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Estimation of Tracer Diffusion Coefficients of Ions in Aqueous Solution

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ESTIMATION OF TRACER DIFFUSION COEFFICIENTS OF IONS IN AQUEOUS SOLUTION

ABSTRACT

Equations are given for estimating tracer diffusion coefficients D_i^0 of ions at infinite dilution in terms of limiting ionic conductances Λ_i^0 . Also given are generalized Nernst-Hartley equations for binary and multicomponent diffusion coefficients D^0 and D_{ij}^0 , respectively, at infinite dilution. Data, estimates, and correlations for Λ_i^0 at 25°C and other temperatures are discussed. Estimated values of Λ_i^0 are tabulated from 0-300°C for ions of waste isolation interest and for ions of economic interest in geothermal brines. Estimates of their tracer diffusion coefficients at infinite dilution are tabulated. A rule of thumb, good to a factor of 2, is presented. Very limited data (available only at 25°C) indicate that D_i/D_i^0 generally declines as the concentration of salt or supporting electrolyte increases.

INTRODUCTION

Transport data are frequently required to accurately model systems of practical interest. Examples are the precipitation of valuable metals from geothermal brines, the diffusive transport of radioactive isotopes away from a flooded repository, the diffusion of salt between the two aqueous layers of a solar pond, the diffusion to and from electrodes in battery systems, etc. Clearly, diffusion coefficients are an important transport property.

Diffusion is complex, since n^2 diffusion coefficients are required for n solutes in a solvent. Fortunately tracer diffusion, useful in some applications, is simpler. Unfortunately diffusion coefficients are difficult to measure even in 1-solute systems, and there are little data--especially at temperatures greater than 25°C. There are much less data in multicomponent systems; there is nothing at higher temperatures except a few tracer results, and the experiments are much more difficult.

It is thus desirable to find ways of estimating diffusion coefficients in binary and multicomponent systems. Unfortunately the concentration dependences of binary systems are too complex to predict in advance, especially for electrolytes. Figure 1 shows examples of this complexity. Moreover, there are not enough systematic data for multicomponent systems to see whether binary data can be successfully used to predict multicomponent properties. There is a method based on irreversible thermodynamics which does work well for 1-1 strong electrolyte mixtures,¹ but which requires extensive binary transport data. However, for higher valence type mixtures, this method has not yet been tested.

For very dilute electrolyte solutions, however, it is possible to make estimates of the diffusion coefficients by generalizing the old Nernst-Hartley equation. The equations¹ are given below [Eq. (3)], and are valid at all concentration ratios. The data required are just the limiting ionic conductances (infinite dilution values) Λ_i^0 as a function of temperature.

In this report, we shall be concerned with estimates of tracer diffusion coefficients at various temperatures, with emphasis on ions with economic value from geothermal brines and on ions of radioactive isotopes. As noted earlier, there are few real data to use as guidance for tracer diffusion

Figure 1. Concentration dependence of diffusion coefficients at 25°C for some electrolytes found in brines, seawater, and ground waters.

coefficients D_i in the high concentrations of other salts associated with either brines or salt beds. There are also few data for Λ_i^0 at higher temperatures for infinite dilution estimates. Moreover, the complex-forming transition metals like Zn, Ca, and Fe are not strong electrolytes. Our expectation is that D_i will be lower for a charged complex ion. Finally, Nernst-Hartley-type equations themselves are poor approximations at finite concentrations.

Despite the above-mentioned difficulties, we shall estimate tracer diffusion coefficients at infinite dilution for a number of ions at different temperatures. To do this will require estimates of Λ_i^0 at different temperatures. The results will be tabulated and rules of thumb given. The effects on D_i from higher concentrations of other salts will be considered in the light of existing data. Finally, it is important to note that the estimates are very approximate.

INFINITE DILUTION ESTIMATES IN GENERAL

Diffusion can be described by Fick's Law.² For a binary system (one solute in a solvent) of any concentration, we write in one dimension:

$$-J = D \frac{\partial c}{\partial x}, \quad (1)$$

and for multicomponent systems of n solutes:

$$-J_i = \sum_{j=1}^n D_{ij} \frac{\partial c_j}{\partial x}, \quad i = 1, \dots, n \quad (2)$$

where J , J_i are flows; D , D_{ij} are diffusion coefficients (cm^2/s); c , c_i are volume concentrations in mol/dm^3 , and x is the distance. By writing out Eq. (2), it is clear that a 2-solute system requires 4 diffusion coefficients and a 3-solute system requires 9, etc. Sometimes the cross terms $i \neq j$ are quite large (and even negative), and can exceed a main term coefficient D_{ii} .³

For infinite dilution in electrolyte solutions which have a common anion (characteristic of brines and many natural waters), the generalizations of the Nernst-Hartley equation can be derived from irreversible thermodynamics.^{1,4}

These equations are presented for convenience if more than tracer results are wanted:

Binary:

$$D^0 = \frac{RT}{F^2} \cdot \frac{\Lambda_1^0 \Lambda_n^0}{\Lambda^0} \left(\frac{1}{z_1} - \frac{1}{z_n} \right) \quad (3a)$$

Multicomponent:

$$D_{ij}^0 = \frac{r_{ja}}{r_{ia}} \cdot \frac{\Lambda_i^0}{\Lambda^0} \frac{RT}{F^2} \left[\frac{\delta_{ij} \Lambda^0}{z_i} - x_i \left(\frac{\Lambda_j^0}{z_j} + \frac{\Lambda_n^0}{z_n} \right) \right] \quad i, j = 1, \dots, n-1 \quad (3b)$$

where

$$\Lambda^0 = \sum_{i=1}^n x_i \Lambda_i^0, \quad (4)$$

and where n refers to the common anion, i (up to $n-1$) refers to the various cations, r_{ia} is the stoichiometric coefficient of ionization for the common anion of the i th salt whose formula is $C_{r_{ic}} A_{r_{ia}}$, Λ_i^0 is the limiting conductance of ion i , R is the gas constant (8.3144 joules/mol K), T is the absolute temperature in K, F is the Faraday (96,493 coulombs/equiv), δ_{ij} is the Kronecker delta, and z_i is the valence of ion i with due regard to sign. The equivalent fraction x_i is given by

$$x_i = \frac{N_i}{N}, \quad (5)$$

where

$$N_i = r_{ic} z_i c_i \quad i = 1, \dots, n-1 \quad (6)$$

and

$$N = \sum_{i=1}^{n-1} N_i, \quad (7)$$

where r_{ic} is the stoichiometric coefficient of cation i , and c_i is the concentration of salt i . The D_{ij} correspond to the flows of salts, not ions. The superscript 0 refers to infinite dilution.

It is easy to show from Eq. (3) that when salt i (i.e., cation i) is present in trace amounts (i.e., $c_i \cong 0$), $D_{ij} = 0$ for $j \neq i$ and the tracer diffusion coefficient D_i^0 is given by

$$D_i^0 = D_{ii}^0 = \frac{RT \Lambda_i^0}{z_i^2 F^2} \quad (\text{trace amount of } i) \quad (8)$$

A similar analysis for a tracer anion in any mixture leads to the same type of result:

$$D_k^0 = \frac{RT \Lambda_k^0}{|z_k|^2 F^2} \quad (\text{trace amount of } k) \quad (9)$$

Although we are not concerned with nonelectrolytes, the valuable book by Reid, Sherwood, and Prausnitz⁵ contains some estimation procedures for nonelectrolyte diffusion coefficients.

Equations (3a), (3b), (8), and (9) are very convenient for infinite dilution estimates since only T and Λ_i^0 as a function of T are required to estimate D_i and D_{ij} .

VALUES OF Λ_i^0 AND THEIR TEMPERATURE DEPENDENCE

Data for a number of ions at 25°C are tabulated in Robinson and Stokes⁶ and Harned and Owen⁷, with a few data listed between 0° and 100°C.⁶ There are also Λ_i^0 data for a few ions at 200 and 300°C given by Quist and Marshall⁸ (H^+ , Li^+ , Na^+ , K^+ , NH_4^+ , OH^- , Cl^- , HSO_4^- , SO_4^{2-}), and data for Λ^0 of NaCl to 800°C by the same authors.⁹

For ions not tabulated at 25°C, estimates must be made by chemical analogy to similar ions which have been tabulated. For the ones which are tabulated at 25°C (but not at some or all of the other temperatures),

estimates may be made by assuming the ionic conductances are parallel to or in between other ions whose Λ_i^0 are close at 25°C and when possible are chemically similar. Thus Sr^{+2} is assumed to be similar to Ca^{+2} , and the value at 50°C is interpolated from a graph of Ca^{+2} data. In addition, values for Cs^+ and I^- at 50°C are averages of 45 and 55°C data in Ref. 6; the error will be not more than 1-2%.

Figure 2 shows plots of some data of Quist and Marshall^{8,9} and Robinson and Stokes,⁶ plus some extrapolations for Ba^{+2} and Ag^+ to 300°C which follow the general curvature of the other ions. The Λ_i^0 for brine ions have been treated as follows: Zn^{+2} about 5% more than Na^+ ; Cu^{+2} as 0.94 of the average between Na^+ and Ba^{+2} ; Fe^{+2} about 2.5% more than Ca^{+2} ; Pb^{+2} as an average between Ba^{+2} and Cl^- . Waste isolation ions have been treated as follows: Cs^+ like Cl^- ; T^+ like H^+ ; Sr^{+2} about 7% less than Ba^{+2} ; Ra^{+2} about 2% more than Ba^{+2} , assuming that Λ_{Ra}^0 at 25° is approximately 65; Ce^{+3} to be like La^{+3} , and La^{+3} to be parallel to Ba^{+2} since $\Lambda_{100}/\Lambda_{25} \cong 3.08 \pm 0.04$ for La^{+3} , Mg^{+2} , Ca^{+2} , and Ba^{+2} (thus Ce^{+3} is about 9.7% more than Ba^{+2}); Pu^{+3} like the rare earths with $\Lambda_i^0 = 64$ and otherwise the same as Ba^{+2} ; I^- like Cl^- ; and TcO_4^- like ReO_4^- at 25°C and about 7.5% more than HSO_4^- at other temperatures.

These estimates are collected in Table 1.

Alternate methods for estimating Λ_i^0 at 25°C have been described in an excellent paper by Nigrini.¹⁰ He suggests correlations with 3rd Law ionic entropies, entropies of hydration, or charge-to-radius ratios. Using the data base of Refs. 6-9, he obtains good results for cations in terms of charge-to-radius ratios. Unfortunately, however, anions do not correlate well with any of his suggested quantities. The uncertainties in Λ_i^0 from estimating cation radii are about the same as from our use of chemical similarity.

Figure 2. Temperature dependence of experimental limiting ionic conductances Λ_i^0 as a function of temperature.

Table 1. Estimates and data for Λ_i^0 at various temperatures.

Ion	$\Lambda_i^0, \text{ cm}^2/(\text{ohm equiv})$							
	0°C	25°C	50°C	100°C	150°C	200°C	250°C	300°C
Experimental Data								
H ⁺	225	350	463	634	752	824	865	894
Na ⁺	26.5	50.1	80	151	226	304	382	459
Cl ⁻	41.0	76.4	117	211	303	391	478	561
HSO ₄ ⁻	--	51.2	75	140	212	290	367	440
SO ₄ ⁻²	41	80	127	246	378	525	672	800
Ions from Geothermal Brines								
Ag ⁺	33.1	61.9	95	175	263	348	427	506
Ba ⁺²	34.0	63.6	101	195	286	372	452	530
Zn ⁺²	28	52.8	84	159	237	319	401	482
Cu ⁺²	29	53.6	85	163	241	319	393	466
Fe ⁺²	30	55	87	167	247	327	403	478
Pb ⁺²	38	69.5	109	203	294	382	465	546
Waste Isolation Ions								
Cs ⁺	44	77.2	116	210	303	390	478	561
T ⁺	225	350	463	634	752	824	865	894
Sr ⁺²	31	59.4	95	180	266	346	420	493
Ra ⁺²	35	65	103	200	292	380	461	541
Ce ⁺³	37	70	111	214	314	408	496	581
Pu ⁺³	34	64	101	195	286	372	452	530
I ⁻	41.4	76.8	117	210	303	391	478	561
TcO ₄ ⁻	--	55	81	150	228	312	395	473

Nigrini¹⁰ also linearly correlated Λ_i^0 up to 300°C in terms of Λ_i^0 at 25°C. Linear coefficients are given at each of several temperatures for +1, +2, +3 cations, and for halogens, monovalent oxyanions, and divalent oxyanions. Because of limited data, few anions could be treated. The difference between Λ_i^0 values from his and our temperature correlations are 6% or less.

ESTIMATES OF TRACER D_i^0 AT INFINITE DILUTION

Table 2 contains the results of using the Λ_i^0 from Table 1 in Eqs. (8) or (9). Because of the T factor in Eqs. (8) and (9), the tracer diffusion coefficient goes up faster with T than does Λ_i^0 . Moreover, because of the valence factor z in the denominator, higher valence cations typically have smaller D_i^0 than univalent ions.

At the bottom of Table 2 are the average D_i^0 , excluding H^+ and T^+ . A rough rule of thumb, good to about a factor of 2 is that the tracer diffusion coefficients of ions other than H^+ , T^+ , and OH^- are: $10^{-5} \text{ cm}^2/\text{s}$ at 25°C, half the 25° value at 0°, double at 50°, 4 times at 100°, 7 times at 150°, 10 times at 200°, 15 times at 250°, and 20 times at 300°. The average values plus upper and lower limits are plotted in Fig. 3 (H^+ and T^+ being excluded). Figure 3 is thus suitable for crude estimates. Campbell¹¹ has noted that the average values in cm^2/s from Table 2 between 25 and 300°C can be described quite well by the equation

$$D_{i \text{ ave}}^0 = 4.205 \times 10^{-3} \exp (-1746/T) \quad (10)$$

The calculated value at 0°C, however, is 40% too high, but still within the factor of 2.

Table 2. Estimates of tracer D_1^0 at various temperatures at infinite dilution.

Ion	$10^5 D_1^0, \text{ cm}^2/\text{s}$							
	0°C	25°C	50°C	100°C	150°C	200°C	250°C	300°C
Experimental Data								
H^+	5.5	9.3	13.4	21.1	28.4	34.8	40.4	45.8
Na^+	0.65	1.3	2.3	5.0	8.5	12.8	17.8	23.5
Cl^-	1.0	2.0	3.4	7.0	11.4	16.5	22.3	28.7
HSO_4^-	--	1.4	2.2	4.7	8.0	12.3	17.1	22.5
SO_4^{2-}	0.50	1.06	1.8	4.1	7.1	11.1	15.7	20.5
Ions from Geothermal Brines								
Ag^+	0.81	1.6	2.7	5.8	9.9	14.7	19.9	25.9
Ba^{+2}	0.41	0.85	1.5	3.2	5.4	7.9	10.6	13.6
Zn^{+2}	0.34	0.70	1.2	2.6	4.5	6.7	9.4	12.3
Cu^{+2}	0.35	0.71	1.2	2.7	4.6	6.7	9.2	11.9
Fe^{+2}	0.37	0.73	1.3	2.8	4.7	6.9	9.4	12.2
Pb^{+2}	0.46	0.93	1.6	3.4	5.6	8.1	10.9	14.0
Waste Isolation Ions								
Cs^+	1.1	2.1	3.3	7.0	11.4	10.5	22.3	28.7
T^+	5.5	9.3	13.4	21.1	28.4	34.8	40.4	45.8
Sr^{+2}	0.38	0.79	1.4	3.0	5.0	7.3	9.8	12.6
Ra^{+2}	0.43	0.87	1.5	3.3	5.5	8.0	10.8	13.8
Ce^{+3}	0.30	0.62	1.1	2.4	4.0	5.7	7.7	9.9
Pu^{+3}	0.28	0.57	1.0	2.2	3.6	5.2	7.0	9.0
I^-	1.01	2.0	3.4	7.0	11.4	16.5	22.3	28.7
TcO_4^-	--	1.5	2.3	5.0	8.6	13.2	18.5	24.2
Average ^a	0.50	1.2	2.0	4.2	7.0	10.4	14.2	18.4

^a All but H^+ , T^+ .

Figure 3. Temperature dependence of tracer diffusion coefficients (boundaries represent extremes of ions other than H^+ , T^+ , OH^-).

Again it is important to note that these infinite dilution values of D_i^0 are very approximate--except for the first group of ions for which Λ_i^0 was experimentally determined. Errors are greatest for ions whose values are based on analogy and/or extrapolation, and are of the order of 20-30%.

Radioactive tracers can be used to measure D_i at high dilution in diaphragm cells at higher temperatures to a few percent. Consequently it would be very desirable to measure some for a number of ions. This may ultimately be an easier way to get Λ_i^0 at high temperatures rather than limiting conductance and transference number measurements.

CONCENTRATION DEPENDENCE OF TRACER DIFFUSION COEFFICIENTS

There are some data for tracer diffusion of one ion in its own solution for +1, +2, and -1 valence ions, often up to several mol/dm³ (Refs. 12-20). There are also some data for univalent ions in 1-1 solutions of other salts.¹²⁻²⁰ There do not appear to be any data for higher valence ions in other solutions.

From an examination of existing data, tracer D_i generally decrease as the overall concentration increases. Some results¹¹⁻¹⁸ for univalent ions in NaCl are shown in Fig. 4, where D_i/D_i^0 at 25°C are plotted against the ionic strength I , where

$$I = \frac{\sum c_i z_i^2}{2}, \quad (11)$$

where c_i is now the concentration (mol/dm³) of ion i and z_i is its valence, and the sum is over all the ions (for a single 1-1 salt, $I = c$; for a 2-1 salt, $I = 3c$; etc.). Figure 5 shows similar plots for +2 ions in their own chloride solutions at 25°C.¹²⁻²⁰

Figure 4. Concentration dependence of D_i/D_i^0 for +1 ions in NaCl at 25°C in terms of ionic strength I .

It will be seen from Fig. 4 that the decline of D_i/D_i^0 in NaCl solutions is much the same for all the ions, except that the H^+ ratio is somewhat lower everywhere. The similarity of D_i/D_i^0 for all ions in a given supporting electrolyte is generally true.²⁰ Saturated NaCl is a good analogy to what would be expected from the nearly saturated Salton Sea geothermal brines and from solutions in bedded salt. Consequently for T^+ , Cs^+ , and I^- , the tracer D_i^0 in such NaCl brines should be about 1/3 to 1/2 of their values at infinite dilution.

Figure 5 shows that all the +2 ions have a similar decline in their own solutions. The ions Mg^{+2} , Ca^{+2} , Ba^{+2} , and Ni^{+2} are all strong electrolytes, so that some similarity is not surprising. However, Cd^{+2} strongly complexes with Cl^- in its own solutions, and the bulk of the complex might have been expected to slow down the trace ion. A possible

Figure 5. Concentration dependence of D_i/D_i^0 for +2 cations in their chlorides at 25°C in terms of ionic strength I .

conclusion is that the complexed Cd^{+2} has about the same relative properties as the hydrated other +2 ions. On the other hand, the D_i/D_i^0 ratio for Cl^- in CdCl_2 is greatly affected by the complexing, whereas the ratio curves for Cl^- in other +2 ion solutions are all much the same. It should also be noted that the ratios for Cl^- in KCl solutions follow a curve different from ratios for Cl^- in NaCl solutions. These 25°C results are shown in Fig. 6.

The only multicomponent system for which tracer data are available is $\text{NaCl-KCl-H}_2\text{O}$.^{21,22} It is found that generally tracer D_i for Na^+ , K^+ , and Cl^- fall in between their values in NaCl and KCl at the same

Figure 6. Concentration dependence of D_i/D_i^0 for Cl^- in various chlorides at 25°C in terms of ionic strength I .

overall concentration. It is expected that this would hold true at least for other strong electrolyte mixtures at the same overall ionic strength.

Owing to inadequate data, it is difficult to offer any general estimation rule for tracer D_i at high concentrations, other than D_i decrease with increasing concentration. There appear to be so few data at other than 25°C that essentially nothing can be said. Perhaps to 200°C, the decline in D_i with concentration may possibly be similar to the results at 25°C. Thus, in bedded salt, an arbitrary choice of $D_i/D_i^0 = 0.5$ in 5M NaCl will probably be good to a factor of 2. Clearly it would be desirable to obtain experimental tracer data in NaCl for many more ions and at some higher temperatures.

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