STUDIES IN INORGANO-ORGANIC GELS IN PINENE

Part I. Gels of Some Sodium Soaps in Pinene and their Cooling and Heating Curves

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THE importance of the study of cooling curves during the sol-gel transformation of organic gels has been stressed from time to time by several workers. Cooling curves for gelatin solutions were determined by Lottermoser and Matthæs[1] and the results obtained were compared with the cooling curves for water so drawn that the course of cooling in the two cases is coincident in the earlier part. They find sharp changes of direction in the cooling curves for gelatin solutions with respect to that for water and conclude that the heat content is smaller in the gel state than in the sol state. On plotting the temperature differences against the mean temperatures, they obtained curves which are irregular for low concentrations but become regular as the concentration of the gelatin is increased. Pleass[2] also studied the cooling curves of gelatin solutions and arrived at the same conclusion, namely, that heat is evolved on the setting of gelatin gels. Hollemann and co-workers[3] found that the heat changes in the solutions of gelatin in water are a function of temperature, and that at constant water content, lowering of temperature causes an evolution of heat over a certain range of temperature. They regard this quantity of heat which is evolved during the formation of gels as the heat of gelation.

Fischer[4] and Lawrence[5] have determined the cooling curves for solutions of various soaps in water-alcohol and nujol, respectively, and in all cases, they find a break in the curves at the point of setting in a direction which indicates that heat is evolved during the gelation of the soap solution. In the course of studies on cooling curves of gelating systems, Lederer[6] found that the evolution of heat on gelation is of the same order of magnitude as the heat of solvation for both hydro-sols and alco-sols of soaps. He also found that the temperature at which gelation begins is independent of the solvent.

The only important reference in literature dealing with the heating curves of organic gels is the one due to Pleass.[2] The heating curves relating to the gelatin gels are found to be very different from that for water. The nature of the curves suggests that the thermal conductivity is lower in the gels than in the sols and also that heat is absorbed on melting the gelatin gels.

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Prasad and Mathur[7] found that sodium oleate dissolves in pinene at a high temperature and the resulting solution sets to a gel on cooling; similar
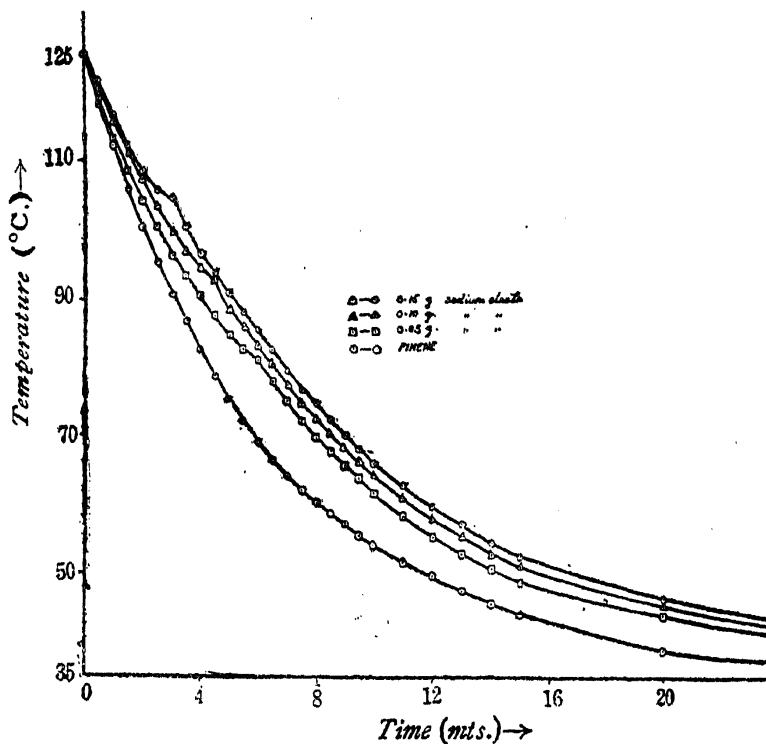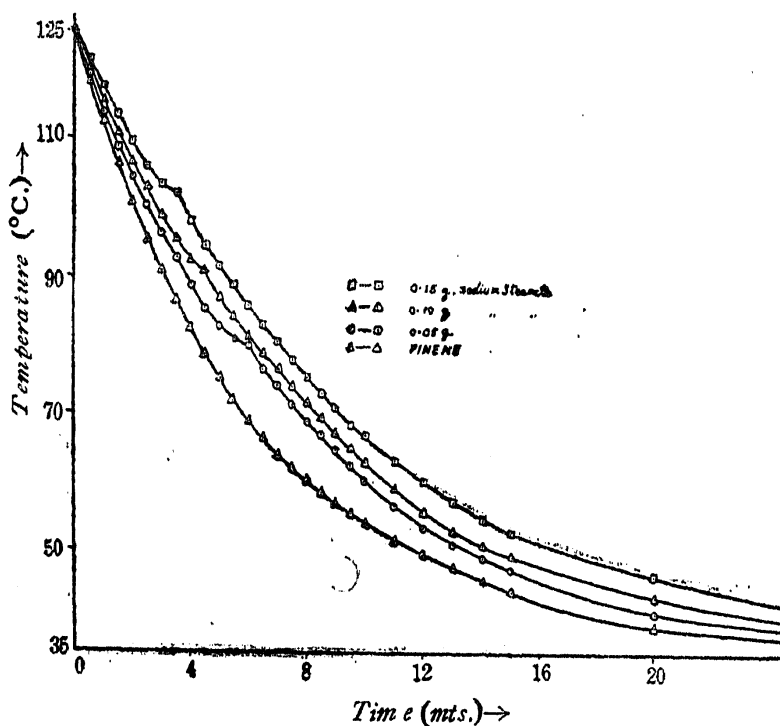

FIG. 1.

FIG. 2.

observations were made by Prasad and Vishvanath[8] in the case of the sodium and potassium soaps of oleic, stearic and palmitic acids. The present investigation deals with the study of (i) the cooling curves of gel-forming solutions of sodium oleate and sodium stearate in pinene, and (ii) the heating curves of their gels.

EXPERIMENTAL

The sodium oleate and sodium stearate used were products of the B. D. House and Messrs. E. Merck & Co., respectively. The pinene used in the preparation of the gels was obtained from Messrs. Eastman Kodak & Co., and was the fraction distilling at 156°.

For the preparation of the gels a known amount of the soap was taken in a test-tube and 10 c.c. of pinene were added to it. The test-tube was then kept in an oil-bath maintained at about 140°, and a long condensing tube was attached to it to avoid any appreciable loss of pinene. The system in the tube was stirred constantly with a stirrer, and when the solution had attained the temperature of the bath and the soap had completely dissolved, the test-tube was taken out and placed in a thermostat maintained at some constant low temperature. After some time it was observed that the solution had set to a gel. It was observed that these solutions do not set when they are allowed to cool at a temperature above 100°.

For determining the cooling curves the test-tube containing the gel-forming solution was placed in an air-thermostat maintained at 35°. The fall in temperature of the system was read periodically on a thermometer dipping in the solution. Such readings were taken with gel-forming solutions containing different amounts of the two soaps and the results obtained are shown graphically in Figs. 1 and 2. To determine the heating curves solutions of either soap were prepared in pinene as described above and were allowed to gelate and 'stand' in a thermostat maintained at 35°. The test-tube containing the gel was then placed in an oil-bath maintained at a constant high temperature (140°), and the rate of increase in the temperature was read on a thermometer dipping in the gel. The results obtained are shown graphically in Figs. 3 and 4.

DISCUSSION OF RESULTS

The cooling curves (Figs. 1 and 2) for solutions of the two soaps in pinene containing different amounts of the soaps are very similar in general characteristics; they have been so drawn that the course of cooling of the solutions coincides in the earlier part with that for pinene. These curves at once show that under the same conditions, pinene cools more rapidly than the gel-forming solutions of either soap in pinene, and that the higher the concentration of the soap the slower is the rate of cooling.

The curves of all the soap solutions show definite arrests; the initial rate of cooling is followed by a change in direction of the curves which continue regularly later on. The point of solidification of the system was recognisable by the appearance of a wavelike surface at the walls of the
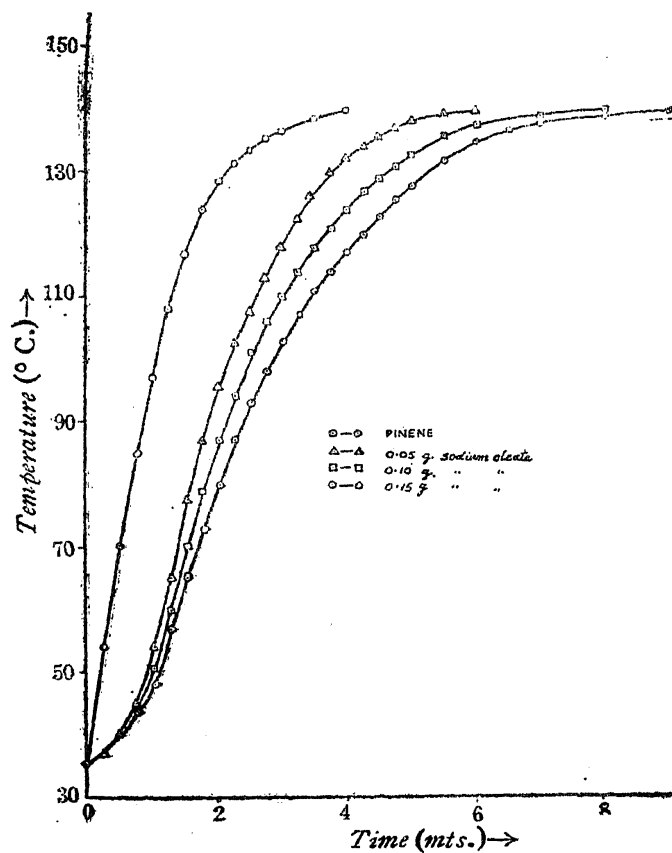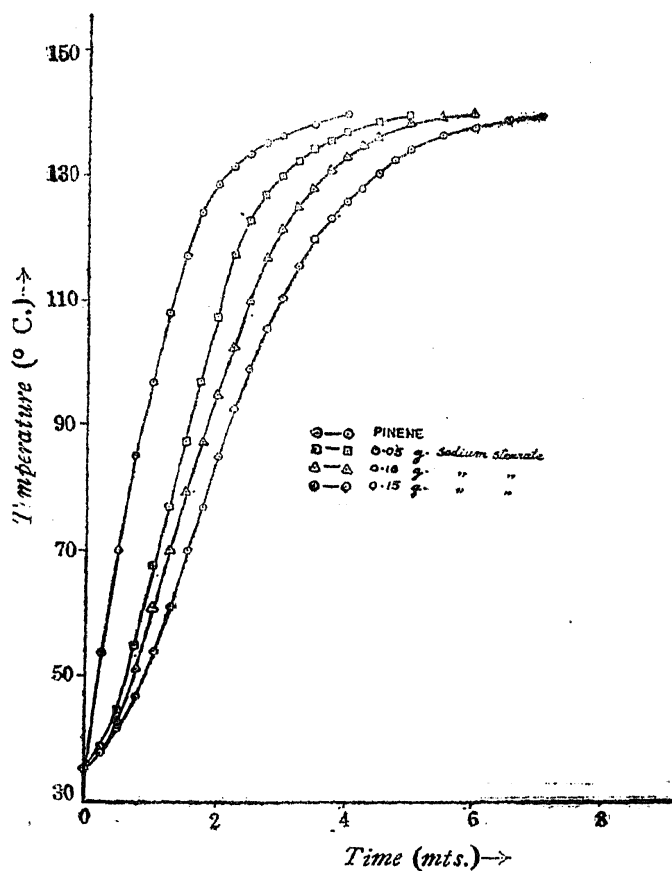
FIG. 3.

FIG. 4.

test-tube; but to get definite results, the time of setting of these soap solutions was measured separately by Flemming's method[9] in the air-thermostat, and these values were found to be nearly the same as the time of appearance of kinks in the cooling curves. This shows that the kink is obtained at the point when the solution sets to the gel state.

It was found that the parts of the various curves above and below the kinks obey the law of cooling. Hence the specific heats of the solutions as well as of gels of the soap systems in pinene were calculated, and the values obtained are given in columns 2 and 3 of the following table:—

TABLE I

Soap content (in g.)	Specific heat of solution	Specific heat of gel.	Heat of gelation (in Calories)	Gram molar heat of gelation (in Calories) (ML)	ML/T
Sodium oleate					
0·05	0·5754	0·5170	9·98	981500	2798
0·10	0·6296	0·5388	19·45	985600	2805
0·15	0·6531	0·5650	32·62	1073000	2846
Sodium stearate					
0·05	0·5234	0·4101	7·37	727600	2067
0·10	0·5924	0·4635	15·26	750600	2067
0·15	0·6642	0·5616	23·56	772300	2062

It will be seen from the table that the specific heats of the solutions as well as those of gels increase as the soap content in the system is increased. Again, the specific heat of the system of a particular soap content is greater in the solution or sol state than in the gel state.

Considering the gel of either soap in pinene as composed of heavily super-saturated micelles of the soap in the form of fibrils or threads, and the space in between the fibrils being occupied by a super-saturated solution of soap in pinene, we have in it a thermodynamic system consisting of a number of homogeneous parts between the boundaries of which are certain non-homogeneous parts. During the change of state when the sol goes over to the gel state, there is a tendency towards the formation of clusters of the primary colloidal particles which adsorb the dispersion medium. In this process a restriction would be imposed on the degree of freedom of the individual particles, which would lead to the reduction of their kinetic energy and cause a release of energy in the form of heat at the point of setting. Since it is not a strictly homogeneous system, the point is not well defined, and during this period there is a thickening stage in which the system passes through all the gradations of viscosity with continual though much quicker fall in temperature. The heat evolved during gelation may be termed as the Heat of Gelation of the system and can be calculated in the same manner as in the change of state.

The heat of gelation has been calculated for the two soap-pinene systems studied and the values are given in column 4 of Table I. It will be observed that the amount of heat evolved during gelation increases as the soap content of the gel is increased, and there appears to be some sort of correlation between the two. The values of the molecular heats of gelation divided by the absolute temperatures of gelation of the two systems, are given in the last column of Table I. It will be seen that they are very nearly constant for the same system. Also there appears to be a vague similarity between these results and Trouton's Rule, a generalisation according to which the ratio of the molar latent heat of vaporisation to the boiling point is constant for most substances.

When considering the curves in Figs. 1 and 2 it should be remembered that the thermometer records the temperature at the centre of the test-tube which is higher than the temperature of the outermost layer of the solution. Thus, there is a temperature gradient in the container at any moment which varies from 35° to the temperature recorded at the centre. Therefore, the outermost layer may have set to a gel, evolving the heat of gelation, while the central portions of the solution may still be at a temperature removed

from the setting temperature. This accounts for the fact that the arrest is gradual. The arms of the curve above the temperature of arrest indicate that the most concentrated solutions cool very slowly. This is due either to differences in the specific heats of the solutions of varying soap concentrations, or to differences in their ability to transmit heat either by conduction or by convection, or it may be due to the evolution of heat which occurs as the gel sets. The concentrated solutions set at higher temperatures than the dilute ones and hence the heat of gelation of the outer layers of the gel-forming mixture would retard the convection or conduction of heat from the central portions and thus decrease the rate of cooling.

The branches of the curves pertaining to the gel-forming solutions below 45° are approximately parallel and indicate therefore that at low temperatures the rate of cooling is almost independent of the soap content.

It will be noticed from curves in Figs. 1 and 2 that the rate of cooling of pinene is much greater than those of the set gels. This may be due to the fact that the loss of heat in the case of pinene takes place both on account of convection and conduction, while in the case of the set gels heat is only transmitted by conduction.

On plotting the differences in the rates of cooling between pinene and the gel-forming solutions against temperature, it was found that the curves regularly rise to a maximum value and then fall down slowly and regularly; no irregularities were observed in any case (cf. Lottermoser and Matthæs[1]).

Preliminary experiments on the heating curves of soap gels in pinene revealed that the variation in the time of " standing" of the gels at 35° makes no difference to the observed results. For the sake of uniformity, all gels were allowed to "stand" at 35° for half an hour before a heating experiment was started. The gels of sodium oleate were, however, allowed to stand for only ten minutes because they synerise if allowed to stand for a longer period.

The progress of the melted shell towards the centre of the container could be seen quite clearly. As the proportion of the melted gel increases gradually, the rate of rise of temperature also increases, and when the last portion of the gel has just melted the rate of rise of temperature immediately shoots up.

Figs. 3 and 4 show that the heating curves for pinene and the soap gels in pinene over the temperature range of 35° to 140° are very different. The curves obtained for varying concentrations of soap are coincident up to about 50°; above this temperature, however, when the proportion of the sol to the gel becomes large, the curves tend to " spray ", the rate of rise of temperature being lowest in the most concentrated gels.

The sigmoid nature of the curves suggests that the conduction of heat in the gel is lower than that in the sol, probably due to the absence of convection currents in the former.

The difference in the rate of increase in temperature on varying the concentration of either soap in the gels is probably due to (i) the difference in the amount of heat absorbed on melting (the heat of gelation varying with the concentration of the soap) and (ii) the effect of the different physical state of the system on the convection currents.

SUMMARY

The cooling curves for gel-forming solutions of sodium oleate and sodium stearate in pinene lie above that for pinene, and show definite arrests at the point of setting of these solutions to the gel state, indicating that heat is evolved during gelation. The Heat of Gelation has been calculated; the ratio of the molar heat of gelation to the absolute temperature of gelation appears to be constant for a system. An attempt has been made to explain the evolution of heat at the point of setting from a thermodynamic standpoint.

The heating curves for gels of either sodium oleate or sodium stearate in pinene are sigmoid, suggesting that conduction of heat in a gel is lower than that in a solution or sol.

ACKNOWLEDGMENTS

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