The Solubility of Sodium and Potassium Soaps and the Phase Diagrams of Aqueous Potassium Soaps*

JAMES W. McBAIN and WILLIAM C. SIERICHS, Department of Chemistry,
Stanford University, California

THE solubility of soaps at room temperature is usually greatly overestimated. The only soaps that do not require elevated temperature for dissolution are potassium laurate, myristate and oleate and sodium oleate, and some less saturated soaps. Sodium stearate is no more soluble in water at room temperature than limestone. Frequently in the literature various mixtures of water and soaps are indiscriminately referred to as solutions, whereas some are pastes, some are plastic liquid-crystalline phases, and some are, of course, actually solutions.

It is the purpose of the present communication to assemble the data for the solubilities in water of the commonest sodium and potassium soaps. Hitherto only preliminary studies of phase diagrams for two potassium soaps, laurate (3) and oleate (2), have been available. We now present detailed phase diagrams for aqueous systems of potassium laurate, myristate, oleate, palmitate, and stearate.

Materials

Special Kahlbaum preparations of potassium palmitate, potassium myristate, and potassium laurate were found to be slightly acid and were dissolved in hot methyl alcohol and neutralized with 6 *m* potassium hydroxide to phenolphthalein endpoint, filtered, and dried under a radiating evaporator. In each case the remaining moisture content was found to be negligible. Eastman Kodak Company stearic acid was dissolved in hot methyl alcohol, neutralized, and treated as above. The moisture content was again negligible. The oleic acid was Kahlbaum's best.

Experimental Method

Hydrolysis is the chief source of error in studies of soap solutions. If exactly neutral potassium soaps are placed in carbon dioxide-free water, hydrolysis occurs. This renders it difficult to secure reproducible results, and the temperature required to produce a solution clear like water is raised by some 5-15° (see literature, and Figure 2). Hence, in most of this work, to each 100 moles of potassium soap was added 4 moles per cent of potassium hydroxide free from carbonate. Thus a 0.1 N potassium soap was measured in 0.004 N KOH, too little to affect solubility but enough to avoid turbidity. Solutions were made up by weight, using carbon dioxide-free distilled water in sealed off tubes.

For solubility determinations, that is, observations of the temperature, T_c, at which the curd just goes completely into isotropic or anisotropic solution, an air oven was used. This oven has windows in front and back, and a light source is placed behind the oven; heating elements are connected directly to a variac transformer for manual control. Sample tubes are placed in a rack that can be rotated from outside to stir the contents.

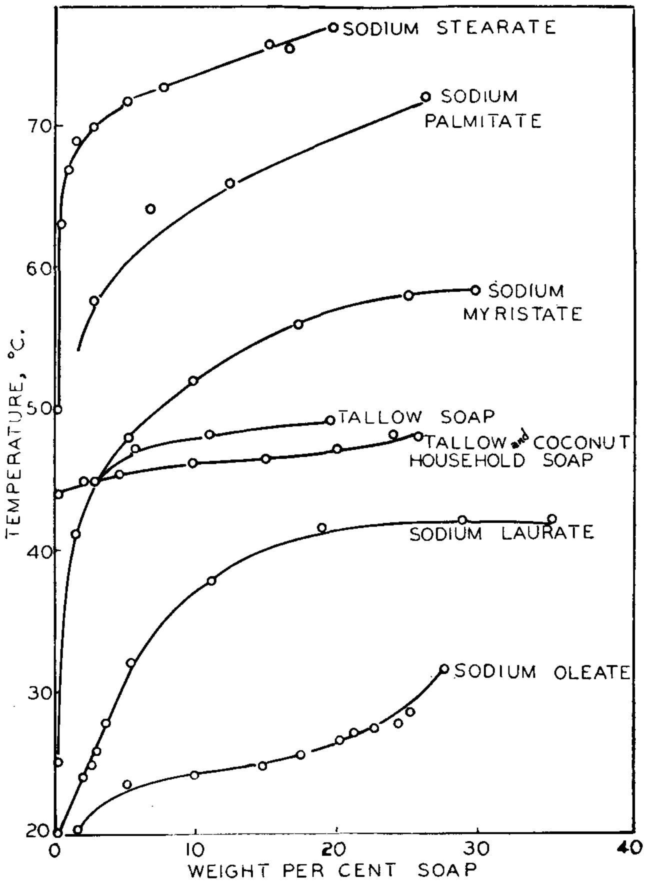

Fig. 1. Solubility of the sodium soaps in gms./100 gms. soap solution, showing the minimum temperature required to dissolve that amount of soap.

For studying phase equilibria, a much smaller furnace was constructed, which can be rotated as a whole to insure stirring. For protection from explosion the sample tube used with this oven was placed inside a brass tube, with small windows opposite those in the furnace. The light in back passes through polaroid and is observed from the front through a second polaroid, which shows clearly when the system changes from anisotropic to isotropic or *vice versa.*

It should be stressed that free potassium hydroxide is present in the solutions to a distinctly greater amount than usual, approximately N/1000 free alkali which is spontaneously produced by all neutral and even acid soaps.

An *ad hoc* experiment by M. E. L. McBain showed that the temperature of solution of sodium laurate in water was not affected by more than 1°C. (4 moles per cent excess of added sodium hydroxide) when 0.25 N sodium laurate was compared with 0.25 N sodium laurate + 0.01 sodium hydroxide. All the other sodium soaps contained slight excesses of alkali. Thus the typical commercial soap in Figure 1 contained 63.4% fatty acids with 0.093% excess sodium

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oxide and 0.41% sodium chloride. The myristate contained 0.04 weight per cent excess sodium hydroxide. The palmitate contained 0.007-0.008 equivalents excess alkali per mole. The stearate contained 99.53% soap and 0.06% free sodium hydroxide. The oleate contained 99.3% soap with 0.006% free sodium hydroxide, according to the respective papers in the literature. Figure 1 should be compared with Figure 11 of the paper by J. W. McBain, M. J. Vold, and J. L. Porter, Industrial and Engineering Chemistry, 1941, Volume 33, p. 1054, which includes a number of soaps made from single commercial oils and fats. McBain, Cornish, and Bowden, Transactions of the Chemical Society, 1912, Volume 101, p. 2054, show that dilute sodium laurate solutions which have been heated may be kept in a supersaturated condition at room temperature for long periods if jarring or scratching is avoided.

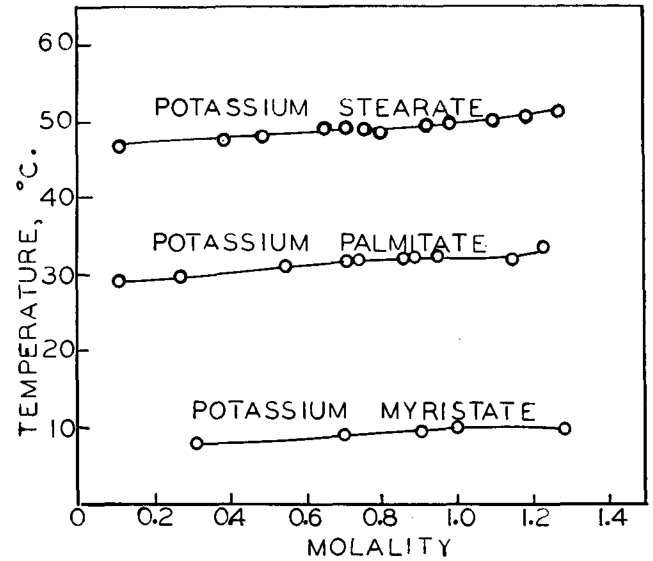

FIG. 2. Solubility of potassium soaps in gm. molecular weight/1,000 gms. water (molality) with 4 moles per cent excess alkali. Potassium laurate and potassium oleate are freely soluble even below 0°C. The same is true of the potassium soap of coconut oil, provided excess alkali is present; otherwise the solutions are turbid nearly up to room temperature.

Discussion of Results

The Solubility of Sodium and Potassium Soaps. Figure 1 assembles data for the five commonest sodium soaps. It includes measurements by A. Van Tuyl and R. B. Dean of the Rubber Reserve Specification Tallow Soap used in the synthesis of rubber and of a tallow and coconut household soap. From a study of Figure 1 it is at once noted that even sodium laurate does not become freely soluble until well above room temperature. It is also apparent that all the sodium salts of the pure fatty acids require much higher temperatures to produce concentrated solutions than do the potassium salts (cf. Figure 2).

The solubility of three potassium soaps is shown in Figure 2, where 4 equivalents per cent of potassium hydroxide was added to suppress hydrolysis. Comparing Figure 2 with Figure 1, a great contrast is seen between the solubility relations of sodium and potassium soaps. First, of course, is the fact that the potassium soaps are much more soluble than the sodium soaps so that concentrated solutions (21%) of potassium myristate are obtainable at 10°C., whereas for sodium myristate a temperature approaching 58°C. is required. Potassium stearate dissolves freely at 50°C., but sodium stearate needs 75-80°C.

The sodium soaps dissolve progressively as the temperature is raised, forming saturated solutions of higher and higher concentration over a wide range of 20°, whereas the potassium soaps almost abruptly become freely soluble up to high concentrations within 1 or 2° of temperature.

The so-called "Krafft Point" is the temperature at which soaps are supposed to become soluble. Demarcq (1) has taken the following as Krafft Points for the alkali stearates: lithium, 145-150°C.; sodium, 79°C. (cf. Figure 1 and the foregoing statements; potassium, 48°C. (our 47-51° of Figure 2); rubidium, 52.5°C. and cesium, 49°C. Stearic acid melts at 69.91°C. It is the "coincidence" of this melting point with the 79°C. of Demarcq (or the 78-80°C. of Figure 1) that is generally remembered as the Krafft Point for sodium soaps. The same temperature is labelled the genotypic point when discussing the slight change in crystal pattern that has been observed with one or two anhydrous soaps though not with others. Naturally there is no coincidence with the melting point of the fatty acid for the soaps of the other alkali metals, three of which lie about 20° lower, and lithium stearate about 80° higher.

Other Krafft Points mentioned by Demarcq are sodium laurate, 38°C. (cf. the 25-42°C. of Figure 1); potassium palmitate, 30.5°C. (cf. the 29-33°C. of Figure 2); lithium oleate, 72°C. The melting points of the three acids are: lauric, 44°C.; palmitic, 62.9°C.; oleic, 13.4°C. for the α and 16.3° for the β form.

Reference to Figure 1 clearly indicates that there is no definite temperature which can be called the Krafft point for sodium soaps unless such point is arbitrarily chosen.

The Effect of Excess Alkali Upon the Turbidity and Solubility of Potassium Soaps. Figure 3 shows the effect upon the apparent solubility or T_c values for several concentrations of potassium palmitate and potassium stearate of progressive additions of excess alkali. Without excess alkali the value is not sharp and the true solubility point T_c is obscured but it is represented rather by a gradual decrease of turbidity over a wide range of temperature. Furthermore, since hydrolysis is more prominent in dilute solutions, T_c apparently decreases for increasing concentration of potassium soap, which would be an impossibility for any pure substance not forming a highly stable stoichiometric hydrate consisting almost wholly of water. Upon subsequent addition of alkali T_c becomes sharp and it increases steadily, although slightly, with increasing concentration of potassium soap. After 5-8 moles equivalents per cent alkali has been added, further addition of alkali has practically no effect. In more concentrated potassium soap solution, such as 1 *m*, only about one equivalent per cent alkali is necessary to avoid any effects of hydrolysis, presumably because the concentration of the simple hydrolyzing fatty ions is less, and any acid soap formed would be incorporated in the micelles.

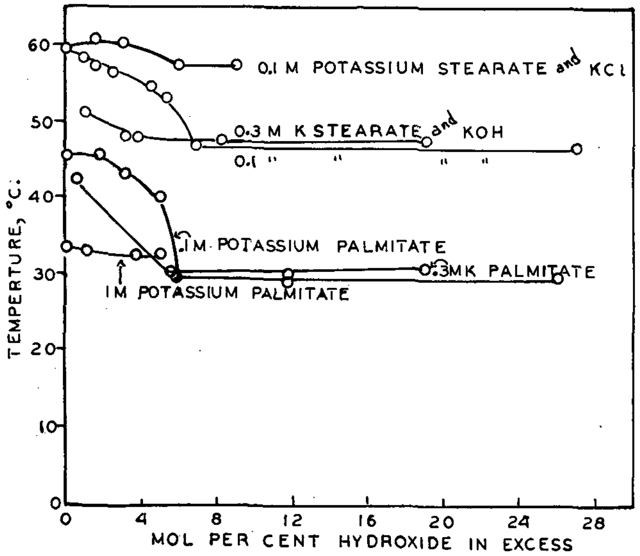

FIG. 3. The effect of excess potassium hydroxide upon the solubility of potassium palmitate and potassium stearate, and of potassium chloride upon the solubility of 0.1 *m* potassium stearate.

Figure 3 includes one curve in which potassium chloride is substituted for potassium hydroxide in 0.1 *m* solution of potassium stearate. The effect is somewhat similar to that of potassium hydroxide, but in less degree.

The data derived from the phase diagram for potassium laurate published in 1926 (3) indicated that potassium laurate dissolved over a range up to 10°C. We now find that solutions without excess alkali are indeed turbid up to 10-15°C., but with excess of alkali form clear solutions up to the high concentration of 2.3 *m* (35.4%) at 0°C. Thereupon the solution becomes a clear, plastic, liquid-crystalline mass. At about 3.6 *m* (46%) some curd remains at 0°C. but dissolves between 5 and 9°C. (Figure 4 is corrected accordingly.)

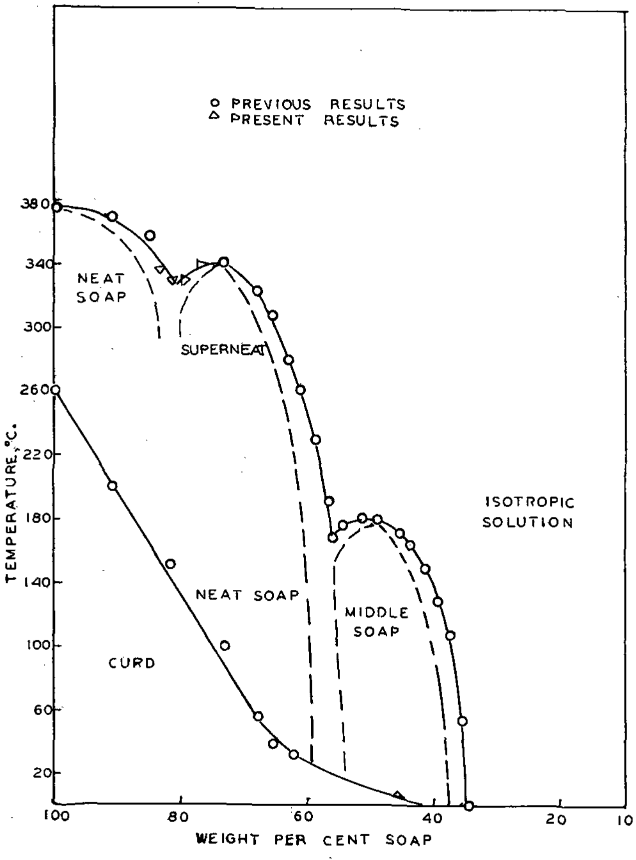

FIG. 4. Phase diagram for potassium laurate.

The Phase Diagrams of Potassium Soaps With Water. The phase diagrams for potassium laurate (3) and oleate (2) have been recalculated and are replotted from the original records in Figures 4 and 5. These figures also embody the further work done here.

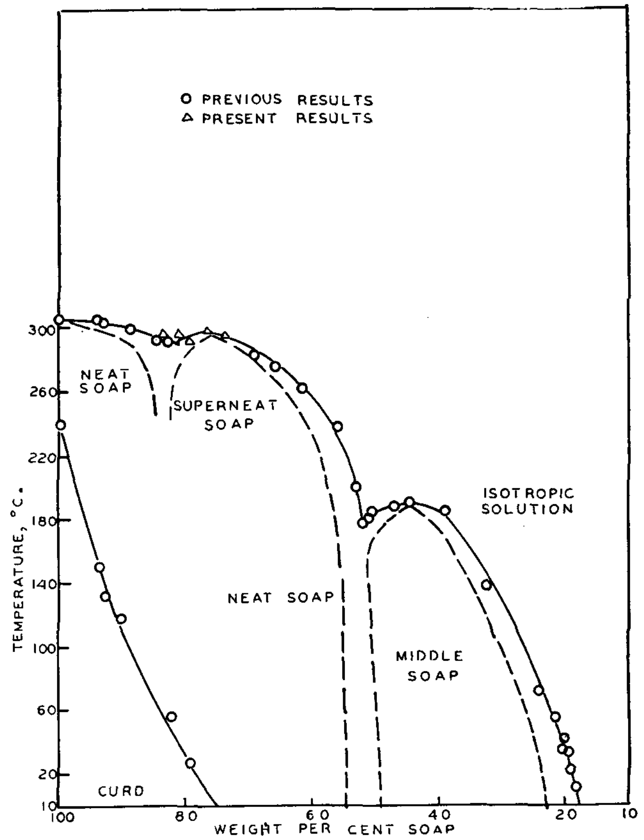

FIG. 5. Phase diagram for potassium oleate.

The phase diagram for potassium myristate and water is reproduced in Figure 6. It shows that a liquid-crystalline phase (clear, plastic, anisotropic liquid) appears at about 25% soap. T_i is designated as the temperature at which, on cooling, an isotropic soap solution just begins to separate out from it a liquid-crystalline phase. As the concentration of potassium myristate increases, T_i increases steeply, until it reaches a maximum at 47.5% soap at 202°C. At higher concentrations T_i first decreases until it reaches a point between middle and neat soap at 60% soap. Thereupon it increases again sharply to a second maximum at 335°C. and 75% soap. There is then a dip to 320°C. at 82% soap; and thereafter T_i rises steadily to the melting point of pure anhydrous potassium myristate at 392°C. Many phase changes occur between room temperature and 392° for anhydrous potassium myristate (5, 6), but these have not been investigated.

Phase diagrams for potassium palmitate and potassium stearate appear as Figures 7 and 8. The phase diagrams for these two, as well as for potassium my-

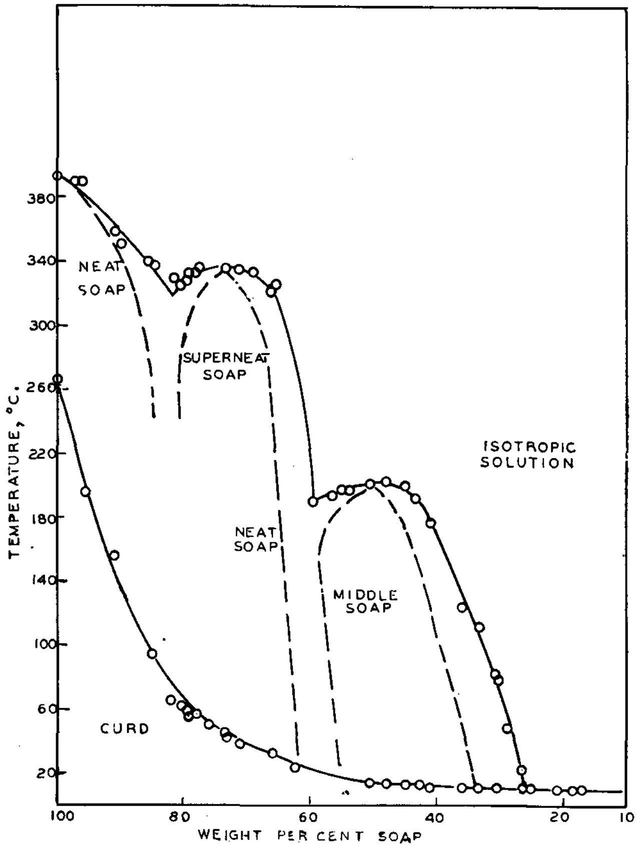

Fig. 6. Phase diagram for potassium myristate.

ristate, are quite incomplete between 90 and 100% soap. However, as a point of comparison, the known transitions for anhydrous potassium palmitate and stearate (6) have been indicated on the figures by crosses, with the temperatures noted.

Comparing Figures 4-8 with each other, it is seen that the diagrams for potassium soaps are similar.

Increasing the number of carbon atoms in a soap molecule decreases the melting point of anhydrous soap. It also decreases the lowest concentration at which liquid-crystalline phase can exist. The dip between middle and neat soap for the five potassium soaps here presented comes at about 60% of soap, and that between neat and super-neat comes at about 80% soap. The maximum melting points of the middle soap to form isotropic solution are nearly the same for all five soaps, namely 200° to 210°C. The maximum temperature of existence of super-neat potassium soap varies from 320-340°C.

Comparing the data for the potassium soaps with those of sodium soaps, the melting points of the potassium soaps are higher, and the super-neat and middle soap phases are stable to higher temperatures for the potassium soaps. The second maximum (e.g. 335°C. at 75% potassium myristate), now established for all the potassium soaps, has not been previously reported, but similar maxima have been established for the sodium soaps (4).

Summary

Solubility data are provided and collected for the pure sodium and potassium soaps. Hydrolysis obscures the temperatures of solution but is obviated by the presence of a small excess of alkali. Each sodium soap has a large range of temperature be-

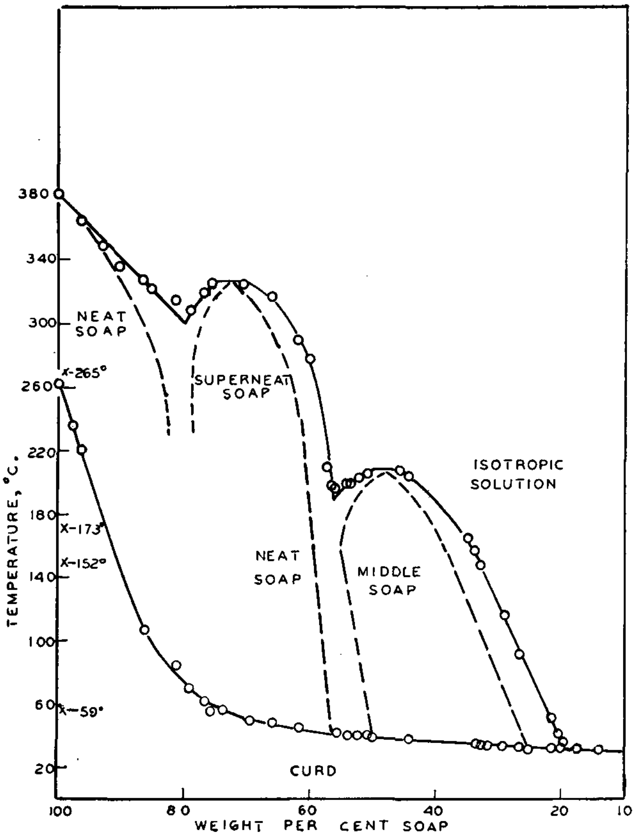

Fig. 7. Phase diagram for potassium palmitate. Crosses indicate known transitions for anhydrous potassium palmitate (6).

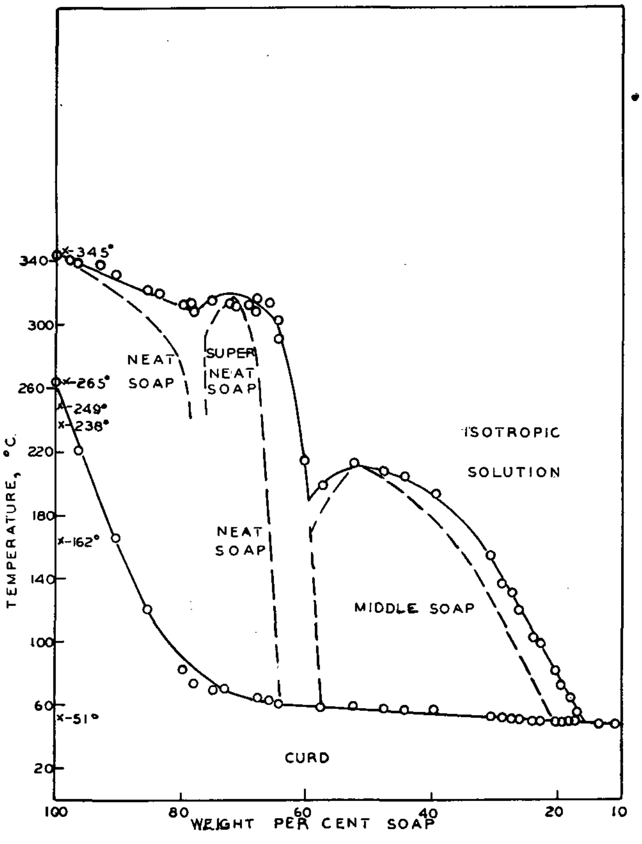

Fig. 8. Phase diagram for potassium stearate. Crosses indicate known transitions for anhydrous potassium stearate (6).

tween fair and high solubility, whereas the potassium soaps go abruptly into solution, at almost the same temperature and concentration of each soap.

The only soaps that are even moderately soluble at room temperature are potassium laurate, myristate, and oleate, the potassium salt of acids from coconut oil, and the sodium oleate. The other sodium and potassium soaps of the saturated fatty acids require elevated temperatures for solution.

Phase diagrams for the five commonest potassium soaps are developed and recorded.

REFERENCES

1. Demarcq, M., Inds. corps. gras., *2*, 341, 370 (1946); *3*, 13 (1947); through Abs. Tech. Press No. 786, 369 (1947).
2. McBain, J. W., and Elford, W. J., J. Chem. Soc., *129*, 421 (1926).
3. McBain, J. W., and Field, M. C., J. Phys. Chem. *30*, 1545 (1926).
4. McBain, J. W., and Lee, W. W., Oil & Soap *20*, 17 (1943).
5. Vold, R. D., J. Am. Soc., *63*, 2920 (1941).
6. Vold, R. D., and Vold, M. J., J. Phys. Chem., *49*, 36 (1945).

Rapid Volumetric Method for the Determination of Silica in Soap

ROBERT M. KELLEY and EUGENE W. BLANK, Research and Development Department,
Colgate-Palmolive-Peet Company, Jersey City, New Jersey

THE gravimetric method for the determination of silica in soaps involves a time-consuming evaporation and dehydration with concentrated sulfuric acid. There is a great chance for error due to spattering and insufficient dehydration. Losses due to the difficulty in handling the gelatinous silica are common. The volumetric method described below eliminates these disadvantages and is both rapid and accurate.

In 1929 Siegel (1) introduced a method for the volumetric determination of alkali-fluorides and silicic acid based on the reaction:

$$SiO_2 + 6NaF + 4HCl \rightarrow Na_2SiF_6 + 4NaCl + 2H_2O$$

Korol and Koluzhskaya (2) found that the determination of SiO_2 in water glass by this method proceeded very slowly and resulted in an indifferent endpoint. The addition of an excess of HCl and back titration with NaOH resulted in ambiguous results due to the fact that Na_2SiF_6 itself is titratable. These workers avoided this difficulty by employing potassium chloride to convert the sodium salt into the less soluble K_2SiF_6 and by titrating in the presence of alcohol.

The method of Korol and Koluzhskaya is capable of good results in the analysis of sodium silicate solutions but, when applied to the determination of SiO_2 in soap, immediate difficulty is encountered. In attempting to apply the method to the determination of SiO_2 in soap, it was found that the presence of phosphates and carbonates necessitated several modifications of their method. As described in this paper, these modifications consist in bringing the hot solution of the ashed sample to exact neutrality by adding an excess of N/2 HCl and back-titrating to a phenolphthalein endpoint with N/2 KOH. The required amount of potassium chloride is then added, followed by an excess of N/2 HCl and the required amount of NaF. After allowing sufficient time for the reaction to proceed to completion, the excess HCl is titrated with N/2 KOH. Boiling of the solution before adjustment of the initial endpoint is necessary to remove CO_2 from the solution.

Procedure

Reagents Required. The following reagents are required for use in the procedure:

N/2 Hydrochloric Acid.
N/2 Potassium Hydroxide.
Phenolphthalein Indicator solution prepared by dissolving 1 gram of phenolphthalein in 120 ml. of alcohol, adding 100 ml. of water, thoroughly mixing and neutralizing with dilute alcoholic KOH to a faint pink color.
Potassium Chloride (KCl).
Sodium Fluoride (NaF).
Neutral alcohol (95% ethyl alcohol, U.S.S.D. Formula 3a) prepared by neutralizing cold alcohol to a phenolphthalein endpoint with dilute alcoholic KOH.

Method

Accurately weigh 2 to 3 grams of the sample into a platinum dish. Carefully ignite over a Meker burner to a white ash. Dissolve the ash in approximately 100 ml. of distilled water (temperature 90-100°C.) and transfer to a 500-ml. Erlenmeyer flask. If difficultly oxidizable char is encountered, dissolve the ash as completely as possible in hot water, filter the solution, return the paper and char to the platinum dish, and again ignite. Dissolve the residue in a small volume of hot water and add to the filtrate already obtained.

Add several drops of phenolphthalein indicator solution and titrate to an approximate phenolphthalein endpoint with N/2 hydrochloric acid. Add an excess of about 5 ml. of the N/2 hydrochloric acid. Bring the solution to a boil to expel CO_2. Rinse down the walls of the flask with distilled water and titrate the contents of the flask with N/2 potassium hydroxide to an exact phenolphthalein endpoint. Cool the titrated solution under a stream of cold tap water.

Transfer the cooled solution to a 1000-ml. Erlenmeyer flask whose interior has previously been coated with paraffin. Use a commercial grade of white paraffin with melting point of 55-60°C. Add 20.0 grams of potassium chloride and exactly 40 ml. of N/2 hydrochloric acid from a burette. Add 5.0 grams of sodium fluoride and allow the mixture to stand for 10 to 15 minutes. Add a volume of cold neutral alcohol equal to the total volume of the solution already present in the flask. Allow to stand for an additional 5 minutes. Back titrate the excess N/2 hydrochloric acid with N/2 potassium hydroxide solution employing phenolphthalein indicator. The endpoint is taken when the color persists for one minute:

Calculation:

$$\%\ SiO_2 = \frac{(B - T) \times N \times F}{W}$$

B = ml. of N/2 KOH equivalent to 40 ml. of N/2 HCl.
T = ml. of KOH required for back titration.
N = Normality factor of N/2 KOH.
F = Equivalent weight of SiO_2 × 100.
W = Weight of sample.

Results

A number of sprayed soaps were analyzed for their silica content by both the usual gravimetric method (3, 4) and the volumetric method described above. The results obtained are shown in Table I.

To determine the precision of the volumetric method several determinations were made on Sample