2H₂O. The molal freezing point lowering of calcium chloride is, however, so great as to make it extremely difficult, at 0°, to obtain points on this curve or to obtain data on the isothermal monovariant point at which the saturated solution is in equilibrium with NaCl and NaCl·2H₂O. The necessary data for these portions of the isotherm were not obtained and the first branch of the solu-
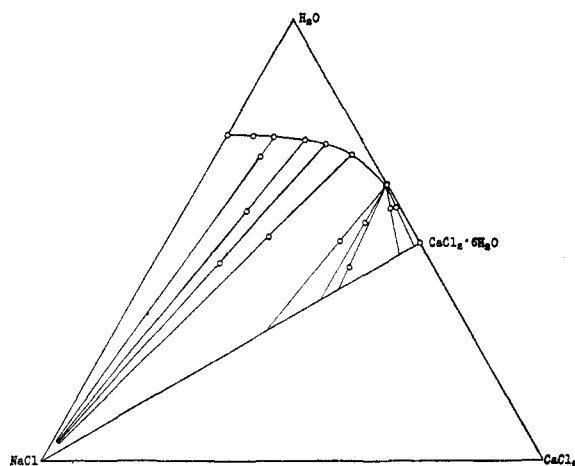

Fig. 3.—The ternary system CaCl₂–NaCl–H₂O at 0°.

bility curve is therefore represented, subject to correction, as for solutions in equilibrium with NaCl. The other branch corresponds to saturated solutions in equilibrium with CaCl₂·6H₂O. Because of the shortness of this curve, no points upon it were obtained, but study of the associated system CaCl₂–KCl–H₂O and MgCl₂–CaCl₂–H₂O

shows that the solid phase is CaCl₂·6H₂O. The composition of the saturated solution at the isothermal monovariant point is 0.31% NaCl and 37.50% CaCl₂.

The isotherm at 0° differs but little from the isotherms for the same system obtained at 25° by Cameron, Bell and Robinson[8] and at 50 and 94.5° by Pelling and Robertson.[9]

Summary

1. The isotherms for the ternary systems MgCl₂–KCl–H₂O, MgCl₂–CaCl₂–H₂O, CaCl₂–KCl–H₂O and CaCl₂–NaCl–H₂O have been determined at 0°.

2. The ternary system MgCl₂–KCl–H₂O, at 0°, is characterized by the extreme insolubility of potassium chloride, or of carnallite, in solutions saturated for MgCl₂·6H₂O.

3. Data for the system MgCl₂–CaCl₂–H₂O agree substantially with those obtained at the same temperature by Prutton and Tower.[6]

4. No evidence of double salt formation was found in the system CaCl₂–KCl–H₂O.

5. Because of the freezing point lowering produced by calcium chloride, it was impossible to obtain points on the solubility curve for NaCl·2H₂O or data for the monovariant point where NaCl·2H₂O, NaCl and solution are in equilibrium. Because of the shortness of this curve, these values are probably not much different from that for the solubility of sodium chloride in pure water.

A Study of Salts of Higher Alkyl Sulfonic Acids

BY R. M. REED AND H. V. TARTAR

The salts of the higher alkyl sulfonic acids are typical colloidal electrolytes with soap-like properties, but are better than soaps for experimental studies because they are salts of strong acids and do not hydrolyze in aqueous solutions.

The preparation of the sodium alkyl sulfonates has been described by the authors in a previous paper.[1] This communication describes the preparation of certain other salts and gives the results of solubility, surface tension and interfacial tension measurements, and determinations of electrical conductivity made on aqueous solutions of various salts.

(1) Reed and Tartar, THIS JOURNAL, 57, 570 (1935).

Solubility Determinations

Introduction.—It has long been known that the solubility of soaps in water increases greatly at certain temperatures.[2] The only work which has been reported on the solubility of salts of alkyl sulfonic acids is that of Murray and Hartley,[3] who studied the solubility of the cetyl derivative and its sodium, lithium and potassium salts. They found that sharp increases in solubility occurred at certain temperatures. This behavior was explained by the assumption that

(2) Krafft, Ber., 28, 2566 (1895); ibid., 29, 1328 (1896); ibid., 32, 1584 (1899).
(3) Murray and Hartley, Trans. Faraday Soc., 31, Part 1, 183 (1935).

Alkyl radical	Calcium salt		Grams of salt per 100 g. of water Magnesium salt		Sodium salt	
	25°	60°	25°	60°	25°	60°
n-Octyl	...	...	...	...	74.40	...
n-Decyl	0.155	0.260	0.268	...	4.55	...
Lauryl	.011	.033	.033	48.0[a]	0.253	>48[a]
Myristyl	.0014	.005	.0035	0.016	.041	38.8[a]
Cetyl	.0005	.0013	.0012	.006	.0073	6.49
n-Octadecyl	.0006	.0007	.0010	.003	.0010	0.131

[a] Approximate values.

when the amount of dissolved salt reaches the "critical concentration for micelles" an abrupt formation of micelles occurs with a consequent sharp increase in solubility. For cetyl sulfonic acid and its salts this occurs in the neighborhood of 0.01 M.

Experimental Methods and Data.—Calcium and magnesium alkyl sulfonates were prepared from the sodium salts by adding calcium or magnesium chlorides to solutions of sodium alkyl sulfonates, thus precipitating the calcium or magnesium salts. These were washed, dried and analyzed. All analyses checked with the calculated values.

The solutions were heated 10 to 20° above the temperature at which the solubility was determined and enough salt added to insure an excess of solid. The solution was placed in a thermostat and allowed to remain for two days with occasional shaking. It was then filtered through a Büchner funnel immersed in the thermostat. The filtrate was transferred to a flask and weighed. The solution was then evaporated to dryness in an oven at 105° and the weight of dry salt determined.

The solubility determinations at 60° gave no difficulty with calcium alkyl sulfonates, and magnesium myristyl, cetyl and n-octadecyl sulfonates. With magnesium lauryl sulfonate, however, the excess solid was jelly-like in appearance, and the saturated solution was quite viscous, resembling a concentrated soap solution.

Definite solubilities were obtained with the sodium n-octadecyl and cetyl sulfonates at 60°, but with sodium myristyl sulfonate the excess solid was a rather hard, transparent mass. The saturated solution was, however, not particularly viscous and quite clear. On heating, the mixture became homogeneous, and very viscous, and on cooling again to 60° a hard jelly-like mass settled out, leaving the solution clear.

A mixture of 48 g. of sodium lauryl sulfonate with 100 g. of water at 60° gave a very thick sirup. The behavior of this transparent mass on cooling was characteristic of all those obtained with these salts. It first solidified to an opaque mass which disintegrated at room temperature to crystals and a quantity of solution of low viscosity. This transition to a crystalline form takes place within the narrow temperature interval of only a few degrees. Lottermoser and Püschel[4] have recently observed a similar behavior with solutions of salts of higher hydrogen alkyl sulfates.

The solubilities of calcium, magnesium and sodium alkyl sulfonates at 25 and 60° are given in Table I.

Discussion of Results.—The extremely low solubilities of most of the calcium and magnesium salts at both 25 and 60° do not support the claims given in the literature since it has been repeatedly claimed that they are very soluble in water.[5]

The solubilities of the sodium alkyl sulfonates at 25° show the effect of the length of the alkyl carbon chain upon solubility. This is shown graphically in Fig. 1, where the logarithm of the solubilities has been plotted as a function of the number of carbon atoms. The relationship is very regular, even though the actual solubilities vary from 74.4 g. per 100 g. of water for the sodium n-octyl sulfonate to 1 mg. per 100 g. of water for the sodium n-octadecyl sulfonate.

The regularity of the relationship between solubility and the length of the carbon chain does not agree very well with the theory of Murray and Hartley,[3] unless it is assumed that the "critical concentration for micelle formation" for sodium n-octyl sulfonate solutions is higher than 3.444 M and that it is higher than 0.19 M

(4) Lottermoser and Püschel, Kolloid Z., 63, 175 (1933).

(5) (a) French patent 711,210; C. A., 26, 1732 (1932); (b) French patent 716,705; ibid., 26, 2288 (1932); (c) British patent 360,539; ibid., 27, 575 (1933); (d) British patent 369,301; ibid., 27, 2661 (1933).

for sodium decyl sulfonate solutions. Since the saturated solutions (at 25°) of the sodium n-octadecyl, cetyl and myristyl sulfonates all fall well below this critical concentration, and the saturated solution of sodium lauryl sulfonate (0.009 molal) is also probably slightly below it, the saturated solutions of the sodium n-octyl and n-decyl sulfonates must also be considered as below the "critical concentration for micelle formation" if the regularity in their solubility is to be reconciled with the viewpoint of Murray and Hartley. An alternative explanation would be that the carbon chains of the sodium n-octyl and n-decyl sulfonates are so short that micelle formation is no longer an important factor and that these salts obey the ordinary relationships of non-micellar solubility throughout all ranges of concentration. Although this explanation is probably partly correct, the soap-like properties of these solutions, together with their surface tension and interfacial tension behavior, as well as the electrical conductivity of solutions of sodium decyl sulfonate, all point to the presence of colloidal micelles in the concentrated solutions.
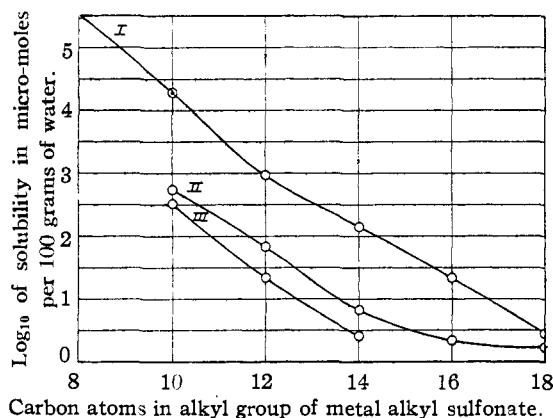

Fig. 1.—The relationship between the solubilities of salts of the alkyl sulfonic acids and the length of the alkyl carbon chain: I, sodium alkyl sulfonates at 25°; II, magnesium alkyl sulfonates at 25°; III, calcium alkyl sulfonates at 25°.

Surface Tension Measurements

Introduction.—Lottermoser and Stoll[6] have recently made surface tension measurements on aqueous solutions of a series of sodium alkyl sulfates. They used the anchor ring method[7] and reported that the values obtained were reproducible, although they did mention that solu-

tions which were five days old gave values slightly different from those of fresh solutions.

A series of surface tension measurements on solutions of sodium alkyl sulfonates and of sodium lauryl sulfate was undertaken in this Laboratory by the anchor ring method. It was found, however, that this method was unsuitable for determining the surface tension of such solutions, because the surface tension changes very markedly with time. The results lead to the conclusion that the results of Lottermoser and Stoll cannot be considered as surface tensions at equilibrium, but rather as surface tensions of fairly fresh surfaces. Such changes of surface tension with time have been repeatedly observed with colloidal solutions, such as aqueous solutions of sodium oleate. Bigelow and Washburn[8] have given a good historical account of such studies, together with further confirmatory results which they obtained. In all such cases the same type of behavior has been observed, namely, an initially rather high value, followed by a more or less regular decrease to a final minimum value, reached usually in a few hours. They concluded that the capillary rise method was the most suitable for observing such behavior since in this way changes in surface tension with time could be observed without any necessity of disturbing the surface.

Surface Tension Measurements by the Capillary Rise Method.—A number of capillarimeters were made according to the design of Richards and his co-workers.[9] They were provided with ground glass stoppers to prevent losses by evaporation or outside contamination. The capillary tubing was all carefully inspected for evenness of bore, and the radii of the capillaries were determined by the method of Harkins and Brown.[10] These values for the radii, which varied from 0.336 to 1.044 mm., checked those obtained by determining the capillary rise of water and benzene using the values of Harkins for the capillary constants at 25°.

The measurements at 20 and 25° were made in a thermostat controlled to 0.1°; at 60° a Freas electric oven was used.

Preliminary experiments showed that the age of the solution at the time it was placed in the capillarimeter had no apparent effect upon its subsequent surface tension behavior.

(6) Lottermoser and Stoll, Kolloid Z., 63, 49 (1933).

(7) DuNoüy, "Surface Equilibria of Colloids," Chemical Catalog Co., New York, N. Y., 1926.

(8) Bigelow and Washburn, J. Phys. Chem., 32, 321 (1928).

(9) Richards and co-workers, This Journal, 37, 1656 (1915); ibid., 43, 827 (1921).

(10) Harkins and Brown, ibid., 41, 449 (1919).

Early experiments also showed that the surface tension of the solutions did not reach a static value after a few hours, but that changes continued for many days. A 0.001 M solution of sodium lauryl sulfonate was prepared and placed in four different capillarimeters, two of which were maintained at 20°, and two at 60°. The apparatus was especially free from vibration, and the capillarimeters were left undisturbed for one and one-half months, several readings of the capillary height being taken each day. After this time, the capillarimeters were shaken, replaced and allowed to remain for a day, after which the two at 20° were interchanged with those at 60° and the surface tensions were observed for three weeks when the same procedure of shaking and interchanging was repeated and the surface tensions were again observed for three weeks. The results of this experiment are given in Fig. 2.[11]

It will be observed that the size of the capillary tube used does not affect appreciably the surface tension behavior of the solution. At 20° (curve IA) the surface tension of the solution decreased quite steadily for several days. The minimum point was followed by a slow increase in surface tension for several days. In three weeks, however, an equilibrium value was reached which was practically the same in both capillarimeters. That this was a fairly stable value is shown by the behavior of the solutions after they were shaken. Although the surface tensions of both solutions increased noticeably on being shaken, they returned to the equilibrium values by the next day.

At 60° (curve IIA) the surface tension of the solution was practically identical in both capillarimeters and a slow but steady increase occurred until a value very near that of pure water at 60° (66.2 dynes) was reached.

Curve IIB shows that when the solution was changed from 60 to 20° there was a definite decrease in surface tension. On changing the temperature back to 60° (curve IIC) the surface tensions soon approached that of pure water.

On changing the capillarimeters from 20 to 60°

(11) In this, as well as in later graphs, an "S" preceding two points on the same day connected by a dotted line indicates that the solution was shaken and maintained at the same temperature.

(curve IB) the surface tensions increased steadily. When the temperature was lowered to 20° (curve IC) a decrease in surface tension was noted.

After the solutions were removed from the thermostats the pH was determined using thymol blue indicator, and in all cases was found to be from about 9.2 to 9.4. This increase from neutrality was attributed to the solution of a small amount of glass during the three months aging period. The data showed definitely that no hydrolytic decomposition of the sodium lauryl sulfonate had occurred.

On the completion of this experiment, the changes in surface tension with time of solutions of the different sodium alkyl sulfonates were
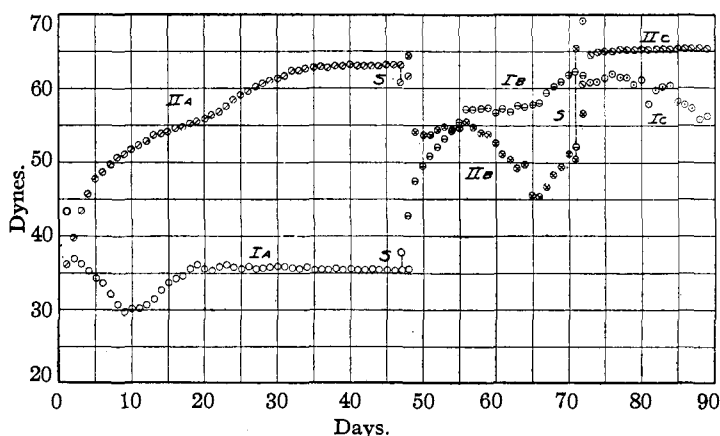

Fig. 2.—Surface tension changes in 0.001 molal sodium lauryl sulfonate solutions: I A ○, solution in capillarimeter of radius 0.374 mm. at 20°; I B ⊖, solution in capillarimeter I placed at 60°; I C ◎, solution in capillarimeter I placed at 20°; II A ⊘, solution in capillarimeter of radius 0.505 mm. at 60°; II B ⊗, solution in capillarimeter II placed at 20°; II C ◐, solution in capillarimeter II placed at 60°.

studied. In addition, solutions of sodium lauryl sulfate were also studied to determine their behavior, as well as a solution of sodium laurate and a solution of magnesium decyl sulfonate. The results of some of these studies are shown in Figs. 3 and 4.

The surface tensions of the sodium n-octyl sulfonate solutions shown in Fig. 3 are especially interesting. While the 0.001 M solution of sodium lauryl sulfonate was very capillary active at 20°, and showed an initially low surface tension at 60°, the 0.001 M solution of sodium octyl sulfonate had practically no effect upon the surface tension of water either at 25 or at 60°. On increasing the concentration to 0.01 molal, the solution at 60° still showed only a slightly lower surface tension than water, but at 25° distinct capil-

lary activity was observed. The initially high surface tension was followed by a rapid drop, after which a slight increase occurred, and then a gradual fall until a fairly steady value was

Fig. 3.—Surface tensions of sodium *n*-octyl sulfonate solutions:

I ○, 0.001 molal solution at 25°.   V ⊖, 0.1 molal solution at 25°.
II ⊙, 0.001 molal solution at 60°.   VI ⊗, 0.1 molal solution at 60°.
III ⊘, 0.01 molal solution at 25°.   VII (‡), 1.0 molal solution at 25°.
IV ⊕, 0.01 molal solution at 60°.   VIII ◎, 1.0 molal solution at 60°.

reached after about ten days. On shaking the solution the surface tension returned to its original high value and then began to fall.

Increasing the concentration to 0.1 *M* caused the surface tension at 25° to be much lower than that of the 0.01 *M* solution. In this case a steady value was reached after about ten days. On shaking the capillarimeter, the surface tension fell slightly, instead of showing an increase, as had the 0.01 molal solution. At 60° the 0.1 *M* solution of sodium *n*-octyl sulfonate showed definite capillary activity, the surface tension fluctuating markedly from day to day, although the surface tensions were somewhat higher than those of the corresponding solution at 25°. The 1.0 *M* solutions were both definitely capillary active, with practically constant surface tensions from the beginning, although the values were higher than those of the 0.1 *M* solution at 25°, and the surface tension of the solution at 60° was lower than that shown by the corresponding one at 25°.

The surface tensions of the various sodium *n*-decyl sulfonate solutions at 25 and 60° were similar

in many respects to those of the sodium *n*-octyl sulfonate solutions, the most notable difference being that the 0.01 *M* solution at 60° showed great capillary activity and was even more active than the corresponding solution at 25°.
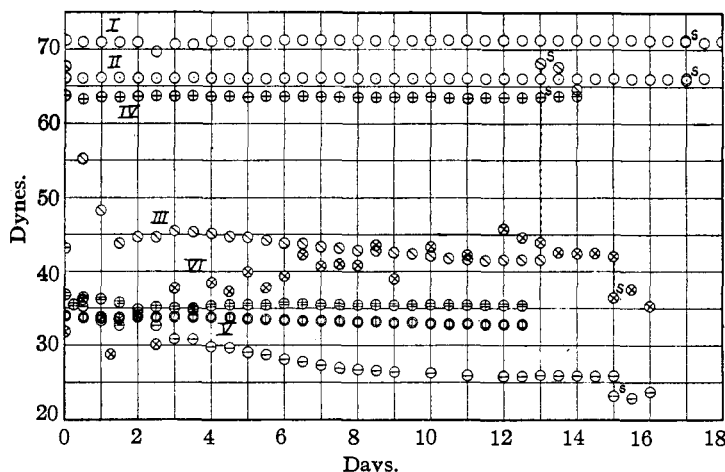
The surface tensions of sodium lauryl sulfate[12] showed a behavior like the sodium alkyl sulfonate solutions. On changing the temperature from 60 to 25° the surface tension fell from 61 dynes to the same low value (23 dynes) as was observed with the corresponding solution originally placed at 25°. This shows that the high surface tension reached by this solution at 60° is not due to a chemical decomposition since it regains its low surface tension on being changed to 25°.

The surface tensions of a number of other sodium alkyl sulfonate solutions are shown in Fig. 4.

To show the effect of a bivalent cation, the surface tension of a 0.005 *M* solution of magnesium *n*-decyl sulfonate was determined at 25 and 60°. No difference in behavior was noted.

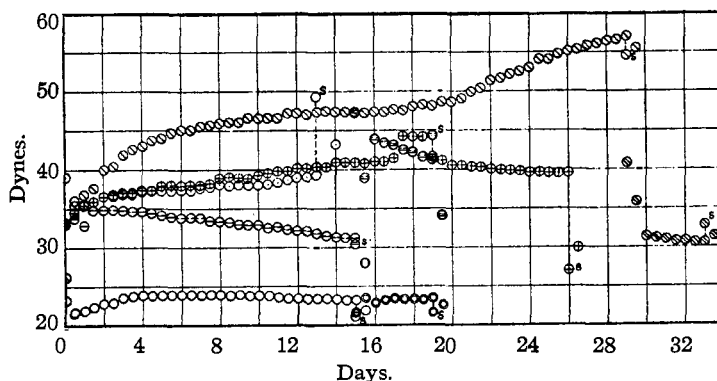To afford data for comparison with a soap, the

Fig. 4.—Surface tensions of various sodium alkyl sulfonate solutions:

I ○, 0.01 m. $C_{12}H_{25}SO_3Na$ soln. at 60°.   IIIA ⊕, Solution III placed at 25°.
IA ◎, Solution I at 25°.   IV ⊕, 0.001 m. $C_{16}H_{33}SO_3Na$ at 60°.
II ⊙, 0.001 m. $C_{14}H_{29}SO_3Na$ Soln. at 25°.   V ⊖, 0.001 m. $C_{18}H_{37}SO_3Na$ at 60°.
III ⊘, 0.001 m. $C_{14}H_{29}SO_3Na$ Soln. at 60°.   VA (=), Solution V at 25°.

surface tension of 0.01 *M* solution of sodium laurate[13] was observed at 25 and 60°. This solu-

(12) Sodium lauryl sulfate was prepared by the method of Lottermoser and Stoll.[6]

(13) Sodium laurate solution was prepared by the method of Fischer; Holmes, "Laboratory Manual of Colloid Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1934, p. 132.

tion was found to act in much the same way as some of the sodium alkyl sulfonate solutions.

General Discussion.—No other study of the surface tension behavior of colloidal solutions over relatively long periods of time, such as the one just described, appears to have been reported. A recently published note on work done by Adam and Shute,[14] however, indicates that such a study is in progress in their laboratory, and the preliminary results on alkyl pyridinium and alkyl trimethyl ammonium bromides confirm the observations reported herein. They used the method of "sessile bubbles" and considered that the slow fall in surface tension with time was due to an aging of the surface and not of the whole solution, since a new bubble blown in a solution several days old was found to follow the same changes as in a fresh solution. That a similar phenomenon has been observed with dilute solutions of other long chain colloidal electrolytes by an entirely different method of measurement is a definite confirmation that the changing surface tension behavior shown by the sodium alkyl sulfonate solutions (as well as by other salts studied) has been due to actual changes occurring in the solutions and not to any effects which might be due to the conditions of aging or the method of measurement.

Wholly apart from this confirmatory evidence, however, the behavior of the solutions has shown enough regularity with respect to molecular weight and concentration to preclude the possibility of environmental effects other than the temperature playing any major role. In addition to this, there were several instances, both in very dilute solutions and in more concentrated ones, at 25° and also at 60°, where the surface tension values remained practically constant throughout the period of measurement. These facts all lead to the same conclusion, namely, that the variations of surface tension with time are due to slowly occurring changes in the surfaces and that these changes depend on: (1) the temperature, (2) the concentration of the salt present in the solution, (3) the length of the carbon chain of the sodium alkyl sulfonate, (4) the age of the surface.

The time effects reported above were not due to changes in the contact angle. A determination of this angle for solutions of sodium lauryl sulfonate against glass was made by the method of Bosanquet and Hartley.[15] Observations over a period of several days showed that at all times the angle was zero.

With the 0.001 M sodium n-octyl and sodium n-decyl sulfonate solutions the carbon chains are not long enough to cause the surface tension to be materially different from that of water. On increasing the carbon chain to twelve or fourteen atoms a distinct change in behavior is apparent in the 0.001 M solutions both at 20 or 25° and at 60°. At the lower temperature the solutions show very definite capillary activity, and slow changes in surface tension occur similar to those obtained by Adam and Shute.[14] At 60° the solutions show an initially fairly low surface tension, which slowly increases until a value approaching that of pure water is reached. The 0.001 M sodium cetyl sulfonate (16 carbon atoms) solution at 60° shows an intermediate behavior. The solution of sodium n-octadecyl sulfonate at 60° resembles the sodium lauryl sulfonate solutions at 20°.

If the average surface tensions shown by the various sodium n-octyl or n-decyl sulfonate solutions at 25° were plotted as a function of the concentration, a definite minimum would be noted in both cases at a 0.1 M concentration. Such minima in surface tension–concentration curves have been observed with solutions of numerous long chain colloidal electrolytes by various workers using widely different methods of measurement.[6,16,17,18]

No entirely conclusive evidence has yet been presented as to just what type of particle is responsible for the capillary activity of solutions of long chain colloidal electrolytes. Walker[16] decided that the surface tension lowering produced by dissolving soaps in water was caused by micelles. To explain the minimum points in the surface tension–concentration curves, as well as the variations in capillary activity produced by changes in molecular weight and temperature, he postulated the presence of two types of micelles, one relatively small, but very effective in lowering the surface tension, and the other quite large, but not very capillary active. With extremely dilute solutions all the soap was considered to be present as simple molecules or ions, both in the solution and in the surface layer, with very little decrease in surface tension resulting. On increasing the concentration of soap, the surface layer

(14) Adam, *Trans. Faraday Soc.*, **31**, 204 (1935).

(15) Bosanquet and Hartley, *Phil. Mag.*, **42**, 456 (1921).

(16) Walker, *J. Chem. Soc.*, **119**, 1521 (1921).

(17) Lottermoser and Tesch, *Kolloid. Beiheft.*, **34**, 339 (1931).

(18) Neville and Jeanson, *J. Phys. Chem.*, **37**, 1001 (1933).

would no longer contain simple molecules, but an increasing number of the small, very capillary active micelles. As a result the surface tension would be lowered to a minimum value, after which a decrease in capillary activity on further concentration would occur due to the formation of an increasing number of the larger, less capillary active micelles in the surface layer.

Through extensive studies of the conductivity and osmotic behavior of different soap solutions, McBain and his students[19] have shown quite definitely the presence of: (1) simple ions, (2) simple undissociated molecules, (3) ionic micelles and (4) neutral micelles.
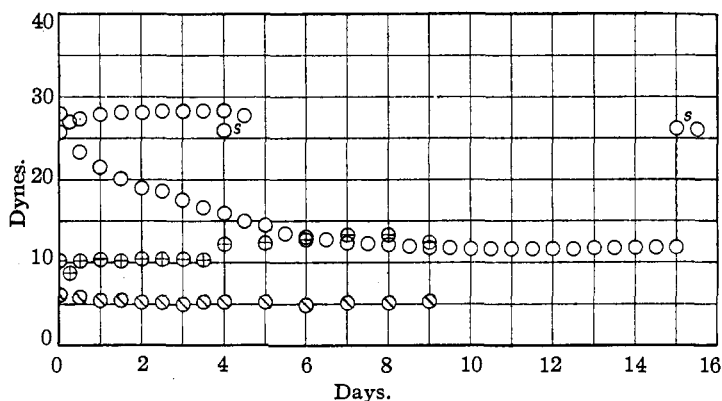

Fig. 5.—Interfacial tensions between benzene and sodium *n*-octyl sulfonate solutions:

I O, 0.01 molal solution at 25°.   III ⊘, 0.1 molal solution at 25°.
II ☉, 0.01 molal solution at 60°.   IV ⊕, 0.1 molal solution at 60°.

Lottermoser and Stoll[6] assumed that the neutral micelles of McBain corresponded to the small, highly capillary active micelles postulated by Walker,[16] and that the ionic micelles corresponded to Walker's larger micelles of lesser activity. By assuming that the equilibrium existing in the solution shifts toward the larger particles with increasing concentrations and molecular weights, and with decreasing temperatures, they were able to arrive at a very satisfactory explanation for the surface tension behavior of the various metal alkyl sulfate solutions. They further assumed, as Walker had done, that neither the simple ions nor molecules exerted any appreciable effect upon the surface tension.

Much of the surface tension behavior of the solutions of sodium alkyl sulfonates reported herein can also be explained quite satisfactorily by adopting the assumptions used by Lottermoser and Stoll. The behavior of the 0.001 *M* solutions

(19) McBain, This Journal, 50, 1636 (1928).

of sodium *n*-octyl and *n*-decyl sulfonate solutions at 25 and 60° and of the 0.001 *M* solutions of sodium lauryl and myristyl sulfonates and sodium lauryl sulfate at 60° may be considered as evidence that the simple ions and molecules are not capillary active, since the first two sulfonates are very probably present in molecular or ionic dispersion while in the last three cases the effect of continued aging is to cause such a dispersion to occur.

Murray[20] has recently given a very ingenious explanation of the presence of minima in surface tension–concentration curves for long-chain colloidal electrolytes. He assumes that three kinds of particles exist in the solutions, namely, ionic micelles, simple metallic cations, and simple long chain anions. The number of simple anions present in the solution will increase with increasing concentrations to a maximum point, after which there will be a decrease due to their rapidly increasing aggregation to form ionic micelles. He considers that the surface tension minimum occurs at the point where the concentration of simple anions in the solution is a maximum, and explains it on the basis that the simple anions are the capillary active particles.

This explanation seems worthy of consideration, but neither it nor any of the others which have been mentioned above seem adequate to explain the "mysterious slow change of surface tension with time"[14] or the large positive temperature coefficients of surface tension. The application of Murray's explanation of surface activity to such a change as that observed in curve IA, Fig. 2, would require that ionic micelles dissociate at 20° over a period of several days to yield simple anions. Furthermore, in more of the same solution kept at 60° (curve IIA, Fig. 2), there should occur a slow change, presumably an association into ionic micelles, since these are the only aggregated particles admitted by Murray to permit a constantly decreasing number of simple anions with a consequent increase in surface tension. Since, however, higher temperatures are almost universally considered as favoring dissociation, while lower temperatures favor aggregation, it would seem that the extremely large differences between the surface tensions of the 0.001 *M* sodium lauryl sul-

(20) Murray, Trans. Faraday Soc., 31, 207 (1935).

fonate solution at 60 and at 20° can best be explained by assuming that the capillary active unit in the solution is some aggregated particle, and not a simple ion.
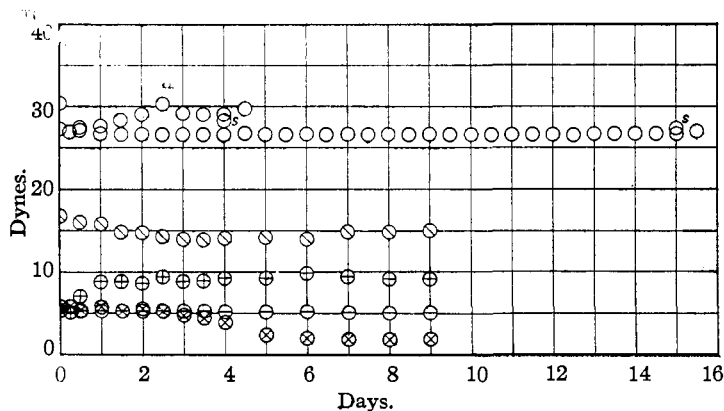

Fig. 6.—Interfacial tensions between benzene and sodium *n*-decyl sulfonate solutions:

I O, 0.001 molal solution at 25°.   IV ⊕, 0.01 molal solution at 60°.
II ⊙, 0.001 molal solution at 60°.   V ⊖, 0.1 molal solution at 25°.
III ⦸, 0.01 molal solution at 25°.   VI ⊗, 0.1 molal solution at 60°.

Interfacial Tension Measurements

Experimental Methods and Results.—Several determinations were made of interfacial tensions between benzene and various solutions of the sulfonates. The recommendations and precautions given by Harkins[21] for interfacial tension determinations were followed, and a special glass-stoppered capillarimeter was constructed, having a capillary tube with a diameter of 2 mm. and a wide tube with a diameter of 80 mm. The general shape and design of the capillarimeter was the same as those used in the surface tension determinations. The wide tube was found to be large enough to provide a definitely flat meniscus between the benzene and water layers.

The benzene used was a chemically pure, thiophene-free grade, and was not further purified. The sodium alkyl sulfonate solutions were the same ones that were used in the surface tension experiments. The benzene was placed in contact with the solution before using in order to mutually saturate both solutions.

The results of the interfacial tension determinations are given in Figs. 5 to 7.

(21) Alexander, "Colloid Chemistry," Chemical Catalog Company, New York City, N. Y., Vol. I, 1926, p. 249.

Discussion of Results.—No other study of the interfacial tensions between benzene and solutions of long chain colloidal electrolytes over a period of time has been reported. The various measurements of interfacial tension which have been made by the anchor ring and drop weight methods do not permit the observation of changes with time, since each measurement necessarily disturbs the interface.

In certain cases definite changes of interfacial tension with time were observed, somewhat similar to the changes in the surface tension measurements. This indicates that the equilibria at the benzene–solution interface were sometimes established quite slowly. Notable cases of such slow changes are shown by curve I, Fig. 5, curves IV and VI, Fig. 6 and curves II and V, Fig. 7. The interfacial tension behavior of the 0.01 M sodium octyl solution at 25° was analogous to the surface tension behavior shown by the same solution (curve III, Fig. 3). Other instances in which practically constant interfacial tension values were obtained are also shown, Figs. 5 and 6.
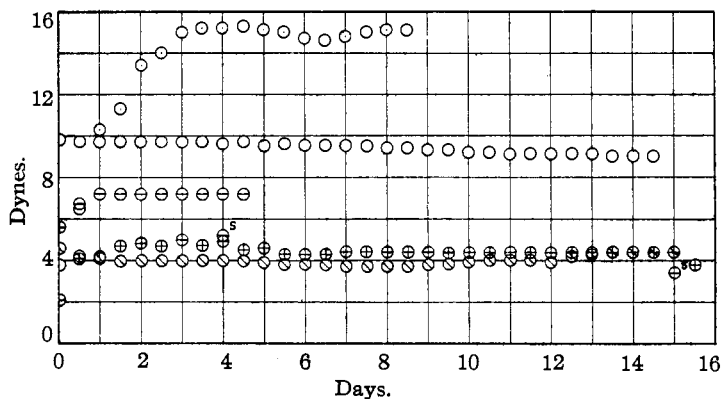

Fig. 7.—Interfacial tensions between benzene and various sodium alkyl sulfonate solutions:

I O, 0.002 molal $C_{12}H_{25}SO_3Na$ solution at 20°.
II ⊙, 0.002 molal $C_{12}H_{25}SO_3Na$ solution at 60°.
III ⦸, 0.01 molal $C_{12}H_{25}SO_4Na$ solution at 25°.
IV ⊕, 0.001 molal $C_{14}H_{29}SO_3Na$ solution at 25°.
V ⊖, 0.001 molal $C_{14}H_{29}SO_3Na$ solution at 60°.

Electrical Conductivities

McBain and his co-workers[19] have studied thoroughly the conductivities of solutions of the sodium and potassium salts of the higher fatty acids at various concentrations and temperatures,

and have found that in very dilute solutions these substances behave as typical electrolytes, but that as the concentration increases they exhibit anomalies.
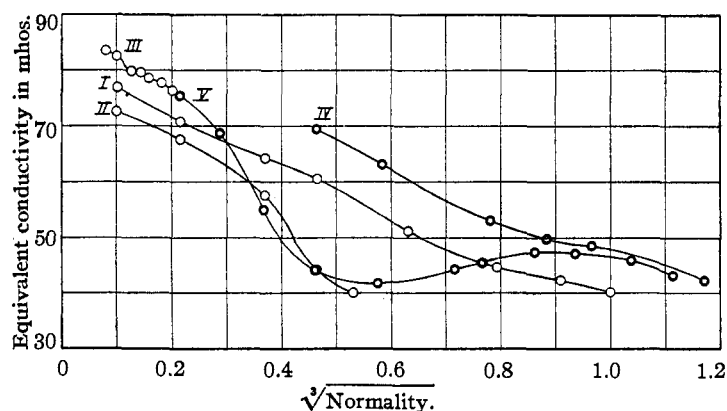

Fig. 8.—Equivalent conductivities of sodium alkyl sulfonates at 25° and potassium soaps at 18° plotted against the cube roots of the concentrations: I, sodium *n*-octyl sulfonate at 25°; II, sodium *n*-decyl sulfonate at 25°; III, sodium lauryl sulfonate at 25°; IV, potassium octoate (McBain's values) 18°; V, potassium laurate (McBain's values) 18°.

Following the suggestion of Kohlrausch[22] the writers have obtained smooth curves by plotting the equivalent conductivities reported by McBain[19] for potassium octoate solutions at 18 and 90° as functions of the cube root of the concentration (Figs. 8 and 9). The potassium laurate solutions gave curves entirely different in form from those of the potassium octoate solutions. Such an increase of equivalent conductivity with concentration was first clearly established by the studies of McBain and his students.[19] It has since been discovered that solutions of other long chain colloidal electrolytes show similar behavior.[2,4]

McBain has explained the conductivity of potassium laurate solutions (as well as others) by showing the presence of highly conducting "ionic micelles."

Reychler, in 1913, discovered the existence of a minimum in the equivalent conductivity–concentration curve for cetyl sulfonic acid. McBain and Williams[23] repeated and extended Reychler's work, and showed that the equivalent

conductivity–concentration curve of cetyl sulfonic acid at 90° is entirely analogous to that of potassium palmitate at the same temperature. Murray and Hartley's conductivity measurements[3] on solutions of potassium cetyl sulfonate at 80° are in accord with those on the acid.

Experimental Methods and Results.—The conductivity measurements were carried out with a Jones conductivity bridge.[24] The calibration of the bridge was checked using resistances which had been standardized by the United States Bureau of Standards. The amplifier[25] and oscillator[26] were of the type recommended.

The conductivity cells were of the Washburn type[27] and had cell constants varying from 0.0139 to 41.12.

The conductivity water was prepared in contact with air, and had a specific conductivity of 1×10^{-6} mhos at 25° and 2×10^{-6} at 60°. This value was subtracted from the measured specific conductivities of the solutions.[28]

The conductivity measurements at 25 and 60° were carried out in a thermostat containing 23
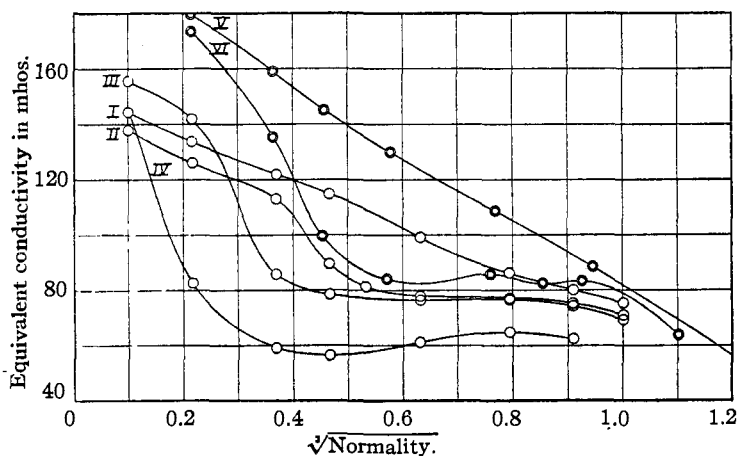
Fig. 9.—Equivalent conductivities of sodium alkyl sulfonates at 60° and potassium soaps at 90° plotted against the cube roots of the concentration. I, sodium *n*-octyl sulfonate at 60°; II, sodium *n*-decyl sulfonate at 60°; III. sodium lauryl sulfonate at 60°; IV, sodium myristyl sulfonate at 60°; V, potassium octoate at 90° (McBain's values with 60 mhos deducted from each one); VI, potassium laurate at 90° (McBain's values with 60 mhos deducted from each one).

(22) Taylor, "Treatise on Physical Chemistry," D. Van Nostrand Co., New York, N. Y., second edition, Vol. 1, 1931, p. 652.

(23) McBain and Williams, THIS JOURNAL, **55**, 2250 (1933).

(24) Dike, *Rev. Sci. Instruments*, July, 379 (1931).

(25) Hall and Adams, THIS JOURNAL, **41**, 1515 (1919).

(26) Jones and Josephs, *ibid.*, **50**, 1049 (1928).

(27) Washburn, *ibid.*, **38**, 2431 (1916).

(28) Kendall, *ibid.*, **39**, 7 (1917).

gallons of light transformer oil. Stirring was accomplished by six stirrers and the temperature was maintained to within ±0.002°. A mercury regulator was used and the heating circuit was controlled by a Thyratron tube.[29]

The sodium alkyl sulfonate solutions were made up by volume, and were also weighed and the molality calculated.

Conductivity measurements were made on solutions of sodium n-octyl, n-decyl, lauryl and myristyl sulfonates at 25 and 60°. The results are given in Table V.

TABLE V

CONDUCTIVITY DATA FOR SODIUM ALKYL SULFONATES

Molal-ity	Volume normality 25°	60°	Sp. conductivity, Mhos × 10^6 25°	60°	Equiv. cond., Mhos 25°	60°
			Sodium n-Octyl Sulfonate			
0.001	0.001	0.000986	76.72	144.3	76.72	146.3
.010	.010	.00986	708.5	1338	70.85	135.7
.051	.050	.0493	3213	6095	64.26	123.6
.102	.100	.0986	6071	11490	60.71	116.5
.262	.250	.247	12800	24820	51.20	100.5
.548	.500	.493	22330	43190	44.66	87.61
.863	.750	.740	31650	60130	42.20	81.26
1.215	1.000	.986	40130	75380	40.13	76.44
			Sodium n-Decyl Sulfonate			
0.001	0.001	0.000986	72.50	137.8	72.50	139.8
.010	.010	.00986	674.6	1261	67.46	127.9
.051	.050	.0493	2879	5658	57.58	114.8
.102	.100	.0986	4403	8967	44.03	90.94
.155	.150	.148	6006	12220	40.04	82.57
.268	....	.250	...	19540	...	78.16
.568	....	.500	...	38560	...	77.12
.907	....	.750	...	56220	...	74.96
1.293	....	1.000	...	70670	...	70.67
			Sodium Lauryl Sulfonate			
0.0005	0.000499	..	41.75	...	83.67	....
.001	.000997	0.001	82.46	155.0	82.71	155.0
.002	.00199	..	159.5	...	80.15	....
.003	.00299	..	239.0	...	79.94	....
.004	.00399	..	314.4	...	78.80	....
.006	.00598	..	465.7	...	77.88	....
.008	.00798	..	610.8	...	76.54	....
.010	....	0.010	...	1420	...	142.0
.051	....	.050	...	4285	...	85.70
.104	....	.100	...	7863	...	78.63
.270	....	.250	...	19100	...	76.40
.579	....	.500	...	38340	...	76.68
.937	....	.750	...	55600	...	74.13
1.350	....	1.000	...	68830	...	68.83
			Sodium Myristyl Sulfonate			
0.001	....	0.001	...	144.6	...	144.6
.010	....	.010	...	829.2	...	82.92
.052	....	.050	...	2969	...	59.38
.104	....	.100	...	5687	...	56.87
.273	....	.250	...	15310	...	61.24
.592	....	.500	...	32430	...	64.86
.966	....	.750	...	46670	...	62.23

The equivalent conductivities have been plotted as a function of the cube roots of the concentrations, these curves being shown in Figs. 8 and 9.

(29) Daniels, Mathews and Williams, "Experimental Physical Chemistry," Second edition, McGraw-Hill Book Co., Inc., New York, N. Y., 1934, p. 456.

For comparison, the corresponding curves for potassium octoate and potassium laurate have also been plotted, using the values obtained by McBain.[19]

Discussion of Results.—McBain[19] found that the conductivity of soap solutions at room temperature changed about 1% on aging. Similar changes in conductivity were noted with dilute sodium alkyl sulfonate solutions at 25°. In order to obtain constant values for the conductivities, all solutions were allowed to stand for a day before their conductivities were determined.

The relatively small aging effects observed with the conductivities in comparison with the large changes in the surface tension, makes it appear probable that equilibria within the bulk of the solution were attained in a short time, and that the surface tension changes were largely due to surface effects.

As will be seen on inspection of the curves in Figs. 8 and 9, the sodium alkyl sulfonate solutions show a conductivity behavior analogous to that of the soap solutions.

McBain[19] has estimated that in a 1.0 molal potassium octoate solution at 18° the total concentration of colloid present (neutral colloid plus ionic micelle) is only about 14%, while in a 1.0 molal potassium laurate solution at 18° the total colloid present amounts to 96%. Judging from the conductivity–concentration curves of Figs. 8 and 9, a similar difference probably exists between the solutions of sodium n-octyl sulfonate and those of sodium lauryl sulfonate.

The regularity in the conductivity–concentration curves for sodium n-octyl sulfonate at both 25 and 60°, as contrasted with the high capillary activity of the solutions of this salt, makes it seem quite probable that the capillary activity is due to colloidal particles which concentrate in the surface, while the bulk of the solution contains the salt in molecular or ionic dispersion.

Summary

Solubility determinations were made with the various metal alkyl sulfonates; the calcium and magnesium salts are much less soluble in water than had been claimed previously.

Measurements of the surface tension of solutions of the sodium alkyl sulfonates were carried out over extended periods of time and revealed that such changes continue over much longer periods than had been observed in previous studies

of this kind. Certain regularities in the surface tension behavior of these solutions were pointed out, and a discussion given of the various hypotheses which have been advanced to explain such types of behavior.

The interfacial tensions between benzene and solutions of sodium alkyl sulfonates showed changes with time, a phenomenon which has not been previously reported.

Conductivity measurements made on solutions of the sodium alkyl sulfonates showed that the conductivity of these substances is analogous to that of the potassium soaps.

The Action of Chloral on β-Phenylethylmagnesium Bromide, γ-Phenylpropylmagnesium Bromide and δ-Phenylbutylmagnesium Bromide

BY PAUL M. DEAN AND WENDELL I. WOLF

Secondary alcohols containing the trichloromethyl group have been prepared by several investigators[1,2,3,4] through the addition of chloral to the corresponding Grignard reagent. Since such carbinols are readily formed from alkyl- and arylmagnesium halides as well as from benzylmagnesium chloride, one would anticipate the formation of analogous compounds from phenyl substituted alkylmagnesium halides. However, numerous attempts, in this Laboratory, to prepare secondary alcohols from chloral and β-phenylethylmagnesium bromide, γ-phenylpropylmagnesium bromide, and δ-phenylbutylmagnesium bromide have failed. In all cases, such by-products as trichloroethanol, styrene or its homologs and 1,4-diphenylbutane or its homologs were obtained. No secondary alcohol could be separated from the reaction mixture by the methods employed. Since no reference to the action of the three Grignard reagents, named above, on the unsubstituted aldehydes has been found in the literature, it is planned to investigate this point in the near future.

Procedure

Action of Chloral on β-Phenylethylmagnesium Bromide.—To the cooled Grignard reagent prepared from a 0.25-mole portion of β-phenylethyl bromide dissolved in 200 cc. of ether was added a solution of 0.25 mole of chloral dissolved in 50 cc. of ether. After refluxing for one hour the gray solid was filtered and washed with ether.

(a) **Examination of the Solid.**—The solid was hydrolyzed with water and the solution cleared with hydrochloric acid. A heavy oil separated which was extracted with ether, washed with sodium bisulfite solution, then with sodium carbonate, and dried over sodium sulfate.

After removal of the ether the residue was distilled under diminished pressure. Nearly all distilled at 67–68° at 25 mm. pressure. This liquid was shown to be trichloroethanol through the preparation of the phenyl urethan, the p-nitrobenzoate and the urethan from α-naphthyl isocyanate. The last named new derivative was prepared by heating the trichloroethanol with α-naphthyl isocyanate for two hours at 120–135°. The white solid crystallized from ligroin melted at 120°; melting point of product from authentic trichloromethanol 119°; mixed melting point 120°.

Anal. Calcd. for $C_{13}H_{10}NO_2Cl_3$: Cl, 33.43; H, 4.40. Found: Cl, 33.90; N, 4.56.

(b) **Examination of the Ether Filtrate.**—The filtrate was hydrolyzed and washed in the same manner as the solid residue above. The following products were obtained on fractional distillation: some trichloroethanol, styrene, 1,4-diphenylbutane, some unidentified material. To facilitate the separation of styrene from the mixture, the dried ether solution was treated with a slight excess of bromine in diffused light, and washed with sodium bisulfite and carbonate solution. The dried ether was distilled off and the residue fractionated under diminished pressure. This procedure was followed in all of the experiments except the one in which the styrene was identified. The results are summarized in Table I.

TABLE I

Products recovered	Yield in grams				
Experiment	1	2	3	4	5
CCl₃CH₂OH from solid	10	14	14	14	14
CCl₃CH₂OH from filtrate	2	2	2	2	1
C₆H₅CH=CH₂	6	..	..	..	..
C₆H₅CHBrCH₂Br	10	29	30	35	34
C₆H₅CH₂CH₂CH₂CH₂C₆H₅	2	..	1	1	1
C₆H₅CH₂CH₂Br	2	1	2	1	2

Action of Chloral on γ-Phenylpropylmagnesium Bromide.—Similarly to the foregoing case γ-phenylpropylmagnesium bromide treated with chloral yielded a solid and filtrate which hydrolyzed separately gave from the solid trichloroethanol, and from the liquid, trichloroethanol, allylbenzene, 1,6-diphenylhexane and a small amount of unidentified material. The allylbenzene was identified

(1) Henry, *Compt. rend.*, **138**, 204 (1904).
(2) Savariau, *ibid.*, **146**, 297 (1908).
(3) J. W. Howard, THIS JOURNAL, **48**, 774 (1926).
(4) J. W. Howard, *ibid.*, **49**, 1068 (1927).