Tracer Diffusion and Electric Mobility of Ions in Aqueous Solutions: A Method for Estimating the Average Charge of Complex Ions

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In the study of complex ions in aqueous solution it is useful to know the charge on the ion being studied. The Nernst equation implies a linear relationship between the charge (z) and the ratio of the electric mobility (μ) to the diffusion coefficient (D). The equation is strictly valid only at infinite dilution, but it might be assumed that the relationship in real solutions would be a fairly simple one. We have tested the assumption by measuring the values of μ and D for a group of cations at low concentration in 1 M $HClO_4$. The ions measured were those of Na, Rb, Cs, Be, Co, Zn, Sr, Cr, Fe, Y, and Eu. The relationship is not linear but can be described by a function of the form $z = A(1 - e^{-Bz})$, where A and B are empirically determined constants. We used radioactive tracers to make the measurements.

Introduction

In the study of coordination complexes in aqueous solution it can be useful to know the charge on a complex ion. For instance, if the charge is known, the number of anionic ligands attached to a cation would be known. Furthermore, if the average charge is known as a function of solution composition, it may be possible to calculate one or more association constants.

The ionic charge (z) is related to measurable quantities by the Nernst equation, $z = RT\mu/(FD)$, where R = the gas constant, T = absolute temperature, μ = the electric mobility of the ion, F = the Faraday constant, and D = the diffusion coefficient of the ion.

The equation is strictly valid only at infinite dilution. Nevertheless, it is reasonable to expect that the charge on an ion would be related in some simple way to the ratio of its electric mobility and its self-diffusion coefficient. In particular, one might hope that this would be true for an ion at low concentration in an electrolyte at much higher concentration (e.g. 10^{-3} M Fe^{3+} in 1 M $HClO_4$). Evidence for at least semiquantitative agreement in solutions of total ionic strength of about 10^{-2} M was reported by Hevesey (1913). Apparently, systems of this type in the more interesting higher concentration range have never been investigated using both self-diffusion and tracer mobility. Mills and Lobo (1989) summarize the data on self-diffusion, and a few mobility measurements have been summarized by Spiro (1986). For example, Fischer and Hessler (1964) measured the tracer mobility of $^{42}K^+$ in KNO_3 solutions up to 0.1 M. However, we are not aware of any study in which both were measured for the same solutions and correlated with ionic charge.

We have tested these assumptions by measuring the values of μ and D for a group of ions in 1 M $HClO_4$ solution. The +1 ions are Na, Rb, and Cs; +2, Co, Zn, and Sr; +3, Cr, Fe, Y, and Eu. Our approach has been completely empirical; we have made no attempt to make corrections for the fact that the solutions are not at infinite dilution. The goal has been to see how well the measurements can be applied to real solutions with a minimum of theoretical complications. The results show that the method can give reasonable, if not precise, results. Our best measurements are on Na, Co, and Fe in 1 M mixtures of HCl and $HClO_4$. From these we were able to calculate association constants for Fe^{3+} and Co^{2+} with Cl^-. We also made measurements on gold in 1 M HCl which confirm the well-known fact that the gold−chloride complex has a single negative charge and is thus $AuCl_4^-$ and not, for example, $AuCl_6^{3-}$.

As an adjunct to the main thrust of the work, we also report values of μ for Na, Rb, and Cs ions in solutions of LiCl, NaCl, KCl, and $CaCl_2$.

In all cases the tracers were at a concentration of about 10^{-3} M. We avoided the use of “carrier-free” tracers because of the complications which can arise from adsorption on the walls and “radio-colloid” formation. For a general discussion, see Bonner and Kahn (1951), and for adsorption on capillary walls, see Gosman et al. (1986).

Experimental Section

Diffusion Measurements. We used the open-ended capillary method of Anderson and Saddington (1949) to measure diffusion coefficients. In this method, a capillary tube, closed on one end, is filled with tracer solution and immersed in a chemically identical solution containing no tracer, and the amount of tracer diffusing out of the capillary is measured. The method is described in detail by several investigators, including Mills (1991), Tyrrell and Harris (1984), and Wang (1951). Our apparatus was very similar to that described by Wang but somewhat larger and with a much slower stirring rate. Our flask had a volume of 2 L and had five necks: a central one for the stirrer and four for sample holders. Each sample holder held two capillaries, so eight samples were run simultaneously. The stirrer was completely sealed and coupled to the motor with magnets. The stirring paddle was about 3 cm long and turned at 1 revolution per second. The flask was immersed in a water bath held at (25.0 ± 0.1) °C. Our capillaries were made from 0.5 mm inside diameter Corning precision bore tubing. They were cut to approximately 4 cm length, the

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ends carefully lapped to be perpendicular to the bore, and sealed by fusing a glass plate to one end. We measured the lengths with a precision of about 0.05% and the volumes to about 0.2%. Before each run, they were cleaned with sulfuric acid−dichromate solution and then treated with Beckman Desicote vapor.

Before diffusion, the capillaries were filled with a degassed tracer solution of known concentration, using fine transfer pipets. A drop of excess tracer solution was left on top, covering the capillary opening. Early experiments had shown that during the filling process appreciable evaporation occurred. This was sometimes enough to change the tracer concentration by a few percent. To avoid this problem, which was not mentioned by previous workers, we constructed a “wet box”, where the capillaries could be filled in an atmosphere of near 100% relative humidity. This procedure made the evaporative losses negligible.

The tracer specific activity was measured by pipetting a known volume into a counting tube and diluting it with inactive solution to the standard height.

For this type of measurement, the solution to the diffusion equation is

$$\frac{C_{\mathrm{av}}}{C_0} = \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left[-(2n+1)^2\pi^2\frac{Dt}{4l^2}\right]$$

where C_0 is the initial amount of tracer in the capillary, C_{av} is the amount remaining after time t, and l is the length of the capillary. The series converges so rapidly that the first term alone gave an adequately precise solution to the equation for our measurements.

Accuracy Check. As a check on the overall accuracy of our diffusion measurements, we measured the diffusion coefficient of trace concentrations of Na^+ in 1 M KCl and compared our value with the values published by Mills (1957, 1961). Our value is 13.2 (±0.03) × 10^{-6} cm^2/s. Mills reported a value of 13.11 ± 0.13. This is well within our experimental error and probably shows that our stirring rate was within the range 1−3 mm/s, as recommended by Mills (1955). Unfortunately, we did not measure the actual flow rate. The only other value which we can compare with published values is that for Zn^{2+} in 1 M $HClO_4$. Our value is 7.54 × 10^{-6} cm^2/s, which is comparable to the value of 7.2 obtained by Marcinowsky et al. (1965) using the porous frit method.

Electric Mobility Measurements. We measured the mobilities by a variant of the method of moving boundaries as described in the classic paper of MacInnes and Longsworth (1932). In the usual method the motion of a stable boundary is followed. In our case there was no boundary because all of the solutions were identical except for the presence of a radioactive tracer in one section. The boundary was the edge of a stopcock, and we measured the amount of tracer moving past this stationary boundary. The lack of concentration gradients means that great care must be taken to avoid convection.

Figure 1 is a diagram of the transference cell. Our final design was very similar to one used by Hoyer et al. (1954) for the measurement of the mobility of detergent micelles.

It is important that the arms of the cell A−C and B−D lead down from the center capillary. If they lead up, convection occurs and erratic results are obtained. The reason appears to be that the major resistive losses occur in the capillary sections of the cell. Despite the low currents and the fact that the cell is immersed in a water bath, there will be some heating in this part of the cell. The densities of the traced and inactive solutions are as close to identical as possible, so if the warmer solution in the capillary is below the cooler solution in the wider parts of the cell, convection will occur.

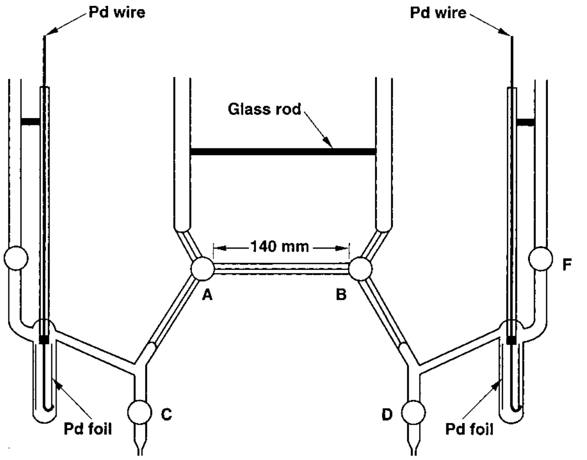

Figure 1. Diagram of transference cell. The drawing is approximately to scale. For clarity the cell is drawn as if it were planar. In fact, the electrode compartments are back, into the plane of the paper, to make it more compact. The cell is firmly clamped to a stainless steel frame for rigidity.

The electrodes were Pd sheets held in place with Pd wire. We tried spot welding the sheet to the wire, but gaseous hydrogen was always produced at the welds. In the final design, the sheet Pd was merely resting on the wire. The electrical contact seemed to be adequate.

In operating, either electrode could be used as cathode, and either compartment could be left open. The results were independent of these variables.

To start a run, the 2 mm capillary between A and B was filled with degassed tracer solution through the vertical arms. The cell was brought to 25 °C in the water bath. The capillary was then closed off with stopcocks A and B and the cell removed from the bath. The excess tracer was very carefully rinsed from the stopcock bores and the side arms through C and D. The rest of the cell was then filled with inactive solution and put back in the water bath with E and F open. After temperature equilibrium had been established, either E or F was closed, A and B were opened, and the current was turned on. Currents were usually between 2 and 10 mA. The constant-current supply had an accuracy and constancy of about 0.2 μA. The runs lasted 15 to 24 h, and the time was known to within 1 s, so the errors in current and time values were negligible.

At the end of the run, stopcocks A and B were closed and the cell was removed from the bath. The solutions on the electrode sides of A and B were carefully collected and washed out through C and D; then the solution remaining in the capillary between A and B was washed out. All samples were then counted. The activity on the cathode side was used to calculate the mobility (if the ion was a cation), the activity on the anode side was used as a check for motion in the wrong direction caused by convection, leaks, and so forth, and the total activity in all three fractions was used as a check on material balance.

If 1% or more of the activity showed up on the anode side, or if the material balance was off by >1%, the run was viewed with suspicion and usually discarded.

The calculation of the mobility from this experiment requires measurement of only A, the amount of tracer transported past the boundary, I, the current, t, the duration of current flow, s, the specific activity of the tracer solution, and L, the specific conductance of the solution.

Table 1. Transference Numbers, Specific Conductances, and Volume Corrections for the Pd/PdH Cathode Compartment in HCl−HClO$_4$ Mixtures

(HCl)	(HClO$_4$)			ΔV	L	correction
mol/L	mol/L	t_{Cl}	$t_{Cl}O_4$	cm^3/F	mΩ^{-1} cm^{-1}	$10^4(\Delta VL/F)$
0.000	1.000	0.000	0.2213	−8.16	0.3306	−0.280
0.100	0.900	0.0148	0.2007	−7.54	0.3308	−0.258
0.250	0.750	0.0375	0.1691	−6.57	0.3311	−0.225
0.500	0.500	0.0764	0.1149	−4.91	0.3316	−0.169
0.750	0.250	0.1169	0.0586	−3.19	0.3321	−0.110
1.000	0.000	0.159	0.000	−1.39	0.3326	−0.048

The measured mobility, μ_m, is the velocity, r, at any point divided by the field gradient, X, at the same point.

In this experiment the velocity is measured by the amount of tracer which has moved past the boundary in a known time and is given by $r = A/(sct)$, where c is the cross-sectional area of the tube in square centimeters at the boundary.

The field gradient at the boundary is $X = I/cL$. Thus

$$\mu_m = r/X = AL/sIt \qquad (1)$$

These results are independent of cell dimensions. In particular, it is not necessary that the capillary section of the cell have a uniform cross section. The volume between the stopcocks A and B is used only to check the material balance.

As a practical matter, the capillary must be reasonably small in diameter to prevent convection, since there are no concentration gradients to stabilize the system. Otherwise, none of the cell dimensions are critical.

The volume of the capillary was about 0.5 cm^3. We normally adjusted the total number of coulombs so that less than half of the tracer was transported out of the capillary. This avoided any possible effects of electroosmosis (Hoyer et al., 1954).

Conductivity Measurements. We measured the specific conductance of the HCl−HClO$_4$ mixtures using a direct current cell. The cell had separate electrodes for measuring the voltage and for carrying the current. It was calibrated against 1.000 M KCl, 0.1000 M KCl, and 1.000 M NaCl. The cell constants for these three measurements were the same within 0.1%. The resulting specific conductances are summarized in Table 1 along with the transference numbers and electrode volume changes. We also measured the conductivities of 3.00 M KCl and 0.045 M, 0.500 M, and 1.00 M CaCl$_2$.These data are included in Table 4.

Electrode Volume Change. To convert the measured mobility relative to the cell to the mobility relative to the solvent, we must take into account the volume change in the electrode compartment on the closed side of the cell. In this cell the two electrodes are the same, so the volume changes are equal and opposite. Thus, it makes no difference to the calculation which side of the cell is open.

The use of nongassing Pd−H electrodes was described by Neihof and Schuldiner (1960). They did not, however, address themselves to the electrode volume change. When Pd is the cathode, hydrogen ion is reduced to elemental hydrogen, which, if the current density is not too great, dissolves in the Pd with no formation of bubbles.

The Pd−H system at 25 °C has been reviewed by Lewis (1967). When hydrogen dissolves in Pd, the Pd lattice (referred to as the α phase) is almost unchanged until the H/Pd ratio reaches about 0.015. At this point a new phase, β, appears. Both phases are face-centered cubic, but the lattice constants are different: α phase lattice constant = 3.894 Å; β phase lattice constant = 4.025 Å. These lattice constants lead to a volume increase, $(V_\beta - V_\alpha)$, of 0.92 cm^3 when 1 g atom of Pd is converted from α to β.

The H−Pd phase diagram shows that at 25 °C the β phase first appears at a H/Pd ratio of 0.015. As the H/Pd ratio increases, α is converted to β, until at H/Pd = 0.58 the α phase is completely converted to β. Thus, 0.58−0.015 = 0.56 g atoms of hydrogen is required to convert 1 g atom of Pd from α to β, or 1/0.56 = 1.79 g atom of Pd are converted per g atom of H and therefore per Faraday. We have assumed that the value is 1.8 and that it is constant over the mixed α−β region.

We always used the electrodes with H/Pd ratios within the range 0.015 to 0.58.

The electrode reaction with Pd as the cathode can thus be written

$$1.8\mathrm{Pd}(\alpha) + \mathrm{H}^+ + \mathrm{e}^- = \mathrm{Pd}_{1.8}\mathrm{H}(\beta)$$

The net changes in the cathode compartment per Faraday are

1.8 g atoms of Pd(α) converted to Pd(β)

t^- mole of anions removed

where t^- is the sum of the transference numbers of ClO$_4^-$ and Cl$^-$ in the solution. If ν is the partial molal volume of the solute, the volume change per Faraday is

$$\Delta V = 1.8(V_\beta - V_\alpha) - (t^-)\nu \qquad (2)$$

From eq 1, $\mu_m = L(A/sIt)$.

The part of the expression in parentheses has units of cm^3/coulomb. Thus, the electrode volume correction can be applied to the measured value of the mobility very simply:

$$\mu = [(A/sIt) \pm \Delta V/F]L = \mu_m \pm \Delta VL/F$$

where the positive sign is used for cations and the negative for anions. For 1 M HClO$_4$, $L = 0.3306$ mΩ^{-1} cm^{-1} so the correction to μ_m is -0.280×10^{-4} cm^2/(V s). This is a <10% correction to the average values of μ_m which we measured, so any errors in the volume corrections will have only a small effect on the final value of μ.

Transference Numbers and Partial Molal Volumes. We have assumed that the mobility of each anion relative to the hydrogen ion is the same in the mixed solutions as in the single acid solution. With this assumption we can calculate the values of the anionic transference numbers in each of our solutions. We have made the same assumption for the partial molal volumes. There is also the implicit assumption that the tracer ion concentration is so low that it does not affect the values.

The transference number of ClO$_4^-$ was obtained from Haase et al. (1964), and that for Cl$^-$ from Harned and Owen (1958). The partial molal volume of HClO$_4$ at 1.000 M was calculated from the data of Wirth and Collier (1950) to be 44.413 cm^3/mol, and that of HCl from Åkerlöf and Teare (1938) to be 19.1689 cm^3/mol.

Using the above values, and applying eq 2, we get the volume corrections in cm^3/Faraday listed in column five of Table 1. Column seven lists the actual corrections applied to the measured μ_m values. The corrections decrease the measured cation values, since the volume decreases in the cathode compartment.

Counting Procedure. The samples to be counted were put into screw-top plastic tubes 15 mm in diameter and 150 mm long. The height of the solution above the bottom of the tube was carefully adjusted by the addition of

Table 2. Values of Mobilities and Diffusion Coefficients for Ions in 1.00 M $HClO_4$

ion	tracer	$10^4\mu$ cm^2/(V s)	n^a	%σ	10^6D cm^2/s	n	%σ	μ/D	Nernst value
Na^+	^{22}Na	3.42	4	1.6	13.56	7	0.9	25.2	
Rb^+	^{86}Rb	4.14	3	5.5	16.50	34	5.2	25.1	
Cs^+	^{137}Cs	3.65	4	1.8	17.10	7	2.4	21.4	38.96
$AuCl_4^-$	^{196}Au	2.76	3	1.0	10.11	4	2.1	27.3	
Be^{2+}	^{7}Be				7.20	8	1.6		
Co^{2+}	^{60}Co	3.16	3	1.0	7.50	12	0.4	42.2	77.9
Zn^{2+}	^{65}Zn	3.14	4	1.0	7.54	6	1.3	41.6	
Sr^{2+}	^{89}Sr	3.54	2	1.7	8.56	8	1.5	41.4	
Cr^{3+}	^{51}Cr	3.22	2	2.0	5.73	6	1.0	56.2	
Fe^{3+}	^{59}Fe	3.04	3	1.0	5.74	11	1.2	53.0	116.9
Y^{3+}	^{88}Y	3.61	4	3.1	6.49	6	2.8	55.6	
Eu^{3+}	$^{152,154}Eu$	3.69	3	0.1	6.38	11	1.0	57.8	

[a] n = number of samples.

Table 3. Values of Mobilities and Diffusion Coefficients in $HCl-HClO_4$ Solutions

	Na			Co(II)			Fe(III)		
(HCl) mol/L	$10^4\mu$ cm^2/(V s)	10^6D cm^2/s	μ/D	$10^4\mu$ cm^2/(V s)	10^6D cm^2/s	μ/D	$10^4\mu$ cm^2/(V s)	D	μ/D
0.00	3.42	13.6	25.2	3.16	7.50	42.1	3.04	5.74	53.0
0.10							2.84	5.8^a	48.9
0.25		13.7		2.97	7.37	40.3	2.58	5.86	44.1
0.50	3.47	13.4	25.8	2.82	7.23	39.0	2.35	5.83	40.3
0.75		13.4		2.70	7.14	37.8	2.19	5.80	37.8
1.00	3.54	13.1	26.9	2.63	6.97	37.7	2.05	5.82	35.2

[a] Interpolated value.

Table 4. Volume Change Corrections for Ag/AgCl Cathode Compartments[a]

solution	partial molal volume cm^3/mol	cation trans no., t^+	L mΩ^{-1} cm^{-1}	ΔV cm^3/F	correction $10^4(\Delta VL/F)$
1.00 M HCl	19.1689	0.841	0.3726	+0.62	+0.024
0.10 M KCl	27.62	0.50	0.0129	−1.69	−0.002
0.30 M KCl	28.43	0.50	0.0365	−1.29	−0.005
1.00 M KCl	30.01	0.50	0.1118	−0.49	−0.006
3.00 M KCl	32.86	0.50	0.2985	+0.93	+0.029
1.00 M NaCl	19.66	0.38	0.0858	−8.03	−0.071
0.090 M LiCl	17.67	0.32	0.0087	−9.85	−0.009
0.099 M LiCl	17.70	0.32	0.0096	−9.84	−0.010
0.99 M LiCl	19.22	0.30	0.0720	−9.73	−0.073
2.99 M LiCl	20.99	0.28	0.1562	−9.62	−0.156
0.045 M $CaCl_2$	20.96	0.41	0.0093	−6.99	−0.007
0.50 M $CaCl_2$	24.60	0.40	0.0776	−5.66	−0.046
1.00 M $CaCl_2$	27.32	0.38	0.1319	−5.12	−0.070

[a] Note: The AgCl to Ag volume change is −15.5 cm^3/Faraday on the basis of the densities.

inactive solution so that it was the same for all samples in a set (30 mm for transference samples and 15 mm for diffusion samples).

The samples were counted in a NaI(Tl) well type scintillation counter. The crystal was 76 mm in diameter and 76 mm high. The well was 19 mm in diameter and 38 mm deep. It was lined with a piece of 18 mm glass tubing to help center the counting tubes and absorb any beta particles escaping from the counting tube. Enough counts were usually accumulated so that the standard deviation due to statistical fluctuations in the count rate was <0.2%.

The iron and cobalt measurements were actually made simultaneously. This was the result of a fortuitous contamination of the ^{59}Fe tracer with ^{60}Co. Some of the iron tracer was rather old and was found to contain the cobalt activity. We were able to measure both Fe and Co in each sample by counting them with a coincidence counter, which counted only the Co, and then correcting the Fe counts for the Co contamination. We made a few independent measurements with ^{60}Co. Within experimental error, they agreed with the other values.

Solution Preparation. The solutions used were of two types—tracer solutions, of which only small volumes were required, and untraced solutions in multiliter volumes.

The large volume solutions (e.g. 1.000 M $HClO_4$) were prepared and standardized by the Analytical Chemistry Division of LLNL. We then added enough of the nonradioactive form of the ion being studied to make the tracer element concentration about 10^{-3} M.

Most of the tracers were obtained from commercial sources (usually New England Nuclear). Some of the tracers were prepared in our laboratory. These were ^{7}Be, ^{88}Y, $^{152,154}Eu$, and ^{196}Au. These were very carefully purified and the half-lives checked when possible. The appropriate amount of tracer solution was evaporated to dryness and taken up in one of the untraced solutions described above. If necessary, for instance if the tracer was delivered as the chloride, and the solution to be made up was perchloric acid, the tracer was evaporated to dryness, a few drops of concentrated perchloric acid added, the solution re-evaporated, a few drops of water added, and the solution evaporated to dryness once again before being taken up in

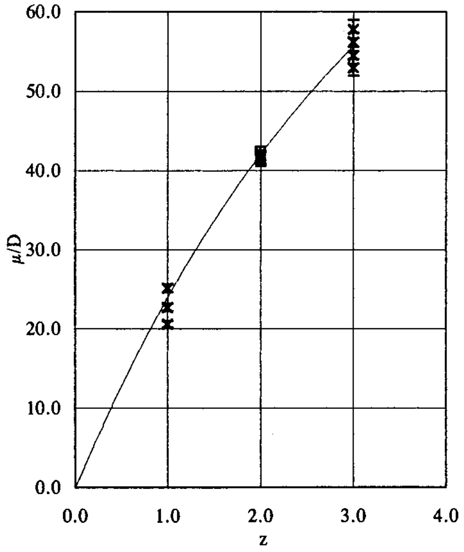

Figure 2. μ/D for 10 positive ions. The curve is $\mu/D = 98(1 - e^{-0.28z})$.

the final solution. The solvent concentrations reported in the body of the paper are the final concentrations after the tracer or carrier had been added. Care was taken to ensure that the traced and untraced solutions were of the same overall concentrations of acid and of traced element.

Results and Discussion

Once we had developed the method for measuring the ionic mobilities, our first task was to determine the relationship between the values of μ/D and the ionic charge. To do this, we measured a series of ions in 1 M $HClO_4$. Our assumption is that in this solution there is very little complexing of the ions with perchlorate, so the ions actually carry the formal charge. (For example, Fe(III) is triply charged.) The data are summarized in Table 2. Our original hope was that all of the values of μ/D for ions of the same charge would be equal within experimental error. As can be seen from the table, the +2 ions are very satisfactory, with a spread of <2%. However, the +1 and +3 ions are not nearly as uniform, although they do cluster.

The values of μ/D fit a function of the form $A(1 - e^{-Bz})$, with $A = 98$ and $B = 0.28$. This form of the curve has no theoretical basis but gives a good fit and seems to be a reasonable shape to allow interpolation. The measured values and the fitted curve are plotted in Figure 2. The error bars are set at 2%. The Nernst equation predicts a linear relationship: $\mu/D = 38.96z$, so it can be seen that the experimental values fall below the Nernst values, with the difference becoming greater as z increases.

The values of μ do not change very much within the entire set of measurements, whereas the diffusion coefficients decrease consistently with increasing charge. In other words, most of the change in μ/D is accounted for by the changes in D. We would have expected the major change to be in the electrical mobility, since it would appear to depend directly on the ionic charge. A simple qualitative explanation is that, as the charge increases, more water is dragged along with the ion, thus increasing its effective size and decreasing the diffusion coefficient. The increased electrical force on the larger charges can then be assumed to fortuitously counteract the slowing of the motion, leading to a nearly constant electrical mobility. The calculations of Nightingale (1959), Marcus (1988), and Ohtaki and Radnai (1993) show an increase of about 30% in ionic radii of +3 ions over +1 but no consistent increase in the number of primary waters of hydration (usually 6).

In contrast, in the experiments described below in HCl−$HClO_4$ mixtures (Table 3), the diffusion coefficients of Fe(III) and Co(II) do not change much with HCl concentration, but the values of μ decrease steadily.

Easteal et al. (1991) have measured diffusion coefficients of Fe(III) in $FeCl_3$ solutions acidified with 1.75 M HCl and 1.85 M $HClO_4$. They see higher values of D as the ionic charge decreases with increasing chloride complexation. They also note that in their lower concentration range the values of D do not change much with chloride concentration.

These observations are consistent with our measurements of D in 1 M $HClO_4$ and in HCl−$HClO_4$ mixtures even though the solutions are not really comparable, since their solutions have very high concentrations of Fe(III).

Fe(III)− and Co(II)−Cl^- Association Constants. After having established a relationship between μ/D and z, we tested the usefulness of the method by measuring the association constants of chloride with Fe(III) and Co(II). We made a series of measurements of the mobilities and diffusion coefficients of Na, Fe, and Co in HCl−$HClO_4$ mixtures in which the sum of the HCl and $HClO_4$ concentrations was 1.000 M. The data are summarized in Table 3. These are our best data, since they were determined last, after our measurement techniques had been refined. The other data were obtained earlier over a period of years, during which time the work was done occasionally when time was available.

In this case we used the measured values for these three ions in 1 M $HClO_4$ to calculate the relationship between μ/D and z rather than the function derived from the larger set of values calculated previously. There were two reasons for this choice. One was that these were our best experimental values. The other was that we were looking for changes in μ/D for Co and Fe as the HCl concentration was changed.

For these three ions in 1 M $HClO_4$, the best fit is with $A = 75.52$ and $B = 0.406$.

For iron, we used the z versus μ/D expression to calculate the average charge, z, of the ions for each HCl concentration. We then used these values in combination with the usual equilibrium constant expressions to calculate the best fit to the association constants. Since the equations are nonlinear, there was no simple analytical way to solve for the constants. We solved them by minimizing the sum of the squares of the weighted residuals by trial and error. The literature values (Martell and Smith, 1976), expressed as betas, are

$$\beta_1 = 4.27 \pm 0.63, \beta_2 = 5.62 \pm 0.69, \beta_3 = 0.20$$

(where β_1 = the first association constant, β_2 = the product of the first two association constants, etc.). In the concentration range of interest, apparently only the first three association constants need be considered. Our best values are

$$\beta_1 = 9.30, \beta_2 = 5.60, \text{ and } \beta_3 = 1.62$$

Unfortunately, the values of these constants are very sensitive to the experimental data. For example, a 1% change in one of the data points can make a change of 10 to 25%. This is largely the result of the fact that we have only five data points to determine three constants and the total change in the average charge is rather small.

Table 5. Values of μ for Na^+, Rb^+, and Cs^+ in Salt Solutions[a]

	Na^+		Rb^+		Cs^+	
	$10^4\mu$		$10^4\mu$		$10^4\mu$	
solution	$cm^2/(V\ s)$	%σ	$cm^2/(V\ s)$	%σ	$cm^2/(V\ s)$	%σ
0.1 M KCl	4.35	1.0	6.75	1.8	6.74	0.1
0.3 M KCl	4.01	1.2				
1.00 M KCl	3.54	4.8	5.89	1.3	5.61	1.0
3.00 M KCl	3.43	1.4	5.57	2.0	4.85	0.9
1.00 M NaCl	3.24	1.9	5.39	1.0	5.23	1.6
0.090 M LiCl	4.24	0.8				
0.099 M LiCl			6.60	1.2	6.34	2.5
0.987 M LiCl	3.10	2.0	5.20	2.7	4.80	2.6
2.99 M LiCl	2.14	1.6	3.80	2.6	3.47	3.3
0.0454 M $CaCl_2$	4.35	0.4	6.76	1.9	6.82	2.8
0.50 M $CaCl_2$	3.19	0.6	5.20	3.5	5.03	3.5
1.00 M $CaCl_2$	2.65	0.9	4.52	0.6	4.29	2.5

[a] Note: We would like to thank W. H. Hutchin, K. V. Marsh, and E. Morimoto for their help in making these measurements.

A further complication arises when we examine the Na data. As the solution composition changes from pure 1 M $HClO_4$ to pure 1 M HCl, μ increases by 3.5%, while D decreases by about the same amount. The net result is that μ/D for Na^+ increases by about 7% in a linear fashion. If we assume that the iron species behave in the same way, the measured values in HCl would be high. We recalculated the betas after reducing the iron values proportionally (i.e. 7% for 1 M HCl, 3.5% for 0.5 M HCl, etc.) to take care of this "solvent effect". In this case the betas become

$$\beta_1 = 8.80, \beta_2 = 3.20, \text{ and } \beta_3 = 0.87$$

It is not clear to us which are the better data, but we lean toward the corrected values.

For Co, the calculation is much simpler. Apparently, only the first association constant is important. Therefore, we can calculate a value of the constant for each HCl concentration. The results, using the uncorrected data, and the data modified by the "solvent effect" are

(HCl)	K	K(solvent effect)
0.25	0.552	0.820
0.50	0.533	0.861
0.75	0.545	0.951
1.00	0.422	0.861
avg	0.513	0.873
std dev	0.061	0.056

We would expect our best value to be at 1 M HCl, since this gives the maximum concentration of $CoCl^+$.

Martell and Smith give the best value as 1.0 ± 0.25. This gives us another reason to favor the corrected values. Furthermore, when the gold values (Table 2) are corrected by 7% (since they were in 1 M HCl), the μ/D value becomes 25.5. This is closer to the average for the +1 ions than the uncorrected value of 27.3.

Other Solutions—Alkali Metal Ions in Chloride Solutions. In the initial exploratory phases of the investigation, we measured the electrical mobilities of Na^+, Rb^+, and Cs^+ in a variety of chloride solutions. For these measurements we used Ag/AgCl electrodes and earlier versions of the transference cell. These cells were very similar to the one in Figure 1 but had either ball joints or standard taper joints at various places to make it possible to disassemble the cell. These cells were subject to leaks and small volume changes as the joints moved, so we went to the one-piece cell. The data obtained with the earlier cells are not as precise as the later data. The standard deviations of a measurement are in the range of 3% instead of the approximately 1% seen in the later measurements. There may well be systematic errors not accounted for, so we estimate that the accuracy is probably of the order of 5%. The cathode compartment volume change corrections are listed in Table 4 and the μ values in Table 5.

The values of μ decrease consistently with increasing salt concentration. The values for Rb seem anomalous, since, except for the lowest salt concentrations, they are higher than those for either Na or Cs. This is also true in 1 M $HClO_4$, as shown in Table 2. The hydrated radius of Rb is approximately the same as that of Cs and smaller than that of Na. However, in 1 M $HClO_4$, the diffusion coefficients are more or less proportional to the radii.

Summary and Conclusions

We have shown that by measuring both the tracer diffusion coefficients and the electric mobilities of dilute ions in aqueous solutions it is possible to make a good estimate of the charge on the ions. In 1 M $HClO_4$ as well as in 1 M $HCl-HClO_4$ mixtures, the ratio μ/D is a better indicator of the charge than either μ or D alone. Our measurement confirming that the charge on the gold−chloride complex is −1 is a simple example.

The method can also be used to estimate association constants of complex ions in aqueous solutions. However, it is difficult to get accurate values. Our measurements on the iron−chloride and cobalt−chloride association complexes point out some of the complications. Since the method can be used with tracers, and in fact requires their use, the method could be useful in some cases in studying the chemistry of those man-made elements which can only be produced in trace amounts.

We would like to have carried the investigations further, but changing conditions followed by retirement prevented our doing so.

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