185. *The Transference of Water. Part III. Its Dependence on Concentration in the Electrolysis of Barium Chloride Solutions.*

By Millicent Taylor and Violet R. Willcox.

In previous investigations on water transport (Part I, J., 1929, 2095; Part II, J., 1932, 2497) it was shown that, during the electrolysis of sodium chloride solutions, water moves from the anode to the cathode, and the quantity of water transported per faraday of electricity decreases with increase in temperature and with increase in concentration; it was concluded that the ions transport water with which they are not chemically combined. Experiments of a similar nature, urea again being used as inert reference substance, have now been carried out with barium chloride solutions. This substance was chosen as a typical salt of a bivalent metal on account of the comparative ease of purification and also because other important and accurate numerical data, such as the transport numbers of the ions and the conductivity of the salt in aqueous solution at various concentrations, were already available (Jones and Dole, *J. Amer. Chem. Soc.*, 1929, **51**, 1073; 1930, **52**, 2245).

The measurements were carried out at 25° with 0·5*M*- and 0·25*M*-solutions of barium chloride. The water transport was found to be very small, as compared with that occurring in corresponding solutions of sodium chloride under the same conditions. In both concentrations water appears to be transported to the cathode, and the quantity transported changes little with concentration although the transport number of the barium ion increases rapidly with increasing dilution.

EXPERIMENTAL.

The migration apparatus was identical with that used in the previous investigations (*locc. cit.*). The container for the stock solution was a large flask with the specially constructed stopper described by MacInnes and Dole (*J. Amer. Chem. Soc.*, 1929, **51**, 1124). Before the migration apparatus was filled, a stream of purified nitrogen, already saturated with water vapour by contact with a portion of the solution, was passed through the main solution and the migration apparatus. On rotation of the stopper of the container through 180°, the solution was driven over into the migration apparatus without further exposure to air.

The anode consisted of a tightly rolled cylinder of pure silver gauze (mesh 60 to the inch) covered, according to the directions of Jones and Dole (*loc. cit.*), with a spongy coating of metallic silver. As in all previous experiments, precipitated silver chloride of known weight was used for the cathode. The use of a silver spiral coated electrolytically with chlorine was found to result in slight alkalinity at the cathode, notwithstanding that air had been removed from the solution.

Materials.—The urea was purified as previously described (*loc. cit.*). Kahlbaum's purest barium chloride dihydrate (" for analysis with guarantee ") was invariably used; its purity was confirmed by the agreement between the results of the analysis of the solution and its composition as prepared.

Analytical Method.—In each experiment the solution was analysed before electrolysis by the method subsequently used for the analysis of each separate portion after electrolysis. The urea was estimated as already described, and the chlorine by the method of Richards and Wells, a platinum sponge Munroe crucible being used, together with a nephelometer to determine dissolved silver chloride. The order of accuracy was equal to that obtained with sodium chloride solutions (Part II, *loc. cit.*).

The electrometric method of MacInnes and Dole (*J. Amer. Chem. Soc.*, 1929, **51**, 1119) was discarded, for, with the limited amount of material available the possibility of undetected error in this method appeared to be greater than in the gravimetric method.

Results.—Four experiments were carried out within 0·1° of 25°, two with 0·25*M*- and two with 0·5*M*-barium chloride solutions, the urea being approximately 0·1*M* in each case.

In each experiment, except No. 1, the results depend upon the analysis of five solutions in all, the anode, the cathode, and three separate middle portions. In Expt. 1 no data are recorded for the cathode solution. This is due to the fact that the cathode portion became alkaline during electrolysis, probably on account of the texture of the silver chloride electrode, which had been prepared by chlorinating a silver spiral. In all subsequent experiments, we reverted to the precipitated silver chloride electrode of the type found satisfactory in Part I (*loc. cit.*) in place of the chlorinated spiral. An exactly known weight of silver chloride was used in the electrode.

The analyses carried out followed exactly the scheme indicated by the detailed results recorded in Part II for similar experiments with sodium chloride solutions. The duration of each experiment varied from 16 hours at 0·06 amp. for the more dilute solutions to 11 hours at 0·096 amp. for the more concentrated solutions. The results are summarised in Table I, n_w representing the total number of g.-mols. of water, n_s the number of g.-equivs. of barium chloride transported, $T_{\frac{1}{2}\mathrm{Ba}}$ and T_{Cl} the true transport numbers, and $T^{\mathrm{H}}_{\frac{1}{2}\mathrm{Ba}}$ and $T^{\mathrm{H}}_{\mathrm{Cl}}$ the Hittorf transport numbers of the ions. The ratio n_w/n_s gives the number of g.-mols. of water transported per equivalent of barium chloride, and n^{F}_w the number of g.-mols. of water transported per faraday. The number of equivalents of silver deposited in the coulombmeters during each experiment is also recorded.

TABLE I.

(i) *Approx.* 0·25M-$BaCl_2$ *solution.*

Temperature 25° ± 0·01°.

	Expt. 1.		Expt. 2.		
Compn. of soln., g.-mols./1000 g. $BaCl_2$	0·24056		0·25382		
Compn. of soln., g.-mols./1000 g. Urea	0·098325		0·098173		
	Anode.	Anode.	Cathode.	Mean.	Mean of Expts. 1 & 2.
n_w	0·00327	0·00633	0·00433	0·0053	—
n_s	0·01387	0·01396	0·01462	0·0143	—
Ag, equivs.	0·034674	0·034759	0·034753	0·034756	—
$T_{\frac{1}{2}\mathrm{Ba}}$	0·40006	0·40155	0·42067	0·4111$_1$	0·4056
T_{Cl}	0·59994	0·59845	0·57933	0·5888$_9$	0·5944
$T^{\mathrm{H}}_{\frac{1}{2}\mathrm{Ba}}$	0·39920	0·39978	0·41945	0·4096$_1$	0·4044
$T^{\mathrm{H}}_{\mathrm{Cl}}$	0·60080	0·60022	0·58055	0·5903$_0$	0·5956
n_w/n_s	0·2361	0·4534	0·2962	0·375	0·305
n^{F}_w	0·094	0·182	0·125	0·153	0·124

Specific gravity of solution 1 = 1·0440 g./c.c.

(ii) *Approx.* 0·5M-$BaCl_2$ *solution.*

Temperature 25° ± 0·02°.

		Expt. 3.			Expt. 4.		
Compn. of soln., g.-mols./1000 g. $BaCl_2$		0·48058			0·47444		
Compn. of soln., g.-mols./1000 g. Urea		0·096786			0·10103		
	Anode.	Cathode.	Mean.	Anode.	Cathode.	Mean.	Mean of Expts. 3 & 4.
n_w	0·00910	0·0019	0·00555	0·01040	0·00639	0·00839	—
n_s	0·01489	0·01485	0·01487	0·01696	0·01691	0·01694	—
Ag, equivs.	0·038562	0·038511	0·038537	0·043967	0·043983	0·043975	—
$T_{\frac{1}{2}\mathrm{Ba}}$	0·3864$_3$	0·3854	0·3859	0·3856$_3$	0·3842$_4$	0·3850	0·3855
T_{Cl}	0·6135$_7$	0·6145	0·6141	0·6143$_7$	0·6157$_6$	0·6150	0·6145
$T^{\mathrm{H}}_{\frac{1}{2}\mathrm{Ba}}$	0·3817$_0$	0·3845	0·3831	0·3810$_7$	0·3814$_6$	0·3813	0·3822
$T^{\mathrm{H}}_{\mathrm{Cl}}$	0·6183$_0$	0·6155	0·6169	0·6189$_3$	0·6185$_4$	0·6187	0·6178
n_w/n_s	0·611	0·127	0·369	0·612	0·378	0·499	0·434
n^{F}_w	0·231	0·0490	0·140	0·236	0·145	0·191	0·166

Specific gravity of solution 4 = 1·09235 g./c.c.

In Table II, the mean values for the transport of barium ion and water at the two concentrations are compared. The anode values are invariably the more reliable. With sodium chloride solutions this was found to be due to the tendency to the formation of alkali at the cathode. In the case of barium chloride, the low solubility of the hydroxide makes the error more difficult to correct. Therefore in Table II are included also the mean values of the above quantities calculated from anode results only. There is no significant difference between the two sets of values.

In view of the possibility of complex formation between the urea and the barium chloride, and also in order to obtain some information regarding the mobilities of the ions in the presence of urea, the effect of the latter on the molecular conductivity of barium chloride solutions of given volume concentrations was observed. The solutions were freshly made and were of about the same concentrations as those used in the main transport experiments.

TABLE II.

Temperature = 25° ± 0·02°.

	Mean of all values.		Mean of anode values.	
Concn.	0·25*M*.	0·5*M*.	0·25*M*.	0·5*M*.
$T_{\frac{1}{2}\mathrm{Ba}}$	0·4056	0·3855	$0·4008_1$	$0·3860_5$
$T^{\mathrm{H}}_{\frac{1}{2}\mathrm{Ba}}$	0·4044	0·3822	$0·3994_9$	$0·3813_9$
$n_{\mathrm{w}}/n_{\mathrm{s}}$	0·305	0·434	0·345	0·612
$n^{\mathrm{F}}_{\mathrm{w}}$	0·124	0·166	0·136	0·234

The same conductivity cell (constant, 8·112) was used for all the solutions. No special precautions were taken for the attainment of extreme accuracy, as merely comparative results were required. The following table records the equivalent conductivities Λ_ϕ at 24·99° of approximately $0·25m_v$ and $0·5m_v$-barium chloride in presence and in absence of $0·1m$-urea, and the equivalent mobilities $U_{\frac{1}{2}\mathrm{Ba}}$ and V_{Cl} of the barium and chlorine ion respectively, as calculated from the conductivities and the true transport numbers in the urea-containing solutions.

Concn.	$\Lambda\phi$.	$U_{\frac{1}{2}\mathrm{Ba}}$.	V_{Cl}.	Concn.	$\Lambda\phi$.	$U_{\frac{1}{2}\mathrm{Ba}}$.	V_{Cl}.
$0·2501m_v$-$BaCl_2$	88·22	—	—	$0·5183m_v$-$BaCl_2$	79·79	—	—
$0·2501m_v$-$BaCl_2$ + $0·1m$-urea	87·82	35·20	52·62	$0·5183m_v$-$BaCl_2$ + $0·1m$-urea	79·36	30·64	48·72

The reduction in conductivity due to urea is of about the same magnitude as that produced by urea in potassium chloride or sodium hydroxide solutions, in which cases it is ascribed to increase in viscosity (Fawsitt, *Z. physikal. Chem.*, 1904, **48**, 585; Chadwell and Asnes, *J. Amer. Chem. Soc.*, 1930, **52**, 3509). Since the urea, acting as a neutral medium in place of water molecules, increases the microscopic viscosity which opposes the movement of an ion in an electric field (Jones and Dole, *J. Amer. Chem. Soc.*, 1930, **52**, 2254), this assumption appears to be justified.

By making use of the densities of the solutions in question, the Hittorf transport numbers of the ions in each case can be compared with the corresponding values for solutions of barium chloride as determined by Jones and Dole (*loc. cit.*, 1929), and embodied in their empirical equation

$$t^{\mathrm{H}}_{\frac{1}{2}\mathrm{Ba}} = 1·4476/(1 + 0·0701\sqrt{c})$$

The required values are collected below.

Soln.	Concn. of soln., g.-mols./1000 g.	*d*, g./c.c.	Concn. of soln., g.-mols./l.	$T^{\mathrm{H}}_{\frac{1}{2}\mathrm{Ba}}$ ($BaCl_2$ + urea).	$T^{\mathrm{H}}_{\frac{1}{2}\mathrm{Ba}}$ (pure $BaCl_2$).
1	0·24056	1·04399	0·25114	0·3992	0·3985
4	0·47444	1·09235	0·51826	0·3811	0·3781

At each concentration the divergence between the Hittorf transport number in the pure barium chloride solution and in that containing urea is almost within the limits of experimental error, and the fact that the Hittorf transference number of the barium ion in the presence of urea is in each case slightly higher than in the pure salt solution emphasises the improbability of union between the barium ion and urea. This conclusion is supported by the spectroscopic investigations of Shibata, Inouye, and Natkatsuka (*Japanese J. Chem.*, 1922, **1**, 1), which indicate that even in $0·5n$-salt solution, there is no complex formation between barium chloride and urea.

DISCUSSION.

It is of interest to compare the quantity of water $n^{\mathrm{F}}_{\mathrm{w}}$ transported per faraday, the true equivalent transport number T_c, and the mobilities Λ_c for barium chloride solutions with the corresponding quantities for sodium chloride. These values are collected in Table III.

TABLE III.

Electrolyte.	Concn., g.-equivs./l.	T_c.	Λ_c.	$n^{\mathrm{F}}_{\mathrm{w}}$.	Electrolyte.	Concn., g.-equivs./l.	T_c.	Λ_c.	$n^{\mathrm{F}}_{\mathrm{w}}$.
NaCl	1·0	0·379	31·27	0·83	$BaCl_2$	1·0	0·386	30·55	0·234
	0·5	0·382	34·93	1·08		0·5	0·401	36·31	0·136

The values for sodium chloride at 0° which are not reproduced here are exactly analogous to the values at 25°, the increase in cathodic water transport on dilution being greater than at 25° (see Part II). In the case of sodium chloride the increase in the quantity of water transported to the cathode both with decrease in concentration and with fall in temperature has been shown not to be entirely ascribable to change in the relative mobilities of ions which are carrying a fixed quantity of water. It therefore appears probable that with decreased concentration as well as with decreased temperature the number of water molecules carried by each ion increases.

The values for water transport recorded in Table III differ markedly for the two electrolyses : they are very much smaller for barium chloride, being of the order of 0·2 mole per faraday, as against approximately 1 mole for sodium chloride. Also, with decrease in concentration, a small increase in the transport number of the sodium ion accompanies considerable increase in water transport to the cathode, whereas in barium chloride solutions for the same concentration change, a five-fold greater increase in the cation transport number, $T_{\frac{1}{2}\mathrm{Ba}}$ is accompanied by a slight decrease in water transport of about 0·1 mole per faraday.

These differences in behaviour may be referred to the bivalency of the barium ion. The electrostatic forces between the doubly charged ion and the surrounding water dipoles will be stronger than in the case of a singly charged ion—in fact, at least four times as great (see Gurney, " Ions in Solution," Cambridge, 1936). Consequently, at any concentration, the water molecules adjacent to the barium ion will be more firmly attached than in the case of the sodium ion, and the effect will be that of a permanent hydration shell. This accounts for the low mobility of the barium ion, which in spite of the double charge differs little from that of the sodium ion, being in the more concentrated solution slightly smaller, and in the more dilute solution slightly larger, than that of the sodium ion (Table III). On increase in the quantity of solvent, the mobilities of both anion and cation will be affected by two opposing influences, *viz.*, decrease in the restraint of the ionic atmosphere, and increase in the retarding load of water due to the larger number of water dipoles oriented round each ion ; but the proportionate increase in the quantity of water associated with the already highly hydrated barium ion will probably be less than in the case of the chlorine ion, and we may expect an increase in the true transport number of the cation, not necessarily accompanied by an increase in cathodic water transport.

This is the phenomenon actually observed in the electrolysis of barium chloride as distinguished from sodium chloride, and it affords evidence of a hydration shell round the barium ion which is more permanent than that round the sodium or chlorine ion, in that it is not affected to the same degree by change in concentration of the solution.

On the other hand, it must not be forgotten that, according to the Debye–Onsager theory, among the neighbours of each ion there is a preponderance of ions of opposite sign which during the passage of a current are moving in the opposite direction and are carrying water with them. Each ion therefore moves in a medium which is not stationary but is streaming in the opposite direction. In any attempt to foretell the water transport, one would have in this connection to take account of the fact that the number of positive ions is only half that of the negative. We are at present without data for estimating the magnitude of this effect in concentrated solution, though it may possibly be an important factor in determining whether the water transport will increase or decrease for a given change in concentration.

There is no need to stress the observation that with increased dilution an increase in cation transport number is accompanied by a decrease in cathodic water transport. The experimental results indicate this relationship, but the largest weight of water actually transported in any single experiment was barely 0·19 g., *i.e.*, about 0·1% of the total weight of the electrode portion in which it was estimated. Consequently, the differences in the water transport in the two different dilutions will be almost within the limits of experimental error. The fact that a large rise in cation transport is not accompanied by a corresponding rise in cathodic water transport is sufficient to prove conclusively that, of the various factors affecting water transport, the decisive one is not a hydration shell of equal permanency and different magnitude attached to each ion.

Therefore, no significance can be attached to ionic hydration values calculated from the equation

$$n_{\mathrm{W}}^{\mathrm{F}} = (1 - n)m_{\mathrm{k}} - nm_{\mathrm{a}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where n^{F}_{w} is the number of g.-mols. of water transported per faraday, n is the true transport number of the anion, and m_a and m_k the number of water molecules assumed permanently attached to the anion and cation respectively.

Brintzinger and Ratanarat (*Z. anorg. Chem.*, 1935, **222**, 119; **223**, 103) have calculated total hydration values for a large number of ions, on the assumption of a hydration of 8 for the sodium and 4 for the potassium ion. These " standard " values are derived by applying equation (1) to the results of transport measurements in N-solution, a membrane having been used to separate the electrode portions (see Remy, *Fortschr. Chem.*, 1927, **19**, No. 2, 67; Baborovský and Wagner, *Z. physikal Chem.*, 1933, *A*, **163**, 132). Brintzinger's experiments consist in a comparison of the rates of dialysis of the ion under investigation and of the standard ion in $0{\cdot}1N$-solutions which are also $2N$ with regard to an alkaline nitrate. Since concentration has a considerable effect on water transport and on the hydration values calculated from it (Part I, *loc. cit.*), no reliance can be placed on values derived from standards which are almost certainly unreal and have been determined in conditions different from those under which the comparison is made. Schmitz-Dumont (*Z. anorg. Chem.*, 1935, **226**, 33) has adduced other evidence that Brintzinger's total hydration numbers have no physical basis; notwithstanding this, his values are quoted as being in exceptionally good accord with other properties of the ions (Tollert, *Z. physikal. Chem.*, 1935, *A*, **174**, 246).

Our results, with respect both to water transport and to the transference numbers of the ions, are at variance with the values recorded by Baborovský and Viktorin (*Coll. Czech. Chem. Comm.*, 1932, **4**, 155) for several concentrations of the salt. These investigators, using a membrane to separate the electrode portions, worked at temperatures varying from 19·5° to 24° and calculated a mean value both for water and for ion transport for each concentration over this temperature range. In all concentrations from 1·0 to $0{\cdot}2n$ they observed transport of water to the anode, transport to the cathode being observed in $0{\cdot}1n$-solution only.

Also, the Hittorf transport values $T^{H}_{\frac{1}{2}Ba}$ calculated from their ' true ' transport values and the water transport by means of Washburn's equation, $T_{\frac{1}{2}Ba} = T^{H}_{\frac{1}{2}Ba} + n^{F}_{w}n_{s}/n_{w}$, where n_{s}/n_{w} is the ratio of the number of equivalents of solute and water in the original solution, differ by about 20% from the values of Jones and Dole for the same concentrations. The available data (I.C.T., Vol. VI, p. 310; Jones and Dole, *loc. cit.*) show that the Hittorf transport numbers $T^{H}_{\frac{1}{2}Ba}$ in barium chloride solutions at 16° are only about 2% less than in the same concentrations at 25°. There must therefore be some disturbing factor in the experiments of Baborovský and Viktorin. Later experiments by these same authors (*Coll. Czech. Chem. Comm.*, 1933, **5**, 216), using the E.M.F. method for the determination of transport numbers, have shown that the presence of a separating membrane in approximately $0{\cdot}2m$-barium chloride solution reduces the barium transport number from 0·39 to 0·29, and that the decrease in cation transport becomes more marked with increasing concentration. This great decrease in transport number must be associated with a corresponding distortion of the water transport values. It is sufficient to account for the difference between our values and those of Baborovský and Viktorin, and emphasises the danger of using a membrane in transport measurements.

SUMMARY.

Transport measurements have been carried out at 25° in $0{\cdot}5M$- and $0{\cdot}25M$-solutions of barium chloride containing $0{\cdot}1M$-urea as non-electrolytic reference substance. The water transport per faraday is found to be from one-quarter to one-eighth of that which occurs in sodium chloride solutions of equal equivalent concentrations. In both concentrations the water transport is to the cathode.

The Hittorf ionic transport numbers agree closely with those determined in the absence of urea by Jones and Dole. Both the Hittorf and true transport numbers of the barium ion show large increase with increasing dilution. Notwithstanding this, the cathodic water transport does not increase with increasing dilution. It is therefore suggested that the double charge on the barium ion produces a hydration shell which is more firmly bound and less sensitive to change in concentration than that round a chlorine or a sodium ion.

Neither the water nor the ion transport values agree with the corresponding values determined by Baborovský and Viktorin. The divergence is ascribed to the use of a membrane by these investigators.

We thank the Colston Research Society for grants for apparatus and materials.

THE UNIVERSITY, BRISTOL. [*Received, April 3rd,* 1937.]