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THE TRANSFERENCE NUMBERS AND THE DEGREE OF SOLVATION OF THE IONS OF LITHIUM CHLORIDE IN CERTAIN ALCOHOLS

J. N. PEARCE AND W. G. EVERSOLE

The low migration velocities of some of the ions of the elements of low atomic weight, as well as the many other phenomena that are not explained by simple electrolytic dissociation, have led to the belief that the ion does not lead an independent existence in the solution, but is solvated, or combined chemically with one or more molecules of the solvent.

If the molecules of the solvent are carried by the ions during electrolysis, there should be a migration of both solvent and solute when the current is passed through the solution. The direction and the extent of this migration can be determined if it is possible to have present in the solution a small amount of a third substance which will neither combine with the ions nor migrate with the current. By referring the concentrations of both the electrolyte and the solvent to this "reference substance" the extent to which the solvent has been transported by the ions can be calculated.

Several attempts have been made to apply this principle to aqueous solutions of electrolytes. Nernst¹ and his students studied solutions of sulphuric, hydrochloric, hydrobromic and nitric acids, using boric acid as the reference substance. Lobry de Bruyn² electrolyzed solutions of silver nitrate between silver electrodes with methyl alcohol for reference. Morgan and Kanolt³ used silver nitrate in mixtures of alcohol and water. The first successful attempt was made by Büchbock.⁴ Working with solutions of hydrochloric acid containing mannite and resorcinol as reference substances he was able to show that water is transported from the anode to the cathode during the electrolysis. With his apparatus he could divide the solution into three portions and he was able to obtain a satisfactory measure of the migration of both solute and solvent.

¹ Nernst, Gerrard and Oppermann, *Nachr. Gesells. Wissensch., Göttingen*, 56, 86 (1900).

² Lobry de Bruyn, *Rec. trav. chim.*, 22, 430 (1903).

³ Morgan and Kanolt, *J. Amer. Chem. Soc.*, 28, 572 (1906).

⁴ Büchbock, *Z. physik. Chem.*, 55, 563 (1906).

The most valuable contribution to this field has been made by Washburn.⁵ His apparatus was of a highly improved design which permitted the removal of the solution in five separate portions. The analysis of the three middle portions shows definitely whether or not any mixing has taken place between the electrode portions and the middle portions during the passage of the current. In this series of experiments he determined the transference numbers of the ions of the chlorides of lithium, sodium and potassium, using raffinose as the reference substance. He found that in all cases there is a migration of the solvent from the anode to the cathode chamber, and he was able to determine with considerable accuracy the relative degree of hydration of the ions. By assuming various degrees of hydration for the chloride ion he was able to estimate the most probable absolute values for the hydration of the potassium, sodium and lithium ions. In addition to this he recalculated the results of Büchbock for hydrochloric acid and estimated the degree of hydration of the hydrogen ion. The degree of hydration of the positive ions was found to increase in the order: H^+ , K^+ , Na^+ , Li^+ .

Since the solvent carried from the anode to the cathode by the cation tends to dilute the solution at the cathode and to concentrate the solution at the anode, the ordinary transference number, which is calculated on the assumption of an absolutely stationary solvent, is not the true transference number of the ion. To obtain the true transference number it is necessary to add to the apparent change in the amount of salt in the electrode portion the amount of salt originally associated with the quantity of solvent which has been carried into, or out of, the electrode chamber by the ions. This true transference number is obtained directly if the change in the concentration of the electrolyte is referred to the reference substance which is present at the end of the electrolysis in the same amount as at the beginning. In the same way the change in the ratio of the solvent to the reference substance gives the change produced in the actual amount of solvent in the electrode chamber during the electrolysis. Washburn has calculated both the ordinary and the true transference numbers and has derived a mathematical relation connecting the two quantities. These will be discussed later.

The purpose of the present investigation is simply an attempt to apply this method to the determination of the transference numbers of the ions of lithium chloride in solvents other than water.

⁵ Washburn, J. Amer. Chem. Soc., 31, 322 (1909).

Such a problem should involve not only the determination of the magnitude of the solvation of the two ions in different solvents, but also the determination of the influence of certain properties of the solvents upon the magnitude of solvation. It should be mentioned that while the difficulties accompanying the determination of accurate transference values in aqueous solutions are numerous they are in a way only trivial in comparison with those encountered when one is working with volatile hygroscopic solvents.

APPARATUS AND MATERIALS

The chief disturbing element in the determination of transference numbers is the mixing of the solution around the electrodes with the remainder of the solution. This may be caused by diffusion, by convection currents caused by local heating while the current is passing, or by currents set up when the different portions of the solution are separated from each other. The Washburn apparatus was designed to reduce these effects to a minimum, and it was therefore selected for this investigation. A detailed description of the apparatus and of the technique involved is given in the original paper by Washburn.

The whole apparatus was immersed in a large Freas thermostat and electrically maintained at $25^{\circ} \pm 0.01$. To detect any possible current leakage the apparatus was placed between two long silver titration coulometers; in no case were leaks detectable. Electrical connection was made through the coulometers with the source of current and the voltage was adjusted to give a current of approximately 5 m. a. Satisfactory results were not obtainable when the current applied exceeded 8 m. a.

REFERENCE SUBSTANCE. Camphor is quite soluble in the alcohols used and it was found to possess to a marked degree all the properties which such a substance should have. A solution of the camphor in each of the pure solvents was placed in the transference apparatus and subjected to a potential of 110 volts for 13 hours. No change in the concentration of the camphor at either electrode could be detected by the polariscope. To test the substance further a solution of camphor and lithium chloride in the solvent under investigation was carefully analyzed and placed in the apparatus. A regular transference experiment was then made, except that the solution was not separated in different portions at the end of the electrolysis. The entire solution was thoroughly mixed and then analyzed. No change could be noted in the total amount of camphor present in the solution.

SOLVENTS. The solvents chosen were methyl-, ethyl- and n-

propyl alcohol. Except for slight differences in the preliminary dehydration the treatment was the same. The alcohols were finally refluxed for 12 to 15 hours over metallic calcium and fractionally distilled. These distillates were then refluxed for several hours with small quantities of pure dry silver nitrate crystals and again fractionally distilled. Only the constant boiling middle portions were retained in each distillation. In every case the solvents were carefully protected by efficient drying trains.

LITHIUM CHLORIDE. Pure lithium carbonate was prepared by repeated precipitation from nitrate solution by ammonium carbonate. The product was then dissolved in pure nitric acid and recrystallized twice as the nitrate, and finally heated in a platinum dish to remove the last traces of ammonium nitrate. The nitrate was converted into the chloride when needed by passing a stream of pure hydrogen chloride gas into a strong hot solution of the nitrate contained in a flask of fused silica. When a test for nitrate could no longer be obtained the reaction flask was placed in an oil bath at 200° and the solution was evaporated to dryness in a stream of dry hydrogen chloride gas. After the last traces of moisture had been driven out the residue was heated for two hours at the same temperature in a stream of pure dry hydrogen to remove the last traces of hydrogen chloride, and the residue was then dissolved in the pure alcohol. The resulting stock solution of alcoholic lithium chloride gave a perfectly neutral solution when mixed with water.

CAMPHOR. A pure sample was twice resublimed and the resulting product was recrystallized from pure dry ether.

ANALYTICAL METHODS

The concentration of the camphor was determined by means of a half-shadow Schmidt and Haensch polariscope which could be read with vernier to 0.01° . The polarizing tube was surrounded by a water jacket through which water was caused to circulate rapidly from a large water thermostat electrically controlled at $25^{\circ} \pm 0.03$. Sodium light from pure sodium carbonate was used for illumination. The average deviation of a set of ten readings was less than 0.01° , and the value of the rotation of a given solution was taken as the mean of ten consecutive readings.

The lithium chloride content of the solutions was determined by titration with a carefully standardized solution of silver nitrate. In making a transference experiment the results of the run were discarded if the chloride contents of the three middle portions failed to check each other within 0.03 percent.

The specific gravity determinations were made by means of 20 c.c. Ostwald-Sprengel pycnometers, each provided with two ground glass caps. In weighing these as well as in weighing other objects a counterpoise was used. The weights were carefully calibrated against a set of quartz weights standardized by the Bureau of Standards and all weighings have been reduced to vacuo.

NOTATION

The various symbols used are identical with those given by Washburn. For the sake of brevity in the following discussion we shall give here only those which are most frequently used.

| | |
|----------------------------|---|
| d , | density of the solution at 25° referred to water at 4°. |
| α , | the angular rotation produced by the solution at 25°. |
| $[A]$, | the specific rotation of the camphor in the solution at 25°. |
| P_e , | percent of electrolyte in the solution. |
| P_c , | percent of camphor in the solution. |
| P_a , | percent of alcohol in the solution. |
| $\Delta m_e, \Delta n_e$, | increase in grams and mols, resp., of lithium chloride in the electrode portion. |
| $\Delta m_a, \Delta n_a$, | increase in grams and mols, resp., of alcohol in electrode portion. |
| N , | the number of equivalents of electricity passed through the solution. |
| T_t , | true transference number. |
| T_o , | ordinary transference number. |
| A, C , | anode portion and cathode portion, resp. |
| M_a, M, M_c , | anode middle, middle, and cathode middle portions, resp. |
| $\Delta n_a/F$, | number of mols of solvent transferred from anode to cathode per faraday of electricity. |
| N_a^{Li} , | number of alcohol molecules combined with one lithium ion. |
| N_a^{Cl} , | number of alcohol molecules combined with one chloride ion. |

The final results of an experiment can be summed up in two equations:

$$T_t^{Li} N_a^{Li} - T_a^{Cl} N_a^{Cl} = \Delta n_a/F \quad (A)$$

$$N_a^{Li} = \frac{\Delta n_a/F}{T_t^{Li}} + \frac{T_t^{Cl}}{T_t^{Li}} N_a^{Cl} \quad (B)$$

The first two terms in (A) are evidently the numbers of mols of solvent carried by the cation and anion, respectively; the difference, therefore, $\Delta n_a/F$, is the net amount of solvent carried by the two ions when one faraday of electricity is passed through the solution. Equation (B) which is obtained directly from (A) by solving for N_a^{Li} , expresses the number of alcohol molecules combined with the lithium ion as a function of the number combined with the chloride ion.

EXPERIMENTAL RESULTS WITH METHYL ALCOHOL

The rotation produced by camphor was first accurately determined for several solutions of definitely known composition by weight. The specific rotation was then calculated by means of the usual relation,

$$[A]_D^{25} = \frac{100\alpha}{P_c \cdot d} = \frac{50\alpha}{P_c \cdot d} \quad (\text{since } l = 2 \text{ dcm.}) \quad (1)$$

The linear relation which exists between the specific rotation of the camphor and its concentration in methyl alcohol is given by the equation,

$$[A]_{\text{calc.}} = 38.68 + 0.1375P \quad (2)$$

This relation holds with considerable accuracy for camphor concentrations less than 16 percent. The observed values of $[A]$ and those thus calculated by (2) are given in Table I.

TABLE I
THE SPECIFIC ROTATION OF CAMPHOR IN METHYL ALCOHOL

| P_c | d | α | $[A]$ obs. | $[A]$ calc. |
|--------|--------|----------|------------|-------------|
| 4.735 | 0.7955 | 2.96 | 39.29 | 39.33 |
| 6.974 | 0.7988 | 4.42 | 39.68 | 39.64 |
| 11.190 | 0.8016 | 7.20 | 40.13 | 40.22 |
| 14.53 | 0.8114 | 9.61 | 40.76 | 40.68 |
| 16.33 | 0.8133 | 10.85 | 40.84 | 40.92 |

To determine the effect of lithium chloride upon the specific rotation of camphor in methyl alcohol suitable amounts of camphor were weighed directly into smaller glass stoppered flasks and dissolved in weighed amounts of lithium chloride solution of known composition. The rotation of the solutions were then determined and the values of $[A]_{\text{obs}}$ and $[A]_{\text{calc.}}$ were calculated by means of (1) and (2). The results are given in Table II. The difference between the corresponding and observed values gives the change in the specific rotation of the camphor produced by the lithium chloride present in the solution. This effect can be expressed in the form:

$$[A]_{\text{calc.}} - [A]_{\text{obs.}} = a \cdot P_e, \text{ or } a = \frac{[A]_{\text{calc.}} - [A]_{\text{obs.}}}{P_e} \quad (3)$$

where a is some function of P_e which must be determined. Combining (3) with (1) and (2), we obtain,

$$a = \frac{38.68 + 0.1375P_c - \frac{50\alpha}{P_c d}}{P_e} \quad (4)$$

By clearing of fractions, transposing and collecting terms, and solving the resulting quadratic for P_e we obtain finally the relation:

$$P_e = \frac{-(38.68 - a \cdot P_e) + \sqrt{(38.68 - a \cdot P_e)^2 + 27.5a/d}}{0.275} \quad (5)$$

Equation (5) gives the concentration of the reference substance in terms of α , P_e , d and a . The first three of these quantities can be determined directly. The value of a for a given solution is read from a large scale plot of the values of a (3), obtained from Table I, against the corresponding values of P_e . The equation for the curve obtained by this plot is,

$$a = \frac{-7.587 + \sqrt{180.74 - 20.497P_e}}{10.248},$$

and this also may be used in calculating the values of a .

TABLE II
THE EFFECT OF LITHIUM CHLORIDE ON THE SPECIFIC ROTATION OF CAMPHOR IN METHYL ALCOHOL

| P_e | P_e | d | α | [A] obs. | [A] calc. | P_e calc. |
|--------|-------|--------|----------|----------|-----------|-------------|
| 14.960 | 6.060 | 0.8568 | 10.25 | 39.99 | 40.74 | 14.957 |
| 10.470 | 4.240 | 0.8338 | 6.90 | 39.54 | 40.12 | 10.466 |
| 7.246 | 2.935 | 0.8203 | 4.61 | 38.77 | 39.66 | 7.247 |
| 4.986 | 2.020 | 0.8107 | 3.05 | 37.73 | 39.44 | 4.996 |
| 3.428 | 1.389 | 0.8031 | 2.05 | 37.23 | 39.12 | 3.418 |

The percentage of camphor in the various solutions have been recalculated by the aid of (5) and the results are placed in the last column of Table II. The agreement is all that can be asked. A further test of the validity of (5) was made on a solution the data for which had not been used in deriving the equation. This solution contained 1.778 p.c. of LiCl and 10.925 p.c. of camphor; its density was 0.8200 and the mean angle of rotation was 7.205° . The value of α was found to be 1.043; the percent of camphor calculated from (5) was 10.929. Equation (5) was, therefore, considered sufficiently accurate for calculating the concentration of the reference substance.

THE EFFECT OF LITHIUM CHLORIDE ON THE SPECIFIC ROTATION OF CAMPHOR IN OTHER ALCOHOLS

Since the concentration range of the reference substance used in the ethyl alcohol solutions is kept within rather narrow limits when the transference experiments are carried out, the specific rotation of camphor in ethyl alcohol was determined only for a

limited range of concentrations. As a result, a constant value was obtained for the specific rotation of camphor. The mean of the values obtained from a number of independent determinations (42.540) was taken as the value of the specific rotation of camphor in ethyl alcohol for the concentration range of 1.5 to 4.0 percent.

The effect of lithium chloride on the specific rotation was determined by measuring the rotation produced in solutions of known composition by weight. The results are recorded in Table III.

TABLE III
THE EFFECT OF LITHIUM CHLORIDE ON THE SPECIFIC ROTATION OF CAMPHOR IN ETHYL ALCOHOL

| P_c | P_e | d | α° | $[A]_D^{25}$ |
|--------|--------|--------|------------------|--------------|
| 4.155 | 1.390 | 0.8056 | 2.839 | 42.40 |
| 3.057 | 3.5465 | 0.8194 | 2.113 | 42.18 |
| 2.068 | 5.103 | 0.8282 | 1.439 | 42.01 |
| 0.9459 | 2.335 | 0.8073 | 0.646 | 42.30 |

A straight line is obtained when the values of $[A]$ are plotted against the corresponding values of P_e . The equation of this line is

$$[A] = 42.540 - 0.1034 P_e \tag{7}$$

In the transference experiments the concentrations of the camphor were calculated by means of the usual formula :

$$P_c = \frac{100\alpha}{[A] d l} \tag{8}$$

A similar series of determinations was made of the specific rotation of camphor in pure n-propyl alcohol and in solutions containing varying amounts of lithium chloride. The results are given in Table IV.

TABLE IV
THE EFFECT OF LITHIUM CHLORIDE ON THE SPECIFIC ROTATION OF CAMPHOR IN n-PROPYL ALCOHOL

| P_c | P_e | d | α° | $[A]_D^{25}$ |
|--------|--------|--------|------------------|--------------|
| 3.6525 | 0.0000 | 0.8047 | 2.604 | 44.299 |
| 3.153 | 0.7245 | 0.8086 | 2.247 | 44.07 |
| 2.832 | 1.3707 | 0.8128 | 2.021 | 43.89 |
| 2.309 | 1.8364 | 0.8164 | 1.649 | 43.75 |
| 3.367 | 4.0754 | 0.8333 | 2.417 | 43.07 |
| 3.452 | 4.1784 | 0.8341 | 2.479 | 43.05 |
| 3.485 | 4.2189 | 0.8345 | 2.503 | 43.03 |

Here again the plot of the values of $[A]$ against the corresponding values of P_e is a straight line for which the equation was calculated to be,

$$[A] = 44.299 - 0.3000 P_e \tag{9}$$

The concentration of the reference substance in the transference experiments was obtained by substituting the proper values in equation (3).

The influence of the three solvents and of lithium chloride upon the specific rotation of camphor is accurately given by equations (2), (7) and (9). The specific rotation in the pure solvent is least in methyl alcohol and greatest in propyl alcohol. The influence of the salt is perhaps best shown by differentiating the above equations with respect to P_e . When this is done we find that the ratio, $d[A]/dP_e$, is positive in methyl alcohol, whereas it is negative in the remaining alcohols, the negative coefficient being greater in the propyl alcohol.

RESULTS OF THE TRANSFERENCE EXPERIMENTS

Transference experiments were carried out with various concentrations of lithium chloride in each of the three alcohols. For the sake of brevity we shall give only the experimental data for a typical determination in propyl alcohol. (Table V).

TABLE V

COMPOSITION OF SOLUTION: 0.940 MOLLS OF LITHIUM CHLORIDE AND 0.21 MOLLS CAMPHOR IN 1000 GRAMS OF PROPYL ALCOHOL; APPLIED E.M.F., 110 VOLTS; CURRENT, 3 MILLIAMPERES; DURATION OF EXPERIMENT 11.5 HOURS; EQUIVALENTS OF ELECTRICITY PASSED, 0.0009716

| | A | Ma | M | Mc | C |
|-------------------------|-----------|-------------|--------|-------------|-----------|
| M_e | 41.400 | | | | 41.530 |
| $\alpha^{0'}$ | 2.189 | | 2.183 | | 2.177 |
| d | 0.8317 | | 0.8318 | | 0.8319 |
| P_e | 3.675 | ± 0.001 | 3.709 | ± 0.001 | 3.742 |
| $[\alpha]_D^{25}$ | 43.200 | | 43.195 | | 43.190 |
| P_c | 2.977 | | 2.969 | | 2.961 |
| P_a | 93.348 | | 93.322 | | 93.297 |
| Δm_e | 0.0182 | | | | 0.0181 |
| Δm_a | 0.0970 | | | | 0.0960 |
| Δn_e | 0.0004292 | | | | 0.0004269 |
| Δn_a | 0.00161 | | | | 0.00160 |
| $\Delta n_a/\Delta n_e$ | 3.76 | | | | 3.74 |
| $\Delta n_a/F$ | 1.66 | | | | 1.64 |
| T_t^{Li} | 0.441 | | | | 0.439 |
| T_t^{Cl} | 0.559 | | | | 0.561 |
| T_o^{Li} | 0.338 | | | | 0.338 |

The results here given are typical of those obtained in the various experiments. The conductivity of solutions in these solvents is relatively very low and hence it was impossible to use currents

greater than a few milliamperes. The concentration changes produced at the electrodes are, therefore, very small and small errors are greatly magnified in making the subsequent calculations. Considering the great difficulties involved, the agreement between the transference numbers calculated from the concentration changes at the two electrodes is satisfactory. Obviously, some values are in error and these errors, if included are sufficient to produce a much larger error in the magnitudes which we wish to calculate, namely, the relative degree of solvation of the ions in the three solvents, and in the effect of change in the concentration of the salt upon these relative values.

In order to compare the true and ordinary transference numbers and the degree of solvation of the ions in the three solvents at the same concentration, the values of the quantities thus determined were each plotted against the corresponding molal concentrations of the lithium chloride, and the most representative straight lines were drawn through the points. The values of T_e^{Li} , T_t^{Li} and $\Delta n_a/F$ for round concentrations were read directly from these plots. The data thus collected is given in Tables VI, VII and VIII.

TABLE VI

THE TRANSFERENCE NUMBERS AND THE DEGREE OF SOLVATION OF THE IONS OF LITHIUM CHLORIDES IN METHYL ALCOHOL

| M | T_o^{Li} | T_t^{Li} | $\Delta n_a/F$ | N_a^{Li} |
|-----|------------|------------|----------------|-------------------------|
| 0.4 | 0.330 | 0.453 | 10.89 | 24.04 + 1.20 N_a^{Cl} |
| 0.5 | 0.312 | 0.446 | 9.95 | 22.31 + 1.24 .. |
| 0.6 | 0.295 | 0.438 | 8.99 | 20.53 + 1.28 .. |
| 0.7 | 0.278 | 0.430 | 8.03 | 18.67 + 1.32 .. |
| 0.8 | 0.260 | 0.425 | 7.08 | 16.66 + 1.35 .. |

TABLE VII

THE TRANSFERENCE NUMBERS AND THE DEGREE OF SOLVATION OF THE IONS OF LITHIUM CHLORIDES IN ETHYL ALCOHOL

| M | T_o^{Li} | T_t^{Li} | $\Delta n_a/F$ | N_a^{Li} |
|-----|------------|------------|----------------|------------------------|
| 0.4 | 0.350 | 0.403 | 3.33 | 8.26 + 1.48 N_a^{Cl} |
| 0.5 | 0.347 | 0.401 | 3.03 | 7.55 + 1.49 .. |
| 0.6 | 0.340 | 0.400 | 2.75 | 6.87 + 1.50 .. |
| 0.8 | 0.331 | 0.398 | 2.18 | 5.48 + 1.51 .. |
| 1.0 | 0.320 | 0.393 | 1.62 | 4.12 + 1.54 .. |

To calculate the number of mols of any alcohol carried by one mol of lithium ions referred to the number of mols of alcohol

carried by the chloride ion it is only necessary to substitute the proper values in equation (2),

$$N_a^{\text{Li}} = \frac{\Delta n_a / F}{T_t^{\text{Li}}} + \frac{T_t^{\text{Cl}}}{T_t^{\text{Li}}} N_a^{\text{Cl}}$$

These calculated values are to be found in the last columns of Tables VI, VII and VIII.

TABLE VIII
THE TRANSFERENCE NUMBERS AND THE DEGREE OF SOLVATION OF THE IONS OF LITHIUM CHLORIDES IN PROPYL ALCOHOL

| M | T_o^{Li} | T_t^{Li} | $\Delta n_a / F$ | N_a^{Li} |
|-----|-------------------|-------------------|------------------|------------------------------|
| 0.4 | 0.320 | 0.410 | 3.19 | $7.80 + 1.44N_a^{\text{Cl}}$ |
| 0.5 | 0.315 | 0.408 | 2.92 | $7.16 + 1.45 \dots$ |
| 0.6 | 0.309 | 0.404 | 2.64 | $6.53 + 1.47 \dots$ |
| 0.8 | 0.298 | 0.400 | 2.08 | $5.20 + 1.50 \dots$ |
| 1.0 | 0.287 | 0.397 | 1.52 | $3.83 + 1.52 \dots$ |

DISCUSSION

When solutions of camphor and lithium chloride in these solvents are electrolyzed between a silver anode and a silver chloride cathode there is an increase in the concentration of the camphor at the anode and a corresponding decrease at the cathode. Since camphor dissolved in the pure solvents does not migrate through the solution when it is subjected to a potential, this change in the concentration of the camphor in the presence of the lithium chloride can only be explained on the basis of one of the following hypotheses. (1) Molecules of camphor are combined with chloride ions and are carried by them from the cathode to the anode during the passage of the current through the solution, or (2) that molecules of the solvent are combined with the lithium ions and are carried by them from the anode to the cathode. In either case there should be an apparent increase in the concentration of the camphor at the anode and a decrease at the cathode. Washburn has shown that for aqueous solutions of the alkali chlorides the first assumption is not sufficient since it requires that the result shall depend upon the concentration of the chloride ion, and shall be independent of the nature of the cation. Experiments with the alkali chlorides showed that this is not at all the case. Further, in order that the hypothesis shall explain the facts, it is necessary to assume not only a complex with the chloride ion, but also the formation to a less extent of a complex with the cation, the amount of the latter complex varying with the nature of the cation, and

increasing in the series — Li^+ , Na^+ , K^+ . An increase in the concentration of the reference substance will affect the two ion-(ion-solute) equilibria differently, the chloride ion complex increasing at a more rapid rate than the cation complex. The mobilities of two ions will not change at the same rate, and the conductivity of the alkali chloride solution with varying concentration of the reference substance should be some other function than a linear one. He cites the work of Masson and Martin⁶ on the conductivity of hydrochloric acid solutions containing sucrose which showed no indication of any combination of sucrose with the ions, the only effect of the sucrose being to increase the viscosity of the medium and to retard both ions. In the light of these facts Washburn considers that the first assumption may be considered as eliminated in so far as any considerable effect is concerned.

This leaves us free to accept the second assumption, namely, that the migration of the solvent with the current is due to the formation of a solvate complex between the solvent and one, or both, of the ions. If this assumption is true, the magnitude of the effect should depend to a large extent on the solvent, since it is one of the reacting substances. The number of molecules of the different alcohols combined with one lithium ion should be expected to decrease with increasing complexity of the solvent molecules, and this has been found to be an experimental fact.

The data in the second and third columns of Tables VI, VII and VIII show that in a given solvent the values of both the ordinary and true transference numbers of the lithium ion decrease with increase in the concentration of the lithium salt. The change in the relative migration velocity of the lithium ion with change in concentration is in the same direction as in aqueous solutions, but the change in the alcoholic solutions is greater. This is probably due to the relatively higher viscosity of alcoholic solutions of lithium chloride, even in only moderately concentrated solutions, and to the subsequent slowing down of the heavier solvated lithium ion. This decrease in the migration velocity of the lithium ion is no doubt opposed but not entirely overcome by the lower degree of solvation and the consequent smaller ion volume in the more concentrated solutions. It is possible also that the smaller transference number of the lithium ion at higher concentrations may be due in some measure to a slight polymerization of the salt molecules and subsequent ionization to form Li^+ and LiCl_2^- ions. The migration of the LiCl_2^- ion from the cathode to the anode during

⁶ Masson and Martin, 79, 707 (1901).

electrolysis would oppose the change in the concentration of the lithium chloride at the electrodes which is produced by the normal migration of the lithium ion.

The data in the last two columns of the above tables show that the relative degree of solvation of the lithium ion and the number of mols of solvent carried through the solution per one faraday of electricity decreased in a given solvent as the concentration of the lithium chloride is increased. This is in complete accord with the fact that the ions in an aqueous solution are solvated to a greater extent in the more dilute solutions.

In this work the transference numbers of the lithium ion were determined for six different concentrations in methyl alcohol, seven in ethyl, and four in propyl alcohol. The data for the round concentrations were interpolated from that part of the curve lying between the maximum and minimum concentrations employed. Washburn has determined the transference number of the lithium ion in an aqueous solution of lithium chloride at one concentration only, (1.2 M). A comparison of the relative degree of solvation of the lithium ion in water and the three alcohols and of the number of mols of solvent transferred during the passage of one faraday of electricity in approximately 1.0 M solutions is given in Table IX.

TABLE IX

| SOLVENT. | M. | $\Delta n_s/F$ | N_s^{Li} |
|----------|-----|----------------|------------------------------------|
| Water | 1.2 | 1.50 | $N_w^{Li} = 4.7 + 2.29 N_w^{Cl}$ |
| Methyl | 0.8 | 7.08 | $N_m^{Li} = 16.66 + 1.35 N_m^{Cl}$ |
| Ethyl | 1.0 | 1.62 | $N_e^{Li} = 4.12 + 1.54 N_e^{Cl}$ |
| Propyl | 1.0 | 1.52 | $N_p^{Li} = 3.83 + 1.52 N_p^{Cl}$ |

From the equations in the last column it would be possible to calculate the absolute solvation of the lithium ion in each solvent, if the value for the solvation of the chloride ion were known. The exasperatingly high values of $\Delta n_m/F$ and N_m^{Li} for solutions in methyl alcohol are apparently entirely out of proportion when compared with the same values in the other solvents. While they are probably due for the most part to slight errors which are greatly magnified in the various calculations involved these values were, nevertheless, consistently high for each of the six concentrations used in this solvent. It would seem entirely reasonable to believe that these values should be higher than the corresponding values for ethyl alcohol. Whether or not they should lie below the same values in water solutions is problematical. Apart from the data for methyl alcohol the degree of solvation of the lithium ion de-

creases as the complexity of the solvent molecules increases. A survey of the previous tables shows that the number on mols of solvent transferred per faraday increases with the dilution of the salt. Making this allowance the value of $\Delta n_w/F$ for water should be slightly higher than the same value for ethyl alcohol. We can therefore conclude that the net amount of solvent transferred per faraday decreases as the complexity of the solvent increases.

SUMMARY

1. The true and ordinary transference numbers of the lithium ion in solutions of lithium chloride in methyl, ethyl and n-propyl alcohol have been determined. Camphor was used as the reference substance.

2. When these solutions are electrolyzed there is an increase in the concentration of the camphor at the anode and a decrease at the cathode. This change in the concentration of the camphor is produced by the migration of the solvent with the lithium ion from the anode to the cathode.

3. In a given solvent the values for the transference numbers and the degree of solvation of the lithium ion decreases as the concentration of the lithium chloride is increased.

4. For a fixed concentration of lithium chloride the observed values of the degree of solvation of the lithium ion decrease as the complexity of the solvent molecules increase.

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