STUDIES ON THE SOL-GEL TRANSFORMATION OF SILICIC ACID SOL IN PRESENCE OF DYES

BY WAHID U. MALIK AND IQBAL A. KHAN

[Chemical Laboratories, University of Roorkee, Roorkee (India)]

Received April 28, 1966

(Communicated by Dr. Putcha Venkateswarlu, F.A.Sc.)

ABSTRACT

The influence of dyes on the gelation of silicic acid sol has been studied with the help of viscometric and pH metric methods. The results indicate that the time of gelation decreases in presence of basic dyes and increases with acid dyes. It has also been found that methylene blue is adsorbed by replacement of H⁺ ions by the big cation of the dye followed by a possible combination between S of the dye and OH of the silanol group of silicic acid. The results on pH variations during gelation support this viewpoint. Similar results have been obtained with malachite green. The interaction of alizarin sulphonie acid with silicic acid is explained in terms of compound formation between the silanol and the phenolic groups while methyl orange undergoes orientation to quinonoid structure in presence of silicic acid. Positive adsorption is found to take place in all cases except methyl orange which is negatively adsorbed.

Very little work has been done on the interaction of the dyes with inorganic colloidal solutions in spite of the fact that some of these systems have been widely employed in dyeing. The only aspect which appears to have attracted some attention is the use of hydrous oxide sols as mordants and the problem of the formation of alizarin lakes.¹ ² Even silicic acid has not so far been systematically studied and the few references available on this compound deal either with the theories of polymerisation of silicic acid,³ or on the adsorption of dyes and related compounds by silica gel.⁴ ⁶ The behaviour of colloidal silicate solutions as revealed by adsorption indicators⁶ has also been studied but no attempt is made to know the real mechanism of the silicic acid-dye interaction.

To investigate the problem a beginning was made, employing a combination of silicic acid sol with a few acid and basic dyes. The present study
describes the results of the influence of alizarin sulphonic acid (Na salt), methyl orange (Na salt), methylene blue and malachite green on the gelation of silicic acid studied with the help of viscometric and pH metric methods with special emphasis on the nature of chemical interaction between the dyes and the sol.

**Experimental**

1. **Reagents**

   (a) *Silicic acid sol.*—Silicic acid sol was prepared by diluting 40 ml of concentrated hydrochloric acid (A.R.) with 125 c.c. of conductivity water. 75 ml of sodium silicate (Riedel) solution (sp. gr. 1.16) was added to the dilute acid with constant stirring. The mixture was dialysed till the pH of the sol was 1.5. The silica content was determined gravimetrically by evaporating 5 ml sol in a weighed crucible to dryness and then heating until the weight was constant. The SiO₂ content was found to be 51.0 gm. per litre. Since the viscosity of the sol was found to vary with time, the viscosity of the pure sol was measured before carrying out experiments with a particular set of dye-sol mixture.

   (b) The dyes: alizarin sulphonic acid (sodium salt), methyl orange (sodium salt), methylene blue and malachite green used in the investigations were of B.D.H. and Merck products.

2. **Apparatus and Technique**

   The viscosity measurements were carried out by using modified Scarpa’s method. pH measurements were made with a Cambridge Bench pH meter.

3. **Procedure**

   Stock solutions of $2 \times 10^{-2} \text{M}$ conc. each of alizarin sulphonic acid (sodium salt), methyl orange (sodium salt), methylene blue and malachite green were prepared in double distilled water. Silicic acid sol was also prepared in double distilled water. The following sets of mixtures were prepared:

   20 c.c. sol + varying amounts of each of the dye solutions (0, 2.0, 6.0, 8.0, 10.0 c.c.) were employed. In each case total volume was made upto 30 c.c. by the addition of double distilled water.

   The viscometric and pH metric studies were carried out during the dialysis of the sets in different dialysing bags of the same size. The measurements were made at a constant temperature of $30^\circ \pm 0.1^\circ \text{C.}$
Dye adsorption measurements.—The silicic acid gel was initially dried overnight at 110°C, and then finely powdered, weighed and presoaked in a small quantity of conductivity water prior to addition of the dye solution. Stock solutions of $1.5 \times 10^{-4}$ M conc. of alizarin sulphonic acid, $4.51 \times 10^{-6}$ M conc. of methyl orange, $3.14 \times 10^{-5}$ M conc. of methylene blue and $1.96 \times 10^{-5}$ M malachite green were then added as follows:

The adsorbents and dye solutions were agitated to equilibrate after each addition of the dye prior to colorimetric measurements of the dye. The readings were taken after 24 hr. of mixing. The concentration of the dye, in the equilibrium solutions, was measured with a Bausch and Lomb “Spectronic 20 colorimeter”. The equilibrium solutions were centrifuged for transmittance measurements. From the difference in optical density, the concentration of the dye adsorbed can be determined using Beer Lambert’s Law.

DISCUSSION

Before discussing the experimental results on the gelation time of silicic acid sol, as influenced by the presence of dyes, it is worthwhile to consider the behaviour of the pure sol when converted into a gel by prolonged dialysis. A plot of time of dialysis against viscosity would reveal that after a certain stage of dialysis, there is an abrupt increase in viscosity. It is at this stage that the optimum conditions necessary for the conversion of the sol into a gel are realised. The time for this change may be termed as gelation time, which is quite distinct from the time of setting which is ordinarily taken as the time required for any system to set into a gel. A perusal of the data (Table I) would reveal that the time of setting is minimum only when the sol has been dialysed sufficiently to cross the limit pertaining to gelation time.

Undoubtedly rise in viscosity of colloidal systems may be explained in the light of factors, viz., solvation, electroviscous effect, aggregation of particles, etc., in the case of pure sols; a forthright explanation is difficult to give for complex systems comprising of mixtures of a sol and a foreign substance (electrolyte or non-electrolyte) or two different sols.

The data on the viscosities of sol-dye mixtures may be studied from two angles.

1. Variations in viscosity with progressive dialysis in presence of a fixed amount of dye, when abrupt change in viscosity takes place.

2. Change in viscosity with the addition of gradually increasing amount of the dye for a dialysed sol.
TABLE I

Time of setting and gelation time for a dialysed silica sol of pH 1.5

<table>
<thead>
<tr>
<th>Time of dialysis (mts.)</th>
<th>Sol I</th>
<th>Sol II</th>
<th>Sol III</th>
<th>Sol IV</th>
<th>Gelation time from curves between time of dialysis and viscosity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Setting time by Fleming's method</td>
<td>Viscosity (centipoise)</td>
<td>Setting time by Fleming's method</td>
<td>Viscosity (centipoise)</td>
<td>Setting time by Fleming's method</td>
</tr>
<tr>
<td>0</td>
<td>60 hrs.</td>
<td>1.213</td>
<td>63 hrs.</td>
<td>0.994</td>
<td>62 hrs.</td>
</tr>
<tr>
<td>60</td>
<td>12 hrs.</td>
<td>1.260</td>
<td>15 hrs.</td>
<td>1.001</td>
<td>14 hrs.</td>
</tr>
<tr>
<td>120</td>
<td>6 hrs.</td>
<td>1.334</td>
<td>4 hrs.</td>
<td>1.483</td>
<td>4 hrs.</td>
</tr>
<tr>
<td>160</td>
<td>3 hrs.</td>
<td>1.526</td>
<td>3 hrs.</td>
<td>1.526</td>
<td>..</td>
</tr>
<tr>
<td>180</td>
<td>1 hrs.</td>
<td>2.315</td>
<td>1.5 hrs.</td>
<td>1.773</td>
<td>..</td>
</tr>
</tbody>
</table>

Although a continuous increase in viscosity with dialysis is observed in all cases, the extent to which this change takes place is dependent on the nature of the dye employed. Thus for a fixed concentration of the dye (4 0 mM./litre of the dye) the extent of variations in different cases are as shown in Table II.

From Table II, it is evident that the overall increase in viscosity is less in the case of acid-dye sol mixtures than in the pure sols. The overall increase being methyl orange (77%), alizarin sulphonic acid (31%) as against 96%.

TABLE II

Variations in viscosity with dialysis of silica-dye sol mixtures

<table>
<thead>
<tr>
<th>Time of dialysis (mts.)</th>
<th>Viscosity pure sol (centipoise) Sol I</th>
<th>Viscosity sol+methyl orange (centipoise) Sol II</th>
<th>Viscosity sol+alizarin sulphonic acid (centipoise) Sol III</th>
<th>Viscosity sol+methylene blue (centipoise) Sol IV</th>
<th>Viscosity sol+malachite green (centipoise)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.213</td>
<td>1.287</td>
<td>0.9940</td>
<td>1.002</td>
<td>1.027</td>
</tr>
<tr>
<td>60</td>
<td>1.260</td>
<td>1.340</td>
<td>1.001</td>
<td>1.017</td>
<td>1.024</td>
</tr>
<tr>
<td>120</td>
<td>1.334</td>
<td>1.445</td>
<td>1.483</td>
<td>1.184</td>
<td>1.066</td>
</tr>
<tr>
<td>150</td>
<td>1.526</td>
<td>1.783</td>
<td>1.526</td>
<td>1.210</td>
<td>..</td>
</tr>
<tr>
<td>180</td>
<td>2.315</td>
<td>2.279</td>
<td>1.773</td>
<td>1.311</td>
<td>..</td>
</tr>
</tbody>
</table>
Studies on Sol-Gel Transformation of Silicic Acid Sol in Presence of Dyes

and 78% of the pure sols respectively. With the basic dyes the results are, however, quite different. Here the overall increase in viscosity is larger 16·5% for methylene blue and 98·6% for malachite green, as against 5·7% and 78% of pure sols respectively.

The large increase in viscosity of the pure sol can be explained in terms of hydration or polymerisation as envisaged by Treadwell and Weiland. The electroviscous effects will be operative to a negligible extent in view of the almost uncharged nature of the silica particles since the sol was prepared at pH 1·5. The difference in the relative variations in viscosity with dialysis between the pure sol and sol-dye mixture, however, cannot be explained in terms of hydration or polymerisation of silica particles but has to be explained in terms of the colloid-chemical behaviour of the new aggregates formed by interaction with the dye. In this context the results on the change in viscosity and pH with concentration after a fixed period of dialysis are worth considering.

A plot of concentration of dye against viscosity would reveal that the viscosity increases with increase in concentration of the dye, both in the case of methylene blue and malachite green although the nature of curves is slightly different in both the cases (Fig. 1). With acid dyes the behaviour

![Diagram](image_url)
is altogether different, the concentration viscosity curves showing a decrease over a long concentration range, followed by a slight increase in the case of alizarin sulphonic acid and marked increase in the case of methyl orange (Fig. 1).

![Equilibrium Conc of Dye](image)

**Fig. 2**

The difference in the behaviour of the acid and basic dyes towards silicic acid gel is also evident from the adsorption studies. A plot of equilibrium concentration of dye against the amount of the dye absorbed per 100 mg. of silica gel ($x/m$) are typical physical adsorption isotherms (Fig. 2) in the case of methylene blue, malachite green and alizarin sulphonic acid, the adsorption data are seen to fit well in Langmuir adsorption equation (Fig. 3). On the other hand methyl orange is found to be negatively adsorbed (Fig. 2, curve 4). From these observations it is evident that the thickness of the material adsorbed is only monomolecular, on the bare surface in the case of methylene blue, malachite green and alizarin sulphonic acid. Methyl orange is found to be negatively adsorbed by silica gel, this would involve swelling of the gel by imbibing water, consequently resulting in an increase of optical density.
Another factor worth taking into account while explaining the gelation tendency of silicic acid in presence of dyes is the structure of the dyes and the molecular re-arrangements they may undergo in the different pH ranges. Since the silicic acid sol has a fairly low pH, the dye molecule may either undergo protonation or is reoriented to give the quinonoid structure.

Since the existence of uncharged silica particles in the sol may be attributed to the strong adsorption of counter H⁺ and subsequent appearance of OH groups on the surface of silica micelle, adsorption of methylene blue would take place in the following ways:

Replacement of H⁺ ions by

\[
\begin{array}{c}
\text{(CH₃)₂N} \\
\text{S} \\
\text{N} \\
\text{(CH₃)₂} \\
\end{array}
\]

followed by its subsequent adsorption. Since such big cation cannot enter into the electronic structure of O⁻ ion, addition of methylene blue would not form a definite compound or group with the cation of the dye, and, therefore the possibility of chemical reaction is very little. Physical adsorption can, therefore, be expected. Our results on the decrease in pH and physical adsorption support this mechanism. The hydration accompanying the adsorption of basic dye seems to be connected with the gradual increase in
aggregation up to a critical size. When hydration is maximum a sudden increase in viscosity leads one to believe that after the critical size has been attained the gel formation starts (Fig. 1). Another factor which should not, however, be lost sight of, is the possible combination between the sulphur of the dye and the OH of the silanol group of silicic acid.

Preliminary experiments have shown that methylene blue does not change its colour either in the acid or basic medium. The addition of sol, however, brings about a slight deepening of the colour which may be due to the chemical interaction between S of the dye and OH of the silanol group. The results on the variation in pH with addition of methylene blue also support this view (Fig. 4). It appears that up to a certain concentration the adsorption phenomenon is operative resulting in the release of H⁺ ions but afterwards chemical combination takes place resulting in irregular variations in pH. The behaviour with malachite green can also be explained on similar lines except for the fact that there is nothing inherent in the structure of the molecule which may point towards some sort of chemical interaction between the dye and the active sites of the silicic acid sol.

Another aspect from which the gelation can be studied is that of controlled coagulation of silicic acid by the addition of dye. On plotting ‘C’ (concentration of dye) and 1/t and 1/C−a and t (time of gelation), typical curves are obtained for Bhattacharya’s equation¹⁴ for coagulation of hydrophobic sols by electrolytes. These curves, however, differ significantly from
the usual ones in one respect, that is, the value of a critical stability concentration comes out to be negative (Fig. 5). Although the negative values of the constants $a$ (c.s.c.) has no real significance, they point towards the fact that in highly hydrated system like that of silicic acid, gelation would not necessarily take place through controlled coagulation. However, controlled coagulation may become operative in presence of foreign substances. It is for this reason that silicic acid sol undergoes gelation in a shorter time in presence of basic dyes for equally dialysed samples. Since both the sol and the dye do not come out of the dialysing bag during dialysis an inter-relationship between the time of gelation and concentration of dye for dialysed samples is justifiable.

![Graph showing the relationship between concentration and time of gelation](image)

**Fig. 5**

Alizarin sulphonlic acid is well known for its tendency to form colour lakes with metal hydrous oxide sols through exchange adsorption. This behaviour would not be exhibited by silicic acid in view of the non-existence of counter ions in its double layer. The only possible way in which alizarin sulphonlic acid can influence the gelation of silicic acid can, therefore, be through compound formation. Since a change in the original colour of the dye from light yellow to violet is observed on the addition of the sol after
prolonged dialysis, there is a good possibility of the combination between the silanol and the phenolic group, resulting in a re-arrangement involving quinonoid structure.

The decrease in viscosity with concentration (Fig. 1, curve 4) as well as marked variation in pH (Fig. 4, curve 3) support this view point. It appears that behaviour of the acid dyes is different from that of the basic dyes and the possibility of realising gelation through controlled coagulation is very remote. Here aggregation is very difficult to achieve. The rate of gelation is very slow and gelation can only set in when the critical size-hydration limit is reached. The initial decrease in viscosity may be attributed to the peptisation of the sol by the small amounts of the dye. However, with increase in concentration of the dye the hydration tendency increases resulting in a large increase of viscosity. Such a behaviour is quite likely since, together with the hydration, orientation of the methyl orange to the quinonoid structure is also likely to take place. The initial decrease of viscosity may be attributed to chemical changes accompanying dye-sol interaction whereas purely adsorption effects seem to be operative in the higher concentration range. It is for this reason that the decrease in pH with concentration is not so marked as in the case of alizarin sulphonic acid (Fig. 4, curve 4). An appreciable decrease in pH is observed only in the later stages.
ACKNOWLEDGEMENT

One of the authors (I. A. K.) is thankful to the C.S.I.R. (India) for the award of Fellowship.

REFERENCES