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ice, and the line width at -5°C is about 2.5 gauss,¹⁶ although it increases at lower temperatures. Pitzer and Coulter¹⁸ report approximately 2/10 as much residual entropy per H_2O molecule in $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ as exists in ice; a tendency toward smoothed-out fine structure in this substance is mentioned in Section 4. If this explanation of the narrower line is correct, the residual entropy per H_2O molecule of borax should approach that of ice. So far as the author knows, this quantity has not yet been determined.

On the basis of these preliminary experiments, the study of nuclear resonance absorption fine structure appears to hold some promise toward extending knowledge not only of the solid state, but also of the role of hydrogen in chemical bonding. Investigations of the latter have been especially hampered by the inability of x-ray methods to locate hydrogen atoms. The method,

¹⁸ K. S. Pitzer and L. V. Coulter, *J. Am. Chem. Soc.* **60**, 1310 (1938).

if it is applicable to the substance in question, is favorable for the determination of internuclear distances, inasmuch as the directly measured quantity is the cube of the distance. Thus, although magnetic field calibration, finite modulation, noise fluctuations, and crudeness of crystal cutting may have introduced as much as 6 percent error in the determination of r^3 , the value of r should not be in error by more than 2 percent.

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The Conductance of Sodium and Potassium Chlorides in 50-Mole Percent Methanol-Water Mixtures

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The conductance of NaCl and KCl in 50-mole percent methanol-water mixtures has been measured at concentrations from 0.0005 to 0.01 *N*. The data can be represented within experimental error by the Onsager-Shedlovsky equation, the limiting conductances being 66.62 and 75.10, respectively. The limiting conductances of chloride ion, obtained from these values, and the limiting transference numbers reported in the accompanying paper, satisfy the rule of independent ionic mobilities, but at finite concentrations the chloride ion conductance is less for the potassium salt than for the sodium. The decrease in limiting ion conductances as compared with those in water is greater than can be accounted for by viscosity alone. The results are also in disagreement with the Bjerrum theory of ion pair formation if the mean ionic diameter, determined thermodynamically, is significant in transport processes.

THE work reported here was undertaken to provide values of the conductance for two typical 1-1 electrolytes in 50-mole percent methanol-water solution, and so make possible a correlation of the transference data¹ given in the accompanying paper.

¹ L. W. Shemilt, J. A. Davies, and A. R. Gordon, *J. Chem. Phys.* **16**, 340 (1948).

The procedure employed was the same as that used in this laboratory for aqueous solutions, *viz.* the direct current method with reversible Ag/AgCl probe electrodes as described by Gunning and Gordon;² for details of cell, circuit,

² H. E. Gunning and A. R. Gordon, *J. Chem. Phys.* **10**, 126 (1942); *ibid.* **11**, 18 (1943); G. C. Benson and A. R. Gordon, *J. Chem. Phys.* **13**, 470 (1945); *ibid.* **13**, 473 (1945).

and experimental procedure see reference 2. All measurements are based on the Jones and Bradshaw 25° 0.01 Demal standard;³ bath temperature in all cases is 25°C as determined by a platinum resistance thermometer with National Bureau of Standards certificate.

The methanol was a 99.6 percent synthetic product, and was rectified in a 250-cm Brunn column⁴ containing 75 bubble caps, operating at a reflux ratio of 5:1 and a normal through-put of 200-ml methanol per hour. The still head supplied with the column contained a metal dividing valve to control the reflux ratio, with a consequent risk of contaminating the distillate. This head was accordingly replaced by a new head consisting of two vertical parallel glass condensers, set off from the column, the wells at the bottom of the condensers being connected by a horizontal glass tube. The bottoms of the wells were standard tapers, the male members being attached to glass rods which passed through and were supported by Neoprene stoppers at the tops of the condensers. The flows from the wells (one back into the head of the column, and the other into the receiver) were regulated by the seating of the tapers, thus controlling the reflux and through-put. Since condensation was complete in the lower half of the condensers, and since nitrogen was supplied through a manifold to the heads of the condensers, there was no contamination of the methanol by the rubber. Preliminary to a run, the whole apparatus including the still pot and the receiver was flushed with carefully purified, dried nitrogen, and an atmosphere of nitrogen at a slight positive pressure was maintained throughout the distillation by means of the manifold mentioned above and a lead to the closed receiver. All transfers of distillate from the receiver to the filling flasks and all subsequent transfers of solution were by nitrogen pressure. In a distillation, first and last fractions of approximately 750 ml and 1000 ml were rejected, only a middle cut of 2000 ml being retained.

The resulting distillate showed less than one part per million of aldehydes by the alkaline mercuric cyanide test described by Hartley and Raikes,⁵ as evidenced by comparison with a series of samples of known formaldehyde content. The Nessler test, described by Morton and Mork,⁶ placed a similar upper limit on acetone. Nessler's reagent can also be used as a test for ammonia and amines since small traces impart a brown color to the reagent; although the starting material gave a noticeable test, the distillate gave none. Spectroscopic analysis showed less than 1-ppm metallic impurities, and a sample concentrated in boron-free glass was negative in methyl borate; we wish to express our thanks to Professor F. E. Beamish of this department for performing these tests.

TABLE I.

10°C	NaCl		KCl	
	Λ_{obs}	Λ_{calc}	Λ_{obs}	Λ_{calc}
5	64.80	64.79	73.12	73.10
10	64.04	64.05	72.24	72.27
20	63.01	63.02	71.09	71.11
30	62.25	62.25	70.24	70.24
50	61.09	61.09	68.91	68.92
70	60.19	60.19	67.90	67.91
100	59.12	59.11	66.73	66.72

The distillate usually contained from 0.005 to 0.007 weight percent of water as determined by titration with Karl Fischer reagent.⁷ The reliability of this method was checked by titration of samples to which small known amounts of water had been added; the reagent was standardized with sodium acetate trihydrate, as suggested by Warren.⁸

The density of the distillate at 25°C was 0.78658 g/ml, corresponding to 0.78657 for the anhydrous alcohol, and its specific conductance from 2.2 to 3.0×10^{-7} . The density found here is slightly higher than 0.78653, that reported by Jones and Fordamwalt,⁹ but the specific conductance is comparable with those reported by Frazer and Hartley¹⁰ in the majority of their experiments. In some of the preliminary work, the crude material before distillation was digested with anhydrous copper sulfate⁶ or 2, 4, 6 tribromobenzoic acid as suggested by Bjerrum and Lund¹¹ to remove amines. The resulting slight improvement in specific conductance after distillation, however, hardly justified the extra labor. It is interesting to note that methanol prepared by the method of Bjerrum and Lund, the distillation being carried out under nitrogen in a 50-plate Stedman column, gave a product of water content similar to that obtained by simple distillation in the Brunn column, but with a specific conductance roughly twice as great; this higher conductance was apparently due to traces of magnesium (identified spectroscopically) in the distillate.

The solutions were prepared gravimetrically from the alcohol, conductivity water (specific conductance 1.0 to 1.3×10^{-6}), and the twice recrystallized salts which had been heated for half an hour at 600° in an atmosphere of purified, dried nitrogen. In computing volume from mass concentrations, the density data of Shemilt, Davies, and Gordon¹ were employed, and all weights have been reduced to vacuum. In arriving at the concentration, allowance has been made for any changes caused by the evaporation of the solvent from the solutions into the space in the flasks above the liquid. The composition of the solvent in the solutions differed by at most a few hundredths of a

³ Grinnell Jones and B. B. Bradshaw, *J. Am. Chem. Soc.* **55**, 1780 (1933).

⁴ J. H. Brunn, *Ind. Eng. Chem. Anal. Ed.* **8**, 224 (1936).

⁵ H. Hartley and H. R. Raikes, *J. Chem. Soc.* **127**, 524 (1928).

⁶ A. J. Morton and J. G. Mork, *Ind. Eng. Chem. Anal. Ed.* **6**, 151 (1934).

⁷ K. Fischer, *Zeits. f. angew. Chemie* **48**, 394 (1935).

⁸ G. G. Warren, *Can. Chem. Proc. Ind.* **29**, 370 (1945).

⁹ Grinnell Jones and H. J. Fordamwalt, *J. Am. Chem. Soc.* **60**, 1683 (1938).

¹⁰ J. E. Frazer and H. Hartley, *Proc. Roy. Soc. A* **109**, 351 (1925).

¹¹ J. Bjerrum and H. Lund, *Ber. d. d. chem. Ges.* **64**, 210 (1931).

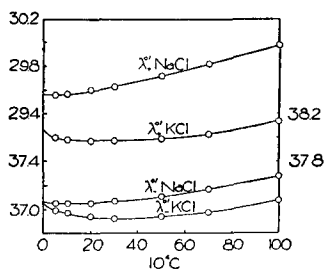


FIG. 1.

mole percent from $NCH_3OH = 0.5$. The specific solvent conductance lay within narrow limits of 1.8×10^{-7} .

The results are given in Table I. To save space only average values of the conductance Λ for round values of the concentration (expressed in moles per liter) are recorded in the table. From the result of each individual run the Shedlovsky function Λ_0' was computed and plotted, and from the resulting $d\Lambda_0'/dC$ a mean value of Λ_0' and, consequently, of Λ for the round concentration was obtained. These corrections for the small concentration differences involved amounted to at most a few hundredth's of a conductance unit in Λ_0' . Each entry in Table I is the average of from 3 to 7 experiments, each with a different solution. The mean absolute deviation was as a rule of the order 0.01 conductance unit.

The last column of Table I gives values of the conductance computed by the Onsager-Shedlovsky equation

$$[\Lambda + 2\sigma(C)^{\frac{1}{2}}]/[1 - \vartheta(C)^{\frac{1}{2}}] = \Lambda_0' \\ = \Lambda_0 + BC + EC \log C, \quad (1)$$

where $\vartheta = 8.204 \times 10^5 / (DT)^{\frac{1}{2}}$, $\sigma = 41.21 / (DT)^{\frac{1}{2}} \cdot \eta$, D is the dielectric constant,¹² viz. 49.84, and η is the viscosity¹³ 0.01326 poise; Λ_0 , B , and E are disposable constants. With $\vartheta = 0.4529$ and $2\sigma = 50.99$, the values of Λ_0 , B , and E used in computing Λ_{calc} are 66.62, 206, and 71 for NaCl, and 75.10, 322, and 155 for KCl. It is evident from Table I that Eq. (1) adequately represents the data; nevertheless the very large value of the ratio E/Λ_0 for the potassium salt suggests that, in this case at any rate, the agreement is some-

what fortuitous.¹⁴ However, we believe that the extrapolation to infinite dilution is reasonably reliable.

From the limiting values¹ of t_+ , 0.4437 and 0.5068, the limiting conductance for chloride ion is 37.06 and 37.04 for NaCl and KCl, respectively. Thus, the results satisfy the Kohlrausch rule of independent ionic mobilities at infinite dilution practically within the precision of the transference numbers. At higher concentrations, however, the situation is different. Figure 1 shows the quantity¹⁵ $\lambda_{\pm}^{0'} = [\lambda_{\pm} + \sigma(C)^{\frac{1}{2}}]/[1 - \vartheta(C)^{\frac{1}{2}}]$ where λ_{\pm} is the ionic conductance computed from Table I of this paper and Table III of reference 1. It will be noted that for both ions of the sodium salt, $\lambda_{\pm}^{0'}$ is more or less constant at high dilutions and then tends to increase with rising concentration—a behavior usually taken as normal for strong 1-1 electrolytes in aqueous solution. For KCl, on the other hand, there is a distinct minimum¹⁶ for both ions at a concentration near 0.003 N , and this has frequently been interpreted as evidence for ion-pair formation, since it corresponds on the familiar $\Lambda - (C)^{\frac{1}{2}}$ plot to the observed conductances lying below the limiting Debye-Onsager slope. Thus sodium chloride on this basis would be "strong" and potassium chloride somewhat associated.¹⁷ Electromotive force measurements in this laboratory on cells with transference (employing the LaMer extension¹⁸ to the Debye-Hückel equation for the activity coefficients) give a mean ionic diameter for NaCl in this solvent of approximately 4.5 Å. The critical Bjerrum¹⁹ distance q_0 , given for 1-1 salts by $q_0 = e^2/2DkT$, is approximately 5.6 Å for a solvent of dielectric constant 50 at 25°C; thus, on the rather naive assumption

¹⁴ L. Onsager and R. M. Fuoss, *J. Phys. Chem.* **36**, 2689 (1932).

¹⁵ D. A. MacInnes, T. Shedlovsky, and L. G. Longworth, *J. Am. Chem. Soc.* **54**, 2758 (1932).

¹⁶ There is, of course, a similar minimum in the Λ_0' versus C curve.

¹⁷ It is interesting to note that Frazer and Hartley's results for NaCl and KCl in anhydrous methanol (reference 10) would also indicate that the sodium salt was strong but that there was association with the potassium. In fact, a test of their data for the more dilute KCl solutions by the method of Shedlovsky (*J. Frank. Inst.* **225**, 739 (1938)) indicates a dissociation constant of approximately 0.06.

¹⁸ T. H. Gronwall, V. K. LaMer, and K. Sandved, *Physik. Zeits.* **29**, 358 (1928).

¹⁹ N. Bjerrum, *Kgl. Danske Vidensk. Selskab* **7**, No. 9 (1926).

¹² P. J. Albright and L. J. Gosting, *J. Am. Chem. Soc.* **68**, 1061 (1946).

¹³ L. G. Longworth and D. A. MacInnes, *J. Phys. Chem.* **43**, 239 (1939). The value given here was obtained from a large-scale deviation plot of their values of the relative viscosity, and the viscosity of water (I.C.T. 5, p. 10).

that the LaMer ionic diameter and the Bjerrum q_0 may be correlated, sodium chloride should also be associated, contrary to observation. It would seem probable that the contradiction arises from the over-simplification of Bjerrum's treatment.

The data also permit a test of the familiar Walden rule connecting the limiting conductance for an ion in two solvents, $\lambda_{\pm}^0 \cdot \eta_r = (\lambda_{\pm}^0)_r$, where η_r is the viscosity of the solvent in question relative to some reference solvent in which the limiting ionic conductance is $(\lambda_{\pm}^0)_r$. Alternatively, the Walden equation is sometimes modified¹³ to give $\lambda_{\pm}^0 \cdot \eta_r^\alpha = (\lambda_{\pm}^0)_r$, where α is a disposable parameter. Taking water as reference solvent, in which the limiting conductances² are 73.50, 50.10, and 76.35 for potassium, sodium, and chloride ions, respectively, and $\eta_r = 1.482$, the resulting values of α , corresponding to the observed limiting conductances found here (38.06, 29.56, and 37.05) are 1.67, 1.34, and 1.84 for potassium, sodium, and chloride. The decrease in conductance as compared with water is thus much greater than can be accounted for by viscosity alone. On the simple Stokes' picture of transport, this would imply, as suggested by Longworth and MacInnes,¹³ an increase in the diameters of the solvated ions in the mixture of from 15 to 30 percent as compared with water, i.e., that in the mixture the ions had a much greater influence in organizing the neighboring solvent dipoles. As against this, once again assuming that the Debye-LaMer diameter is significant in transport processes, is the fact that, for sodium chloride at any rate, this diameter is practically identical²⁰ in water and in the 50-mole percent mixture.

That this curious situation is not confined to mixtures of two highly polar solvents is evidenced by the extensive series of measurements

carried out in the Yale laboratories on hydrochloric acid in dioxane-water mixtures. If the limiting conductances of Owen and Sweeton²¹ and the transference numbers of Harned and Dreby²² be combined, and if water once again be taken as reference solvent, the exponent α of the relative viscosity is 1.09, 1.37, 1.88, and 2.54 for chloride ion in 20, 45, 70, and 82 percent dioxane solution, respectively, at 25°C; the corresponding values for hydrogen ion are 0.90, 1.50, 2.40, and 3.85. Even ignoring the results for H_+ (which might be expected to behave anomalously in any solvent containing water²³) the chloride results show a steady increase in α with increasing dioxane concentration. Alternatively, on the basis of the simple Walden rule, the diameter of the chloride ion in 70 percent dioxane solution would have to be nearly twice its diameter in water; yet Harned,²⁴ from e.m.f. measurements has shown that there is an increase of only about one third in the LaMer diameter on passing from water to 70 percent solution.

We believe that our results and those for the dioxane-water mixtures indicate that any interpretation of electrolytic transport as a function of solvent medium will ultimately require a knowledge of ion conductances as distinct from equivalent conductances. We also feel that the use of a mixed solvent may complicate the problem unduly, possibly through preferential ion solvation with one solvent constituent rather than the other, and that, consequently, a one-component solvent may yield data which are more easily interpreted.

In conclusion we wish to thank the National Research Council of Canada for the grant of a fellowship to one of us (H.I.S.) and also Dr. G. F. Wright of this department for his advice and assistance in purifying the methanol.

²⁰ Brown and MacInnes, J. Am. Chem. Soc. **57**, 1356 (1935), give 4.45Å in water. The smaller value quoted by Janz and Gordon, J. Am. Chem. Soc. **65**, 218 (1943), viz. 4.12Å, arises from the fact that Janz and Gordon employed the semi-empirical Hückel extension, involving a term linear in the concentration, to represent their activity coefficients over a greater concentration range than is possible with the Debye-Hückel equation itself. It is the former result that should be compared with the value 4.5Å, quoted above for the methanol-water mixture.

²¹ B. B. Owen and G. W. Waters, J. Am. Chem. Soc. **60**, 2371 (1938).

²² H. S. Harned and E. C. Dreby, J. Am. Chem. Soc. **61**, 3113 (1939).

²³ L. Onsager, Ann. N. Y. Acad. Sci. **46**, 241 (1945).

²⁴ H. S. Harned and J. O. Morrison, J. Am. Chem. Soc. **58**, 1908 (1936); H. S. Harned, *ibid.* **60**, 336 (1938); H. S. Harned and C. Calmon, *ibid.* **60**, 2130 (1938); H. S. Harned, J. G. Donelson, and C. Calmon, *ibid.* **30**, 2133 (1938).