

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

The Hydration of Curd Fibers of Sodium Palmitate and Sodium Oleate

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A soap curd is an opaque white felt of curd fibers. The fibers are long, but of ultramicroscopic thinness. Necessarily, the interstices and spaces between the bundles of interlacing fibers represent a fine capillary system of every gradation of pore size. When water is added to such a felt or gel the problem is twofold; first, how much are the ordinary phase rule relations overlaid and even obscured by capillary effects, and second, is it still possible in spite of such effects to distinguish between free and bound solvent. We here show that in all such systems the capillary effects must be recognized and allowed for, and second that in soap curds some of the water is free and some is bound, the amount depending upon the value of the relative humidity.

The fact that the fibers separating from a soap solution retain some water definitely associated with the soap in a union firmer than simple mechanical sponge action was discovered in 1911.¹ Since then attempts have been made to determine how much water was held, and in what way. The methods have been measurement of the water abstracted by curd fibers from solution through increase in the concentration of some reference substance,² measurement of the vapor pressure of water in equilibrium with soap curds of varying composition³ (by several techniques, including the use of saturated salt solutions as reference substances), study of the X-ray diffraction patterns of soap curds as a function of composition,⁴ measurement of the collapse pressures of sodium palmitate in a high speed air-driven centrifuge,⁵ microscopic and ultramicroscopic examination,⁶ and study of the sorption of methylene

blue on the surface of soap curd.⁷ The present communication contains an interpretation of further vapor pressure studies and of a new method of attack, namely, dilatometric measurement of the amount of ice formed at various temperatures in soap curds of varying composition.

I. Vapor Pressure of Water in Equilibrium with Curd Fibers of Sodium Palmitate

Two different procedures have been employed to measure the amount of water taken up by curd fibers as a function of its partial pressure. That here presented is a modification of the Robinson and Sinclair⁸ isopiestic method in which the same vapor is brought to equilibrium with both curd fibers and solution of potassium chloride of known composition. It proved readily applicable at relative vapor pressures from 0.96 to unity. Reference is also made to as yet unpublished investigations of W. W. Lee, J. L. Porter and R. D. Vold using the McBain-Bakr sorption balance which is best used at relative humidities from zero up to not more than 0.97 or 0.98.

Experimental.—The sodium palmitate used for the vapor pressure measurements at 25° was a 0.1074 *Nw* curd made by allowing a 0.1074 *Nw* solution of neutral sodium palmitate (prepared from palmitic acid "Kahlbaum") to cool in a Jena glass bottle, and stand since 1929, with vaselined glass stopper. The same sample was used throughout, but after dehydration and rehydration the fibers can no longer be assumed to be well-aged. Kahlbaum potassium chloride "for analysis" was thoroughly dried before use.

The apparatus consisted of four square silver dishes 2 cm. deep and 4 × 4 cm. wide set in a silver plate 12 cm. in diameter, 0.8 cm. thick to a depth of 3 mm. Thus adequate thermal contact between all parts of the system was assured. The plate was placed in a brass box 3.4 cm. high. The box was closed by a cover bolted down over a thin sheet rubber gasket. Evacuation, and the small vapor space, increase the rapidity of attainment of equilibrium. The entire apparatus was completely immersed in a thermostat operating at 25 ± 0.005°, on a device rotating at an angle of 20° to the horizontal, at 30 r. p. m. Weighed amounts of soap curd and of solutions of potassium chloride of known concentration were introduced into the dishes (2 samples of each in diagonally opposite corners). Care was used during evacuation to prevent

(1) J. W. McBain and M. Taylor, *Z. physik. Chem.*, **76**, 179 (1911).

(2) (a) J. W. McBain and M. Taylor, *J. Chem. Soc.*, **115**, 1300 (1919); (b) J. W. McBain and H. E. Martin, *ibid.*, **119**, 1369 (1921); (c) H. B. Bennett, *ibid.*, **125**, 1971 (1924); (d) M. E. Laing, *ibid.*, **119**, 1669 (1921).

(3) (a) J. W. McBain and C. S. Salmon, *ibid.*, **119**, 1374 (1921); (b) J. W. McBain, H. I. Bull and L. S. Staddon, *J. Phys. Chem.*, **38**, 1075 (1934); (c) R. H. Ferguson and R. D. Vold, *Oil and Soap*, **15**, 181 (1938); (d) R. D. Vold and R. H. Ferguson, *THIS JOURNAL*, **60**, 2066 (1938); (e) R. D. Vold and M. J. Vold, *ibid.*, **61**, 37 (1939).

(4) (a) S. H. Piper and E. N. Grindley, *Proc. Phys. Soc. (London)*, **35**, 5 (1923); (b) P. A. Thiessen and R. Szychalski, *Z. physik. Chem.*, **A156**, 345 (1931); (c) J. Stauff, *Kolloid-Z.*, **89**, 224 (1939).

(5) J. W. McBain and T. F. Ford, *THIS JOURNAL*, **62**, 866 (1940).

(6) (a) W. F. Darke, J. W. McBain and C. S. Salmon, *Proc. Roy. Soc. (London)*, **A98**, 395 (1921); (b) K. MacLennan, *J. Soc. Chem. Ind.*, **42**, 393T (1923).

(7) J. W. McBain, J. McDowell and M. E. Worden, *THIS JOURNAL*, **61**, 2540 (1939).

(8) (a) D. A. Sinclair, *J. Phys. Chem.*, **37**, 495 (1933); (b) R. A. Robinson and D. A. Sinclair, *THIS JOURNAL*, **56**, 1830 (1934).

spattering as dissolved air comes out of the solutions. The composition of each sample was determined by weighing after equilibration. While solutions of electrolytes reach equilibrium after a few hours, several days are required for soap curd to attain it. All samples were therefore allowed to equilibrate for at least one week. The curves both on hydration and dehydration are reproducible. The well known equation $p - p_s = p_s N_s g$ was used, with values of g , the osmotic coefficient, from the work of Scatchard and Prentiss,⁹ (p/p_s is the vapor pressure of the solution relative to water at the same temperature, and N_s the mole fraction of potassium chloride.) G. W. Fuller has shown that values of g at 0° can be used in this case at 25° with less than 0.08% error.¹⁰ As far as the experimental manipulations are concerned a weighing error of 1 mg. would give rise to a difference of 1 part in 10⁸ in the calculated value of p/p_s .

Data and Results.—The results obtained for the vapor pressure of water above sodium palmitate curd fibers at 25° are tabulated in Table I and plotted in Fig. 1. The logarithmic plot serves

TABLE I
RELATIVE VAPOR PRESSURE OF WATER ABOVE CURDS OF SODIUM PALMITATE AT 25°

Wt. % NaP	$(1 - p/p_s) \times 10^4$	Wt. % NaP	$(1 - p/p_s) \times 10^4$
A. First dehydration		B. Second dehydration	
2.903	3.20	50.432	52.75
3.036	3.68	53.883	59.90
3.165	4.17	57.540	71.59
3.328	4.19	65.741	97.69
3.484	4.98	70.912	131.37
3.714	5.48	77.761	195.11
3.849 ^a	3.93	84.685	385.91
5.393	15.89	85.308	399.01
9.653	16.39		
12.500	16.44	C. Third dehydration	
21.192	18.36	65.999 ^a	97.23
22.350	19.48	56.818	68.61
23.334	20.20	57.730	71.48
25.631	21.50	60.446	81.00
27.270	23.47	62.351	87.88
43.192	40.86	65.436	97.61
59.175	77.16		
61.950	81.60		

^a Points obtained during rehydration to make sure that true reversible equilibrium was being achieved.

to exhibit all the significant features in a single diagram. These are (1) the fact that although at least two phases, curd fibers and isotropic solutions are demonstrably present over most of the concentration range, the vapor pressure is not constant, (2) the fact that the vapor pressure is reproducible on successive dehydrations and hydra-

tions, (3) there is a flat portion of the curve between 5.5 wt. % and 17 wt. % sodium palmitate, (4) there is a small, poorly defined but apparently real and reproducible break in the continuous curve between 58% and 61% sodium palmitate, at approximately the composition NaP·10H₂O found by Bennett,^{3c} not by any discontinuity but by negative sorption using glycerol as reference substance. The results of Lee fit on satisfactorily at lower relative pressures; furthermore they show approximate constancy of composition over a wide range of vapor pressure in the neighborhood of the monohydrate NaP·1H₂O.

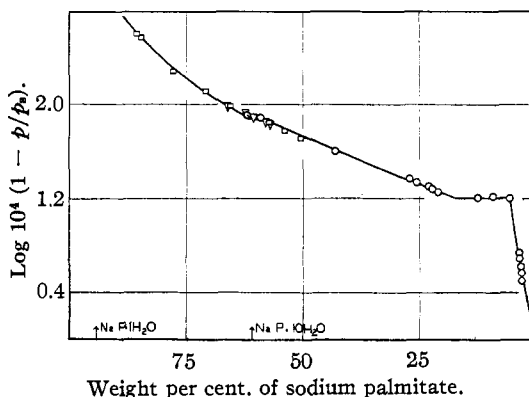


Fig. 1.—Relative vapor pressure of water above curd fibers of sodium palmitate at 25°: O, first dehydration; □, second dehydration; ▽, third dehydration.

The results clearly prove that the vapor pressure in a gel containing free water is not constant and cannot be expected to be constant where there are capillary spaces of varying diameter. The well-known Thomson¹¹ equation of the lowering of vapor pressure by placing any liquid in a capillary space of exposed radius r is

$$r = \frac{2\sigma d_{gas}}{p_s d_{liquid}} \ln \frac{p}{p_s}$$

where d refers to density and σ the surface tension; showing that for every relative vapor pressure capillaries will be filled to all levels whose radii are less than the radius given in the equation, and that the extent to which these capillaries of varying diameter will be filled is a function of relative vapor pressure. A further instance of these considerations is that even where the main equilibrium is between two finely divided hydrates, there must at high relative vapor pressures be free water present in all sufficiently fine interstices.

(9) G. S. Scatchard and S. S. Prentiss, THIS JOURNAL, 54, 2696 (1932).

(10) G. W. Fuller, Master's Thesis, Stanford University, June, 1936.

(11) W. Thomson, Phil. Mag., [4] 42, 448 (1871).

II. Freezing Experiments with Curds of Sodium Palmitate or Sodium Oleate with Water

Measurements have been made dilatometrically of the amount of ice that forms when soap curd is cooled substantially below 0° , both for sodium palmitate and for sodium oleate. The amount formed in any given sample is found to be independent of the temperature and duration of freezing between about -7 and -30° .

Since some of the water which freezes is held in the small spaces formed by the criss-crossing of the curd fibers, it is subject to the same kind of forces as water held in fine capillaries. E. A. Fisher¹² has derived an equation relating the change in density of liquid water in a capillary to the diameter of the capillary, assuming that the surface tension undergoes no change. For very small capillaries, of the order of 10 \AA . in radius, a decrease in density of 8.5% is expected. However, since the observed volume change all occurs between -7 and 0° the smallest capillaries containing significant amounts of water are approximately 250 \AA . in radius, and the calculated decrease in density is at most 0.3%. This can affect the result obtained for the weight of ice formed using the bulk densities of water and ice, by at most 3%, a figure scarcely outside the experimental error.

The dilatometric method involves using the difference in specific volume between ice and water at 0° as a constant factor in converting the experimentally measured increase in volume into a weight of ice formed. The value of this factor calculated from the densities of ice and water given in "International Critical Tables"¹³ is 0.0907 cc./g. Dilatometric experiments by several authors have given values ranging from 0.0930 to 0.0965 cc./g.^{13b,c,d} We obtained 0.0953 ± 0.002 in nine trials. Possibly the formation of cracks which are not filled by the dilatometer fluid, and the release of dissolved air on freezing contribute to the observed fluctuations. We used the factor 0.0953 throughout.

Experimental.—The sodium palmitate was specially made by Kahlbaum, previously described.¹⁴ The sodium oleate was prepared by neutralizing to phenolphthalein a

solution of oleic acid in ethyl alcohol with a solution of sodium ethylate and removing alcohol and water under reduced pressure at 40° . The oleic acid had been obtained from British Drug Houses, Ltd., and purified by fractional crystallization of the acid potassium dioleate from ethyl alcohol according to McBain and Stewart.¹⁵ The final product had a molecular weight by titration of 288.3, an iodine value of 85.8, calculated as oleic acid, and was exactly neutral. The residual 0.66% water was allowed for in making up samples.

One-gram samples were prepared by weighing out the desired amounts of soap and water into Pyrex tubes of 6 mm. diameter. These were sealed and heated to such a temperature that the entire contents formed a homogeneous isotropic liquid. After thorough mixing the tubes were cooled, opened, and sealed onto capillaries whose internal diameter had been carefully determined at several points by weighing the mercury contained per unit length. The finished dilatometers were cooled in ice and salt and filled with mercury.¹⁶

Most runs were made by first freezing the samples, either in ice and salt, or acetone cooled by adding dry-ice, allowing them to remain frozen for a measured time interval, and then measuring the change in height of the mercury level in the capillary as the temperature was gradually raised. A correction must be applied for the decrease in volume of the mercury as it passes from the stem at room temperature (25°) into the bulb of the dilatometer at 0° . The actual magnitude of this correction, however, seldom exceeds 1 mm. The dilatometer bulbs were immersed in the mechanically stirred freezing bath, contained in a double-walled glass vessel of 2.5 liter capacity to a depth of 10 cm. The temperature was controlled by adding small amounts of ice, salt, or water, dry-ice or acetone as needed. A few experiments were performed by gradually lowering the temperature, observing the change in height of the mercury level. Except for undercooling, the results were identical, but the persistent tendency of the bulbs to crack when suddenly frozen below 0° in this way led to the abandonment of this procedure.

Data and Results.—A typical result is shown in Fig. 2. On warming from -13° the volume increases continuously and very nearly linearly until point A at -2.2° is reached. The subsequent decrease is caused by melting ice. Twice, at a and at b, the temperature was lowered. Ice began immediately to reform, giving points a' and b'. These points show that a close approach was kept to equilibrium conditions during the melting process. When no more ice would melt at -0.1° , the temperature was allowed to rise above 0° and the melting soon became complete. Point O, dividing the total decrease in volume into a part occurring below zero and a part occurring at 0° is seen to be only roughly determined. The total decrease in volume, measured at 0° (VV') is good to about 2 mm. in a total of 197, or 1%, although

(12) E. A. Fisher, *J. Phys. Chem.*, **28**, 380 (1924).

(13) (a) "International Critical Tables," Vol. III, McGraw-Hill Co., New York, N. Y., 1926, p. 43; (b) H. W. Foote and B. Saxton, *THIS JOURNAL*, **39**, 627 (1917); (c) I. D. Jones and R. A. Gortner, *J. Phys. Chem.*, **36**, 387 (1932); (d) T. F. Buehrer, *J. Phys. Chem.*, **43**, 941 (1939).

(14) J. W. McBain, R. D. Vold and W. T. Jameson, *THIS JOURNAL*, **61**, 30 (1939).

(15) J. W. McBain and A. Stewart, *J. Chem. Soc.*, 1392 (1927).

(16) R. D. Vold and M. J. Vold, *THIS JOURNAL*, **61**, 808 (1939).

measurements on duplicate samples have shown extreme deviations as large as 6%.

Data for other samples of sodium oleate and sodium palmitate are given in Table II, and

TABLE II

RESULTS OF DILATOMETRIC MEASUREMENTS ON THE MELTING OF FROZEN SOAP CURD, GIVING THE NUMBER OF GRAMS OF ICE MELTED PER GRAM OF MIXTURE, A IF THE WATER AND ANHYDROUS SOAP WERE AN INDIFFERENT MIXTURE, B TOTAL ACTUALLY OBSERVED, C THAT NOT MELTED UNTIL IN THE NEIGHBORHOOD OF 0°, AND THE TEMPERATURES AT WHICH THE OBSERVED MELTING BEGINS AND IS COMPLETE

Wt. % soap	Expts. done	A	B	C	Begins	Ends
Sodium Palmitate						
11.13	2	0.889	0.846	0.795	-0.6°	0°
13.4	1	.866	.845	.778	-.5	0
13.9	2	.861	.790	.703	-.9	0
23.9	5	.761	.616	.547	-2.2	0
24.7	3	.753	.555	.475	-3.0	0
40.0	2	.600	.473	.356	-3.0	0
41.4	2	.586	.397	.213	-3.7	0
50.1	2	.499	.243	.167	-3.0	0
58.5	3	.415	.173	.005	-5.3	0
60.2	2	.398	.211	.019	-4.7	0
71.5	3	.295	.058	.000	-5.5	0
80.2	2	.198	.022	.000	-3.2	-0.9
90.7	1	.093	.007	.000	-3.5	-1.0
96.1	1	.039	.000	.000
Sodium Oleate						
8.95	5	0.910	0.879	0.695	-2.0	0
17.0	4	.830	.751	.454	-3.1	0
24.9	5	.751	.658	.373	-2.9	0
34.8	4	.652	.606	.131	-3.1	0
38.7	2	.613	.500	.055	-3.8	0
41.4	2	.586	.548	.013	-3.8	0
45.4	3	.546	.476	.011	-3.7	0
48.4	2	.516	.425	.006	-3.8	0
51.8	2	.482	.374	.021	-4.6	0
63.4	2	.366	.252	.000	-5.6	-0.1
77.6	2	.224	.091	.000	-5.4	-1.9
87.4	2	.126	.043	.000	-6.1	-2.7
91.4	2	.086	.029	.000	-7.0	-3.0
96.2	2	.038	.000	.000

plotted in Figs. 3 and 4. The significant features of the results are (1) not all the water in the curd (difference between columns A and B) can be frozen even at -30°; (2) of that which does freeze (column B) a considerable portion (difference between columns B and C) melts below 0° (the saturated soap solution at 0° is so dilute that its freezing point is not sensibly different from 0°); (3) melting begins at progressively lower temperatures as the soap content increases; (4) in highly concentrated systems the ice is completely melted at temperatures below 0°.

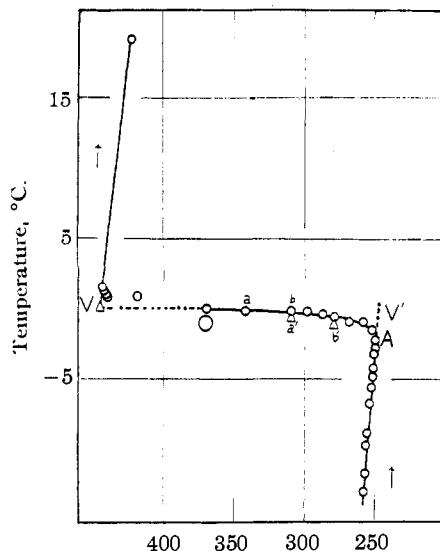
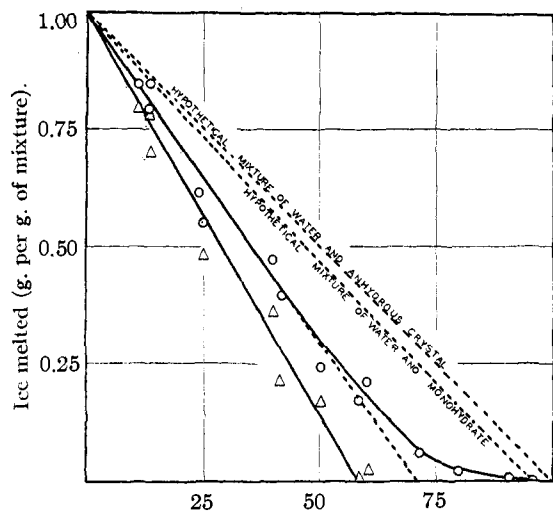


Fig. 2.—A typical dilatometer curve showing changes in volume when a frozen curd of sodium oleate (24.9% soap) is melted: O, points obtained on heating; Δ, points obtained on cooling. Point a' followed point a, and point b' followed point b. A is the temperature at which melting began. O is an estimate of the equilibrium volume just below 0° in which not all the ice is melted. V' - V gives the total decrease in volume due to melting ice.

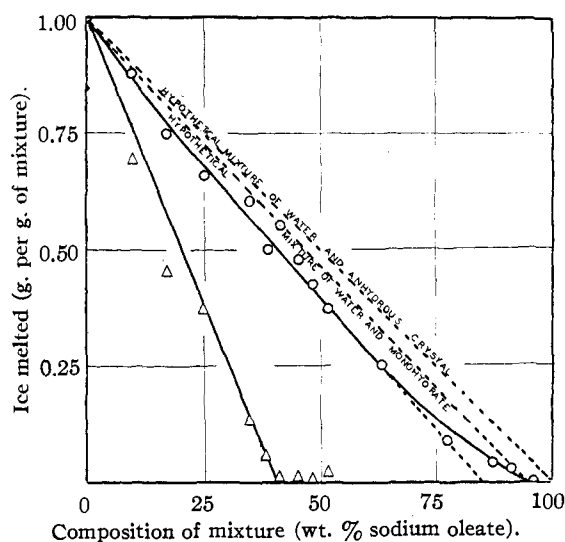
Discussion

The Equivalence of Vapor Pressure and Freezing Experiments.—The measurement of the equilibrium water content of soap curd as a function of the vapor pressure, or thermodynamic activity of the water, can be shown to be entirely equivalent, theoretically, to the measurement of the freezing properties of the soap curd. In the vapor pressure measurement the activity of the water is fixed by fixing the vapor pressure and temperature, and the composition of the soap curd adjusts itself by condensation or evaporation of water until equilibrium is reached. In the freezing measurement, the activity of the water is fixed by the fact that ice is maintained in the system at a given temperature. The composition of the soap curd adjusts itself through the freezing out of more water or the melting of ice until equilibrium is reached. The measurement of the hydration of soap curd by increase in the concentration of a reference substance not taken up by soap, such as glycerol, is also equivalent to the extent that the solubility of the soap in mixtures of water and glycerol, and the sorption of glycerol by the soap are both negligible. Here again the activity of the water is fixed by adding



Composition of mixture (wt. % sodium palmitate).

Fig. 3.—Ice melted in sodium palmitate curds of varying composition: O, total; Δ, ice which does not melt until nearly 0° is reached.



Composition of mixture (wt. % sodium oleate).

Fig. 4.—Ice melted in sodium oleate curds of varying composition: O, total; Δ, ice which does not melt until nearly 0° is reached.

a solute at constant temperature, and the composition of the soap curd adjusts itself by direct sorption of water from the solution.

The demonstration that this equivalence is experimentally real is complicated by the fact that the measurements by different methods have been made at somewhat different temperatures, and by lack of precision in the experimental results. To make the comparison we have assumed that the relative vapor pressure, p/p_s , does not change with temperature. We have also compared the p/p_s for sodium oleate, obtained in freezing ex-

periments, with vapor pressure measurements for sodium palmitate at 25°, thus neglecting the slight differences between the two soaps.

If a sample of soap curd is cooled to such a temperature that the vapor pressure of water over it is equal to that above ice at the same temperature, ice should just form, or, in our experiment, when the sample reaches this temperature on warming, all the ice should just be melted. A curve has been calculated from the vapor pressure measurements showing as a function of soap concentration the temperature at which all the ice should just be melted. The results have been compared with those obtained experimentally. Figure 5 shows that this temperature does decrease in the manner predicted. It is in general too high, ice persisting longer under the given experimental conditions than it should if equilibrium were continuously maintained. Most of the ice that should melt between -1 and 0° was allowed to persist up to 0° or even apparently slightly higher because melting at 0° occurs so very slowly.

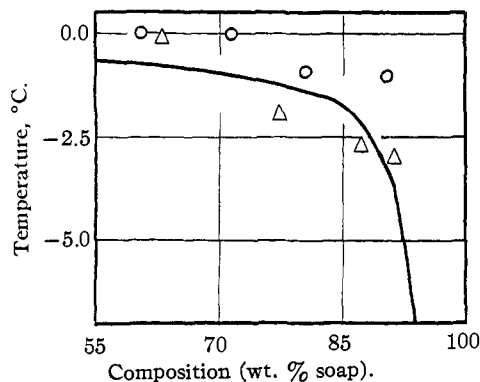


Fig. 5.—Comparison of the temperatures of complete melting with predictions from measurement of vapor pressure: —, calculated curve; O, results on sodium palmitate; Δ, results on sodium oleate.

Another comparison of the two methods is to convert the measurements of the amount of ice formed at various temperatures into a curve of p/p_s as a function of the actual composition of the soap by subtracting from the total water present that which is frozen, and obtaining the activity of the water from the vapor pressure of ice at that temperature. These results as a function of composition of curd can be compared directly with the vapor pressure measurements. The residual curd formed by freezing a sample of sodium palmitate containing 60% soap contains 67% soap at

the temperature corresponding to $p/p_s = 0.974$. The value observed at 25° was 0.99. For sodium oleate containing 60% soap the residual curd has 80% soap at a temperature corresponding to p/p_s of 0.968. The value for sodium palmitate at 25° at this composition was 0.976.

Bennett^{2c} found in a mean of five experiments that the curd fibers separating at room temperature from a solution containing 22 wt. % sodium palmitate and 5.2 wt. % glycerol, with a value¹⁷ of p/p_s of 0.987 contained 77.6% soap. According to our present direct vapor pressure measurements, p/p_s for a curd of this composition is 0.981 at 25° .

Classification of the Water in Soap Curd into Four Categories.—Three entirely independent experimental methods are thus found to be in agreement in showing that the activity of the water in the two component system water and soap is definitely not constant at constant temperature over the range of composition from about 3% soap to about 94% soap between 0 and 25° . This result constitutes a departure from the phase rule requirement of one or more flats or steps, *as derived for a system whose properties are determined solely by pressure, temperature and composition*, since the vapor pressure should be constant when two condensed phases are present in a two component system.

Numerous phase rule diagrams for binary systems of soap and water published from this Laboratory¹⁸ have represented this region as consisting of two phases, curd fiber phase and dilute mother liquor, in equilibrium. In samples containing up to about 30–40% soap, the simultaneous presence of the two phases is visibly demonstrable. The curd as a whole, however, has a rigid structure, with the water trapped in fine capillaries, and offers a definite measurable resistance to collapse. McBain and Ford⁵ calculated a value for the diameter of the capillaries based on the rate of collapse of sodium palmitate curd in a centrifugal field. For a sample containing 1.3% sodium palmitate they obtained an idealized average radius of 1.1×10^{-4} cm. If the entire vapor pressure lowering is assumed to be

caused by confinement of mother liquor in capillaries, the maximum radius of the capillaries can be calculated from the Thomson equation. At 1.3% sodium palmitate, σ is taken to be 30 dynes, D to be unity. Then from Fig. 1 and the vapor pressures of pure water in bulk, the maximum value of r in the graduated interstices is found to be 2.5×10^{-4} cm., in satisfactory agreement with the result of McBain and Ford.

The circumstances surrounding the appearance of the discontinuity in the curve of vapor pressure *vs.* composition between 5 and 17% sodium palmitate (Fig. 1) give support to the hypothesis that retention of water in fine capillaries is responsible for the lack of constancy of the vapor pressure. The curd was observed to collapse when its composition was about 5% soap, presumably due to the contractive effect of surface tension; this collapse reduced the diameters of the capillary spaces.

Each value of the relative humidity corresponds to a different curvature for the surface of the water. The calculated radii vary from 25,000 Å. at a relative humidity of 99.98% to about 100 Å. at 95%. The actual capillary structure of the soap curd certainly does not vary as much as this with concentration. The interstices must be of continuously variable diameter and are merely filled to a given radius at each vapor pressure.

The relative humidity does not decrease at a uniform rate as the soap concentration is increased. Between 60 and 85% sodium palmitate the drop is over twenty times more rapid than that occurring between 5 and 60%. In the freezing experiments, this effect makes it possible to divide the total amount of ice formed into two categories, one melting near 0° and the other substantially below 0° . In the case of sodium palmitate all water in excess of 40% is in the first category; for sodium oleate all above 60%. Expressed in thermodynamically inexact, but none the less practically real, terms this water is "free" as opposed to "bound." It is held in relatively coarse capillary spaces; it can be pressed out with moderate ease or frozen out at temperatures only slightly below the freezing point of pure water.

The amount of water which is "free" in the limited sense described above varies nearly linearly with the soap concentration (Figs. 3, 4), *i. e.*, the composition of the curd fibers themselves including the "bound" water remains nearly constant independent of total composition of the

(17) A. W. Lawrie, "Glycerol and the Glycols," A. C. S. Monograph No. 44, Chem. Catalog Co., New York, N. Y., 1928, p. 172.

(18) J. W. McBain, L. H. Lazarus and A. W. Pitter, *Z. physik. Chem.*, **A147**, 87 (1930); J. W. McBain, G. C. Brock, R. D. Vold and M. J. Vold, *THIS JOURNAL*, **60**, 1870 (1938); R. D. Vold, *J. Phys. Chem.*, **42**, 1218 (1939); J. W. McBain, R. D. Vold and M. Frick, *ibid.*, **44**, 1013 (1940); R. D. Vold, R. Reivere and J. W. McBain, *THIS JOURNAL*, **63**, in press (1941).

system at constant temperature, as is required by the phase rule. Likewise, the actual deviation of the relative humidity from constancy, while real, is also small on an absolute basis (*ca.* 1%) up to about 50% sodium palmitate.

The measurements of vapor pressure by Lee show that the composition of the soap curd is nearly independent of the relative humidity ranging from $p/p_s = 0.14$ to 0.86, and nearly that of sodium palmitate monohydrate. In the freezing experiments correspondingly, even when the temperature was reduced to -30° (which corresponds to a relative humidity of about 0.73), no ice ever formed in samples containing less than 6% water, and in more dilute systems the amount of ice formed was never great enough to leave the curd fibers with less than 6% of unfrozen water. This was true also for sodium oleate.

Thus we have identified two categories into which the water retained by soap curd can be classified. There is water of hydration, apparently chemically combined to the extent of one mole of water per mole of soap, and there is dilute solution, really uncombined, but having a slightly lowered activity due to its mechanical confinement in small capillary spaces.

This picture is not complete, however, for it fails to account for the behavior of systems containing between 60 and 94% sodium palmitate or 40 to 94.5% sodium oleate. The vapor pressure measurements above 60% sodium palmitate at 25° are not quite continuous with those below 60%. Moreover, even by going to temperatures well below that (-15°) where the activity of water lies on the vertical portion of the vapor pressure curve corresponding to the monohydrate, it was in no case possible to freeze out all the water in excess of $\text{NaP}\cdot\text{H}_2\text{O}$. The residual unfrozen water corresponds to a composition for the soap fibers themselves of 70% sodium palmitate or about $\text{NaP}\cdot 6.7\text{H}_2\text{O}$ (85% NaOl or $\text{NaOl}\cdot 3\text{H}_2\text{O}$), as can be seen by extrapolating the first nearly linear portion of the curves for total ice formed to their intersection with the soap axis (Figs. 3, 4).

Thus the water in a sodium palmitate curd between 60 and 70% sodium palmitate (or 40 to 85% sodium oleate) can be considered as either "bound" (in capillaries only) or "free," depending on how drastic an effort is made to remove it. It will freeze out, or it can be removed by lowering the relative humidity to about 0.98. On the

other hand such soap curds have considerable mechanical rigidity and the expulsion of water by pressure or extreme centrifugation is difficult or impossible.

The water in a curd between 70 and 94% sodium palmitate (or 85 to 94.5% sodium oleate) is sufficiently firmly "bound" not to freeze out in samples initially containing more water than this. Yet some ice is always formed in curds initially made up in this composition range, and the temperature of its formation is closely that predictable from the vapor pressure measurements.

These results can be summarized in tabular form as follows:

TABLE III
CLASSIFICATION OF THE WATER CONTAINED IN SOAP CURD
(0° up to 30° for NaP , 20° for NaOl)

Category	Composition limits	
	% NaP	% NaOl
1. Water of hydration. Removed only at low relative humidity ($< 10\%$)	100-94	100-94.5
2. "Firmly bound" water. Not removed from dilute curds by freezing. Only partly frozen out down to -30° . Removed at a relative humidity less than about 87%	94-70	94.5-85
3. "Loosely bound" water. Easily removed by freezing at -1 to -5° , or by moderate lowering of the vapor pressure	70-60	85-40
4. "Free" water. Held mechanically in small interstices; slightly lowered activity	60-0	40-0

Systems containing water in category 4 behave essentially as two phase systems with relatively small departures from the "ideal" behavior arising from the confinement of the water in capillaries. Those in category 3 behave superficially more like one phase systems, though perhaps they should be considered as mixtures of the monohydrate and a more highly hydrated phase, together with sorbed water which brings about pronounced departure from simple phase rule requirements. Little information is available concerning the properties of samples in category 1. The existence of category 3 in which some of the water present can be considered either as "bound" or "free" at the discretion of the experimenter, corresponds to the fact that the discontinuity between water considered "free" and that considered combined with the soap is not an absolute one and corre-

sponds to no gross discontinuity in the curve of activity *vs.* concentration

Obviously the present data give no information as to the way in which the water held by curd fibers is arranged except to confirm the conclusion of McBain and Ford⁵ that in dilute curds the water held mechanically exists in capillary spaces filled to such a level that the effective diameter is about 10^{-4} cm.

This discussion has omitted reference to the fact that moist soap curds are electrolytically conducting systems¹⁹ and to the effects of electrolytic charges on hydration such as are considered, for example, by von Nitsch.²⁰

Summary

1. The activity of water in soap curd has been

(19) M. E. Laing McBain, *Trans. Faraday Soc.*, **31**, 153 (1935).

(20) W. von Nitsch, *Kolloid-Z.*, **93**, 114 (1940).

determined by two independent methods: namely, measurement of the vapor pressure at constant temperature, and of the amount of ice formed at various temperatures, both as functions of total composition.

2. Sodium palmitate and sodium oleate can contain up to nearly one mole of combined water per mole of soap. Fibers crystallizing from more dilute systems contain more water than this (30–40% for NaP, 15–60% for NaOl) depending on the criterion for "bound" water.

3. Water in excess of 40% for sodium palmitate or 60% for sodium oleate is not chemically combined or sorbed, although its activity is slightly and progressively lowered by confinement in capillary spaces of the order of magnitude of 10^{-4} cm. in diameter.

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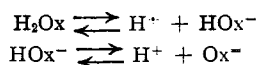
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Ionization Constants of Oxalic Acid at 25° from Conductance Measurements

BY LAWRENCE S. DARKEN¹

The success of the conductance method in determining the ionization constants of monobasic acids, together with the various general tendencies learned from the work on these, led the author to believe that the ionization constants of certain dibasic acids could be determined by a similar method, due account being taken of the rather small increment in conductance occasioned by the second ionization.

The ionization of oxalic acid in aqueous solution may be represented as



The ionization constant for the first dissociation cannot be determined by the method used for the ionization constant of a monobasic acid for two reasons: first, the measured conductance includes the contributions of both the first and the second ionizations; second, the equivalent conductance of the theoretical strong acid dissociating according to the first of the above equations only, Λ_0 , defined by the equation

$$\Lambda_0 = l_{\text{H}^+} + l_{\text{HOx}^-}$$

(where the l 's are the equivalent ionic conductances), cannot be obtained in the customary manner from data on the sodium salt since the sodium salt undergoes secondary ionization to a marked extent.

The latter difficulty can be overcome by use of the empirical rule, developed in previous work,² that the plot of the logarithm of the ionization constant versus the concentration of un-ionized acid is linear; Λ_0 is selected so that the plot is linear. Successful application of this method to the measured conductances of a dibasic acid requires first a correction for the second ionization. If C is the concentration of the oxalic acid, α the degree of dissociation for the first step, and Δ the concentration of the Ox^- ion, then

$$C_{\text{H}_2\text{Ox}} = C(1 - \alpha); \quad C_{\text{H}^+} = C\alpha + \Delta; \quad C_{\text{HOx}^-} = C\alpha - \Delta; \quad C_{\text{Ox}^-} = \Delta$$

$$k_1 = \frac{C_{\text{H}^+} C_{\text{HOx}^-}}{C_{\text{H}_2\text{Ox}}} = \frac{C\alpha^2}{1 - \alpha} - \frac{\Delta^2}{C(1 - \alpha)}$$

$$K_1 = \frac{C\alpha^2\gamma_1^2}{1 - \alpha} - \frac{\Delta^2\gamma_1^2}{C(1 - \alpha)}$$

$$k_2 = \frac{C_{\text{H}^+} C_{\text{Ox}^-}}{C_{\text{HOx}^-}} = \frac{(C\alpha + \Delta)\Delta}{C\alpha - \Delta} \frac{\Delta}{\Delta}$$

$$K_2 = \frac{(C\alpha + \Delta)\Delta\gamma_+ \gamma_-}{(C\alpha - \Delta)\gamma_-}$$

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(2) Saxton and Darken, *THIS JOURNAL*, **62**, 846 (1940).