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

Leading soln., 0.01 N KCl			Leading soln., 0.01 N KCl		
Indicator	Current, milliamp.	Vol., ml.	Indicator	Current, milliamp.	Vol., ml.
KIO_3	0.11	0.6109	LiCl	0.36	0.6108
KIO_3	.36	.6109	LiCl	.36	.6113
KIO_3	.36	.6112	LiCl	.36	.6114
KIO_3	.36	.6110	Leading soln., 0.01N NaCl		
KIO_3	.36	.6106	$NaIO_3$	0.24	0.6112
KIO_3	.66	.6108	$NaIO_3$	.36	.6109
NaCl	.36	.6106	$NaIO_3$	.56	.6109
NaCl	.56	.6110	Mean 0.6110 ± 0.0002		

In conclusion, we wish to express our thanks to the Advisory Committee on Scientific Research of the University of Toronto for a grant in aid, and to the National Research Council of Canada for the award of studentships to J. W. L. and to J. R. G.

TORONTO, ONTARIO, CANADA

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

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

BY J. R. GRAHAM AND A. R. GORDON

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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 R_f (see Fig. 1 of ref. 1) was set at about one tenth of the resistance across the channel R_o when the leading solution was between the microelectrodes 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-

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(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.

cedure described by Davies, Kay and Gordon[3a]; in the case of the lithium salt, however, the reaction between the bicarbonate and the purified acid required digestion at 60° for several hours. It should be noted that the measured transference numbers recorded in the tables are based on the time intervals between electrode pairs 1–4, 2–4, 1–5 and 2–5 to minimize the percentage error in the elapsed time; the intervals 2–3 and 3–4 were only employed to detect any significant change in boundary velocity with boundary movement. Volume corrections for the concentrations employed here are entirely negligible, and solvent corrections amount at most to a few units in the last decimal place.

While the anion transference numbers so obtained satisfied all internal criteria for a stable boundary—absence of "progression," independence of current and of initial indicator concentration over an appreciable concentration range[6]—we were unable to find suitable cation indicators. Falling 0.002 N NaCl/LiCl boundaries gave traces approximately ten times as long as those for the anion boundaries, and the duration of the "event" tended to increase as the boundary moved down the channel. Since the duration is primarily a function of the spread of the a.c. current lines,[1] rather than of physical boundary thickness, this raised serious doubts as to whether a boundary in the usual sense of the term existed at all, in spite of the fact that the computed t_+ was consistent within half a per cent. or so with the known value of t_-. If one assumes that cations are more highly solvated than anions, a possible explanation is that the random passage of a cation across the boundary would produce a more serious disturbance than would a similar passage of an anion across an anion boundary, particularly when, as is the case here, density stability is slight. Dodecylammonium chloride as indicator showed similar behavior, while hyamine 1622 chloride with a rising boundary showed an erratic variation of apparent transference number with boundary movement and again a steady increase in the length of the trace. Cadmium chloride as an indicator for rising cation boundaries was eliminated since it proved from rough conductance measurements to be such a weak electrolyte that it was impossible to maintain even an approximately constant direct current during a run.

It should also be noted that when rising 0.0005 N NaCl boundaries with triiodobenzoate as indicator were studied, while the traces were not significantly different from those obtained at higher concentrations, the apparent t_- varied erratically as the boundary moved up the channel. This was unquestionably due in part to difficulty in setting the shearing stopcock correctly, since the same behavior was noted at higher concentrations with a definitely incorrect setting; possibly a more sophisticated method of forming the junction such as that employed by Longsworth[7] might eliminate this difficulty, although the possibility of leakage with his apparatus, even with the lithium stearate lubricant[3a] used here, might be serious. A second possibility is that at high dilutions with consequently slight density stability, turbulent electroendosmotic flow may disturb the boundary, the effect being more pronounced the more dilute the solution. If this be the case, it puts a lower limit to the concentration at which moving boundary measurements are possible.

Results

As an example of the reproducibility of the measurements, the individual experimental results for 0.001 N NaCl are listed in Table I. Each measurement involves a solution prepared by dilution from a different stock solution[8]; the concentration of the NaCl solutions differed only negligibly from 0.001 N as far as variation of t_- with concentration was concerned. The first line of the table gives the initial value of the indicator concentration, the second the current in microamperes and the third the transference number corrected for solvent conductance. It is apparent that within experimental precision t_- is independent of initial indicator concentration and of current; it is also evident (and this is generally true of the results obtained) that the reproducibility of the measurements is inferior to that obtained with water and methanol as solvents.

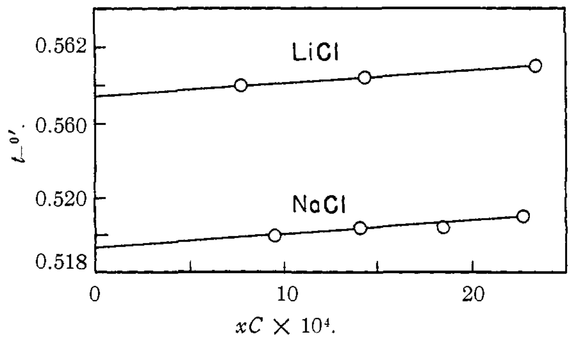

Fig. 1.—The Longsworth function plotted against ionic concentration.

TABLE I

TRANSFERENCE NUMBERS FOR 0.001 N NaCl AT 25°

$10^4C^\circ_i$	9.5	10.5	11.0	9.5	9.5	9.5	10.0
I, µamp	12	17	17	18	18	19	22
t	0.5208	0.5202	0.5205	0.5199	0.5204	0.5208	0.5204

The results for the other solutions are summarized in Table II. The first column gives the concentration of the leading solution in equivalents/liter, the second the number of independent measurements, the third the current range in microamperes, and the fourth the mean value of t_- corrected for solvent conductance; the figure in brackets indicates the mean absolute deviation of the individual results from the average as printed. The fifth column gives the degree of dissociation of the ion pairs,[9] and the sixth the value of the modified Longsworth function[7] $t_-^{0\prime}$, computed on the basis of ionic rather than stoichiometric concentration

TABLE II

TRANSFERENCE NUMBERS FOR NaCl AND LiCl IN ETHANOL AT 25°

$10^4 \times C$	No. of meas.	I, µamp.	t_-	x	$t_-^{0\prime}$
		Leading soln., NaCl			
10	7	12–22	0.5204(3)	0.954	0.5190
15	4	16–26	.5209(3)	.938	.5192
20	7	22–46	.5212(3)	.925	.5192
25	2	42	.5218(1)	.913	.5195
		Leading soln., LiCl			
9	2	12–16	0.5657(3)	0.968	0.5610
15	2	18–31	.5674(1)	.954	.5612
25	5	28–42	.5698(3)	.937	.5615

$$t_-^{0\prime} = (t_-\Lambda' + \sigma(xC)^{1/2})/(\Lambda' + 2\sigma(xC)^{1/2}) \qquad (1)$$

where $\Lambda' = \Lambda_0 - (\vartheta\Lambda_0 + 2\sigma)(xC)^{1/2}$, and ϑ and σ are the Debye–Onsager coefficients 1.330 and 44.66, respectively.[4]

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(6) To take the case of 0.002 N NaCl as an example, the initial indicator concentration was varied from 0.0017 N, approximately the Kohlrausch value, to 0.002 N without appreciable effect on the measured t_-.

(7) L. G. Longsworth, THIS JOURNAL, **54**, 2741 (1932).

(8) In computing volume from mass concentrations, the density data of ref. 4 were employed.

(9) The values of x were obtained from the values of ΛS of Table II of ref. 4 except for 0.0009 and 0.0025 N, when they were computed by means of eq. 4 of ref. 4 from the known value of the dissociation constants.

Discussion

In Fig. 1, the modified Longsworth function is plotted against ionic concentration for the two salts, and it is at once evident that it is linear in xC well within experimental precision, thus permitting an unambiguous extrapolation to infinite dilution. The resulting values of t_+^0 are 0.5187 and 0.5607 for NaCl and LiCl, respectively. The fact that such an extrapolation is possible here is encouraging, since it suggests that limiting transference numbers may be obtained in this way with other solvents where ion pair formation occurs without the necessity of making measurements at fantastic dilutions.

It should also be noted, in contrast to results in aqueous solution, that although the transference numbers are greater than one half, the limiting slope is approached in both cases from above. Potassium chloride in methanol showed similar behavior,[3a] and we believe that about the only generalization that can be made, based on the results in the three solvents, is that the deviation from the limiting law at finite concentrations is numerically least when the transference numbers are close to one-half.

Smisko and Dawson[10] have recently reported transference numbers for KCNS solutions in ethanol, based on measurements in an autogenic cell; a discussion of the correlation of their results with ours, and of the mutual consistency of our NaCl and LiCl data, is reserved for the accompanying paper.[4] Suffice it to say here that while the ethanol data are not of the precision obtained with water and methanol as solvents, they nevertheless fix a limiting conductance for chloride ion in ethanol which is probably reliable to a few hundredth's of a conductance unit.

In conclusion we wish to express our thanks to the National Research Council of Canada for the award to J. R. G. of two studentships.

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

TORONTO, ONTARIO, CANADA

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

Equivalent and Ionic Conductances for Lithium, Sodium and Potassium Chlorides in Anhydrous Ethanol at 25°

BY J. R. GRAHAM, G. S. KELL AND A. R. GORDON

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The conductance of lithium, sodium and potassium chlorides in anhydrous ethanol has been determined for concentrations from 0.0001 to 0.0020 N. All three salts show definite ion-pair formation, the dissociation constants for the pairs (determined by the Shedlovsky procedure) being greatest as might be expected for LiCl and least for KCl. In conjunction with the transference numbers, the LiCl and NaCl results yield a limiting conductance for chloride ion of 21.85; this is probably reliable to 0.02 or 0.03 conductance units, and consequently should fix other limiting ion conductances within similar limits. The correlation of the ion conductances in ethanol with those in methanol and water is discussed.

If the transference measurements of the preceding paper[1] are to yield information as to ion conductances in ethanol solution, it is obvious that reliable equivalent conductances are necessary. Previous conductance studies of the alkali halides in ethanol have given an extraordinarily wide variation in conductance values. To take the case of Λ_0 for NaCl as an example, Goldschmidt and Dahll[2] give 46.5, Thomas and Marum[3] 43.0, and Barak and Hartley[4] 42.5. Admittedly, some of the spread is due to the methods of extrapolation employed (see below) but nonetheless such results indicate the necessity for measurements carried out under conditions much more carefully controlled than those obtaining in the earlier work. Here we report conductance data at 25° for lithium, sodium and potassium chlorides.

Experimental

The measurements were effected by the direct current method, developed in this Laboratory, employing the cells previously used with methanol[5] as solvent; their calibrations are based on the Jones and Bradshaw 25° 0.01 demal standard.[6] Bias potentials between the probe electrodes were in general no greater than in water and methanol, but great care had to be exercised, particularly in the more dilute solutions, to avoid the passage of any appreciable current through the probes as the result of significant off-balance in the initial setting of the potentiometer; if this occurred, the probes behaved erratically and had to be reanodized. It was also found impossible to determine the solvent conductance for ethanol by the direct current method; it was accordingly determined in a conventional conductance cell (cell factor 0.1005 cm.$^{-1}$) with an alternating current bridge. Work in methanol[5a] had shown that the two methods were in agreement to better than 1%.

The principal difficulty with ethanol is its preparation as a solvent with, at the same time, low water content and low specific conductance. The starting material was a Gooderham and Worts "anhydrous" alcohol, rectified by ethylene glycol distillation; it contained approximately 0.25% water, 0.01% esters and traces of aldehydes and acids, and its specific conductance was of the order 6×10^{-8} mho/cm. The procedure finally adopted was to reflux 4.5 l. of the starting material overnight under a 30-cm. Allihn condenser (condenser temperature 30°) while a slow stream of nitrogen (from which traces of oxygen, carbon dioxide and water vapor had been removed) bubbled through the charge; this removed the low-boiling impurities, which were taken off by a slight suction applied at the top of the condenser. The subsequent distillation was carried out under a slight positive pressure of the purified nitrogen, only a middle cut of 3 l. being retained. While this procedure left the water content unaltered, the specific conductance of the distillate was in general $0.5\text{–}0.8 \times 10^{-8}$ mho/cm.

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[1] J. R. Graham and A. R. Gordon, THIS JOURNAL, **79**, 2350 (1957).

[2] H. Goldschmidt and P. Dahll, *Z. physik. Chem.*, **114**, 1 (1925).

[3] L. Thomas and E. Marum, *ibid.*, **143**, 191 (1929).

[4] M. Barak and H. Hartley, *ibid.*, **A165**, 272 (1933).

[5] (a) J. P. Butler, H. I. Schiff and A. R. Gordon, *J. Chem. Phys.*, **19**, 752 (1951); (b) R. E. Jervis, D. R. Muir, J. P. Butler and A. R. Gordon, THIS JOURNAL, **75**, 2855 (1953).

[6] G. Jones and B. B. Bradshaw, *ibid.*, **55**, 1780 (1933).