[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

A Moving Boundary Method for the Measurement of Non-electrolyte Transport in Mixed Solvents[1]

BY L. G. LONGSWORTH

Introduction

In a discussion of the moving boundary method for the determination of the transference numbers of electrolytes G. N. Lewis,[1a] in 1910, suggested that the method could also be used to measure "ionic hydration" if one could follow the movement, on passage of an electric current, of a boundary between a solution of a salt and the same solution to which an "electrically inert" reference substance had been added. Actually, however, there appears to be no way at present of demonstrating that the reference material is more, or less, inert than the solvent, usually water. Consequently it seems preferable to consider the reference substance as one component of a mixed solvent and to call boundaries of the type suggested by Lewis *solvent boundaries*. Unlike an ordinary salt boundary, diffusion at a solvent boundary proceeds essentially independently of the current and such a boundary soon loses the sharpness with which it is initially formed. The method of observation in use at the time Lewis wrote was not applicable to diffuse boundaries and his suggestion received no experimental test. With the recent development of the schlieren method for the observation of boundaries it is now possible, however, to record the refractive index gradients, and hence the concentration distribution, in a diffuse boundary. Consequently the position of a boundary whose gradients may be spread over several centimeters can now be defined with almost the same precision as one in which the transition occurs within a fraction of a millimeter. In this manner the displacements of the solvent boundaries have been measured in the work described below. It is the purpose of this report to outline the experimental procedure and to show that this adaptation of the moving boundary method yields results that confirm and extend the work of Buchbock[2] and Washburn[3] on "water transport" in ionic solutions, although the new results indicate that their interpretation was incorrect.

Experimental

The experimental procedure and apparatus are the same as that used in the study of concentration boundaries.[4] As in this earlier work a boundary is formed in each of the two sides of the U-shaped channel of a modified Tiselius cell. The modification consists in a redesign of the top section of the cell to include the electrode cups, thereby eliminating the rubber connections, the expansion, or contraction, of which during an experiment in the conventional Tiselius assembly may be a source of error. After the boundaries are formed they are shifted into view and current is then passed. For the first few minutes after closing the circuit the current through the cell increases somewhat as the steady-state distribution of temperature is established in the channel and then changes but slowly. Since the product of the average current and the time is an adequate measure of the quantity of electricity passed, regulation of the current is unnecessary if the potential of the power supply is reasonably constant. Small volume changes accompany the initial temperature adjustments, however, and the first photograph of the boundaries was not taken until current had been flowing from five to ten minutes. Additional photographs, also with the current flowing, were taken after about two hours and again after four hours, after which the current was reversed and a fourth photograph taken after the boundaries had moved in the opposite direction for another interval of two hours. In this manner three values for the displacement, per faraday, of the boundary in each side of the channel were obtained or a total of six values. The constancy of these values affords an important check on the experiment. As was shown[5] in the work on concentration boundaries the failure of this displacement to be independent of the direction and magnitude of the current can usually be traced to the disturbing influence of convective circulation.

An idea of the magnitude of the displacements that are observed is afforded in Fig. 1 by the superimposed tracings of the first three photographs of the 1.5% raffinose boundaries in 0.1 N lithium chloride. Since the displacements are small the boundary positions are determined with the same care as in the work with concentration boundaries. The fact that the diffusion coefficient that may be computed from the boundary spreading shown in Fig. 1 differs by only a few per cent. from the value measured independently with no current flowing is good evidence that the thermal and electro-osmotic effects of the current did not disturb the boundaries appreciably.

Results

The results are summarized in Table I, which is self-explanatory except for the last three columns. In column 7 the value of the observed boundary displacement per faraday, ΔV_b, is the mean of

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[1] A report of this research was made at the Pittsburgh meeting of the American Chemical Society in September, 1943.

[1a] Lewis, THIS JOURNAL, **32**, 862 (1910).

[2] Buchbock, *Z. physik. Chem.*, **55**, 563 (1906).

[3] Washburn, THIS JOURNAL, **31**, 322 (1909).

[4] Longsworth, *ibid.*, **65**, 1755 (1943).

[5] Reference 4, footnote 23, p. 1760.

TABLE I

NON-ELECTROLYTE TRANSPORT ON PASSAGE OF AN ELECTRIC CURRENT, AT 0.5°, THROUGH SOLUTIONS OF ELECTROLYTES

1 Expt.	2 Electrolyte	3 Concn., eq./liter	4 Non-electrolyte	5 Concn., %	6 Current, ma.	7 $-\Delta V_b$, ml./faraday	8 ΔV_e, ml./faraday	9 n_w, moles/faraday
1	LiCl	0.1	Raffinose	1.5	20	26.2 ± 2.1	9.3	1.97
2	LiCl	.2	Raffinose	1.0	30	23.7 ± 1.8	9.8	1.86
3	LiCl	.2	Raffinose	1.0	29	23.5 ± 0.7	9.5[a]	1.83
4	LiCl	.2	Raffinose	2.0	30	21.5 ± 0.6	9.5	1.72
5	LiCl	1.0	Raffinose	2.0	38	11.3 ± 0.5	9.9	1.18
6	LiCl	0.2	Resorcinol	2.0	28	27.4 ± 0.8	6.4[b]	1.88
7	LiCl	.2	Mannitol	2.0	29	11.9 ± 0.9	9.5	1.19
8	LiCl	.2	Urea	2.0	30	10.3 ± 0.6	9.5	1.10
9	LiCl	.2	Urea	4.0	30	9.3 ± 1.1	9.5	1.04
10	NaCl	.2	Raffinose	1.5	27	10.4 ± 1.1	8.65	1.06
11	NaCl	.5	Raffinose	1.0	38	7.5 ± 1.7	9.3	0.93
12	NaCl	1.0	Raffinose	1.5	31	5.4 ± 0.2	8.9	0.80
13	NaCl	1.0	Raffinose	1.5	40	5.2 ± 0.5	8.9	0.79
14	KCl	0.2	Raffinose	1.0	36	9.35 ± 1.3	1.3	0.59
15	KCl	1.0	Raffinose	1.5	50	7.1 ± 0.7	1.4	0.47
16	KCl	1.0	Raffinose	1.5	30	6.2 ± 0.8	1.4	0.42
17	NH_4Cl	0.2	Raffinose	1.0	36	16.8 ± 0.7	−3.0	0.77
18	NH_4Cl	1.0	Raffinose	1.5	30	11.2 ± 1.0	−3.0	0.46
19	HCl	0.2	Raffinose	1.0	46	5.7 ± 0.8	0.6	0.35
20	HCl	1.0	Raffinose	1.5	51	3.1 ± 0.4	0.4	0.20
21	HCl	1.0	Resorcinol	1.5	30	5.1 ± 0.8	0.4	0.30
22	HCl	1.0	Resorcinol	1.5	50	5.8 ± 0.5	0.4	0.34

[a] The concentration of lithium chloride around the cathode (closed) differed from that of expt. 2. [b] A silver–silver bromide cathode was inadvertently used in the closed side in this experiment.

the six figures obtained in an experiment as described above. The average deviation of the individual figures from this mean, also included in column 7, indicates that the precision of the measurements is about 1 ml./*F*. Since all of the boundaries moved against the current the values of ΔV_b are taken as negative.

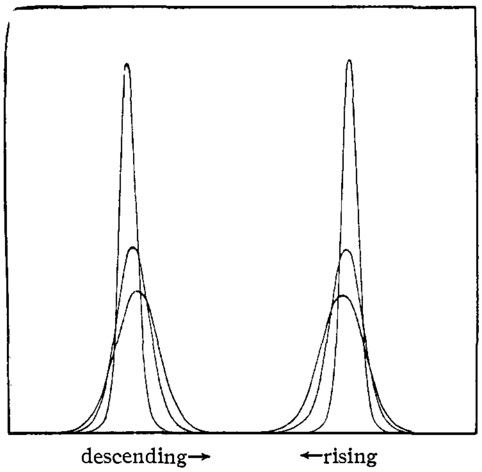

Fig. 1.—The refractive index gradients in the 1.5% raffinose boundaries in 0.1 *N* lithium chloride.

The displacement, ΔV_b, is observed with respect to the cell whereas the displacement required, ΔV, is that with respect to the solvent. Due to the volume changes at the electrodes the solvent itself undergoes a displacement, ΔV_e, and this must be subtracted from ΔV_b, *i. e.*, $\Delta V = \Delta V_b - \Delta V_e$. The computed values of ΔV_e are

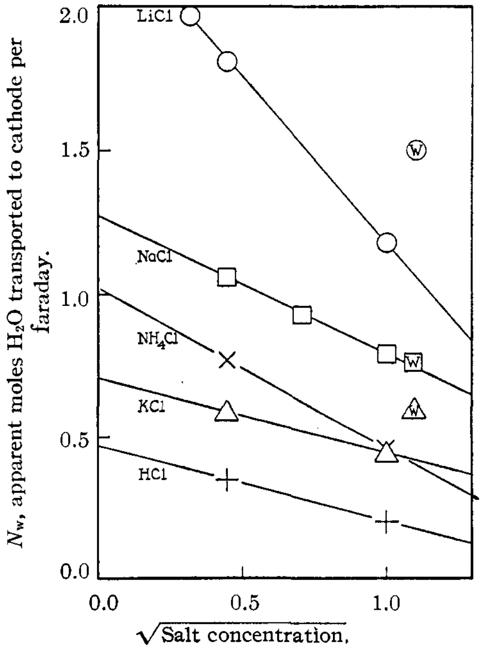

Fig. 2.

given in column 8 of Table I and tests[4,6,7] on other types of boundaries indicate that these values are also correct to within 1 ml./F. If, now, the assumption is made, as was done by Buchbock and Washburn, that the added non-electrolyte does not move on passage of the current the relation $n_w = -(\Delta V_b - \Delta V_e)/18$, column 9, then gives the number of moles of water that are transported, per faraday, from the anode to the cathode.

Discussion

Although Washburn's data were obtained at 25°, whereas those of Table I are for 0.5°, it is of interest, nevertheless, to compare the moving boundary results with those given by the gravimetric procedure. This is done in Fig. 2 where the values of n_w from Table I in which raffinose is the non-electrolyte are plotted as ordinate against the square root of the salt concentration as abscissa. On this abscissa scale the three points for sodium chloride, and also those for lithium chloride, fall on a straight line. In this figure Washburn's values are indicated by a *W*. In the case of sodium chloride the agreement is complete and even for potassium and lithium chlorides it is satisfactory when one considers the difficulties that are encountered in the gravimetric method. Although not shown in Fig. 2, Buchbock's value of $n_w = 0.29$ for 1.1 N hydrochloric acid in 2.2% resorcinol is also in good agreement with the moving boundary value of 0.32, experiments 21 and 22 of Table I, under similar conditions. The conclusion that the two methods measure the same property of the solution appears to be justified.

The interpretation of the moving boundary results is, however, complicated by the possible effect of the non-electrolyte on the transference number of the salt. If this number is different in the two solutions forming a boundary, passage of the current may lead to an accumulation, or impoverishment, of the salt in the boundary layer that complicates the interpretation of the refractive index gradient curves.[8] Correction for this effect is made by determining n_w for different concentrations of the non-electrolyte and extrapolating to zero concentration of that material. As is shown in Table II, sufficient data are given in Table I for 0.2 N solutions of lithium chloride to permit linear extrapolation when raffinose and urea are the non-electrolytes. As these data indicate, it is one of the advantages of the moving boundary method that the concentrations of the added non-electrolyte can be kept low enough to make this effect relatively small.

TABLE II

THE VARIATION OF n_w IN 0.2 N LITHIUM CHLORIDE SOLUTIONS WITH THE NATURE AND CONCENTRATION OF THE ADDED NON-ELECTROLYTE

Non-electrolyte/concn., %	0.0	1.0	2.0	4.0
Raffinose, n_w	1.94	1.83	1.72	..
Resorcinol, n_w	..	..	1.88	..
Urea, n_w	1.16	..	1.10	1.04
Mannitol, n_w	..	..	1.19	..

Also included in Table II are the values of n_w with resorcinol and mannitol as the added non-electrolytes. These, together with the corresponding values for raffinose and urea, indicate, in contrast with Buchbock's results, that the so-called water transport, n_w, is not independent of the nature of the non-electrolyte. This is sufficient to demonstrate the incorrectness of the assumption, made by the early workers, that the added substance, but not the water, is electrically inert. Thus it is clear that n_w is not a measure of the water transport but is merely a convenient parameter with which to express the experimental results. Its physical significance remains to be assigned in the light of modern theory.[9]

Other Moving Boundary Work on Non-electrolyte Transport.—In a recent paper Janssen[10] describes experiments similar to those reported above. Apparently he used the conventional Tiselius apparatus, unmodified for precise moving boundary work as described earlier in this paper, with both electrode vessels open to the atmosphere and without making a correction for the volume changes due to the electrode reactions. Since he observes much larger boundary displacements than would be expected from the work of Buchbock and Washburn, for example, he concludes that a hitherto undiscovered electrokinetic effect is operating. Moreover, he interprets his results as indicating that this new effect depends on the electric field strength. In contrast, experiments 12 and 13 of Table I with sodium chloride, 15 and 16 with potassium chloride and 21 and 22 with hydrochloric acid indicate that the boundary displacement per faraday is independent, within the limits of error of the method, of the field strength so long as the currents are not excessive. It is thus clear that Janssen's results differ from those reported here.

On the basis of the experience of this Laboratory the current of 50 ma. employed by Janssen produced sufficient convective circulation in his relatively dilute solutions to disturb the boundaries. His own observations support this conclusion since he notes, in contrast with my experience, that all of the boundaries spread faster than from diffusion alone and in some instances were seriously distorted. It has also been my experience that precise moving boundary work is not possible unless one of the electrode vessels is closed and unless the rubber connections of the conventional Tiselius assembly are eliminated. Moreover, re-

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(6) Smith, *Bur. Standards J. Research*, **8**, 457 (1932).

(7) MacInnes and Longsworth, *Chem. Rev.*, **11**, 171 (1932).

(8) With 0.2 N barium chloride in a 1% raffinose solution, for example, this effect is sufficient to produce a noticeable asymmetry in the boundary patterns.

(9) The problem of non-electrolyte transport in solutions of electrolytes through which current is passing is considered from the modern point of view in a forthcoming paper by A. M. Squires and J. G. Kirkwood.

(10) Janssen, *Rec. trav. chim.*, **65**, 564 (1946).

versal of the current provides an important check on the experiment that was not made by Janssen. As was shown in the work on concentration boundaries[5] it should also be noted that electroosmotic streaming is not negligible, even in the Tiselius cell, at the lower salt concentrations studied by Janssen. The existence of the new electrokinetic effect postulated by him still remains, therefore, to be demonstrated.

Acknowledgments.—The author is indebted to Dr. D. A. MacInnes of these Laboratories for his sustaining interest in this research and for valuable criticism of the manuscript.

Conclusion

A moving boundary method is described for the determination of non-electrolyte transport in solutions of electrolytes through which current is passing. Although measuring the same property of the solution as the gravimetric procedures previously available it has several advantages. No analyses are required and, since the non-electrolyte is not present at the electrodes, it does not have to be stable against electrochemical decomposition. Consequently a variety of non-electrolytes may be studied. As sensitive criteria for the validity of a result are the requirements that the boundary displacement per faraday be independent of the direction and magnitude of the current and that the spreading of a boundary with time does not differ appreciably from that due to diffusion alone. The time and effort involved in an experiment is but a fraction of that required by the gravimetric procedure.

Since the boundary displacement per faraday varies with the nature of the added non-electrolyte it is now clear that the early interpretation is incorrect. It is to be hoped, however, that with the aid of a more elaborate theory the results may yield information as to the composition of the mixed solvent in the immediate neighborhood of an ion in terms of the bulk composition and the electrical properties of the components.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, AUCKLAND UNIVERSITY COLLEGE]

The Measurement of Vapor Pressures of Aqueous Solutions by Bi-thermal Equilibration Through the Vapor Phase

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Introduction

The isopiestic method[1a] of determining the vapor pressures of aqueous solutions, though it has proved easily the most practical of the various techniques available, has been hampered from the first by uncertainties about the vapor pressures of the reference solution. Most of the isopiestic measurements have been made against potassium chloride or sodium chloride, so that they are limited to the region of water activities greater than 0.75. Robinson[2] has recently surveyed the existing measurements for these two salts at 25°, and correlated them with many others by means of isopiestic measurements. As a result a reasonably reliable set of standard data is now available. For more concentrated solutions, however, the position has been far from satisfactory. Hitherto we have generally used sulfuric acid as the reference substance, as it is obtainable in good purity and can be readily analyzed. Unfortunately however it is not easy to select a "best" set of vapor pressure data for its concentrated solutions at 25°. The most recent measurements are those of Shankman and Gordon[3] by the static method. They pointed out serious discrepancies between their results and those derived from e.m.f. measurements by Harned and Hamer.[4] Recent calculations[5] show that these e.m.f. measurements, made on two different types of cell, with different cell reactions, show a remarkable degree of internal self-consistency in regard to both the water activities and the partial molal heat contents of the water. This makes the choice between them and the direct vapor pressure measurements more difficult. Attempts to check the vapor pressure of sulfuric acid by isopiestic measurements against other solutions have not been helpful; thus the isopiestic ratios of sulfuric acid to sodium hydroxide[6] show that the water activities calculated by Åkerlöf and Kegeles[7] from their e.m.f. measurements on sodium hydroxide are not consistent with either of the above sets of data for sulfuric acid. Gibson and Adams[8] using the same design of apparatus as was later used by Shankman and Gordon, measured the vapor pressures of lithium chloride solutions at 20.28°. Robinson[9] has measured the isopiestic ratios of sulfuric acid to lithium chloride at this temperature, from which he obtains values for sulfuric acid by taking the

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[1] Present address: Chemistry Department, University of Western Australia, Nedlands, W. A.

[1a] R. A. Robinson and D. A. Sinclair, THIS JOURNAL, **56**, 1830 (1934).

[2] R. A. Robinson, *Trans. Roy. Soc. N. Z.*, **75** (II), 203 (1945).

[3] S. Shankman and A. R. Gordon, THIS JOURNAL, **61**, 2370 (1939).

[4] H. S. Harned and W. J. Hamer, *ibid.*, **57**, 27 (1935).

[5] R. H. Stokes, *ibid.*, **67**, 1686 (1945).

[6] R. H. Stokes, *ibid.*, **67**, 1689 (1945).

[7] G. Åkerlof and G. Kegeles, *ibid.*, **62**, 620 (1940).

[8] R. E. Gibson and L. H. Adams, *ibid.*, **55**, 2679 (1933).

[9] R. A. Robinson, private communication, 1945.