# Studies on the Mixed Gels of Silica, Alumina and Ferric Oxide

By WAHID U. MALIK[1]), HASAN ARIF and FASIH A. SIDDIQI

With 4 Figures

## Summary

Sol-gel transformation of mixed gels of silica, alumina and ferric oxide has been studied by determining the variations in pH with time of dialysis. For silica-alumina mixtures a pH of 2.9 is invariably reached irrespective of the alumina content of the mixtures. The amount of alumina present in the mixture influences the time of setting of the gel to a very great extent and it decreases with increase of the alumina content of the mixtures. These results have been explained in light of chemical interaction between the two gels to give aluminosilicates as well as in terms of controlled coagulation phenomenon with alumina behaving as a foreign electrolyte for bringing about the gelation of silicic acid.

The results of silicic acid, ferric oxide gel forming mixtures are altogether different. In this case the time of gelation increases with the increase in the amount of ferric oxide in the gelation mixture, while a pH of 4.2 is reached irrespective of the amount of ferric oxide present. No evidence for the formation of ferric-silicate is obtained nor the gelation of these mixed sols can be explained in terms of controlled coagulation.

The colloidal silica appears to act as protective colloid for the highly acedic ferric oxide sol. Viscometric and pH metric studies on the addition of alumina sol to mixtures of ferric oxide and silica sols indicate that alumina competes with ferric oxide in the formation of mixed gels. Here, too a pH of 2.9 is invariably reached irrespective of the alumina content in the mixed gels.

A considerable amount of literature, mostly in the form of patents, is reported on silica gel but very little is known about the colloidal behaviour of mixed gels of silica obtained from various metal hydrous oxide sols. In view of the importance of such gel forming systems in the building materials and allied industries it was considered desirable to carry out some fundamental work on these gels. The present communication deals with the results on the variation in the viscosity and the pH of silica-alumina, Silica-ferric oxide and Silica-alumina-ferric oxide sols during gelation.

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[1]) Department of Chemistry, University of Roorkee, Roorkee, India.

# Experimental

## Preparation of Silicic acid sol

Silicic acid sol²) was prepared by diluting 40 ml. of concentrated hydrochloric acid with 125 ml. of conductivity water. 75 ml. of sodium silicate (sp. gr. 1.16) was added to the dilute acid with constant stirring. The mixture was dialysed till the pH of the sol became 1.5. The $SiO_2$ content was determined gravimetrically by evaporating 5 ml. sol in a weighed crucible to dryness and then heating until the weight was constant. The $SiO_2$ content was fixed to 48 gms/litre by dilution.

## Preparation of aluminium hydroxide sol

Alumina sol was prepared by the peptisation method as recommended by Weiser³). The pH of the sol was fixed to 3.5 by dialysing the sol in parchment bag. The $Al_2O_3$ content was determined gravimetrically⁴) and was found to be 10.2 gms/litre.

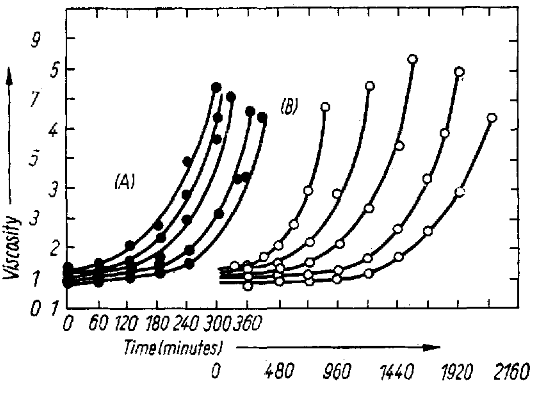

Fig. 1

## Preparation of ferric hydroxide sol

Ferric hydroxide sol was prepared by Grahm's⁵) method. The pH of the sol was brought to 1.8 by dialysing the sol in a parchment bag. The $Fe_2O_3$ content was determined gravimetrically⁶) and was found to be 16 gms/litre.

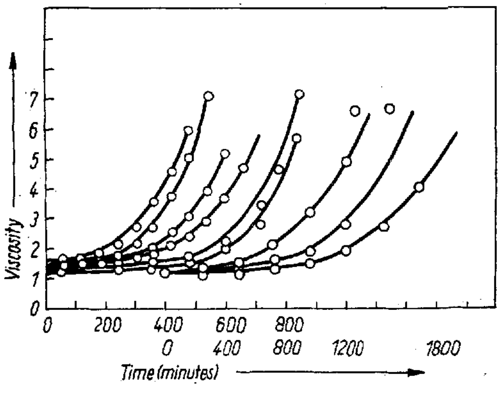

Fig. 2

## Procedure

100 ml. of silicid acid (pH 1.5) was taken in each set of experiments ($SiO_2$ = 48 gms/litre). Vary-

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²) Emil Hatschek (Laboratory manual of elementry colloid, Second Edition, London J. & A. Churchill publication page 50).

³) H. B. Weiser, J. phys. Chem. **24**, 525 (1920).

⁴) Arthur I. Vogel (A test book of quantitative inorganic analysis, Second edition, Longmans, Green and Co., London, page 410).

⁵) Grahm, J. chem. Soc. (London) **15**, 249 (1862); Philos. Trans. Roy. Soc. London **151**, 208 (1861).

⁶) Arthur I. Vogel (A test book of quantitative inorganic analysis, Second edition, Longman, Green and Co., London, page 407).

ing amount of aluminium oxide and ferric hydroxide sols (pH = 3.5 and 1.8 respectively) were mixed (Viz; 100, 80, 40, and 20 ml.), in order to get the silica-alumina and silica-ferric oxide mixed gels and the total volume was made up to 200 ml. in each case. To get mixed gels comprising of three constituents, 90, 80, 70, 60, 50, 40, 30, 20, and 10 ml. of alumina and 10, 20, 30, 40, 50, 60, 70, 80, and 90 ml. of ferric oxide were mixed to 100 ml. silica and the total volume made up to 200 ml. The mixtures were then put in the parchment bag and gelation was studied by following changes in viscosity and pH during dialysis (Figs. 1 and 2). Modified SCARPA's[7]) method was used for viscosity measurements while pH measurements were carried out with the help of BECKMAN pH meter model "G".

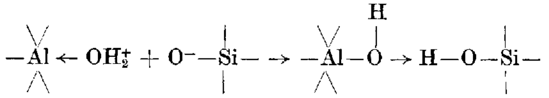
## Discussion

Ordinarily polysilicic acid does not combine with metals to give metal silicates due to the destruction of SiOH groups during the course of polymerisation. However, this is possible, although without realising definite compound formation, in the pH range 2 to 3 when the chances of polymerisation are very slight[8]). In this pH range various possibalities including the adsorption of metal hydroxides on silica, and combination between SiOH and a basic metal ion such as $[Fe(OH)]^{+2}$, have been proposed but none of them explains satisfactorily the chemistry of such systems. Moreover, the problem becomes all the more interesting when looked upon from an entirely new angle involving the study of systems obtained by mixing silicic acid sol with various metal hydroxide sols.

In the systems under investigation the physical properties may be influenced by two important factors, one purely chemical, and the other physical, viz: (i) interaction of the two sols under suitable conditions to give metal silicates of varying compositions; (ii) mutual interaction between them, hydrous oxide sol influencing the gelation of silicic acid sol.

The following facts emerge out from the studies on the gelation of silicic acid- alumina mixtures of different alumina content (designated as $SiO_2/Al_2O_3$): (i) a pH of 2.9 is invariably reached in all the mixtures, and (ii) the time of setting of the gel as evidenced from viscosity data (table 1; fig. 1; curves A) decreases with the increase in the alumina content of the mixtures.

The results on the variation in pH may be explained by considering a series of reactions involving the formation of alumino-silicate gel accompanied by simultaneous hydrolysis of the reaction products: (i) Formation of alumino-silicate gels:



$$-\overset{\diagdown\;\diagup}{\underset{\diagup\;\diagdown}{\text{Al}}}\leftarrow \text{OH}_2^+ + \text{O}^- -\overset{|}{\underset{|}{\text{Si}}}- \rightarrow -\overset{\diagdown\;\diagup}{\underset{\diagup\;\diagdown}{\text{Al}}}-\overset{\overset{\text{H}}{|}}{\text{O}}\rightarrow \text{H}-\text{O}-\overset{|}{\underset{|}{\text{Si}}}- \qquad (A)$$

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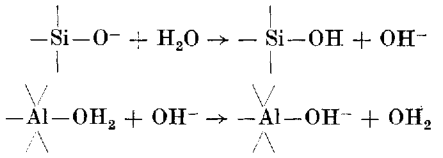
[7]) SCARPA, Gazetta **40**, 271 (1910).

[8]) R. K. ILER, J. physic. Chem. **57**, 604 (1953).

Table 1
Data on pH and time of setting of different silica-alumina gel forming mixtures

| Molar ratio $SiO_2/Al_2O_3$ | Time of abrupt changes from viscosity data (minutes) | Initial pH | Final pH |
|---|---|---|---|
| 4.70 : 1 | 210 | 2.12 | 2.9 |
| 5.89 : 1 | 240 | 2.10 | 2.9 |
| 7.84 : 1 | 270 | 2.05 | 2.9 |
| 11.75 : 1 | 312 | 1.95 | 2.9 |
| 23.53 : 1 | 336 | 1.90 | 2.9 |

(ii) Followed by hydrolysis of the gel:



$$-\overset{|}{\underset{|}{Si}}-O^- + H_2O \rightarrow -\overset{|}{\underset{|}{Si}}-OH + OH^- \quad (B)$$

$$-\overset{\backslash\,/}{\underset{/\,\backslash}{Al}}-OH_2 + OH^- \rightarrow -\overset{\backslash\,/}{\underset{/\,\backslash}{Al}}-OH^- + OH_2 \quad (C)$$

Reactions (A), (B) and (C) when considered together should mean no change in the pH of the different gel forming mixtures. But the increase in pH observed on keeping the mixture indicates that only a portion of the hydroxyl ions released from reaction (B) are used up by the alumina end of the mixed gel. However, on keeping the mixture for long the hydrolytic tendencies diminish due to enhanced interlinking and subsequent disappearance of $-\overset{|}{\underset{|}{Si}}-O^-$ group with the result that further change in pH does not take place. Another interesting aspect of these studies is that a pH of 2.9 is invariably reached in all mixtures.

From the mechanism proposed above, it may be inferred that a coherent gel structure, consisting of interlaced alumino-silicate particles, is achieved by the mutual interaction of alumina and silica sols. Further confirmation is forth-coming from the thixotropic character exhibited by these gels which readily reset after losing their original structure on vigorus shaking.

It is a matter of common experience that gelation is difficult to achieve with either purely lyophobic or purely lyophilic systems. The particles in the latter case would never come in contact to give the gel structure while in the former complete contact in between the particles would result in the formation of floccules rather than gels. An intermediate stage involving partially lyophilic particles should, therefore, favour gel formation. In the present study the two systems can be represented by the metal hydrous oxide and silica sols respectively. Silica as such takes a very large time for gelation (and that too at a certain critical pH and due to structural changes like the destruction of the silanol group etc.) but once the alumina sol is added the time of setting decreases (table 1). It may, therefore, be said that alumina sol almost acts as an electrolyte for the setting of the silicic acid sol by the mechanism of controlled coagulation, differing only in this respect that the solid phase would consist not merely of silica but is covered with a highly insoluble alumino-silicate. Reference to such blended structure have been made by JEPHCOTT and JOHNSTON[9]) for alumina-silica systems.

Indirect evidence of controlled coagulation phenomenon in alumina-silica mixtures is available in other ways also. Firstly, on plotting log t (time of setting as obtained from viscosity data) against concentration of $Al_2O_3$ a straight line conforming to the FREUNDLICH[10]) relationship, $\log \theta = A - BC$ (where $\theta$ is the time of setting, C is the concentration of electrolyte, A and B are constant), for ferric oxide sol undergoing gelation by the addition of electrolyte is obtained (Fig. 3; curve-1, the values of constants are $A = 2.586$ and $B = 0.225$). Secondly, the experimental results on the time of setting in presence of varying amounts of alumina sol fit in quite satisfactorily in BHATTACHARYA's equation[11]) for slow coagulation

$$c = a + \frac{m\, 1/t}{n + 1/t}$$

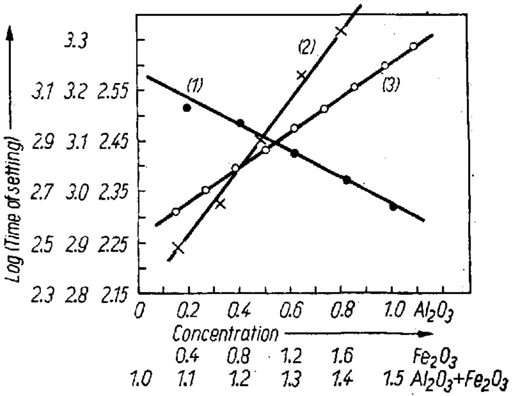


Fig. 3

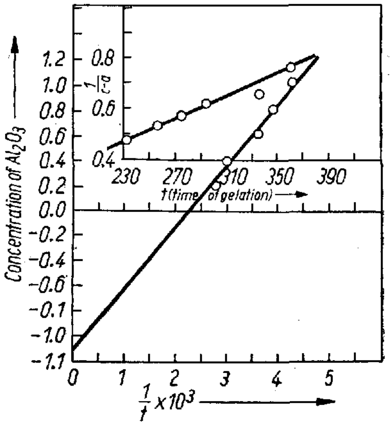


Fig. 4

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[9]) C. M. JEPHCOTT and JOHNSTON, Arch. Ind. Hyg. and Occupational Med. **1**, 323 (1950).

[10]) H. FREUNDLICH, "Thixotropy", Paris **29**, 7 (1935).

[11]) A. K. BHATTACHARYA and RAM KUMAR, J. Ind. Chem. Soc. **28**, No. 4, 179 (1951); **28**, 638 (1951).

where 'a' is the maximum amount of electrolyte which can be added to the sol without affecting any coagulation, m and n are constants and 'c' the concentration of the electrolyte and 't' the time of coagulation.

On plotting 1/t (t being taken as the gelation time at abrupt changes in specific viscosity) and c (c the concentration of aluminium oxide), straight line is obtained (Fig. 4) which, however, cuts the concentration axis on the negative side. The values of the various constants are as follows: $a = -1.1$; $m = 2.128$; $n = 0.0048$.

This anomalous behaviour, that is having a negative value of critical concentrate apparently dubious is not altogether without significance. The system under study is distinctly different from the lyophobic ones in which coagulation or gelation is realised by the addition of electrolyte. Here hydration besides slow coagulation also influences gel formation. With progressive dialysis the silica particles get hydrated and, therefore, take quite a large time to assume the gel structure. However, on adding alumina the preventive action of excessive hydration is checked resulting in the formation of micelles easily disposed to gel formation. A negative value of 'a' would then mean that a sol as such would either not undergo gelation or it would do so only with great difficulty (the time of setting being extremly large). The entire system is, however, quite complicated due to the existence of factors like chemical interaction, adsorption, and hydrolysis.

The behaviour of silicic acid-ferric hydroxide gel forming mixture is altogether different from the corresponding silicic acid alumina mixture (Table 2). It differs in the following respects: (i) the time of gelation increases with increase in the amount of ferric oxide in the gelation mixture; (ii) the change in pH is more marked than in the alumino-silicate gel: a maximum pH of nearabout 4.2 is reached on complete gelation irrespective of the amount of ferric oxide in the gelation mixture; (iii) BHATTACHRYA's equation is not applicable.

Table 2
Data on pH and time of setting of different Silica-ferric oxide gel forming mixture

| Molar ratio $SiO_2/Fe_2O_3$ | Time of abrupt changes from viscosity data (minutes) | Initial pH | Final pH |
|---|---|---|---|
| 3.00 : 1 | 1848 | 1.80 | 4.15 |
| 3.75 : 1 | 1512 | 1.76 | 4.18 |
| 5.00 : 1 | 1128 | 1.72 | 4.18 |
| 7.50 : 1 | 840 | 1.68 | 4.20 |
| 15.00 : 1 | 696 | 1.65 | 4.20 |

The mechanism involved in this case is quite different from the one put forward for the alumina-silica mixtures. It appears that the colloidal silica simply acts as a protective colloid for the highly acidic ferric hydrous oxide sol and that no homogenous gel of ferric silicate is formed. The large increase in pH is due to hydrolysis:

$$-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}^- + \mathrm{H_2O} \rightarrow -\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{OH} + \mathrm{OH}^-.$$

Silica at this high pH would continously polymerise with the result that the amount of metal bound to silica will be too small. Similar explanation has been given by VAIL[12]) to explain the behaviour of metal silicates formed by interaction of the silicic acid with acid reacting metal salts.

The ferric oxide-silica mixed gel system, however, exhibits thixotropic behaviour and a FREUNDLICH relationship is followed on plotting log t against concentration of ferric-oxide (Fig. 3, curve 2, the values of constants are $A = 2.73$ and $B = -0.327$). As stated earlier BHATTACHARYA's relationship is not applicable here and, therefore, gelation cannot be explained by controlled coagulation. Other factors like hydrolysis, adsorption and hydration are, however, operative and the presenence of ferric oxide sol sould very much influence gelation with the result that the setting time varies with the change in concentration of ferric oxide sol.

Interesting results are obtained on adding alumina sol to the mixture of ferric oxide-silica sols (Table 3).

Table 3

Data on pH and time of setting of different iron oxide alumino-silicate gel forming mixtures

| Molar ratio $SiO_2/Al_2O_3 + Fe_2O_3$ | Time of abrupt changes from viscosity data (minutes) | Initial pH | Final pH |
|---|---|---|---|
| 4.45 : 1 | 270 | 2.08 | 2.9 |
| 4.22 : 1 | 330 | 2.08 | 2.9 |
| 4.00 : 1 | 396 | 2.02 | 2.9 |
| 3.83 : 1 | 463 | 2.00 | 2.9 |
| 3.66 : 1 | 560 | 2.00 | 2.9 |
| 3.50 : 1 | 680 | 2.00 | 2.9 |
| 3.33 : 1 | 840 | 1.85 | 2.9 |
| 3.23 : 1 | 1020 | 1.85 | 2.9 |
| 3.12 : 1 | 1200 | 1.80 | 2.9 |

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[12]) J. G. VAIL, "Soluble silicate" (A.C.S. Monograph Series, New York, Reinhold publishing Corp. 1952, Vol. I and II).

It appears that alumina competes with ferric oxide in the formation of mixed gels. Irrespective of the amount of ferric oxide in silica-ferric oxide mixture, the presence of a little amount of alumina brings down the pH to 2.9 which is specific for the formation of aluminosilicate. This means the presence of alumina checks the polymerisation of silicic acid to a very great extent and helps in the formation of metal silicates. The time of setting also starts decreasing instead of increasing after the addition of alumina.

The mixed Iron oxide-aluminosilicate gel shows a thixotropic behaviour, indicating the formation of a uniform reversible gel of the mixed type. The plot of log t against concentration of $Al_2O_3 + Fe_2O_3$ (Fig. 3, curve 3) gives a straight line with $A = 0.91$ and $B = -1.40$ in FREUNDLICH relationship.

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