

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Transference Numbers and Hydration of Some Quaternary Ammonium Salts¹BY CECIL H. HALE² AND THOMAS DE VRIES

It is a generally accepted fact that ions in aqueous solution are hydrated to some extent. The degree of hydration depends, amongst other factors, upon the nature and size of the ion. Von Hevesy³ has shown that nearly all univalent organic ions are so large and the strength of the electric field surrounding them so weak that hydration should not occur. If organic ions are not hydrated, the electrolytic transfer of water in solutions of tetraalkylammonium salts should show a transfer of water to the anode equivalent to the amount of water carried by the anions alone or, more probably, the results should show a trend of less hydration for the larger organic cations. In this research, the electrolytic transfer of water in solutions of tetramethyl-, tetraethyl-, tetra-*n*-propyl-, and tetra-*n*-butylammonium iodides was studied. Maltose was used as the non-electrolyte because it has a high optical rotation and its concentration can be measured very accurately by means of a polarimeter. Some experiments were also made in which acetone and ethyl acetate were the reference substances. The well-known Nernst method as developed by Washburn⁴ was used in this investigation.

Apparatus and Experimental

The transference apparatus shown in Fig. 1 is a modification of the one described by MacInnes and Dole.⁵ It was constructed of Pyrex glass tubing of 19 mm. internal diameter. The stopcocks which separated the anode and cathode compartments were hollow and open at each end to permit the circulation of water through them when the apparatus was in the constant temperature bath. The apparatus consisted of two sections, connected by a spherical joint to allow the anode and cathode compartments to be weighed. The total length of 130 cm. contained 10 bends, spaced to reduce convection and diffusion during electrolysis. For analysis the solution in the apparatus was divided into five portions. The approximate volumes of the different compartments were: cathode, 115 ml.; anode, 150 ml.; cathode middle, 40 ml.; anode middle, 40 ml.; middle, 90 ml. There was never any appreciable variation in the concentrations of the three middle compartments, which proved the effectiveness of the design of the apparatus in the prevention of diffusion and convection.

The electrodes were made of silver and silver iodide, deposited electrolytically on 18-gage platinum wire.

Silver coulometers were used to measure the current. The silver nitrate solutions from the platinum crucibles were filtered through sintered glass crucibles to prevent the loss of deposited silver. One coulometer was connected to each electrode in order to detect any electrical leaks. It was necessary to coat the glass joints with picein wax to prevent such leaks.

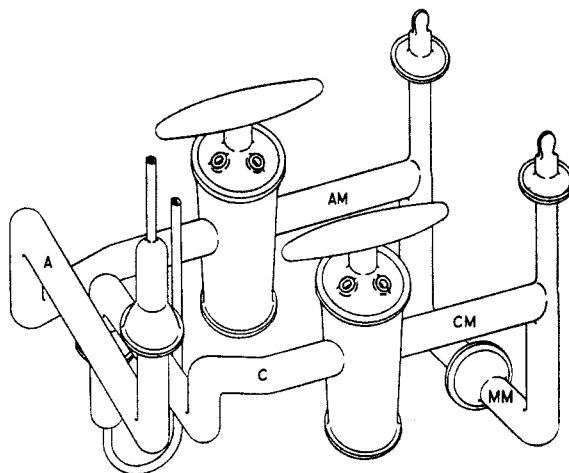


Fig. 1.—Transference apparatus: A, anode compartment; AM, anode middle; MM, middle middle; CM, cathode middle; C, cathode compartment.

The polarimeter was a Schmidt and Haensch instrument which could be read to ± 0.01 degree of rotation. Light of wave length 5893 Å. was obtained from a tungsten bulb by means of a monochromator. A four decimeter tube was used.

Electrolysis experiments were carried out in a thermostat maintained at $25 \pm 0.02^\circ$.

Quaternary ammonium iodides were prepared from alkyl iodides and the corresponding tertiary amines. The compounds were purified by repeated recrystallizations from ethyl acetate to which a small amount of ethanol had been added.

The silver cyanide solution for silver plating the electrodes was prepared by the dissolution of 46 g. of silver nitrate, 70 g. of potassium cyanide, 31.5 g. of sodium carbonate and 0.5 g. of sodium thiosulfate in one liter of distilled water.

The maltose used was Merck, "purified" grade. Electrical conductivity measurements showed it to be free from electrolytes.

In the transference experiments, the electrolysis was allowed to continue for about forty-eight hours. A potential of about 50 volts was necessary to obtain the desired current of about 5 milliamperes. At the end of the electrolysis, the stopcocks were closed and the anode middle, cathode middle and middle solutions were transferred by means of a pipet to weight burets. The apparatus was then removed from the bath and the two sections separated, cleaned and dried, the stopcocks remaining closed. The two sections were first weighed before the solutions were transferred to weight burets.

Analysis.—The quaternary ammonium salt solutions were titrated with 0.05 *M* silver nitrate at about 50° . The end-point was determined potentiometrically using a Garman and Droz⁶ titrimeter. Weight burets were used in all the titrations.

The concentration of the maltose in grams per 100 ml. in the solutions were found from the equation $0.1923\alpha - 0.010$, where α is the optical rotation. This relation was established by measuring the rotation of solutions of known concentration. The presence of the quaternary

(1) Presented before the Physical and Inorganic Division at the 113th meeting of the American Chemical Society, Chicago, Ill., April 19–22, 1948.

(2) Abstract of the Ph.D. dissertation of C. H. Hale whose present address is Esso Laboratories, Baton Rouge, La.

(3) G. von Hevesy, *Z. Elektrochem.*, **27**, 77 (1921).

(4) E. W. Washburn, *THIS JOURNAL*, **31**, 322 (1909).

(5) D. A. MacInnes and M. Dole, *ibid.*, **53**, 1357 (1931).

(6) R. L. Garman and M. E. Droz, *Ind. Eng. Chem., Anal. Ed.*, **11**, 398 (1939).

ammonium iodides was found to have no measurable effect on the optical rotation of the solution.

Acetone determinations were made by a method based on the formation of iodoform.⁷ The deviation of triplicate determination was 0.1%.

Ethyl acetate was determined by hydrolysis in alkaline solution. A measured excess of carbonate-free 0.35 *N* sodium hydroxide solution was added to a weighed sample and refluxed for forty-five minutes, and back titrated with 0.1 *N* sulfuric acid. With a correction from blank determinations the deviation of triplicate determinations was 0.05%.

The transference numbers of sodium and potassium iodide were determined to test the apparatus and the techniques. The values obtained at the anode and the cathode agreed well with each other and with the values in the literature to within 0.001.

The quaternary ammonium iodides invariably gave a much larger value for the cation transference number at the anode than at the cathode. A typical set of values are presented in Table I. The deposit on the anode did not have the appearance of pure silver iodide, but was white and somewhat flocculent. Further, the transference numbers calculated from the analysis of the anode solutions did not agree in successive experiments. These facts indicated that formation of solid solutions of the quaternary ammonium iodide with silver iodide. A solution of tetramethylammonium iodide was electrolyzed in a small beaker with no attempt made to separate the solutions at the silver-silver iodide electrodes. The final solution was analyzed for iodide ion concentration and it was found that approximately one mole of tetramethylammonium iodide had disappeared for every four moles of silver iodide deposited at the anode. The transference numbers obtained from measurements of anode solutions were recalculated on the assumption that solid solutions of the quaternary ammonium iodide and silver iodide were formed in the ratio of one to four. The values were in approximate agreement with those obtained at the cathode. In every case, the ratio necessary to give complete agreement was between one to three and one to five.

TABLE I

TRANSFERENCE NUMBER OF TETRAETHYLAMMONIUM IODIDE

Experiment no.	15	16
Initial concn., mole/kg.	0.1013	0.1013
Final concn., anode soln.	0.0888	0.0864
Final concn., cathode soln.	0.1094	0.1113
Final concn., anode middle	0.1010	0.1012
Final concn., cathode middle	0.1011	0.1011
Wt. of anode soln., g.	144.695	144.467
Wt. of cathode soln., g.	115.370	115.107
Wt. of Ag in coulometers, g.	0.4352	0.5477
<i>t</i> _c at anode	0.467	0.437
<i>t</i> _c at cathode	0.236	0.237

The transference numbers of the quaternary ammonium iodides were first measured with no reference substance added and these results are presented in Table II. The concentrations of the salts were about 0.1 *M* except in the case of the tetra-*n*-butylammonium iodide where, because of limited solubility, it was necessary to use about 0.07 *M* solutions. Several attempts to electrolyze solutions of the tetrabutylammonium salt were unsuccessful because of the formation of hydrogen at the cathode. This difficulty was overcome by the use of a silver bromide electrode for the cathode.

Hydration of Ions.—The electrolytic transfer of water in solutions of the quaternary ammonium iodides was

(7) M. B. Jacobs, "The Analytical Chemistry of Industrial Poisons, Hazards and Solvents," Interscience Publishers, Inc., New York, N. Y., 1941, p. 535.

TABLE II

TRANSFERENCE NUMBERS OF QUATERNARY AMMONIUM IODIDES

Salt	Cation transference number	
Tetramethylammonium iodide	0.321	0.323
Tetraethylammonium iodide	.236	.237
Tetra- <i>n</i> -propylammonium iodide	.179	.171
Tetra- <i>n</i> -butylammonium iodide	.106	.103

measured with maltose as the reference non-electrolyte. The results of a typical experiment with 0.1 *M* solutions of tetraethylammonium iodide are given in detail in Table III. The results with tetramethyl- and tetra-*n*-propylammonium iodides are included in Table IV, which also shows the values found with the other reference substances. Experiments in which tetra-*n*-butylammonium iodide and maltose were used were unsuccessful because of the formation of crystals at the cathode and slight gassing at the anode.

TABLE III

HYDRATION OF TETRAETHYLAMMONIUM IODIDE, MALTOSE AS REFERENCE SUBSTANCE

Experiment no.	—23—		—24—	
	Salt ^a	Mal-tose ^b	Salt ^a	Mal-tose ^b
Initial concn.	0.0949	3.268	0.0949	3.271
Final concn., anode soln.	.0758	3.280	.0823	3.284
Final concn., cathode soln.	.1110	3.238	.1090	3.249
Final concn., anode middle	.09490949	...
Final concn., cathode middle	.09490949	...
Final concn., middle middle	.0949	3.267	.0948	3.276
Density of initial soln., g./ml.	1.0166		1.0169	
Density of final anode soln.	1.0154		1.0159	
Density of final cathode soln.	1.0177		1.0177	
Density of final middle middle	1.0164		1.0169	
Wt. of anode soln., g.	151.321		150.589	
Wt. of cathode soln., g.	116.745		116.528	
Wt. of Ag in coulometers, g.	0.7916		0.7419	
<i>t</i> _c at cathode	0.263		0.245	
Moles H ₂ O transferred to cathode per faraday	4.9		4.9	

^a Concentration expressed as moles per kg. of solution.
^b Concentration expressed as g. per 100 ml. of solution.

TABLE IV

SUMMARY OF HYDRATION MEASUREMENTS

Salt	Moles H ₂ O transferred to cathode per faraday		
	Maltose	Ethyl acetate	Acetone
(CH ₃) ₄ NI	3.9	20	6.4
	4.4		5.7
(C ₂ H ₅) ₄ NI	4.9	20	...
	4.9		
(C ₃ H ₇) ₄ NI	3.9
	3.2		
(C ₄ H ₉) ₄ NI	...	35	...

Acetone and ethyl acetate also were used as reference non-electrolytes. Two experiments were made with 0.1 *M* tetramethylammonium iodide which contained 0.1% acetone. The limited accuracy of the analytical method for determining acetone casts some doubt on the values of the actual amount of water transported. However, the results confirmed at least qualitatively those obtained with maltose, and a transfer of water toward the cathode apparently occurred in each case. Acetone could not be used as a reference non-electrolyte with solutions of the other quaternary ammonium iodides because the addition of iodine, involved in the determination, formed precipitates with the higher salts.

Ethyl acetate was used as the reference substance in the electrolysis of tetramethyl-, tetraethyl- and tetrabutylammonium iodide. In each case water was apparently transferred toward the cathode, as was the case with maltose. These results are included in Table IV.

The transfer of water toward the cathode during the hydrolysis indicates that the cation is more highly hydrated than the anion, which is contrary to the prediction that large organic ions should not be hydrated. A plausible explanation of this failure to follow prediction is that the changes in concentration of the reference substance are not only caused by the transfer of water but also by the transfer of the non-electrolyte to the anode. The assumption that the reference substance is carried along with the iodide ion is substantiated by the fact that the anion transference number is decreased by the addition of non-electrolyte. The effects of the non-electrolytes on the cation transference numbers are shown in Table V.

TABLE V

EFFECTS OF NON-ELECTROLYTE ON CATION TRANSFERENCE NUMBERS

Salt	Cation transference number		
	Nothing added	Maltose added	EtOAc added
(CH ₃) ₄ NI	0.322	0.340	0.356
(C ₂ H ₅) ₄ NI	.237	.254	.278
(C ₃ H ₇) ₄ NI	.175	.153	...
(C ₄ H ₉) ₄ NI	.105110

The association of non-electrolytes with ions in solution has been suggested by Fisher and Koval.⁸ They found that sucrose, acetone and urea reduced the transference number of the hydrogen ion in solutions of sulfuric acid and concluded that complex ions of the type, H₃O⁺-non-electrolyte, exist. Longworth⁹ recently used the moving boundary method to measure water transport in solutions of alkali chlorides with various reference non-electrolytes. He also concluded that the reference substances were not electrically inert and therefore not stationary during the electrolysis.

If one assumes that neither the iodide ion nor the quaternary ammonium ion is hydrated, that is, that the water molecules are stationary, then the amount of reference non-electrolyte carried along by the iodide can be calculated. The results for such a calculation are presented in Table VI based on the data obtained with maltose, ethyl acetate and acetone. Only about one per cent. of the iodide ions need to be associated with an equivalent amount of maltose to explain the experimental results. One might also assume that the iodide ion but not the quaternary ammonium ion is hydrated and calculate

(8) P. Z. Fisher and T. E. Koval, *Univ. etat Kiev. Bull. sci., rec. chim.*, No. 4, 137 (1939).

(9) L. G. Longworth, *THIS JOURNAL*, 69, 1288 (1947).

the amount of reference substance associated with the iodide ion. In Table VII are given the results of such a calculation for maltose when the iodide ion is arbitrarily assigned hydration values of five and of ten molecules of water.

TABLE VI

AMOUNT OF REFERENCE SUBSTANCE ASSOCIATED WITH IODIDE IONS ASSUMING WATER STATIONARY

Salt	Moles of non-electrolyte per mole of iodide ions		
	Maltose	Ethyl acetate	Acetone
(CH ₃) ₄ NI	0.011	0.10	0.029
	.012		.029
(C ₂ H ₅) ₄ NI	.011	.12	...
	.008		
(C ₃ H ₇) ₄ NI	.008
	.006		
(C ₄ H ₉) ₄ NI09	...

TABLE VII

AMOUNT OF MALTOSE ASSOCIATED WITH IODIDE IONS HYDRATION VALUES OF IODIDE ION ASSUMED

Salt	Mole of maltose per mole of iodide ion		
	I ⁻	I ⁻ ·5H ₂ O	I ⁻ ·10H ₂ O
(CH ₃) ₄ NI	0.011	0.020	0.028
	.012	.020	.029
(C ₂ H ₅) ₄ NI	.011	.019	.028
	.008	.017	.025
(C ₃ H ₇) ₄ NI	.008	.015	.023
	.006	.016	.024

Summary

The transference numbers of 0.1 M solutions of tetramethyl-, tetraethyl-, tetra-*n*-propyl- and tetra-*n*-butylammonium iodide have been measured. The cation transference numbers were found to decrease as the size of the cation increased.

The electrolytic transport of water was measured in solutions of the same quaternary ammonium iodides with maltose, acetone and ethyl acetate as reference non-electrolytes. The results indicated that the reference substances were associated with a small fraction of the iodide ions and could not serve to determine the degree of hydration of the ions.

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