

hydrogen peroxide. With constant stirring, the reaction was carried out on the water-bath, cooled and left overnight. The unchanged material, being soluble in water, was removed while the white product was crystallized from boiling water. It gave no aldehyde test with semicarbazide or Schiff's reagent, but gave a dark purple coloration when treated with aqueous ferric chloride. This derivative decomposes at 290° and has the form of long, white, rhombic crystals soluble in glacial acetic acid but insoluble in ether. The yield was only 20%.

Anal. Calcd. for $C_7H_8O_6S$: S, 14.54. Found: S, 14.31.

6-Sulfonic Acid of Hydroxyhydroquinone Trimethyl Ether.—The 2-methyl ether was methylated with dimethyl sulfate, giving the sodium salt of the 6-sulfonic acid of hydroxyhydroquinone trimethyl ether. The compound was analyzed as the sulfonyl chloride which melts at 98° and is soluble in acetone, chloroform and glacial acetic acid.

Anal. Calcd. for $C_8H_{11}O_6ClS$: S, 12.00. Found: S, 11.95.

Summary

A number of new derivatives of hydroxyhydroquinone have been prepared, and the structures of the following have been established. (1) Fabinyi and Széki's dibromohydroxyhydroquinone trimethyl ether is the 3,5-dibromo compound. (2) Bromination of the 6-bromotrimethyl ether gives the 3,6-dibromo compound as proved by quinone formation. (3) The α -nitrotriacetate is the 5-nitro compound. (4) The α -nitro- α,α -dibromohydroxyhydroquinone is the 5-nitro-3,6-dibromo body. (5) The side-product occurring with the α -nitrotriacetate is the 1,4-diacetoxy-2-hydroxybenzene. (6) Direct sulfonation of hydroxyhydroquinone trimethyl ether gives the 5-sulfonic acid since, on treatment with nitric acid, the sulfur derivative is converted into the 5-nitro compound.

WORCESTER, MASS.

RECEIVED OCTOBER 8, 1938

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

The Hittorf Transference Numbers of Sodium and Ammonium Acetates in Anhydrous Acetic Acid¹

BY W. CLARENCE LANNING AND ARTHUR W. DAVIDSON

Since the determination of transference numbers in non-aqueous solutions presents a number of difficulties not encountered in aqueous solutions, the data on this subject to be found in the literature² are comparatively scarce, and, with a few exceptions, not very accurate. Among studies of solutions in anhydrous acetic acid which have been made in this Laboratory, a few measurements of transference numbers have been included. Longworth³ made use of the moving boundary method on solutions of sodium and potassium acetates in this solvent. The transference numbers so found were between 0.4 and 0.5, and increased with increasing dilution. In later work by Davidson and Holm,⁴ the results of some preliminary determinations by the Hittorf method were reported. The results appeared to indicate highly abnormal behavior, as the apparent cation transference numbers decreased with increasing dilution, and were practically zero in the most dilute solutions stud-

ied. It would be difficult to account for such extreme abnormality in the dilute solutions; furthermore, it has been shown⁵ that in aqueous solutions closely concordant results can be obtained by moving boundary and Hittorf methods. In view of these facts it seemed of interest to re-determine the transference numbers by the Hittorf method under conditions which promised greater accuracy.

The chief difficulty encountered in such determinations lies in the fact that solutions of electrolytes in acetic acid are very much poorer conductors of electricity than similar aqueous solutions. In order to make possible the passage of a satisfactory quantity of electricity, either the distance between electrodes must be comparatively short or the cross section of the cell must be large. These conditions are exactly opposite to those which would be favorable to sharp separation of the several compartments of a cell and to the attaining of accuracy in the measurement of transference numbers. Further, electrode reactions which are suitable with regard to density changes, absence of gas evolution and accurate

(1) Presented before the Division of Physical and Inorganic Chemistry at the Dallas meeting of the American Chemical Society, April, 1938.

(2) Walden, "Elektrochemie nichtwässriger Lösungen," Johann Ambrosius Barth, Leipzig, 1924, p. 176.

(3) Longworth, Thesis, University of Kansas, 1928.

(4) Davidson and Holm, *University of Kansas Science Bulletin*, 21, 9 (1933).

(5) MacInnes and Dole, *THIS JOURNAL*, 53, 1357 (1931); MacInnes and Longworth, *Chem. Rev.*, 11, 213 (1932).

analysis of the solutions are not numerous. In fact, in the case of acetic acid solutions, it has thus far been possible to meet this difficulty only by the introduction of an additional ion at each electrode of the cell. In the work reported here, cation transference numbers have been obtained for solutions of sodium acetate and ammonium acetate in acetic acid over as wide a range of concentrations as the limitations imposed by solubilities and conductances would permit.

Materials.—Anhydrous acetic acid of m. p. 16.58–16.60°, ammonium acetate,^{6a} sodium acetate^{6b} and lead acetate^{6c} were prepared as previously described. In order to obtain lead in a form which would dissolve readily in mercury, lead of reagent grade was melted under purified hydrogen and allowed to solidify in sheet form. The tank hydrogen employed was freed of oxygen by being passed over platinized asbestos and then through drying towers. Mercury was purified by being shaken with mercurous nitrate and dilute nitric acid solution for a week, and by subsequent distillation under vacuum.

Apparatus and Method.—The transference apparatus is shown in Fig. 1. The cell used in the final determinations

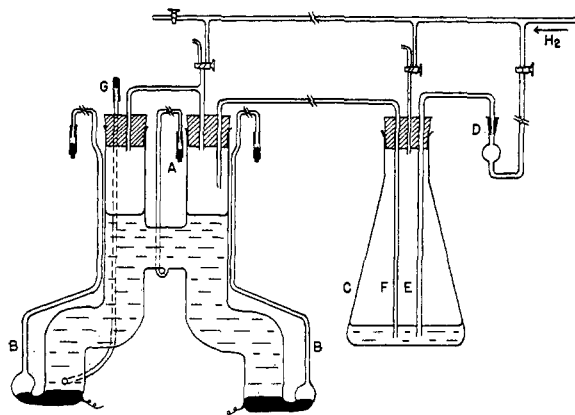


Fig. 1.

was of a modified H-type, the dimensions of which may be estimated from the fact that the two arms of the "H" were made from 1 by 8-inch (2.5 × 20.0 cm.) Pyrex test-tubes. The cross arm was 1 inch (2.5 cm.) in diameter and 1.5 inches (3.8 cm.) in length. The electrodes were placed at the bottom of the two arms of the cell, electrical contact being made by means of platinum wires sealed in at the base. The 250-cc. Erlenmeyer flask C contained the original test solution. The overhead system of tubing and stopcocks was so arranged that air could be swept out of the cell and solution with hydrogen, and the cell could be filled and emptied without access to the air. Drain tubes A, B and B were sealed to the cell so that the solution could be withdrawn in three separate portions without removal of the cell from the constant temperature bath. The tube A sealed to the bottom of the cross arm served to drain

the solution to that level, thus removing a middle portion and separating the anode and cathode compartments. The latter could then be drained through B, B. The bulbs at the base of these tubes had a capacity of about 2 cc. each and served to trap the mercury of the electrodes.

The constant temperature bath, filled with light mineral oil to avoid any current leakage through the bath liquid, was maintained at 25.0°. The source of current was a rectifier built to deliver a maximum of 700 v., d. c., and quantities of electricity were measured with two silver coulometers, one placed ahead of the transference cell and the other following it in the electrical circuit.

To carry out a typical experiment, the cell was supported in the oil-bath, and about 2 cc. of mercury was introduced into each side of the cell. A suitable quantity of freshly cut lead was dropped into the anode side. The overhead system, without flask C, was then put into place and the cell swept free of air. The removal of air was necessary in order to prevent appreciable oxidation of lead at the anode other than by electrolysis. Before the flask C was attached, a small amount of anhydrous acetic acid was introduced into the bulb at D. This minimized the evaporation of solvent, and subsequent crystallization of salt in the tube E, during the sweeping out process. The flask was then slipped into place and, after air had been removed, solution was forced through F to rinse the electrodes and fill the cell, the drain tubes being capped against an outflowing stream of solution to exclude air.

It was necessary to provide for the cathode reaction, which consisted of the reduction of plumbous ion to lead, after the cell had been filled. Pure plumbous acetate was dissolved in a few cc. of the test solution, and a suitable quantity of this dense solution was introduced above the mercury cathode through the tube G, by means of a pipet. The anode reaction consisted of the quantitative oxidation of lead to plumbous acetate; hence no gassing occurred at either electrode. At the end of an electrolysis, the several compartments of the cell were emptied into weighed, stoppered flasks, and each electrode was rinsed with test solution poured directly into the opened cell.

Ammonium acetate solutions were analyzed by distillation of the ammonia into standard acid. Lead was determined in separate small samples as sulfate. Sodium was determined as sulfate in covered platinum crucibles, the lead sulfate having previously been removed by filtration followed by thorough washing.

Results.—The optimum conditions as to time and current were determined by means of a preliminary series of some 15 experiments, carried out with ammonium acetate solutions. The results showed also that the region of concentration change moved toward the middle compartment more rapidly from the anode than from the cathode, and further that the minute changes in the middle might correctly be added to those occurring at the anode. Further evidence that there was no appreciable mixing from the cathode compartment was given by the fact that the total quantity of lead found in both the anode and

(6) (a) Davidson and McAllister, *THIS JOURNAL*, **52**, 507 (1930); (b) *ibid.*, **52**, 519 (1930); (c) Davidson and Chappell, *ibid.*, **55**, 4524 (1933).

middle compartments at the end of a run always agreed closely with that which was dissolved electrically at the anode.

The complete experimental data for one typical run with ammonium acetate are given in Table I. In order to conserve space, detailed data for the remaining nine experiments with this salt have been omitted, and the results only are collected in Table II, where A, C and M designate anolyte, catholyte and middle solutions, respectively.

TABLE I
TYPICAL RUN—AMMONIUM ACETATE

Molality.....	0.9789
Ag in coulometer, g.....	.3874
Amperes.....	.012
Hours of electrolysis.....	8
Wt. of anolyte, g.....	56.418
NH ₄ OAc in anolyte, g.....	3.7951
Pb(OAc) ₂ in anolyte, g.....	0.577
NH ₄ OAc transferred from anolyte, g.....	.1323
Wt. of middle solution, g.....	38.243
NH ₄ OAc in middle, g.....	2.6791
Pb(OAc) ₂ in middle, g.....	0.004
NH ₄ OAc transferred from middle.....	.0042
Wt. of catholyte, g.....	57.994
NH ₄ OAc in catholyte, g.....	4.1605
Pb(OAc) ₂ in catholyte, g.....	0.450
NH ₄ OAc transferred to catholyte.....	.1323
T ₊ (anode).....	.478
T ₊ (anode + middle).....	.493
T ₊ (cathode).....	.478

TABLE II
SUMMARY OF DATA FOR AMMONIUM ACETATE

Molality	T ₊ (A)	T ₊ (A + M)	T ₊ (C)
0.1923	0.45	0.52	0.52
.2198	.41	.49	.48
.300350
.3814	.40	.48	.48
.5214	.445	.473	.486
.6714	.499	.518	.487
.9790	.478	.493	.478
1.4455	.460	.467	.469
1.6053	.466	..	.463
2.4298	.435	.440	.449

Changes in concentration in the middle were very small but uniformly negative. As a result, the anode transference numbers are slightly low and somewhat erratic. The cathode values therefore have been accepted as the more nearly correct ones, and it is these which have been plotted in Fig. 2. The spread of points from a smooth curve indicates the approximate lower limit of concentration to which our results can be considered reliable. Below 0.5 molal, the effective capacity of the electrode compartments was too quickly ex-

ceeded, and, also, the analyses were less precise in the presence of so high a concentration of acetic acid. Above 0.5 molal, the regions of concentration change were well separated, and individual determinations fall less than 0.003 unit from the curve.

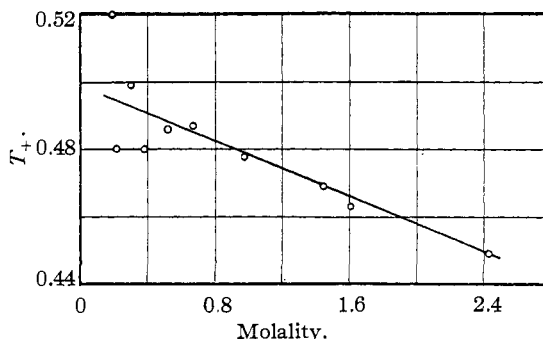


Fig. 2.—Transference number of the ammonium ion in ammonium acetate.

In the case of sodium acetate the rates of mixing from the two end compartments were more nearly equal, so that the constant concentration of sodium acetate in the middle did not constitute an altogether reliable indication of the separation of anolyte and catholyte. However, the duration of the electrolyses was so restricted that the amount of lead acetate in the middle compartment rarely exceeded 0.02 g., and was usually only about 0.01 g. Because of the difficulty of determining sodium acetate accurately in the presence of lead, the errors of analysis were probably larger than any due to imperfect separation of the cell compartments. A summary of the data is given in Table III. In most of the experiments the change

TABLE III
SUMMARY OF DATA FOR SODIUM ACETATE

Molality	T ₊ (A + M)	T ₊ (C)	Av. T ₊
0.3439	0.45	0.52	0.48
.4809	.47	.45	.46
.5578	.41	.48	.45
.5831	.51	.42	.47
.6268	.41	.46	.44
.6727	.47	.42	.45
.6783	.40	.47	.44
.7093	.45	.40	.43
.7973	.41	.46	.43
.8869	.39	.39	.39

in concentration in the middle was negligible, and, since the anode and cathode transference numbers are of equal reliability, an average of the two values from each experiment has been taken. The averages are plotted in Fig. 3, where deviations from the curve amount to 0.02 unit or less.

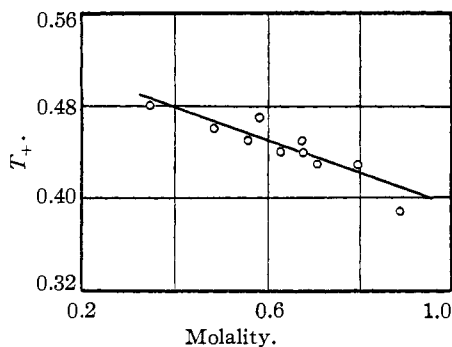


Fig. 3.—Transference number of the sodium ion in sodium acetate.

Discussion

If Stokes' law could be assumed to hold for ions in solution, it would be expected that the limiting values of transference numbers for a given electrolyte, in solvents in which the ions have the same diameter, would be identical. Since there is little reason to suppose the effective diameters to be the same in water and acetic acid, it is not surprising that there should be differences in the limiting values in these two solvents. For aqueous ammonium acetate at 25°, T_+^0 is 0.645,⁷ and for sodium acetate, T_+^0 is 0.551,⁷ while the corresponding values for both salts in acetic acid, insofar as they may be estimated from the data given here, are not far from 0.50. The differences might well be due to variation in the relative solvation of ions in the two solvents. The values obtained for acetate ion in acetic acid, though somewhat high, are certainly not sufficiently anomalous to warrant the assumption of any such conductance mechanism as was suggested by Hammett and Lowenheim⁸ for barium bisulfate in anhydrous sulfuric acid. The transference number of acetate ion in acetic acid is, in fact, much less abnormal than that observed for the analogous hydroxyl ion in water.

As for the variation of the transference numbers with concentration, it is unlikely that this is due to unequal changes in mobilities of the ions, because the total ion concentration, and consequently the effect of electrostatic forces, must be very small in the solutions here studied. The minimum in the equivalent conductance curve for sodium acetate⁹ in acetic acid, which occurs at a concentration of 0.06 N, may be explained, ac-

ording to the theory of Fuoss and Kraus,¹⁰ by the hypothesis that triple ions such as $\text{Na}_2\text{C}_2\text{H}_3\text{O}_2^+$ and $\text{Na}(\text{C}_2\text{H}_3\text{O}_2)_2^-$ exist in the solution, but the further assumption of these authors that positive and negative triple ions are formed to an equal extent can scarcely account for the observed variation of the transference numbers with concentration. It may be shown, however, when reasonable assumptions are made as to the relative mobilities of the ions involved, that if the negative triple ions of this sort were formed to a greater extent than positive ones, the transference numbers might then be expected to show the observed variation, *i. e.*, an approximately linear decrease in T_+ with increasing concentration. However, since an adequate test of this hypothesis would require a quantitative knowledge of the mobilities of all the ions involved, and since such data are not yet available, the evidence for such a mechanism cannot be considered to be conclusive.

Whatever may be the correct explanation of the observed transference numbers, it is of interest to compare them with Longworth's results, obtained by the moving boundary method, which were mentioned in the introduction. The values of T_+ found in the work reported here vary between 0.4 and 0.5, and hence are in substantial agreement with those of Longworth. The data for these non-aqueous solutions therefore offer further evidence for the assumption⁵ that the moving boundary and Hittorf methods measure the same property of the solution.

Summary

1. Cation transference numbers for solutions of ammonium acetate in anhydrous acetic acid have been determined by the Hittorf method at various concentrations between 0.16 and 2.4 molal, and have been found to vary from 0.49 to 0.449 over this range.
2. Similar determinations have been made for sodium acetate at concentrations between 0.3 and 0.9 molal, and the transference numbers have been found to vary from 0.48 to 0.41.
3. The possibility of interpreting the data in terms of the hypothesis of triple ion formation has been discussed.
4. It has been pointed out that transference numbers obtained for such solutions by the moving boundary and the Hittorf methods are in substantial agreement.

LAWRENCE, KANSAS

RECEIVED JULY 25, 1938

(7) (a) "International Critical Tables," Vol. VI, p. 230; (b) MacInnes, Shedlovsky and Longworth, *Chem. Rev.*, **13**, 40 (1933).

(8) Hammett and Lowenheim, *THIS JOURNAL*, **56**, 2620 (1934).

(9) Hopfgartner, *Monatsh.*, **33**, 123 (1912).

(10) Fuoss and Kraus, *THIS JOURNAL*, **55**, 2387 (1933).