A Phase Study of Sodium Soap - Sodium Silicate - Water Systems

By Yasushi KIMURA, Terunosuke SHIMO and Hitoshi SEKIGUCHI

(Received July 22, 1964)

Since it was established by McBain and his collaborators that the ordinary phase rule applies strictly to the phase diagrams of soap, various phase diagrams of soap - water or soap - alkaline electrolyte - water systems have been determined by McBain and by others.[1-3] However, the number of soap systems is so large, and the field to be covered is so extensive, that only minor portions of a few typical systems have as yet received quantitative study.[4] One of the practical industrial applications of these works is to predict the amounts of various builders which will dissolve in soaps at crutching temperatures.[3]

In the soap industry, particularly that concerned with the manufacture of commercial soaps, soap-silicate-water systems are important. However, although the amounts of silicates which can suitably be added to the soap at crutching temperatures have been known empirically for various soaps with different fatty acid compositions, these amounts have been determined incompletely from the phase-rule point of view.

Merrill,[5] using a typical commercial mixed soap and some industrially important silicates or other salts, measured the salting-out power of these salts at the arbitrarily chosen soap concentration of 24%, on the assumption that the relative efficiency is the same for different soap concentrations. However, no one has yet determined the phase behavior of the soap-silicate-water systems using a silicate and soaps with various structures and compositions.

For the purpose of supplying some date on the correlation of the suitable amounts of sodium silicate with the composition of sodium soaps, a phase study of some sodium soap - sodium silicate - water systems has been made using a silicate with a SiO_2/Na_2O weight ratio of 2.1, and six single soaps or their mixtures. This report will describe the T_c temperature in the systems with a 24% soap concentration, at which hydrated crystals or curd fibers change completely to liquid crystals, isotropic solutions, or both upon heating, as determined by the synthetic method.[5] The single sodium soaps used were laurate, palmitate, stearate, oleate, elaidate, and isoöleate(L). The data cover the silicate concentrations to 10 or 15%, and the temperatures to 80°C.

Experimental

Materials.—*Single Soaps.*—Table I gives the properties and compositions of the methyl esters which are the raw materials of these six soaps.

Methyl laurate, palmitate, and stearate were prepared by methanolysis and subsequent fractional distillation from the corresponding reagent grade fatty acids. Methyl oleate was prepared from commercial-grade rice oil by methanolysis and fractional distillation to isolate the C-18 fraction, followed by two low-temperature crystallizations from 15 volumes of acetone at −70°C and one distillation.[6] Methyl elaidate was prepared by the elaidinization[7] of the oleate with potassium nitrite and nitric acid at 30—35°C and four low-temperature crystallizations of the reaction mixture from 10 volumes of acetone at −40°C.

Figure 1 shows the infrared spectra of methyl oleate and methyl elaidate. Methyl elaidate has a strong absorption at 10.36μ, arising from a trans C=C bond;[8] the melting point of elaidic acid prepared from methyl elaidate was found to be 43.9°C, which is in agreement with the published value of Swern.[9] Therefore, the methyl elaidate used is considered to be pure.

For the purpose of obtaining the position isomers of elaidic acid, which have a double bond in $\Delta^{11:12}$ or $\Delta^{12:13}$ and different melting points,[10] the isoöleates (S) and (L) were prepared from caster oil containing ricinoleic acid by the following procedure: the oil was hydrogenated, using methanol as the solvent and 5% of a Raney nickel catalyst at 57°C and 44 atm. The hydrogenated product, after the solvent and the catalyst, had been removed, was dehydrated with 2% of sodium bisulfate at 200°C and 100 mmHg; the product was then separated by low-temperature fractional crystallization from the acetone solution into two fractions, one from

---

[1] J. W. McBain, G. C. Brock, R. D. Vold and M. J. Vold, *J. Am. Chem. Soc.*, **60**, 1870 (1938).

[2] J. W. McBain, R. D. Vold and W. T. Jameson, ibid., **61**, 30 (1939).

[3] J. Davidsohn, E. J. Better and A. Davidsohn, "Soap Manufacture," Coll. Vol. 1, Interscience Publishers, New York (1953), p. 59.

[4] J. C. McBain, R. D. Vold and K. Dardiner, *Oil & Soap*, **20**, 221 (1943).

[5] R. C. Merrill, *Ind. Eng. Chem.*, **39**, 158 (1947).

[6] D. Swern, H. B. Knight and T. W. Findley, *Oil & Soap*, **21**, 133 (1944).

[7] G. L. Vandone, *Ind. Vernice*, **4**, 42 (1950); *Chem. Abstr.* **44**, 10354-h (1950).

[8] R. T. O'Connor, *J. Am. Oil Chemists' Soc.*, **33**, 1 (1956).

[9] D. Swern, H. B. Knight, O. D. Shreve and M. R. Heether, *Oil & Soap*, **27**, 17 (1956).

[10] W. F. Huber, *J. Am. Chem. Soc.*, **73**, 2730 (1951).

TABLE I. PROPERTIES AND COMPOSITIONS OF METHYL ESTERS

Methyl ester	Iodine value*	Saponification value	M.p. °C	n_D^{40}	Composition,**% by wt.				
					C_{12}	C_{14}	C_{16}	C_{18F_0}	C_{18F_1}
Laurate	0.02	261.6	7.0	1.4242	100.0				
Palmitate	0.02	208.0	31.4	1.4331	0.2	0.4	99.4		
Stearate	0.01	188.4	30.5	1.4365			3.2	96.8	
Oleate	84.7	191.2		1.4444					100.0
Elaidate	85.0	189.8	12.5	1.4432			0.7		99.3
Isoöleate(L)	83.7	190.6		1.4435			0.4		99.6

* Determined by Wijs method at 15—20°C

** Determined by gas chromatography

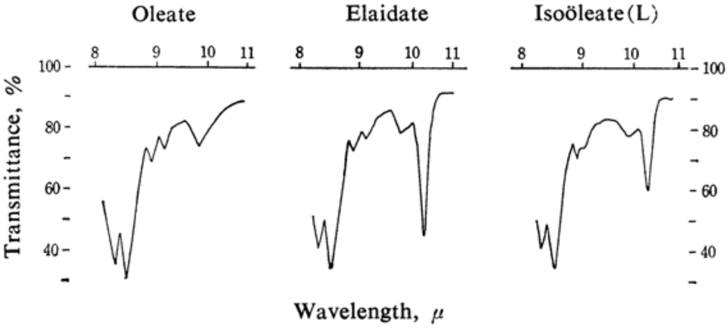


Fig. 1. Infrared absorption spectra of methyl esters of unsaturated fatty acids.

10 volumes of acetone at −30°C and the other from 15 volumes of acetone at −70°C. The solvent was removed, and, by the fractional distillation of the residues, the isoöleates (S) and (L), respectively, were obtained. However, the results of gas chromatography showed that the isoöleate (S) contains about 10% saturated ester. Therefore, this isoöleate was discarded.

Moreover, in the results of the paper chromatography of the mono-basic acids obtained by the periodate-permanganate oxidation of the isoöleate (L), contrary to expectations, it was seen that the isoöleate (L) consists of some position-isomers, $\Delta^{13:14}$ 24.4, $\Delta^{12:13}$ 18.0, $\Delta^{11:12}$ 35.9, $\Delta^{10:11}$ 14.1, and $\Delta^{9:10}$ 5.1, and the saturated 2.5%.

As Fig. 1 shows, furthermore, the isoöleate (L) has a rather weaker absorption intensity at 10.36 μ than that of elaidate; therefore, it is considered that some cis-geometrical isomers are also included.

Partially-hydrogenated commercial oils contain various isoöleates, owing to selective addition or isomerization during the hydrogenation of such elements as the isomers included in the isoöleate (L), and they are used in the manufacture of commercial soaps; therefore, this isoöleate (L) was used as one of raw materials of the soaps for the determination.

All of the single soaps were prepared by the neutralization of the fatty acids obtained from the corresponding methyl esters by saponification and subsequent acidification, and the free alkali of these soaps was adjusted to have a slight excess (less than 0.05%). The isoöleate soap, prepared from the methyl isoöleate (L) by the same procedure, is also described for the sake of convenience as a single soap in spite of its complex composition.

In the following figures, sodium soaps of laurate, palmitate, stearate, oleate, elaidate, and the isoöleate (L) are abbreviated as NaL, NaP, NaOl, NaEl, and Na*i*Ol (L) respectively.

Two-Single Soaps and Commercial Type Soap.—Equimolar mixtures of two-single soaps, with such combinations as saturated - saturated soaps and saturated - unsaturated soaps, were prepared from the corresponding single soaps.

A mixed soaps with almost the same composition as that of typical commercial laundry soap was prepared from sodium laurate, palmitate, oleate, and stearate in the ratio of 6.1, 32.6, 42.6, and 18.5% respectively. Hereafter, this mixed soap will simply be described as "commercial soap."

Sodium Silicate.—The sodium silicate of the JIS No. 1 grade of the Nihon Chemical Industry, Ltd., was used; the composition as determined by the JIS analytical method (K-1408) was 38.2% SiO_2 and 18.2% Na_2O; i.e., the SiO_2/Na_2O weight ratio was 2.10.

Procedure.—*The Preparation of Materials.*—All date were obtained by the synthetic method,[5] consisting of observing the temperature at which phase changes occur in systems of known compositions. To facilitate the visual observation for the soap phases, the determination was made at the relatively low soap concentration of 24%.

The calculated quantities (total weight 1.65 g.) of soap, silicate, and distilled water were weighed into a 2.35-ml. stainless steel micro-autoclave in the order named. In order to transform the contents into a single homogeneous solution, the autoclave was then heated in an electric muffle-furnace at about 210°C for a quarter hour and then quenched into ice water to settle the contents in an unseparated state. A part of the solid soap obtained, about 0.5 to 0.6 g., was taken into a 0.75-ml. glass micro-cell (inside diameter, 11 mm.; height, 8 mm.); this cell was covered with a slide glass and then sealed by epoxy adhesives (Bond-E7, Konishi Gisuke Co.).

The Determination of the T_c Temperature.—The determination was made by using an electric oven of the hot-plate type, Model MHS-3 (Union Optical Co.), with quartz-glass windows and jackets.

The micro-cell was heated slowly in order to allow adequate time for the soap system to acquire the successive temperature, and then the determination was made of the temperature, T_c, at which all traces of the opaque white solid disappeared to complete the formation of an isotropic liquid, an anisotropic liquid crystalline phase, or a mixture of the two. The curve of T_c values is, therefore, a solubility curve.4) The identification of the phases in a state of equilibrium at the T_c temperature was made by crossed polaroid disks.11)

The heating rate was rather quick, about 1°C/10 min., until 2—3°C below the T_c temperature; then the system was allowed to reach equilibrium, for which it took more than two hr.11) Stirring was effected by rotating the oven as a whole slowly and frequently. When the T_c temperature of the materials was lower than 30°C, the cell was dipped in ice-salt solution prior to the determination in order to transform the contents into a completely rigid solid. Moreover, the oven was kept 5°C below the T_c temperature by pumping cold water or a cold salt solution through the jackets, and then the determination was started.

The T_c values are reproducible to within 1°C; the values which were determined in single soap-water binary systems agreed closely with those reported by McBain and Lee,12) who used the vapor pressure method (Table II). Temperatures were measured with a calibrated thermometer.

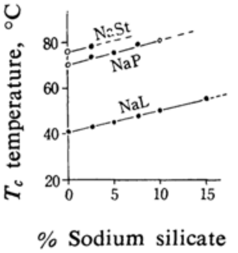
TABLE II. THE T_c TEMPERATURE OF A SINGLE SOAP-WATER BINARY SYSTEM IN °C

	NaL	NaP	NaSt	NaOl
McBain and Lee12)	41.5	70.0	77.5	29.0
The present authors	41.0	72.0	77.0	28.5

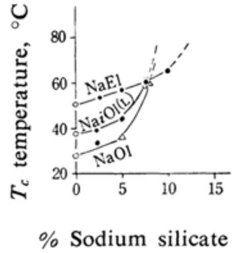
Results and Discussion

Figure 2 shows the effect of the silicate on the transition temperatures of these six single soaps. The effects on the equimolarly mixed soaps and on the commercial soap are shown in Figs. 3 and 4 respectively.

In the T_c values for single-soap systems, there is a characteristic tendency arising from the structure of the fatty acids of the soaps. Within the range determined, the T_c values for the saturated soaps are raised in proportion to the amounts of the silicate and their T_c value curves are parallel. While the amount of the

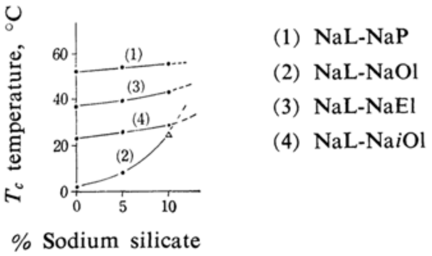


(1) Saturated soaps

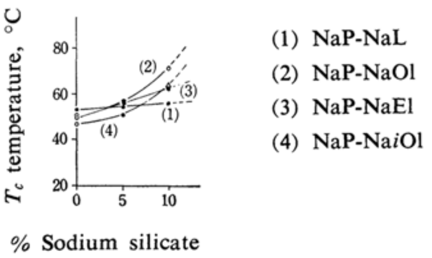


(2) Unsaturated soaps

Fig. 2. The T_c curves of single soap-silicate-water systems. Open circles, filled circles, and open triangles represent the compositions forming liquid crystals, isotropic solutions, and both liquid crystals and isotropic solutions on heating, respectively.



(1) Two-single soaps with sodium laurate



(2) Two-single soaps with sodium palmitate

Fig. 3. The T_c curves of two-single soaps-silicate-water systems.

---

11) J. W. McBain and W. J. Elford, *J. Chem. Soc.*, **1926**, 421.

12) J. W. McBain and W. W. Lee, *Oil & Soap*, **20**, 17 (1943).

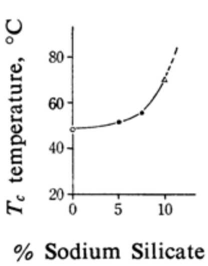
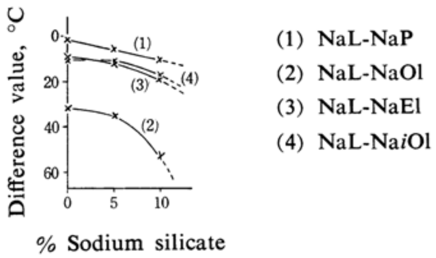
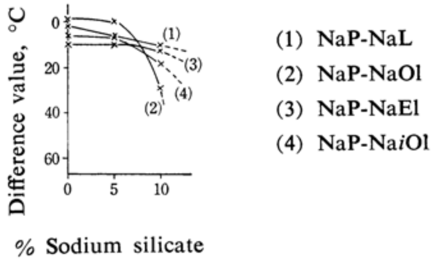


Fig. 4. The T_c curve of commercial soap - silicate - water system.



(1) Two-single soaps with sodium laurate



(2) Two-single soaps with sodium palmitate

Fig. 5. The difference-value curves of two-single soap - silicate - water systems.

silicate in the system is small, the T_c value of oleate soap is lower than any of the former, but it is elevated steeply when the concentrations of the silicate increase to more than 5%. These results agree with those of McBain et al.,⁴⁾ who found that oleate soap is salted out more easily (by sodium chloride) than are saturated fatty acid soaps.

As elaidic acid has a trans structure and its molecular form is similar to that of saturated acid, it may be assumed that the behavior of its soap, which has not yet been determined in any system, resembles that of the saturated soaps.¹³⁾ However, the T_c value curve obtained was in the middle of the oleate and palmitate soaps, and that of isoöleate (L) soap, though not pure, resembles that of the oleate. It seems that the influence of the tendency to salt out of cis unsaturated soap present in small amounts is very great.

In the systems of the two-single soaps, also there is a characteristic tendency arising from three main combinations; laurate soap - palmitate soap, the said saturated soap - oleste soap, and the said saturated soap - elaidate soap. The T_c value for the saturated - saturated soap systems is raised in proportion to the amounts of the silicate, as is the case with single-saturated-soap systems. The T_c values for the saturated soap - oleate soap systems are raised rather steeply as the silicate contents become relatively large. In the case of the combination with laurate soap, the T_c shows extremely low values with small amounts of the silicate. The T_c curves for saturated soap - elaidate soap systems are similar to the curves for the saturated - saturated soaps. However, the T_c curves for the saturated soap - isoöleate soap systems do not show any consistent behavior in the combinations with palmitate and with laurate.

As a rule, the T_c values which have been determined in the present experiment are lower than those estimated on a molecular basis from the T_c values for the ingredient soaps on the assumption that the T_c value has an additive property. The same is true also on a weight basis. These differences between determined and estimated values are shown in Fig. 5 as "difference values." It seems likely, as has been suggested previously,²⁾ that a less soluble soap can be prevented from separating as "curd" simply by adding it to the system of a soap with a shorter chain length. Mixed micelles of a smaller size, less orientation, and greater solubility must be produced by the presence of the shorter laurate molecules among the longer homologs, which is an example of mutual solubilization.²⁾ In other words, the solubility of sodium palmitate is effectively raised to near that of laurate soap by the addition of laurate soap to the system. The difference in the oleate soap - saturated soap system increases steeply when the silicate contents increase to more than 5%. This phenomenon shows that the tendency of oleate soap to salt out is substantially prevented by the saturated soap. In the commercial soap system, the T_c value determined is also lower than the estimated value. This difference is shown in Fig. 6.

In the manufacture of soap, the temperature at which silicates are mixed into soaps, i.e., the crutching temperature, is about 70—80°C. In this case, for the silicate to be mixed in homogeneously the T_c temperature of these systems must be lower than the crutching temperature.³⁾ However the T_c temperature increases with the amounts of the silicates added. Therefore, the amounts of the silicates which can be added are restricted. From the findings

---

13) H. Ezaki, K. Ohwada and S. Noguchi, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zassi*), **62**, 543 (1959).

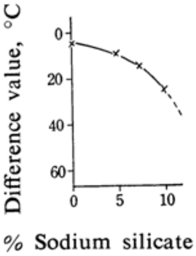


Fig. 6. The difference value curve of the commercial soap - silicate - water system.

concerning two-single soap systems, it may be concluded that, in order to increase the amounts of sodium silicate which can be added to the soap of higher saturated fatty acid, the combination with the lower saturated soap is suitable, because of the effect of lowering the T_c values through the higher concentrations of the silicate (Fig. 3).

Together with the combination of soaps, the mixing ratio of the two-single-soaps also influences the T_c value of two-single-soap systems greatly. This influence was determined for the ternary system of laurate roap - oleate soap - water. As Fig. 7 shows, when the substances are mixed with each other the T_c value is lowered, and at an equimolar ratio the value reaches a minimum, at which it is lower than that of a single-oleate-soap system with a low T_c value. This phenomenon is also due to the multiplicity of mutual effects.

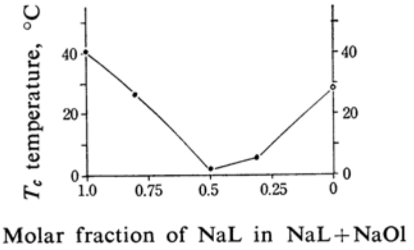


Fig. 7. Molar fraction and the T_c temperature in sodium laurate - sodium oleate - water ternary system.

Summary

The T_c temperatures of sodium soap - sodium silicate - water systems, which are important but are usually neglected, have been determined using a silicate with an SiO_2/Na_2O weight ratio of 2.1, and six single soaps or their mixtures.

It has been found that there is a characteristic tendency arising from the structure of the fatty acids of the soaps, saturated (higher or lower) and unsaturated (cis or trans). The T_c values of the saturated - fatty acid soap systems increase linearly in proportion to the silicate in the system. The T_c value curves of the unsaturated soaps are rather complicated. Their T_c values, while the contents of the silicate in the system are small, are relatively lower than those for the former, but when the silicate concentrations increase to relatively large amounts, the T_c values are elevated rapidly. This inclination is more remarkable for cis unsaturated soap than for the trans isomer.

In the system of the mixed soaps, there is a complex mutual effect. By the combination with a lower saturated-soap, the solubility of the higher saturated-soap is increased, and by the combination with a saturated soap, the tendency of unsaturated soap to salt out is substantially prevented. Consequently, the rising of the T_c curve for unsaturated soap becomes mild.

As a rule, the T_c values determined, therefore, are lower than those estimated from the T_c values for the ingredient soaps. It seems that, in order to increase the amount of builder which can be added to the soap of higher saturated-fatty acid, combination with a lower saturated-soap is suitable.

Moreover, in the case of the sodium laurate - sodium oleate - water system, it has been shown that the mixing ratio of the two-single soaps influences the T_c value greatly.

The Research Laboratory
of the Lion Fat and Oil Company
Edogawa-ku, Tokyo