SOLUBILITY OF SOME SODIUM SOAPS IN PINENE

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PRASAD, HATTIANGDI, *et al.* [1, 5, 6, 7] have made extended investigations on the behavior and properties of numerous alkali soap systems in pinene. It is interesting theoretically to correlate the solubility data of soap-solvent systems with their physico-chemical characteristics, and an attempt has been made in this direction in the present paper which deals primarily with the solubility of sodium oleate, stearate and palmitate in pinene, over the temperature range in which the above mentioned authors have measured numerous properties and observed different phenomena.

Earlier references to solubility measurements of soaps in organic solvents are more or less of a qualitative nature. Leggett, Vold and McBain[2] made the first detailed investigations on the solubility of sodium palmitate in nineteen different organic solvents over a wide range of temperatures, and correlated their results with the polarity, internal pressure, spacing, length, etc., of the solvent molecules, as also with the position and nature of the attached groups. More recently, Palit and McBain[4] have conducted extensive measurements on the co-solvency and mix-solvency of several alcohol-hydrocarbon-glycol mixtures for both alkali and heavy metal soaps.

MATERIALS USED

Eastman Kodak pinene was distilled and the middle portion of the distillate, collected at 156° C., was used. The refractive index and specific gravity of the pinene, as determined at 30° C., were 1·4658 and 0·858 respectively.

Sodium oleate and sodium palmitate were products of the British Drug House, and sodium stearate of Messrs. E. Merck & Co. Their melting points as measured by a capillary-type melting point apparatus were 232°, 270° and 260° C. respectively.

EXPERIMENTAL TECHNIQUE

The procedure adopted for solubility determinations was as follows: About 20 g. of pinene and a slight excess of the dry soap were taken in a

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glass-stoppered bottle, and the soap was allowed to swell by keeping the system overnight in an air-thermostat maintained at some constant desired temperature. The soap pinene system was then stirred continuously in a mechanical shaking device for about 6 hours during which interval the solution became saturated with respect to the soap. (Some preliminary experiments showed that equilibrium with respect to saturation was reached within about 4 or 5 hours' shaking, but 6 hours' shaking was considered safe and was therefore adopted in making quantitative estimations). After shaking, the system was allowed to stand at that temperature for a further period of 2 hours after which it was filtered quickly under air pressure through glass-wool in a small fritted glass Buchner funnel. The glass-wool and the whole filtering arrangement were kept at the same temperature as that of the soap-pinene system, thus reducing to a minimum any change in the saturation state.

Pinene reacts fairly vigorously when treated with mineral acids, and hence the chemical method of analysis could not be adopted. The soap content of the solutions was determined as follows: A portion of the filtrate was taken in a shallow weighing bottle, weighed and evaporated carefully to dryness over a sand-bath. It was dried till a constant weight of the white residual soap was obtained. The method was tested with known amounts of soap and pinene, and was found to give results with a reproducibility better than 2 per cent. Care had to be taken while drying the system over the sand-bath to prevent charring of the pinene.

The results obtained are presented in Table I in which the solubility of the soaps in pinene is expressed on a weight-percent basis.

TABLE I

Solubility of some Sodium Soaps in Pinene

Temperature (°C.)	Weight-percent solubility of		
	Sodium palmitate	Sodium stearate	Sodium oleate
30	0·04	0·045	0·05
50	0·25	0·43	0·58
70	0·56	0·85	1·28
90	1·04	1·56	2·17
100	1·57	1·98	2·75
110	1·65	2·10	3·34
120	1·77	2·29	3·37
130	1·94	2·55	3·44
140	2·20	3·01	3·65
150	2·92	..	3·93

RESULTS AND THEIR DISCUSSION

The appearance of the soap-pinene systems at various temperatures is interesting. At room temperature and at moderately high temperatures (30° to 50° C.), the soaps do not swell to any appreciable extent. The soap particles exist as semi-fluffy semi-swollen flakes and, in general, do not coalesce to form larger aggregates. The swelling and degree of solvation of the soap particles is considerable at higher temperatures, the undissolved soap existing in the system as a highly swollen gel-like lump. At still higher temperatures, namely above 110° C. the soaps dissolve more freely than at lower temperatures, sodium oleate being the most soluble. If soap-pinene systems are saturated with respect to a high temperature in the abovementioned range and then cooled to about 80° C. or lower, a mixture of clear solution and crystals is not obtained but either a semi-translucent smoky viscous suspension or a very weak and precarious pseudo-gel results.

On cooling the soap-pinene systems of concentrations less than 0·5% the soap sediments out in the form of slightly solvated amorphous or crystalline flakes or as gel-like lumps; the soap, recovered from such systems and dried thoroughly, has the same melting point as that of the original dry soap. At concentrations larger than 0·5%, jellies are obtained which are initially soft and transparent but change over to stiff, translucent or opaque gels on standing. These observations are made at temperatures below 100° C. Above about 110° C. systems of reasonable concentrations (upto about 5% of soap) do not set to jellies or gels even on long standing.

The term "jelly" has been used in the same sense as that suggested by McBain, *et al.*,[3] and signifies a one-phase homogeneous transparent isotropic elastic system. A "gel", on the other hand, is a discontinuous system of two or more components involving a phase of swollen soap, and frequently intermeshed with sol, jelly or liquid crystalline material. Gels are usually opaque or translucent, but can be transparent as a result of suitable combination of the refractive indices of the phases involved. "Pseudo-gels" have a visual appearance resembling that of gels but possess none of their other characteristic properties; according to Prasad, *et al.*,[7] pseudo-gels are systems consisting of a large number of micro-crystallites which enmesh the dispersion medium at random, and have extremely low yield values.

In previous communications to this journal,[1, 5, 6] Prasad, *et al.*, have referred to the "sol-gel" transformation of soap systems in pinene. In actuality, it is a "solution-sol-jelly-gel" transformation, with (*a*) sols and jellies bridging the gap between true molecular solutions and gels, and (*b*) jellies and gels bridging the gap between dry crystalline soaps and their sols in pinene.

It will be seen from the data presented in Table I that the difference in the solubility of sodium palmitate, stearate and oleate is very slight at room temperature and at moderately high temperatures up to about 70° C. At

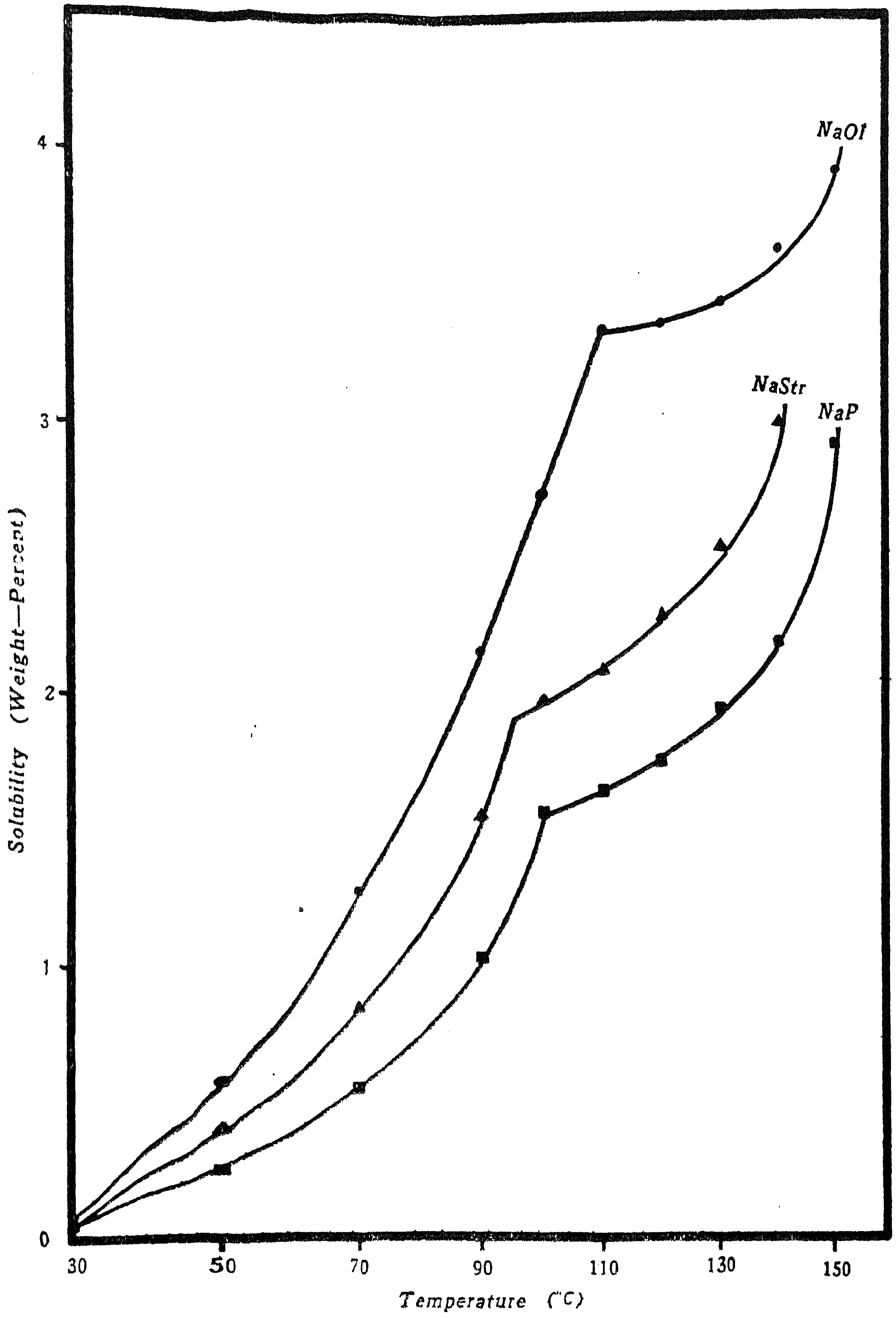

FIG. 1. Solubility Curves of Some Sodium Soaps in Pinene.

elevated temperatures, the solubility of these sodium soaps increases appreciably, being the most for the oleate and the least for the palmitate.

The solubility data when presented graphically as in Fig. 1 shows an interesting point. The solubility curves lie close to the temperature axis initially but shoot upwards after about 70° C. indicating enhanced solubility above this temperature. The solubility increases very slowly in the vicinity of 110° C. and then starts increasing very rapidly as the boiling point of pinene is approached although the absolute solubility remains low. The curves thus show a kink or change in direction nearabouts 100–10°.

These kinks in the solubility temperature curves may be caused by either (*a*) the formation of colloidal micelles, or (*b*) a phase transition of the soap. Prasad, Hattiangdi and Vishvanath[6] have determined the vapour pressures of soap-pinene systems and report that the values of ΔP are measurable within the temperature range 110° to 150° C. below which they are very low. They conclude that the soap-pinene systems exist as true solutions above 110° C. whereas below this temperature aggregation becomes very great and the lowering of vapour pressure is negligible. The close analogy of this observation with the appearance of an elbow or kink in the solubility curves is very interesting and leads one to surmise that the sudden change in solubility is due to saturation and the formation of micelles in the lower temperature range.

The change in the saturation phase, responsible for a change in the direction of the solubility curves, may also be due to a phase transition of the non-solvated soap. The kinks in the solubility curves of sodium palmitate, stearate and oleate in pinene, appear at 100°, 90° and 110° C. respectively, and these temperatures approximate closely to some of the transition temperatures reported by Vold, *et al.*[8] for these soaps in the anhydrous state, namely 114°, 89° and 115° C. The slight deviations in the temperatures at which the actual phase changes take place may be due to either the presence of solvated soap particles in considerably larger amounts of pinene or traces of impurities in the soap sample.

It is possible to construct a partial temperature-composition phase diagram for soap-pinene systems on the basis of the present solubility data and the results reported earlier by Prasad, Hattiangdi, *et al.*[6,7] on the behavior of these same systems. The diagram in Fig. 2 is a generalized schematic representation of the regions of existence of true molecular solutions, colloidal solutions or sols, crystals, pseudo-gels, jellies and gels. It should be noted that the Gibbs' Phase Rule is applicable only to true reversible equilibria such as are found in sols and jellies. Owingto the defective fluidity

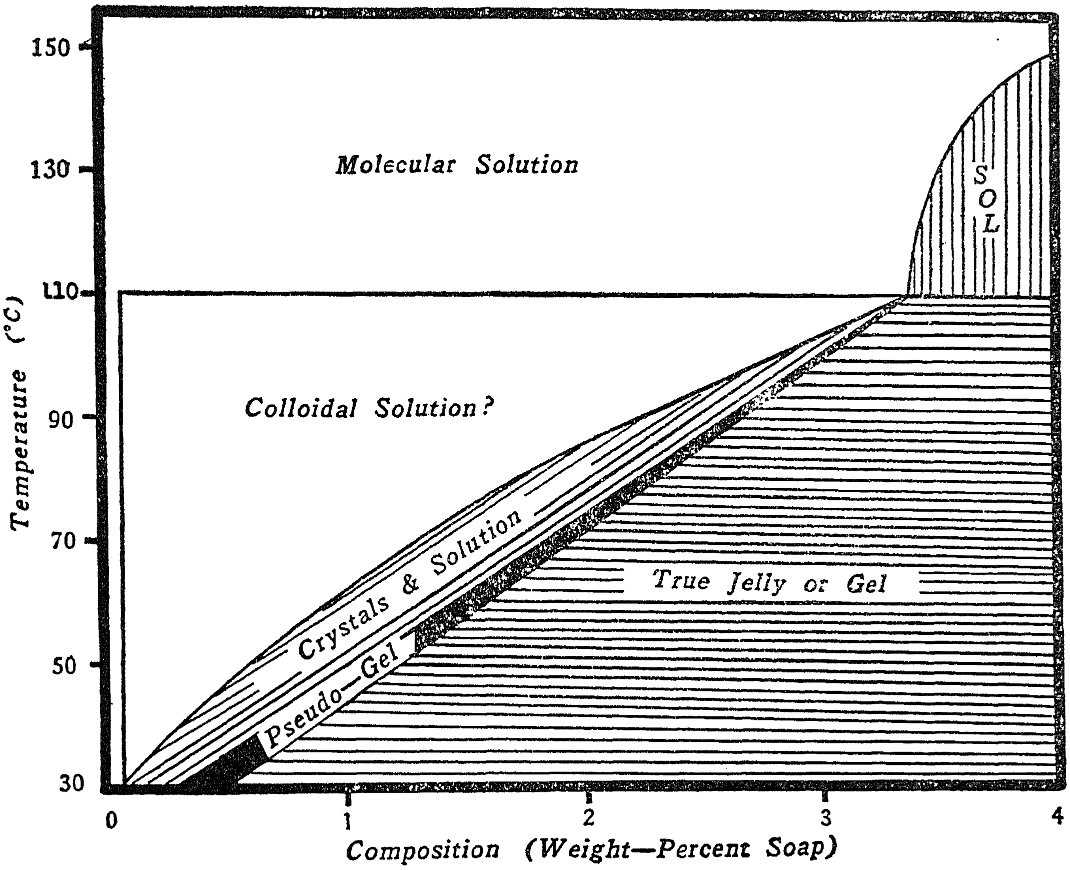

FIG. 2. Schematic Representation of the Regions of Existence of Solutions, Sols, Jellies, Gels, etc., in the system Sodium Oleate—Pinene.

of the liquid crystalline phases, other phases with which they are in equilibrium (such as sol, jelly, crystals and liquid crystals) cannot quite frequently separate or aggregate.

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SUMMARY

1. Solubility curves have been determined over the temperature range 30° to 150° C. for sodium palmitate, stearate and oleate in pinene. The solubility of the three soaps decreases in the order

$$\mathrm{NaOl} > \mathrm{NaStr} > \mathrm{NaP}.$$

2. The solubility curves show a kink or change in direction at about 100° to 110° C. which is caused possibly by either the formation of colloidal micelles or a phase transition of the soap.

3. The regions of existence of solutions, sols, crystals, jellies, gels, etc., in the system sodium oleate-pinene have been indicated in a schematic partial phase diagram.

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