

STUDIES IN INORGANO-ORGANIC GELS IN PINENE

Part II. Gels of the Sodium and Potassium Soaps of Oleic, Stearic and Palmitic Acids in Pinene, and the Factors which influence their Time of Setting

BY MATA PRASAD, G. S. HATTIANGDI AND C. V. VISHVANATH

(From the Chemical Laboratories, Royal Institute of Science, Bombay)

Received September 18, 1944

THE time of setting is the main property which characterises a gel. A search through literature shows that although in recent years the measurements on the time of setting have been made in the case of several inorganic gels, very little information is available in the case of organic gels in spite of the fact that their preparation was known for a long time. This is probably so because in the case of the inorganic gels all the processes involved in the setting operation take place at the same temperature and hence the time of setting has a definite value at a constant temperature. In the case of the organic gels, the transformation of the solution of the gel-forming substance into a gel takes place either by cooling or heating the solution and hence it is impossible to determine the time of setting of these gels at one fixed temperature. Prasad¹ suggested that the time of setting in the case of organic gels could be defined as the time taken by a gel-forming system to set when it is allowed to cool from one fixed temperature to another fixed temperature. The same procedure has been adopted by Olsen² and others for the measurement of the time of setting of gelatin gels, but its definition is not clearly stated in any of these publications.

It has been reported³ that the gels of sodium and potassium soaps of oleic, stearic and palmitic acids in pinene have been prepared by the authors for the first time. This investigation deals with the measurement of the time of setting of these gel-forming systems. The concentration of the gel-forming substance as well as the temperature at which the system is allowed to set have a profound influence on the time of setting. Several workers have noted marked changes in the structure of the gels on varying the concentration and temperature. Therefore, the effects of soap content as well as of temperature on the time of setting of these gel-forming systems have been determined.

Some of the important methods employed for the determination of the time of setting are due to Flemming,⁴ Fells and Firth,⁵ Hurd and Letteron⁶

and Prasad and Hattiangadi.⁷ None of them gives the exact time at which all the processes involved in gelation are complete; it appears that the process of gelation nearly reaches its maximum of activity when the gel-forming system is considered to have set by the abovenamed methods, whereas the final slow changes continue for a long time afterwards. Prasad and Parmar⁸ have shown that the above-mentioned methods give values widely different from each other, and are therefore useful for comparative purposes only. In the present investigation, Flemming's method has been employed for the determination of the time of setting. It consists in measuring the time which the gel-forming system takes to reach a consistency when it will not flow out of the container when it is inverted.

EXPERIMENTAL

Sodium oleate and sodium stearate used in this investigation were Merck's pure products. Sodium palmitate and the potassium soaps of oleic, stearic and palmitic acids were prepared in the laboratory according to standard methods. The pinene used in the preparation of the gels was obtained from Messrs. Eastman Kodak & Co., and was the fraction distilling off at 156°.

The gels in pinene were prepared in the same manner as described in Part I of this series.⁹ Test-tubes containing gel-forming solutions of either soap in pinene at about 140° were placed in a water-thermostat at a constant low temperature. The system was examined at different intervals of time to see whether the solution flows out of the tube or not. When the solution did not flow out of the tube on inverting it, it was considered to have set to a gel. The exact time of setting of the system was determined by repeating this process, each time disturbing the system as little as possible. The results obtained are given in the following tables in which the time of setting at a temperature means the time required to set when cooled from 140° to that temperature.

DISCUSSION OF RESULTS

It will be seen from the foregoing results that the time of setting of gels of sodium oleate, sodium stearate, sodium palmitate, potassium oleate, potassium stearate and potassium palmitate in pinene decreases as the amount of the soap in the system is increased. The manner in which the time of setting decreases with an increase in the amount of the soap content is shown in the case of sodium oleate gels by various curves in Fig. 1. It will be noted that all the curves are very steep in the beginning but, later on, the changes become very slow and gradual.

TABLE I. *Time of Setting of Sodium Oleate Gels in Pinene*

A (in g.)	40°	50°	60°	70°	80°	90°
0-01	11' 0"	Very loose setting after 25'	Does not set	Does not set	Does not set	Does not set
0-02	3' 45"	5' 45"	20' 0"	No tendency to set for 40'	"	"
0-03	3' 15"	5' 0"	9' 0"	25' 0"	30' 0"	No tendency to set for 1½ hrs.
0-04	3' 0"	4' 0"	6' 0"	17' 0"	23' 0"	No setting for 1 hour
0-05	2' 55"	3' 30"	5' 0"	12' 0"	17' 0"	30' no perfect setting
0-07	2' 35"	3' 0"	4' 0"	7' 0"	8' 30"	22' 0"
0-10	2' 20"	2' 40"	3' 15"	4' 30"	5' 50"	6' 30"
0-15	2' 0"	2' 17"	2' 36"	3' 10"	4' 0"	4' 45"
0-20	1' 42"	2' 5"	2' 15"	2' 30"	3' 0"	4' 15"
0-25	1' 25"	1' 40"	1' 48"	2' 5"	2' 25"	..
0-30	1' 15"	1' 25"	1' 35"	1' 50"	2' 12"	..
0-35	1' 10"	1' 15"	1' 25"	1' 35"	2' 0"	..
0-40	1' 5"	1' 8"	1' 15"	1' 25"	1' 50"	..
0-45	0' 55"	1' 4"	1' 8"	1' 18"	1' 40"	..

TABLE II. *Time of Setting of Sodium Stearate Gels in Pinene*

A (in g.)	40°	50°	60°	70°	80°
0-25	2' 30"	2' 50"	3' 15"	3' 40"	5' 50"
0-30	2' 12"	2' 35"	2' 52"	3' 10"	4' 0"
0-35	2' 0"	2' 25"	2' 35"	2' 50"	3' 15"
0-40	1' 50"	2' 5"	2' 24"	2' 35"	2' 50"
0-45	1' 40"	1' 52"	2' 5"	2' 20"	2' 35"

TABLE III. *Time of Setting of Sodium Palmitate Gels in Pinene*

A (in g.)	40°	50°	60°	70°	80°
0-10	10' 50"	Sets to a loose gel
0-15	7' 8"	23' 0"	Sets to a loose gel
0-20	4' 32"	11' 0"	27' 0"
0-25	3' 0"	4' 35"	6' 30"	12' 0"	Sets to a loose gel
0-30	2' 18"	2' 40"	3' 30"	6' 10"	12' 30"
0-35	2' 0"	2' 10"	2' 25"	3' 15"	6' 15"
0-40	1' 45"	1' 55"	2' 10"	2' 30"	4' 30"
0-45	1' 38"	1' 45"	1' 58"	2' 15"	3' 20"

TABLE IV. *Time of Setting of Potassium Oleate Gels in Pinene*

A (in g.)	40°	50°	60°	70°	80°
0.10	2' 20"	2' 58"	3' 30"	4' 6"	6' 0"
0.15	2' 8"	2' 20"	2' 50"	3' 26"	4' 15"
0.20	2' 0"	2' 10"	2' 18"	2' 48"	3' 30"
0.25	1' 50"	2' 0"	2' 12"	2' 25"	2' 50"
0.30	1' 42"	1' 50"	2' 0"	2' 10"	2' 24"
0.35	1' 36"	1' 46"	1' 52"	2' 0"	2' 15"
0.40	1' 29"	1' 40"	1' 45"	1' 55"	2' 5"
0.45	1' 24"	1' 32"	1' 40"	1' 48"	1' 58"

TABLE V. *Time of Setting of Potassium Stearate Gels in Pinene*

A (in g.)	40°	50°	60°	70°
0.08	7' 4"	9' 33"	13' 45"	20' 48"
0.09	4' 40"	6' 30"	9' 5"	12' 55"
0.10	3' 33"	4' 48"	7' 4"	9' 35"
0.15	2' 36"	3' 26"	4' 30"	6' 19"
0.20	2' 5"	2' 45"	3' 48"	5' 8"
0.25	1' 24"	1' 57"	2' 40"	3' 38"

TABLE VI. *Time of Setting of Potassium Palmitate Gels in Pinene*

A (in g.)	30°	40°	50°	60°
0.08	12' 25"	Very loose setting	Does not set	Does not set
0.09	9' 55"	14' 5"	"	"
0.10	5' 30"	11' 25"	Loose setting	"
0.15	2' 45"	4' 20"	8' 5"	Loose setting
0.20	1' 33"	2' 40"	5' 3"	9' 5"
0.25	0' 45"	1' 30"	2' 35"	5' 0"

It will be observed from Tables I to VI that the time of setting of gels containing the same amount of the soaps increases as the gel-forming solutions are allowed to cool at higher temperatures. It was observed that if this temperature was 100° and above, the gel-forming solutions did not set at all. These observations are similar to those made by Pleass¹⁰ and Olsen² in the case of gelatin gels.

Hurd and Letteron⁶ found that the variation of the time of setting of silicic acid gels with temperature could be represented by Arrhenius' equation in which the time of setting could be substituted for the velocity constant.

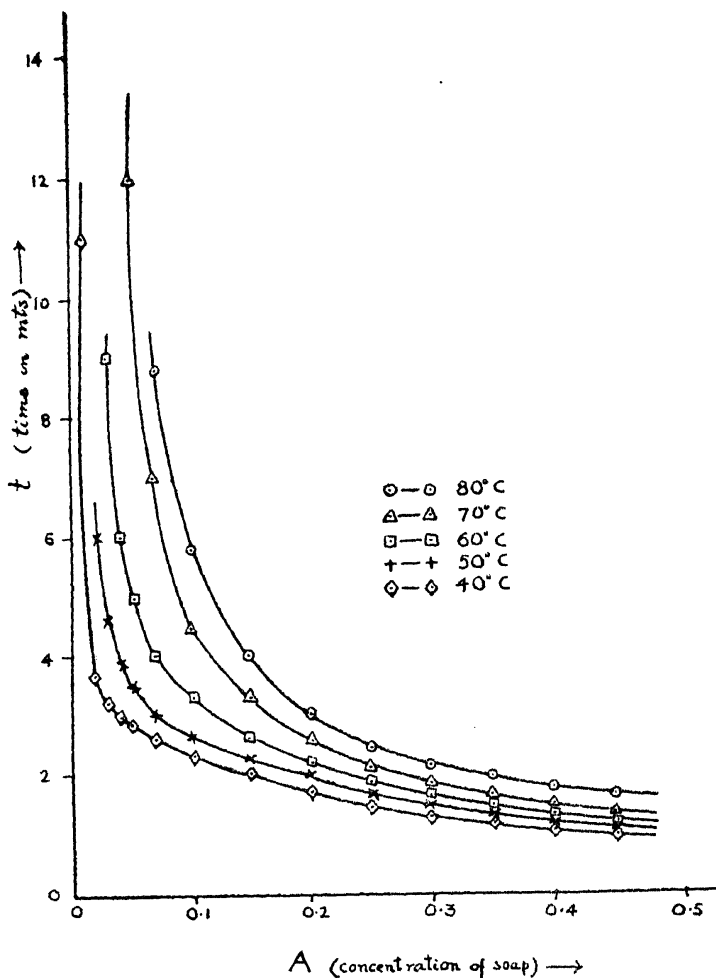


FIG. 1

This equation can be written as

$$\frac{d \log t}{dT} = \frac{Q}{RT^2},$$

$$\text{or } \log t = -\frac{Q}{2.303 R} \cdot \frac{1}{T} + c.$$

It has been found to apply in the case of gels of several inorganic substances by Prasad and Desai.¹¹ In order to examine its applicability to the case of soap gels in pinene, the values of $\log t$ were plotted against $1/T$, and the curves obtained are almost sets of parallel straight lines in all the soap-pinene systems. Slight deviations from the straight line nature are however noticed at higher temperatures with all the gels. Curves for sodium oleate in pinene are shown in Fig. 2; those for the other soaps are very similar to these curves in general characteristics. This shows that the Arrhenius' equation is applicable to all the gels studied in this investigation. The values of Q , the Heat of Activation, have been calculated from the slopes of the lines, and they are given in Table VII.

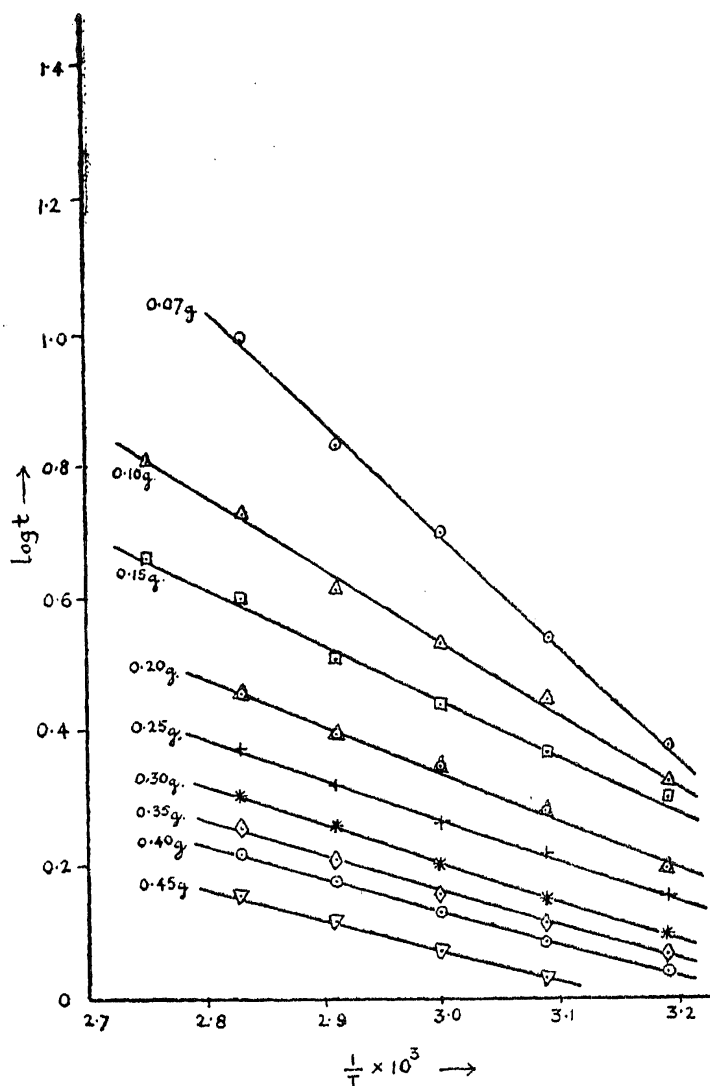


FIG. 2

TABLE VII

A (in g.)	Slope (in degrees)					
	Sodium oleate	Sodium stearate	Sodium palmitate	Potassium oleate	Potassium stearate	Potassium palmitate
0.08	-1566	..
0.09	-1500	..
0.10	- 933	-1466	- 3000
0.15	- 875	- 633	-1433	- 2433
0.20	- 840	- 500	-1433	- 2633
0.25	- 622	- 855	..	- 433	-1466	- 2700
0.30	- 633	- 650	..	- 400
0.35	- 615	- 525	-166	- 366
0.40	- 577	- 533	-166	- 400
0.45	- 700	- 466	-166	- 366
Mean slope Q (in cal.)	- 695 -3202	- 612 -2820	-166 -760	- 504 -2322	-1477 -6800	- 2692 -12400

It will be seen from the above table that the values of the heat of activation in the case of these gels appear to be independent of the soap contents within the range indicated in the table, in several cases.

The applicability of the above relation to the various soap gels shows that the process of formation of these gels is allied to, though not identical with, the process of gel-formation in the case of inorganic gels.

The setting point of a gel may be defined as the convergence temperature at which the "time of relaxation" becomes infinite. To measure these points for soap gels in pinene, the fall in temperature of the gel-forming system with time was studied under the same conditions as employed for the measurement of the time of setting. The setting points were obtained by reading the temperature (T') attained by the gel-forming mixtures at the time of setting (t). Some of the important cases for each soap are given in Table VIII.

TABLE VIII

A	t	T'	t	T'	t	T'
<i>Sodium Oleate</i>						
		30°		60°		80°
0.01 g.	8' 0"	30°		60°		80°
0.02 g.	3' 0"	38°	20' 0"	60°		80°
0.05 g.	2' 0"	56°	5' 0"	61.6°	17' 0"	80°
<i>Sodium Stearate</i>						
		40°		50°		60°
0.25 g.	2' 30"	56°	2' 50"	51°	3' 15"	70°
0.30 g.	2' 12"	62°	2' 35"	67°	2' 52"	75°
0.35 g.	2' 0"	69°	2' 25"	72°	2' 35"	79°
<i>Sodium Palmitate</i>						
		40°		50°		60°
0.25 g.	3' 10"	50°	4' 10"	51°	6' 30"	60°
0.30 g.	2' 18"	57°	2' 40"	57°	3' 30"	63°
0.35 g.	2' 0"	63°	2' 10"	64°	2' 25"	69°
<i>Potassium Oleate</i>						
		40°		50°		60°
0.20 g.	2' 0"	53°	2' 10"	58°	2' 18"	64°
0.25 g.	1' 50"	56°	2' 00"	61°	2' 12"	67°
0.30 g.	1' 42"	62°	1' 50"	66°	2' 0"	69.5°
<i>Potassium Stearate</i>						
		40°		50°		60°
0.09 g.	4' 40"	42.8°	6' 30"	50.1°	9' 5"	60°
0.10 g.	3' 33"	47.5°	4' 48"	53.5°	7' 4"	60°
0.15 g.	2' 36"	56.0°	3' 26"	59.0°	4' 30"	63.5°
<i>Potassium Palmitate</i>						
		40°		50°		60°
0.15 g.	2' 45"	44°	8' 5"	50°		60°
0.20 g.	1' 33"	60.5°	5' 3"	52.1°	9' 5"	60°
0.25 g.	0' 45"	74°	2' 35"	64°	5' 0"	61.5°

A critical examination of these results shows that the setting of the quick-setting gels takes place much before the gel-forming system has attained the temperature of the thermostat. It is evident that, in such cases, no stage of the process of setting is completed at the temperature at which the gel-forming solutions are cooled.

Before making an attempt to explain the observed results of the effects of concentration and temperature on the time of setting of soap gels in pinene, it was thought essential to obtain some information regarding the nature of dispersion of the soap in pinene when a solution was prepared at 140°. For this purpose, some experiments were conducted on the measurements of (i) the elevation of the boiling point of pinene and (ii) the lowering of its vapour pressure (ΔP) due to the addition of a soap. For the former, the standard Beckmann's apparatus was used, and for the latter, an apparatus was assembled and used along the lines suggested by Pickett.¹² The values of ΔP were read by employing a suitable reading arrangement. Below 110°, the reliability of the results is not high for ΔP could not be determined with any fair degree of accuracy. The results obtained are given in Tables IX and X.

TABLE IX

Soap	Amount of soap (g.)	Amount of pinene (g.)	Elevation in b.p. (ΔP)	Molar wt. (calculated)	Molar wt. (theory)
Sodium Oleate	0.30	25.8	0.20°	313.6	304.4
	0.60	25.8	0.42°	298.7	
			Mean =	306.15	
Sodium Stearate	0.30	25.8	0.20°	313.6	306.4
	0.60	25.8	0.41°	306.0	
			Mean =	309.8	

The values of ΔP are negligible at and below 110°. Above 110° they increase rapidly with both temperature and the concentration of the system. It will be seen that the observed values of molar weights of the soaps obtained by the two methods are in fair agreement with the theoretical values, indicating that a solution of either soap in pinene is a true molecular solution at the boiling point. This shows that the soap remains in the molecular state in the solution when it is cooled from 150°–140° to about 110° or so. When it is gradually cooled below 110°, it first becomes saturated and then partly super-saturated with the soap because of the low solubility of the soap in pinene at low temperatures, and subsequently the soap goes over to the colloidal state with the saturated solution as the dispersion medium (this may be one of the causes of the low value of ΔP). On further cooling,

TABLE X

Temp. (° C.)	P ₀ (in mm.)	Δ P (in mm.)	Molecular weight
(1) 0.75 g. of sodium oleate dissolved in 75 c.c. pinene			
30	8.5
40	13.0
50	19.5
60	27.0
70	46.0
80	66.0
90	102.0
100	144.0
110	197.0	1.0	311.6
120	294.0	1.5	299.9
130	378.0	2.0	298.8
140	498.0	2.6	302.8
150	650.0	3.4	302.3
(2) 1.125 g. of sodium oleate dissolved in 75 c.c. pinene			
120	294.0	2.2	316.9
130	378.0	2.9	309.1
140	498.0	3.8	310.8
150	650.0	5.0	308.2
(3) 1.50 g. of sodium oleate dissolved in 75 c.c. pinene			
120	294.0	3.0	307.9
130	378.0	4.0	296.1
140	498.0	5.0	315.4
150	650.0	6.8	299.6
Mean molecular wt.			306.1
Molecular wt. of sodium oleate (empirical)			304.4

further super-saturation takes place which causes an increase in the size of the already existing particles and probably effects an increase in the number of colloidal particles. All the aforesaid changes take place more rapidly, the lower the temperature to which the solution is allowed to cool, and hence its setting to the gel state which results from the union of colloidal particles in certain abundance is quicker. The observed results of the effect of concentration on the time of setting can be explained on this hypothesis; an increase in the amount of soap in the gel-forming mixtures increases the number of micelles, and reduces the time of setting. This supports the concept that the essential factor in the formation of a gel is the union of micelles present in certain abundance in the gel-forming system. The rapid decrease upto a certain concentration and the gradual one subsequently indicates that the optimum conditions are reached at some soap content of the gel-forming mixture.

SUMMARY

Measurements of the time of setting of several alkali soap gels in pinene under different conditions show that they behave like organic gels; the time

of setting increases with increase in temperature, and decreases with increasing concentration. The plots of $\log t - 1/T$ are straight lines, suggesting that Arrhenius's equation is applicable to these systems; the values of the Heat of Activation have been calculated for each system. Setting points have also been measured. Molecular weight determinations show that a solution of either soap in pinene is a true solution at its boiling point.

ACKNOWLEDGEMENTS

One of the authors (G.S.H.) is grateful to the authorities of the University of Bombay for awarding a University Research Scholarship which has enabled him to carry out this investigation.

REFERENCES

1. Prasad .. *Presidential Address (Chem. Sec.)—20th Ind. Sc. Cong.*, 1941, 2.
2. Olsen .. *J. Phys. Chem.*, 1932, 36, 529.
3. Prasad and co-workers .. *Curr. Sci.*, 1940, 9, 119, 459.
4. Flemming .. *Zeit. Physik.*, 1902, 41, 427.
5. Fells and Firth .. *Trans. Farad. Soc.*, 1927, 23, 623.
6. Hurd and Letteron .. *J. Phys. Chem.*, 1932, 36, 606.
7. Prasad and Hattiangadi .. *J. Indian Chem. Soc.*, 1929, 6, 653
8. ——— and Parmar .. *Curr. Sci.*, 1935, 4, 310.
9. ——— and Hattiangadi .. *Proc. Ind. Acad. Sci.*, 1945, 21, 1.
10. Pleass .. *Proc. Roy. Soc.*, 1930, 126 A, 406.
11. Prasad and Desai .. *J. Indian Chem. Soc.*, 1939, 16, 117.
12. Pickett .. *J. Ind. Eng. Chem. (Anal. Edn.)*, 1929, 1, 36.