cal concentration, ceases to fall in moderate dilution and may even increase. In order to investigate this phenomenon further, we have calculated the osmotic coefficients from our activity data. These results are plotted in Fig. 2 along with the values for potassium laurate from McBain and Bolduan. Although the curve of activity against concentration above the critical shows no discontinuity, or even deviation from a straight line, the osmotic coefficient curve calculated therefrom ceases to fall and even rises more abruptly than that of potassium laurate. Thus this "outstanding property of colloidal electrolytes (g ceasing to fall in moderate dilution)" would appear to be due entirely to the nature of the osmotic coefficient, and not to any changes occurring in the solution.

Similarly, the interpretation of the minimum as a "critical concentration for completion of the formation of micelles"[19] is unwarranted.

We do not wish to imply from the above that these data prove that no change does occur, but merely wish to point out that one must be extremely careful in attaching significance to a change in direction of a curve.

Summary

1. Thermodynamic activity of 1-dodecanesulfonic acid in aqueous solution at 40° in the concentration range 0–0.4 m has been determined by e.m.f. measurements.

2. The activity of 1-dodecanesulfonic acid in aqueous solution agrees with that expected on the basis of the mass law.

[19] Johnston and McBain, *Proc. Roy. Soc.* (*London*), **A181**, 127 (1942).

Seattle 5, Washington Received August 25, 1947

[Contribution from the Department of Chemistry and Chemical Engineering of the University of Washington]

The Electrical Conductance and Density of Solutions of Potassium 9,10-Dihydroxystearate and Potassium Stearate at 60°

By N. W. Gregory and H. V. Tartar

To determine the effect of substitution of hydroxyl groups in the middle of the carbon chain of a fatty acid soap on electrical conductance and micelle formation, studies have been made on solutions of the potassium salts of stearic and 9,10-dihydroxystearic acids.

A comparison of this type has not been made previously. Data concerning the electrical conductance of solutions of potassium 9,10-dihydroxystearate are not on record. The conductance of solutions of potassium stearate and related compounds has been reported by Bunbury and Martin[1] and by McBain and co-workers.[2,3,4] In these studies, however, any break in the conductance curves, indicating a critical concentration at which micelles are formed, would likely be masked by hydrolysis with the concomitant formation of slightly soluble acid soaps. This difficulty has been obviated in the investigation reported herein by using as a solvent an alkaline solution of sufficient concentration to repress hydrolysis. Measurements were made at 60° because of the slight solubility of potassium stearate at room temperature.

Experimental Part

Preparation of Materials.—The 9,10-dihydroxystearic acid (high melting form) was prepared by the oxidation of oleic acid with alkaline permanganate in dilute solution. Oleic acid (U.S.P. quality) was purified by a treatment modified from the methods described by Brown and Shimarowa[5] and Smith,[6] and conversion of oleic acid to dihydroxystearic acid effected by oxidation in a manner similar to that reported by Smith.[6]

The impure 9,10-dihydroxystearic acid resulting from the oxidation was extracted twice with boiling water to remove any hexa- or tetra-hydroxy acids, and recrystallized from 95% alcohol. After drying, the acid was extracted with both petroleum and ethyl ethers to remove any stearic acid and the residue recrystallized four times from 95% alcohol. The resulting compound was crystalline and melted at 131.6°. This is in excellent agreement with the melting point reported by Le Sueur–Freundler,[7] and others.[8]

Four hundred grams of oleic acid (U.S.P.) yielded 150 g. of the purified dihydroxystearic acid. The yield from the oxidation was very good and the principal losses incurred were in the purification procedures.

The potassium salt of dihydroxystearic acid was prepared in a manner adapted from the method of preparation of sodium stearate reported by McBain, Vold and Frick.[9] A hot alcoholic solution of dihydroxystearic acid was neutralized with an alcoholic solution of potassium ethoxide using phenolphthalein as an indicator. Upon cooling the resulting solution, the potassium salt separated as a silky crystalline precipitate. The crystals were washed thoroughly with alcohol, dried at 110°, and recrystallized from alcohol. The purity of the salt was checked by regenerating the acid from a small aliquot and determining the melting point.

Potassium stearate was prepared in an analogous manner from stearic acid (U.S.P. stearic acid recrystallized

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[1] Bunbury and Martin, *J. Chem. Soc.*, **105**, 424 (1914).

[2] McBain and Taylor, *Z. physik. Chem.*, **76**, 179 (1911).

[3] McBain, Cornish and Bowden, *J. Chem. Soc.*, **101**, 2042 (1912).

[4] McBain and Salmon, This Journal, **42**, 426 (1920).

[5] Brown and Shimarowa, *ibid.*, **59**, 16 (1937).

[6] Smith, *J. Chem. Soc.*, 974 (1939).

[7] Melting point of 9,10-dihydroxystearic acid reported to be 131–132° by Le Sueur–Freundler, *J. Chem. Soc.*, 1316 (1901).

[8] K. S. Markley, "Fatty Acids," Chapter XV, Interscience Publishers, Inc., New York, N. Y., 1947.

[9] McBain, Vold and Frick, *J. Phys. Chem.*, **44**, 1013 (1940).

from alcohol) and was purified as directed by Scheringa.[10] The salt was recrystallized eight times from 66% alcohol. Upon regeneration of stearic acid from an aliquot of the final material, it was found to have a melting point of 69.0°.[11]

The potassium hydroxide solution used as a solvent in the conductivity measurements was prepared in the following manner: a 50% aqueous (conductivity water) solution of potassium hydroxide (analyzed reagent grade) was prepared and the small amount of carbonate present precipitated with dilute barium hydroxide solution. The barium ion concentration of the solution was reduced to a minimum by careful titration against dilute potassium carbonate solution until the two were balanced. The total volume of the solution was 100 ml. and contained 50 g. of potassium hydroxide. Five-tenths ml. of this solution was diluted with conductivity water to a normality of approximately 0.001. Standardization of the dilute solution was effected with potassium acid phthalate, using a weight buret and neutral phenolphthalein. The titrations were carried out in an atmosphere of nitrogen.

Equipment and Procedure.—Conductance measurements were made using a Jones and Josephs-Dike conductivity bridge[12,13] calibrated to an accuracy of 0.02%, with current supplied by an a.c. vacuum-tube oscillator. A two-stage amplifier with telephone formed the detecting circuit. Measurements were made at a frequency of 1000 cycles, occasionally checking at 2000 cycles.

Measurements were made at 60° using an oil-bath with temperature controlled to ±0.001°. The temperature of the bath was determined by means of a platinum resistance thermometer (calibrated by the National Bureau of Standards).

Cells of the Jones and Bollinger type[14] were used for the conductivity measurements. It was found necessary to modify the cells slightly, to permit passage of nitrogen over the liquid in the filling tubes during the measurements, in order to eliminate drifts caused by absorption of carbon dioxide from the air by the alkaline solvent. By the use of nitrogen, drifts in the measured resistance were reduced to less than 0.005% per minute. The lowest resistance measured over a period of ten minutes after thermal equilibrium had been attained was the value used in calculating the conductance of the solution. The two cells used were found to have constants at 60° of 2.6841 and 25.904, respectively.[15]

All solutions were made up by weight. The samples were weighed on an analytical balance with an accuracy of 0.1 milligram, and the solvent on a larger balance (accuracy ± one milligram). The conductance of the stock potassium hydroxide was checked from time to time during the period in which measurements were made and was found not to vary beyond the limits of experimental error. Transfer of solutions was effected in glass systems by applying a pressure of nitrogen and solutions were maintained under nitrogen at all times. The bottles in which the solutions were stored had been carefully aged and paraffined before use.

In the case of the stearate, which is rather insoluble at room temperatures, it was found necessary to fill the conductance cell at 60°. This requirement renders the probable error in the stearate measurements somewhat greater than those for the dihydroxystearate. The latter is sufficiently soluble at room temperature to enable the cells to be filled without difficulty.

The density of the solutions was measured at 60° in a modified Sprengel type pycnometer,[16] which consisted of a 25 ml. pipet with the ends drawn down to capillary dimensions and fitted with ground glass caps. The pycnometer was calibrated with water at 60°. The accuracy of the density measurements is estimated to be ±0.00003.

The authors estimate that values for the conductance of the solutions, except those at very low concentrations, have a maximum probable error of the order of 0.1%.

Results and Discussion

The results of the density and conductance measurements are tabulated in Tables I and II and are illustrated graphically in Figs. 1 and 2. The solvent for all but the values designated *a* for the dihydroxystearate was 0.001317 N_w po-

TABLE I

DENSITY OF SOLUTIONS

Potassium 9,10-dihydroxystearate in 1.317 × 10^{-3} N KOH		Potassium stearate in 1.038 × 10^{-3} N KOH	
Molality × 10^2	Density	Molality × 10^2	Density
0.09062	0.98324	0.1713	0.98324
2.145	.98396	1.460	.98337
7.020	.98597	4.428	.98339
15.97	.98916	8.908	.98343
		14.93	.98345

TABLE II

CONDUCTANCE OF SOLUTIONS

Normality, N_v × 10^3	Specific conductance of solution, K × 10^3 mho	Specific[b] conductance of solvent, K × 10^4 mho	Equivalent[b] conductance of soap, mho
Potassium 9,10-Dihydroxystearate			
0.5083	0.69110	6.070	165.4
1.503	.84376	6.038	159.7
2.982[a]	.91625[a]	4.513[a]	155.9[a]
5.634[a]	1.2985[a]	4.470[a]	151.1[a]
6.690[a]	1.4516[a]	4.454[a]	150.4[a]
7.323	1.6901	5.933	149.8
9.810	1.9993	5.933	143.3
9.819	1.9939	5.933	142.6
19.587	3.2059	5.933	133.4
27.330	4.1096	5.933	128.7
37.816	5.2306	5.933	122.6
67.526	8.4126	5.933	115.8
84.764	10.210	5.933	113.5
149.71	17.162	5.933	110.7
202.64	22.724	5.933	109.2
Potassium Stearate			
0.4551	0.53291	4.594	161.5
.9091	.57937	4.594	132.0
2.712	.72495	4.594	97.92
3.231	.75566	4.594	91.71
4.415	.82286	4.594	82.33
9.831	1.1739	4.594	72.68
14.290	1.4046	4.594	66.14
24.931	1.9578	4.594	60.14
29.666	2.2926	4.594	61.80
42.931	2.9068	4.594	57.01
64.794	4.2152	4.594	57.97
70.028	4.5791	4.594	58.83
91.946	5.8111	4.594	58.21
140.06	9.1259	4.594	61.88

[a] Different solvent (see text).
[b] Approximated as indicated in text.

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[10] Scheringa, *Chem. Weekblad*, **29**, 605 (1932).

[11] "I. C. T.," Vol. IV, McGraw-Hill Book Co., Inc., New York, N. Y., 1930, p. 10. Melting point of stearic acid reported as 69.3°.

[12] Dike, *Rev. Sci. Inst.*, **2**, 379 (1931).

[13] Jones and Josephs, THIS JOURNAL, **50**, 1049 (1928).

[14] Jones and Bollinger, *ibid.*, **53**, 411 (1931).

[15] The authors are indebted to A. B. Scott for the determination of these cell constants.

[16] This pycnometer was designed by Scott: doctorate thesis, University of Washington, 1941.

tassium hydroxide; that for the a values was 0.001038 N_w potassium hydroxide. The latter solvent was used entirely for the potassium stearate measurements. All data were obtained at 60°.

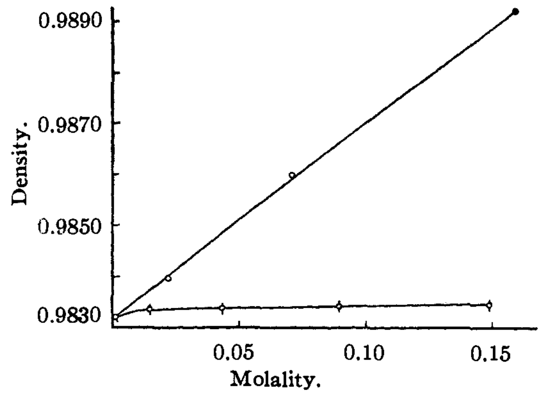

Fig. 1.—Change of density with concentration at 60°: O, potassium 9,10-dihydroxystearate; -O-, potassium stearate.

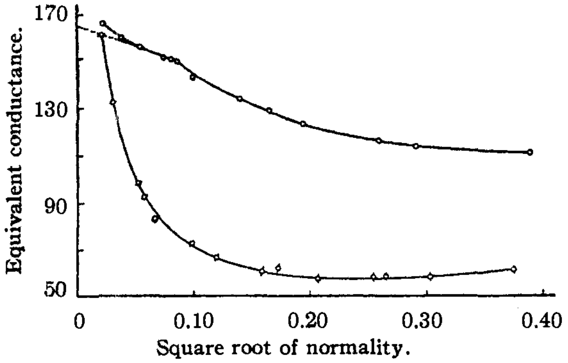

Fig. 2.—Equivalent conductance curves for solutions of potassium 9,10-dihydroxystearate and potassium stearate: O, potassium 9,10-dihydroxystearate; -O-, potassium stearate.

The concentration of potassium hydroxide necessary to repress hydrolysis of the soaps was computed on the basis of an assumed ionization constant for stearic acid. The constant for dihydroxystearic acid was assumed not to be appreciably different from that of stearic acid. Since ionization data for these acids are not available, a constant of 1.5×10^{-5} at 60° was taken, based on the known values of other members of the stearic acid homologous series up to caprylic acid. Using K_w for water as 9×10^{-14} at 60°, a concentration of hydroxyl ion of 0.001 mole/liter was calculated as sufficient to repress the concentration of the acid soap below 10^{-5} mole/liter. That this concentration was sufficient was confirmed by the observation that the more dilute solutions were either clear or only faintly colloidal, indicating negligible formation of acid soaps due to hydrolysis.

The use of the potassium hydroxide solution as the solvent requires a correction to be applied to the measured resistance of the solution, if the true conductance of the soap is to be determined. According to the Onsager theory, the conductance is determined by the total ionic strength of the solution. The concentration of the potassium hydroxide in the solvent remains constant and is sufficiently dilute to be treated by the Onsager equation. The soap has been assumed to be completely ionized at concentrations below that at which formation of micelles is indicated.

On this basis, the Onsager correction for the conductance of the potassium hydroxide, due to changing ionic strength of the solution, has been made up to the concentration at which micelles begin to form. The Onsager correction was computed from the general relation

$$\Lambda = \Lambda_0 - (\alpha\Lambda_0 + \beta)\sqrt{\mu}$$

where

Λ = equivalent conductance
Λ_0 = equivalent conductance at infinite dilution
$$\left.\begin{aligned}\alpha &= 0.2627\\ \beta &= 119.6\end{aligned}\right\}\text{Onsager constants at } 60^\circ$$
μ = total ionic strength

Since Λ_0 may be obtained from the measured conductivity of the standard potassium hydroxide by assuming an Onsager slope, the actual specific conductance due to the solvent may be found by calculating the total ionic strength of the solution, and substituting this value in the expression above. This involves the assumptions that the potassium hydroxide and the soap are completely dissociated up to the concentration at which micelles are formed. The difference between the total measured conductance and the value calculated for the solvent yields the value for the conductance of the soap.

In solutions of soaps in micellar form, determination of the ionic strength is not straightforward. Consequently, for lack of a precise method of treatment, a constant correction (the value calculated at the critical concentration) was applied to correct the measured conductance data for the contribution of the solvent. While it is realized that the equivalent conductance values determined on this basis are only approximate, it is doubtful that appreciable errors are involved, and certainly would not be of such a nature to change materially the over-all form of the curve.

Comparison of the two equivalent conductance curves illustrated in Fig. 2 reveals a striking difference. The dihydroxystearate is more soluble than the stearate, as would be expected from the influence of the hydroxyl groups. Its equivalent conductance is considerably greater than that of the stearate over most of the concentration range investigated.

There is a small break in the equivalent conductance curve for the dihydroxy compound occurring at a concentration of approximately 0.0075 N, at which point micelles may be formed. Below this concentration the curve follows an Onsager slope (indicated by the dotted line). The apparent upward trend of the conductance curve in the region of very low concentration is not felt to be real. The conductance of the solution in this region is almost entirely due to the solvent and the value for the soap is obtained only by taking the difference of two relatively large numbers. Neglecting the two values at high dilution, the soap exhibits a behavior characteristic of a strong electrolyte until the critical concentration is reached.

The change in slope in the equivalent conductance curve for potassium 9,10-dihydroxystearate at the critical concentration is not nearly as great as has been observed in the studies of sulfonates and other soaps in which the carbon chain does not contain substituted hydrophilic groups. This would indicate that the micelle formed is possibly somewhat smaller and of a different type as the result of the influence of the hydroxyl groups in the middle of the chain, and hence does not change the ionic characteristics of the soap as markedly.

In studying the conductance curve of potassium stearate, the critical concentration for micelle formation was not established. The soap behaved as a colloidal electrolyte throughout the concentration range investigated. It may be seen from Fig. 2 that the critical concentration must lie very close to 0.0005 N (the lower limit of the concentration range studied), in order that the curve for the stearate intersect the ordinate at a reasonable value of Λ_0. Since measurements were not made below the critical concentration, as an approximation, a constant correction for the conductance of the solvent (the value of the conductance of the pure solvent) was applied in reducing the data.

Qualitative observations of the stearate solutions confirm the colloidal nature of the soap as indicated in the conductance measurements. All solutions were observed to be faintly opalescent whereas those of the dihydroxy compound were clear in dilute solution. The conductance curve obtained for potassium stearate is similar to that given by Bunbury and Martin,[1] if the fact that their measurements were made at 90° without repression of hydrolysis is considered.

While the critical concentration for the formation of micelles may be somewhat different in solutions not alkaline in character, the value indicated by these data is, without question, characteristic of the soap in the solvent used, and serves to evaluate the effect of the hydroxyl groups.

The change in density of solutions of the dihydroxystearate with concentration in the potassium hydroxide solvent presents an interesting contrast with that observed for potassium stearate. The density curves are illustrated in Fig. 1 and re-emphasize the pronounced effect of the hydroxyl groups in the molecule. It seems quite likely that the higher density observed for the potassium dihydroxystearate indicates association of water molecules by the hydroxyl groups.

Summary

1. The electrical conductance and density of solutions of potassium 9,10-dihydroxystearate and potassium stearate in 0.001 N potassium hydroxide have been determined at 60°. A comparison of data for the two compounds reveals that the hydroxyl groups have considerable influence.
2. The critical concentration for the formation of micelles in 0.001 N potassium hydroxide is indicated at 0.0075 N for potassium 9,10-dihydroxystearate. The value for potassium stearate was not established but is probably in the vicinity of 0.0005 N.

SEATTLE, WASHINGTON RECEIVED SEPTEMBER 16, 1947

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Solubility of Cesium and Rubidium Dichloroiodides in Hydrochloric Acid Solutions

BY PAUL BENDER AND ROGER A. STREHLOW

Introduction

In the usual procedure for the purification of cesium or rubidium salts the repeated recrystallization of the dichloroiodide from hydrochloric acid solution is employed for the elimination of the other alkali metals. The quantity of material to be processed is ordinarily limited and the solubility of the complex salt appreciable, so that the attainment of efficiency in the purification process can be accomplished only through a quantitative knowledge of the solubility relationships involved. The present study was carried out to supply the required data which have not previously been available in the literature.

Experimental

Preparation of Materials.—Cesium chloride of spectroscopic purity was prepared from Pollucite by the method of Wells.[1] Rubidium chloride was prepared from Lepidolite (from Pala, Calif.) essentially as described by Kennard and Rambo.[2] The five-fold recrystallization as rubidium acid tartrate recommended by Archibald[3] was carried out to ensure the removal of cesium. Other reagents employed were of analytical grade.

In the preparation of the dichloroiodides a slight excess of iodine was added to a hot hydrochloric acid solution of the alkali chloride and chlorine gas bubbled through the

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(1) H. L. Wells, *Am. Chem. J.*, **26**, 265 (1901).

(2) T. G. Kennard and A. I. Rambo, *Am. J. Sci.*, **28**, 102 (1934).

(3) E. H. Archibald, "The Preparation of Pure Inorganic Substances," John Wiley and Sons, New York, N. Y., 1932.