

OPACITY CHANGES DURING THE SOL-GEL TRANSFORMATION OF SOAP-PINENE SYSTEMS

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PRASAD *et al.*³ have investigated systematically the opacity changes taking place during the sol-gel transformation of several inorganic gel-forming systems. In their earlier work, they determined the extinction coefficients of gel-forming systems, but later they measured the changes in opacity using either a thermopile or an amplified photo-cell unit, and more recently by using a compensated photo-electric arrangement in which all possible errors are avoided. Their extensive studies have shown that there are two types of gels, (i) those that increase, and (ii) those that decrease, in opacity, during gelation. The changes in opacity taking place during gelation have been attributed by them to changes in the size, shape and state of aggregation of the gel particles during the formation of gels.

The intensity of light scattered by gel-forming solutions of gelatin and agar-agar, and the extent to which it is depolarized, have been investigated by Krishnamurthy,¹ using incident light unpolarized. He finds that the particles in the gel state are bigger and/or greater than those in the sol state. Prasad and Guruswamy⁴ have investigated the intensity and depolarization factors of scattered light using unpolarized, and horizontally and vertically polarized light, during the sol-gel transformation of several inorganic gel-forming substances in water, and report a continuous increase in micellar size with progress of gelation, the increase continuing in some cases even after the gel had set.

The effects of various factors which influence the process of gel-formation have been studied by Mardles² who has measured the changes in the Tyndall Number during the sol-gel transformation of cellulose acetate in benzyl alcohol. He finds that the curves obtained on plotting the Tyndall Number against the concentration rise at first, reach a maximum, and then fall, the peak of the curve indicating the existence of an optimum concentration at which maximum particle size is obtained. Similar maxima are revealed in the curves of Tyndall Number against temperature.

Gels of alkali soaps in pinene were prepared for the first time by Prasad *et al.*, and the results of their investigations on several properties of these gels have been published in a series of papers in the *Proceedings of the Indian Academy of Sciences*.^{5, 6} The opacity changes taking place during the gel-formation of these soap-pinene systems have been investigated by the author with a view to determining the mechanism of formation of these gels, as also the manner in which the size, number and degree of solvation of the colloidal particles change during setting.

MATERIALS USED

Sodium oleate and sodium palmitate used were pure products of the B. D. House, whereas sodium stearate was obtained from Messrs. E. Merck & Co; pinene was a product of Messrs. Eastman Kodak & Co., and was the fraction distilling at 156° C.

EXPERIMENTAL TECHNIQUE

The opacity measurements were made by means of a Klett-Summerson glass-cell photo-electric colorimeter. A projection-type electric lamp (100 watts; 230 volts) fitted with a blue filter (400 to 465 millimicrons) was used as the source of light, and the current produced by the photo-cells was measured by means of a suspension-wire type galvanometer. The opacity or intensity of transmitted light was measured in terms of the divisions on the potentiometer slide-wire which are necessary to nullify the torsion applied to the galvanometer needle. The instrument was found to yield results of considerably high accuracy; several observations, taken with the same system under identical conditions, did not differ by more than ± 0.3 per cent. These results therefore represent fairly accurately the changes in opacity which take place in the gel-forming systems during setting.

The experimental procedure adopted was as follows: the instrument was corrected for the zero error and the galvanometer needle brought to the zero position. Gel-forming solutions containing different known amounts of a soap in 10 c.c. of pinene were prepared, as described by Prasad and Hattiangdi,⁵ in the glass-cell, provided with the instrument, which was then immediately placed in position. The lamp was switched on and the opacity values were determined at successive known intervals of time until the system attained a constant value of opacity at the room temperature (30° C.).

The results obtained for systems containing different amounts of sodium oleate and sodium stearate are presented graphically in Figs. 1 and 2 in which the values of opacity are plotted against time.

DISCUSSION OF RESULTS

It will be noticed from the data presented in Figs. 1 and 2 that the values of opacity increase with time during the setting of sodium oleate and sodium stearate gels. It was found that the opacity of systems containing 0.045 g., 0.055 g., and 0.065 g. of sodium palmitate did not change at all with time throughout the process of gel-formation. This anomalous behaviour is due to the fact that whereas the former two soaps dissolve in pinene to give clear mobile solutions, sodium palmitate does not dissolve completely even at the boiling point of pinene. The latter exists as a sufficiently viscous system, and on cooling it, the fairly solvated aggregates of soap particles which are dispersed in this system, coalesce and set to a gel; hence, its opacity does not undergo any change during the process of gel-formation.

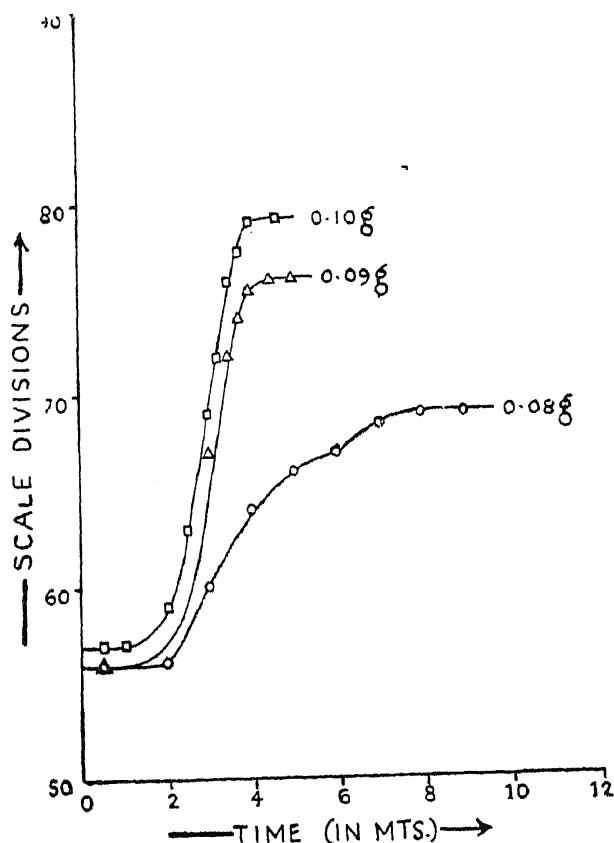


FIG. 1. Sodium Oleate in Pinene

The various opacity-time curves in Figs. 1 and 2 rise very slowly at first, then very rapidly and once again very slowly to reach an almost constant value of opacity. At this stage, for systems containing 0.08 g. of the soap, the curves rise sufficiently rapidly once again and later on tend to run parallel to the time axis. The general nature of the latter curves is thus different from the S-shaped curves reported by previous workers.

The nature of the various opacity-time curves can be explained as follows: Prasad *et al.*⁶ have found that sodium oleate and sodium stearate form true solutions in pinepe at its boiling point and that they exist in this state until the temperature has fallen down to about 110° C. or a little lower. The approximate constancy in the initial opacity values is due to the fact that the absorption of light by true molecular solutions does not change unless saturation or suspended particles interfere. Even if primary colloidal particles are formed during this period of initial cooling, their size as well as their number will be extremely small, and hence the opacity values will not be affected appreciably.

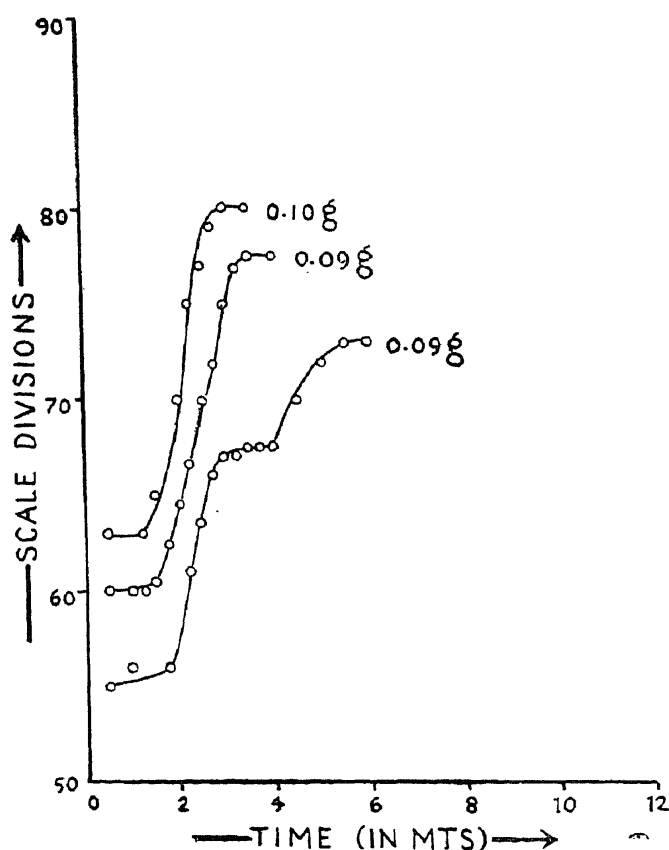


FIG. 2. Sodium Stearate in Pinene

Further cooling of these solutions increases their degree of super-saturation and causes the formation of a number of colloidal particles. An increase in the size and number of these particles brings about the observed rapid rise in opacity with time which persists until both the size and the number of the particles have reached almost the maximum value. After this period, the particles take up plenty of the dispersion medium and the micelles become heavily solvated. During this process of solvation, the changes in the intensity of the scattered light are not large for reasons of

refractive index, and hence the opacity increases rather slowly to reach almost a constant value; this is indicated by the portion of the curve which tends once again to run parallel to the time axis. This period was found to coincide approximately with the setting time of the gel system determined by other methods.

The peculiar behaviour exhibited by systems containing 0.08 g. of sodium oleate and sodium stearate, that is the sudden change in the direction of the curves, is very interesting and is caused probably by the structural changes which take place in these set gels on further cooling. The curves show that these changes are rapid at first, and then slow down until a final structure is formed. It is not very easy to visualise as to how these structural changes actually take place. However, in view of the fact that these gels set at a temperature much higher than the room temperature, it can be surmised that the structural changes are brought about on account of the separation of the soap from the state of solution or suspension which exists either in the intermicellary or in the inter-fibrillary liquid.

It is evident from the several curves in Figs. 1 and 2 that as the soap content of the gel-forming systems is increased, (i) the changes in opacity take place at a quicker rate and the final constant value is obtained earlier, and (ii) the change in direction of the curves after the S-shaped portion has been completed, which is predominant at lower concentrations, appears to flatten out and is not noticeable. This may be due to the fact that in the case of gels of larger soap content, the rate of the structural changes in these gels, or in other words the rate of growth of the particle size, after the setting point has been reached is the same as that prior to gelation.

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SUMMARY

Measurements of the opacity changes with time taking place during the gel-formation of some soap-pinene systems yield opacity-time curves which change their nature considerably with variations in concentration. The curves obtained for systems of high concentrations are S-shaped whereas those for low soap content show a distinct change in direction after the S-shaped stage is reached. The curves for sodium oleate and sodium stearate gels in pinene are very similar in their general characteristics but the opacity values for the sodium palmitate-pinene systems remain constant

throughout the process of gel-formation. An attempt has been made to correlate the data with the manner in which the size, number and degree of solvation of the colloidal particles change during gelation.

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