PHYSICAL AND INORGANIC CHEMISTRY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TORONTO]

Optical and Electrical Methods of Determining Transference Numbers of Electrolytes in Dilute Solutions by the Moving Boundary Technique

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With a view to transference studies in non-aqueous solvents, methods of determining transference numbers at low concentrations have been investigated. The use of rectangular channels permits the identification of the boundary by the conventional optical methods at concentrations well below those permissible in the usual circular channel; there is, however evidence of boundary instability (at 25° at any rate) and with the familiar Tiselius cell, the solvent conductance is sufficiently large and erratic as to render the results at low concentrations valueless. As an alternative, boundary movement in the channel can be followed by measuring the change in resistance across the channel between microelectrodes when the leading solution is replaced between the electrodes by the indicator. A suitable circuit is described, and it is shown that boundary movement can be followed in this way with satisfactory precision. The advantages (and disadvantages) of this technique are discussed.

It has become apparent in recent years[1,2] that the quantity significant in studies of electrolytic transfer in solution is the ionic rather than the equivalent conductance. This implies, in addition to the usual conductance measurement, the determination of the transference number, and even now only a few such data for anhydrous solvents have been reported; the conventional moving boundary measurements with KCl and NaCl in methanol, carried out in this Laboratory,[3] and Smisko and Dawson's KCNS determinations in ethanol[4] suggest the difficulties which may be encountered in non-aqueous solutions. Moreover, if as is the case with many solvents, ion-pair formation occurs, the measurements should be carried to concentrations well below those hitherto used, and this in turn requires improved methods for following boundary movement. The Kohlrausch ratio technique[5] does provide an alternative as far as limiting ion conductances are concerned, but when used as an absolute method suffers under the disadvantage that the resulting limiting ionic quantities are at best no more precise percentually than is the difference in the limiting equivalent conductances of the leading and indicator salts.

This research was therefore undertaken to determine (a) whether optical methods could be employed at high dilutions, and (b) whether alternative criteria could be used to follow boundary movement. The studies of the optical methods are discussed briefly below, the bulk of the paper being concerned with a conductimetric method of following the boundary, which seems to offer distinct advantages.

Experimental

An elementary treatment of the Abegg and Gaus[6] method of observing a sharp boundary between two solutions of different refractive index (sometimes referred to as the total reflection method[7]) shows that, other things being equal, the minimum detectable refractive index difference is roughly inversely proportional to the path length through he cell. This at once suggests the use of a rectangular channel, as in the conventional Tiselius cell, particularly since this would permit, if desirable, the use of more sophisticated optical mthods. The cell chosen was a modified form of the usual 3 mm. × 25 mm. type discussed by Longsworth and MacInnes.[8] It differs in that there are three center sections (labeled II and III in their Fig. 1) the upper two being fused to the header; the third is fused to the bottom section (IV in their figure) thus leaving only one shearing surface to minimize leakage. The electrode compartments were much reduced in size, and the cell was

(1) C. A. Kraus, *Ann. N. Y. Acad. Sci.*, **51**, 789 (1949).

(2) R. E. Jervis, D. R. Muir, J. P. Butler and A. R. Gordon, THIS JOURNAL, **75**, 2855 (1953).

(3) J. A. Davies, R. L. Kay and A. R. Gordon, *J. Chem. Phys.*, **19**, 749 (1951).

(4) J. Smisko and L. R. Dawson, *J. Phys. Chem.*, **59**, 84 (1955).

(5) D. R. Muir, J. R. Graham and A. R. Gordon, THIS JOURNAL, **76**, 2157 (1954).

(6) R. Abegg and W. Gaus, *Z. physik. Chem.*, **40**, 737 (1902).

(7) D. A. MacInnes and L. G. Longsworth, *Chem. Revs.*, **11**, 171 (1932).

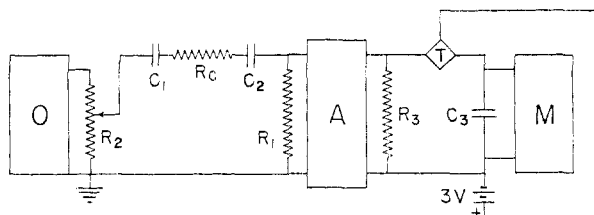(8) L. G. Longsworth and D. J. MacInnes, *ibid.*, **24**, 271 (1939).

Fig. 1.—Schematic diagram of the alternating current circuit.

mounted in a Rockefeller type of frame (see Fig. 2, ref. 8); we wish to thank Dr. Longsworth for supplying us with the blue prints. The measurements were carried out in a carefully controlled air thermostat placed in a constant temperature room.

To determine the volume swept out by the boundary, two methods were employed. The boundary after passing a reference mark was displaced backward through a known volume by additions of mercury to the closed side of the cell from a calibrated pipet. Alternatively, the channel was calibrated from the known value of t_+ for 0.01 N KCl[9,10] by following boundary movement against a graticuled scale. It was found as expected that while a 0.01 N KCl/KIO$_3$ boundary is about the most dilute that can be observed satisfactorily in a 2.5 mm. circular channel, a 0.001 N KCl/KIO$_3$ boundary in the Tiselius cell could be seen with ease. Unfortunately, measurements at high dilutions proved unreliable because of large and erratic solvent conductances determined in the cell; this apparently was due, in part at least, to contamination from slight fissures where the end and side members of the channel are fused together. Moreover, in measurements at 25° in contrast to those near 4°, there was evidence of boundary instability, notably a tendency for the boundary to be arched; this may be due to the non-symmetrical temperature distribution in a channel of this shape.

As an alternative, conventional rising and falling boundary cells were constructed (types V and VIII, see Fig. 1, ref. 11) except that the channel, including that in the shearing stopcock, was of rectangular 2 mm. X 10 mm. glass tubing.[12] The cells were calibrated as to volume with 0.02 and 0.01 N KCl, using KIO$_3$ and LiCl as indicators for rising and falling boundaries, respectively, and as expected, visible boundaries were obtained at concentrations one quarter to one fifth those for a 2.5 mm. channel. Solvent conductances, determined in the cell, were now reproducible, but again at high dilutions there was some hint of boundary instability; even the volume calibrations showed a scatter of a part in 1500 or so, as compared with a part in 4000 at these concentrations in a 2.5 mm. circular channel. With more dilute solutions, the precision was considerably less; for example, a series of measurements with 0.0025 N KCl and potassium diiodobenzoate as indicator, gave $t_- = 0.5097 \pm 0.0005$.

The Conductimetric Method.—This procedure takes advantage of the fact that there must be a change in resistance across the channel when the leading solution is replaced by the indicator. Preliminary measurements suggested certain obvious conditions to be fulfilled if good precision were to be obtained. In the first place, the electrodes used to determine the conductivity of the solution must be as small as possible in the vertical direction to sharpen the timing of the "event" and to minimize the possibility of their acting as bipolar electrodes to the direct current. Secondly, for continuous recording, the conductance electrodes must be capacity coupled in the a.c. measuring circuit.

To construct the channel, the procedure finally adopted was to stretch a platinum ribbon, 0.07 mm. thick and 1.0 mm. wide, across the upper end of a glass tube, 2.5 mm. i.d. 0.7 mm. wall thickness. Since the ribbon was rather fragile, it was first welded to 0.5 mm. leads of platinum wire, the length of ribbon being so chosen as to leave the leads in close proximity to the glass. Another section of tubing was pressed down on the first, and the two sections were
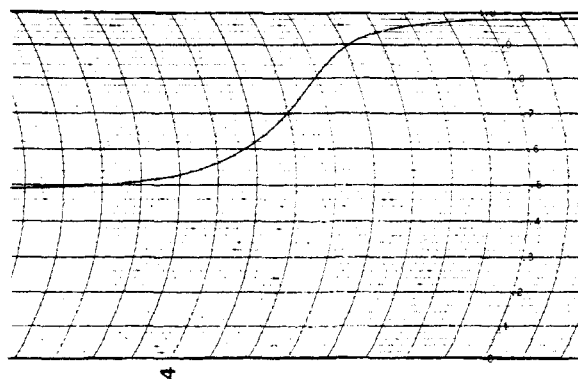
(9) L. G. Longsworth, THIS JOURNAL, **54**, 2741 (1932).

(10) R. W. Allgood, D. J. LeRoy and A. R. Gordon, *J. Chem. Phys.*, **8**, 418 (1940).

(11) A. R. Gordon and R. L. Kay, *ibid.*, **21**, 131 (1953).

(12) Supplied by the Fischer and Porter Co., Hatboro, Pa.

Fig. 2.—Trace on recording milammeter for passage of 0.01 N KCl/0.0069 N KIO$_3$ boundary; boundary velocity 0.04 mm./sec.

fused at the lowest temperature consistent with obtaining a satisfactory seal, leaving the ribbon extending from wall to wall of the tube. A thin thread of glass was next wound around the lead and fused to it and to the wall of the tube, thus protecting the ribbon from mechanical strains. A sharpened steel rod, slightly smaller than the internal diameter of the tube, was pressed down, cutting the ribbon near the walls, and any protruding platinum was removed with a stiff piano wire coated with carborundum powder and glycerol. It was found, as might be expected, that there was considerable variation in apparent resistance with different pairs of electrodes; accordingly, for reasons discussed below, a "cell factor" (using 0.01 N KCl) was determined for each pair of electrodes, and only those pairs with factors differing by not more than a few per cent. were incorporated in a channel. Each channel had as a rule five pairs of such microelectrodes spaced some 40 mm. apart. It should be noted in passing that even with an ohmic drop as high as 1 volt per mm., due to the passage of the direct current, the voltage drop across the surface of a microelectrode is only 0.07 volt.

In order to test the method in the same cell with both rising and falling boundaries, the earlier designs (after annealing) were fitted with a Type III shearing stopcock[11] at the base of the channel and a Type VIII at the top; subsequent cells, for simplicity, were designed *either* for a rising or a falling boundary. The platinum leads were soldered to stout copper wires which lead to a Lucite distributor plate at the top of the cell; the wires were enclosed in glass tubes which carried the shielding. The distributor plate carried sockets for the electrodes and an additional pair for a variable resistance which permitted the oscillator and amplifier (see below) to operate without passing alternating current through the cell.

The cell was mounted in an oil-bath, operating at 25.00 ± 0.01°, and cadmium and silver–silver chloride electrodes served as anode and cathode. The indicator concentrations were a few per cent. below the Kohlrausch values[5,11] for NaCl and LiCl, and a few per cent. above with KIO$_3$ and NaIO$_3$; the preparation of the salts and the solutions has been described previously.[2,10] To clean, the cell was washed with redistilled carbon tetrachloride, ethanol and water, then repeatedly with distilled and conductivity water; it was then drained and dried with a stream of dried filtered air. Periodically, before the final washing, the cell was allowed to stand filled with 20% hydrochloric acid to remove surface alkalinity. In general, the solvent conductance measured in the cell differed only negligibly from that of the stabilized conductivity water used in making up the solutions, viz., 0.7–0.8 X 10^{-6}.

One essential precaution was the removal of any moisture from the inside of the glass tubes which enclose the copper wires leading from the distributor plate to the microelectrodes. To do this, the tubes were flushed with anhydrous ethanol and dried with dried, filtered air immediately before filling the cell. In addition, particularly in humid weather, it was found necessary to dehumidify the laboratory if leakage of the direct current through the microelectrodes to the grounded shielding on the glass tubes was to be avoided.

The a.c. circuit is indicated in Fig. 1. Here R_0 is the resistance across the channel; C_1 and C_2 are 0.02 μf. condensers (rated at 10,000 working volts, leak resistance $\gg$ 50,000 megohms); O is a Hulett–Packard model AB oscillator, normally operating at 20,000 c.p.s.; R_2 is a 6000 ohm voltage divider with taps in 0.05 volt steps up to 1 volt; and R_1 is the amplifier feed resistor. A is a Williamson amplifier (maximum voltage gain 1400 at 20,000 c.p.s., internal input impedance 1.5 megohms); in general, the input, feed resistor and amplification were adjusted to give approximately full scale deflection on the recording ammeter when the leading solution was between the electrodes. R_3 is a 500 ohm load-matching resistor, T a Texas Instrument Co. Type 201 transistor, C_3 an 0.8 μf. condenser, and M an Esterline–Angus Model AW recording ammeter (1 milliamp. full scale deflection, internal resistance 1400 ohms, chart speeds 2.5 mm./sec. and 2.5 mm./minute). We wish to thank Dr. F. S. Goulding of Atomic Energy of Canada Limited, Chalk River, Ont., for suggesting the rectifier circuit to us. To correlate the time scale of the chart with the effective time for the run, a spring-returned stylus was used to record on the chart two datum points, one just before the boundary passed a given pair of electrodes, the second just after it had passed; tests showed that 30 second intervals on the chart were correct to 0.2 sec. or better.

Results

A typical trace for a 0.01 N KCl/0.0069 N KIO₃ boundary is shown in Fig. 2; the current here is 0.36 milliamp. and the actual boundary velocity slightly over 0.04 mm./sec. Zero signal is at the bottom of the chart, which is moving from left to right, the time arcs corresponding to 5 second intervals. At first glance, the duration of the event— approximately 65 seconds—is surprising, but while any calculation of the distribution of the current lines is impossible, an extremely naive estimate of the column of solution involved in the resistance measurement can be made. Since the resistance across the channel for 0.01 N KCl is approximately 12000 ohms, the factor "A/l" is 0.6 mm. If the current were confined vertically to the plane of the electrodes and horizontally to their width, the ratio of length to width would be of the order of 2.5; if this ratio were valid for the actual measurement, the corresponding "height" would be 1.5 mm., which is certainly an underestimate. Moreover, MacInnes and Longsworth's eq. 49 shows[7] that if the thickness of the boundary be taken as the distance from the plane in which the concentration of the indicator is 2% of that of the leading salt, to the plane where the concentration of the leading salt is 2% that of the indicator, the boundary thickness for the conditions obtaining here will be approximately 0.16 mm.; thus the boundary must move at least 1.66 mm. for the transition from leading to indicator solution to be complete, corresponding to an interval of 40 seconds or more—an estimate not inconsistent with the time actually observed.

In addition, if the trace be replotted on rectangular coördinate paper, and the tangent be drawn at the point of inflection, the slope of the tangent should be a measure of boundary velocity near the first moment of the boundary, and for given leading and indicator solutions and fixed a.c. circuit characteristics, the slope should be proportional to the direct current; this is in fact found to be the case.

An approximate circuit analysis shows that with the a.c. circuit components used here, the signal for fixed input voltage should be proportional to $R_1/(R_1 + R_c)$. Thus, with $R_1 = 1400$ ohms, as is the case in Fig. 2, the ratio of the signal when 0.01 N KCl is between the microelectrodes to that when it has been replaced by 0.0069 N KIO₃ solution,[11] should be 1.80; as is evident from the chart, the actual ratio is some 10% greater than this, and this is in general found to be the case, the observed signal ratio being greater than that computed from R_1, the cell factor and the specific conductances of the two solutions. The explanation lies in the fact, as shown by tests with known resistances in place of R_c, that the response in the circuit is not strictly linear, the recorded signal being somewhat more than proportional to $R_1/(R_1 + R_c)$. However, for given leading and indicator solutions, the observed ratio for a pair of electrodes is reproducible to 1%, is independent of the direct current passing, of the a.c. input voltage, and of the amplification, and varies only a few per cent. from one pair of electrodes to another, $i.e.$, essentially the same phenomenon is occurring at all the electrode pairs.

Since it is the time required for the boundary to move from one electrode pair to another that is the experimentally significant quantity, this suggests that any easily identified point on a trace be used to time the event and thus to compute the interval. The one we have chosen is that corresponding to the average of the signals when only leading or indicator solution is between the electrodes. In Fig. 2, this corresponds to an ordinate of 73.5 units with an uncertainty in the time of less than 0.5 second.

As an example of the results that may be obtained in this way, a volume calibration between two pairs of electrodes is summarized in Table I. With this cell, both rising and falling boundaries could be used; the values of t_+ (to which the appropriate solvent and volume corrections[7] were applied) on which the calibration is based were 0.4902 and 0.3918 for 0.01 N KCl[9,10] and 0.01 N NaCl,[9,13] respectively. It is at once evident from the table that the measured volume is independent of the leading ion, of the indicator, of the direct current employed, whether the boundary is anion or cation, and whether it is rising or falling; in other words, the volume is a function only of the cell geometry. It should be mentioned that with the later cells, designed for use with either a rising or a falling boundary, the reproducibility for a given leading solution was definitely better—a part in four thousand, which is the precision at best of transference data. We believe this was due in these cells to the elimination of the shearing stopcock from the closed side of the cell.

It is naturally pertinent to enquire as to the disadvantages and advantages of the technique as described above—particularly in comparison with optical methods of following boundary movement. Its first and most obvious disadvantage lies in the difficulties always encountered with complicated high resistance circuits—here in particular possible leakage of the direct current through the microelectrodes to ground through the shielding of the a.c. leads. A second is the fact that the recorded trace can give no information as to the actual boundary structure such as is supplied by the famil-

(13) R. W. Allgood and A. R. Gordon, $J.$ $Chem.$ $Phys.$, 10, 124 (1942).

iar schlieren technique. On the other hand, there is much greater flexibility here in the choice of indicator ion; the ion must of course be slower than the leading ion and either lighter or heavier depending on the type of boundary, but any requirement as to its optical properties in the solvent disappears. For example, the KCl/LiCl boundary of Table I would be completely invisible under the conditions obtaining here, while the trace obtained is almost indistinguishable from that of Fig. 2. Again, with any optical procedure, there is always a minimum current below which the boundary becomes too diffuse to be observed; here this restriction disappears. It is true that halving the current, for example, and consequently the boundary velocity, roughly doubles the uncertainty in fixing the midpoint of the trace; however, the interval from one electrode pair to the next is also doubled, so that percentually the precision of the computed volume calibration or transference number is unaffected; this can be a matter of real importance where Joule heating is a serious factor. Finally, the method can be employed at concentrations well below those accessible to the optical methods and, as is shown in the accompanying paper, should be generally applicable to non-aqueous solvents.

TABLE I

VOLUME CALIBRATION, CELL λ, 25.00°

Electrode pair No. 2 · Electrode pair No. 5

Indicator	Leading soln., 0.01 N KCl Current, milliamp.	Vol., ml.	Indicator	Leading soln., 0.01 N KCl Current, milliamp.	Vol. ml.
KIO₃	0.11	0.6109	LiCl	0.36	0.6108
KIO₃	.36	.6109	LiCl	.36	.6113
KIO₃	.36	.6112	LiCl	.36	.6114
KIO₃	.36	.6110	Leading soln., 0.01N NaCl		
KIO₃	.36	.6106	NaIO₃	0.24	0.6112
KIO₃	.66	.6108	NaIO₃	.36	.6109
NaCl	.36	.6106	NaIO₃	.56	.6109
NaCl	.56	.6110	Mean 0.6110 ± 0.0002		

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TORONTO]

The Transference Numbers of Sodium and Lithium Chlorides in Anhydrous Ethanol at 25°

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RECEIVED JANUARY 14, 1957

The conductimetric method of following boundary movement has been used to determine the transference numbers for NaCl and LiCl in anhydrous ethanol at concentrations from 0.001 to 0.0025 N. Triiodobenzoate served as a satisfactory rising anion indicator, the observed t_- satisfying the usual experimental criteria, but it was not possible to find a satisfactory cation indicator in this solvent. Moreover, even the anion boundaries showed evidence of boundary instability at 0.0005 N. However, the Longsworth function, computed on the basis of ionic rather than stoichiometric concentration, is linear in the ionic concentration, thus permitting an unambiguous extrapolation to infinite dilution. While the results are not as precise as those obtained with water and methanol as solvents, they nevertheless demonstrate, we believe, that reasonably reliable transference data can be obtained in many if not most anhydrous solvents.

In this paper we report the results of transference measurements, effected by the technique described in the preceding paper,[1] on sodium and lithium chlorides in anhydrous ethanol at 25°. The reasons for selecting these two salts were (a) that their ions were of the simple noble-gas type, and (b) that transference and ion conductance data were available for them in water[2] (over a range of temperatures) and in methanol.[3] While for purposes of continuity it was desirable to investigate their transport properties in another solvent in the same homologous series, the fact remains that the relatively low solubility of the salts and their low conductivity in ethanol raised special problems—in particular that of finding suitable indicator ions.

The fact that it was possible to carry out these measurements at all, argues (we believe) that transference measurements are generally possible with this procedure in non-aqueous solutions subject to certain restrictions discussed below.

Experimental

The general technique already has been described.[1] In general, the amplifier feed resistance R₁ (see Fig. 1 of ref. 1) was set at about one tenth of the resistance across the channel R₀ when the leading solution was between the micro-electrodes and, owing to the relatively low specific conductance of the solutions, the boundary velocities were considerably lower than those employed in aqueous solution to minimize Joule heating. The preparation and purification of solvent, salts and solutions are discussed in the accompanying paper.[4] For rising anion boundaries[5] sodium and lithium triiodobenzoate served as suitable indicators; in fact the traces recording boundary passage are almost indistinguishable from those obtained with similar boundary velocities in aqueous solution; see for example Fig. 2 of ref. 1. The 2,3,5-triiodobenzoates were prepared by the pro-

(1) J. W. Lorimer, J. R. Graham and A. R. Gordon, THIS JOURNAL, **79**, 2347 (1957).

(2) (a) H. S. Harned and B. B. Owen "The Physical Chemistry of Electrolytic Solutions," 2nd Edition, Reinhold Publ. Corp. New York, N. Y., 1950, p. 590; (b) G. C. Benson and A. R. Gordon, J. Chem. Phys., **13**, 473 (1945).

(3) (a) J. A. Davies, R. L. Kay and A. R. Gordon, ibid., **19**, 749 (1951); (b) J. P. Butler, H. I. Schiff and A. R. Gordon, ibid., **19**, 752 (1951); (c) R. E. Jervis, D. R. Muir, J. P. Butler and A. R. Gordon, THIS JOURNAL, **75**, 2855 (1953).

(4) J. R. Graham, G. S. Kell and A. R. Gordon, ibid., **79**, 2352 (1957).

(5) The volume calibrations between the various pairs of electrodes are based on the values of t_+ for KCl in aqueous solution at 25°, 0.4902 and 0.4901 for 0.01 N and 0.02 N, respectively; see footnotes 9 and 10 of ref. 1.