity mesurements are to have any meaning. By means of pipettes, 50 cc of silicate and acetic acid were

were carefully measured and placed in separate, dry 100 cc beakers. Then 50 cc of the third constituent were added to the beaker containing the acetic acid. In some instances the third portion was pure water and in others it was one of some ten electrolytes. The beakers were then covered with suitable watch glasses and placed in a water thermostat which maintained a temperature of 25 1/10° C. When the separate solutions attained the bath temperature, they were removed from the thermostat and thoroughly mixed by first pouring the silicate into the acid and then pouring the mixture back and forth between the beakers. At this stage the mixtures were considered ready for viscosity determinations.

The Ostwald Viscometer:

Since only relative viscosities were desired, the Ostwald Viscometer was used. Prased and Desai (10) have already applied Scarpa's modification of Ostwald's Viscometer to the study of silicic acid gel mixtures with success. Hurd and Fraser (13) in their preliminary studies on the viscosity utilized the Ostwald type as well as the Stormer type and found that the Ostwald type had distinct advantages because of its simplicity although they admitted the greater possibilities of the Stormer viscometer.

The Ostwald viscometer consists essentially of a U-tube with a capillary in the middle of one limb above which is placed a bulb. A given volume of liquid is placed in the instrument and the time measured that is required for the meniscus to pass two marks one above a and one below the bulb (shown in diagram I) under the influence of the hydrostatic pressure of the liquid only. If the relative viscosity of the liquid under investigation is desired, then the dimensions of the instrument may be disregarded and the instrument may be calibrated with some standard liquid possessing a viscosity in the range of the liquid being studied. Water was used in calibrating the viscometers I and II of which number II was used finally throughout the investigations because of the following reasons which were arrived at after considering the data recorded in tables I, II, III, and IV together with the graph number I. Graph I represents the viscosity curves obtained from both viscometers using identical solutions. Although viscometer I has the advantage of longer time of flow which would tend toward greater accuracy, it must be remembered that an unusual mixture is being studied in which the viscosity is continually varying with time after mix. Therefore, the longer the time of flow, the greater will be the change in viscosity per measurement, and the greater will be the error. From graph number I, it can be seen that the time of flow obtained with viscometer I lies entirely above that of viscometer number II. Furthermore, the vertical line indicating the time of set is obtained more readily and more precisely with viscometer II. Another good characteristic of the viscometer is its ability to give reproducible results to within 1 %. In any case, results have been checked to within the above limits. For example, graph two represents a curve drawn from two different sets of data. The conditions of both experiments were the same but were made several months apart. It can be seen that some of the points along the curve were found to be identical. Other checks made throughout the present studies are just as illustrative of the accuracy which can be attained with the viscometer if conditions are controlled.

Determination of time of set with tilted rod:

There is no method for determining the absolute time of set since the process of gelation occurs in three indefinite stages. At best only a relative measure can be made using the tilted rod method as described by Hurd and Letteron (16). The method consists os inserting a small stirring rod into the gel at an angle of about 20° to the vertical until the gel is stiff enough to sustain the rod in the tilted position. The glass rod is about 3m.m. in diameter, about 10cm. long and drawn to a point. It has been found that this method gives results in time accurate to two percent.

Determinations of the pH

Hurd and Griffeth (8) have found that the quinhydrone method of determining the pH gives reliable results. Since the present work was wholly in the acid region, the quinhydrone method was applied to the determination of pH in the various gel-forming mixtures. A diagram of the calomel cell and the set-up is contained at the end of the thesis as figure (2).

EXPERIMENTAL

The process of gelation was studied by the indirect method of noting the effects of added electrolytes such as: NaBr, NaCl, NaI, Na_2SO_4, $NaNo_3$, LiCl, and KCl in addition to the $NaC_2H_3O_2$ which results naturally from the combination of the sodium silicate a nd acetic acid. Sufficient quantities of the salts were added to make their final concentrations $\frac{1}{2}$M in the gel-forming mixtures. These mixtures were prepared as described above and a 10cc portion of the mixture was placed in the thermostated viscometer. As time progressed, times of flow were made by means of an accurate stop-watch and the time after mix was noted at each measurement. The pH of each mixture was observed as well as the time of set by the tilted rod method. The data obtained are recorded at the end of the paper in the tables from Vto X. Graphs from 3 to 13 were drawn from these data. These salts were chosen so that the effect of anions as well as cations could be studied.

The effect of temperature on the viscosity was also studied. Gel-forming mixtures containing water as the third constituent were studied at 20°, 30.1°, and 40.0° C, the 25° C run having been taken earlier in the year. The data obtained are in tables IV, XI, XI^1,and XIII. Graphs 14, 15, 16, show curves drawn from these data. As a matter of interest, since the times of set by the tilted rod method had not been taken for these particular runs, the times of set as obtained from the vertical line in the viscosity curve were used to calculate the energy of activation. Plotting the log of the times of set as ordinates and the reciprocal of the absolute temperature as abscissae, a line was obtained with four points having a slopeof 3.61 and a resulting energy of activation of 16,480 calories. These results give an energy which compares favorably with the average value found by other investigators.

Viscosity curves were made as the concentration of a salt was varied. NaCl was used as the third constituent in concentrations of $\frac{1}{4}$M, $\frac{1}{2}$M, 1M, and 2M, all easily obtainable. The curves and data are contained in the graph number 17 and tables XIV, XV, and XVI.

RESULTS AND DISCUSSION:

All the salts used were found to have a decided effect in decreasing the time of set in the neighborhood of a pH of 4.70. Graph number 9 shows that the coagulating power of the salts is in the following order in so far as the cations are concerned: $K^+ > Na^+ > Li^+$ The coagulating power of the anions are as follows: $I^- > Br^- > NO_3^- > Cl^- > SO_4^=$. Prasad and Hattiangadi (1) and Hurd and Hallstrom (9) found the same order as the above with the cations.

The difficulty of presenting any plausible explanation of the results mentioned is due primarily to the fact that the process of gel formation itself is not fully understood. Furthermore, the mechanism of the lyotropic influence is not fully understood when associated with the velocity of chemical reactions, with the coagulation of colloidal particles by means of dehydration or charge neutralization, with the variation of surface tension when salts comprising the lyotropic series are added to the liquid under investigation, or with other phenomena. There are, however, several theories which attempt a solution. Kruyt (11) postulates that the lyotropic influence on the above phenomena is due to a dehydration effect, charge neutralization, shift in the water equilibrium which may be represented as $nH_2O \rightleftarrows H_2O_n$, or a regular orientation of the water dipoles by the ions of the salts. Anothhr theory states that the lyotropic series influences the rate of a chemical reaction because of the ability of the ions to act as catalysts. The inversion of cane sugar has been found to be influenced by the lyotropic series.

Now, as for the theories concerning the formation of silicic acid gels, there are at present the condensation and coagulation theories. The former explains the gel formation on the basis of a chemical reaction wherein silicic acid condenses into long chains of silicon and oxygen with a splitting out of water. The latter theory states that the gel results from a coagulation of hydrated particles. It may be that a reconciliation of the two theories would be helpful in explaining the formation of a gel of silicic acid. It would seem improbable that the slow growth of silicic acid particles should not be accompanied by a hydration of the same. Moreover, the coagulation of the particles would aid in the condensation process. One phenomenon is superimposed upon the other. To repeat, a compromise would help in visualizing how a gel possessing a crystal structure can contain such large quantities of water.

But if the gel formation is purely a condensation, then the lyotropic series may influence the reaction in the role of a catalyst as it presumably does with the reaction of sugar and water. The two reactions may be written as:

$$\text{Sugar} + H_2O \rightarrow \text{products}$$

$$\text{Silicic acid} \rightarrow H_2O + \text{condensed products}$$

The lyotropic series comes into play in the first and probably in the second in the same capacity.

If, on the other hand, the process is one of coagulation of hydrated particles only, then one would expect the lyotropic influence to exert itself. The order of the coagulating power of the ions as given in Houwink and Kruyt is as follows:

$I^- > NO_3^- > Br^- > Cl^- > SO_4^{=}$ and $K^+ > Na^+ > Li^+$ The order is about the same as obtained in this experiment. Also, it is interesting to note that Klobusitzky (18) in his studies on the speed of blood coagulation indicated that the relative influence of ions on the decrease in the blood clotting is in the following Hofmeister series:

$I^{-} > SCN^{-} > Br^{-} > NO_3^{-} > Cl^{-} > SO_4^{=}$, in the same order noted in the present experiment. To continue, it can be said that the vertical portion of the viscosity curve comes when the concentration of the hydrated colloidal particles exceeds that concentration permitted by the coagulating power of the ion present. If both condensation and coagulation occur, then the ions would be expected to continue to exert their influence as members of the lyotropic series.

It is noticed from graph 17 that an increased concentration of the salt results in a decrease of the setting time. This influence one on would expect either from the theory that a catalysis was being effected or that a greater coagulating power was manifest because of the increased amount of salt.

Summary;

(1) The Ostwald viscometer has been used to study the viscosity of gel-forming mixtures of sodium silicate, acetic acid, and a third constituent consisting of either water or some electrolyte dissolved in water.

(2) The effect of salts in decreasing the time of set as noted by the vertical line in the viscosity curves was found to vary in a typical lyotropic series.

(3) The time of set was found to decrease with increase in temperature and a calculation of the heat of activation was made using data from the viscosity curves and was found to be in good agreement with the previous calculations.

(4) The effect of increased concentration of a salt such as NaCl was to decrease the time of set.

(5) The viscometer was found to give results which were accurately reproducible.

(6) The pH of the gel-forming mixtures as prepared was found to vary little with addition of the particular salts studied.

(7) An attempt was made to reconcile the condensation and coagulation theories in order to obtain a more plausible explanation of the lyotropic influence of the salts.

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