rect can be established only by calorimetric measurement. It should be noted that Hildebrand and Ruhle[7] mention that W. C. Bray has suggested an alternative to complete dissociation which would equally well explain the observed effects.

Summary

The melting points of barium hydroxide and of solutions of barium carbonate, barium chloride, barium bromide and sodium hydroxide in fused barium hydroxide have been measured by the cooling curve method.

The observed m. p. of barium hydroxide was 408 ± 1°, and its heat of fusion calculated as 3400 ± 100 cal. per mole.

The observed freezing point lowerings are consistent with complete dissociation with ion activities proportional to their mole fractions.

State College, Pa. Received April 9, 1945

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[7] Hildebrand and Ruhle, This Journal, 49, 728 (1927).

[Contribution from the Department of Chemistry, Stanford University]

An Equation for the Conductance of Colloidal Electrolytes in the Region of the Minimum

By Emanuel Gonick

The equivalent conductivity curves of uni-univalent colloidal electrolytes typically pass through three regions: (1) the very dilute region in which the conductivity decreases with increasing concentration at a rate similar to that of ordinary strong uni-univalent electrolytes, (2) a region at intermediate concentration in which the conductivity drops abruptly, as the simple ions aggregate to colloidal particles, and (3) a region in which the conductivity definitely increases with concentration. It is with the portion of the conductivity curve about the minimum between regions (2) and (3) that this paper is concerned.

This minimum suggests a relation of the form: $\Lambda = A/f(\mathrm{C}) + Bg(\mathrm{C})$, where A and B are constants and $f(\mathrm{C})$ and $g(\mathrm{C})$ represent functions of concentration. It is now found, in fact, that nearly all colloidal electrolytes for which data are available obey the equation

$$\Lambda = A/\sqrt{C} + B\sqrt{C} \qquad (1)$$

in the region under discussion. The only exceptions so far found are the long chain substituted ammonium acetates (Fig. 2).

Multiplication of equation (1) by $\sqrt{C}$ gives

$$\Lambda\sqrt{C} = A + BC \qquad (2)$$

A plot of $\Lambda\sqrt{C}$ *vs.* C should be linear with slope B and intercept A, if equation (1) holds. Figure 1 shows such plots for a number of sodium and potassium salts. Figure 2 shows similar plots for several long-chain substituted ammonium chlorides. Undecyl, lauryl, and myristyl sulfonic acids at 25° are shown in Fig. 3. Some of the conductivities published for these acids appear to be definitely in error, as they cannot be fitted to the same conductivity *vs.* concentration curve with the other data. These points have been designated by ● on Fig. 3, but have been ignored in drawing the curves. The short bars drawn across the plots at right angles indicate the concentration, $C_{\mathrm{min.}}$, at which the conductivity minimum occurs. It should be emphasized that equation (1) applies only to the concentration range about the minimum, where the colloidal

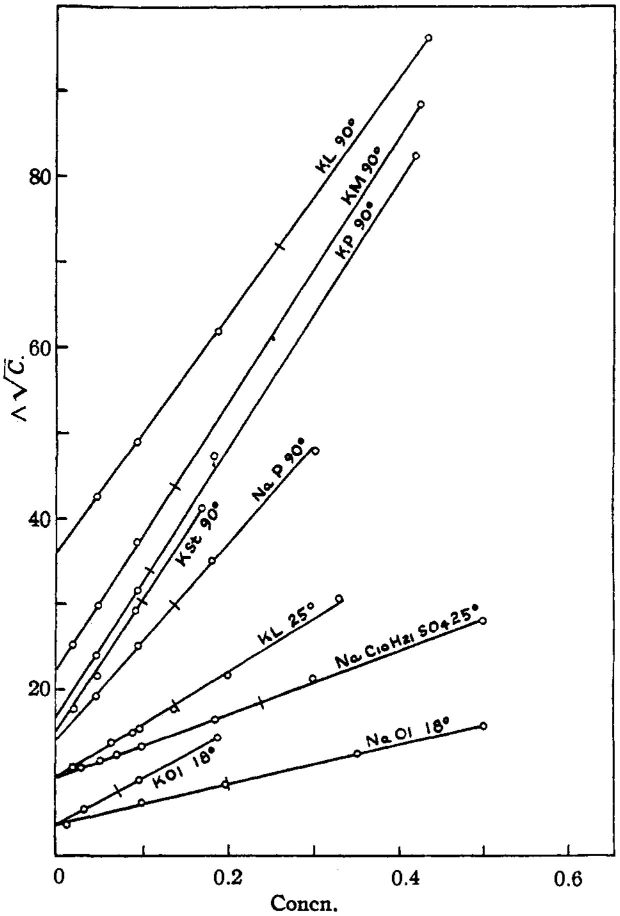

Fig. 1.—Plot of equation (2) for sodium and potassium salts of long-chain fatty acids.

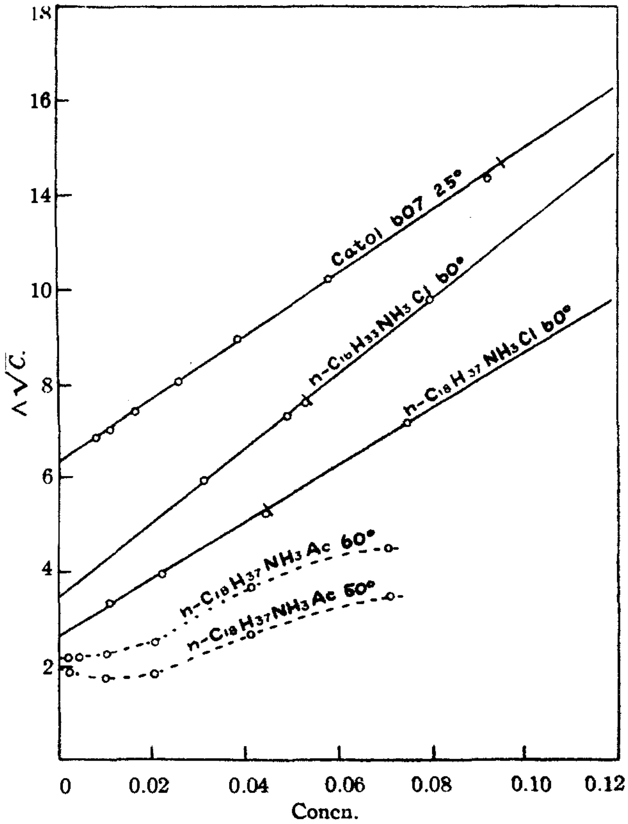

Fig. 2.—Plot of equation (2) for hexadecyl- and octadecylammonium chlorides and Catol 607 (N-(lauryl-colaminoformyl-methyl)-pyridinium chloride). Octadecylammonium acetate is given for comparison.

electrolyte is largely or entirely in colloidal form, and does not extend back into the dilute region below the critical concentration.[1]

If equation (1) is differentiated with respect to concentration and the derivative set equal to zero, we have

$$\frac{d\Lambda}{dC} = -AC^{-3/2} + BC^{-1/2} = 0$$

$$A = B \times C_{\text{min.}} \qquad (3)$$

Table I shows the close agreement between the values A and $B \times C_{\text{min.}}$. $C_{\text{min.}}$ was found by plotting conductivity *vs.* concentration on an expanded scale.

A comparison of the plots for the fatty acid salts (Fig. 1) discloses some interesting relations.

TABLE I

APPLICATION OF THE EQUATION $\Lambda = A/\sqrt{C} + B\sqrt{C}$ TO PUBLISHED CONDUCTIVITY DATA FOR COLLOIDAL ELECTROLYES (CONCENTRATIONS C ARE IN VOLUME NORMALITY)

Compound	$C_{\text{min.}}$	B	A	$BC_{\text{min.}}$
Pot. laurate[a] 90°	0.26	138	36	35.9
Pot. myristate[a] 90°	.14	155	22.4	21.7
Pot. palmitate[a] 90°	.11	155	17	17.1
Pot. stearate[a] 90°	.10	154	15	15.4
Sod. palmitate[b] 90°	.14	114	14	16
Pot. laurate[c] 25°	.14	61	9.5	8.6
Sod. decyl-sulfate[d] 25°	.24	37.5	9.5	9.0
Pot. oleate[e] 18°	.073	55	4.0	3.9
Sod. oleate[e] 18°	.20	22	4.4	4.4
Catol 607[c] 25°	.10	67.3	6.27	6.73
n-$C_{18}H_{37}NH_3Cl$[f] at 60°	.045	58	2.8	2.6
n-$C_{16}H_{33}NH_3Cl$[g] at 60°	.053	78.3	3.95	4.15
n-$C_{14}H_{29}NH_3Cl$[g] at 60°	.16	64	10.7	10.55
n-$C_{12}H_{25}NH_3Cl$[f] at 60°	.062	43.8	26.3	27.1
n-$C_{12}H_{25}NH_3Cl$[f] at 25°	.5	21.4	10	10.7
Undecyl sulfonic acid[h] 25°	.16	215	33.2	34
Layryl sulfonic acid[h] 25°	.15	209	24	24
Myristyl sulfonic acid[h] 25°	.09	200	16	18

[a] Bunbury and Martin, *J. Chem. Soc.*, 105, 417 (1914).

[b] McBain and Taylor, *Z. physik. Chem.*, [2] 26, 179 (1911).

[c] A. P. Brady, Ph.D. Thesis, Stanford University, 1944.

[d] Haffner, Piccione and Rosenblum, *J. Phys. Chem.*, 46, 662 (1942).

[e] McBain, Laing and Titley, *J. Chem. Soc.*, 115, 1283 (1919).

[f] Ralston and Hoerr, THIS JOURNAL, 64, 97 (1942).

[g] Ralston and Hoerr, *ibid.*, 64, 772 (1942).

[h] McBain and Betz, *ibid.*, 57, 1905 (1935).

(1) The slope, B, at a given temperature appears to depend on the cation only. The various potassium soaps at 90° have substantially the same slopes. For potassium stearate, potassium palmitate and potassium myristate the slopes are practically identical at 155, 155, and 154, respectively. If allowance is made for the difference in temperature, the same situation is found to hold for potassium laurate and potassium oleate at ordinary temperatures, a slope of 61 being found for the laurate at 25° and 55 for the oleate at 18°, the somewhat higher value for the laurate corresponding to the higher temperature.

(2) The intercept, A, depends mainly on the anion. Thus, sodium oleate and potassium oleate at room temperature have substantially the same intercepts of 4.4 and 4.0, respectively. Sodium palmitate and potassium palmitate, both at 90°, have intercepts of 14 and 17, respectively. The smaller the anion (hence the more mobile), the higher the value of A. Thus, the values at 90° for potassium stearate, palmitate, myristate, and laurate with 18, 16, 14, and 12 carbons, respectively, increase in the order listed. The same

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(1) At higher concentrations, the conductivity passes through a maximum and begins to fall off again. A second minimum is reported for potassium laurate at 90° at 0.68 N_v (by interpolation). The data for this region also give a straight line when plotted according to equation (2), with A = 59.5, B = 85, and $A \times B$ = 57.8. Aerosol OT (Haffner, Piccione and Rosenblum, *J. Phys. Chem.*, 46, 662 (1942)) also shows two distinct regions: between 0.005057 N and 0.01618 N, A = 3.8 and B = 228; from 0.02023 N to 0.03236 N, A = 6 and B = 100. There are no minima in the conductance curve, but the calculated minimum for the lower portion is 0.01667 N, the point at which the two portions intersect; while the calculated minimum for the higher portion is 0.06 N, beyond the range of the measurements.

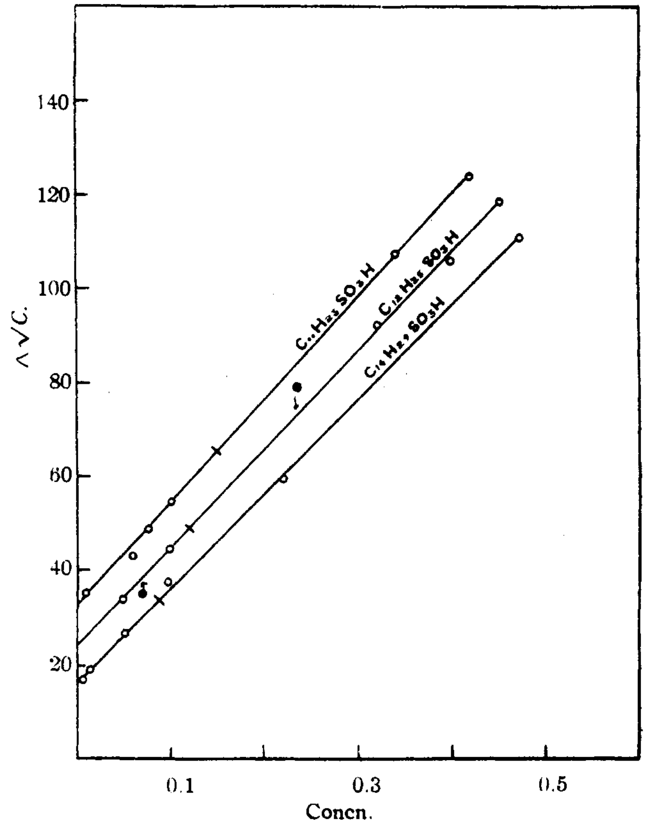

Fig. 3.—Plot of equation (2) for undecyl, lauryl, and myristic sulfonic acids (all at 25°).

holds true for potassium oleate and laurate at room temperature.

(3) The values of both A and B increase with temperature, as does $C_{\text{min.}}$. The regularities set forth in the foregoing paragraphs are further illustrated by the data for sodium myristate[2] at 90, 80, 70, 60, 50 and 40°.

(4) The position of the minimum in the conductivity–concentration curve is determined by the mobilities of the cation and anion, respectively, but in opposite sense. The greater the mobility of the *cation*, the *lower* is $C_{\text{min.}}$ (compare sodium and potassium oleate at room temperature, or sodium and potassium palmitate at 90°). On the other hand, increasing the mobility of the *anion* shifts $C_{\text{min.}}$ to *higher* concentrations, as shown by the plots for the potassium soaps at 90°. These relations necessarily follow from equation (3), which can be put in the form $C_{\text{min.}} = A/B$.

From the foregoing it is evident that the equivalent conductivity of these colloidal electrolytes may be represented as the superposition of two parts, one of which varies inversely and the other directly as the square root of concentration. This is schematically represented in Fig. 4, where the term $A/\sqrt{C}$ for two different anions (or alternatively, the same anion at two different temperatures) is represented by the rectangular hyperbolas, and the term $B\sqrt{C}$ is represented for two different cations (or alternatively, the same cation at two different temperatures) by the straight lines. Division of equation (3) by $\sqrt{C_{\text{min.}}}$, yielding

$$A/\sqrt{C_{\text{min.}}} = B\sqrt{C_{\text{min.}}} \qquad (4)$$

shows that the contributions of the two parts are equal at the minimum, as is also evident from Fig. 4, in which the intersections determine $C_{\text{min.}}$.

Of interest in this connection is an unpublished observation made by A. P. Brady[3] formerly at this Laboratory. The concentration of osmotically active particles can be calculated from the freezing point depression, and a theoretical maximum conductivity of the solution can be calculated by assigning to all the osmotically active particles a mobility equal to that of the fastest simple ion into which the compound dissociates. Brady found that at the concentration corresponding to the conductivity minimum, the conductivity so calculated is actually considerably less than the observed value. This points to the presence in the solution of other (colloidal) conductors of considerably greater mobility than the fastest simple ion. He made the further surprising observation, moreover, that the ratio of observed to calculated conductivity is substantially constant at 1.25 to 1.30

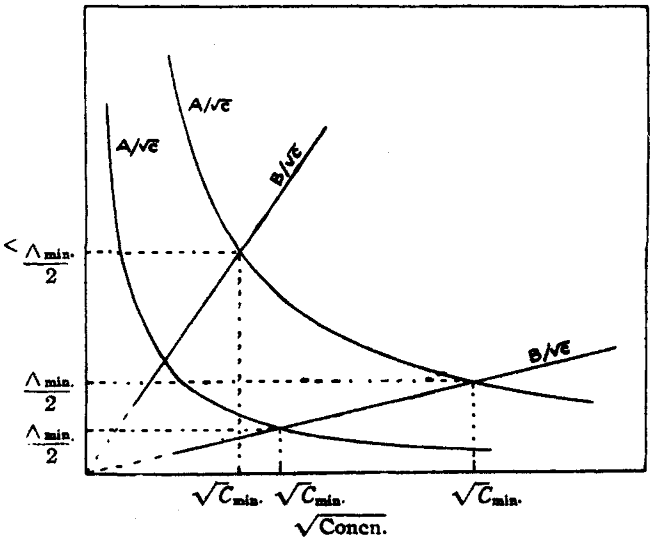

Fig. 4.—Schematic representation of equation (1), showing dependence of $C_{\text{min.}}$ on mobility of anion and cation or, alternatively, on temperature. The upper curves represent the faster ions, or, alternatively, the higher temperature.

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[2] McBain, Cornish and Bowden, *Trans. Chem. Soc.* (London), 101, 2051 (1912); Table VII, mislabelled as laurate.

[3] Present address: American Cyanamid Company, Stamford, Conn.

for all colloidal electrolytes tested, whether the fastest ion is the relatively slow sodium or the highly mobile hydrogen ion. It is as though the mobility of the colloid adjusted itself to that of the gegen ion. Reference to Fig. 4 shows a qualitative parallel between the observations made here and Brady's observations. The steeper of the two straight lines, corresponding to the more mobile of two cations, intercepts the hyperbolas at a higher point, the point of intersection determining the contribution of the "hyperbolic" part to the total conductivity. If the "hyperbolic" part corresponds to conducting micelles, the latter automatically adjust their contribution to the mobility of the gegen ion as a necessary consequence of equation (1).

TABLE II

COMPARISON OF CALCULATED THEORETICAL MAXIMUM AND OBSERVED CONDUCTIVITY AT THE $C_{\text{min.}}$ (BRADY)

Substance	$\alpha_{\text{calcd.}} = \Lambda_{\text{calcd.}}/\Lambda_0$	$\alpha_{\text{obs.}} = \Lambda_{\text{obs.}}/\Lambda_0$	$\alpha_{\text{obs.}}/\alpha_{\text{calcd.}} = \Lambda_{\text{obs.}}/\Lambda_{\text{calcd.}}$
Lauryl sulfonic acid	0.317	0.390	1.24
Catol 607	.287	.371	1.29
Potassium laurate	.389	.507	1.30

Since the specific conductivity, L, being based on a fixed volume of solution, directly reflects changes of concentration and mobility of the conducting species present in the solution, it is worth noting that from equation (1) one gets

$$\Lambda C = 1000L = AC^{1/2} + BC^{3/2} \qquad (5)$$

Thus colloidal electrolytes in the region under discussion behave as though the conductivity were due to two ionic species, the mobility–concentration product of one of which is increasing with the square root and that of the other as the three-halves power of the solute concentration.

Our present knowledge of colloidal electrolytes does not permit an interpretation of these facts in terms of chemical equations consistent with all available data. Therefore, for the present, it is safer to regard this as purely formal analysis, which, however, must have a physical basis.

Acknowledgment.—The author wishes to express his sincere thanks to Professor J. W. McBain for his valuable assistance and suggestions in the preparation of this manuscript.

Summary

1. The equivalent conductivity of the majority of colloidal electrolytes, in the region of the conductivity minimum, has been shown to follow the law: $\Lambda = A/\sqrt{C} + B\sqrt{C}$, where A and B are constants depending primarily upon anion and cation, respectively.

2. The minimum in the conductivity curve occurs at a concentration equal to A/B.

3. The two parts of the equivalent conductivity, $A/\sqrt{C}$ and $B\sqrt{C}$, are equal when the conductivity is at its minimum.

STANFORD UNIVERSITY, CALIFORNIA

RECEIVED MARCH 5, 1945

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

The Synthesis and Directed Chlorination of 2,2-Difluorobutane

BY ALBERT L. HENNE AND JAMES B. HINKAMP

The chlorination of $CF_3CH_2CH_3$, $CH_3CF_2CH_3$, and $CH_3CFClCH_2Cl$ is known to be strongly directed.[1] To determine how far and in what direction the effect of a CF_2 group would extend, $CH_3CF_2CH_2CH_3$ was synthesized and chlorinated.

The difluoromethane was obtained by hydrofluorination of $CH\equiv CCH_2CH_3$,[2,3] and also by the action of hydrogen fluoride upon $CH_3CCl{=}CHCH_3$,[3,4] $CH_2{=}CClCH_2CH_3$ and $CH_3CFClCH_2CH_3$. Since large amounts of reagents were handled, the experimental procedures were modified as follows, for the protection of the operator.

A five-liter, three-necked steel cylinder was fitted with a copper Dry Ice reflux condenser, a stirrer, and a copper inlet tube reaching the bottom. A quantity of commercial 70% $CH_3CCl{=}CHCH_3$ corresponding to 22 moles of the pure compound was placed in the cylinder, and a stream of hydrogen fluoride was led through it. The reaction started at once, and as soon as it was well under way a large ice-bath was placed around the vessel. The reaction was conducted as fast as the capacity of the reflux condenser would allow. The hydrogen chloride discharged from the top of the condenser was absorbed in water. After feeding about one hundred moles of hydrogen fluoride (slightly more than twice the amount needed) the reaction mixture was stirred for two hours at room temperature. The reflux condenser was replaced by a scrubber containing continuously changed hot water, attached to an ice-cooled receiver. The steel vessel was progressively heated to 90° to boil off the reaction products. After washing, drying and fractionally distilling, the distillate gave 11.3 moles (1062 g. or 51.3% yield) of pure $CH_3CF_2CH_2CH_3$ and about 8% of intermediate $CH_3CFClCH_2CH_3$ from which more difluoride was obtained by subjecting to a

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(1) (a) Henne and Whaley, THIS JOURNAL, **64**, 1157 (1942); (b) Henne and Renoll, *ibid.*, **59**, 2434 (1937); (c) Henne and Haeckl, *ibid.*, **63**, 2692 (1941).

(2) (a) Henne and Plueddemann, *ibid.*, **65**, 587 (1943); (b) Grosse and Linn, *ibid.*, **64**, 2289 (1942).

(3) Henne and Plueddemann, *ibid.*, **65**, 1271 (1943).

(4) Renoll, *ibid.*, **64**, 1115 (1942).