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THE IONIC HYDRATION AND TRANSFERENCE NUMBERS OF CAESIUM CHLORIDE.[1]

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1. Outline of the Investigation.

In a previous investigation by one of the authors[2] the transference numbers and relative ionic hydrations of the chlorides of lithium, sodium and potassium in 1.2 *M* aqueous solution at 25° were measured by means of transference experiments in the presence of a suitable nonelectrolyte as a reference substance. The object of the present investigation was to extend these data so as to include caesium chloride, since there was much reason to believe that caesium ion is the least hydrated of all the alkali ions and there was the interesting possibility that it might be so little hydrated that the water transference would take place from cathode to anode. The previous work with sodium chloride was repeated and attempts, only partially successful, were made to include the alkali nitrates in the investigation also.

2. Purification of Materials.

Raffinose.—The raffinose was purified by recrystallization as described by Washburn and Williams,[3] until a 0.1 *M* solution of the crystals had a specific conductance of less than 3×10^{-6} reciprocal ohms at 25°.

Caesium Chloride.—Part of the raw material consisted of 700 g. of pollucite containing about 35% of caesium. The caesium extracted from this mineral was mixed with some caesium salts obtained from various dealers and the whole subjected to purification by recrystallization of the dichloriodide.[4] The final product was tested with a spectroscope and found to be free from all other alkali metals except a faint trace of sodium arising from the glass vessels used as containers.

Incidentally it was found that prolonged boiling of a caesium chloride solution does not result in the volatilization of even a trace of the salt, which is contrary to a statement made by Bailey[5] that caesium chloride is volatile with steam.

3. Apparatus and Method of Procedure.

The transference apparatus, the method of carrying out the transference experiments and the analytical methods were identical with

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[1] Part of a thesis submitted by Earl Bowman Millard to the Graduate School of the University of Illinois in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1914.

[2] Washburn, THIS JOURNAL, 31, 322 (1909).

[3] Washburn and Williams, THIS JOURNAL, 35, 751 (1913).

[4] Wells, *Am. J. Sci.*, 43, 17 (1892).

[5] Bailey, *J. Chem. Soc.*, 65, 445 (1894).

4. Notation.

d_4^{25}	specific gravity of the solution at 25° referred to water at 4°.
P_r	percentage of reference substance in solution.
P_s	percentage of the electrolyte in the solution.
Ag	grams of silver deposited in the coulometers.
m^e	total mass in grams of electrode portion.
Δm_w, Δn_w	increase in grams (or mols) of water in the electrode portion.
Δm_s, Δn_s	increase in grams (or mols) of electrolyte in the electrode portion, referred to raffinose.
$\Delta \mathrm{m}_s$, $\Delta \mathrm{n}_s$	increase in grams (or mols) of electrolyte in the electrode portion, referred to *water*.
N	equivalents of electricity passed through the solution.
T^c, T^a	true transference number of the cation (or anion) calculated on the assumption that the raffinose remains stationary during the passage of the current.
T_H^c, T_H^a	ordinary or Hittorf transference number.
Δn_w^F	number of mols of water transferred from anode to cathode per faraday of electricity.
A	anode portion.
M_a, M, M_c	anode middle, middle, cathode middle portions.
C	cathode portion.

5. Data and Results with Sodium Chloride Reference Substance—Raffinose.

Composition of the solution:

Sodium chloride 1.12 formula weights of NaCl per 1000 g. of water.
Raffinose 0.073 formula weights $C_{18}H_{32}O_{16}$ per 1000 g. of water.
Applied e. m. f. 20 volts.
Current 0.10 ampere.
Time of run 12 hours.

	A.	M_a.	M.	M_c.	C.
Rotation.....	51.107°	50.694°	50.653°	50.648°	50.000°
d_4^{25}..........	1.0461	1.0522	1.0522	1.0522	1.0590
P_r...........	3.376	3.331	3.330	3.330	3.264
P_s...........	5.0467	5.9262	5.9250	5.9263	6.8703
Ag...........	5.6694	...	...	...	5.6699
m^e...........	120.23	...	...	...	108.99
Δm_w.........	—0.58	...	...	...	0.98
Δn_w..........	—0.032	...	...	...	0.054
Δm_s..........	—1.1605	...	...	...	1.1555
Δn_s..........	—0.01958	...	...	...	0.01976
$\Delta \mathrm{m}_s$..........	—1.1221	...	...	...	1.0915
$\Delta \mathrm{n}_s$..........	—0.01919	...	...	...	0.0188
N...........	0.05255	...	...	...	0.05255
$T^c = \Delta n_s/N$..	0.377	...	...	...	0.376
T^a..........	0.623	...	...	...	0.624
T_H^c..........	0.365	...	...	...	0.355
T_H^a..........	0.635	...	...	...	0.645
$\Delta n_w/\Delta n_s$.....	1.6	...	...	...	2.7
Δn_w^F..........	0.61	...	(Mean 0.82)	...	1.04

6. Data and Results with Caesium Chloride—Reference Substance—Raffinose.

Run I.

Composition of the solution:

Caesium chloride 1.07 formula wts. of CsCl per 1000 g. of water.

Raffinose 0.071 formula wts. of $C_{18}H_{32}O_{16}$ per 1000 g. of water.

Applied e. m. f. 20 volts. Current 0.1 ampere.

Time of run 12 hours.

Run II.

Composition of the solution:

Caesium chloride 1.10 formula wts. of CsCl per 1000 g. of water.

Raffinose 0.081 formula wts. of $C_{18}H_{32}O_{16}$ per 1000 g. of water.

Relative viscosity 1.08. Applied e. m. f. 20 volts.

Current 0.1 ampere. Time of run 12 hours.

	Run I.					Run II.				
	A.	M_a.	M.	M_c.	C.	A.	M_a.	M.	M_c.	C.
Rotation...	48.671°	48.225°	48.131°	48.116°	47.452°	55.865°	55.137°	55.137°	55.127°	54.421°
d_4^{25}........	1.1105	1.1357	1.1357	1.1357	1.1642	1.1152	1.1409	1.1409	1.1409	1.1689
P_r.........	3.0320	...	2.9319	2.9310	2.8197	3.4653	3.3433	3.3433	3.3428	3.2208
P_S.........	12.077	14.772	14.770	14.750	17.713	12.383	15.152	15.160	15.161	18.063
Ag.........	5.5048	...	...	...	5.5044	5.4787	...	...	...	5.4787
m^e.........	132.58	...	...	...	119.77	...[1]	...	...	...	121.12
Δm_w.......	—0.30	...	...	...	0.36	...	...	...	...	0.25
Δn_w.......	—0.166	...	...	...	0.020	...	...	...	...	0.014
Δm_S........	—4.243	...	...	...	4.198	...	...	...	...	4.190
Δn_S........	—0.02521	...	...	...	0.02495	...	...	...	...	0.02490
$\Delta \mathrm{m}_S$........	—4.191	...	...	...	4.137	...	...	...	...	4.147
$\Delta \mathrm{n}_S$........	—0.02491	...	...	...	0.02459	...	...	...	...	0.02465
N.........	0.051027	...	...	...	0.051023	0.050785	...	...	...	0.050785
$T^c = \Delta n_S/N$	0.494	...	...	...	0.489	...	...	...	...	0.490
T^a........	0.506	...	...	...	0.511	...	...	...	...	0.510
$T_H^c = \Delta n_S/N$	0.488	...	...	...	0.482	...	...	...	...	0.485
T_H^a........	0.512	...	...	...	0.518	...	...	...	...	0.515
$\Delta n_w/\Delta n_S$...	0.64	...	...	...	0.80	...	...	...	...	0.56
Δn_w^F.......	0.33	...	(Mean 0.36)	...	0.39	0.45	...	...	...	0.28

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[1] The anode residues were scorched in drying in this experiment, thus rendering uncertain the weight of the electrode portion.

those employed in the previous work and need not be described again.

The polarimeter employed for determining the concentration of the raffinose was a better and more accurate instrument than the one employed in the previous work and it was largely due to this fact that conclusive and satisfactory results were obtained with caesium chloride, the water transference being so small in amount, that a very high degree of accuracy was necessary in the polarimetric readings in order to measure its magnitude. The instrument was a triple field Schmidt and Haensch polarimeter of sufficient size to enable the use of a 100 cm. jacketed observation tube. In this tube all the solutions employed were polarized. The light was furnished by a quartz mercury vapor lamp, and was further purified by passing it through a spectroscope. The green mercury E-line was the one employed and this fact also contributed to the increase in the degree of accuracy over that obtained in the previous investigation, since the specific rotatory power of raffinose for the E-line is $[\alpha]_E = 144.55°$ as against $[\alpha]_D = 123.00°$ for the D-line.[1] The addition of 1.2 mol of caesium chloride to a liter of the raffinose solution was found to increase the specific rotatory power to $[\alpha]_E = 144.64$ which is the same increase as that produced by potassium chloride.

The experimental data and results are shown above.

7. Results with Potassium Nitrate.

Several runs were made on 1.2 *M* potassium nitrate solution in the presence of 0.08 mol of raffinose, using a silver chloride cathode and rejecting the anode side altogether. Membranes of silk gauze were inserted in the connecting tubes of the stopcocks and a cooling coil was used at the cathode side to increase the density of this portion, in an effort to prevent mixing. In every experiment, however, chloride was found in the middle portions, indicating that mixing had taken place. On account of this mixing it did not seem worth while to complete the analyses. In one case, however, the solutions were analyzed, and it was shown that the ratio of raffinose to water had decreased at the cathode. In other words, the potassium ion carries water with it to the cathode in a potassium nitrate solution or, if one wishes to ascribe the change in the raffinose-water ratio to a complex formed between the chloride ion and the raffinose, then a similar complex must also be assumed in the case of the nitrate ion.

8. Comparison of Degrees of Hydration of the Ions.

For purposes of comparison the transference and hydration data for the four alkali chlorides and hydrochloric acid are summarized in Table I.

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[1] Bates, *Bureau of Standards Bulletin* **2**, 239.

TABLE I.[1]

Electrolyte (Conc. 1.3 N).	n_w^F/T^c.	Δn_w^F.	T^c.	T^c_∞.	T^c_H.
HCl........	0.28 ± 0.04	0.24 ± 0.04	0.844	0.821	0.82
CsCl........	0.67 ± 0.1	0.33 ± 0.06	0.491	0.491	0.485
KCl........	1.3 ± 0.2	0.60 ± 0.08	0.495	0.495	0.482
NaCl.......	2.0 ± 0.2	0.76 ± 0.08	0.383	0.396	0.366
LiCl........	4.7 ± 0.4	1.5 ± 0.1	0.304	0.330	0.278

$$N_w^H = 0.28 \pm 0.04 + 0.185\ N_w^{Cl} \tag{1}$$

$$N_w^{Cs} = 0.67 \pm 0.1 + 1.03\ N_w^{Cl} \tag{2}$$

$$N_w^K = 1.3 \pm 0.2 + 1.02\ N_w^{Cl} \tag{3}$$

$$N_w^{Na} = 2.0 \pm 0.2 + 1.61\ N_w^{Cl} \tag{4}$$

$$N_w^{Li} = 4.7 \pm 0.4 + 2.29\ N_w^{Cl} \tag{5}$$

The values of the true transference number of the cation in 1.2 *M* solution (T^c) and at infinite dilution (T^c_∞) as well as the ordinary Hittorf number (T^c_H) appear in the first part of the table. In the second part of the table N_w indicates the average number of water molecules carried by the ion (indicated by the superscript) as it moves through the solution. From Equations 2 and 5 we obtain the relation,

$$N_w^K - N_w^{Cs} = 0.65,$$

or in words, the caesium ion carries on the average 0.65 less molecules of water than the potassium ion and is, therefore, the least hydrated of the alkali ions. If we assign to the chloride ion the hydration values (1) zero and (2) four molecules, the corresponding hydration values for the other ions are shown in Table II.

TABLE II.

$N_w^{Cl^-}$.	$N_w^{H^+}$.	$N_w^{Cs^+}$.	$N_w^{K^+}$.	$N_w^{Na^+}$.	$N_w^{Li^+}$.
0	0.3	0.7	1.3	2.0	4.7
4	1.0	4.7	5.4	8.4	14.0

All of the data given above are, of course, based upon the assumption that the raffinose remains absolutely stationary during the passage of the current. There is thus far no evidence indicating that this assumption is invalid to an extent which would appreciably affect the results. With the polarimetric apparatus at present at our disposal it will be possible to work with considerably smaller salt concentrations and also to reduce the concentration of the reference substance as low as 0.01 *M* in the case of lithium chloride solutions. By substituting trehalose for raffinose it will probably even be possible to use a considerably lower concentration than this and thus to remove all reasonable doubt as to the validity of the assumption in question. Work along these lines will be continued in this laboratory.

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[1] In this table the values given are the *means* of the two results obtained at each electrode independently.

9. Summary.

1. By transference experiments in the presence of raffinose as a reference substance, the true transference number of caesium ion in 1.2 *M* caesium chloride solution at 25° has been found to be 0.491 and the water transference 0.33 ± 0.06 formula weights of H_2O per faraday, from anode to cathode. Caesium ion is thus the least hydrated of the alkali ions. It carries on the average 0.65 mol less H_2O than potassium ion.
2. Similar experiments with potassium nitrate solutions showed that the water transference was from anode to cathode with this salt also.
3. The effect of caesium chloride upon the specific rotatory power of raffinose is the same as that of potassium chloride. It increases $[\alpha]_E$, 0.09° per mol of salt added to a liter of the 0.1 *M* raffinose solution.
4. Contrary to a statement in the literature, caesium chloride is not appreciably volatile with steam.

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THE HEAT OF NEUTRALIZATION OF HYDROXYLAMINE AND TETRAMETHYLAMMONIUM HYDROXIDE.

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Recent thermochemical measurements by Richards and his co-workers, using the adiabatic calorimeter, have shown conclusively that many of the thermochemical data in the literature are of very questionable accuracy. The adiabatic calorimeter permits a degree of accuracy heretofore unattainable in thermochemical measurements and for the first time puts these measurements on a par with the measurements of other physicochemical constants. Since considerable of the thermochemical data in the literature have been determined by but two investigators (Berthelot and Thomsen), and as the data are often the results of single measurements, by methods which at best could give only approximate values, it has seemed highly desirable that these measurements be repeated, using the methods for precise calorimetry now available.

This paper deals with the measurement of the heat of neutralization of hydroxylamine and tetramethylammonium hydroxide when neutralized with hydrochloric, sulfuric, and trichloroacetic acids in aqueous solutions, using an adiabatic calorimeter. The method followed was practically the same as that used by Richards and Rowe,[1] and the adiabatic bath employed was similar to the one designed by Richards and Burgess[2] and by Richards and Jesse.[3]

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[1] *Z. physik. Chem.*, 64, 187 (1908); *Proc. Am. Acad.*, 43, 475 (1908).

[2] THIS JOURNAL, 32, 431 (1910).

[3] *Ibid.*, 32, 268 (1910).