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THE DENSITIES, EQUIVALENT CONDUCTANCES AND RELATIVE VISCOSITIES AT 25°, OF SOLUTIONS OF HYDROCHLORIC ACID, POTASSIUM CHLORIDE AND SODIUM CHLORIDE, AND OF THEIR BINARY AND TERNARY MIXTURES OF CONSTANT CHLORIDE-ION-CONSTITUENT CONTENT

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The object of this investigation was to make a systematic study, over a wide range of concentration, of the conductances of solutions of pairs of uni-univalent electrolytes, having a common-ion constituent, with the hope of disclosing the nature of such solutions, and to test the value of the methods of calculating the conductances of solutions of such mixtures of electrolytes, that have been proposed by earlier workers in this field.

According to the original theory of electrolytic dissociation, the ratio of the equivalent conductance of a solution at any concentration to its equivalent conductance at infinite dilution is a measure of the degree of dissociation of the electrolyte present, provided that the viscosity of the solution does not differ appreciably from that of pure water. In solutions of greater viscosities, the frictional resistance to the motion of the ions may be appreciably different from that in very dilute solutions. The conductance ratio, therefore, cannot be an exact measure of the ionization. Later, with the assumption that the mobilities of the separate ions vary inversely with the viscosity, the conclusion was reached that the product of the measured equivalent conductance and the relative viscosity of a solution of an electrolyte to its equivalent conductance at infinite dilution afforded a truer measure of its degree of dissociation in that solution.

As a means of computing the concentration of ions present in a given solution, the conductance-viscosity ratio has lost much of its value. Researches in recent years have shown that the concentration-ionization product is not a measure of the quantity of ions present, in the sense of the ordinary mass-action law. But the property of viscosity is quite intimately related to the conduction of electricity by solutions of electrolytes, for such conduction is accompanied by transference of matter through the solutions. Therefore, a supplemental study of the relative viscosities of a number of solutions was made, with the desire of correlating, if possible, these two properties.

In all previous conductivity work, with the exception of that of Stearn,[1] the concentrations have been computed upon a volume basis. In certain respects it is more advantageous to employ the weight molal basis of reckoning concentration, that is, moles per thousand grams of water. In the present paper this method has been employed. For the computation of the equivalent conductances, accurate density measurements were required. These measurements were made with a pycnometer. With these density data the conductance and relative viscosity measurements of this investigation were compared with measurements of other investigators who employed volume concentrations, and were found to be in moderately satisfactory concordance.

The electrolytes chosen for study were hydrochloric acid, potassium chloride and sodium chloride, which show wide differences in the properties under investigation but which are typical uni-univalent electrolytes, having an ion constituent in common. In addition to the investigation of the three properties of solutions of electrolytes and of their binary mixtures, a similar study of their ternary mixtures was made.

The electrical conductances of solutions of hydrochloric acid, potassium chloride and sodium chloride, varying in concentrations from 0.0001 *N* to 1 *N* have been thoroughly studied,[2] but relatively little work has been done upon mixtures of solutions of these electrolytes. In 1911 Bray and Hunt[3] made measurements of the conductances of solutions of sodium chloride and hydrochloric acid at 25° (in none of which the total electrolyte concentration exceeded 0.2 mole per liter).

Stearn has made a study of the equivalent conductances, densities and relative viscosities of solutions of some of the alkali halides and of their mixtures. He employed weight concentrations in his work and his selection of the concentrations studied coincides to some extent with that employed in this work.[4] Where comparison is possible, that is, in the cases of the potassium and sodium chloride solutions and their mixtures, the agreement between the electrical conductance data given in his paper and those

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[1] Stearn, THIS JOURNAL, **44**, 670 (1922).

[2] Noyes and Falk, *ibid.*, **34**, 454 (1912).

[3] Bray and Hunt, *ibid.*, **33**, 781 (1911).

[4] The experimental work of this paper was completed before September, 1921.

in this article is not so concordant as can be expected, for the numerical differences do not lie within the limits of experimental error, but the trends of the two sets of data are identical.

Employing the assumption that the apparent equivalent conductances of the mixtures can be computed by the alligative formula from the equivalent conductances of solutions of pure salts of concentrations equal to the total salt concentrations of the mixture, he compared his observed figures with these calculated values. In almost all cases he found that the calculated values were the larger, and that the differences increased with increasing total salt concentration. He suggested that these results could be explained upon the basis of complex formation, but no quantitative computations involving the formation of complex ions were offered.

The most precise data on the densities of potassium and sodium chloride solutions are those of Baxter and Wallace[5] whose results at 25° when recalculated to a weight molal basis were found to be in close agreement with the measurements of this paper. Equally accurate measurements on hydrochloric acid are not available. With the exception of the figures of Stearn, density measurements upon solutions of mixed electrolytes made in a systematic manner are not available.

There are at present no accurate measurements on the relative viscosities of the solutions studied in this investigation, since even the work of Stearn on this property of mixed electrolytes must be regarded as only approximate.

Preparation of the Solutions

The hydrochloric acid was purified by the method of Hulett and Bonner.[6] The exact strength of the stock solution thus produced was determined in the usual manner by precipitation and weighing of silver chloride.

The solutions, hereinafter termed "primary solutions," of each of the electrolytes were prepared by combining appropriate weights of the stock solutions of hydrochloric acid, and of the crystals of potassium and sodium chlorides with the calculated quantities of distilled water, in order to produce the desired concentrations. All weights were reduced to vacuum. Seven concentrations of the primary solutions were studied, namely, 0.1, 0.2, 0.5, 1, 2, 3 and 4 weight normal.

The binary mixtures of the three pairs of electrolytes were made by mixing appropriate weights of the primary solutions, so that the mole-per cent. ratios of the two electrolytes were 20:80, 40:60, 60:40, 80:20. For each of the total concentrations of 1, 2 and 4 weight normal, twelve binary mixtures were studied, while for the lower concentrations fewer binary mixtures were examined, because it became apparent that for

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[5] Baxter and Wallace, This Journal, **38**, 70 (1916).

[6] Hulett and Bonner, *ibid.*, **31**, 390 (1909).

concentrations less than 0.5 weight normal, all of the properties investigated became practically linear.

The ternary mixtures of the three electrolytes were prepared by mixing different amounts by weight of the three primary solutions and computing the concentration ratios. An effort was made to approximate to the ratios 20:20:60, 20:40:40, 20:60:20, 40:20:40, 40:40:20 and 60:20:20, in mole percentages of the three electrolytes, but no attempt was made to secure these exact ratios.

For each of the total concentrations of 1, 2 and 4 weight normal, six ternary mixtures were examined; for the concentrations of less than 0.5 weight normal, no ternary mixtures were studied; for the 0.5 weight normal concentration, one ternary mixture was investigated. The values of the three properties of mixtures, whose total electrolyte concentrations are 0.1 weight normal or less, can be computed by the alligative formula.

Methods of Procedure and Degrees of Precision Obtained

Electrical Conductance.—The usual conductivity apparatus, consisting of a Kohlrausch bridge, a four-dial, Curtis-coil resistance box, a constant speed, high-frequency generator, a telephone, adjustable condensers and conductivity cells, was used for making the conductance measurements. The central tenth of the bridge wire was calibrated with the help of resistances precise to one part in five thousand. The precision attainable in reading the bridge was never less than one part in two thousand. The wire leads were in all cases of negligible resistance in comparison with the resistances measured. All measurements were made at a temperature of 25° ± 0.02°, whose constancy was maintained by the use of an asbestos jacketed thermostat fitted with a stirring device, a heating coil, and a thermoregulator. Two conductivity cells were employed whose constants, 33.29 and 659.9, respectively, were determined by the aid of a solution of potassium chloride having the composition of one part of potassium chloride to 12.998 parts of water, and a specific conductance at 25° of 0.1118 mhos. The precision of the recorded conductance data is not less than one part in one thousand, and may be somewhat better.

Densities.—The density measurements made at 25° ± 0.02° by the use of a glass pycnometer of the Sprengel type having a volume of 18.6896 cc. are not less precise than one part in twenty-five hundred. That the solutions studied had no appreciable solvent action upon the pycnometer was shown by its substantial constancy of weight throughout this investigation.

Relative Viscosities.—The measurements of relative viscosities were made with an instrument of the Ostwald type, for the construction of which, as well as for the construction of the two conductivity cells great thanks are due to Professor F. G. Keyes of this Laboratory. In the designing and construction of the instrument, the precautions given by Washburn and Williams[7] were carefully observed. The viscosimeter was immersed in a constant-temperature thermostat (25° ± 0.02°) provided with a glass window, through which the times of flow could be observed.

The period of time of flow was measured with the aid of a stop watch which was compared with a standard chronometer. Readings with this instrument could be duplicated to a fifth of a second, yielding a precision of measurement of at least one part in three thousand. The precision of the recorded relative-viscosity measurements is not less than one part in two thousand.

Discussion of the Data

Equivalent Conductances.—In Table I are given the measured data on the equivalent conductances, densities and viscosities of all the solutions studied, together with the conductance-relative viscosity values.

Four theories have been advanced to account for the conductances of solutions of mixtures of electrolytes.

1. The first theory regards such solutions as mixtures of simple and complex ions and un-ionized molecules. This theory cannot be discussed from the standpoint of data obtained in this investigation, as it does not readily permit quantitative examination.

2. The second theory is based upon the principle of isohydry. This theory was employed by Bray and Hunt in the treatment of their results, but its application to the data of several of the mixtures studied in this investigation has shown it to be of little value.

3. A third method to correlate these data consists in the assumption that the conductance of any mixture may be computed from the equation $\Lambda = \overline{\gamma}\overline{\Lambda}_0$. $\overline{\Lambda}_0$ is the apparent equivalent conductance of the mixture at infinite dilution, and may be computed by the equation $\overline{\Lambda}_0 = x\Lambda_0' + y\Lambda_0'' + (1-x-y)\Lambda_0'''$ in which the Λ's with the zero subscripts are the equivalent conductances at infinite dilution of the pure electrolytes, and x, y and $(1-x-y)$ are the mole fractions of the electrolytes present in the mixtures; $\overline{\gamma}$ is the apparent or "mean" ionization in the mixture, and may be computed from the ionizations of the pure electrolytes in solutions of the same total electrolyte concentration by the equation, $\overline{\gamma} = x\gamma' + y\gamma'' + (1-x-y)\gamma'''$, where γ', γ'' and γ''' are the ionizations of the pure electrolytes in solutions of the same total electrolyte concentration and x, y and $(1-x-y)$ are the mole fractions of these electrolytes present in the mixture. The resulting expression (for the binary mixtures) $\Lambda = [\Lambda_0'\gamma'] + [(1-x)\Lambda_0''\gamma''] + [1-x][\Lambda_0''\gamma' + \Lambda_0'\gamma'']$ is a quadratic in x, which may yield curves convex upward or downward depending upon the values of the constants of the equation but generally convex upward,

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[7] Washburn and Williams, THIS JOURNAL, 35, 737 (1913).

that is, with maxima. This equation is applicable as it stands only to series of mixtures of the type studied, since only implicitly does it contain the concentrations of the electrolytes present.

Table I

Observed Values of Equivalent Conductances, Densities, Relative Viscosities and Equivalent Conductance—Relative Viscosity Products

Concns., moles per 1000 g. of water						
HCl	KCl	NaCl	Λ	δ	η	$\Lambda\eta$
0.1	0.0	0.0	391.33	0.9989	1.0068	394.00
.0	.1	.0	129.02	1.0018	1.0003	129.06
.0	.0	.1	106.82	1.0012	1.0095	107.83
.2	.0	.0	381.25	1.0007	1.0137	386.47
.0	.2	.0	124.11	1.0064	0.9997	124.07
.0	.0	.2	101.69	1.0053	1.0184	103.56
.08	.0	.12	210.03	1.0033	1.0165	213.49
.12	.0	.08	264.92	1.0025	1.0156	269.05
.5	.0	.0	361.31	1.0058	1.0317	372.76
.4	.1	.0	312.67	1.0086	1.0250	320.48
.3	.2	.0	263.56	1.0114	1.0182	268.30
.2	.3	.0	215.27	1.0143	1.0112	217.64
.1	.4	.0	165.65	1.0171	1.0048	166.48
.0	.5	.0	117.52	1.0199	0.9983	117.32
.0	.3	.2	107.80	1.0188	1.0169	109.63
.0	.2	.3	103.08	1.0183	1.0264	105.76
.0	.0	.5	93.94	1.0172	1.0456	98.26
.2	.0	.3	196.84	1.0127	1.0398	204.71
.3	.0	.2	250.93	1.0104	1.0369	260.21
.167	.167	.166	188.63	1.0145	1.0242	193.16
1.0	.0	.0	333.52	1.0143	1.0617	354.11
.8	.2	.0	291.07	1.0198	1.0483	305.13
.6	.4	.0	247.82	1.0253	1.0351	256.52
.4	.6	.0	202.38	1.0308	1.0221	206.85
.2	.8	.0	157.23	1.0362	1.0102	158.83
.0	1.0	.0	112.29	1.0416	0.9985	112.12
.0	0.8	.2	106.88	1.0405	1.0166	108.65
.0	.6	.4	101.54	1.0395	1.0352	105.11
.0	.4	.6	96.24	1.0384	1.0537	101.41
.0	.2	.8	91.14	1.0374	1.0736	97.85
.0	.0	1.0	86.07	1.0363	1.0936	94.13
.2	.0	.8	132.98	1.0320	1.0862	144.44
.4	.0	.6	182.07	1.0275	1.0797	196.58
.6	.0	.4	232.12	1.0231	1.0736	249.20
.8	.0	.2	283.19	1.0187	1.0676	302.33
.5984	.2007	.2009	237.08	1.0244	1.0538	249.84
.4023	.1990	.3987	189.33	1.0286	1.0593	200.56
.4013	.3973	.2014	195.91	1.0297	1.0412	203.98
.2051	.5920	.2029	152.11	1.0350	1.0296	156.61
.2000	.3996	.4004	145.00	1.0441	1.0471	151.83
.2044	.1988	.5968	143.95	1.0325	1.0667	153.55

Table I (*Concluded*)

Concns., moles per 1000 g. of water						
HCl	KCl	NaCl	Λ	δ	η	Λη
2.0	0.0	0.0	285.10	1.0300	1.1210	....
1.6	.4	.0	254.00	1.0410	1.0972	....
1.2	.8	.0	220.00	1.0514	1.0735	....
0.8	1.2	.0	183.70	1.0616	1.0506	....
.4	1.6	.0	145.40	1.0717	1.0285	....
.0	2.0	.0	105.80	1.0820	1.0076	....
.0	1.6	.4	99.45	1.0800	1.0431	....
.0	1.2	.8	93.05	1.0781	1.0811	....
.0	0.8	1.2	87.02	1.0762	1.1209	....
.0	.4	1.6	81.25	1.0743	1.1632	....
.0	.0	2.0	75.46	1.0722	1.2065	....
.4	.0	1.6	115.14	1.0643	1.1870	....
.8	.0	1.2	158.00	1.0558	1.1684	....
1.2	.0	0.8	200.90	1.0471	1.1509	....
1.6	.0	.4	244.10	1.0386	1.1350	....
1.2291	.3707	.4002	212.58	1.0484	....	....
0.7860	.8199	.3941	173.14	1.0600	....	....
.8079	.3878	.8043	166.29	1.0574	....	....
.3778	.3667	1.2555	119.53	1.0663	....	....
.4218	.7811	0.7971	133.84	1.0674	....	....
.3969	1.2153	.3878	138.02	1.0698	....	....
3.0	0.0	0.0	240.40	1.0450	1.1783	....
0.0	3.0	.0	101.00	1.1188	1.0274	....
.0	0.0	3.0	67.40	1.1006	1.3453	....
4.0	.0	.0	210.60	1.0590	1.2378	....
3.2	.8	.0	195.51	1.0781	1.2068	....
2.4	1.6	.0	176.24	1.0981	1.1713	....
1.6	2.4	.0	153.01	1.1168	1.1341	....
0.8	3.2	.0	126.02	1.1349	1.0954	....
.0	4.0	.0	96.12	1.1528	1.0570	....
.0	3.2	.8	88.13	1.1498	1.1309	....
.0	2.4	1.6	80.52	1.1468	1.2118	....
.0	1.6	2.4	73.22	1.1438	1.3022	....
.0	0.8	3.2	66.30	1.1407	1.4030	....
.0	.0	4.0	59.76	1.1375	1.5136	....
.8	.0	3.2	89.64	1.1220	1.4484	....
1.6	.0	2.4	120.69	1.1066	1.3877	....
2.4	.0	1.6	151.91	1.0980	1.3329	....
3.2	.0	0.8	182.01	1.0750	1.2834	....
2.4449	.7888	.7662	168.16	1.0935	1.2477	....
1.6840	.7915	1.5244	138.40	1.1085	1.2916	....
0.8698	1.4879	1.6423	113.15	1.1266	1.2664	....
.8656	0.7636	2.3708	105.42	1.1239	1.3502	....
.8827	2.2355	0.8818	115.41	1.1286	1.1784	....
1.7110	1.4833	.8057	140.93	1.1113	1.2195	....

4. The fourth method of computing the apparent equivalent conductances of mixtures at any given total concentration is expressed by the

alligative formula $\Lambda = x\Lambda' + y\Lambda'' + (1-x-y)\Lambda'''$ in which Λ', Λ'' and Λ''' are the equivalent conductances of the pure salts in solutions of a concentration equal to the total electrolyte concentration of the mixtures, and x, y and $(1-x-y)$ are the mole fractions of the electrolytes present. This equation can be given graphical representation in the case of binary mixtures by straight lines.

A graphical study of the conductivity measurements shows that the curves of equivalent conductances against concentrations exhibit positive, negative and (practically) zero curvature. The equations of the preceding paragraph give rise to surfaces and curves of zero curvature only, so that such equations are inadequate for the computation of the apparent equivalent conductances of these mixtures. The equations of Method 3 have more generality, but a comparison of the values computed by their use, with the actual measurements, does not show satisfactory concordance. In fact, the equations of Method 4 apply quite well at the lower concentrations, and show a maximum deviation of 7% at the highest concentrations studied, while the equations of Method 3 seem in general less applicable, although in certain cases the agreement is fair. Curiously, these equations of Method 3 are in general more applicable to concentrated than to dilute mixtures. The ternary mixtures do not exhibit anomalous behavior at any concentrations.

Densities.—As was to be expected, the densities of the mixtures show only very slight variations from the densities computed by the rule of mixtures, $\delta = x\delta' + y\delta'' + (1-x-y)\delta'''$, where the δ's refer to the densities of solutions of the pure electrolytes at concentrations equal to that of the total electrolyte concentration of the mixtures, and x, y and $(1-x-y)$ are the corresponding mole fractions of the electrolytes present. In all cases where appreciable differences between the observed and computed densities exist, the observed values are invariably the greater. This regularity of behavior for mixtures of solutions of these three electrolytes affords a strong contrast to the somewhat irregular nature of the equivalent conductance curves.

Relative Viscosities.—Tested by the equation, $\eta = x\eta' + y\eta'' + (1-x-y)\eta'''$, where η is the relative viscosity of any mixture of total electrolyte concentration, c, whose composition is given by the mole fractions x, y and $(1-x-y)$, and η', η'' and η''' are the relative viscosities of solutions of the pure salts of concentration c, the observed relative viscosities are consistently less in value, the percentage variation at one molal being as great as 0.25%. A somewhat more sensitive method of expressing this degree of variation is given by the equation, $\alpha = (\eta\text{calcd.} - \eta\text{obs.})/(\eta\text{obs.} - \eta\text{water})$. For 1 M mixtures, the value of α may become as great as 0.04, while for mixtures of 0.1 M and less, it is less than the experimental error.

An examination of the data of relative viscosity in terms of its reciprocal, the relative fluidity, was made but this property proved to be less amenable to treatment than did the relative viscosities.

It is exceedingly unfortunate that relative viscosities of solutions whose densities differ appreciably from that of water cannot be determined with a high degree of precision by means of an instrument such as that employed in this investigation. Measurements have been carried out upon mixtures whose total electrolyte concentrations were 4 *M*, and while they are perhaps of slight intrinsic value, they serve to show qualitatively the trend of this property at such concentrations. It is of interest to note that the curvatures of these quasi-accurate viscosity-mole-fraction curves are of the same sign as those of the curves for the 1 *M* mixtures.

In attempting to relate Λ and η with other measured quantities such as the concentration and the transference number, the product $\Lambda\eta$ (and in some cases the product $\Lambda\eta^n$ where ^{n} is a number less than unity) has been used by earlier investigators. The usual method of computing the value of $\Lambda\eta$ for a given mixture is expressed by the linear equation, $\Lambda\eta = x\Lambda'\eta' + y\Lambda''\eta'' + (1-x-y)\Lambda'''\eta'''$, in which $\Lambda'\eta'$, $\Lambda''\eta''$ and $\Lambda'''\eta'''$ are the equivalent-conductance–relative-viscosity products of the pure salts in solutions of a concentration equal to the total electrolyte concentration of the mixtures and x, y and $(1-x-y)$ are the mole fractions of the electrolytes present.

The concordance between the observed and the so-calculated values of the $\Lambda\eta$ products is generally better than the agreement between the observed and calculated values of the equivalent conductances. But the agreement is proportionately less satisfactory in the 0.5 *M* solutions than in the 1.0 *M* solutions—a fact which tends to discount the value of this particular relationship.

Summary

The densities, equivalent conductances and relative viscosities at 25° of a series of solutions of hydrochloric acid, potassium chloride and sodium chloride, and of a series of their binary and ternary mixtures of constant chloride-ion-constituent contents have been measured, and the results have been tabulated.

The densities of the mixtures of these electrolytes are a linear function of the compositions of the solution to within 2% in the cases of the most concentrated solutions (4 moles per 1000 g. of water); for solutions of strengths of one mole per thousand grams of water and of greater dilutions, the differences between the measured values of the densities and those computed by the rule of mixtures are negligible.

The equivalent conductances of the mixtures of these electrolytes can be fairly well represented by the straight-line relation, although the differences between the measured values and those computed by the rule of mixtures amount in some cases to more than 7%. Curves presenting the equivalent conductances of the mixtures as functions of their relative compositions show all modes of behavior, and any equation advanced to account quantitatively for the equivalent conductances of such mixtures must be of a power greater than linear.

The relative viscosities of the mixtures of these electrolytes are consistently less than values computed by the rule of mixtures from the relative viscosities of pure solutions of their constituent electrolytes, save in the cases of the most dilute mixtures studied, where the differences between the measured and computed values are negligible. The presentation of the relative-viscosity data in terms of its reciprocal, the relative fluidity, is less satisfactory.

The values of the $\Lambda\eta$ products of the mixtures of these electrolytes of the concentrations of 0.5 M and 1.0 M can be computed by the alligative formula somewhat more exactly than can the equivalent conductances of the same mixtures. For concentrations of greater magnitude, the data are not sufficiently accurate to warrant making such calculations.

CAMBRIDGE 39, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NEBRASKA]

THE MANGANESE DIOXIDE-PERMANGANATE ELECTRODE

BY D. J. BROWN AND RALPH F. TEFFT

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The values in the literature for the potential of the manganese dioxide-permanganate electrode differ by more than 0.1 volt. Inglis[1] has been the only person to measure directly the potentials of the manganese dioxide-permanganate electrode in acid solutions with any degree of accuracy. His measurements are consistent to within a few millivolts, but the error is probably somewhat greater than this. Inglis prepared the manganese dioxide by plating it on platinum electrodes which were then electrolyzed as anodes in sulfuric acid. He does not state the nature of the electrolyte from which the manganese dioxide was prepared, but it was probably a solution of some manganous salt. Neither does he give details concerning the applied potential or the current density during the electrolysis. Attempts by the authors to prepare pure manganese dioxide electrolytically failed. Analyses showed that the product, even after being dried at 300°, did not have the oxidizing power of an equal weight of manganese dioxide. Small variations in the conditions used in preparing the electrodes by this method also produced a large deviation in the observed potential. On the basis of a number of preliminary measurements made in this Laboratory

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[1] Inglis, *Z. Elektrochem.*, 9, 226 (1903).