or aluminum) is greater in the liquid than in the solid solutions, and the same for (potassium or ammonium) ferric alum, the results do not of course have the significance of those shown above in Table VII and Fig. 6, since Roozeboom's classification applies only to ternary systems.

Summary

1. The system Tl_2SO_4–$Al_2(SO_4)_3$–H_2O has been studied at 25° and the isotherm found to consist of the three solubility curves of Tl_2SO_4, $TlAl(SO_4)_2 \cdot 12H_2O$, and $Al_2(SO_4)_3 \cdot nH_2O$, respectively (n being probably 17).

2. The 25° isotherms for the ternary systems consisting of water and the three alum pairs thallium alum–ammonium alum, thallium alum–potassium alum and ammonium chrome alum–potassium chrome alum have been studied. In all three a complete series of solid solutions has been found, and their assignment to Roozeboom's Class I demonstrated.

3. That part of the quaternary system ferric ammonium alum–potassium alum–water, where the total compositions can be expressed in terms of $NH_4Fe(SO_4)_2$, $KAl(SO_4)_2$ and H_2O, has been studied at 25°. Where the concentration of $KAl(SO_4)_2$ relative to that of $NH_4Fe(SO_4)_2$ in the total composition is large, the behavior becomes that of a system of more than four components, apparently because of slight hydrolysis; all the quaternary solids, however, are solid solutions of alums.

NEW YORK, N. Y. RECEIVED JANUARY 23, 1940

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF STANFORD UNIVERSITY]

Some Properties of Sodium Palmitate Curd as Studied in the Centrifuge

BY JAMES W. MCBAIN AND T. FOSTER FORD

Soap curd[1] is a felt of hydrated crystalline fibers enmeshing a mother liquor that is slightly alkaline water with almost no soap. The fibers, although exceedingly fine,[2] yield good X-ray patterns as has been shown by Thiessen and others, and they are strikingly visible in the ultramicroscope. Ordinary solutes diffuse and sediment freely through their interstices.[3] The mechanical structure of the felt is sufficiently firm that sodium palmitate curd more concentrated than 0.2 M does not sediment or crush in a centrifugal field of 250,000 times gravity. Incidentally, this is likewise true of household soap, liquid crystalline sulfonic acid solution of 2 M, and of a potassium coconut oil liquid crystalline neat soap.

The densities of sodium palmitate curds at 20° with and without added salt, referred to water at 20° as 0.99820, are given in Table I. Compositions are given in true weight %.

TABLE I

Wt. % NaP	Wt. % NaCl	Wt. % H_2O	Density of curd
1.39	0	98.61	1.0000
2.105	0	97.895	1.0014
2.78	0	97.22	1.0014
2.065	1.92	96.0	1.0136
2.025	3.77	94.2	1.0269
2.725	1.91	95.3	1.0130
2.67	3.74	93.5	1.0194

The density of the hydrated curd fibers themselves was found by adding sodium palmitate solution to saturated sodium chloride solution until the curd fibers just began to sediment, instead of having a tendency to float. The result, 1.15, agrees fairly well with that calculable from Table I.

Observations in the Air-Driven Spinning Top.—For observation of sedimentation in the one-piece rotor the effective arrangement shown in Fig. 1 was devised. By looking obliquely down into the top, as shown by the arrow, it is possible to see directly the separation of water from curd. Calibration was by observation when known weights of water were added to the empty top, the internal radius of which was 0.80 cm., with opening of radius 0.5 cm., height of annular space 0.26 cm., and volume of annular space 0.32 cc. Forty seconds are required for the 20 mm. rotor to attain its full speed of 2650 r. p. s. at 80 lb. (5 atm.) pressure of air.

Separation of curd from water occurred so rapidly, in about one minute, that sedimentation velocity of curd fibers has not yet been accurately

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[1] Jerome Alexander, "Colloid Chemistry, Theoretical and Applied," Vol. I, Chemical Catalog Co., Inc., New York, N. Y., 1926, p. 138.

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

[3] J. W. McBain and C. Alvarez-Tostado *ibid.*, **59**, 2489 (1937).

measured. However, s is about 5×10^{-11}. The method of using a scraping tool was found inadmissible for soap curds as this may press water out of the structure.

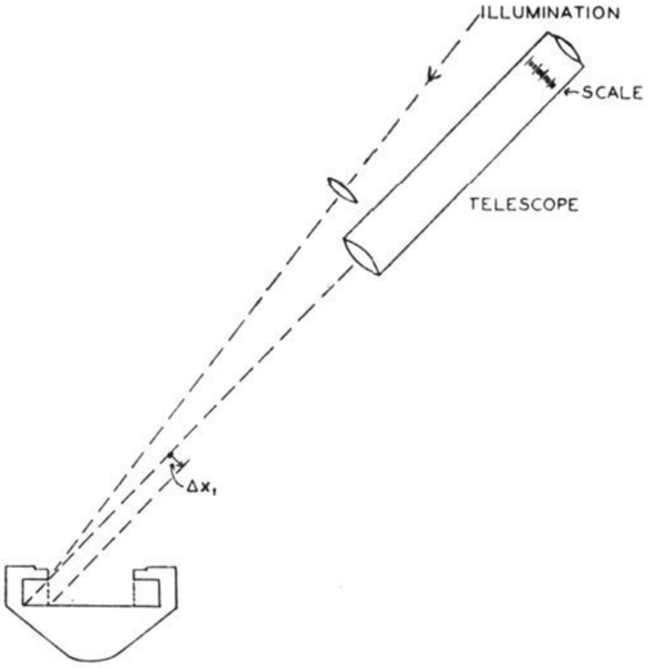

Fig. 1.

Tenth normal sodium palmitate curd shows no sedimentation at 2650 r. p. s.; one-fifteenth normal curd begins to collapse at 1500 r. p. s.; and one-twentieth normal at 1000 r. p. s. A curd collapsed at a high speed does not noticeably rebound when the speed is reduced, although in most cases a slight blurring of the originally sharp boundary between curd and separated water is noticed. This is due perhaps to the Brownian motions and slight diffusion of the curd fibers, but possibly also to a collision effect of molecules that are diffusing back after displacement in the high centrifugal field.

The amount of collapse increases as the centrifugal force increases, but it takes an observable time. The time lag must be due to friction of the water forced through the interstices of the curd structure. With the usual Poiseuille formula for membranes, idealized as consisting of parallel equal capillaries, the radius r of these equivalent capillaries was deduced from the measurements. For example, with a ring of 0.05 N curd of average radius 0.68 cm., 0.32 cc. of curd contained 0.0045 g. of sodium palmitate, of which the effective weight (above that of the aqueous medium) is 0.00067 g., the centrifugal force exerted on the periphery at 2000 r. p. s. is therefore $4\pi^2$ (0.00067) (0.68)$(2000)^2$ = 42,000 dynes. The rate of collapse at twenty seconds from the beginning of the experiment calculated from the slope of the collapse curve is 0.0234 g. H_2O/sec. The inner cylindrical surface of the curd being 1.11 sq. cm., by assuming that 1 sq. cm. of this is total pore cross section, it follows that the flow is equivalent to that through twenty-six million capillaries, each 0.3 cm. long and 0.00022 cm. in diameter. The initial calculated pore size is somewhat greater and that at forty seconds somewhat smaller, but the cessation of collapse is not due to the interstices becoming too small to permit capillary flow, but because the structure is stronger. A similar measurement at 800 r. p. s. gave also 0.00022 cm. for the effective pore diameter.

An alternative approach is to evaluate the diameter of the fibers themselves, or much more probably bundles of fibers, from the approximate sedimentation velocity constant, $s = 5 \times 10^{-11}$. Whereas for spheres this would correspond to a radius of about 390 Å., for very long cylinders the diameter would be about 400 Å. Judging by the well-known ultramicroscopic appearance of sodium palmitate curds, this is an effective diameter due to bundling of the parallel individual fibers which, according to the sorption of methylene blue,[2] are much less than 100 Å. in diameter.

Fig. 2a.—N sodium palmitate curd.

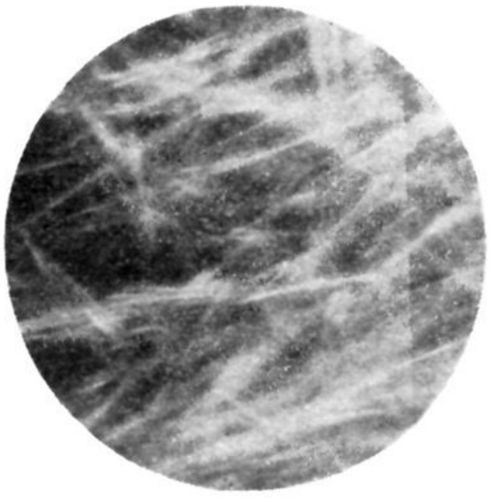

Fig. 2b.—0.25 N sodium palmitate curd.

Photographs of N and 0.25 *N* sodium palmitate curd as seen in the cardioid ultramicroscope are shown in Fig. 2, clearly showing that we are dealing with discrete bundles of fibers.

In Table II is given the final radial thickness, *d*, of the ring of water separated from 0.05 *N* sodium palmitate curds in experiments carried out in triplicate at 10, 20, 40 and 80 lb./sq. in. air pressure, respectively. In all cases the original thickness of the ring of curd was 0.30 cm. In Table III, glycerol was added in two experiments, raising the density to 1.0268, but separations at the higher pressures were greater than without glycerol despite the greater buoyancy of the medium.

TABLE II

FINAL THICKNESS, *d*, OF WATER LAYER SEPARATED FROM 0.30 CC. OF CURD

Lb./sq. in.	(R. p. s.)^2 × 10^{-6}	A	B	C
10	1.117	0.014	0.008	0.005
20	2.66	.052	.034	.030
40	4.92	.078	.052	.052
80	7.02	.090	.070	.070

TABLE III

FINAL THICKNESS, *d*, OF AQUEOUS GLYCEROL LAYER SEPARATED FROM 0.30 CM. OF CURD

Lb./sq. in.	(R. p. s.)^2 × 10^{-6}	D	E
10	1.17	...	...
20	2.66	0.030	0.045
40	4.92	.090	.170
80	7.02	.125	.180
100	8.4	.160	...

Since the properties of sodium palmitate curds depend upon their structure, the exact procedure used in their preparation is important. Thus if the soap solution has been cooled sufficiently that it has already begun to form curd fibers before placing in the top, it forms a soft "mushy" curd yielding considerably more water on collapse than if it were introduced while clear but just above the melting point and allowed to form and set in the slowly rotating top.

The mat separated from mush curd remains in one piece whereas the ordinary curd usually breaks into about seven equal segments in the rotor used owing to radial collapse of the inner circumference. This indicates that the mush curd possesses less oriented structure which agrees with the fact that more free water may be mechanically squeezed from such a mat than from a stiff curd collapsed to an equal extent.

When a curd refuses to collapse further at a given speed, the strength of the structure in the peripheral layer just balances the centrifugal force exerted by the unbalanced mass of the upper (or inner) layers of curd upon this peripheral layer. This pressure exerted inward radially by the outermost or peripheral layer is known as the swelling pressure, although here there is no marked tendency to swell but chiefly a tendency to resist further collapse.

This is a clear case where the origin of the swelling pressure[4] is mechanical rather than osmotic, whereas for many jellies and gels the two factors have not been distinguished in recording swelling pressures and the thermodynamically related vapor pressures. The data are collected in Table IV.

TABLE IV

FINAL THICKNESS, *d*, OF WATER LAYER FROM 0.30 CM. OF VARIOUS CURDS OF SODIUM PALMITATE AND THE SWELLING PRESSURES, *P*, IN DYNES/SQ. CM.

Description of curd	(R. p. s.)^2 × 10^{-6}	*d*	*P* × 10^{-4}
0.05 *N* NaP curd formed in top from soap soln. in which crystals just beginning to form, least collapse obtained	2.66	0.04	4.7
0.05 *N* NaP curd formed from soap soln. just above m. p., least collapse obtained	4.92	0.05	8.7
0.05 *N* NaP curd formed from soap soln. just barely melted clear, least collapse obtained	7.02	0.08	12.8
N/15 NaP curd formed from soap soln. just above melting point, least collapse obtained	7.02	0.038	17.0

Curds were made from 0.05 *N* sodium palmitate solutions with additions of sodium chloride and glycerol, respectively, in such amounts as to make the two curds equal in density. Compared with the original curd in water alone, the glycerol curd collapsed faster and to a greater extent. However, the sodium chloride curd was too rigid to collapse and showed a coarse radial structure yielding water readily upon cutting. The cut curd then collapsed. Since the glycerol medium has a higher viscosity, it is clear that the effect is one of structure and possibly of reduced hydration rather than any retardation of "capillary" flow.

Summary

The behavior of soap curd in the centrifuge is in accord with its brush heap structure with greater or less orientation depending upon previous history; the effective diameter of the interstices between the ultramicroscopic fibers being 10^{-4} cm., that of the fibers, or more probably fiber

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[4] J. W. McBain and R. F. Stuewer, *Kolloid-Z.*, **74**, 10 (1936).

bundles, themselves 400 Å.; and the swelling pressure from a chiefly mechanical origin being 10^5 dynes/sq. cm. for 0.05 N sodium palmitate curd. Glycerol softens the curd whereas sodium chloride makes it more rigid.

STANFORD UNIVERSITY, CALIF.

RECEIVED JANUARY 19, 1940

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTH CAROLINA]

Dialkyl Adipates

BY ROBERT A. FEAGAN, JR., AND J. E. COPENHAVER[1]

This work was carried out because of the growing commercial importance of the higher alcohols and adipic acid, as well as to study the type of melting point curve exhibited by the esters of this dibasic acid. This investigation covers the normal alkyl esters from pentyl to eicosyl. Since the first four have been described previously, they were not prepared in this series but for completeness they are included in the curve.

TABLE I

MELTING POINTS AND ANALYSES OF THE DIALKYL ADIPATES

Diester	M. p. (cor.), °C.	Carbon, %		Hydrogen, %	
		Calcd.	Found	Calcd.	Found
Methyl	8[a]	...	...	...	...
Ethyl	−21[b]	...	...	...	...
Propyl	−20.25[c]	...	...	...	...
Butyl	−37.5[c]	...	...	...	...
Pentyl	−14	67.10	66.07	10.56	10.08
Hexyl	−9 to −7	68.75	68.78	10.90	11.08
Heptyl	3.8–4.5	...	...	...	...
Octyl	9.5–9.8	71.31	70.77	11.43	11.56
Nonyl	21.6[d]	72.31	72.50	11.63	11.37
Decyl	27.4	73.19	74.22	11.88	12.02
Undecyl	34.7	73.96	74.57	11.97	11.56
Dodecyl	39.3	74.63	75.17	12.11	12.04
Tridecyl	45.9	75.24	75.33	12.24	12.14
Tetradecyl	49.4	75.78	75.52	12.35	12.55
Pentadecyl	55.0	76.27	76.36	12.45	12.27
Hexadecyl	57.3[e]	76.71	76.63	12.54	12.31
Heptadecyl	61.8	77.11	76.53	12.62	12.27
Octadecyl	63.4	77.48	76.49	12.69	12.08
Nonadecyl	66.7	...	...	...	...
Eicosyl	65.2	...	...	...	...

[a] Bouveault, *Bull. soc. chim.*, **29**, 1042 (1920); M. van Rysselberge, *Bull. soc. acad. roy. Belg.*, [5] **11**, 171–192 (1926).

[b] Timmermans, *Bull. soc. chim. Belg.*, **36**, 502–518 (1927), gave m. p. −21°, while H. Serwy, *Bull. soc. chim.*, **42**, 482–501 (1933), gave −19.9°.

[c] Timmermans, *Bull. soc. chim. Belg.*, **36**, 502 (1927).

[d] Staudinger and Schwalenstöcker, *Ber.*, **68**, 745 (1935), gave m. p. 17–18.5°.

[e] Staudinger and Schwalenstöcker, *ibid.*, gave the m. p. of 53°.

The esters up to and including dinonyl were colorless liquids at room temperature and above that compound they were white waxy solids. The melting points are given in Table I and plotted in Fig. 1. The alternation between the esters of the even and odd carbon alcohols was very slight, the odd esters exhibiting the unusual property of being a little above the mean curve. It will be noted that there is an even number of carbon atoms in all of these compounds.

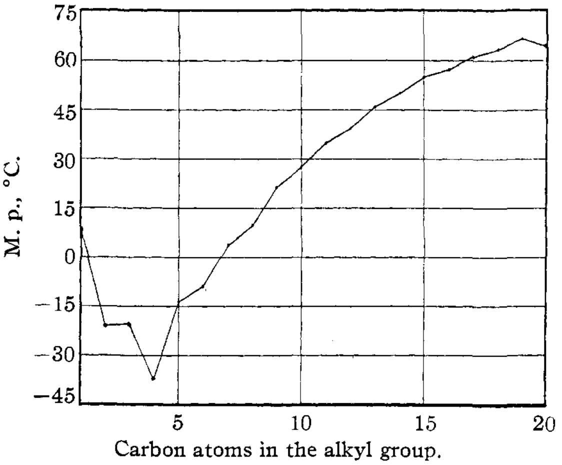

Fig. 1.—Melting points of the dialkyl adipates.

Experimental

Two methods were used for their preparation, *viz.*, the action of the alcohols on the acid or on adipyl chloride. In several cases, both methods were used and the products checked. A slight excess of the acid or the acid chloride was used above the theoretical quantity necessary for the formation of the diester. When adipic acid was used, the reaction mixture was heated at 150–155° for several hours, whereas with adipyl chloride, only slight warming was necessary.

The crude product from either method was dissolved in ether and thoroughly washed with 10% sodium carbonate. The recovered ester was recrystallized from

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[1] Presented in part before the Organic Division of the American Chemical Society at its 97th meeting, Baltimore, Maryland, April, 1939.