[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Conductance of Salts in H_2O–D_2O Mixtures

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Introduction

The dependence of the mobility of ions upon the viscosity of the medium has long been the subject of investigation. Fair agreement with the Walden rule $\Lambda_0\eta$ = constant has been found for electrolytes on changing the solvent.[1,2] However, on changing the solvent, other properties, in addition to the viscosity, which may have an effect upon the conductance, have been altered. The empirical relationship, $\Lambda_0\eta^m$ = constant,[3] where m is a constant less than unity, specific to the electrolyte, applies when the viscosity is changed by varying the temperature or by adding small amounts of non-electrolytes. When the viscosity is varied by changing the pressure, no simple relation has been found.[4]

As has been pointed out by Baker and La Mer,[5] the dependence of the conductance upon the viscosity can be studied under ideal conditions in H_2O–D_2O mixtures since the most significant properties affecting ionic behavior, namely, the dielectric constant[6] and the molar volumes, [7,8,9] are almost if not precisely identical, whereas the viscosity[10] increases by 23% on passing from H_2O to D_2O. If there are factors controlling the conductance of electrolytes which are not accounted for by the viscosity and the dielectric constant of the solvent, they will be brought to light by such an investigation. The measurement of the conductance of electrolytes in H_2O–D_2O mixtures accordingly has been extended to include that of sodium chloride, lithium chloride and potassium acetate for comparison with the earlier study of potassium chloride.[5]

For the interpretation of the kinetics of reactions in D_2O catalyzed by acids and bases it is necessary to have an accurate knowledge of the dissociation constant of the acid. The previous conductimetric measurements of the dissociation constant[11] of acetic acid in D_2O were undertaken with only a fraction of a gram of heavy water. The deuterium content of the water was not accurately known and doubtful assumptions were made concerning the ratio of the conductance of the ions in H_2O and D_2O; the conductance of the solvent was 10% of the total conductance of the solution. The stoichiometric constant has accordingly been redetermined under conditions which give a precision of 0.3%.

Apparatus and Reagents.—The thermostat and the apparatus for the measurement of the resistance were the same as that used by Baker and La Mer and have been described previously.[5]

Two small cells, free from by-pass capacity and inductance effects, with approximately 5-cc. capacity and constants 4.8988 and 0.48315 were employed. The electrodes were platinized as directed by Jones and Bollinger[12] to reduce polarization. A third cell having a constant of 0.1484 and unplatinized electrodes was used to determine the specific conductance of the solvent. Each cell was filled by means of a tube fitted with a ground glass joint. The tube was removed and the cell closed by ground glass caps during measurements. The cell constants were determined by the method of Parker and Parker.[13]

The H_2O–D_2O mixtures obtained from various sources were purified by distillation under atmospheric pressure from acid chromate, similar distillation from alkaline permanganate, and vacuum distillation. The last step was carried out in an all Pyrex vacuum still with mercury sealed caps. In order to remove electrolytes, vacuum distillation from a solution made alkaline by a small pellet of sodium hydroxide was sufficient to produce water having a specific conductance not exceeding 2×10^{-6} mho. The increase in specific conductance of water kept in Pyrex flasks was negligible over a period of several days. The atom fraction of deuterium of the solvent was calculated from the densities by the expression

$$F_{\mathrm{D}} = \Delta S/0.1079 \quad \text{where} \qquad (1)$$
$$\Delta S = (d^{25}{}_{25}) - 1$$

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(1) Kraus, "Properties of Electrically Conducting Systems," Chem. Catalog Co., Inc., New York, 1922, pp. 109, 114, 121.

(2) Walden, "Acids Bases and Salts," McGraw-Hill Book Co., Inc., New York, 1929, pp. 283–323.

(3) Johnston, THIS JOURNAL, **31**, 1010 (1909).

(4) Washburn, "Principles of Physical Chemistry," 2d ed., McGraw-Hill Book Co., Inc., New York, 1921, p. 260.

(5) Baker and La Mer, *J. Chem. Phys.*, **3**, 406 (1935).

(6) Muller, *Physik. Z.*, **36**, 1009–11 (1935).

(7) Abadie and Champetier, *Compt. rend.*, **200**, 1387 (1935).

(8) Lewis and Macdonald, THIS JOURNAL, **55**, 3057 (1933).

(9) Longsworth, *ibid.*, **59**, 1483 (1937).

(10) Lewis and Luten, *Phys. Rev.*, **45**, 161 (1934).

(11) Lewis and Schutz, THIS JOURNAL, **56**, 1913 (1934).

(12) Jones and Bollinger, *ibid.*, **57**, 280 (1935).

(13) Parker and Parker, *ibid.*, **46**, 312 (1924).

Recently Longworth[10] has shown, that contrary to earlier statements, there is no significant volume contraction on mixing H_2O and D_2O. He proposes the formula $F_D = 0.92351\ \Delta S/(1 - 0.327\,\Delta S)$, based upon the Princeton value for $\Delta S = 0.1079$ for 100% D. Until the minor discrepancy between this value and the Norwegian value ($\Delta S = 0.1076$) is reconciled, the simple linear formula (eq. 1) can serve as a sufficiently accurate index of the deuterium content.

Acetic anhydride was distilled four times in an all Pyrex still under anhydrous conditions. The third quarter fraction was retained each time. Standard solutions made up by weight were titrated and found to have the calculated concentration within three parts per thousand.

A small bulb weight buret was designed to transfer acetic anhydride without the possibility of contamination with stopcock grease or moisture. It was filled by warming the bulb and then cooling to room temperature with the tip below the surface of the liquid. The cap was then firmly replaced and the buret weighed. The desired amount of anhydride was ejected into the solvent by warming the bulb by hand. Precaution was taken to protect the glass from the bare hand by means of lens paper.

Reagent quality potassium chloride, recrystallized twice from water and dried at 600°, was found to be pure within one part per thousand by a gravimetric silver chloride analysis.

The other salts, twice recrystallized and dried, were found to be pure within one part per thousand by comparing conductance values in H_2O with those calculated by means of the Shedlovsky equation.[14]

Experimental Procedure.—All glassware was cleaned with chromic acid, rinsed with water and steamed or filled with distilled water for several days before use.

The solutions were made up by weight. The weight of small amounts of salt in a tiny platinum bucket could be reproduced to within 0.03 mg., *i. e.*, 1 to 2 parts per thousand in the concentration. This is the limiting factor in the precision of the results.

Before the measurement of the salt solutions, the conductance cell was freed from heavy water by drawing clean dry air through it, distilled water passed through continuously for fifteen minutes, dried, filled with solution and placed in the thermostat for an hour. The cell was then refilled and the measurements repeated until the resistance of successive fillings agreed within 0.02%. After the measurement of the first solution the acetic acid cell was not washed with water but merely dried.

Calculation of Results

The normal concentration of the solutions (Table I, II and III) was calculated from the weight of the solute, weight of the solution "*in vacuo*," density of the solution and the equivalent weight of the solute. The density of the solutions was calculated by assuming that the density of solutions in D_2O exhibited the same percentage increase with concentration as they do in H_2O. Baker and La Mer[5] have shown this to be valid within one part per hundred thousand. Correction for the specific conductance of the solvent was made in the calculation of the equivalent conductance of the salts. No solvent correction[15] was made to the conductance of acetic acid since the concentration of the hydrogen ion from any carbonic acid present would be repressed to a negligible value.

The viscosity of the H_2O–D_2O mixtures was calculated by means of the fluidity formula developed by Jones and Fornwalt.[16]

$$\varphi = \frac{1}{\eta} = 1 - 2.06855\,\Delta S + 3.1122\,(\Delta S)^2 \qquad (3)$$

The limited quantities of heavy water available did not permit the measurement of equivalent conductance in increasingly dilute solutions in order to obtain the value of Λ at infinite dilution by extrapolation of experimental data. Fortunately this procedure is unnecessary.

The Onsager[17] equation

$$\Lambda_c = \Lambda_0 - [\alpha\Lambda_0 + \beta]\sqrt{C}$$

$$\text{where } \alpha = \frac{8.173 \times 10^5}{(DT)^{3/2}} \text{ and } \beta = \frac{83.4}{(DT)^{1/2}}\frac{1}{\eta} \qquad (4)$$

should hold equally well in D_2O as in H_2O when the appropriate values for the viscosity and dielectric constant are employed. Let $\beta' = \beta\eta$, then α and β differ in H_2O and D_2O only by the ratio of the dielectric constants which has been shown to be nearly unity.

$$\text{Then} \quad \Lambda_c/\Lambda_0 = 1 - [\alpha + \beta'/\Lambda_0\eta]\sqrt{C} \qquad (5)$$

$$\text{And } \frac{[\Lambda_c/\Lambda_0]_{H_2O}}{[\Lambda_c/\Lambda_0]_{D_2O}} = 1 + \frac{\beta'\sqrt{C}\left[\frac{1}{(\Lambda_0\eta)_{H_2O}} - \frac{1}{(\Lambda_0\eta)_{D_2O}}\right]}{1 + [\alpha + \beta'/\Lambda_0\eta)_{D_2O}]\sqrt{C}} \qquad (6)$$

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(14) Shedlovsky, THIS JOURNAL, **54**, 1405 (1932).

(15) Davies, "The Conductivity of Solutions," Chapman and Hall, 1930, p. 64.

(16) Jones and Fornwalt, *J. Chem. Phys.*, **4**, 30 (1936).

(17) Onsager, *Physik. Z.*, **28**, 277 (1927).

TABLE I

LITHIUM CHLORIDE

Concn.	κ soln.	$\kappa \times 10^6$ water	Λ_c	Λ_0	η	F_D	d^{25}_{25} = Sp. g.
0.02594	0.002671	1.2	102.9	114.6	1.000	0.0	1.0000
.02410	.002493	1.2	103.4	114.6	1.000	.0	1.0000
.02045	.002129	1.2	104.0	114.5	1.000	.0	1.0000
.02076	.001957	1.2	94.2	103.6	1.109	48.1	1.05167
.02446	.002289	1.2	93.5	103.5	1.109	48.1	1.05167
.02439	.002086	1.1	85.5	94.5	1.216	93.5	1.10107
.02665	.002277	1.1	85.4	94.7	1.216	93.5	1.10107
				(93.5)	(1.230)	100.0	(1.1079)

TABLE II

SODIUM CHLORIDE

Concn.	κ soln.	$\kappa \times 10^6$ water	Λ_c	Λ_0	η	F_D	d^{25}_{25} = Sp. gr.
0.02243	0.002583	1.1	115.1	126.5	1.000	0.0	1.0000
.01830	.002129	1.1	116.3	126.7	1.000	.0	1.0000
.01907	.002211	1.2	115.9	126.4	1.000	.0	1.0000
.01923	.002223	1.2	115.5	126.1	1.000	.0	1.0000
.01893	.002123	0.8	112.1	122.3	1.034	15.1	1.0161
.01891	.002121	.8	112.2	122.3	1.034	15.1	1.0161
.02121	.002224	1.1	104.8	114.6	1.115	48.1	1.05162
.01914	.002010	1.1	105.0	114.3	1.115	48.1	1.05162
.02005	.002100	1.2	104.7	114.2	1.115	48.1	1.05167
.02218	.002127	1.6	95.8	104.8	1.215	93.6	1.10091
.02169	.002081	1.7	95.9	104.8	1.215	93.7	1.10118
.01944	.001872	1.7	96.2	104.7	1.215	93.7	1.10118
				(103.4)	(1.230)	100.0	(1.1079)

TABLE III

POTASSIUM ACETATE

Concn.	κ soln.	$\kappa \times 10^6$ water	Λ_c	Λ_0	η	F_D	d^{25}_{25} = Sp. gr
0.01928	0.002004	1.2	103.9	114.1	1.000	0.0	1.0000
.02421	.002499	2.1	103.2	114.3	1.000	.0	1.0000
.01304	.001306	3.1	99.9	108.0	1.064	28.4	1.03038
.01286	.001289	1.9	100.1	108.2	1.064	28.6	1.03038
.02418	.002269	0.9	93.8	103.9	1.115	48.1	1.0518
.01250	.001200	.9	95.9	103.5	1.115	48.1	1.0518
.01080	.001042	.9	96.4	103.6	1.115	48.1	1.0518
.01685	.001534	2.5	90.9	99.2	1.169	76.4	1.0822
.01212	.001106	1.5	91.1	98.2	1.179	78.0	1.0839
.01891	.001647	1.4	87.0	96.1	1.213	93.0	1.1002
.01966	.001722	1.4	87.5	96.2	1.213	93.0	1.1002
.01771	.001550	1.2	87.5	95.7	1.215	93.4	1.1007
.01572	.001384	1.2	88.0	95.8	1.215	93.4	1.1007
	(extrapolated)			(94.8)	(1.230)	100.0	(1.1079)

TABLE IV

ACETIC ACID

F_D	0.0	28.4	48.4	77.1	93.0	97.0	100
K' Acetic	1.840	1.352	1.088	0.741	0.608	0.575	(0.555)
A eq. 9	148.6	134.8	126.5	117.2	114.2	113.7	
Λ_0 (HAc – DAc)	390.6	345.6	320.7	297.5	285.9	285.2	
η	1.000	1.064	1.115	1.177	1.213		(1.230)
$\Lambda_{0\text{KCl}}$	149.8	141.5	135.7	129.1	125.4		(123.8)

Values for potassium chloride are calculated from data obtained by Baker and La Mer, ref. 5.

The experimental data show that $(\Lambda_0\eta)$ D_2O differs from $(\Lambda_0\eta)$ H_2O by less than 2% with the salts measured. Therefore, equation (6) reduces without appreciable error to

$$\left(\frac{\Lambda_c}{\Lambda_0}\right)_{H_2O} = \left(\frac{\Lambda_c}{\Lambda_0}\right)_{D_2O} \quad (7)$$ [18]

for dilute solutions.

Values of Λ_0 in H_2O–D_2O mixtures, calculated by means of the Shedlovsky equation

$$\Lambda_c = \Lambda_0 - [\alpha\Lambda_0 + \beta]\sqrt{C} + BC(1 - \alpha\sqrt{C}) \quad (8)$$

under the assumption that the empirical constant B is the same in D_2O as in H_2O agreed with those obtained by means of equation (7) to within 0.1%, which is of the same order of magnitude as our present experimental error.

TABLE V

Salt	$\Lambda_{0(D_2O)}$	$\lambda_{0(D_2O)}$	T_+°
KCl	123.8	61.23 (K^+)	0.4906 + 0.004 F_D
NaCl	103.4	40.83 (Na^+)	.3963 − .001 F_D
LiCl	93.5	30.93 (Li^+)	.3368 − .006 F_D
KAc	94.8	33.57 (Ac^-)	.643 + .003 F_D

TABLE VI

Salt	A	θ	Δ
LiCl	0.0175	2.05918	+0.05918
NaCl	0.0350	2.1014	+0.1014
KCl	.0794	2.1755	+ .1755
KAc	.0923	2.05843	+ .05843
Ion	a	ϑ	Δ
Li^+	− 0.180	1.5866	0.5866
Na^+	+ .0122	1.6998	.6998
K^+	+ .162	1.8623	.8623
Cl^-	+ .043	1.8825	.8825
Ac^-	+ .158	1.6017	.6017

The stoichiometric dissociation constant for approximately 0.02 N acetic acid was calculated for each concentration of D_2O using the method developed by MacInnes and Shedlovsky.[19]

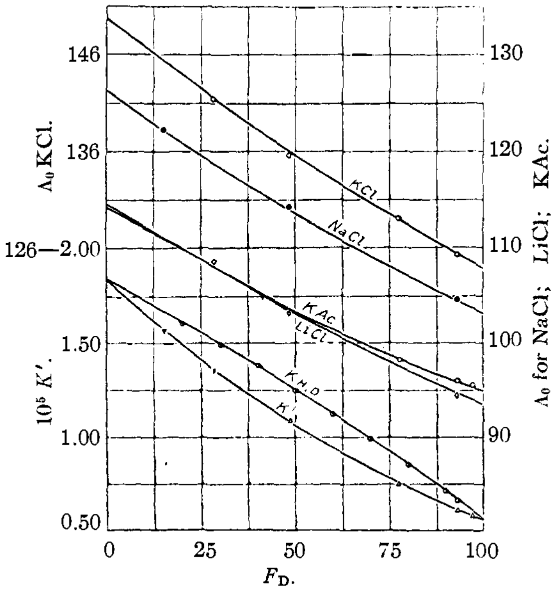

Fig. 1.

Discussion of Results

If the Stokes relation

$$\lambda = K/6\pi\eta' r \quad (10)$$

where λ is the mobility of an ion, K is a constant, η' is the coefficient of viscosity of the medium and r is the radius of the ion can be applied to salt in H_2O–D_2O mixtures, the mobility of an ion should vary linearly with $1/\eta'$. Therefore, the ratio of the conductance of all salts in D_2O to that in H_2O should be a constant at infinite dilution. However, it is evident from Fig. (1) that the Λ_0, equivalent conductance at infinite dilution, exhibits a decrease specific to each salt.

For the purpose of making a discriminating comparison of the behavior of the conductance of the different salts in H_2O–D_2O mixtures, the empirical expression

$$\Lambda_0\eta^m = k \quad (11)$$

where η is the relative macroscopic viscosity, may be transformed to

$$\log(\Lambda_0\eta) = A \log \eta + \Delta \quad (12)$$
$$\text{where } A = 1 - m$$

Figure 2 was obtained by plotting log $(\Lambda_0\eta)$ *vs.* log η where the slope, A, is a small positive number much less than unity. Values of A are listed in Table VI.

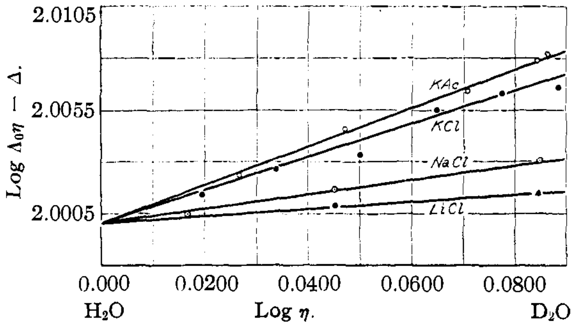

Fig. 2.

The Kohlrausch law of independent ion mobilities requires that the decrease in mobility of the chloride ion with increasing viscosity should be independent of the co-ion. Since the conductance of each alkali halide exhibits a specific dependence upon the viscosity on passing from H_2O to D_2O, it is evident that the transference numbers of the ions will not remain constant on pass-

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[18] La Mer and Chittum, THIS JOURNAL, **58**, 1642 (1936).

[19] MacInnes and Shedlovsky, *ibid.*, **54**, 1429 (1932).

ing from H_2O to D_2O. An equation similar to (12) can be developed for each ion.

$$\log \lambda_0\eta = a \log \eta + \vartheta \qquad (14)$$

where λ_0, a and ϑ are, respectively, the mobility, the slope of log $\lambda_0\eta$ *versus* log η curve and a constant for each ion. If the arbitrary assumption is made tentatively that the mobility of the chloride ion is linearly proportional to the viscosity (*i. e.*, a = zero), the corresponding values of a for the cations becomes $Li^+ = 0.0122$, $Na^+ = 0.0767$ and $K^+ = 0.206$. This assumption would predict a 2% increase in transference number of the potassium ion in potassium chloride on passing from H_2O to D_2O. Dr. Longsworth has measured the transference number of the potassium ion in potassium chloride in 99.35% D_2O by the moving boundary method. He finds that for 0.05 N KCl: $T_{K^+} = 0.4899 + 0.0040\ F_D$, and that the transference numbers of other salts change in a way which is consistent with the Kohlrausch law. For zero concentration of potassium chloride[20] then $T^0_{K^+(KCl)} = 0.4906 + 0.0040\ F_D$ or approximately 0.82% increase in D_2O. Our tentative assumption that chloride ion might be unaffected is incorrect, and

$$T^0_{Cl^-(KCl)} = 0.5094 - 0.0040\ F_D$$

Since $\Lambda_{0(KCl)} = 123.8$, then $\Lambda_{0Cl^-(D_2O)} = 62.5_7$. Using this value we have computed the corresponding values of the mobilities, and transference numbers tabulated in Table V. In Table VI we give the constants for eq. (14) consistent with our measurements.

Recently, Lange and Martin[21] have shown that the "isotopic effect," $\Delta L = L^{H_2O} - L^{D_2O}$, of H_2O and D_2O upon the heats of hydration of the alkali halides is small for lithium fluoride (−155 cal.) and increases regularly with atomic weight to a value of 955 cal. for cesium iodide. The existing theories of Born and Bjerrum for heats of hydration do not account for the gradation in isotopic effect. These data give indication that conditions around a lithium ion in H_2O and in D_2O are more nearly equal than around atomic ions of higher molecular weight. Whether fluoride, bromide and iodide ions will exhibit a corresponding deviation from the Walden rule is being investigated.

As was found by Baker and La Mer[5] for potassium chloride, the value of $\Lambda_{0.01}$ for the various salts exhibits a negative deviation from linearity of approximately 4%. On the other hand, the dissociation constant of acetic acid exhibits a much larger deviation amounting to 11%.

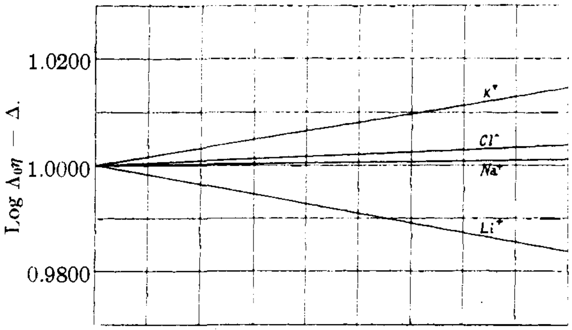

Fig. 3.

It is difficult to attach any significance to the stoichiometric dissociation constant of a weak acid calculated from conductance data in the H_2O-D_2O mixtures as outlined above (see ref. (5)). The mobility of the hydrogen and deuterium ions is complicated by proto- and deuterotropic exchange, the value for $\Lambda_{0.01}$ for (HCl–DCl) showing a negative deviation from linearity of 11% for $F_D = 0.5$. Therefore, the concentration of acid ions in acetic acid solutions cannot be obtained from the simple expression

$$C_i = C\alpha = C\Lambda_c/\Lambda^e \qquad (15)$$

As pure D_2O is approached, the complications disappear and the value in D_2O obtained from the extrapolation from points at 93 and 97% D_2O is the true stoichiometric constant for DAc in D_2O.

The constant, $K_{H,D}$, defined by Korman and La Mer[22] for H_2O–D_2O mixtures (see Fig. 2)

$$K_{H,D} = \frac{[(H^+) + (D^+)]\,(A^-)}{[(HA) + (DA)]} \qquad (16)$$

and showed by them to be equal to the quantity

$$K_{H,D} = K_{DA} \left\{ \frac{1 + 7.1\,\dfrac{(H_2O)}{(HDO)}}{1 + 7.1\,\dfrac{K_{DA}}{K_{HA}}\,\dfrac{(H_2O)}{(HDO)}} \right\} \qquad (17)$$

where the numerical values are obtained from exchange constants, does not depend upon the mobility of the ions. It is not the same constant as that calculated from conductance data. However, at the limits H_2O and D_2O, the two constants are identical as is borne out by the agreement of values calculated by each method in D_2O.

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[20] Longsworth, THIS JOURNAL, **54**, 2741 (1932).

[21] Lange and Martin, *Z. Elektrochem.*, **42**, 662-668 (1936).

[22] Korman and La Mer, THIS JOURNAL, **58**, 1396 (1936).

Temperature Dependence

Preliminary measurements of the temperature coefficients of the resistance of sodium chloride solutions (Table VII) indicate a more negative value in D_2O than in H_2O. As is shown in Fig. 5, the percentage decrease in resistance per degree, $\frac{1}{R_{25}}\frac{(\Delta R)}{(\Delta T)}$, varies linearly with the deuterium content of the water up to 48% D_2O. Lack of experimental data at the present time prevents the description of the behavior of the curve in the region of pure D_2O. The indications are that the temperature coefficient of *conductance* for sodium chloride solutions is *greater* in D_2O than in H_2O so that the conductance-temperature curves of sodium chloride in H_2O and D_2O may approach each other at higher temperatures.

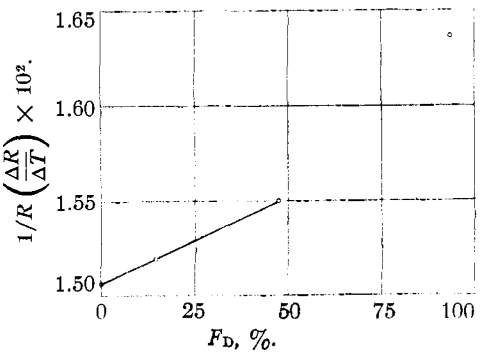

Fig. 4.

TABLE VII

% D_2O	Concn. of NaCl sol'ns	$R_{25°}$	$R_{45°}$	ΔR	$\frac{1}{R_{25}}\frac{(\Delta R)}{(\Delta T)} \times 10^2$
0.00	0.01923	2205.5	1540.0	665.5	−1.505
15.07	.01893	2308.6	1607.1	701.5	−1.519
48.13	.01914	2438.5	1682.6	755.9	−1.550
93.01	.01944	2616.8	1760.6	856.2	−1.636

$$\Delta R = R_{45} - R_{25}$$
$$\Delta T = 45° - 25° = 20°$$

The authors wish to thank Dr. Longsworth and Dr. MacInnes of the Rockefeller Institute for their kind interest and helpful criticism during the investigation.

Summary

1. The equivalent conductance of approximately 0.02 N solutions of lithium and sodium chlorides and potassium acetate has been measured in various H_2O–D_2O mixtures at 25.000°.

2. A sensitive and discriminating comparison of the viscosity dependence of the conductance of the salt solutions is obtained by plotting log $\Lambda_0\eta$ *vs.* log η.

3. The mobilities in D_2O of the lithium, sodium, potassium, chloride and acetate ions have been calculated from the present conductance data and a measurement by Longsworth of the transference number of potassium ion in D_2O from measurements on potassium chloride.

4. The transference number of lithium ion appears to decrease about 2% on passing from H_2O to D_2O, the other ions affected less.

5. The stoichiometric dissociation constant (K') of acetic acid is obtained for pure D_2O. The origin of a difference between the values of K' calculated from conductance data and $K_{H,D}$ defined by Korman and La Mer in H_2O–D_2O mixtures is explained.

6. Preliminary measurements indicate that the temperature coefficient of the equivalent conductance of solutions of sodium chloride is larger in D_2O than in H_2O between the temperatures of 25 and 45°.

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