[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KENTUCKY]

Solvents Having High Dielectric Constants. VII. Transference Numbers of Potassium and Chloride Ions in Formamide at 25°[1]

BY LYLE R. DAWSON AND CARL BERGER

RECEIVED APRIL 4, 1957

Approximate transference numbers of potassium and chloride ions in formamide at 25° have been determined by the Hittorf method within the concentration range of 0.2 to 0.6 *N*. Extrapolation of a plot of the Longsworth function yielded a limiting cation transference number of 0.406. From the present results and conductance data reported previously the calculated limiting transference number of the solvated proton in a solution of hydrogen chloride in formamide was found to be 0.37 at 25°.

The electrical conductances of solutions of potassium chloride in formamide have been reported in an earlier paper[2] from this Laboratory. It was shown that the slope of the plot of Λ *vs.* $\sqrt{C}$ corresponds closely to the theoretical slope below 0.01 *N* and that potassium chloride is completely dissociated in formamide even at concentrations considerably above 0.1 *N*.

Transference data have been obtained by the moving boundary method in ethanol and in methanol[3] but numerous experimental difficulties prevented using this method for formamide solutions. The present investigation was designed to apply the Hittorf method in an attempt to obtain information concerning the relative solvent–solute interaction in this medium and in other more familiar solvents for which reliable data are available in the literature.

Experimental

Apparatus.—Use was made of the familiar type of Hittorf cell[4] which was constructed from large Pyrex glass tubing. The cell was held in a thermostated water-bath. Care was exercised to avoid exposure of the solution to the atmosphere and to prevent its contamination in any other way.

Silver and silver–silver chloride electrodes were constructed from No. 24 B. and S. gage silver wire. A device employing a 6F6 pentode tube on a power line with relatively small voltage fluctuation maintained a constant current.

A Richards silver coulometer was used in the circuit. Specially constructed weight burets were used for the transfer of larger amounts of solutions.

Salt.—Potassium chloride which had been purified especially for accurate *p*H work was purchased. The salt was dried at 110° for ten hours and used without further treatment.

Solvent.—Commercial grade formamide was distilled three times at reduced pressure over calcium oxide. The middle portion retained from the third distillation was carried through several fractional freezing cycles using the procedure described by the present authors in an earlier paper.[5] Physical properties at 25° of the solvent used were as follows: density = 1.129 g./ml.; viscosity = 0.0331 poise; dielectric constant = 109.5 at 10 mc.; conductivity = $1\text{–}5 \times 10^{-5}$ ohm^{-1} cm.$^{-1}$.

The solvent was used as promptly as possible after final purification and was protected from light while in storage.

Procedure.—Dissolution of the salt required several hours with frequent agitation of the solution. All solutions were prepared out of contact with air and dry nitrogen was bubbled through a solution for one hour before it was transferred to the cell. Lubriseal was used on the stopcocks and the usual precautions were observed to ensure tight seals and the absence of air bubbles in the cell.

After the cell had been in the thermostat long enough to establish temperature equilibrium the circuit was closed and electrolysis allowed to proceed for from 24 to 30 hours at 1–3 ma. At higher concentrations the current became larger and the time was decreased.

Changes in salt concentration were measured by potentiometric titration for chloride ion in the formamide solutions. This titration procedure has been described previously.[5]

Results and Discussion

The data presented in Table I represent averages of consistent duplicate or triplicate determinations. Owing to the instability of formamide and the difficulty of maintaining it anhydrous as well as the problems involved in potentiometric titrations in this solvent, there may be inherent errors in the results amounting to 2 or 3%.

TABLE I

POTASSIUM CHLORIDE IN FORMAMIDE

Concn. $\times 10^2$	I (ma.)	G. of Ag^+ deposited	t_+
20.04	1.0	0.1247	0.40
20.80	1.0	.1214	.40
24.37	1.2	.1337	.40
28.98	1.4	.1612	.39
57.28	2.0	.1871	.38
58.91	2.2	.1917	.38

Although experimental difficulties prevented extension of the study to dilute solutions, an attempt was made to obtain an approximate value for the limiting transference number by extrapolating a plot of the Longsworth function.[6]

$$t_+^{0\prime} = (t_+\Lambda^1 + {}^1/_2\beta C^{1/2})/(\Lambda^1 + \beta C^{1/2})$$

In this expression, $\Lambda^1 = \Lambda_0 - (\alpha\Lambda_0 + \beta)C^{1/2}$, $\beta = 82.42/(DT)^{1/2}\eta$ and $\alpha = 8.204 \times 10^5/(DT)^{3/2}$. D is the dielectric constant, η is the viscosity and C is the concentration in equivalents per liter. The entries in Table I correspond to the plot in Fig. 1. A value of 0.406 for the limiting transference number of the potassium ion was obtained by extrapolation of the plot; therefore, the limiting transference number of the chloride ion is 0.594. Above 3×10^{-2} *N* the plot deviates sharply from a straight line. Conductance data from another study in progress in this Laboratory, which support the general validity of these values, will be reported in a subsequent paper.

Using data from the work of Dawson, Newell and McCreary[2] with a value of approximately 29.7 ohms^{-1} cm.^{2} equiv.$^{-1}$ for the limiting equivalent conductance of potassium chloride at 25° and our value for t_{K^+}, the limiting equivalent ionic con-

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(1) Taken from a Ph.D. dissertation submitted by Carl Berger.

(2) L. R. Dawson, T. M. Newell and W. J. McCreary, THIS JOURNAL, **76**, 6024 (1954).

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

(4) D. A. MacInnes and M. Dole, THIS JOURNAL, **53**, 1357 (1931).

(5) C. Berger and L. R. Dawson, *Anal. Chem.*, **24**, 994 (1952).

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

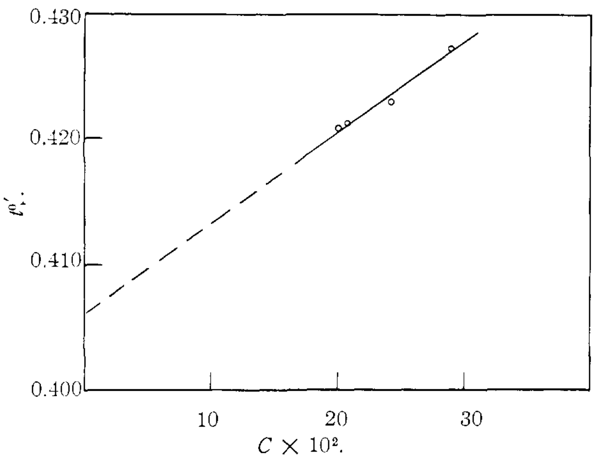

Fig. 1.—The concentration dependence of the Longsworth function for potassium chloride in formamide.

ductances become $\lambda^0_{K^+} = 12.1$, and $\lambda^0_{Cl^-} = 17.6$. Similarly from a value of 27.9 ohms^{-1} cm.$^{-2}$ equiv.$^{-1}$ for the limiting equivalent conductance of hydrogen chloride in formamide at 25°, and $\lambda^0_{Cl^-} = 17.6$, the calculated λ^0 value for the solvated hydrogen ion is 10.3 and its transference number is 0.37.

In passing from water ($t^0_{K^+}$ in KCl = 0.49) to formamide solutions the limiting transference number of the potassium ion in potassium chloride is decreased 17%. The relatively larger solute–solvent interaction with the potassium ion in the latter solvent probably is an ion–dipole effect resulting from the greater dipole moment of the formamide.[7] Evidence that the large dipole moment of formamide produces strong ion–dipole forces appears also in the decrease in transference numbers of the solvated proton from 0.82 in water to 0.37 in formamide. In formamide dissociated protons are held by the solvent molecules with sufficient force to prevent easy transfer from molecule to molecule as occurs in aqueous solutions.

The limiting equivalent ionic conductance–viscosity products for the potassium ion at 25°, in ohm^{-1} cm.^{2} equiv.$^{-1}$ poise, in methanol, ethanol, formamide and water are 0.283, 0.255, 0.400 and 0.656. A complete explanation of the relative magnitudes of these values would involve not only direct ion–solvent interactions but also short-range viscosity effects resulting from the influence of the ions in modifying the normal solvent structure.

[7] W. W. Bates and M. E. Hobbs, THIS JOURNAL, **73**, 2151 (1951).

LEXINGTON, KY.

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

The Copper(II)–Pyridine Complexes and their Reaction with Hydroxide Ions

BY D. L. LEUSSING AND R. C. HANSEN[1]

RECEIVED FEBRUARY 21, 1957

The formation constants have been evaluated at an ionic strength of 1.0 and 25.0° for the reactions: $Cu^{++} + py \rightleftarrows Cupy^{++}$, $Cu^{++} + 2py \rightleftarrows Cupy_2^{++}$, . . ., $Cu^{++} + 5py \rightleftarrows Cupy_5^{++}$. The values found are 3.92×10^2, 2.14×10^4, 8.5×10^5, 3.5×10^6 and $1.0_6 \times 10^7$, respectively. Mixtures of these complexes react with hydroxide to form a dimer: $py_2Cu(OH)_2Cupy_2^{++}$. The constant for the reaction $2Cu^{++} + 2OH^- + 4py \rightleftarrows py_2Cu(OH)_2Cupy_2^{++}$ is $5.1 \times 10^{+24}$. The absorption spectra of each of the complexes were determined and the spectral behavior of the solutions was found to be in accordance with the interpretation based upon equilibrium concentration measurements.

Recent publications have described the formation of mixed hydroxy complexes of copper(II) with ethylenediaminetetraacetate,[2] ethylenediamine,[3] 1,10-phenanthroline,[4] α,α'-dipyridyl[5] and ammonia.[6] The hydroxide was shown to occupy a fifth or sixth coördination position on the copper in the case with bis-ethylenediamine and ethylenediaminetetraacetate. However, with 1,10-phenanthroline and α,α'-dipyridyl the coördination of copper is lower (excluding water) as only one molecule of the bidentate ligand per copper was observed in the mixed complexes. The existence of the hydroxy ammonia complex[6] was inferred from spectral evidence and its composition was assumed to be $Cu(NH_3)_3OH^+$. Only in the case of ethylenediaminetetraacetate was the constant for the formation of the mixed complex evaluated. This was found to have a pK of 11.3 for the reaction

$$CuY^= + OH^- \rightleftarrows CuYOH^\equiv$$

The reactions of the copper–pyridine complexes were investigated in order to throw more light on the nature of the reactions of the copper ammines with hydroxide. Pyridine was chosen because it is a monodentate ligand and its activity in aqueous solutions can be determined very easily by measuring the distribution into toluene. The conventional pH method of Bjerrum[7] cannot be used in the present case to determine the nature and stability of the mixed complexes because the pyridinium ion does not exist in appreciable quantities at the pH values optimum for the reaction with hydroxide. In Bjerrum's method the concentration of

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(1) The authors wish to express their gratitude for partial support of this work by the Wisconsin Alumni Research Foundation and the du Pont Grant-in-Aid. Preliminary experiments were carried out by W. E. Ohnesorge at the Massachusetts Institute of Technology supported by a research grant of the Atomic Energy Commission.

(2) M. C. Bennett and N. O. Schmidt, *Trans. Faraday Soc.*, **51**, 1412 (1955).

(3) H. B. Jonassen, R. E. Reeves and L. Segal, THIS JOURNAL, **77**, 2748 (1955).

(4) R. T. Pflaum and W. W. Brandt, *ibid.*, **76**, 6215 (1954).

(5) T. Wagner-Jauregg, B. E. Hackley, Jr., T. A. Lies, O. O. Owens and R. Proper, *ibid.*, **77**, 922 (1955).

(6) J. Bjerrum, C. J. Ballhausen and C. K. Jorgensen, *Acta Chem. Scand.*, **8**, 1275 (1954).

(7) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, Denmark, 1941.