# A Study of the Constitution of Aqueous Solutions of the Hydrogen Soap, Cetyl Sulfonic Acid

BY JAMES W. McBAIN AND ROBERT C. WILLIAMS

Cetyl sulfonic or hexadecane sulfonic acid ($C_{16}H_{33}SO_3H$) is a hydrogen soap whose aqueous solutions are typical of higher soaps and of colloidal electrolytes in general.   The conductivity of its solutions has been studied by Reychler[1] and Miss Norris[2] but they used specimens of doubtful purity.

Hydrogen soaps are invaluable for study because the disturbing and indeed frustrating factor of hydrolysis in dilute solution is absent.   This one is a white solid at room temperature and resembles the higher fatty acids in texture.   It becomes markedly soluble only above 50°.

The present communication describes the preparation of the soap in a pure condition, followed by a study of the conductivity, hydrogen-ion concentration, and lowering of vapor pressure of its solutions into the range of extreme dilution.   Miss Norris' conductivity results are thus extended through a wider range of concentration and confirmed with purer material.

## Preparation of Cetyl Sulfonic Acid

The least unsatisfactory method hitherto[3] has been the quantitative formation of hexadecyl mercaptan from an alcoholic solution of cetyl iodide (Kahlbaum) by prolonged heating with sodium hydrogen sulfide.   The mercaptan is oxidized by potassium permanganate to form potassium cetyl sulfonate, and after decomposition of the excess permanganate and separation of manganese dioxide, the hot filtrate is treated with alcoholic solution of lead acetate and the lead salt so formed converted into the free acid by the action of hydrogen sulfide in hot alcohol.   On evaporation the acid remains as a soft white solid.   However, the yield is poor and any attempt to remove the last of the alcohol or hydrogen sulfide resulted in a blackening of the substance.

The most successful modification by W. T. Smith (University of Bristol, 1925) consisted in the preparation of lead mercaptide by the action of hot alcoholic lead acetate upon the hexadecyl mercaptan, and its subsequent purification by extraction with acetone.   At Dr. G. H. Christie's suggestion, 1925, 50% nitric acid was used for oxidation, thus avoiding the troublesome filtration of manganese dioxide.   After the vigorous action is complete, the flask is cooled and distilled water added which causes the lead cetyl sulfonate to separate as a heavy white powder.   If the acid is in excess, some cetyl sulfonic acid is formed.   Therefore, to ensure formation of the salt, excess acidity is removed by powdered lead carbonate.   After filtration the salt is again purified by extraction with acetone.

The last step in the preparation of the acid was difficult owing to the insolubility of the lead salt in almost all solvents.   Double decomposition with the stronger mineral acids also failed.   Hence, hydrogen sulfide was again used.   The filtrate was distilled

(1) Reychler, *Bull. soc. chim. Belg.*, **27**, 110, 217, 300 (1913); *Z. Chem. Ind. Kolloide*, **12**, 277 (1913); *Kolloid-Z.*, **13**, 252 (1913).

(2) M. H. Norris (with D. H. Falkner and M. C. Price), *Trans. Chem. Soc.*, **121**, 2161 (1922).

(3) Previously prepared only by A. Reychler, *Bull. soc. chim. Belg.*, **27**, 110, 217, 300 (1913) and M. H. Norris, Ref. 2.

under reduced pressure and a white waxy cetyl sulfonic acid of melting point 42–43° was obtained. This, however, still contained 16% alcohol. Since all attempts to remove the alcohol merely discolored the acid, owing probably to small traces of hydrogen sulfide, the present authors introduced a further modification at the suggestion of Dr. D. Davidson (Stanford University, 1928). The lead cetyl sulfonate is refluxed in isopropyl alcohol while dry hydrogen chloride gas is introduced. The soap formed is quite soluble in the isopropyl alcohol while the lead chloride is not, and thus a separation can be effected. After completion of the reaction the mixture is cooled, filtered and heated on a steam-bath to remove hydrogen chloride and alcohol. The heating is carried out in an atmosphere of nitrogen to minimize decoloration of the soap through possible oxidation. Recrystallization by cooling the hot ethereal solution gives a white solid now melting at 53–54°. All chemicals used were Kahlbaum's best.

## Macroscopic Observations[4]

Aqueous solutions of the cetyl sulfonic acid soap at room temperatures range in appearance from slightly turbid liquid at a dilution of 0.0008 $N_w$ to an opaque gelatinous mass or soft curd, which does not flow when the container is inverted, at a concentration of about 0.3 $N_w$. Most of the solutions exhibit a "silkiness" on stirring which apparently is due to shimmering microcrystals.

Turbidity and opacity of the solutions disappear through a short temperature range above 50° regardless of concentration. This phenomenon is analogous to that in the case of ordinary sodium and potassium soaps (Krafft's rule of melting points).[5] The cetyl sulfonic acid solutions remain perfectly clear to the eye at 90° on long standing. All solutions froth freely. At 90° the viscosity of a 1.0 $N$ solution is so great that bubbles of hydrogen can rise through it only very slowly.

## Measurements of Electrical Conductivity

The conductivity experiments were carried out, as in previous investigations, using Leeds and Northrup equipment in a thermostat controlled to a temperature of 90.0 ± 0.05° read on a thermometer standardized by the Bureau of Standards. The special high resistance cell[6] had a cell constant of 13.2 at 25.0° and 13.16 at 90.0°.

The concentrations of the solutions were obtained either by titrating samples taken from the cell after the readings or by making up definite weight normal solutions

## TABLE I
### CONDUCTANCE DATA FOR SOLUTIONS OF CETYL SULFONIC ACID

| $N_w$ | $N_v$ | $d_{4^\circ}^{90^\circ}$ | $\kappa_{25^\circ}$ | $\kappa_{90^\circ}$ | $\mu_{90^\circ}$ | $\alpha_{90^\circ}$ |
|---|---|---|---|---|---|---|
| 0.6840 | 0.5429 | 0.9597 | 0.001272 | 0.1196 | 220.4 | 31.4 |
| .5000 | .4169 | .9613 | .001904 | .08706 | 208.9 | 29.8 |
| .2500 | .2236 | .9634 | .002545 | .04504 | 201.5 | 28.7 |
| .1000 | .09359 | .9647 | .0003722 | .01650 | 176.4 | 25.2 |
| .0473 | .04502 | .9651 | .0009492 | .009502 | 211.0 | 30.0 |
| .0100 | .009625 | .9653 | .0006978 | .002468 | 256.2 | 36.5 |
| .00814 | .007838 | .9653 | .0009214 | .002148 | 273.8 | 39.0 |
| .005 | .004820 | .9653 | .0004228 | .001467 | 304.1 | 43.3 |
| .001 | .0009650 | .9653 | .0001959 | .0005289 | 548.0 | (78.0) |
| .0005 | .0004827 | .9653 | .0001274 | .0002623 | 543.0 | (77.3) |
| .0001 | .00009653 | .9653 | .00002515 | .00005780 | 598.0 | 85.2 |

(4) Compare ultramicroscopic observations of Darke, McBain and Salmon, *Proc. Roy. Soc.* (London), **98A**, 395 (1921); also observations by Adam, *ibid.*, **103A**, 676 (1923).

(5) Krafft and Wiglow, *Ber.*, **28**, 2566 (1895).

(6) McBain, Laing and Titley, *Trans. Chem. Soc.*, **115**, 1281 (1919).

(gram equivalents soap per 1000 g. of water) and diluting by addition of weighed quantities of soap solution and water. The densities of the soap solutions were taken from the values given by Miss Norris.

The results are collected in Table I in which the columns reading from left to right represent weight normality $N_w$, volume normality $N_v$, density $D$, specific conductivity $\kappa_{25}°$ at 25° (mostly solids or pastes), specific conductivity of liquid solutions $\kappa_{90}°$ at 90°, molar conductivity at 90° $\mu_{90}°$, and the conductivity ratio $\alpha_{90}°$ at 90° in per cent.

As in all soap solutions, the degree of dissociation is very far from complete, no matter how evaluated. Taking the value for equivalent conductance at infinite dilution as 702, the Arrhenius degree of dissociation (conductivity ratio) varies from 25.2% for 0.1 $N_w$ to 85.2% for 0.0001 $N_w$ and to 29.8% for 0.5 $N_w$. These values would become on the Debye–Hückel theory, assuming such uni-univalent electrolytes as potassium chloride or hydrochloric acid to be 100% dissociated, about 29% for 0.1 $N_w$, 86% for 0.0001 $N_w$, and 34% for 0.5 $N_w$ cetyl sulfonic acid, respectively.[7] At concentrations greater than 0.1 $N_w$, the apparent degree of dissociation increases to 31% for 0.6840 $N_w$ because of the well-known increase in conductivity when ionic micelle is substituted for its constituent simple ions.

The results are graphed in Fig. 1, in which results of a typical soap, potassium palmitate at 90°, are also given for comparison. Such a graph clearly shows the essential similarity of the hydrogen soaps to the usual hydrolyzing soaps. The minimum value for conduction is obtained at approximately $N/10$, and the conductivities of all concentrations are greater than those of the palmitate and stearate soaps.

The specific conductance results at 25° were obtained by measuring the (solidified) solutions after standing overnight at 25°. The values increase



Fig. 1.—The molar conductivities of cetyl sulfonic acid (circles) and of potassium palmitate (triangles) at 90° plotted against concentrations in molalities.

(7) McBain [THIS JOURNAL, 50, 1636 (1928)] has pointed out that the ionic strength of soaps is that of a uni-univalent electrolyte even in concentrated solution.

regularly from a dilution of 0.0001 to 0.005 $N_w$, but from here on anomalous results are obtained, probably due to surface conduction of the soap curd. It would appear that somewhat below 0.005 $N_w$ saturation has been reached, because the specific conductivity is not exceeded by that of a well crystallized $N/10$ solution at 25°, although slight turbidity was noticed at 0.001 $N_w$. However, the equivalent conductivity of the 0.005 $N_w$ solution is an even smaller fraction ($\alpha$ = about 27%) of that for infinite dilution than it is at 90°.

**Measurement of Osmotically Active Constituents by Means of Vapor Pressure Lowering.**—Measurements of the lowering of freezing point and the lowering of dew point at 90° have been employed[8] for determination of the osmotically active constituents of soap solutions, but freezing point is here excluded and dew point is not accurate enough in the case of the dilute solutions obtainable with cetyl sulfonic acid. Hence, the dynamic differential method of Washburn[9] has been adopted for vapor pressure lowering at 90°, and although a higher order of accuracy has been attempted, precision is impossible in the most dilute solutions.

In principle this method consists in saturating air or inert gas by passing it over pure water, absorbing the water vapor, and then passing the same gas over the solution, again absorbing the saturated vapor. By comparing the weights of vapor obtained from the solvent and the solution and knowing the barometric pressure, the ratio $(p_0-p)/p_0$ is calculated. In these experiments with rocking Berkeley–Washburn saturators there is no back pressure and the equation of Washburn and Heuse[9] becomes

$$\frac{p_0 - p}{p_0} = \frac{D_m(B - p_0)}{m_0(B) - D_m(p_0)}$$

Experiments with dextrose (0.5 $N_w$) indicated that the apparatus was trustworthy, and the Arrhenius dissociation of 75% obtained with 0.5 $N_w$ potassium chloride agrees with other data. The total crystalloid calculated in Table II is based upon the Raoult equation $(p_0 - p)/p_0 = n/(N + n)$.

Usually the passage of 2 or 3 liters of nitrogen per hour was necessary for saturation. If any back pressure developed throughout the experiment, the results were discarded. As the saturated gas left each set of loops in the apparatus, it was conducted through tubes heated with chromel wire above 90° to prevent condensation which finally took place completely in the cooled weighed absorbers. The formation of soap bubbles was prevented by using an amount of solution in the loops which was insufficient to close any of the tubes when the saturators were tilted to the maximum angle. For convenience the first loop of the set containing the solution was filled with water. This obviated continual addition of

(8) For references see McBain, Taylor and Laing, *Trans. Chem. Soc.*, **121**, 621, 1101, 2161 (1922); also Quick, *ibid.*, **127**, 1401 (1925).

(9) Washburn and Heuse, THIS JOURNAL, **37**, 309 (1915); accuracy estimated at 0.25 to 0.5% of lowering for 1 $N_w$ solution of sucrose at 25°.

soap solution in small quantities between experiments. Equilibrium took place in the remaining two saturators as shown in the blank experiments with potassium chloride and soap solution when approached from both sides.

As the saturated gas left the final saturator it passed .through a tube, heated to prevent condensation, into absorbers placed in ice. What vapor was not there condensed by chilling was taken up by "dehydrite" (Na-$(ClO_4)_2$) contained in the tubes in the upper part of the absorbers.

TABLE II

VAPOR PRESSURE LOWERING FOR SOLUTIONS AT 90.00 $\pm$ 0.05°

| Solution | Bar. B mm. | Solvent vaporized $m_0$ | Difference solution $D_m$ | $\dfrac{p_0 - p}{P_0}$ | Total crystalloid[a] $N_w$ | Activity coefficient $\gamma$ |
|---|---|---|---|---|---|---|
| 0.5 $N_w$ dextrose | 760.2 | 12.455 | 0.376 | 0.00878 | 0.493 | .. |
| | 764.5 | 6.645 | .153 | | | |
| 0.5 $N_w$ KCl | 758.7 | 11.510 | .652 | .0154 | .869 | .. |
| | 761.5 | 9.711 | .417 | | | |
| 0.5 $N_w$ C₁₆H₃₃SO₃H | 764.0 | 10.712 | .110 | | | |
| | 764.8 | 12.029 | .138 | .00344 | .192 | 0.054 |
| | 763.7 | 15.998 | .176[b] | | | |
| 0.1 $N_w$ C₁₆H₃₃SO₃H | 754.4 | 15.672 | .074 | | | |
| | 769.6 | 12.050 | .086 | .00191 | .106 | .21 |
| | 763.0 | 15.490 | .100[b] | | | |
| 0.01 $N_w$ C₁₆H₃₃SO₃H | 761 | 31.45 | .028 | .00027 | .015 | .63 |
| 0.003 $N_w$ C₁₆H₃₃SO₃H | 762 | 38.195 | .011 | .000101 | .0056 | .87 |

[a] By Raoult's formula.

[b] These values were weighted in calculating the average value for $(p_0 - p)/p_0$ inasmuch as they were taken after the technique was thoroughly established.

Again it is seen from Table II that the activity coefficient of cetyl sulfonic acid is only that of a partially dissociated electrolyte. The Arrhenius degree of dissociation of a 0.5 $N_w$ solution is 0.192/0.5 = 38.4%. By comparison with hydrochloric acid (taken as 100% dissociated) this becomes 44%.

**The Activity Coefficient of Soap Solutions.**—A misprint in the tables of Landolt–Börnstein–Roth[10] for the vapor pressure of water at 89.9° has systematically distorted the calculations of Randall, McBain and White,[11] as was noticed in computing the present results in 1929. Their data have been recalculated and will be published elsewhere. The activity coefficients $\gamma$ in Table II for cetyl sulfonic acid are calculated by their method but the data extend to far lower concentrations than do previous data. Finally, it is most striking that $h/\sqrt{m}$ attains the very high value of 2.5 for $\sqrt{m} = 1$. The lower sulfonic acids likewise show this high value in dilute solution at 0°.

(10) Landolt–Börnstein–Roth, "Tabellen," 1923, page 1318.
(11) Randall, McBain and White, THIS JOURNAL, **48**, 2517 (1926).

**Determination of the Hydrogen-Ion Concentration.**—The apparatus and method have been fully described by McBain and Martin.[12] All known precautions were taken. The results are corrected to 760 mm. pressure of hydrogen. The cells investigated were of the following type:

| Pt, | H₂ | C₁₆H₃₃SO₃H | Satd. KCl | N/10 KCl | HgCl, Hg |
|-----|-----|------------|-----------|----------|----------|
| 90° | 235 mm. | 90° | 90° | 90 to 25° | 25° |
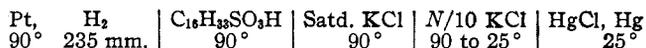
It was shown that the temperature of the bridging solution had no effect upon the potential by connecting a decinormal calomel electrode and a saturated calomel electrode, both at room temperature, with a saturated solution of potassium chloride. The junction between decinormal and saturated potassium chloride was varied from 1 to 90°, but the e. m. f. remained at 0.0880 ± 0.0002 volt. This is of importance in discussing the remarkably uncertain value for the degree of dissociation of water at higher temperatures as well as determining the absolute temperature coefficient of the hydrogen electrode (see McBain and Martin, Ref. 12, p. 963). The time allowed was too short for the development of Soret or electrolytic thermocouple effects.

First, the following data were obtained with hydrochloric acid at 90°, replacing the cetyl sulfonic acid in the cell quoted.

| $N_w$ HCl | 0.000846 | 0.00167 | 0.00562 | 0.0156 | 0.0414 |
|-----------|----------|---------|---------|--------|--------|
| E. m. f. | .5007 | .4822 | .4389 | .4096 | .3776 |
| $N_w$ HCl | .0660 | .0863 | .1036 | .1705 | .2110 |
| E. m. f. | .3666 | .3576 | .3508 | .3387 | .3333 |
| $N_w$ HCl | .2855 | .3142 | .4337 | .6550 | .9475 |
| E. m. f. | .3241 | .3205 | .3143 | .3011 | .2931 |

Then, the following results were obtained for cetyl sulfonic acid, and from interpolation from the results just quoted the concentration of hydrochloric acid which would have given the same e. m. f. was found. The results would indicate that cetyl sulfonic acid is less dissociated than hydrochloric acid. Assuming as a provisional basis of calculation that hydrochloric acid is 100% dissociated, the ratio between the concentrations of the two acids with the same e. m. f. gives approximately the interionic attraction degree of dissociation of the sulfonic acid.

| $N_w$ C₁₆H₃₃SO₃H | E. m. f. | = $N_w$ HCl | $N_w$ C₁₆H₃₃SO₃H | E. m. f. | = $N_w$ HCl |
|------------------|----------|-------------|------------------|----------|-------------|
| 0.000886 | 0.4987 | 0.000873 | 0.1158 | 0.3585 | 0.0841 |
| .00351 | .4590 | .00314 | .2084 | .3410 | .155 |
| .00723 | .4395 | .00550 | .2432 | .3382 | .173 |
| .0103 | .4350 | .00639 | .4225 | .3220 | .300 |
| .0369 | .3960 | .0235 | .6640 | .3058 | .565 |
| .0700 | .3774 | .0415 | 1.0208 | .2934 | .931 |

The Arrhenius degree of dissociation of cetyl sulfonic acid at 90° (based upon the usual Nernst concentration formula for e. m. f. or the Arrhenius

(12) McBain and Martin, *J. Chem. Soc.*, **105**, 957 (1914).

dissociation of hydrochloric acid)[13] is 63% for all concentrations from 0.01 to 1.0 $N_w$.　It is 79, 86 and 96% for 0.00723, 0.00351 and 0.000886 $N_w$, respectively.

In view of the fact that the results here assembled are remarkable, the question arises as to whether conductivity, osmotic measurements, and electrodes yield valid results with a soap solution.　Linderstrøm-Lang[14] has indeed suggested that ordinary ions interspersed between the long chain ions of soap may be so entangled as to simulate a false low degree of dissociation.　One of us has shown this to be hardly reconcilable with the varied information now available.[15]　Furthermore, this suggestion would appear to be completely negatived by the fact that added electrolytes exert even more than their usual effect in the presence of soap, according to all three methods.　Here, for example, a mixture of equal volumes of hydrochloric acid and cetyl sulfonic acid at 90° exhibits, according to the hydrogen electrode, a greater acidity than either constituent, the e. m. f. of the cell being less than for either alone, and the Arrhenius concentration of hydrogen ion being greater than the sum of the two taken separately in the same total volume of solvent.

| $N_w$ $C_{16}H_{33}SO_3H$ | E. m. f. $C_{16}H_{33}SO_3H$ | $N_w$ HCl | E. m. f. HCl | E. m. f. mixture | Sum of $C_{H^+}$ | $C_{H^+}$ observed |
|---|---|---|---|---|---|---|
| 0.2144 | 0.3412 | 0.1445 | 0.3415 | 0.3342 | 0.1327 | 0.1688 |
| .0796 | .3761 | .0417 | .3756 | .3723 | .0447 | .0493 |
| .000845 | .4986 | .000160 | .4783 | .4770 | .00112 | .00112 |
| .000845 | .4986 | .000846 | .5007 | .4997 | .000846 | .000816 |

Only in extreme dilution does the influence of the hydrochloric acid upon the cetyl sulfonic acid become slightly evident.　It is also clear that the ionic strength of the soap cannot appreciably exceed that of a uni-univalent electrolyte.

**Comparison of the Degree of Dissociation Determined by Conductivity, Vapor Pressure and Hydrogen Electrode.**—The degrees of dissociation of 0.5 $N_w$ cetyl sulfonic acid at 90° by conductivity, lowering of vapor pressure and e. m. f. are 29.8, 38.4 and 63%, respectively.　These, if hydrochloric acid is 100% dissociated, become approximately 34, 44 and 80%, respectively.　It is reasonably possible to equate the first two by assuming that the second is enhanced by a degree of hydration similar to that already shown to exist in soap solutions.[16]　It is quite impossible to reconcile with either the number for e. m. f. as it stands.　Even the allowance of the maximum diffusion potential obtainable from the Henderson formula, by assuming that the anions have no mobility, does not suffice to lower the e. m. f. values sufficiently.

The discrepancies are quite beyond the experimental error and must be

(13) Noyes, Publication No. 63, Carnegie Institution of Washington, D. C. (1907).

(14) K. Linderstrøm-Lang, *Compt. rend. trav. laboratoire Carlsberg*, **16**, No. 6 (1926).

(15) McBain, THIS JOURNAL, **50**, 1636 (1928).

(16) McBain and Jenkins, *J. Chem. Soc.*, **121**, 2325 (1922); and further unpublished work.

attributed to the respective methods themselves. Here, therefore, we have a third unexplained example of Hammarsten[17] effect; that is, of hydrogen ions revealed by electrode measurements but only in distinctly lesser degree by osmotic measurements and here even less by conductivity. This study will be continued more advantageously at 0° and room temperature with the lower, more soluble sulfonic acids, now synthesized by Professor C. R. Noller and Mr. J. J. Gordon,[18] which may be studied by the ordinary precision methods.

Constitution Diagram.—The constitution diagram for the various concentrations of cetyl sulfonic acid is so similar to that previously found by Miss Norris that it is not reproduced here. The chief difference is that we find somewhat less ionic micelle in solutions in the neighborhood of 0.1 $N_w$. The effect of allowing for 100% dissociation of hydrochloric acid is merely to push up the boundary lines by a few per cent.

## Summary

1.   A method for the preparation of pure cetyl sulfonic acid is described.

2.   The electrical conductivity, lowering of vapor pressure, and hydrogen electrode potential of cetyl sulfonic acid solutions have been measured.

3.   No matter how evaluated, it is seen that this hydrogen soap is only partially dissociated even in dilutions where colloid is absent. In concentrated solutions it is with difficulty that the results of the three methods, particularly that of e. m. f., can be brought into quantitative agreement.

4.   The activity coefficients have been calculated, and an error in the published calculations of McBain, Randall and White has been noted.

(17) Hammarsten, *Biochem. Z.*, **144**, 383 (1924); Hammarsten, *Biochem. Z.*, **147**, 481 (1924); see also Pauli and Ripper, *Kolloid-Z.*, **62**, 162 (1933).

(18) Noller and Gordon, THIS JOURNAL, **55**, 1090 (1933).