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Studies on the Sol-Gel Transformation of Aluminium Hydroxide in the Presence of Dyes

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The influence of dyes on the gelation of aluminium hydroxide sol has been studied with the help of viscometric and pH metric methods. From these studies it is inferred that the behaviour of acid dyes towards alumina is different from that of basic dyes. The results have been interpreted in terms of various structural changes taking place in the dye molecule. Adsorption studies reveal that the data do not fit well into the Langmuir or Freundlich adsorption isotherm equation in the case of alizarin sulphoric acid, while in the cases of methyl orange, methylene blue, and malachite green, the data are found to fit well into the Langmuir adsorption equation.

A large amount of work has been done on the adsorption of dyes, especially of the alizarin class, on hydrous oxide sols. Mokuskin and Esin,1) White and Gorden,2) and Porter3) have studied the association of several dyes with hydrous oxides. Weiser4) has also made several studies in this direction. Other problems, however, for instance, the nature of the binding between sol and dye, the determination of the miceller size of hydrous oxide sols by dye interaction, and the influence of dyes on the gelation of sols, have not yet been comprehensively studied. In the present paper the results of the gelation of aluminium hydroxide in the presence of acid (alizarin sulfonic acid and methyl orange) and basic (methylene blue and malachite green) dyes are reported.

Experimental

Reagents. *(a) Aluminium Hydroxide Sol.* Positively-charged aluminum hydroxide sol was prepared by the method described by Weiser.5) 10 g of aluminium chloride (E. Merck) was dissolved in 500 cc of doubly-distilled water, and the resulting solution was heated to boiling. Aluminium hydroxide was precipitated with a slight excess of ammonia, and the suspension was boiled for five minutes. The precipitate was then placed in a centrifuge tube and suspended in doubly-distilled water, after which the suspension was centrifuged for 15 min. The supernatant liquid was poured off, doubly-distilled water was again added, and the precipitate was washed. The process of washing was repeated many times. The precipitate was then transferred to a 500 cc Pyrex beaker and suspended with doubly-distilled water. The suspension was then heated to boiling. The precipitate of $Al_2O_3 \cdot xH_2O$ was peptized to alumina sol by gradually adding 0.2 N HCl in 1 cc portions and boiling the solution for ten minutes after each addition. The pH of the solution containing the alumina sol was lowered to the required value by the addition of the requisite amount of a 0.1 N HCl solution. The concentration of alumina in the colloidal solution was determined gravimetrically6) by precipitating it

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1) G. W. Mokuskin and G. L. Esin; *J. Russ. Phys. Chem. Soc.*, **58**, 882 (1926); *Kolloid-Z.*, **41**, 104 (1927).

2) P. L. Marker and G. Gorden, *Ind. Eng. Chem.*, **16**, 1188 (1924); C, E. White and G. Gorden, *J. Phys. Chem.*, **31**, 1764 (1927).

3) J. L. Porter *J. Phys. Chem.*, **31**, 1704 (1927).

4) H. B. Weiser, *ibid.*, **26**, 401 (1922).

5) H. B. Weiser, *ibid.*, **26**, 525 (1926).

6) A. I. Vogel, "A Text Book of Quantitative Inorganic Analysis," 2nd edition, Longman's Green and Co., London, p. 410; and W. W. Scott, "Standard Method of Chemical Analysis" Vol. 1, ed. by H. Furman, D. Van Nostrand Company, Inc., New York (1945), p. 9.

as $Al_2O_3\cdot xH_2O$ in the pH range 7—7.5 and by then igniting the precipitate to Al_2O_3.

b) The dyes, alizarin sulphonic acid (sod. salt), methyl orange (sod. salt), methylene blue (chloride), and malachite green (chloride) were either B. D. H. or Merck products.

Apparatus and Technique. The viscosity measurements were carried out using a modification of Scarpa's method.[7] The pH measurements were made with a Cambridge bench pH-meter. Adsorption experiments were carried using the Bausch and Lomb "Spectronic 20."

Procedure. 2.0×10^{-2} M stock solutions of the dyes (alizarin sulphonic acid, methyl orange, methylene blue and malachite green) were prepared in doubly distilled water and kept in all-Pyrex glass vesseles. The following sets of mixtures were used for gelation measurements. (i) 20 cc sol + a varying amount of the dye (0, 0.5, 1.0, and 1.5 cc of 2.0×10^{-2} M methyl orange); (ii) 20 cc of sol + a varying amount of the dye (0.5, 1.0, and 1.5 cc of 2.0×10^{-2} M alizarin sulphonic acid); (iii) 20 cc sol + a varying amount of the dye (0.5, 1.0, and 1.5 cc of 2.0×10^{-2} M methylene blue); (iv) 20 cc sol + a varying amount of the dye (0.5, 1.0, and 1.5 cc of 2.0×10^{-2} M malachite green). In each case the total volume was made up to 30 cc with doubly-distilled water.

The viscometric and pH metric studies were carried out at 30±0.1°C during the dialysis of the above sets (i, ii, iii and iv in) different dialysing bags of the same size.

Dye Adsorption Measurements. The alumina gel (the adsorbent) was prepared by the continuous dialysis of the sol, and then dried between 50 and 80°C. The finely powdered gel was weighed and presoaked in a small quantity of doubly-distilled water prior to the addition of a dye solution. The following sets of mixtures were prepared: (i) 100 mg of alumina gel + a varying amount of the dye (1.0, 2.0, 3.0, 4.0, and 5.0 cc of 1.5×10^{-4} M alizarin sulphonic acid); (ii) 100 mg of alumina gel + a varying amount of the dye (1.0, 2.0, 3.0, 4.0, and 5.0 cc of 4.51×10^{-5} M methyl orange); (iii) 100 mg of alumina gel + a varying amount of the dye (1.0, 2.0, 3.0, 4.0, and 5.0 cc of 3.14×10^{-5} M methylene blue); (iv) 100 mg of alumina gel + a varying amount of the dye (1.0, 2.0, 3.0, 4.0, and 5.0 cc of 1.96×10^{-5} M malachite green). In each case the total volume was made up to 10 cc with doubly-distilled water.

Adsorption isotherms were run by making successive additions of 1.0, 2.0, 3.0, 4.0, and 5.0 cc of the dye solution to 100 mg of alumina gel. The adsorbent and the dye solution were agitated to equilibrium after each addition of dye prior to a colorimetric measurement of the dye solute. The volume of the solutions was 10 cc. The readings were made after a sufficient time of mixing, when the solution had attained equilibrium. The equilibrium solutions were then centrifuged for transmittance measurements.

Discussion

Before discussing the experimental findings on the sol-gel transformation of aluminium hydroxide in the presence of dyes, it is worthwhile considering the behaviour of the pure sol when converted into a gel by prolonged dialysis. A plot of the time of dialysis against the viscosity (Fig. 1) reveals that, after a certain stage of dialysis, there is an abrupt increase in the viscosity. This means that with a progressive dialysis the optimum conditions necessary to bring about gelation are realized, and that the time after which an abrupt increase in viscosity takes place may conveniently be termed the "gelation time"[8,9] (it is quite distinct from the time of the setting of a gel-forming mixture).

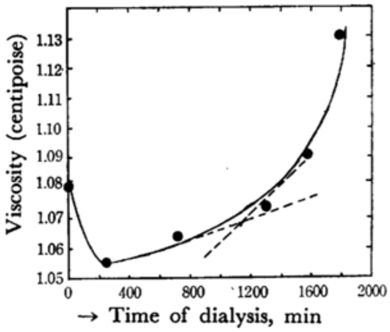

Fig. 1

The data (Table 1) show that, although the time of setting is different for samples subjected to dialysis for different time intervals (the minimum time being 4.5 hr), when samples are dialysed for 30 hr, the time required for all the samples of one mixture to attain the optimum conditions for gelation had the same value, ranging between 1040 and 1300 min.

Although an abrupt rise in viscosity in colloidal systems may be explained in the light of several factors, the solvation, the electroviscous effect, and adhesion of particles, *etc.*, in the case of pure sol, a forthright explanation is difficult in complex systems comprising mixtures of a sol and a foreign substance, or of two different sols. In such cases due consideration has to be given to structural changes accompanying the interaction of the different chemical entities involved besides the factors enumerated above.

Gelation of an Alumina Sol - Dye Mixture. With (acid or) anionic dyes the viscosity of the mixtures first decreases, and then increases near the gelation time, while with (basic or) cationic dyes the behaviour is quite different: the viscosity shows an initial decrease, followed by a gradual increase. These data may be discussed from the following two angles. (i) the variation in the viscosity with a progressive dialysis in the presence of a fixed amount of dye, and (ii) a change in the

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7) O. Scarpa, *Gaz. Chim.*, **40**, 271 (1910).

8) W. U. Malik and F. A. Siddiqui, *J. Phys. Chem.*, **66**, 357 (1962).

9) W. U. Malik and F. A. Siddiqui, *Kolloid-Z.* (U. Z. polymer), **184**, 41 (1962).

TABLE 1. TIME OF SETTING AND GELATION TIME FOR DIALYSED ALUMINA SOL AT pH=3.7

Time of dialysis	Time of setting by Fleming's method	Viscosity (centipoise)	Gelation time as determined from the abrupt rise in viscosity
0	—	1.081	1040 to 1300 min
4.25 hr (255 min)	—	1.060	
12.25 hr (735 min)	—	1.063	
22.5 hr (1300 min)	24 hr	1.074	
26.2 hr (1575 min)	20 hr	1.091	
30.0 hr (1800 min)	4.5 hr	1.13	

TABLE 2. VARIATIONS IN VISCOSITY WITH DIALYSIS OF ALUMINA SOL - DYE MIXTURE CONTAINING 1.0 mmol/l OF DYE

Time of dialysis min	Viscosity				
	Pure sol (centipoise)	Sol + methyl orange (centipoise)	Sol+aliz. s. acid (centipoise)	Sol + methylene blue (centipoise)	Sol + malachite green (centipoise)
0	1.08	2.12	2.30	1.08	1.09
255	1.06	1.55	1.64	1.08	1.07
735	1.06	1.32	1.56	1.07	1.06
1300	1.07	1.26	1.47	1.06	1.07
1575	1.09	1.18	1.47	1.08	1.13
1800	1.13	1.20	1.50	1.08	1.13

TABLE 3. VARIATIONS IN VISCOSITY AND pH OF A DIALYSED ALUMINA SOL CONTAINING VARYING AMOUNTS OF DYES

Concn. of dye mmol/l	Sol + methyl orange mixture		Sol + aliz. s. acid mixture		Sol + methylene blue mixture		Sol + malachite green mixture	
	Viscosity (centipoise)	pH	Viscosity (centipoise)	pH	Viscosity (centipoise)	pH	Viscosity (centipoise)	pH
0	1.09	5.40	1.09	5.40	1.09	5.40	1.09	5.40
0.33	1.12	4.47	1.05	4.69	1.04	4.72	1.05	4.76
0.66	1.17	4.52	1.09	4.55	1.10	4.71	1.07	4.74
1.0	1.18	4.57	1.47	4.37	1.08	4.60	1.13	4.84

viscosity with gradually increasing amounts of the dye in a sol dialysed for a fixed period of time. In (i) a continuous decrease in viscosity with dialysis is observed with acid dyes, the extent to which this change takes place being dependent on the nature of the dye employed. In the presence of a fixed concentration of the dye, 1.0 mmol/l, the following variations are observed.

On considering the viscosity data for samples dialysed for a period greater than the gelation time of the pure sol (say, 30 hr), it will be seen that there is considerable decrease in viscosity, 42.5% and 36.0% in the cases of methyl orange and alizarin sulphonic acid respectively, although there is an overall increase of 0.92% in the case of pure sol. With the basic dyes the results are different; the viscosity changes are very small, and only slight increases in viscosity are observed (0.18% for methylene blue and 3.4% for malachite green).

The decrease in viscosity on prolonged dialysis may be explained in terms of peptization. The

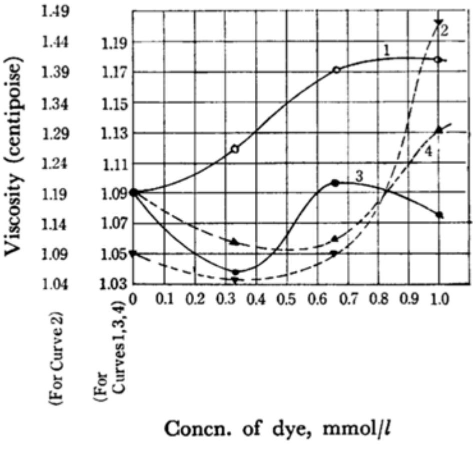

Fig. 2

○ 1. Al_2O_3sol + methyl orange mixture
▼ 2. Al_2O_3sol + aliz. S. acid mixture
● 3. Al_2O_3sol + methylene blue mixture
▲ 4. Al_2O_3sol + mal. green mixture

dye used may prevent agglomeration by the adsorption of the anionic part of the dye on the sol particles, which may keep the sol in the stable state and not allow it to undergo gelation. These data are supported by the work of Ghosh and his coworkers,10) who observed that hydrous oxides, especially of the amphoteric type, develop a large adsorption capacity for anions. The findings on the changes in viscosity and pH with a variation in the concentrations of dyes after a fixed period of dialysis are worth considering.

Figure 2, indicates that the final viscosity increases with an increase in the concentration of the dye, in the cases, of both methyl orange (Curve 1) and alizarin sulphonic acid (Curve 2), although the natures of the two curves are different; in the case of alizarin sulphonic acid viscosity slightly decreases in the initial state (Table 3, Column 4), while in the case of methyl orange there is a continuous increase in viscosity. With basic dyes the behaviour is quite different; that is, the concentration-viscosity curve shows a decrease over a wide concentration range, followed by an abrupt increase in the case of malachite green (Curve 4), while there is an initial decrease, followed by an increase and then a slight decrease again, in the case of methylene blue (Curve 3). The difference in the nature of the products obtained with basic and acid dyes is also evident from the stability curves (a plot of the stability against C_e, where C_e is the concentration of the dye). That is, the stability of the sol increases slightly and then dedecreases rapidly with an increase in the concentration of the dye in the case of basic dyes, but in the case of acid dyes no such decrease is marked (Fig. 3, Curves 1 and 2).

Another factor worth taking into account in explaining the gelation tendency of alumina in the presence of dyes in the structure of the dyes and the molecular rearrangements in the different pH ranges. Since the alumina sol has a fairly low pH, the dye molecule may either undergo protonation or reorientation to give the quinoidal structure.

Preliminary experiments have shown that methylene blue does not change its colour in either an acidic or a basic medium. The addition of sol, however, brings about a slight fading of the coluor, indicating the possibisity of adsorption. The change in the pH of the sol upon addition of methylene blue supports this view (Fig. 4, Curve 3). The behaviour with malachite green can 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 interaction between the dye and the sol.

With acid dyes a lake formation takes place. The alizarin lakes of the hydrous oxides are ordinarily formed by an exchange adsorption process

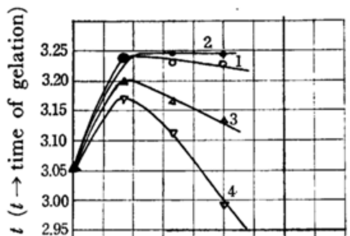

Fig. 3.

Stability curves
○ 1. Al_2O_3 sol + methyl orange
● 2. Al_2O_3 sol + aliz s. acid
△ 3. Al_2O_3 sol + methylene blue
▽ 4. Al_2O_3 sol + mal. green

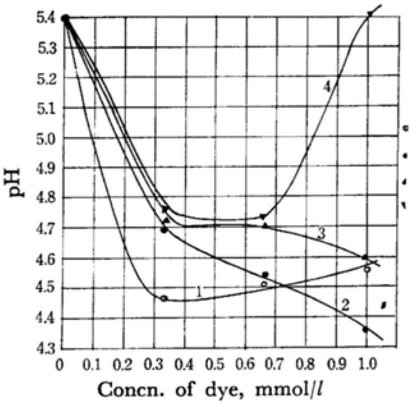

Fig. 4

○ 1. Al_2O_3 sol + methyl orange
● 2. Al_2O_3 sol + aliz. s. acid
▲ 3. Al_2O_3 sol + methylene blue
▼ 4. Al_2O_3 sol + mal. green

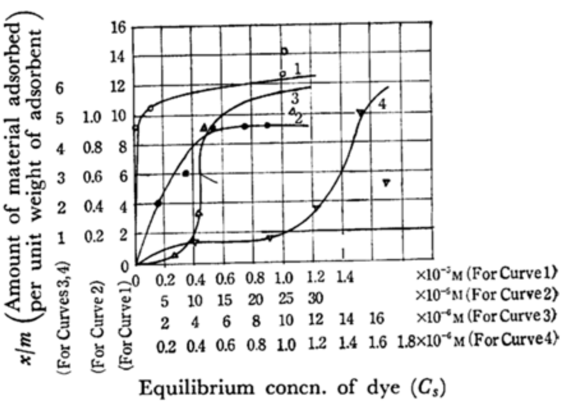

Fig. 5

○ 1. Al_2O_3 gel + aliz. s. acid
● 2. Al_2O_3 gel + methyl orange
△ 3. Al_2O_3 gel + methylene blue
▽ 4. Al_2O_3 gel + mal. green

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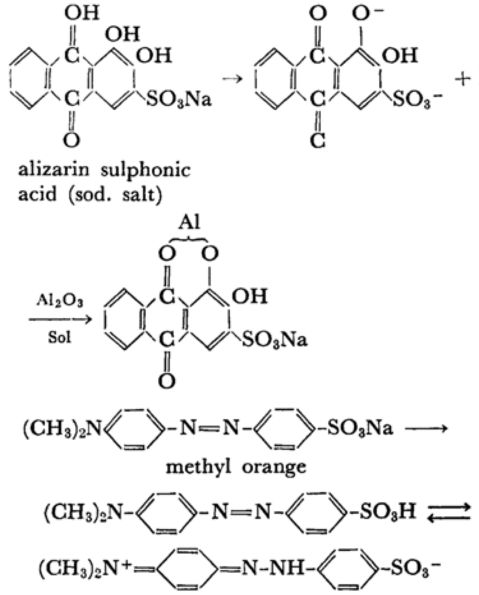
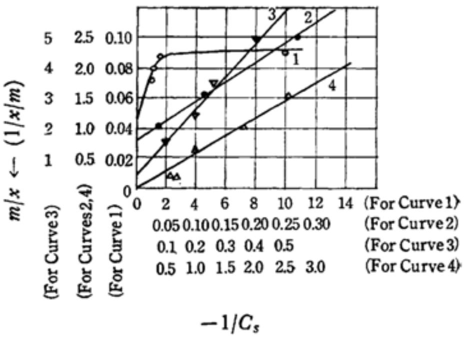
10) S. Ghosh *et at.*, *Z. anorg. u. allgem. Chem.*, **271**, 150 (1952).

in which the relatively strongly-adsorbed alizarate ions displace such more weakly desorbed ions as chloride from the hydrous oxide. According to the view of Morgan,[11] the alizarin lakes are definite metal chelate compounds.

The various changes taking place can be represented by the following scheme:





C_s (Equilibrium concn. of dye)

Fig. 6

○ 1. Al_2O_3 gel + ariz. S. acid
● 2. Al_2O_3 gel + methyl orange
▽ 3. Al_2O_3 gel + methylene blue
△ 4. Al_2O_3 gel + mal. green

In the case of alizarin sulphonic acid, the data on adsorption do not fit well into either the Langmuir or the Freundlich adsorption equation (Figs. 5 and 6, Curve 1). The extent of adsorption in this case is probably more closely related to the chemical nature of the substances than to their molecular size or molecular weight. In the case of methyl orange, methylene blue, and malachite green, the data are found to fit the Langmuir adsorption equation well (Figs. 5 and 6, Curves 2, 3, and 4 respectively).

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[11] G. T. Morgan and J. D. Wain-Smith, *J. Chem. Soc.*, **119**, 704 (1921); **121**, 160, 1956, 2857, 2866 (1922).