that the mutual energy per unit volumes, a_{12}, is equal to $\sqrt{a_{11}a_{22}}$ leads to the result

$$E_{vx}^M = -(\sqrt{a_{11}} - \sqrt{a_{22}})^2 V_x^0 z_1 z_2 \qquad (22)$$

For an equimolal mixture this yields $E_{vx}^M = 3.8$ cal. per mole instead of the measured 20.7. However, if we calculate $-a_{12}$ from the relation

$$E_{vx}^M = (2a_{12} - a_{11} - a_{22}) V^0 z_1 z_2 \qquad (23)$$

and the measured 20.7 for equimolal mixtures, we obtain $-a_{12} = 69.34$, which is only 0.5% less than $\sqrt{72.96 \times 66.54} = 69.67$. So, quadratic combination gives a very good approximation for a_{12}, and the small error is in the direction predicted by the quantum theory. The treatment of solutions makes too drastic demands for a simple theory in requiring a small difference between large numbers. On the other hand, measurements on solutions afford a correspondingly accurate measure of one of these quantities if the others are known.

Summary

The vapor–liquid equilibrium pressure and compositions of carbon tetrachloride–cyclohexane mixtures have been measured at 40 and 70° over the whole composition range, and at 30, 50, and 60° for approximately equimolal mixtures. The densities have been determined at 25°.

These measurements have been expressed analytically, and corresponding equations derived for the thermodynamic functions, including the energy and entropy of mixing at constant total volume.

The dependence upon composition agrees with the predictions of the simple theory. The deviation from regularity is relatively large but most of it is explained by the volume change on mixing.

The unexplained entropy increase on mixing is only one-thirteenth as large as for benzene–cyclohexane mixtures.

Solutions of the Paraffin-Chain Sulfonic Acids as Colloidal Electrolytes

By Evelyn Laing McBain, Walter B. Dye and Stewart A. Johnston

Colloidal electrolytes since their first recognition by McBain in 1913 have received steadily increasing attention, because of their interesting departures from the behavior of ordinary electrolytes and because they embrace such large groups of substances. The soaps originally studied do not lend themselves to precise examination in very dilute solution on account of the prominent effects of hydrolysis. It remained therefore for Lottermoser and Püschel[1] to show that in great dilution many non-hydrolyzable salts of alkyl sulfuric acids conform to the behavior of the Debye–Hückel theory, rather suddenly departing from it at a very low concentration designated, by Bury and collaborators, the critical concentration for micelles. This has been confirmed by many subsequent investigators, and necessitated a modification of the original formulation to conform more closely to later conceptions of interionic attraction. Different authors, however, differ in their formulations. It is desirable to have exact measurements of many different properties of a non-hydrolyzable pure

material of simple chemical composition sufficiently soluble that it may be studied over a wide range of concentrations.

The present communication comprises measurements of lowering of freezing point, conductivity, viscosity and density of straight chain sulfonic acids with special emphasis upon dodecyl sulfonic acid. The results for diffusion have been published[2] and a provisional discussion is being given elsewhere,[3] although it is not until our measurements of transport number are completed that a sufficient number of equations will be available for a definitive solution of the problem, except in its principal outlines which are already generally known.

Experimental

An especially pure preparation of laurylsulfonic acid was made by M. E. Synerholm by the method of Noller and Gordon[4]; its equivalent weight by titration was 100.05% of the theoretical, the excess probably being water. The other sulfonic

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

(2) Evelyn Laing McBain, Proc. Roy. Soc. (London), A170, 415 (1939).

(3) Van Rysselberghe, Colloid Symposium, 1939.

(4) Noller and Gordon, This Journal, 55, 1090 (1933).

acids from C_2 to C_{14} were prepared by F. M. McMillan. The potassium methyl, ethyl and propyl sulfonates were purchased from Kahlbaum, their solutions being filtered before use. The acids were made up by weight on the basis of their titrated value with conductivity water, from a Barnstead still, of specific conductance 0.3 to 0.4×10^{-6} mho.

The conductivity measurements were made with complete Leeds and Northrup Jones–Dike equipment, with an oil thermostat at 25°. Potassium chloride solutions were made up by the Jones and Bradshaw method. The cells were H-shaped with electrode leads from opposite ends, one[5] for use with stronger solutions and another shortened one for the most dilute solutions.

The Conductivity Data

To save space the density and conductivity results obtained by one of us (W. B. D.) for the lower members of the homologous series are given graphically in Figs. 1 and 2, which also include for comparison the "I. C. T." values for hydrochloric acid. Figure 2 also includes the data for the higher homologs and for the potassium salts. It will be noted that the first clear indication of departure from the behavior of ordinary strong electrolytes occurs with C_7 and that in concentration above about 0.4 N. There is a slight effect in solutions of C_6 approaching 1 N, and it is possible that in still greater concentrations the lower homologs of the free acids would give similar indications.

The conductivity data for the higher homologs are given in Tables I to IV for the sulfonic acids C_9, C_{11}, C_{12}, and C_{14}. The necessary density data by one of us (E. L. M.) were included in a previous

TABLE I

EQUIVALENT CONDUCTIVITY OF AQUEOUS SOLUTIONS OF NONYL SULFONIC ACID AT 25°, AT VARIOUS MOLALITIES

m	μ	m	μ	m	μ
0.0008505	369.3	0.006366	362.5	0.04908	329.7
.001993	367.8	.007159	365.0	.05560	320.1
.002917	366.6	.01270	359.8	.06556	305.8
.003226	366.9	.01984	354.4	.07450	293.1
.003801	365.7	.03032	347.5	.08232	283.9
.004756	364.7	.03610	342.9	.08804	277.1
.005604	363.9				

(5) McBain, Laing and Titley, *Trans. Chem. Soc.*, **115**, 1279 (1919).

TABLE II

SPECIFIC AND EQUIVALENT CONDUCTIVITY OF UNDECYL SULFONIC ACID AT 25°

m	k	μ	m	k	μ
0.0007187	0.0002627	366.7	0.006113	0.002199	361.3
.001486	.0005405	365.0	.006432	.002319	362.2
.001597	.0005820	365.5	.006704	.002410	361.1
.002348	.0008533	364.7	.007233	.002598	360.8
.002515	.0009123	364.0	.008332	.002982	359.6
.003102	.0011237	363.6	.009027	.003236	360.3
.003818	.001382	363.3	.009303	.003523	359.0
.004059	.0014655	362.5	.009860	.003518	358.6
.004552	.001645	362.8	.01732	.006021	350.0
.005175	.001871	363.0			

publication,[6] except those for nonylsulfonic acid where very little material was available and where the density is so nearly that of water (d^{25}_4 0.9994
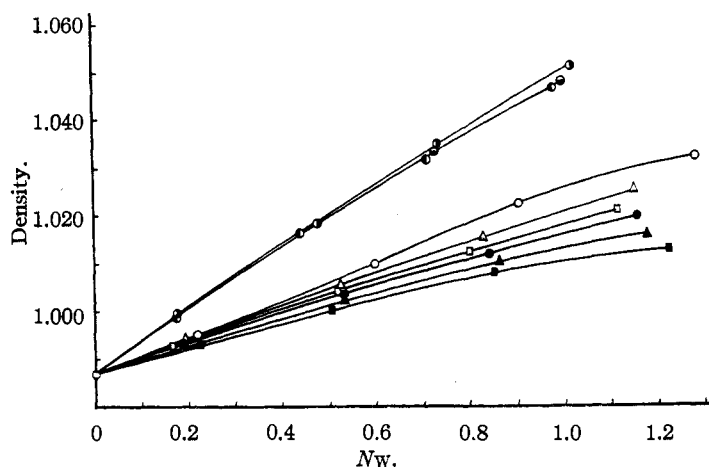

1.060

1.040

Density.

1.020

1.000

0   0.2   0.4   0.6   0.8   1.0   1.2
Nw.

Fig. 1.—The density (at 25/4°) of the sulfonic acids C_2 to C_7: of the potassium sulfonates C_1 to C_3: ◑, CH_3SO_3K; ◐, $C_2H_5SO_3K$; ◓, $C_3H_7SO_3K$; ○, $C_2H_5SO_3H$; △, $C_3H_7SO_3H$; □, $C_4H_9SO_3H$; ●, $C_5H_{11}SO_3H$; ▲, $C_6H_{13}SO_3H$; ■, $C_7H_{15}SO_3H$.

for 0.098 m) that other concentrations are based upon a linear graph.

TABLE III

SPECIFIC AND EQUIVALENT CONDUCTIVITY OF DODECYL SULFONIC ACID AT 25°

m	k	μ	m	k	μ
0.00002466	0.000009135	371.5	0.004630	0.001628	360.8
.00004183	.00001550	371.5	.004677	.001684	361.2
.0001303	.00004816	371.2	.005325	.001924	359.7
.0001462	.00005424	370.8	.005546	.001987	358.6
.0001903	.00007060	372.0	.005867	.002107	359.8
.0003937	.0001462	371.1	.006592	.002347	356.1
.0004098	.0001519	371.2	.007037	.002513	358.0
.0004130	.0001532	371.2	.007920	.002806	355.2
.0004183	.0001550	371.5	.007941	.002821	356.1
.000547	.0002024	371.1	.008067	.002874	356.6
.0006454	.0002395	371.0	.009581	.003188	333.6
.0008925	.0003298	370.5	.01077	.003211	299.1
.001398	.0005185	370.9	.02059	.004345	211.4
.001693	.0006250	369.6	.03018	.005411	180.6
.001828	.0006842	369.1	.0510	.007991	159.8
.002149	.0007861	367.6	.0516	.008098	156.5
.002377	.0008746	367.1	.0705	.01054	146.8
.003473	.001255	362.8	.0958	.01505	147.6
.003750	.001352	362.0			

(6) McBain and Betz, THIS JOURNAL, **57**, 1906 (1935).
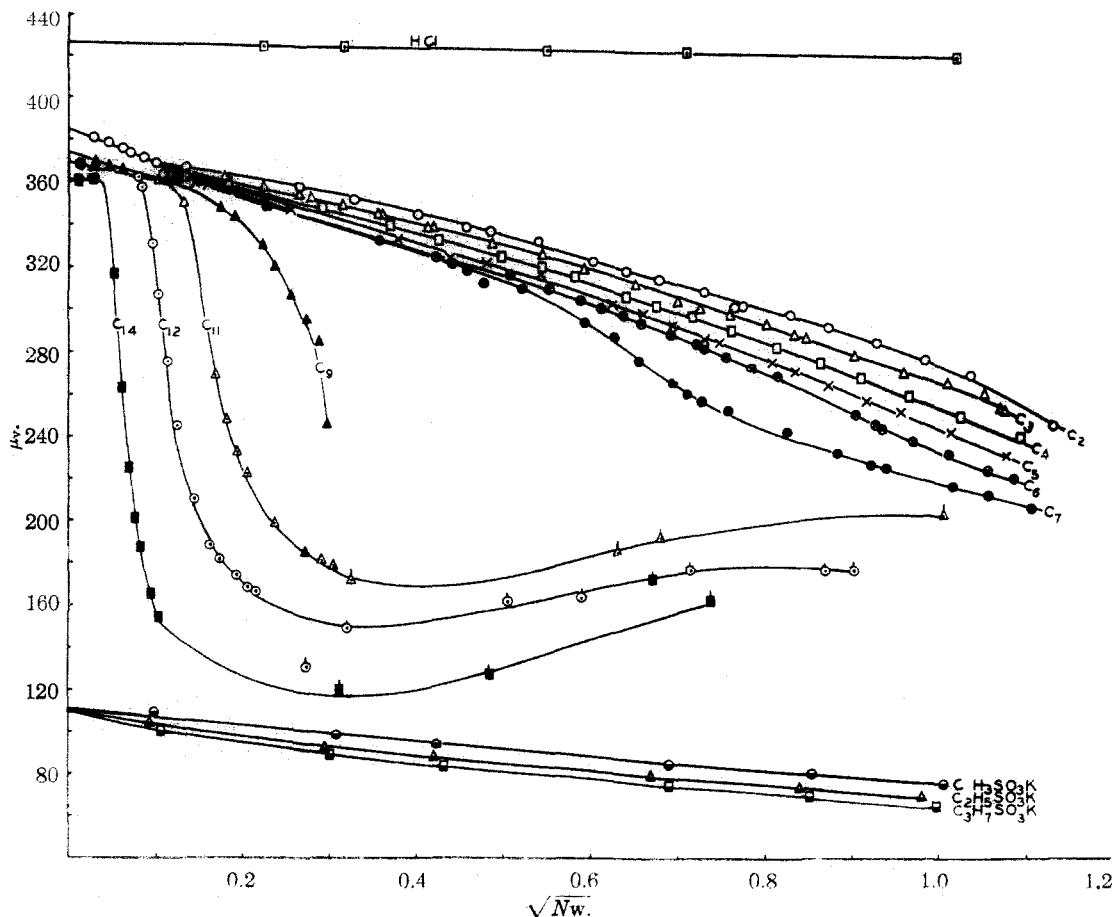
Fig. 2.—The molar conductance at 25° of HCl, the sulfonic acids and some of their salts: ⬠ ⊙ ■. Values by Miss Betz.

TABLE IV

EQUIVALENT AND SPECIFIC CONDUCTIVITY OF TETRADECYL SULFONIC ACID AT 25°

m	k	μ	m	k	μ
0.0001089	0.00003914	360.5	0.002556	0.0008045	315.9
.0001384	.00004968	359.9	.003419	.0008941	262.5
.0001802	.00006464	359.7	.004458	.0009953	224.2
.0002221	.00008002	361.3	.005459	.001089	200.4
.0004878	.0001754	360.6	.006265	.001163	186.5
.0007667	.0002758	360.8	.007110	.001247	176.2
.0010570	.0003806	361.2	.008317	.001365	165.0
.001852	.0006739	359.3	.010065	.001537	153.6

The most interesting portions of the data for the present purpose are those for extreme dilution which are plotted in Fig. 3; the measurements of the most dilute solutions of C_{11} and C_{14} (by W. B. D.) may possibly be affected by some systematic error. Indeed, it was found to be the case in the corresponding measurements of C_{12} (by W. B. D.). However, it does not show in the measurements with C_2 in the same dilutions.

Figure 3 also includes the straight line representing the Onsager slope $\mu_e = \mu_\infty - [0.2274\ \mu_\infty + 59.78]\ \sqrt{N_V}$ for complete dissociation. The

limiting equivalent conductances are, for the acids, 385 for C_2, 374 for C_9, 372 for C_{12} and 361 for C_{14}; and for the potassium salts 109, leaving 35.5 for the C_2 anion. From this the limiting mobilities of the anions are, for C_2 35, for C_9 24, and for C_{12} 22. For sodium dodecyl sulfate, Ward[7] obtained $\mu_\infty = 65.46$ at 20°, from which we deduce for the anion 22 to 23 depending upon whether one uses the data for Na$^+$ from "I. C. T.," Ward or MacInnes, Shedlovsky and Longsworth.[8] Howell and Robinson for the same sulfate had $\mu_\infty = 85.1$ at 25°, but with a systematic error still to be corrected, meanwhile leaving 35.1 mhos for the C_{12} ion. Reed and Tartar had $\mu_\infty = 86$ for the sodium dodecyl sulfonate or 36 mhos for the anion, but their more recent paper[9] contains conductivities for this particular substance that differ by as much as 6 to 20% from their previous paper.

(7) Ward, J. Chem. Soc., 522 (1939).
(8) MacInnes, Shedlovsky and Longsworth, THIS JOURNAL, 54, 2762 (1932).
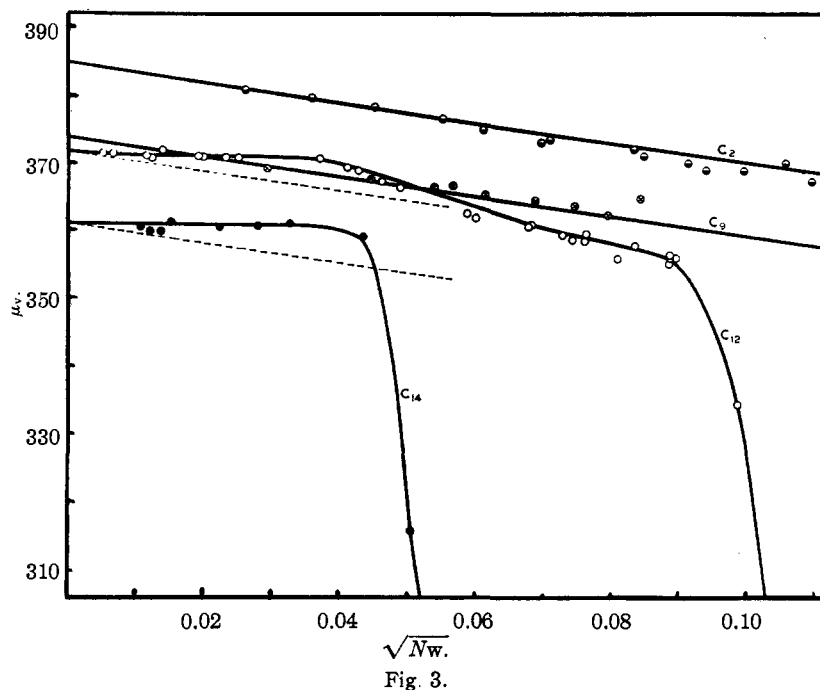(9) Wright, Abbot, Sieverts and Tartar, ibid., 61, 550 (1939).

Fig. 3.

Their value for C_{14} at $40°$ was 2 mhos less. Lottermoser and Püschel obtained $\mu_\infty = 75$ for sodium dodecyl sulfate at $25°$ (but extrapolating linearly against $\sqrt[3]{N}$) giving 24.5 mhos for this anion, and a value for C_{12} 4 mhos less than C_{14} at $40°$. We shall take our own value of 22 mhos as being the most likely for C_{12} anion with 35 mhos for the C_2 anion, which may be compared with the "I. C. T." value of 36.7 mhos for acetate and the MacInnes, Shedlovsky and Longsworth value of 40.87 mhos for the acetate ion.

The slope of the conductivity curve at extreme dilution in Fig. 3 is exactly the Onsager value for C_2 but with the higher members the conductivity of the colloidal electrolyte in this range decreases less than expected with concentration. Tartar's collaborators likewise noted the same effect. For example, for sodium dodecyl sulfonate at 40, 60 and $80°$, they obtained slopes of 80, 109 and 140; whereas Onsager's equation would demand 106, 115 and 203, respectively. A noticeable increase of conductivity above that derived by the Onsager equation at infinite dilution could in these great dilutions only be accounted for on the basis of small amounts of highly conducting ionic micelle. Indeed, the fact that in dilutions such as 0.0004 N the conductivity of methylene blue is very greatly above the value for infinite dilution (of the order of 25–30% excess) was explained similarly by Moillet, Collie, Robinson and

Hartley. They noted that even when with m-benzopurpurin the conductivity slope appeared normal, transport measurements conclusively proved the presence of micelles conducting better than the ions from which they were formed.

The mass law requires that for small micelles or complexes their formation must be gradual and extend over the whole range of concentration. A sharp break in the slope, at the "critical concentration to form micelles," is incompatible with the mass law even for the largest micelles. Writers since Lottermoser and Püschel have tended to overstress the sharpness of this break. Our critical concentrations are C_9 0.04, C_{11} 0.015, C_{12} 0.08 and C_{14} 0.0026 N, as read from the graph of equivalent conductivity, Fig. 3, with slightly different and likewise arbitrary values if read from the graph of specific conductivity, Fig. 4. The value for C_{12} is less than would be expected from those of the sodium salts,[9] whereas that for C_{14} is slightly greater.
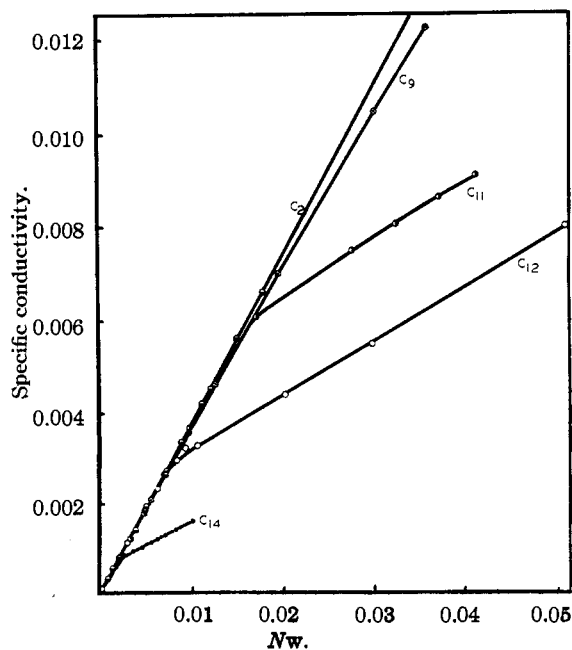

Fig. 4.

Those for the acids of uneven carbon atoms lie likewise at lower concentrations than those predicted for the sodium salts, being more nearly equal to the next highest homolog of even carbon number. The curve is very smoothly rounded for C_9 with increasing abruptness for the higher homologs.

Refractive Index

Refractive index, being essentially a measurement of atomic volumes, is but little affected by change from crystalloid to colloid. Lifshitz and Brandt[10] found that the molar refraction for the soaps as observed in soap solutions agreed with that calculated for ordinary organic chemicals. For this reason refractive index is frequently a valuable method of analysis of soap solutions since with the dipping refractometer and auxiliary prism only 0.03 cc. is required for measurement and the readings at 25° are linear when plotted against % or against equivalent weights in 1000 g. of total solution, as shown in Fig. 5. The slopes for the first four homologs are as shown in the figure 0.0293, 0.0247, 0.0210, and 0.0186, respectively.
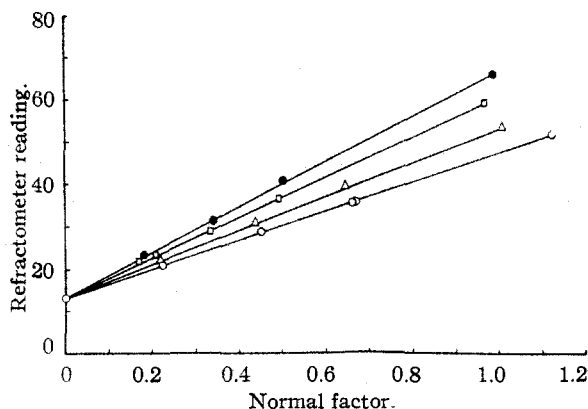

Fig. 5.—The refractometer reading at 25° of the sulfonic acids C_2 to C_5 plotted against the normal factor (equiv./1000 g. of solution): $\bigcirc$, $C_2H_5SO_3H$; $\triangle$, $C_3H_7SO_3H$; $\square$, $C_4H_9SO_3H$; $\bullet$, $C_5H_{11}SO_3H$.

Viscosity Data

The following results were obtained (by E. L. M.) for the viscosity of dodecyl sulfonic acid solutions at 25°, taking the value for water as unity, and employing an Ostwald viscometer.

N_W	0.020	0.035	0.050	0.060	0.090	0.105	0.302	0.36
r	1.14	1.19	1.21	1.22	1.26	1.30	1.82	2.01
N_W	0.455	0.565	0.77	0.805	0.95	1.026	1.052	
r	2.28	3.01	4.64	5.04	7.54	10.93	13.4	

The viscosity results are graphed in Fig. 6. The rapid rise in the more concentrated solutions

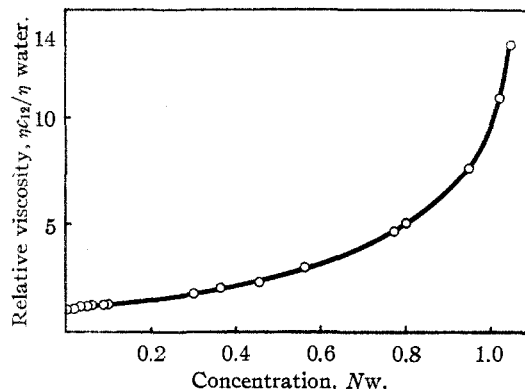(10) Lifshitz and Brandt, *Kolloid Z.*, **22**, 142 (1918).

Fig. 6.

corresponds to structural viscosity. Thus the equivalent conductivity throughout the most concentrated range is rising in spite of an increase in viscosity amounting to many fold. Were it not for this, the increase of conductivity with increase of concentration evidently would be still greater. In the most concentrated solutions diffusion and conductivity show definite signs of reduction.

Freezing Point Data (by S. A. J.)

The freezing equipment was modelled after that of Scatchard.[11] The e. m. f. across the twenty-four junction thermocouple is measured by a relatively inexpensive null method designed by Dr. Stuart W. Grinnell, Fig. 8, and sensitive to 5×10^{-5} degree or 5×10^{-8} volt. The voltage divider AB (ratio 1:1627.3), like the galvanometer circuit, is of copper; P is a simple potentiometer to give a fine adjustment.

The thermocouple is calibrated directly by measuring the thermal e. m. f. produced by the freezing point lowering of approximately 0.15 N potassium chloride solutions, and calculating the freezing point depression using g values obtained by Scatchard.

The freezing point results for dodecylsulfonic acid are assembled in Table V and are shown

TABLE V					
Concn.	θ	g	Concn.	θ	g
0.08713	0.05297	0.1636	0.01211	0.03704	0.8231
.07778	.05101	.1765	.01148	.03686	.8638
.05674	.04492	.2130	.01029	.03581	.9367
.05612	.04589	.2200	.009233	.03254	.9483
.05373	.04635	.2321	.006843	.02427	.9543
.03466	.04038	.3135	.005985	.02135	.9599
.02978	.04111	.3714	.005797	.02079	.9649
.02208	.03915	.4772	.004470	.01592	.9584
.02045	.03856	.5074	.003469	.01238	.9604
.01804	.03888	.5799	.002716	.009817	.9726
.01778	.03847	.5822	.002174	.007905	.9785

(11) Scatchard, Jones and Prentiss, THIS JOURNAL, **54**, 2676 (1932).

graphically in Fig. 7. The concentrations are in moles per 1000 g. of water, θ is the number of degrees lowering of freezing point, and g is the Bjerrum osmotic coefficient, $g = \theta/2 \lambda m$, where $\lambda = 1.858°$ and $g =$ van't Hoff's $i/2$ and Lewis and Randall's $l - j$.
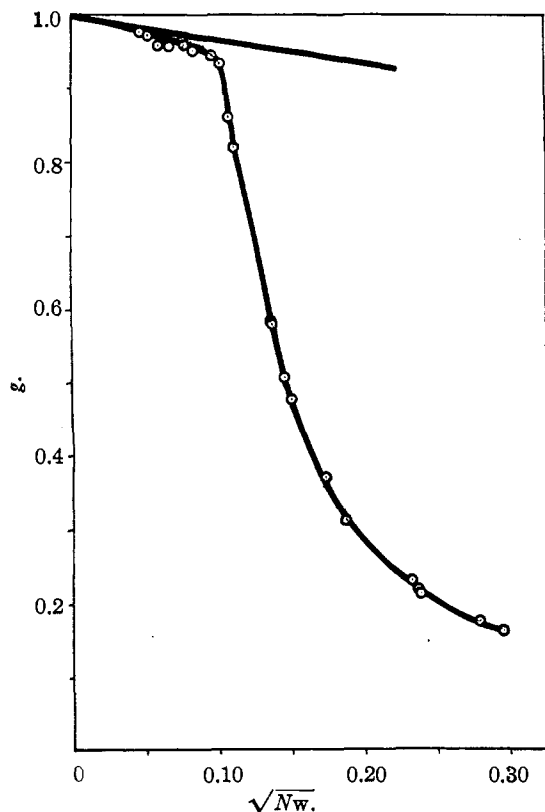

Fig. 7.

Attention may be called to the extremely steep drop in the values of g in the neighborhood of 0.02–0.03 N where the actual freezing point, $-\theta°$, is only just progressively lowered by increase in concentration. In other words, these dilute solutions are almost on the verge of separating into a heterogeneous mixture of two solutions both dilute and within this range. The requirement that θ should increase continuously with concentration to prevent such separation is paralleled by the requirement that $g/N + \mathrm{d}g/\mathrm{d}N$ must be positive where N is the mole fraction of the solute.

Discussion

The salient features of the data are, first, the regularity within the homologous series showing a gradual transition from typical fully dissociated electrolytes in the lowest members to well characterized colloidal electrolytes in the higher mem-
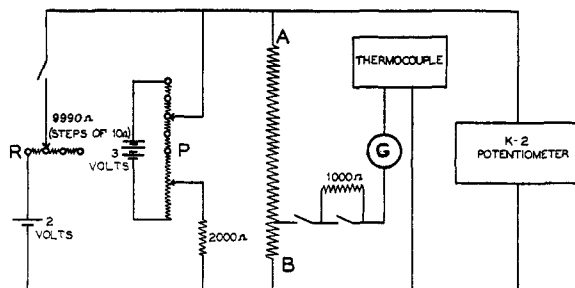

Fig. 8.

bers. In the latter there is the region in extreme dilution corresponding approximately to the Debye–Hückel–Onsager behavior followed by the region of concentration in which conductivity and lowering of freezing point fall to a fraction of their former values, and then after a minimum the third characteristic region where equivalent conductivity and molar lowering definitely increase with increasing concentration.

The transition from the first to the second region occurs over a very appreciable range of moderately concentrated solutions for heptyl- and nonylsulfonic acids, the transition being very gradual. This transition zone is commonly called the critical concentration for micelles. We believe, as is indeed evident from a comparison with freezing point lowering, that even in the solutions of greater dilution there is at least some ionic micelle that enhances the conductivity. After the transition zone or critical concentration, the much larger micelles of low conductivity like ordinary colloidal particles, which McBain called "neutral colloid," are formed so rapidly that they destroy much of the conductivity and freezing point lowering, in spite of any relatively small increase of highly conducting or ionic micelles. However, after the minimum, the effects due to the latter gain the upper hand by their steady increase, and the conductivity rises again.

Summary

1. Conductivity measurements are presented for the homologous series of straight chain sulfonic acids from two to fourteen carbon atoms, together with data for density and refractive index. The data show the gradual transition from the behavior of fully dissociated electrolytes for the lowest homologs through the intermediate members in higher concentration to the typical behavior of colloidal electrolytes for the higher homologs. The latter approximate to complete

dissociation in extreme dilution, then rather suddenly lose much of their conductivity through association of ion-pairs and ions to form colloidal particles of low conductivity, but after a well-defined minimum in moderately dilute solution, regain some of their conductivity through increasing formation of better conducting or ionic micelles.

2. This interpretation is in agreement with exact freezing point and diffusion data for dodecylsulfonic acid.

# Naphthoquinones of the Vitamin K₁ Type of Structure[1]

By Louis F. Fieser, William P. Campbell, Edward M. Fry[2] and Marshall D. Gates, Jr.

The synthesis of various allyl derivatives of α-naphthoquinone[3,4] by utilization of the Claisen rearrangement reaction was undertaken to provide model substances of the structural types postulated for vitamins K₁ and K₂. It was recognized that methods involving use of this reaction probably would not be applicable to the synthesis of the vitamins themselves, and the present paper reports attempts to develop methods suitable for accomplishing this second objective.

One scheme tried without success consisted in the attempted addition of a Grignard reagent to a naphthoquinone oxide. The reaction between allylmagnesium bromide and 2,6-dimethyl-1,4-naphthoquinone oxide (I) was studied because addition in the desired direction would lead to 2,6-dimethyl-3-allyl-1,4-naphthoquinone,[3] which was already characterized. The chief product isolated, however, proved to be the bromohydrin II, the structure following from the analysis of the colorless product and from its conversion to

a yellow bromodimethylnaphthoquinone of the composition of III. That cleavage of the oxide ring is due, as in comparable cases,[5] to interaction of the oxide with magnesium bromide present in the Grignard solution was established by the observation that the bromohydrin can be obtained in 73% yield from the oxide and magnesium bromide in ether. On attempted coupling of the MgBr derivative of II with allylmagnesium bromide there was isolated a small amount of the oxide, indicating that the cleavage reaction is reversible. When 2-methyl-1,4-naphthoquinone oxide was treated with methylmagnesium chloride and the oily product refluxed with alcoholic hydrochloric acid, a colorless substance resulted which appears to be formed by the addition of the elements of methane and of hydrogen chloride. The investigation was not pursued beyond these unpromising observations. A useful outcome of the brief study is the development of a method of preparing 1,4-naphthoquinone oxides which is much more convenient than Zincke's[6] hypochlorite procedure.

A few trials were made of the method of introducing a β-unsaturated group by direct C-alkylation of a phenolic salt, and it was observed that a small amount of 2-methyl-3-benzyl-1,4-naphthoquinone can be isolated from the very dark mixture produced by refluxing of 2-methyl-1,4-naphthohydroquinone with benzyl bromide and potassium carbonate in acetone. When the reaction was conducted at room temperature with two equivalents of benzyl bromide the mixture remained light in color and the sole crystalline product was methylnaphthohydroquinone dibenzyl ether (73% yield). With one equivalent

I   II   III
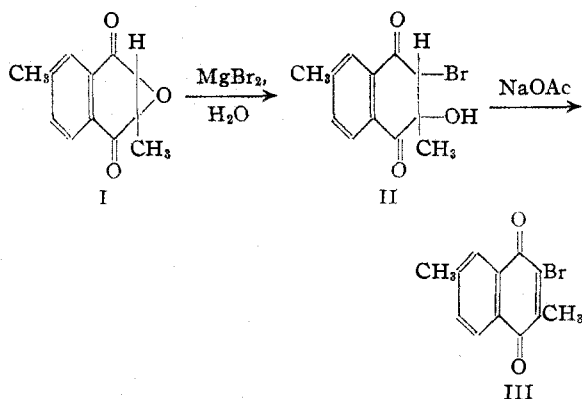
(1) For a preliminary account of a part of this work see Fieser, Campbell, Fry and Gates, This Journal, 61, 2559 (1939).

(2) Du Pont Research Fellow.

(3) Fieser, Campbell and Fry, This Journal, 61, 2206 (1939).

(4) Fieser, Bowen, Campbell, M. Fieser, Fry, Jones, Riegel, Schweitzer and Smith, ibid., 61, 1925 (1939).

(5) Gilman, "Organic Chemistry," Vol. I, John Wiley and Sons, Inc., New York, N. Y., pp. 428–429, 1938.

(6) Zincke, Ber., 25, 3602 (1892).