JOURNAL OF THE
AMERICAN CHEMICAL SOCIETY

VOLUME 70 JUNE 30, 1948 NUMBER 6

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

Studies of Sulfonates. IX. Transference Numbers and Activity of 1-Dodecanesulfonic Acid in Aqueous Solutions at 40°[1,2]

BY L. L. NEFF,[3] O. L. WHEELER,[4] H. V. TARTAR AND E. C. LINGAFELTER

One of the most important properties for the interpretation of the behavior of solutions is the thermodynamic activity. While many studies have been made of solutions of paraffin-chain salts as colloidal electrolytes, the only activity data are the freezing point measurements of McBain and co-workers[5] and of Ralston and associates,[6] the vapor pressure measurements of McBain and co-workers,[7] and, appearing since the completion of the present study, the electromotive force measurements of Walton.[8]

It was felt that an independent determination of these activities would be desirable. We have therefore determined the activity of 1-dodecanesulfonic acid in aqueous solutions at 40° up to 0.4 *m* by electromotive force measurements. Two types of cells were used. In the concentration range 0–0.02 *m* we have used cells of the type

$$\mathrm{Pt, H_2|C_{12}H_{25}SO_3H}(m_1)|\mathrm{C_{12}H_{25}SO_3H}(m_2)|\mathrm{H_2, Pt} \quad (1)$$

(concentration cells with liquid junction). In the concentration range 0.01–0.4 *m* we have used cells of the type

$$\mathrm{Pt, H_2|C_{12}H_{25}SO_3H}(m)|\mathrm{Hg_2(C_{12}H_{25}SO_3)_2{\cdot}2H_2O(s), Hg} \quad (2)$$

(concentration cells without liquid junction).

The transference numbers necessary for the calculation of activities from the measured electromotive force of cells of type (1) were determined by the Hittorf method over the concentration range 0–0.6 *m*.

Experimental

Materials.—The 1-dodecanesulfonic acid was prepared from its sodium salt by the method of Zuffanti.[9] The sodium 1-dodecanesulfonate had been prepared by the action of aqueous sodium sulfite on *n*-dodecyl bromide in a bomb at 160°.

The mercurous 1-dodecanesulfonate for use in the mercury–mercurous electrodes was prepared by precipitation from a solution of either the 1-dodecanesulfonic acid or its sodium salt with an excess of mercurous nitrate. The precipitated salt was washed thoroughly with distilled water and stored until used under 0.1 *m* 1-dodecanesulfonic acid in contact with mercury. Microscopic examination showed the solid to consist of very small, well-formed crystals. Analysis of the solid for mercury by the method of Hager and Hulett[10] gave results in agreement with the composition $\mathrm{Hg_2(C_{12}H_{25}SO_3)_2{\cdot}2H_2O}$ (% Hg found: 42.77, 42.99, 43.00; calcd. 42.86).

The solubility of mercurous 1-dodecanesulfonate in water at several temperatures was determined by evaporating to dryness 50-ml. samples of the saturated solutions. At 40° the result obtained was 5.7×10^{-5} *M*.

The mercury used in the preparation of the mercury–mercurous sulfonate electrodes had been washed with nitric acid and distilled twice *in vacuo*.

Commercial tank hydrogen was used for the hydrogen electrodes, the oxygen being removed by passing the gas through a quartz tube filled with granular copper filings heated electrically to about 700°.

Conductivity water from a Barnstead still was used for the preparation of all solutions. The solutions were made up by weight from a stock solution of 1-dodecanesulfonic acid. This stock solution was standardized by weight titration against a sodium hydroxide solution which had been standardized against twice-recrystallized Baker C. P. grade potassium acid phthalate.

Apparatus and Procedure.—The transference numbers were determined in a modified Washburn[11] apparatus con-

---

(1) Presented at the New York Meeting of the American Chemical Society, New York, September, 1944.

(2) Taken in part from theses submitted by L. L. Neff and by O. L. Wheeler in partial fulfillment of the requirements for the Ph.D. degree.

(3) Present address: Union Oil Company of California, Wilmington, California.

(4) Present address: Plastics Division, Monsanto Chemical Company, Springfield, Massachusetts.

(5) (a) J. W. McBain and Betz, THIS JOURNAL, **57**, 1909 (1935); (b) E. L. McBain, Dye and Johnston, *ibid.*, **61**, 3210 (1939).

(6) Ralston, Hoerr and Hoffman, *ibid.*, **63**, 2576 (1941).

(7) (a) J. W. McBain and Williams, *ibid.*, **55**, 2250 (1933); (b) Randall, J. W. McBain and White, *ibid.*, **48**, 2517 (1926); (c) J. W. McBain and Barker, *Trans. Faraday Soc.*, **31**, 149 (1935).

(8) Walton, THIS JOURNAL, **68**, 1180 (1946).

(9) Zuffanti, *ibid.*, **62**, 1044 (1940).

(10) Hager and Hulett, *J. Phys. Chem.*, **36**, 2095 (1932).

(11) Washburn, THIS JOURNAL, **31**, 322 (1909).

structed of 2-cm. Pyrex glass tubing according to the specifications of MacInnes and Dole.[12]

Two silver coulometers, constructed according to the specifications of the U. S. Bureau of Standards,[13] were placed in series with the transference cell, one on either side.

The temperature was held to 40 ±0.03° in a Freas water thermostat. The cathode of the transference cell was a coiled silver wire coated with silver chloride. The anode was of lead (anode reaction, $Pb + 2C_{12}H_{25}SO_3^- = Pb(C_{12}H_{25}SO_3)_2 + 2e^-$) for concentrations of sulfonic acid below 0.05 *m*, and of platinum (anode reaction, $2H_2O = 4H^+ + O_2 + 4e^-$) for concentrations above 0.05 *m*.

In all runs, the transference numbers were calculated from data on both anolyte and catholyte and the two values were averaged. In solutions below 0.05 *m* these two values agreed within 1% in all cases. Above 0.05 *m* the agreement was somewhat less satisfactory, but always within 3%.

The electromotive forces were measured by means of a Leeds and Northrup Type K potentiometer with a Type R galvanometer. The standard cell was checked by means of a White potentiometer against a pair of cells recently standardized by the United States Bureau of Standards.

The temperature was controlled at 40±0.05° by means of an air thermostat.

The cells used were very similar to those described by Tartar, Newschwander and Ness.[14]

Results and Discussion

The transference numbers are given in Table I. The data are quite similar to those obtained by McBain[15] at 20°, although our data indicate no change in transference number below the critical concentration.

TABLE I

TRANSFERENCE NUMBERS OF THE HYDROGEN ION IN AQUEOUS SOLUTIONS OF DODECANE SULFONIC ACID AT 40°

Molality	Transference number	Molality	Transference number
0.0000	0.930	0.1124	0.680
.00526	.924	.1632	.721
.00795	.929	.1971	.733
.01743	.816	.2300	.762
.03134	.740	.3134	.738
.04038	.715	.3490	.730
.0554	.680	.4651	.738
.0671	.718	.6067	.753
.0801	.694		

The expression of e.m.f. in terms of activities for a cell containing a colloidal electrolyte such as 1-dodecanesulfonic acid is complicated by the transference of micelles, as well as single ions, across the liquid junction. It can be shown, however, that the expression assumes a form identical with that for an ordinary electrolyte.

In calculating and discussing the results, we may make use of an activity coefficient defined as the ratio of the mean ionic activity to the total stoichiometric molality, $\gamma = a_{\pm}/m$.

The activity coefficients in the concentration range 0–0.02 *m* were calculated from the measured e. m. f. of the cells of type (1) by the method outlined by MacInnes.[16]

Table II gives measured e. m. f. and molality of solution 2, solution 1 being constant at 0.00526 *m*. Table III includes the values of the mean ionic activity of 1-dodecane sulfonic acid at rounded concentrations. The data are plotted in Fig 1.

TABLE II

ELECTROMOTIVE FORCES OF CELLS WITH TRANSFERENCE

Molality (m_2)	E. m. f., mv.	Molality (m_2)	E. m. f., mv.
0.00301	−2.13	0.00898	1.66
.00372	−1.19	.01008	1.91
.00416	−1.11	.01031	2.01
.00526	0.00	.01039	1.81
.00590	0.56	.01094	2.00
.00638	0.52	.01147	2.38
.00657	0.98	.01321	2.13
.00697	1.28	.01408	2.31
.00781	1.41	.01532	2.40
.00794	1.97	.01567	2.40
.00878	1.79	.02287	2.91
.00885	2.12		

TABLE III

ACTIVITY OF 1-DODECANESULFONIC ACID IN AQUEOUS SOLUTION FROM E. M. F. OF CELLS WITH TRANSFERENCE

Molality	Activity	Molality	Activity
0.00300	0.00293	0.01200	0.00846
.00400	.00384	.01300	.00856
.00500	.00481	.01400	.00848
.00600	.00587	.01500	.00860
.00700	.00691	.01600	.00878
.00800	.00780	.01700	.00888
.00900	.00808	.01800	.00898
.01000	.00814	.01900	.00906
.01100	.00835	.02000	.00915

It was found that the mercury–mercurous 1-dodecanesulfonate electrode was not constant or reproducible in very dilute solutions and measurements in solutions below 0.01 *m* were made with hydrogen electrodes in concentration cells with liquid junction (type 1). In solutions of concentration 0.01 *m* and greater, the mercurous sulfonate electrode functioned satisfactorily and cells without liquid junction (type 2) were used. Their reversibility was proven by the calculation of E^0 in a series of concentrations where the activity coefficients had been determined from the electromo-

TABLE IV

E^0 OF THE MERCURY–MERCUROUS 1-DODECANESULFONATE ELECTRODE

$2Hg + 2C_{12}H_{25}SO_3^- + 2H_2O = Hg_2(C_{12}H_{25}SO_3)_2 \cdot 2H_2O + 2e^-$

Concentration (*m*)	E^0, volts
0.00992	−0.3856, −0.3828
.01030	− .3870, −0.3863
.01532	− .3844
.02100	− .3870
	− .386 (mean)

---

[12] MacInnes and Dole, THIS JOURNAL, 53, 1357 (1931).

[13] U. S. Bur. Stand. Bull. No. 285 (1916).

[14] Tartar, Newschwander and Ness, THIS JOURNAL, 63, 28 (1941).

[15] M. E. L. McBain, *J. Phys. Chem.*, 47, 196 (1943).

[16] MacInnes, "The Principles of Electrochemistry," Reinhold Pub. Corp., New York, N. Y., 1939.

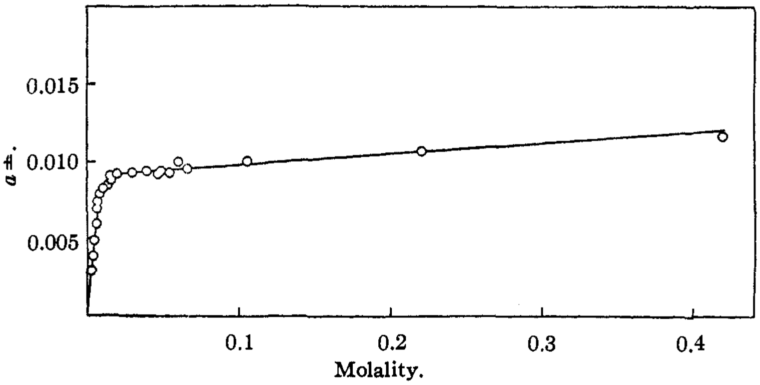

Fig. 1.—Mean ionic activity of 1-dodecanesulfonic acid in aqueous solution at 40°.

tive force of cells with liquid junction; these values of E^0 are shown in Table IV. The average value, 0.386 volt, is identical with the value obtained by Walton[8] at 25°.

The average value of E^0 was used to calculate the solubility of mercurous 1-dodecanesulfonate to check the result obtained analytically; the result obtained was 2.5 × 10^{-5} mole per liter. This agrees quite well with the analytical value of 5.7 × 10^{-5} mole per liter. Part of the difference may be due to the value of the standard potential of the mercury–mercurous ion electrode. Since its value was not known experimentally at 40°, an approximation was made from its value and temperature coefficient at 25° assuming that the temperature coefficient was constant from 25 to 40°. This temperature coefficient was calculated from the standard entropy change of the reaction $2Hg + 2H^+ = Hg_2^{++} + H_2$ reported by Latimer, Pitzer and Smith.[17] The analytical value is undoubtedly high because of the nature of the salt; minute crystals were present in the filtrate as shown by a carbon arc and because of the limited solubility these caused a rather large error in the result.

Data from cells of type 2 were used to calculate activities in solutions of 1-dodecanesulfonic acid where the sulfonate electrodes would function. The activity in a reference solution (near 0.01 *m*) was obtained from those determined by means of cells with liquid junction, and the activity in the other solutions calculated from the electromotive force of the above cell. The mean ionic activities are listed in Table V and are plotted in Fig. 1.

It may be seen from Fig. 1 that the behavior to be expected on the basis of the mass law is shown by these solutions. Below the critical concentration the activity of the 1-dodecanesulfonic acid increases with concentration as expected for an ordinary univalent strong electrolyte. Above the critical concentration, the activity is almost constant, rising only very slowly with increasing concentration.

Our results agree very well with those of Walton.[8] The extent of the agreement is indicated by the fact that our data, if plotted on Fig. 2 of his paper, fall almost exactly on the dashed line. Thus the three sets of data, at 0, 25 and 40°, form a consistent body, both with respect to the values of the activities and the position of the critical concentration.

TABLE V

ACTIVITY OF 1-DODECANESULFONIC ACID IN AQUEOUS SOLUTION FROM E. M. F. OF CELLS WITHOUT TRANSFERENCE

Molality	Activity	Molality	Activity
0.01030	0.00819	0.05485	0.00932
.01532	.00917	.05554	.00944
.02100	.00925	.05995	.01001
.03030	.00933	.06594	.00956
.04009	.00931	.10630	.01012
.04678	.00922	.22105	.01070
.04860	.00933	.39871	.01184

McBain and Bolduan[18] in discussing osmotic coefficients of colloidal electrolytes seem to attach considerable importance to the fact that the coefficient, after dropping markedly above the criti-

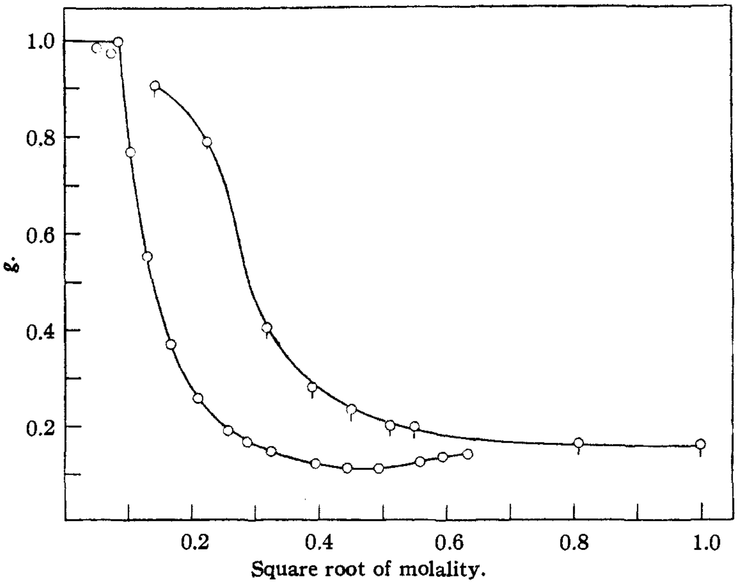

Fig. 2.—Osmotic coefficients: O, 1-dodecanesulfonic acid (this research): ♀, potassium laurate (McBain and Bolduan).

---

[17] Latimer, Pitzer and Smith, THIS JOURNAL, **60**, 1829 (1938).

[18] McBain and Bolduan, *J. Phys. Chem.*, **47**, 94 (1943).

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

---

[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).