Both indicators were also studied in acetate-acetic acid buffers. The results are summarized in Table III and Figs. 3 and 4.

From Figs. 3 and 4 the ratios of the thermodynamic dissociation constants of chlor phenol blue and iodo phenol blue to that of acetic acid are 2.05 and 3.5, respectively. The thermodynamic dissociation constant of acetic acid is 1.75×10^{-5},[4] which yields 3.6×10^{-5} for chlor phenol blue and 6.1×10^{-5} for iodo phenol blue. These values are to be compared with 3.8×10^{-5} and 6.7×10^{-5} from the benzoate buffers. The average values of the thermodynamic dissociation constants increase in the order chlor phenol blue 3.7×10^{-5}, brom phenol blue 6.0×10^{-5} and iodo phenol blue 6.4×10^{-5}.

Summary

The thermodynamic dissociation constants of chlor phenol blue and iodo phenol blue have been determined.

PHILADELPHIA, PENNA. RECEIVED JUNE 21, 1937

[4] Harned and Owen, THIS JOURNAL, **52**, 5079 (1930); MacInnes and Shedlovsky, *ibid.*, **54**, 1429 (1932).

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

The Conductance of Mixtures of Strong Electrolytes[1]

BY K. A. KRIEGER AND MARTIN KILPATRICK

Of the two effects which tend to diminish the velocity of an ion in solution, only one, the field effect or relaxation effect, will have a different value in a mixture of salts than it would have in a pure salt. According to Onsager and Fuoss[2] the decrease $\Delta\overline{X}_j$ in the external electric field $\overline{X}$ acting upon a j ion in a mixture of ions is

$$\frac{\Delta\overline{X}_j}{\overline{X}} = -\frac{\epsilon^3}{3}\sqrt{\frac{N\pi}{250k^3}}\Big/\frac{\Gamma^{1/2}}{(DT)^{3/2}} z_j' \, (I - H^{1/2})_{j\sigma} \, r_\sigma \qquad (1)$$

where[3] $\Gamma = n_\sigma e_\sigma^2$

ϵ is the unit of electrostatic charge

N is Avogadro's number

z_j' is the valence of the jth ion and z_j is its absolute magnitude

I is the unit or identical matrix

H is a matrix with elements

$$h_{ji} = \mu_\sigma \omega_{\sigma j} \delta_{ji} + \mu_i \omega_{ij}$$

r is a vector with elements

$$r_i = z_i' - \frac{z_\tau \mu_\tau}{\mu_\pi z_\pi} \cdot \frac{\Lambda^\circ{}_\pi z_i}{\Lambda^\circ{}_i}$$

μ_i is the ratio of the concentration of i ions to the total ion concentration

ω_i is the mobility of the ith ion and

$$\omega_{ij} = \omega_i/\omega_i + \omega_j$$

δ_{ji} is the Kronecker symbol:

$$\delta_{ji} = 0 \quad \text{if } j \neq i$$
$$\delta_{ji} = 1 \quad \text{if } j = i$$

Inspection of equation (1) shows that the decrease in velocity due to the field effect is not a function of the properties of the j ion alone, but is a function of the properties of all the ions in the solution.

Bray and Hunt[4] have measured the conductance of mixtures of sodium chloride and hydrochloric acid and Onsager has compared their results with those computed from equation (1). The agreement between observed and calculated values is good at low concentrations, but at higher concentrations the observed mixture effect appears to be about half that calculated.

Due to the high mobility of the hydrogen ion, the mixture effect in an acid-salt mixture is much larger than in a salt-salt mixture and in this respect an acid-salt mixture is more suitable for such measurements. The advantage that might be gained in this way is, however, offset by the fact that measurements of conductance of acids in dilute solution are relatively inaccurate for two reasons. First, it is impossible to make correction for the conductance of the solvent, and, second, small amounts of impurities will often produce changes in conductance large enough to mask entirely an effect as small as the mixture effect. For these reasons it was thought advisable to measure the conductance of a mixture of salts, rather than that of a salt-acid mixture.

A detailed description of the method of computation of the mixture effect will be reserved for a later section.

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[1] Abstracted from the dissertation of K. A. Krieger submitted in April, 1937, to the Graduate School of the University of Pennsylvania in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Onsager and Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

[3] Throughout this paper Greek letters used as subscripts will indicate summation.

[4] Bray and Hunt, THIS JOURNAL, **33**, 781 (1911).

Experimental Part

Alternating Current Bridge.—The alternating current bridge and associated apparatus already has been described by Brockman and Kilpatrick[5] and, in fact, was identical with that used by them, with the exception of the amplifier. A more sensitive amplifier consisting of three resistance coupled stages was used.

Temperature Control.—The cell containing the solution, the resistance of which was to be measured, was immersed in an oil thermostat, whose temperature could be maintained at 25 ± 0.002°. The temperature was determined by means of a Beckmann thermometer checked against a platinum resistance thermometer calibrated by the Bureau of Standards.

Cell.—The cell used in all measurements was a Pyrex cell with a Jena glass side arm after the design of Shedlovsky.[6] The cell constant was determined with a 0.01-demal solution of potassium chloride, containing 0.745263 g. of potassium chloride in 1 kg. of water (weights reduced to vacuum) whose specific conductance, according to Jones and Bradshaw,[7] is 0.00140877 ohm^{-1} cm.$^{-1}$ at 25°. On the basis of these data the cell constant was found to be 14.5480 ± 0.0003. The platinum electrodes of this cell were platinized lightly, according to the directions suggested by Jones and Bollinger.[8] Frequent tests for polarization by measuring the conductance at different frequencies (1050 and 2730 cycles) showed that polarization was negligible.

Conductivity Water.—Pure water was prepared by redistillation from alkaline permanganate in a Barnstead electrically heated still similar to that described by Kraus and Dexter.[9] The conductivity of the water was between 8×10^{-7} and 1.5×10^{-7} ohm^{-1} cm.$^{-1}$.

Procedure.—The procedure followed that described by Shedlovsky[6] except that all solutions were made up by the dilution of more concentrated solutions contained in weight burets.

Purification of Compounds

Lithium Chloride.—Baker C. P. lithium chloride (400 g.) was dissolved in 400 cc. of distilled water. Lithium carbonate was precipitated from the warm solution by the addition of a solution of 550 g. of Baker C. P. ammonium carbonate. The precipitated carbonate was washed three times by decantation and finally filtered. (At this stage in the purification a flame test indicated the absence of sodium, although a similar test on the original sample showed sodium clearly.) The carbonate was sucked as dry as possible on the filter and made into a paste with about 300 cc. of conductivity water. Pure hydrogen chloride evolved by the gentle heating of Baker C. P. hydrochloric acid was distilled into the paste through an all glass apparatus. During the distillation the paste was stirred and kept near the boiling point. The resulting solution (which of course contained some ammonium chloride and hydrochloric acid) was evaporated until lithium chloride was about to crystallize and then cooled rapidly in ice. The crystallized lithium chloride was filtered with suction, made into a paste with a few cc. of conductivity water and again sucked dry. The lithium chloride so obtained was twice recrystallized from conductivity water. Since the loss by this method is very large the mother liquors from the recrystallizations were concentrated by evaporation and a second crop obtained. This second crop was likewise twice recrystallized from conductivity water. Both crops of lithium chloride were examined for impurities by means of photographs of the spark spectrum taken with panchromatic plates in a quartz spectrograph. The electrodes were of pure silver and the cell used for the solutions to be examined was of the kind described by Lucian.[10,11] No other metals were found. The pure lithium chloride was dried *in vacuo* over calcium chloride. Considerable difficulty was encountered in connection with fusion of lithium chloride because at first the fused salt persistently attacked the platinum boat[12] in which the fusions were made. It was found that this difficulty could be eliminated if the nitrogen used during fusion (as an inert atmosphere) were freed of traces of oxygen by passing it over reduced copper at about 800°.

The technique finally evolved consisted in heating the lithium chloride for about an hour at 100–150° in a vacuum in a Richards[13] bottling apparatus, breaking the vacuum with nitrogen and slowly raising the temperature while the salt was surrounded by an atmosphere of nitrogen containing a little hydrogen chloride. When all the ammonium chloride had been driven off, the atmosphere was replaced by one of pure dry hydrogen chloride and the fusion carried out in a slow stream of the latter gas. The fused salt was cooled in an atmosphere of dry hydrogen chloride, and finally the system was evacuated and the hydrogen chloride replaced by dry nitrogen. The salt so prepared was found to be colorless and neutral.

Potassium Chloride.—The potassium chloride was part of the sample prepared and used by Brockman and Kilpatrick.[5] It was tested spectroscopically and found to be pure except for a possible trace of sodium. It was fused in a current of pure nitrogen in the Richards apparatus.

Densities.—Since the salt solutions were made up by weight and the concentrations used in the theory are on a volume basis (molarity and ionic strength) it was necessary to know the density of the solutions. It was found that the density of the lithium chloride solutions was a linear function of the concentration up to the highest concentration used, and obeyed the equation

$$d = 0.99707 + 0.00585C_{\mathrm{LiCl}}$$

where d is the density of a solution of C_{LiCl} per cent. concentration in lithium chloride and

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(5) Brockman and Kilpatrick, THIS JOURNAL, **56**, 1483 (1934).

(6) Shedlovsky, *ibid.*, **54**, 1411 (1932).

(7) Jones and Bradshaw, *ibid.*, **55**, 1780 (1933).

(8) Jones and Bollinger, *ibid.*, **57**, 272 (1935).

(9) Kraus and Dexter, *ibid.*, **44**, 2469 (1922).

(10) The authors wish to acknowledge the kind assistance and advice of Dr. Lucian and Mr. Bancroft of Randall Morgan Laboratory of Physics in connection with the spectrographic examination of lithium and potassium chlorides.

(11) Lucian, unpublished work.

(12) When this occurred the lithium chloride would appear dark after the fusion and upon solution in water left a residue of small metallic plates almost crystalline in appearance. Metallic platinum was suspected and its presence confirmed by a microanalysis.

(13) Richards and Parker, *Proc. Am. Acad. Arts Sci.*, **32**, 59 (1896).

0.99707 is the density of pure water at 25°.[14] 0.00585 is a constant calculated from the density tables for lithium chloride[14] (p, 77). The mixture of lithium chloride and potassium chloride obeyed the equation

$$d = 0.99707 + 0.00585C_{\text{LiCl}} + 0.00635C_{\text{KCl}}$$

where d is the density of a solution of C_{LiCl} per cent. concentration in lithium chloride and C_{KCl} per cent. concentration in potassium chloride.

The values of the coefficients of C_{LiCl} and C_{KCl} were calculated from the densities given in the "International Critical Tables" and confirmed by the experimental determination of the density of the most concentrated mixture with a pycnometer of the type described by Shedlovsky.[15] The equation was found to be accurate within 0.01% up to 0.1 molar.

The Conductance of Lithium Chloride.—The conductance of lithium chloride has been measured by Hosking, Kohlrausch and Grotrian, Washburn and MacInnes,[16] and Shedlovsky[6] but the results are widely discrepant and only the measurements of Shedlovsky were believed to be reliable. The authors therefore measured the conductance of this salt and the results are given in Table I. In this table the concentrations are in gram equivalents per liter (weights reduced to vacuum). Λ_K obsd. is the observed value of the equivalent conductance as determined by the authors, Λ_S obsd. is the observed value of the equivalent conductance according to Shedlovsky, Λ_S calcd. is the value of the equivalent conductance as calculated from the equation given by Shedlovsky[17] and Λ_K calcd. is the value as calculated from the equation

$$114.97 = \frac{\Lambda + 59.79\sqrt{C}}{1 - 0.2274\sqrt{C}} - 94.6C \qquad (2)$$

determined by the application of the theory of least squares to the data recorded in the column headed Λ_K obsd. Figure 1 affords a comparison of Shedlovsky's data and those of this paper.

TABLE I

CONDUCTANCE OF LITHIUM CHLORIDE

	Concentration	Λ_K Obsd.	Λ_S Obsd.	Λ_S Calcd.	Λ_K Calcd.
b	0.000052613	114.40		114.38	114.35
b	.00011271	114.02		114.10	114.07
b	.00018787	113.79		113.84	113.81
b	.00034888	113.44		113.43	113.40
	.00047210		113.18	113.17	113.14
b	.00065987	112.73		112.85	112.82
a	.0012694	111.93		112.05	112.03
a	.0021683	111.11		111.15	111.14
	.0023455		111.04	111.04	111.03
b	.0030191	110.58		110.54	110.53
a	.0037533	110.05		110.07	110.06
	.0058866		108.91	108.92	108.92
a	.0068854	108.50		108.48	108.48
	.009836		107.33	107.34	107.36
a	.010151	107.31		107.22	107.25
c	.010185	107.25		107.22	107.25
	.0107786		107.03	107.01	107.04
c	.015021	105.88		105.76	105.81
a	.017111	105.36		105.23	105.30
c	.018067	105.14		105.00	105.07
	.018515		104.91	104.90	104.97
	.0199375		104.64	104.59	104.67
	.032581		102.34	102.27	102.41
d	.041239	101.30		101.05	101.24
d	.048113	100.48		100.23	100.44
	.049924		100.10	100.02	100.25
d	.055974	99.60		99.38	99.64
d	.063524	98.85		98.68	98.98
	.064021		98.70	98.62	98.92
	.10000		95.83	96.09	96.57

The specific conductance of the water used in each of the series above was as reported below:

a 8.6×10^{-7} ohm^{-1} cm.$^{-1}$
b 3.91×10^{-7} ohm^{-1} cm.$^{-1}$
c 3.53×10^{-7} ohm^{-1} cm.$^{-1}$
d 6.47×10^{-7} ohm^{-1} cm.$^{-1}$

Shedlovsky's data are based on the specific conductance of a 0.1 demal solution of potassium chloride as determined by Parker and Parker[18] while the data of Jones and Bradshaw[7] form the basis of this paper.

If Shedlovsky's equation (2b) is rewritten to conform to the data of Jones and Bradshaw, it becomes

$$115.02 = \frac{\Lambda + 59.79\sqrt{C}}{1 - 0.2274\sqrt{C}} - 90.7C \qquad (3)$$

which is in good agreement with our data between about 0.004 and 0.04 molar although the value

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(14) "International Critical Tables," Vol. III, p. 25.

(15) Shedlovsky, THIS JOURNAL, **56**, 1066 (1934).

(16) (a) Hosking, *Phil. Mag.*, **7**, 469 (1909); (b) Kohlrausch and Grotrian, *Ann. Physik*, **154**, 1, 215 (1875); (c) Washburn and MacInnes, THIS JOURNAL, **33**, 1686 (1911).

(17) It will be observed that the values in column Λ_S calcd. differ considerably from the values reported by Shedlovsky as calculated from his original equation

$$115.00 = \frac{\Lambda + 59.79\sqrt{C}}{1 - 0.2274\sqrt{C}} - 89.1C \qquad (2a)$$

Upon informing Dr. Shedlovsky of these discrepancies Dr. Shedlovsky recalculated his reported values and found that they were incorrect. The writers have also informed Dr. Shedlovsky that the application of the theory of least squares to his (Shedlovsky's) data does not yield equation (2a) but rather

$$114.99 = \frac{\Lambda + 59.79\sqrt{C}}{1 - 0.2274\sqrt{C}} - 90.7C \qquad (2b)$$

To this last communication Dr. Shedlovsky has not, at the present writing, replied.

(18) Parker and Parker, "International Critical Tables," Vol. VI, p. 230.

of the equivalent conductance at infinite dilution, 115.02, is probably too high.

The Conductance of Potassium Chloride.—Shedlovsky's values for the conductance of potassium chloride have been used in the calculation of the mixture effect. As noted under lithium chloride the equation has been rewritten on the basis of Jones and Bradshaw's values for the conductance of 0.1 demal potassium chloride. Thus corrected, Shedlovsky's equation becomes:

$$149.86 = \frac{\Lambda + 59.79\sqrt{C}}{1 - 0.2274\sqrt{C}} - 94.9C \qquad (4)$$

In order to be sure that Shedlovsky's data could be used for the conductance of potassium chloride, the conductances of three solutions of potassium chloride were measured and compared with the values calculated from equation (4). The results which follow agreed with Shedlovsky's equation within the experimental error.

Concentration	Λ obsd.	Λ calcd.
0.00045579	147.95	147.89
.0010146	147.06	146.97
.0025007	145.43	145.40

Conductance of Mixtures of Lithium and Potassium Chlorides. Method of Computation.—Equation (1), upon the substitution of numerical constants, becomes for aqueous solutions at 25°

$$\Delta\overline{X}_i/\overline{X} = -[0.5502\, z_j'(I - H^{1/2})_{j\sigma}r_\sigma]\Gamma^{1/2} \qquad (5)$$

and since

$$\frac{\Delta\overline{X}_i}{\overline{X}} = \frac{\Delta\Lambda_j}{\Lambda_j^\circ} \qquad (6)$$

we may write

$$\Delta\Lambda_j = -[0.5502\, z'\Lambda_j^\circ(I - H^{1/2})_{j\sigma}r_\sigma]\Gamma^{1/2} \qquad (7)$$

Equation (7) expresses the increase, $\Delta\Lambda_j$, due to the field effect, in the conductance of the jth ion in a mixture of finite total salt concentration $\Gamma/2$ over its conductance at infinite dilution. Now for either pure lithium chloride or pure potassium chloride $\Delta\Lambda_j$ is given by the expression

$$\Delta\Lambda_j = -0.1611\Lambda_j^\circ\Gamma^{1/2} \qquad (8)$$

according to Onsager.[19]

The difference between equations (7) and (8), which may be represented by the symbol $\Delta\Delta\Lambda_j$, is, therefore, the increase in conductance of the jth ion in a mixture over the conductance which it would have in either pure lithium chloride or pure potassium chloride. Thus

$$\Delta\Delta\Lambda_j = -[0.5502\, z_j'(I - H^{1/2})_{j\sigma}r_\sigma - 0.1611]\Lambda_j^\circ\Gamma^{1/2} \quad (9)$$

Since the tensor $(I - H^{1/2})$ is a function of μ_1, and Γ also appears in the expression, it is clear that unless either μ_1 or Γ is kept constant $\Delta\Delta\Lambda_j$ is a function of two independent variables. Experimentally it is not convenient to keep either μ_1 or Γ constant and both were in fact allowed to vary. The labor of computation, at best sufficiently burdensome, would, however, be almost intolerable if it were necessary to compute the elements of H corresponding to the particular value μ_1 for each of the nineteen mixtures studied. If both members of (9) be divided by $\Gamma^{1/2}$ the function

$$\frac{\Delta\Delta\Lambda_j}{\Gamma^{1/2}} = -[0.5502\, z_j'(I - H^{1/2})_{j\sigma}r_\sigma - 0.1611]\Lambda_j^\circ \quad (10)$$

becomes a function of μ_1, alone.

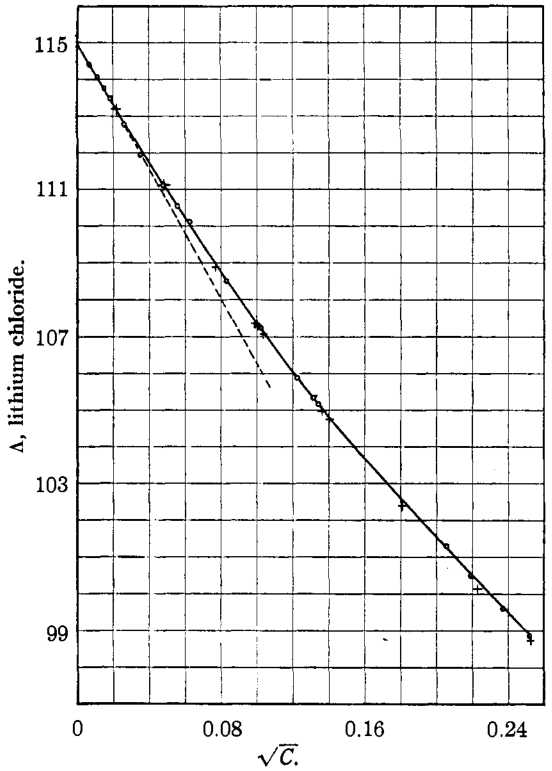

Fig. 1.—○, K. and K.; +, Shedlovsky; ---, Debye slope; width of circles 0.1%.

Accordingly, the values of the right member of (10) were calculated for $\mu_1 = 0$, $\mu_1 = 0.2$, $\mu_1 = 0.25$, $\mu_1 = 0.3$ and $\mu_1 = 0.5$ for each of the three ions involved and plotted against μ_1. The curves obtained are shown in Figs. 2 and 3 following. The actual plots (here much reduced in size) were sufficiently large to allow the values of $\Delta\Delta\Lambda_j/\Gamma^{1/2}$ to be read directly for any desired value of μ_1.

The other data essential to the calculation of the elements of the matrix H are given in Table II below.

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[19] Onsager, *Physik. Z.*, **27**, 388 (1926); **28**, 277 (1927).

TABLE II

Ion	j	$\Lambda_j^{\circ\,a}$	
Li	1	38.73	$\omega_{12} = 0.3451$
K	2	73.50	$\omega_{23} = .4907$
Cl	3	76.30	$\omega_{31} = .6633$

[a] The values of Λ_j° and ω_{ji} are computed from the conductance measurements of Shedlovsky,[6] the data of Table I and the transference numbers of Longsworth, THIS JOURNAL, **54**, 2741 (1932).

The theoretical increase in specific conductance for the whole mixture is given by the equation

$$1000\,\Delta C_{\text{sp.}} = \sum_{j=1}^{j=3} m_j\,\Delta\Delta\Lambda_j \qquad (11)$$

where $\Delta C_{\text{sp.}}$ is the theoretical increase in specific conductance due to the mixture effect; m_j is the concentration of the j ions in gram ions per liter. The right member of (11) obviously can be calculated from the plots of (10) by multiplying the term $\Delta\Delta\Lambda_j/\Gamma^{1/2}$ for each ion by m_j for that ion, summing for all ions (three in the present case), and multiplying the sum by $\Gamma^{1/2}$ for the mixture involved. This has been done in Table III and the results, divided by one thousand times the observed specific conductance and multiplied by 100 are reported in the last column under the heading $\Delta C_{\text{sp.}}$ (%) calcd.

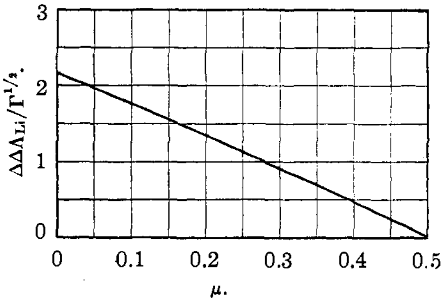

Fig. 2.

TABLE III

	Γ	μ_1	1000 $C_{\text{sp.}}$ Obsd.	$\Delta C_{\text{sp.}}$ (%) Obsd.	$\Delta C_{\text{sp.}}$ (%) Calcd.
b	0.0019650	0.26847	0.12621	+0.04	0.02
b	.0027141	.19404	.18064	.00	− .02
b	.0036447	.27253	.23176	− .05	− .03
a	.0051647	.30424	.32116	+ .03	− .03
b	.0061831	.15970	.41370	− .08	− .03
a	.0071920	.21774	.46593	.00	− .04
b	.0091018	.26999	.57026	− .08	− .05
a	.0099320	.29625	.61263	.00	− .05
a	.014681	.19881	.94590	− .03	− .05
c	.016563	.35075	.97812	− .01	− .06
a	.022184	.30239	1.3353	− .02	− .07
a	.030469	.21702	1.9030	− .03	− .08
c	.033039	.17224	2.1074	− .05	− .07
a	.041355	.29416	2.4477	− .03	− .10
c	.044354	.25880	2.6702	− .05	− .10
c	.051780	.21967	3.1662	− .05	− .11
c	.063780	.27525	3.7473	− .05	− .13
c	.087088	.19566	5.2749	− .05	− .13
c	.100401	.23984	5.8916	− .08	− .16

The specific conductance of the water used in each of the series above was as reported below.

a 3.46×10^{-7} ohm^{-1} cm.$^{-1}$
b 2.85×10^{-7} ohm^{-1} cm.$^{-1}$
c 1.64×10^{-7} ohm^{-1} cm.$^{-1}$

Now if there were no change in conductance due to the mixture effect, the conductance of a mixture m_1 molar in lithium chloride and m_2 molar in potassium chloride would be given by

$$1000\,C_{\text{sp.}} = m_1\Lambda_{\text{LiCl}} + m_2\Lambda_{\text{KCl}} \qquad (12)$$

where Λ_{LiCl} is the observed conductance of a solution of pure lithium chloride of molarity $(m_1 + m_2)$ and Λ_{KCl} is the observed conductance of a solution of pure potassium chloride of molarity $(m_1 + m_2)$. The values of $C_{\text{sp.}}$ for the mixtures studied have been computed from this equation with the help of equations (2) and (4) and the differences between these values and the observed values of the conductance of the mixtures, again expressed as percentage of the observed conductances, are reported in Table III under the heading $\Delta C_{\text{sp.}}$ % observed. An examination of Table III indicates that the calculated mixture effect leads to a correction of the proper magnitude and in the right direction. The writers believe that no significance is to be attached to the two mixtures which show corrections in the wrong direction because the experimental error at low concentration is comparatively large. (Note that Γ is *twice* the total salt molality.)

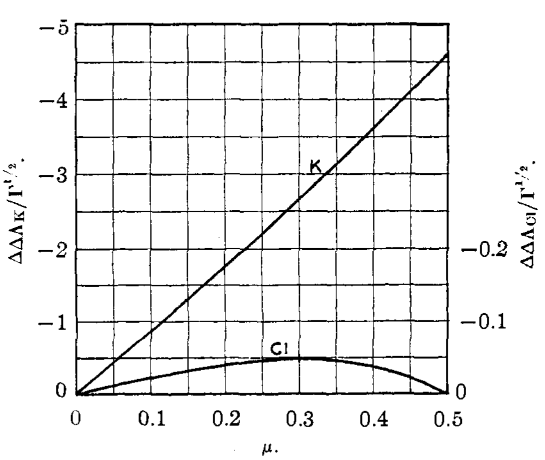

Fig. 3.

Experience with the same apparatus in the measurement of the conductance of lithium chloride indicates a probable average deviation of individual measurements of the order of 0.04%. These are, of course, arranged in a random manner as to sign so that it can be stated safely that the observed changes in conductance are not due to experimental error. The measured values of the changes in conductance appear to indicate that the observed $\Delta C_{\text{sp.}}$ is about half that calculated by Onsager and Fuoss at higher concentrations and tends to agree with them at lower concentrations. The same statement, it will be remembered, is made by Onsager and Fuoss in connection with the measurements of Bray and Hunt on mixtures of hydrogen chloride and sodium chloride.

The authors would like to make due acknowledgment of a research grant made to one of us (M. K.) by the Faculty Research Committee of the University.

Summary

The conductance of lithium chloride at 25° has been measured and compared with the values in the literature.

The conductances of nineteen mixtures of potassium chloride and lithium chloride have been measured and compared with the theoretical conductances.

PHILADELPHIA, PENNA. RECEIVED JULY 1, 1937

[CONTRIBUTION FROM THE BIOLOGICAL LABORATORIES, HARVARD UNIVERSITY]

Monomolecular Films of α-Aminostearic Acid, Stearic Acid, and Heptadecylamine

BY ELIOT F. PORTER

Monomolecular films of proteins have been studied by many investigators, including ourselves in unpublished work. Unfortunately, the results so far obtained have not added as much as was originally hoped to an understanding of the properties of these large dipolar ions (or zwitterions). In particular, as in the case of other compounds, estimates of the dipole moments based on the contact potentials associated with the films are of a smaller order of magnitude than those calculated from dielectric constant measurements.

In order to throw some light on this difficult problem it seemed desirable to study a simpler type of dipolar ion in a monomolecular film and to compare its behavior, both mechanical and electrical, with that of other related molecules lacking the dipolar ionic structure. Unfortunately the smaller and more familiar amino acids, which at first suggest themselves for the purpose, are too soluble to form monomolecular films on aqueous substrates. For this reason in the following study we have made use of α-aminostearic acid and for comparison of two closely related compounds without the dipolar ionic structure, namely, heptadecylamine and stearic acid. Although it has never been measured directly, there is every reason to believe the dipole moment of this amino acid to be the same as that of other α-amino acids, whose moments, estimated from dielectric constant studies, are found to be very nearly independent of the length of the hydrocarbon chain.[1]

So far as we know the measurements here reported for α-aminostearic acid are the only ones of their kind ever made on dipolar ions, except of course, for the complicated case of the proteins.[2] In the case of heptadecylamine some mechanical, but no electrical, measurements are on record.[3,4] A large number of studies, both mechanical and electrical, have of course been made on long chain fatty acids.

Materials and Solutions.—The aminostearic acid and heptadecylamine used in these experiments were synthesized for us by Dr. T. L. McMeekin of the Department of Physical Chemistry at the Harvard Medical School. The stearic acid was purchased from the Eastman Kodak Company.

The amino acid is insoluble in all common organic solvents with the exception of glacial acetic and formic acids, but uniform films could not be obtained by spreading from solutions in these solvents, partly, at least, because of their high specific gravity. A sufficiently concentrated solution was finally obtained in a mixture of methyl alcohol and diethyl ether by first converting the amino acid into the hydrochloride. The procedure used was to add to weighed samples in a 100-cc. volumetric

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[1] Wyman and McMeekin, THIS JOURNAL, **55**, 908 (1933).

[2] A preliminary note by van Ormondt [*J. Biol. Chem.*, **114**, lxxvii (1936)], which has just come to our attention, states that he is investigating the mechanical properties of films of certain lipopeptides.

[3] Lyons and Rideal, *Proc. Roy. Soc.* (London), **A124**, 333 (1929).

[4] Adam, *ibid.*, **126**, 526 (1930).