[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY, UNIVERSITY OF BRISTOL]

THE TRANSFERENCE NUMBERS OF SODIUM AND HYDROGEN IN MIXED CHLORIDE SOLUTION

BY MILLICENT TAYLOR

RECEIVED AUGUST 4, 1925 PUBLISHED MARCH 5, 1926

In 1923 Schneider and Braley[1] published a number of transference data for solutions of mixtures of sodium and potassium chlorides ranging in total normality from 0.1 to 1.6 *N* and varying in the proportions of sodium and potassium salts from 3KCl:1NaCl to 1KCl:3NaCl.

They obtained the remarkable result that there was no apparent movement of the sodium in the solution which was 0.15 *N* in potassium chloride and 0.05 *N* in sodium chloride. From this, the far-reaching conclusion was drawn that the ions in such solutions are not the simple ions universally assumed but that the sodium must enter into a complex anion, and that the migration of the complex anion must just counterbalance the migration of the sodium ion.

Schneider and Braley themselves pointed out that their experimental error is high, on account of the indirect method of estimating the sodium and it is evident that the effect of this inaccuracy must be accentuated in those solutions in which the proportion of potassium chloride is highest, namely, in the mixture under discussion. Further, for the determination of the chlorine content, the authors used the Mohr volumetric method, which is inaccurate as compared with gravimetric determination.

It is essential to test such an unexpected conclusion, not by a mere repetition of the same measurement but by choosing such conditions that the accuracy of the results can be placed beyond question.

To ensure this it is advisable to eliminate the inherent difficulty of the analysis of mixtures containing both potassium and sodium. At the suggestion of Professor James W. McBain a mixture of hydrochloric acid and sodium chloride was employed so that evaporation would give sodium chloride directly and these substances were used in the proportions 0.15 *N* hydrochloric acid and 0.05 *N* sodium chloride for migration measurements. This mixture provides the same anions as that used by Schneider and Braley and affords a crucial test of the credibility of their conclusion.

If the sodium enters with chlorine into any complex anion, such as ($NaCl_2$), which was suggested by Schneider and Braley, we shall expect in the case of the mixture of sodium and hydrogen chlorides, to find the value of the ratio T_{Na}/T_H much below that corresponding to the mobilities of sodium and hydrogen, calculated either on the Arrhenius theory or on any hypothesis of complete dissociation.

---

[1] Schneider and Braley, THIS JOURNAL, **45**, 1121 (1923).

Materials Used, Apparatus and Method

The materials used were Kahlbaum's purest sodium chloride, and pure hydrochloric acid, obtained of definite concentration by distillation according to the method of Hulett and Bonner.[2]

Both in the case of this acid and of the conductivity water, with which the solutions were made, the distillation was carried out immediately before use of the distillate.

The migration apparatus consisted of a pair of borosilicate glass U-tubes of about 2.5 cm. in diameter and a total capacity of some 350 cc. The U-tubes communicated through side tubes, united by a ground-glass joint.

The electrodes passed through hollow ground-glass stoppers, each of which was provided with a second opening for the escape of gas.

The cathode consisted of platinum and the anode of pure silver, previously plated with electrolytic silver.

Silver coulometers were inserted at each end of the migration apparatus, and each invariably contained the same weight of deposited silver, within 0.1%.

The solutions were made up in a liter flask to a volume normality of approximately 0.05 N NaCl and 0.15 N HCl affording 0.2 N total chloride, and in each case the total solution was weighed so that the initial weight composition was accurately known by synthesis as well as by analysis.

The Analytical Method

This consisted in determining the weight of sodium chloride directly by evaporation[3] of a known fraction of each portion of the solution, while the total chlorine was determined gravimetrically as silver chloride in the remaining fraction.

It was observed in preliminary experiments, that conductivity water which has stood in Jena glass flasks left upon evaporation a measurable solid residue. Consequently, in the recorded experiments, rinsing was avoided, and each tube was weighed with a small quantity of clinging liquid, which amounted to about 0.3 cc. and was taken into account in the final calculation.

In the first experiment the liquid round the anode remained perfectly clear and no silver could be detected in it when tested by reduction with alkaline formaldehyde, according to the method of Armani and Barboni[4] who claim to detect one part in 240,000. In this experiment the total chlorine in the anode portion was not determined directly as silver chloride, but by difference.

In the second experiment a haze of silver chloride was seen in the liquid around the anode. This necessitated filtration with consequent decrease in accuracy, as far as the anode portion is concerned. Thus in both cases the anode portion should give less accurate values than the cathode portion.

---

[2] Hulett and Bonner, THIS JOURNAL, **31**, 390 (1909).

[3] To avoid loss of sodium chloride, the evaporation was carried out at a low temperature (about 60°) in a steam oven, and the platinum dish containing the solution was covered by a platinum lid, leaving a clearance of about 1 cm. between the edge of the dish and the lid.

[4] Armani and Barboni, *C. A.*, **4**, 2428 (1910).

This is actually the case, as the final values for the transport numbers are not as concordant for the anode as for the cathode portions.

During the experiment the anode became coated with chloride and there was no escape of gaseous chlorine. In the latter part of each experiment the formation of chloride ceased, and oxygen escaped. The anode was therefore weighed at the beginning of each experiment, and again at the end it was washed and weighed, after being dried at 150° together with the silver chloride filtered from the anode solution. The weight of deposited chlorine was thus determined, and the weight of liberated oxygen could be calculated.

In calculating the final composition of the anode solution, account has been taken of the oxygen and chlorine so removed, while the weight of the cathode solution has been corrected for the equivalent quantity of hydrogen lost. The weights used were standardized at the National Physical Laboratory, and all weighings have been corrected for air buoyancy. The

TABLE I

EXPERIMENTAL RESULTS

Expt.	IV	VII
Concn. of original solution, N_v at 18°, HCl	0.1500	0.1502
NaCl	.0498	.05002
Total	.1998	.20022
G. per 1000 g. of H_2O, HCl	5.4981	5.5028
NaCl	2.9284	2.9383
Wt. of soln. in migration apparatus, g.	330.301	334.0999
Corrected[a] wt. of anode solution, g.	104.0342	113.01234
Wt. of NaCl in anode solution, g.	0.29418	0.32374
Wt. of total Cl in anode solution, g.	.65439	.71869
Further wt. of Cl_2 deposited on anode, g.	.10300	.10514
Wt. of water in anode soln., g.	103.1475	112.0463
Wt. of total Cl initially in water, g.	0.73468	0.79916
Wt. of NaCl initially in water, g.	.30206	.32912
Equivalents of Cl_2 migrated to anode portion, g.	.0006405	.0006958
Equivalents of Na migrated from anode portion, g.	.0001353	.00009204
Corrected[a] wt. of cathode solution, g.	103.2885	104.5338
Wt. of NaCl in cathode solution, g.	0.30650	0.31087
Wt. of total Cl_2 in cathode solution, g.	.70536	.71813
Wt. of water in cathode solution, g.	102.4449	103.6753
Equivalents of Cl_2 migrated from cathode portion	0.0006853	0.0006013
Equivalents of Na migrated to cathode portion.	.00011121	.00010863
Wt. of HCl in middle portion, g.	.67142	.63534
Wt. of NaCl in middle portion, g.	.35739	.33916
Wt. of HCl initially in water, g.	.67049	.63601
Wt. of NaCl initially in water, g.	.35712	.33950
Wt. of silver deposited in coulometers, g., A.	.38066	.34093
C.	.38058	.34083

[a] Corr. for wt. of Cl_2, O_2 or H_2 as indicated in the preceding paragraph.

atomic weights used are H = 1.008, Cl = 35.457, Na = 22.997, Ag = 107.880. Seven experiments with different procedures were carried out, of which two are recorded as being most complete and embodying all the precautions.

The experimental results are collected in Table I.

Table II contains the transference numbers of the sodium, chlorine and hydrogen ions, calculated from the experimental values in Table I.

TABLE II

CALCULATED TRANSFERENCE NUMBERS

Expt.	Pole	T_{Na}	T_{Cl}	T_H
1	Anode	0.0383	0.1817	0.7800
	Cathode	.0315	.1942	.7743
	Mean	.0349	.188	.7771
2	Anode	.0291	.2203	.7506
	Cathode	.0342	.1902	.7756
	Mean	.0317	.2053	.7631

Table III shows in Col. 1 the mean values of the transference numbers as calculated from the two experiments and in Col. 2 the values for these numbers deduced on the assumption that the ionic mobilities have the same value in mixtures as in solutions of the pure salts of the same total salt concentration.[5]

TABLE III

MEAN VALUES OF TRANSFERENCE NUMBERS

	Observed mean	Theoretical values
T_{Na}	0.0333	0.0311
T_{Cl}	.197	.206
T_H	.770	.763

In calculating the values contained in Col. 2, the following equations have been employed:

$$1000\,L = (\Lambda_{Na} + \Lambda_{Cl})\,\gamma_{0\cdot 2NaCl} \times C_{NaCl} + (\Lambda_H + \Lambda_{Cl})\,\gamma_{0\cdot 2HCl} \times C_{HCl}$$
$$= \Lambda_{0\cdot 2NaCl}\,C_{NaCl} + \Lambda_{0\cdot 2HCl}\,C_{HCl} \qquad (1)$$

since $\gamma_{0\cdot 2} = \dfrac{\Lambda_{0\cdot 2}}{\Lambda_K \times \Lambda_A}$

$$T_{Na} = \frac{C_{NaCl}\,\gamma_{0\cdot 2NaCl}\,\Lambda_{Na}}{1000\,L} \qquad (2)$$

with the corresponding value for T_H

$$T_{Cl} = (C_{NaCl} \times \gamma_{0\cdot 2NaCl} + C_{HCl}\,\gamma_{0\cdot 2HCl})\,\Lambda_{Cl} \qquad (3)$$

In these equations L denotes the specific conductivity of the solution of mixed salts, $\gamma_{0\cdot 2}$ the ratio of the molar conductivity of the pure salt at concentration 0.2 N to its molar conductivity at infinite dilution, C_{NaCl} and C_{HCl} denote the concentrations of the salts in the mixed solution, $\Lambda_{0.2NaCl}$ and $\Lambda_{0.2HCl}$ the molar conductivities of the pure salts at concentra-

---

[5] Bray and Hunt, THIS JOURNAL, **33**, 781 (1911).

tion 0.2 N, Λ_{Na}, Λ_{H}, Λ_{Cl} the mobilities and T_{Na}, T_{Cl}, T_{H}, the transference numbers of the respective ions in mixed solution. Kohlrausch's values at 18°, 315.0, 65.5 and 43.5 have been used for the ionic mobilities of hydrogen, chlorine and sodium, respectively.[6]

The agreement between the mean observed values of the transference numbers, and the values calculated on the normal behavior of mixed salts in solution, is complete and conclusive.

Thus none of these four independent analyses affords any support to the suggestion of Schneider and Braley, that any complex anion exists containing sodium and chlorine.

It is important to emphasize that the expression for the mobility of the ion at any given concentration, such as $\Lambda_{0.2\mathrm{Na}} = \Lambda_{0.0\mathrm{Na}} \times \Lambda_{0.2\mathrm{Na}}/\Lambda_{0.0\mathrm{NaCl}}$, has been employed without reference to the question of whether the apparent decrease in the mobility of the ion with increasing concentration is due to decrease in dissociation, or to an actual change in mobility. These results and their interpretation therefore remain valid, no matter whether the classical theory of Arrhenius or a theory of complete dissociation is accepted. In any case the behavior is quantitatively in accordance with the existence of the simple ordinary ions and not those advocated by Schneider and Braley to explain their experimental results.[7]

Summary

Transference numbers have been determined in a solution of sodium chloride containing hydrochloric acid. The results show that only simple ions and no complex ions are present in such solutions.

BRISTOL, ENGLAND

---

[6] Landolt-Börnstein, "Physikalisch-Chemische Tabellen," Julius Springer, Berlin, 5th edition, **1923**, p. 1104.

[7] Since this paper was submitted a paper has appeared [Dewey, THIS JOURNAL, **47**, 1927 (1925)] in which the experiments of Schneider and Braley have been directly repeated and not confirmed. Bjerrum and Ebert [*Det. Kgl. Danske Videnskabernes Selaskab.*, VI, 9, p. 5, **1925**] have criticized Schneider and Braley's work from internal evidence, ascribing the reputed deviations to experimental error. MacInnes developed a formula for the prediction of the transference numbers in the mixture giving values which agree even better with our experimental results than those given in the last column of Table III of the present paper.