

Studies on the Sol-gel Transformation of Ferric Hydroxide Sol in Presence of Dyes

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With 4 Figures

Summary

The influence of dyes on the gelation of ferric hydroxide sol has been studied with the help of viscometric, pH metric and cataphoretic methods. From these studies it has been concluded that out of the four dyes it is only alizarin sulphonic acid which brings about appreciable change in the above physical properties. The results have been interpreted in terms of structural changes in the dye molecule. Positive adsorption is found to take place in all cases except malachite green which is negatively adsorbed on the gel. In the case of alizarin sulphonic acid the adsorption data do not fit in well either in LANGMUIR or FREUNDLICH adsorption isotherms.

Investigations on the sol-gel transformation of inorganic gel forming systems containing dyes have not so far been studied. The few references available in the existing literature do not deal with this aspect of the problem but describe the influence of dyes on the stability of hydrophobic sols. Since hydrous oxide sols are widely employed as mordants, the study of their gelation in presence of acid and basic dyes was considered worth attempting. In this paper the results of the studies on the interaction of alizarin sulphonic acid, methyl orange, malachite green and methylene blue dyes with ferric oxide sol employing pH metric, viscometric and cataphoretic studies have been discussed.

Apparatus and Technique

The viscosity measurements were carried out by using SCARPA's method¹⁾, pH measurements were made with a Cambridge bench pH meter. Adsorption measurements were carried out by Bausch and Lomb "Spectronic 20".

Cataphoretic measurements: BURTON's method²⁾ recommended by FREUNDLICH³⁾ for determining the cataphoretic velocity of colloidal particles was employed.

¹⁾ SCARPA, Gazz. chim. Ital. **40**, 271 (1910).

²⁾ BURTON, "Burton's Colloidal Solution" 3rd edition, p. 173, London (1938).

³⁾ FREUNDLICH, Z. phys. Chem. **85**, 398 (1913).

Discussion

Before discussing the experimental results on the sol-gel transformation of ferric hydroxide 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 (Fig. 1)

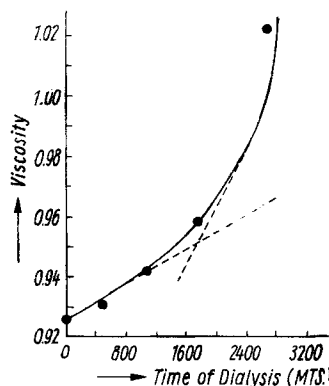


Fig. 1

would reveal that after a certain stage of dialysis there is an abrupt increase in viscosity. It is at this stage that conditions necessary for the conversion of the sol into a gel are realized. The time after which this change takes place 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 gel forming mixture to set into a gel. A perusal of the data (Table 1) would reveal that the time of setting becomes minimum (10 hrs) only when the sol has been dialysed beyond the gelation time.

Table 1

Time of setting and gelation time for dialysed Fe_2O_3 sol

Time of dialysis (mts.)	Time of setting by FLEMMING'S method	Viscosity (centipoise)	Gelation time from curve between time of dialysis and viscosity
0	—	0.926	1740 mts. (29 hrs.)
480	—	0.931	
1080	—	0.943	
1740	24 hrs.	0.959	
2640	10 hrs.	1.023	

Undoubtedly variations in viscosity of colloidal systems may be explained in the light of factors, viz., solvation, electroviscous effect, adhesion 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 or mixture of two different sols. In such cases due consideration has to be given to structural changes accompanying the interaction of the different chemical entities present therein. As will be seen from the discussion given below that simple techniques like viscosity, pH and electrophoresis may be usefully employed to elucidate a few aspects of the problem.

The data on the viscosities of sol-dye mixtures may be considered 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.

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 certain concentration of the acid dye viz., 1.0 mM/litre and 2.33 mM/litre of the basic dyes the extent of variations in different cases are as shown in Table 2.

From the Table 2 it is evident that in the case of pure sol the extent of increase in viscosity for a period of dialysis larger than the gelation time, say, 2640 mts (44 hrs) is 10.4% while the extent of increase in viscosity in the case of methyl orange and alizarin sulphonic acid (anionic dyes) is 8.9% and 25% respectively. With basic dyes e.g. methylene blue and malachite green the extent of increase in viscosity is 7.7% and 8.7% respectively. From these results it is evident that out of the four dyes it is only alizarin sulphonic acid which brings about appreciable increase in viscosity.

Cataphoretic studies under similar conditions show that in the case of pure sol the extent of decrease in ζ -potential is 62.4%, the extent of increase in ζ -potential in the case of methyl orange, alizarin sulphonic acid, methylene blue and malachite green is 63.2%, 2.9%, 69.0% and 45.2% respectively.

The increase in viscosity and decrease in ζ -potential in the case of pure sol can be explained simply in terms of hydration or solvation although electroviscous effects may also be operative. With progressive dialysis the stabilizing ions necessary to keep the sol stable are removed which result in the increase in viscosity and the decrease in ζ -potential. According to KRUYT and BRIGG⁴) the ζ -potential is related to the stability of the system.

In the case of complex systems the only effective way of having such an increase in viscosity and ζ -potential with small amount of suspended material (2.49% Fe₂O₃) can, therefore, be explained in terms of the aggregates formed by the interaction of dyes with sol. For ascertaining this the results on the change in viscosity and ζ -potential with concentration after a fixed period of dialysis are worth considering.

⁴) KRUYT and BRIGGS, Proc. K. Akad. Wetensch. **32**, 372 (1929).

Table 2
 Variations in viscosity and ζ -potential with dialysis of ferric oxide sol-dye mixture
 Conc. of sol = 24.9 gms Fe_2O_3 per litre

Time of dialysis (mts.)	Viscosity pure sol (centipoise)	ζ -potential pure sol (volts)	Viscosity sol + me-thyl orange mixture (centipoise)	ζ -potential sol + me-thyl orange mixture (volts)	Viscosity sol + aliz. s. acid mixture (centipoise)	ζ -potential sol + aliz. s. acid mixture (volts)	Viscosity sol + me-thylene blue mixture (centipoise)	ζ -potential sol + me-thylene blue mixture (volts)	Viscosity sol + mala-chite green mixture (centipoise)	ζ -potential sol + mala-chite green mixture (volts)
0	0.926	5.07×10^{-8}	0.939	2.57×10^{-8}	0.950	5.21×10^{-8}	0.924	1.27×10^{-8}	0.941	1.28×10^{-8}
480	0.931	3.83×10^{-8}	0.939	2.57×10^{-8}	0.957	5.24×10^{-8}	0.927	2.54×10^{-8}	0.949	1.27×10^{-8}
1080	0.943	2.58×10^{-8}	0.954	2.61×10^{-8}	0.967	6.20×10^{-8}	0.936	3.86×10^{-8}	0.950	2.60×10^{-8}
1740	0.959	2.12×10^{-8}	0.974	4.20×10^{-8}	1.00	5.49×10^{-8}	0.970	4.00×10^{-8}	0.962	2.70×10^{-8}
2640	1.023	2.00×10^{-8}	1.023	7.00×10^{-8}	1.18	5.36×10^{-8}	0.995	4.09×10^{-8}	1.03	2.82×10^{-8}

Table 3

Variations in viscosity, pH and ζ -potential with dialysis of ferric oxide sol-dye (anionic) mixture

Conc. of dye mM/lit.	Viscosity sol + aliz. s. acid mixture (centipoise)	ζ -potential sol + aliz. s. acid mixture (volts)	pH sol + aliz. s. acid mixt.	Viscosity sol + methyl orange mixture (centipoise)	ζ -potential sol + methyl orange mixture (volts)	pH sol + methyl orange mixture
0	1.02	2.00×10^{-8}	5.28	1.02	2.00×10^{-8}	5.28
0.33	0.99	2.31×10^{-8}	5.34	—	—	—
0.66	0.99	5.09×10^{-8}	5.32	1.17	8.02×10^{-8}	5.34
1.00	1.18	5.36×10^{-8}	5.36	1.02	7.00×10^{-8}	5.28

Table 4

Variations in viscosity, pH and ζ -potential with dialysis of ferric oxide sol-dye (cationic) mixture

Conc. of dye mM/lit.	Viscosity sol + methylene blue mixt. (centipoise)	ζ -potential sol + methylene blue mixt. (volts)	pH sol + methylene blue mixt.	Viscosity sol + malachite green mixt. (c.p.)	ζ -potential sol + malachite green mixt. (volts)	pH sol + malachite green mixt.
0	1.023	2.00×10^{-8}	5.28	1.02	2.00×10^{-8}	5.28
1.66	1.04	9.96×10^{-8}	5.28	1.03	5.03×10^{-8}	5.31
2.00	1.00	8.23×10^{-8}	5.18	1.06	4.37×10^{-8}	5.25
2.33	0.995	4.09×10^{-8}	5.15	1.03	2.82×10^{-8}	5.18

A plot of concentration of dye against viscosity would reveal that the viscosity of the dialysed sols vary slightly from the viscosity of the original sol. In the light of these observations it may be argued that the gelation of ferric oxide sol is not dependent on the concentration of the dye present. In the case of alizarin sulphonic acid the presence of even a small amount of the dye was quite enough to make it more viscous on dialysis than the untreated sol. The variations in ζ -potential (Fig. 2) also support the fact

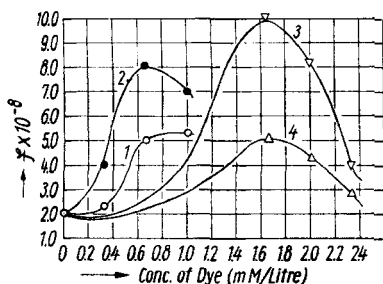


Fig. 2. Variations in ζ -Potential. \circ Aliz. s. acid and Fe_2O_3 sol, \bullet Me. orange and Fe_2O_3 sol, ∇ Meth. blue and Fe_2O_3 sol, \triangle Mal. green and Fe_2O_3 sol.

that the gelation tendency of the sol can not be enhanced merely by increasing the amount of the dye. On the otherhand the sol after attaining optimum condition for gelation gets more peptized on the addition of the dye. The fact that the dialysed sample of ferric oxide remains unattacked by the dye is also supported by the fact that no appreciable change in pH takes place on the gradual addition of the dye. It means that adsorption of the dyes on the ferric oxide gel does not take place otherwise it would have resulted in the release of H^+ from the inner part of the sol and consequent decrease in pH.

Another factor worth taking into account while explaining the gelation tendency of ferric oxide sol in presence of dyes is the structure of the dyes and the molecular rearrangements they may undergo in the different pH ranges. Since the ferric oxide sol has a fairly low pH (3.76), the dye molecule may either undergo protonation or is reoriented to give the quinonoid structure.

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 deepening of the colour resulting into bluish pink colour which may be due to the adsorption of its cationic part on the sol particles. Similar behaviour with malachite green is observed but here the change in colour are observed only after keeping the sol-dye mixture for some time. With alizarin sulphonic acid the colour of the sol changes from light yellow to blood red while in the case of methyl orange it changes from yellow to deep red.

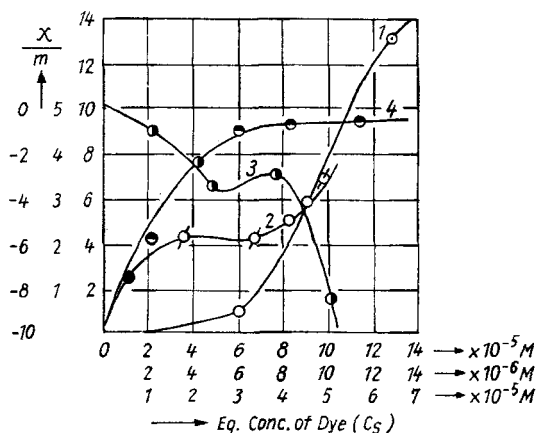
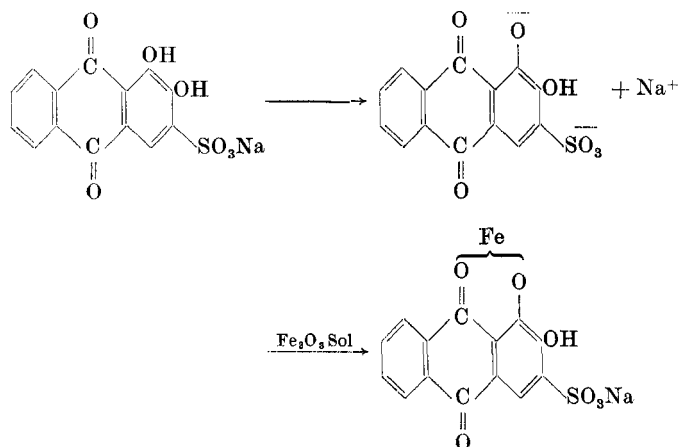


Fig. 3. 1 = Fe_2O_3 gel and me. or. 2 = Fe_2O_3 gel and M. Blue. 3 = Fe_2O_3 gel and M. G. 4 = Fe_2O_3 gel and Ali₃ s. acid.

Alizarin sulphonic acid is well known for its tendency to form colour lakes with metal hydrous oxide sols through exchange adsorption. The only possible way in which alizarin sulphonic acid can influence the gelation of

Fe_2O_3 can therefore, be through compound formation. Since a change in the original colour of the dye from light yellow to blood red takes place on the addition of the sol, it appears that a mechanism involving the combination of the sol particles with the dye is as follows,



In the case of alizarin sulphonic acid the adsorption data do not fit well either in LANGMUIR or FREUNDLICH adsorption isotherm (Fig. 3 and 4, curve 4 and 3) showing the possibility of chemisorption or interstitial adsorption. In the case of methyl orange and methylene blue the data fit in well in LANGMUIR isotherm (Fig. 3 and 4, curve 1, 2, 2). On the otherhand with malachite green negative adsorption is observed (Fig. 3, curve 3).

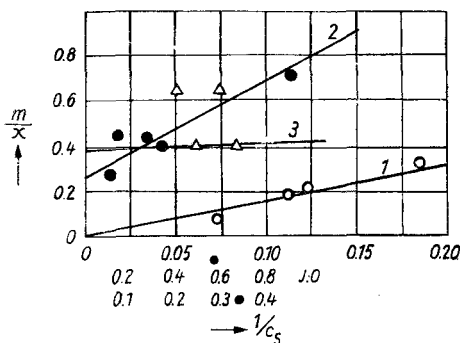


Fig. 4. 1 = Fe_2O_3 gel and me. or. 2 = Fe_2O_3 gel and M. Blue. 3 = Fe_2O_3 gel and Ali₃ s. acid.

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