The Conductance of Potassium Chloride and of HydrochloricDeuterochloric Acid H2O—D2O Mixtures. The Viscosity of H2O—D2O

Weldon N. Baker and Victor K. La Mer

Additional information on J. Chem. Phys.

The Conductance of Potassium Chloride and of Hydrochloric-Deuterochloric Acid in H₂O–D₂O Mixtures. The Viscosity of H₂O–D₂O.

WELDON N. BAKER AND VICTOR K. LA MER, *Department of Chemistry, Columbia University*

(Received May 15, 1935)

The conductances of 0.01 normal solutions of potassium chloride and of hydrochloric-deuterochloric acid in H_2O–D_2O mixtures, have been investigated as a function of D_2O concentration at 25°C. The viscosity of D_2O is 23 percent greater, the conductance of potassium chloride in D_2O is 17 percent less, and the conductance of deuterochloric acid in D_2O is 26 percent less, than the corresponding values in H_2O. The viscosity, and the conductance of potassium chloride solutions and of hydrochloric-deuterochloric acid solutions show a maximum deviation of 0.4, 0.8 and 5.4 percent of the total values, respectively, from linearity. The decreased conductance of potassium chloride solutions in D_2O is due mainly to the increased viscosity of the solvent. The marked deviation from linearity of the hydrochloric-deuterochloric acid curve is interpreted on the basis of a statistical correction to the proton exchange mechanism for the mobilities of H_3O^+ and D_3O^+ in H_2O–D_2O mixtures.

G. N. LEWIS and his co-workers,[1, 2] using a fraction of a cc of heavy water (90–97 percent D_2O, depending on the experiment), have shown that the mobilities of ions in D_2O are less than, and that the viscosity of D_2O is greater than, the corresponding values for H_2O. Because of the small quantities employed, the accuracy is open to question, and a more exact study of the problem is highly desirable. Furthermore their use of linear extrapolation to obtain the values for pure D_2O from the experimental values in H_2O–D_2O mixtures is not always a correct procedure as will be emphasized below.

The conductances of 0.01 normal solutions of potassium chloride and of hydrochloric-deuterochloric acid in H_2O–D_2O mixtures, and the viscosities of H_2O–D_2O mixtures, were investigated as a function of D_2O concentration at a temperature of 25°C.

MATERIALS

Potassium chloride was twice recrystallized from water and dried at 600°C. The constant boiling hydrochloric acid was prepared according to the usual method.[3] After atmospheric distillations from an alkaline permanganate solution and from an acid chromate solution, the water samples were distilled in vacuum. The water in the vacuum still was frozen, the apparatus evacuated, the ice melted completely to allow the dissolved gases to escape, and the freezing, evacuation and melting repeated. The distillation was conducted at 40°C with the receiving flask at 0°C. The waters averaged about 1×10^{-6} mho in specific conductivity. The D_2O concentration was determined from the increase in specific gravity, ΔS, by using the corrected Lewis formula, $N_{D_2O} = 9.377 \Delta S - 1.01 \overline{\Delta S}^2.$[4]

APPARATUS

A vacuum tube oscillator of the beat frequency type[5] constructed in this laboratory[6] produced a current free from harmonics, and from any direct current component. The frequency was 1740 cycles per second. The Leeds and Northrup conductivity bridge is described in detail elsewhere.[7] An L. and N. impedance coupled amplifier amplified the bridge output sufficiently that a cell resistance of about a thousand ohms could be determined to within ±0.001 percent.

A small cell, shown in Fig. 1, having a capacity of 4.5 cc, was constructed of Jena 16^{III} glass. The cell constant was determined according to the directions of Parker and Parker.[8] As a change of the frequency from one thousand to five thousand cycles produced a decrease in the measured resistance of only 0.01 percent, the cell was sensibly free from the Parker effect.

The ordinary Ostwald U-shaped type of viscometer was employed. The time of outflow at 25.00°C was 75 sec. for five cc of H_2O.

[1] Lewis and Doody, J. Am. Chem. Soc. **55**, 3504 (1933).
[2] Lewis and MacDonald, J. Am. Chem. Soc. **55**, 4730 (1933).
[3] Bonner and Titus, J. Am. Chem. Soc. **52**, 633 (1930).
[4] La Mer and Baker, J. Am. Chem. Soc. **56**, 2641 (1934).
[5] Lampkin, *Radio Broadcast*, July, 1928, p. 156.
[6] The authors wish to express their thanks to Mr. Samuel Korman under whose direction the oscillator was constructed.
[7] Paul H. Dike, Rev. Sci. Inst. **2**, 379 (1931).
[8] Parker and Parker, J. Am. Chem. Soc. **46**, 312 (1924).

EXPERIMENTAL PROCEDURE

Preparations of solutions

The limiting factor in the precision of the measurements is the accuracy with which the concentration of the solution is known. In the preparation of potassium chloride solutions, between 20 and 35 mg of potassium chloride was transferred from a weighing bottle to a 50 cc flask. If the weights of the potassium chloride, determined by the difference in the weight of both the flask and the weighing bottle, did not check within 0.06 mg, the sample was discarded.[9] The average of the two weights was taken as the weight of potassium chloride used. Enough water was now added to make an approximately 0.01 normal solution.

The method of preparing the hydrochloric acid solutions differed from that employed for potassium chloride solutions, since the principal error arises from the loss by evaporation during transfer. The water for the solution (specific conductivity about 1×10^{-6} mho) was placed in a 25 or 50 cc volumetric flask and about 45 mg of hydrochloric acid of constant boiling point added from a small weight burette, the amount of acid added being checked by the increase in the weight of the solution in the flask. In two-thirds of the cases the results agreed to within 0.1 mg, and the maximum variation was 0.2 mg. As this loss in weight is more likely to be water, the only opportunity for evaporation of the hydrochloric acid solution being from the tip of the burette while the water has an opening about one $(cm)^2$ in area from which to evaporate, the decrease in the weight of the burette was taken as the weight added.

Determination of conductance

The conductivity cell was filled with the solution until the electrodes were in equilibrium with the solution, after which the cell was never washed with pure water. When ready for use, it was drained, dried, filled with the solution being tested and placed in the constant temperature bath until its conductance became constant which required about an hour. It was now rinsed three times and refilled. After the first filling the difference in conductance between successive
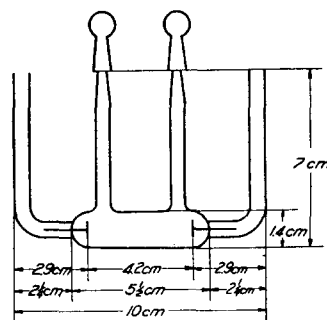
[9] The weighings were reproducible to ±0.03 mg.

FIG. 1. Conductivity cell.

fillings was rarely more than 0.02 percent and usually about 0.005 percent.

Viscosity determinations

After the viscometer, containing five cc of water, had been in the 25°C bath for ten minutes, the time of outflow was measured six or eight times and the results averaged. The water was removed, the viscometer dried, and the experiment repeated. Chromic acid "cleaning" solution was used but once as it has a solvent effect on the glass, the apparatus being merely air-dried between runs. At the conclusion of the experiments, the H_2O value was rechecked, and the time of outflow for H_2O at 40° determined in order to evaluate the constants of the viscometer, C and C', in the equation for relative viscosity $(\eta = \rho(Ct - C'/t))$.[10, 11]

Calculation of results

The calculation of the conductance is evident from Table I, where the data of a typical run are given for both potassium chloride solutions and hydrochloric acid solutions. The data for the potassium chloride solutions were corrected for the conductance of the solvent. This correction is of no importance in HCl solutions, where the conductance of traces of H_2CO_3 is completely repressed.[12]

Experimental data

The conductances of 0.01 normal potassium chloride solutions in H_2O–D_2O mixtures is given in the second column of Table II and curve I of

[10] Hatschek, *The Viscosity of Liquids*, D. Van Nostrand Co., 1928, p. 41.
[11] Reilly and Rae, *Physico-Chemical Measurements*, 2nd ed., D. Van Nostrand Co., 1932, Chap. 37.
[12] Davies, *The Conductivity of Solutions*, 2nd ed., John Wiley and Son, 1933, Chap. IV.

TABLE I. *Typical conductance data.*

KCl Solutions

Sp.gr. Solvent	KCl (g)	Sol'n (g)	Sp.gr. Sol'n	Eq./cc ($\times 10^6$)	R (ohms)	$10^6\,\kappa = \dfrac{4.902}{R\cdot 10^{-6}}$	$10^6\,\kappa$ water	$10^6\,\kappa$ KCl	$\Lambda_C = \kappa/C$	$\Lambda_{0.01}$	N_{D_2O}
1.02202	0.02740	37.720	1.02249	0.9933	3640.0	1346.7	2.1	1344.6	135.4	135.4	
	0.02263	32.029	1.02247	0.9661	3724.0	1316.3	2.1	1314.2	136.0	135.9	0.2060
	.02678	34.532	1.02252	1.0605	3406.6	1439.0	2.1	1436.9	135.5	135.7	

HCl Solutions

	20.25% HCl							$\Lambda = 4.902/R\cdot C$			
1.05923	0.04458	26.391	1.05930	0.9907	1484.8		1.2		333.2	333.2	0.5511
	.04906	26.439	·1.05931	1.0884	1351.8		1.2		333.2	333.6	0.5510
	.04368	26.429	1.05930	0.9693	1514.6		1.2		333.9	333.8	0.5511

TABLE II. *Summary of results.*
All measurements at 25°C; electrolyte concentrations, 0.01 normal; values in parentheses are extrapolated.

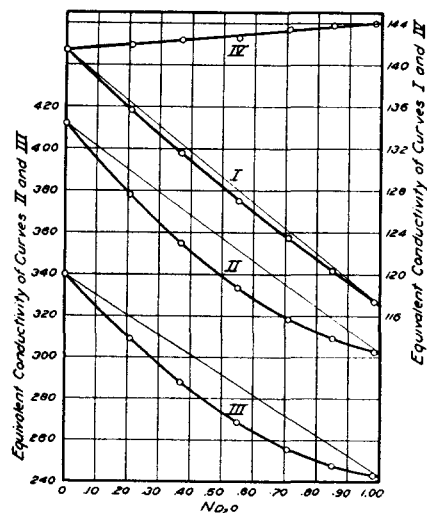| N_{D_2O}	Λ_{KCl}	$\lambda_{Cl^{-1}}$	$\Lambda_{(HCl+DCl)}$	$\lambda_{(H_3O^+ + D_3O^+)}$[2]	Relative viscosity	$\Lambda_{KCl}(\eta)^{0.913}$
0.000	141.4	72.1	411.9	339.8	1.000	141.4
.206	135.7	69.2	378.1	308.9	1.046	141.4
.368	131.6	67.1	354.9	287.8	1.082	141.4
.550	127.0	64.8	333.5	268.7	1.123	141.2
.709	123.5	63.0	318.7	255.7	1.161	141.5
.848	120.3	61.3	309.2	247.9	1.195	141.5
.980	117.3	59.8	303.0	243.2	1.228	141.4
1.000	(117.0)	(59.7)	(302.1)	(242.4)	(1.232)	

[1] T_{Cl^-} in KCl equals 0.5098 (MacInnes, Shedlovsky and Longsworth, J. Am. Chem. Soc. **54**, 2758 (1932).
[2] $\lambda_{(H_3O^+ + D_3O^+)} = \Lambda_{(HCl+DCl)} - \lambda_{Cl^-}$.

Fig. 2. The value of $\Lambda_{0.01}$ in H_2O, 141.4 Kohlrausch units, agrees well with Shedlovsky's value[13] of 141.32. The value in 100 percent D_2O, extrapolated from 98.34 percent D_2O, is 117.0, a decrease of 17.2 percent in the conductance compared to the value in H_2O. Lewis and Doody,[1] using an 0.086 molar potassium chloride solution, obtained a decrease in conductance of about 14 percent. The change in conductance with D_2O concentration is not quite linear. The maximum deviation (50 percent D_2O) is 0.8 percent.

As the ratio of the conductances of K^+ and Cl^- is very nearly independent of viscosity,[10, 14] the conductance of Cl^- may be calculated if the assumption is made that the relative degrees of hydration remain the same. The values of λ_{Cl^-} thus calculated, with 0.510 as the transference number of Cl^- ion in KCl,[15] are given in the third column of Table II.

The results for 0.01 N HCl–DCl solutions are given in Table II and curve II of Fig. 2. The

FIG. 2. Curve I, Λ_{KCl}. Curve II, $\Lambda_{(HCl+DCl)}$. Curve III, $\lambda_{(H_3O^+ + D_3O^+)}$. Curve IV, $(\Lambda_{KCl}\cdot\eta)$.

[13] Shedlovsky, J. Am. Chem. Soc. **54**, 1411 (1932).
[14] Kraus, *The Properties of Electrically Conducting Solutions*, The Chemical Catalog Co., 1922, Chap. 5.
[15] MacInnes, Shedlovsky and Longsworth, J. Am. Chem. Soc. **54**, 2758 (1932).

value of $\Lambda_{0.01}$ for HCl in H_2O, 411.9 Kohlrausch units agrees very well with Shedlovsky's value[13] of 411.88. The value of $\Lambda_{0.01}$ for DCl in D_2O extrapolated from the three values between 97.50 percent D_2O and 98.75 percent D_2O is 302.1, a decrease of 26.6 percent from the conductivity of HCl in H_2O. Lewis and Doody,[1] using 0.017 M HCl obtained a decrease of about 28 percent. The conductance at 50 percent D_2O is less by eighteen Kohlrausch units (5.4 percent of the total conductivity at that D_2O concentration) than a linear relation would give. This departure from linearity is shown in Table III and

TABLE III. *Deviation of conductance of (HCl+DCl) from linearity.*

N_{D_2O}	$\Lambda_{(linear)}$	$\Lambda_{(exp.)}$	$\Lambda_{linear} - \Lambda_{exp.}$	$\dfrac{\Lambda_{linear} - \Lambda_{exp.}}{\Lambda_{exp.}} \times 10^2$
0.2060	389.3	378.1	11.2	2.96
.3682	371.5	354.9	16.6	4.68
.5511	351.4	333.5	17.9	5.37
.7095	334.0	318.7	15.3	4.80
.8488	318.7	309.2	9.5	3.07

Fig. 3 where

$$(\Lambda_{linear} - \Lambda_{exp.}) \quad \text{and} \quad \left(\frac{\Lambda_{linear} - \Lambda_{exp.}}{\Lambda_{exp.}}\right) \times 10^2$$

are given as functions of the D_2O concentration.

The viscosity of H_2O–D_2O mixtures is given in column 6 of Table II. The maximum deviation from linearity is 0.4 percent of the total at 50 percent D_2O. The relative viscosity extrapolates to 1.232 for pure D_2O, and the absolute viscosity to 1.103 centipoises,[16] in exact agreement with Lewis and MacDonald's value.[2]

POTASSIUM CHLORIDE SOLUTIONS

Numerous studies of the relationships between conductance of ions in aqueous solution and the viscosity of the medium[10, 14] have shown that the experimental results may be expressed satisfactorily by the equation, $\Lambda \cdot (\eta)^p$ equals a constant where p is usually less than one and, in general, approaches unity as the size of the ion increases.

To investigate the influence of viscosity, the addition of a second solvent or a change in temperature has been employed. Unfortunately these procedures introduce a variation in other
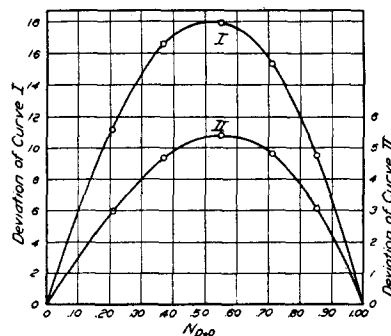

FIG. 3. Deviation of conductance of (HCl+DCl) from linearity. Curve I, $(\Lambda_{linear} - \Lambda_{exp.})$. Curve II, $[(\Lambda_{linear} - \Lambda_{exp.})/\Lambda_{exp.}] \times 10^2$.

important properties of the medium, so that the effects cannot be ascribed exclusively to viscosity. By varying the proportions of H_2O and D_2O, the viscosity of the medium can be changed without producing these complications; the temperature, the electrolyte concentration, the size of the solvent molecules, and even the dielectric constant[17] remains practically unchanged.

The product $(\Lambda_{KCl} \cdot (\eta)^{0.913})$ gives a constant value within the limits of experimental error as shown in the last column of Table II. η is the relative viscosity of the pure solvent, which may be used since the viscosity of 0.01 N KCl solutions in H_2O is only 0.04 percent greater than pure H_2O.[18] Even on the assumption of a linear dependence upon the viscosity 90 percent of the decrease in conductance is accounted for by the increase in viscosity of the D_2O.

HYDROCHLORIC-DEUTEROCHLORIC ACID SOLUTIONS

It has been recognized for many years that the conducting ions in acid solutions are not free protons, but hydrated protons (H_3O^+)— oxonium ions.[19, 20] When an H_3O^+ ion is in sufficiently close contact with a water molecule, as in aqueous solutions, it need not retain its extra proton since there is another configuration of equal energy in which the extra proton has changed molecules, thus:

[16] Viscosity of H_2O at 25°C = 0.895 centipoise, I.C.T.

[17] Lewis, Olson and Maroney, J. Am. Chem. Soc. **55**, 4731 (1933) find D for D_2O is 99 percent of that of H_2O.
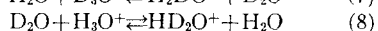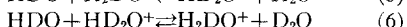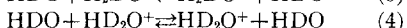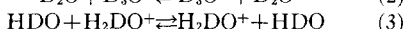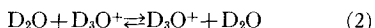[18] Jones and Talley, J. Am. Chem. Soc. **55**, 624 (1933).
[19] Bernal and Fowler, J. Chem. Phys. **1**, 515 (1933).
[20] Eucken, Jette and La Mer, *Fundamentals of Physical Chemistry*, McGraw-Hill, 1925, p. 445.

$$H_2O + H_3O^+ \rightleftharpoons H_3O^+ + H_2O. \qquad (1)$$
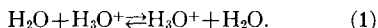
At any given time there is an equal probability of the proton being on either of the water molecules. However, if there is an applied field, F, the probability of the proton being found on one or the other of the water molecules is altered by an amount proportional to F, the migration of the proton being directed toward the region of lower potential energy.

The ions Cs^+, Rb^+, Th^+, K^+, NH_4^+, Cl^-, Br^- and I^- have about the same mobility in aqueous solutions, which is the maximum mobility of any ions except H_3O^+ and OH^-. The ordinary mobility of ions of the same charge is *primarily* a function of their effective ionic volume and not of their mass. The conductance of H_3O^+ is about five times that of the ions just mentioned. If the mechanism of conduction of H_3O^+ were the same as that of other ions, the radius, calculated on the basis of Stokes' law, would be absurdly small (2.6×10^{-9} cm). According to the present view, the conductance of H_3O^+ must be considered as composed of two parts, (1) ordinary conduction similar to that shown by other ions and (2) proton exchanges leading to a Grotthus chain type of conduction. In H_2O–D_2O solutions, in addition to proton exchanges between H_2O molecules, several other types of proton and deuteron exchanges are possible.

$$D_2O + D_3O^+ \rightleftharpoons D_3O^+ + D_2O \qquad (2)$$
$$HDO + H_2DO^+ \rightleftharpoons H_2DO^+ + HDO \qquad (3)$$
$$HDO + HD_2O^+ \rightleftharpoons HD_2O^+ + HDO \qquad (4)$$
$$HDO + H_2DO^+ \rightleftharpoons HD_2O^+ + H_2O \qquad (5)$$
$$HDO + HD_2O^+ \rightleftharpoons H_2DO^+ + D_2O \qquad (6)$$
$$H_2O + D_3O^+ \rightleftharpoons H_2DO^+ + D_2O \qquad (7)$$
$$D_2O + H_3O^+ \rightleftharpoons HD_2O^+ + H_2O \qquad (8)$$

The exchanges represented by Eqs. (2), (3) and (4) are similar to that represented by (1) in having the same energy after the proton or deuteron transfer as before, while if the exchanges represented by (5), (6), (7), or (8) occur, an absorption of energy from, or an evolution of energy to, the surrounding medium must occur. The frequency of the exchanges illustrated by (1), (2), (3) and (4) are all of the same order of magnitude, while the frequency of those illustrated by (5), (6), (7) and (8) will be less

because of the necessity of exchanging energy simultaneously with the surrounding medium. At a concentration of 50 percent D_2O, we have the maximum probability that an acid ion will not be next to a water molecule with which its extra proton or deuteron can exchange readily. We should accordingly expect a lower conductance than that calculated according to the additivity law. The conductance of $(H_3O^+ + D_3O^+)$; i.e., of $\Lambda_{(HCl+DCl)} - \lambda_{Cl^-}$, is given in the fifth column of Table II, and in curve III of Fig. 2, on the assumption that the conductance of Cl^- is the same in 0.01 normal solutions of both KCl and HCl–DCl.[15] The equivalent conductance of H_3O^+ in H_2O is 339.8 Kohlrausch units; that for D_3O^+ in D_2O is 242.4, a decrease in conductance of 28.6 percent. The equivalent conductance of $(H_3O^+ + D_3O^+)$ in 50 percent D_2O is 17.6 units less (6.5 percent of the total conductance) than linear extrapolation would give.[21] This marked deviation from linearity is exhibited by the empirical equation, $\Lambda_{(H_3O^+ + D_3O^+)} = 339.8$ (H_2O) $+ 255.8$ (HDO) $+ 242.4$ (D_2O), which fits the experimental points with an average deviation of 0.2 unit. The conductance constant for HDO, instead of being the average of the constants for H_2O and D_2O, is only slightly larger than that for D_2O.

It is important to point out that the deviation of the conductance curve for $(H_3O^+ + D_3O^+)$ from linearity discussed above is not due to the effect considered by Onsager and Fuoss.[22] They show that the conductance of a solution of two electrolytes with a common ion but with non common ions of widely differing mobilities should not follow the additivity law. For NaCl and HCl at a concentration of 0.005 molar each (total concentration 0.01 molar), the deviation from linearity is only 0.76 percent, although the mobilities of Na^+ and H_3O^+ stand in the ratio of one to seven. The phenomenon we have observed is of considerably greater magnitude.

---

[21] This deviation from linearity was predicted qualitatively by Dr. Otto Halpern of New York University in private conversation in April, 1934.
[22] Onsager and Fuoss, J. Phys. Chem. **36**, 2758 (1932).