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DIFFUSION AND THERMAL DIFFUSION IN ELECTROLYTE SOLUTIONS ¶

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1. Introduction

Isothermal and thermal diffusion in electrolyte solutions are transport properties that may give important clues to the understanding of the complex structure of those electrolyte solutions. Furthermore, and once diffusion is a very common phenomenon, experimental data on diffusion coefficients D are in high demand, both from industrial areas and from other scientific fields. In fact, not only the availability of these data is very scarce, [1], but their accurate experimental measurement has been so difficult that only a few researchers in this century have managed to obtain diffusion coefficients with reasonable accuracy. Harned's [2] conductimetric technique, Miller's [3] optical system and our open-ended capillary cell have provided reliable data on D. Harned's and Miller's methods are experimentally very difficult to operate and the former is only good for dilute solutions, whereas the latter, being an optical method, only works for relatively concentrated solutions. Our system is operationally much simpler than any of the above and has successfully been used with solutions more diluted than possible with Harned's cell and also with reasonably concentrated solutions. It has been possible to have a precision similar to that of the highly precise Harned method and, we believe, also equally accurate [4]. It has been successfully used in a range of concentrations from 0.001 M (and sometimes lower) to 0.1 M and higher in aqueous solutions of the following electrolytes: HCl [5]; $KClO_4$ [6]; KCl with sucrose [7]; $CdCl_2$ [8]; $CdSO_4$ [9]; $NiCl_2$ [10]; $Al(NO_3)_3$ [11]; $Ca(NO_3)_2$ [12]; $Ba(ClO_4)_2$ [13]; $BaBr_2$ [14]; KSCN [15]; $Mg(NO_3)_2$ [16]; $MgSO_4$ [17]; $BeSO_4$ [18]; $CoCl_2$ [19]; NH_4VO_3 [20]; $LiClO_4$; $NaCH_3COO$; $MnCl_2$; $CuCl_2$; CsI; $Ba(ClO_4)_2$; CdI_2; $Cd(NO_3)_2$; $BaBr_2$; CdI_2; $CdBr_2$; $AlCl_3$; $MnSO_4$. It has also been adapted to measure diffusion coefficients of electrolytes imbibed in polymers [21-24], and, to study diffusion in solutions subjected to magnetic fields [25].

The cell was initially developed for measurements of Soret coefficients by thermal diffusion, using the initial rate procedure, that is the rate of the initial ion migration in a solution where a temperature gradient is suddenly applied. In fact, such a procedure requires the knowledge of the isothermal diffusion coefficient D. Soret coefficients, and consequently heats of transport,

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entropies of transport, etc., are important thermodynamic parameters for the understanding of the kinetic entity associated with an ion that moves in a solution. For example, using this procedure for polyelectrolytes Lobo at al. [26] have proved that these polyelectrolytes with n monomer units behave approximately as a collection of connected spheres where each monomer unit seems to contribute additively to the total heat of transport of the electrolyte.

2. The open-ended capillary diffusion cell

The isothermal diffusion cell we developed, Fig. 1, consists of two vertical capillaries, each closed at one end by a platinum electrode and positioned one above the other with the open ends separated by a distance of about 10 mm. The upper and lower tubes, initially filled with solutions of concentration 0.75 $\bar{c}$ and 1.25 $\bar{c}$, respectively, are surrounded with a solution of concentration $\bar{c}$. This ambient solution is contained in a glass tank 200 X 140 X 60 mm immersed in a thermostat at 298 K. The tank is divided internally by Perspex sheets and a glass stirrer creates a slow lateral flow of the ambient solution across the open ends of the capillaries. The flow has been adjusted so that the concentration (c) at each of the open ends is equal to the ambient solution value $\bar{c}$.

Diffusion is followed by measuring the ratio of resistances of the upper and lower tubes by an alternating current transformer bridge, or by high precision digital voltmeters, highly stable AC sources, controlled by specifically designed software.

In order to measure the differential diffusion coefficient D at a given concentration $\bar{c}$, "top" solution of concentration 0.75 $\bar{c}$ and "bottom" solution 1.25 $\bar{c}$ are prepared, each in a 2 l volumetric flask. The "bulk" solution of concentration $\bar{c}$ is prepared by mixing 1 l "top" solution with 1 l "bottom" solution, accurately measured. Solutions from 0.001 M up to 0.1 M and higher are normally studied. In the case of HCl we managed to go down to 0.005 M for testing theories in connection to the electrophoretic effect [30].

The capillaries are then filled with "top" and "bottom" solutions and allowed to diffuse on to the "bulk" solution and resistance ratio readings are taken at recorded times. The diffusion coefficient is finally evaluated using a computerized least-squares procedure to fit the data. A theory has been developed for the calculation of the diffusion coefficients from the resistance ratio readings [27].

This cell received the Gold Medal at the Geneve International Exhibition of Inventions and New Techniques, 1987.

The reasons for attempting to built a cell where

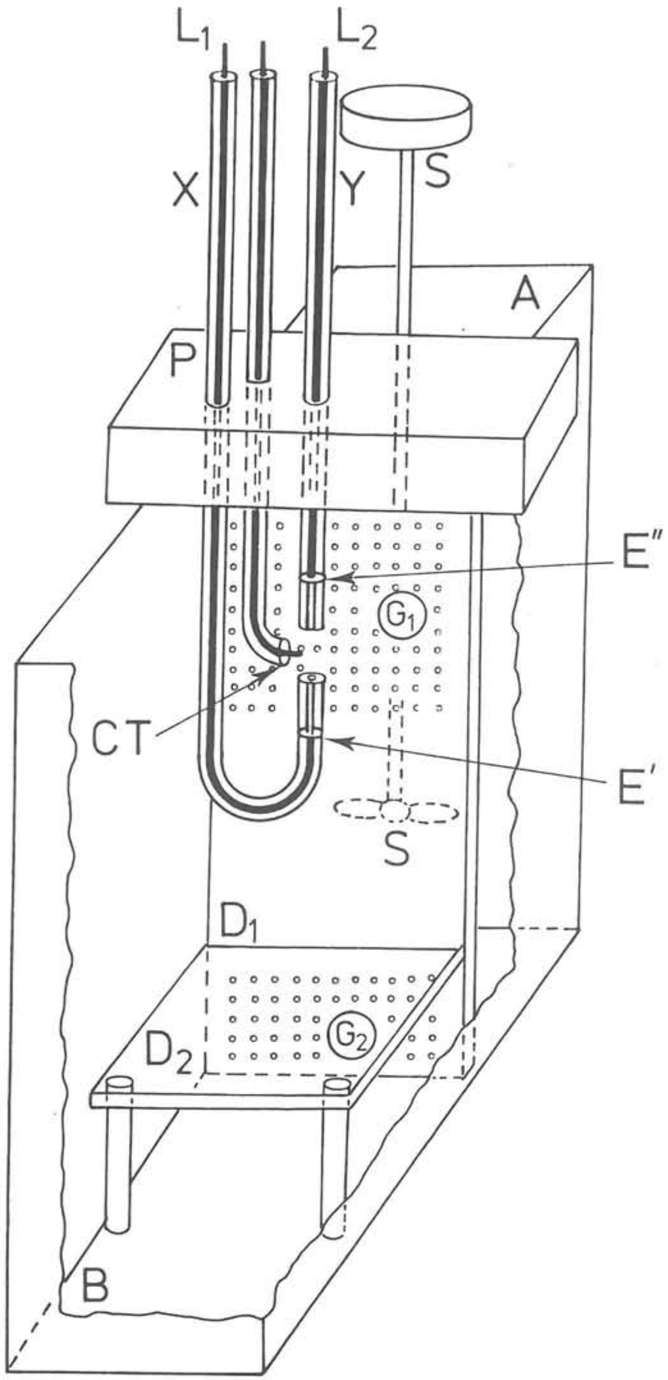

FIGURE 1. ILLUSTRATION OF THE CELL SHOWING LOCATION OF CAPILLARIES AND CENTRE TAP ELECTRODE, AND ARRANGEMENTS FOR CIRCULATION OF SOLUTION.

diffusion is confined to a capillary tube are:

1 - To avoid convection currents. In fact, the most serious problem of Harned's cell is its very high sensitivity to convection currents which rendered most of the experiments useless. It was difficult to have a meaningful experiment as we clearly see from the papers above cited, though the cell was in a cellar, away from sources of vibration, attached to the four corners of the ceiling with springs, in total darkness, etc. Simply by switching on a 50 W lamp, the whole solution in the cell was completely stirred, a fact used when necessary.

   We have performed a number of tests whereby we proved that with the capillary diametre used (2.3 mm) there are no convection currents inside the capillary in normal conditions. We have also proved that surface effects are insignificant for the purpose.

2 - Confining diffusion to one dimension. This makes the mathematical treatment much easier, but maintains its validity for the purpose.

3 - Symmetry in the design. With capillaries it is possible to have a situation where diffusion of solute to the bulk solution in the bottom capillary, is symmetrical to the diffusion of solute from the solution into the upper capillary.

4 - With capillaries it was possible to design an elegant composition whereby a streamlined flow of solution across the mouth of the capillaries effectively eliminates the Δl-effect [27].

3. Diffusion and the structure of electrolyte solutions

It is well known that the structure of electrolyte solutions is very complex. They lack the order of the solid state or the independence and freedom of movement of the entities of the gaseous state and consequently it is not so easy to treat mathematically electrolyte solutions as for solids or gases. Furthermore, electrolytes in a solvent are subject to electric interactions difficult to account in any model attempting to describe this structure. We all know that the situation concerning the understanding of solutions was chaotic before the genius of Arrhenius set his epic model, but we also know that scientific contributions ever since Arrhenius have shown an even more complexing picture, notwithstanding the brilliant work of Debye and Huckel, but, quantitatively applicable only in so diluted solutions that someone said "good only for distilled water slightly polluted". May be we should hope for some genius that "riding some white horse along a sunday beach in a very foggy morning" ends up our bewilderment and provides us with a clear theory of the structure of electrolyte solutions that quantitatively accounts for not only mutual diffusion coefficients, but viscosity, conductance, and all thermodynamic and transport properties in a solution of any electrolyte in any solvent ! A kind of Isaac Newton imposing an order (eventually to be "broken up" by Albert Einstein, but we have already broken up Arrhenius order).

The calculation of diffusion coefficients from equations based on some model describing the movement of matter in electrolyte solutions, is, in the end, a process of contributing to the knowledge of their structure, provided we have accurate experimental data to test these equations.

Assuming that each ion of the diffusing electrolyte can be regarded as moving under the influence of two forces, (a) the gradient of the chemical potential for that ionic species, and (b) an electrical field produced by the motion of oppositely charged ions, we come up to the Nernst-Hartley equation

$$D = \frac{(\nu_1 + \nu_2)\lambda_1^\circ\lambda_2^\circ}{\nu_1|Z_1|(\lambda_1^\circ + \lambda_2^\circ)} \frac{RT}{F^2} \left(1 + \frac{d \ln y\pm}{d \ln c}\right) \qquad (1)$$

or

$$D = D^\circ \left(1 + \frac{d \ln y\pm}{d \ln c}\right) \qquad (2)$$

(the meaning of the letters used is well-known, see e.g. [28], and with the described below). Considering the activity coefficient as unit, the "thermodynamic factor" [parenthesis in (1) and (2)] vanishes and we have the so-called Nernst equation, valid for infinitesimal concentrations (infinite dilution as used to be called).

After the epic contribution by Debye and Huckel, Onsager and Fuoss [29] improved the Nernst-Hartley approach by considering the electrophoretic effect [30].

Thus, the Onsager-Fuoss equation [29] is expressed by

$$D = \left(1 + c\,\frac{d \ln y\pm}{dc}\right)(D^0 + \Sigma\Delta_n) \qquad (3)$$

where D is the mutual diffusion coefficient of the electrolyte, the first term in parenthesis is the activity factor, $y\pm$ is the mean molar activity coefficient, c is the concentration in mol dm^{-3}, D^0 is the Nernst limiting value of the diffusion coefficient, and Δ_n are the electrophoretic terms given by

$$\Delta_n = K_B\, T A_n \frac{(z_1^n\, t_2^0 + z_2^n\, t_1^0)^2}{a^n\, |z_1\, z_2|} \tag{4}$$

where K_B is the Boltzmann's constant; T is the absolute temperature; A_n are functions of the dielectric constant, of the viscosity of the solvent, of the temperature, and of the dimensionless concentration-dependent quantity (κa), being the reciprocal of average radius of the ionic atmosphere; t_1^0 and t_2^0 are the limiting transport numbers of the cation and anion, respectively; z_1 is the algebraic valency of a cation and z_2 is the algebraic valency of an anion.

Since the expression for the electrophoretic effect has been derived on the basis of the expansion of the exponential Boltzmann function because that function had been consistent with the Poisson equation, we only would have to take into account the electrophoretic term of the first order (n = 1). For symmetrical electrolytes we can consider the second term.

Thus, the experimental data D_{exp} can be compared with the calculated D_{OF} on the basis of eq. (5) and (6)

$$D = (D^0 + \Delta_1 + \Delta_2)\,\left(1 + c\,\frac{d \ln y\pm}{d\,c}\right) \tag{5}$$

$$D = (D^0 + \Delta_1)\,\left(1 + c\,\frac{d \ln y\pm}{d\,c}\right) \tag{6}$$

for symmetrical and non-symmetrical electrolytes, respectively.

The theory of mutual diffusion in binary electrolytes, developed by Pikal [31], includes the Onsager-Fuoss equation, but has new terms resulting from the application of the Boltzmann exponential function for the study of diffusion.

The electrophoretic correction appears now as the sum of two terms

$$\Delta\nu_j = \Delta\nu_j^{\,L} + \Delta\nu_j^{\,S} \tag{7}$$

where $\Delta\nu_j^{\,L}$ represents the effect of electrostatic interactions of long-range, and $\Delta\nu_j^{\,S}$ represents them as short-range.

Designating by $M = 10^{12}\, L/c$ the solute thermodynamic mobility, where L is the thermodynamic diffusion coefficient, ΔM can be represented by the equation

$$\frac{1}{M} = \left(\frac{1}{M^0}\right)\left(1 - \frac{\Delta M}{M^0}\right) \tag{8}$$

where M^0 is the value of M for infinite dilution, and

$$\Delta M = \Delta M^{OF} + \Delta M_1 + \Delta M_2 + \Delta M_A + \Delta M_{H1} + \Delta M_{H2} + \Delta M_{H3} \tag{9}$$

The first term on the right hand in equation (9), ΔM^{OF}, represents the Onsager-Fuoss term for the effect of the concentration in the solute thermodynamic mobility, M; the second term, ΔM_1, is a consequence of the approximation applied on the ionic thermodynamic force; the other terms result from the Boltzmann exponential function.

The relation between the solute thermodynamic mobility and the mutual diffusion coefficient is given by

$$D = \frac{L}{c}\, 10^3\, RT\nu\, \left(1 + c\,\frac{d \ln y\pm}{d\,c}\right) \tag{10}$$

where R is the gas constant, and ν is the number of ions formed upon complete ionization of one solute "molecule". From equations (8) and (10) we obtain a version of Pikal's equation more useful for estimating the mutual diffusion coefficients of electrolytes, D_{Pikal}:

$$D_{Pikal} = \frac{10^3\, RT\nu}{\dfrac{1}{M^0}\left(1 - \dfrac{\Delta M}{M^0}\right)}\,\left(1 + c\,\frac{d \ln y\pm}{d\,c}\right) \tag{11}$$

Many other equations have been proposed, but using so many empirical parameters that we think they are not useful for considerations of the structure of the electrolyte solutions.

Are those expressions any good ? Yes and no, but perhaps we should ask: is the structure of the solutions according to the models assumed to develop those expressions ? Unfortunately, the extensive set of D measurements taken with the previously described cell in electrolyte solutions clearly shows that, though for very diluted solutions (as Harned had already shown), the theory and experimental data seem to agree for "simple" (e.g. KCl) electrolytes, the situation is totally different for even moderately concentrated solutions, or, even diluted, when we take less "simple" electrolytes, e.g. $CdCl_2$.

Trying to use diffusion to understand solutions, that is, trying to use theories capable of predicting the values of diffusion coefficients with any reliability has been one of our main goals. The latter, if successful, would be of great industrial and scientific interest, because the measurement of diffusion coefficients is always a difficult task, and some equation which would save us of those troubles would be most welcome by those who merely need the numbers, to go ahead with their productive industries, or by researchers in some other fields.

Before we proceed with this approach to the structure of electrolyte solutions, let us analyse some of the problems encountered when pursuing that task.

4. Availability of thermodynamic and transport data on electrolyte solutions

Looking at eq. (3) we see that in order to calculate D, we need density, viscosity, conductance, transport numbers, and activity coefficients. We soon found out that literature on these data is spread over an enormous variety of journals, from many countries, in many different languages, using many different units and ways of expressing results, and covering a period of about a century. To attain our objective of studying the structure of electrolyte solutions through diffusion (and thermal diffusion) we had to compile all that information and "normalize" it so as to be accessible to a modern applied scientist or researcher in other fields. After some 20 years of searching dusty cellars of libraries, from Australia to the USA, we published [1] in two volumes with 2354 pages. This Handbook has data on density, viscosity, conductance, transport numbers, diffusion coefficients and activity (and osmotic) coefficients in aqueous solutions of over 500 "inorganic" electrolytes. As a spin-off of the bibliographic searches undertaken, we also published "Self-diffusion in Electrolyte Solutions: a Critical Examination of Data Compiled from the Literature" [32]. We are currently preparing an addenda to the above publications, and we are also preparing similar publications for "organic" electrolytes in aqueous solutions, and electrolytes in any other solvents.

At the invitation of the British Science and Engineering Research Council, and with a NATO grant, we organized an Electrolyte Solutions Database [33].

5. Precision and accuracy in thermodynamic and transport data in electrolyte solutions

In order to test theories and equations we need accurate data. We tried to guarantee that our experimental determinations are accurate, but are the data published for the other properties equally accurate ? Some of the other properties are easy enough to measure so as to allow a high degree for precision and accuracy. For example, using a sophisticated equipment of the Australian National University we have measured electrical conductivity with a precision connected to an error of less than 0.01% and we had reasons to believe that the accuracy was equally high. However, we felt it was important to check the precision and accuracy of published data.

To attain that objective tables like Table I were organized for all the electrolytes and the 6 properties of [1]. By appropriate interpolation, the values of the respective properties were calculated for round concentrations of 0.01, 0.05, 0.10, 0.50, 1.0, 2.0 and 3.0 M. Then, the results of one of the authors were chosen as "reference" (not the one thought to be the most accurate, but simply the more convenient for comparing purposes, usually the one covering a wider range of concentrations). Data from the other authors were compared with the "reference" and the percentual error was calculated. The conclusions are the following.

1. Density

In many 1:1 electrolytes it is possible to be confident that the literature values may guarantee an error up to 0.01% in obtaining d, though in some electrolytes one cannot trust the results to better than 1%. In polyvalent electrolytes only rarely can one be sure of an error of 0.01%; in most, an uncertainty of 1% is more likely and in some uncertainties of 1 to 10% are possible.

2. Viscosity

In some 1:1 electrolytes we cannot trust the results within 0.1% (already much greater than the experimental error of 0.01%), but for many we cannot trust the results to much better than 1% and in some cases the uncertainties are greater than 1%. Polyvalent electrolytes: generally worst than 1%.

3. Conductivity

Though conductivity can be measured with high precision (better than 0.01%), only in a few 1:1 electrolytes can we be sure the results are right within 1.0 - 0.1%. In many others the uncertainty is higher than 1%. Polyvalent electrolytes show still higher discrepancies: many electrolytes show discrepancies higher than 10%.

TABLE I

Data relative to equivalent conductance from different sources but, in each case, for the same aqueous solution at 298 K.

A - 1:1 ELECTROLYTES (Λeq / S cm^2 g-equiv.$^{-1}$; c / mol dm^{-3})

Inv.	Conc.	0.01	dif. %	0.05	dif. %	0.10	dif. %	0.50	dif. %	1.0	dif. %	2.0	dif. %	3.0	dif. %
							$AgClO_4$								
Campbell	'59|121					110.1	- 2.90	97.6	- 3.15	89.47	- 3.98	77.36	- 0.73	66.58	
Hognas	'69|364	120.89		116.38		113.39	R	100.78	R	93.18	R	77.93	R		
							$AgNO_3$								
MacInnes	'27|526					109.23	+ 0.21								
Shedlovsky	'32|739	124.72	+ 0.18	115.20	+ 0.10	109.1	+ 0.09								
Campbell	'50|112					109.1	+ 0.09	95.26	+ 6.50	77.95	+ 0.02	64.19	+ 0.01	55.22	- 0.01
Campbell	'59|121					109.1	+ 0.09	89.50	+ 0.06	77.93	0.00	63.93	- 0.38	51.72	- 6.35
Campbell	'59|110	124.75	+ 0.20	115.15	+ 0.06	108.94	- 0.05	89.65	+ 0.23	77.92	- 0.01				
McKenzie	'69|552	124.48	- 0.008	115.15	+ 0.06	109.77	+ 0.70								
Miller	'72|558	124.49	R	115.08	R	109.00	R	89.44	R	77.93	R	64.18	R	55.23	R

4. Transport number

Though in some cases of 1:1 electrolytes one can reasonably expect an error of about 0.5% in the values from the literature, in most 1:1 electrolytes the discrepancies shown in different researchers do not give us a confidence much better than 2% and in some cases that figure is higher. Polyvalent electrolytes show higher discrepancies, generally 1 - 5%, but sometimes much higher.

5. Diffusion

There are not many cases where we can compare results from independent researchers. The author believes we can trust the results of Harned, Miller, Vitagliano and Lobo within less than 1%, but other sources from the literature are to be taken with care.

6. Activity coefficient

In many of the 1:1 electrolytes we can trust the results within 0.5% or better. (But one find discrepancies of 4.4% for HCl 0.1 m and similar anomalies). In many others, one cannot expect better than 1% and in some still higher errors. The situation in polyvalent electrolytes is generally considerably worse: errors from 1 - 10% are common and in some cases the researcher may find that the literature findings may have errors much higher than 10%.

Presently we are trying to organize, for all the above indicated properties, tables like Table II. The idea would be to give to the applied researchers or researchers in other fields, a recommendation on what value to take for each specific case, in a similar manner of what we do when we need a value for the atomic weight of a specific element: consult the table published by IUPAC's Atomic Weights Commission and use the value indicated by them. As we know, that commission periodically analyses data published by researchers all over the world, and decides that some "mean" value is the recommended number to be published.

However, whereas we only have about one hundred of elements, we have hundreds of electrolytes, many properties and a wide range of concentrations to cover (and obviously not the human and material resources of that IUPAC commission).

6. Computation of diffusion coefficients from Onsager-Fuoss and Pikal theories

A theory of mutual diffusion in liquid systems of a solvent and an electrolyte capable of accurately predicting diffusion coefficients has not yet been successfully developed, due to the complex nature of the systems and to the shortage of experimental results [1].

TABLE II

DIFFUSION COEFFICIENTS IN AQUEOUS ELECTROLYTE SOLUTIONS:

AVAILABLE DATA AT ROUND CONCENTRATIONS

c/(mol dm^{-3}); D/(10^{-9} m^2 s^{-1})

conc. c/(mol dm^{-3}) author/year	DEV	FSP	0.001	0.01	0.05	0.10	0.50	1.0	2.0	3.0	5.0
							$AgNO_3$ 1 °C				
Albright 72	8E-4	F					0.712	0.620			
							$AgNO_3$ 13 °C				
Albright 72	3E-3	F					1.040	0.918			
							$AgNO_3$ 25 °C				
Longswor.59	0E0	P					1.423				
Janz 66	1E-2	F	1.749	1.715	1.649	1.598	1.373	1.204	0.986	0.846	0.687
Miller 72	1E-2	F	1.734	1.704	1.649	1.605	1.408	1.248	1.017	0.846	0.518
Albright 72	8E-3	F				1.594	1.426	1.261	1.016	0.841	0.624
D° = 1.766	$D_{av.}$		1.742	1.710	1.649	1.599	1.408	1.238	1.006	0.844	0.610
	σ		0.011	0.008	0.000	0.006	0.024	0.030	0.018	0.003	0.085
	100σ/$D_{av.}$		0.609	0.455	0.000	0.348	1.727	2.414	1.751	0.342	14.01
							$AgNO_3$ 37 °C				
Albright 72	8E-3	F					1.879	1.692			

However, for dilute electrolyte solutions, Onsager and Fuoss introduced a theory which allowed the estimation of diffusion coefficients for symmetrical electrolytes of the type 1:1 with a good approximation [29].

The failure of this theory for other electrolytes, where significant deviations were observed [2], was attributed to the formation of ion-pairs. In fact, the mobility of an ion-pair was introduced as an adjustable parameter, and a reasonable agreement between theory and experimental results was observed [2]. Pikal has developed a similar theory, but using the full Boltzmann exponential instead of the Boltzmann exponential first three terms of a series expansion [31], as in the Onsager-Fuoss theory.

As a result of this procedure, a term representing the effect of ion-pair formation appears in the theory as a natural consequence of the electrostatic interactions. The mobility of an ion-pair is not an adjustable parameter but is determined by the theory.

Both Onsager-Fuoss and Pikal's theories introduce the ion size parameter *a*, "distance of closest approach" from the Debye-Huckel theory and it is well known that there is no direct method for measuring *a*. It may be estimated from experimental data (e.g. activity coefficients, conductance measurements) assuming the validity of some Debye-Huckel based equation. Also, from a table of ionic sizes presented by Kielland [34], we have estimated values of *a*, calculating the average of the radii for the ionic species of an electrolyte. Similarly, we have calculated *a* from Marcus [35] data.

We have calculated the values of the diffusion D_{OF} and D_{PIKAL} according to the Onsager-Fuoss and Pikal theories, respectively, for all the electrolytes in the Handbook of Electrolyte Solutions [1], except when lack of data made it impossible, trying to choose the most appropriate value of the distance of closest approach *a* for each specific case. Calculations were done for 29 concentrations from 0.0 to 1.0 M. Table III shows some examples of those results.

The above calculations were compared with our data, whenever possible, and the basic conclusions are the following:

- No theory on diffusion in electrolyte solutions is capable of giving generally reliable data on D. However, for estimating purposes when no experimental data are available, we suggest, for electrolytes in aqueous dilute solutions:
  - . Symmetrical uni-univalent (1:1)
    Onsager-Fuoss eq. with any *a* (ion size) from the literature (e.g. Lobo's publication) because parameter *a* has little effect on final calculation

TABLE III

Diffusion coefficients calculated from Onsager-Fuoss, [$D_{OF}/(10^{-9}$ m^2 s$^{-1})$], and Pikal [$D_{Pikal}/(10^{-9}$ m^2 s$^{-1})$] theories from 0.000 to 1.000 mol dm^{-3} assuming indicated Λ°/(cm^2 Ω^{-1} eq^{-1}) and distances of closest approach $a/10^{-10}$ m.

Electrolyte	$AgClO_3$		$AgClO_4$		AgF		$AgNO_2$	
	Λ^0=126.5 a=1.75		Λ^0=129.2 a=2.91		Λ^0=117.3 a=3.0		Λ^0=133.9 a=2.8	
Conc.	**Dof**	**Dpikal**	**Dof**	**Dpikal**	**Dof**	**Dpikal**	**Dof**	**Dpikal**
0.000	1.683	1.683	1.717	1.717	1.556	1.557	1.772	1.772
0.001	1.657	1.656	1.690	1.689	1.533	1.532	1.745	1.743
0.002	1.647	1.647	1.681	1.679	1.524	1.523	1.735	1.733
0.003	1.640	1.640	1.675	1.672	1.519	1.517	1.728	1.726
0.004	1.635	1.635	1.669	1.667	1.514	1.512	1.723	1.720
0.005	1.630	1.630	1.664	1.662	1.510	1.507	1.718	1.715
0.006	1.626	1.626	1.660	1.658	1.506	1.504	1.713	1.711
0.007	1.622	1.623	1.657	1.654	1.503	1.500	1.710	1.707
0.008	1.621	1.620	1.653	1.651	1.500	1.498	1.706	1.703
0.009	1.618	1.617	1.651	1.648	1.498	1.495	1.703	1.700
0.010	1.616	1.614	1.648	1.645	1.495	1.492	1.700	1.697
0.020	1.595	1.595	1.629	1.625	1.479	1.474	1.680	1.676
0.030	1.582	1.582	1.618	1.611	1.469	1.462	1.668	1.661
0.040	1.572	1.572	1.610	1.601	1.463	1.453	1.660	1.651
0.050	1.564	1.564	1.605	1.592	1.458	1.445	1.654	1.642
0.060	1.559	1.557	1.601	1.585	1.455	1.438	1.649	1.634
0.070	1.554	1.550	1.599	1.578	1.453	1.432	1.646	1.627
0.080	1.550	1.544	1.596	1.572	1.451	1.426	1.644	1.620
0.090	1.547	1.531	1.594	1.566	1.449	1.420	1.642	1.614
0.100	1.545	1.526	1.592	1.560	1.448	1.415	1.640	1.609
0.200	1.541	1.479	1.592	1.508	1.450	1.361	1.637	1.557
0.300	1.543	1.435	1.606	1.450	1.463	1.301	1.652	1.502
0.400	1.553	1.389	1.621	1.385	1.478	1.269	1.666	1.439
0.500	1.568	1.342	1.639	1.355	1.495	1.199	1.684	1.370
0.600	1.585	1.293	1.659	1.281	1.513	1.124	1.704	1.341
0.700	1.605	1.244	1.680	1.205	1.533	1.046	1.725	1.267
0.800	1.629	1.195	1.701	1.127	1.553	0.970	1.747	1.191
0.900	1.648	1.145	1.724	1.051	1.574	0.896	1.770	1.115
1.000	1.668	1.097	1.747	0.977	1.595	0.825	1.793	1.041

of D_{OF}.

- Symmetrical polyvalent (basically 2:2)
  Pikal eq. Because D_{PIKAL} is strongly affected by the choice of *a*, we suggest calculation with two (or more) reasonable values of *a*, assuming that the actual value of D should lie between them.

- Non-symmetrical polyvalent
  Both Onsager-Fuoss and Pikal, assuming the actual value of D should lie between them. Now, the choice of *a* is irrelevant, within reasonable limits.

- Concerning more concentrated solutions, no definite conclusion is possible.

The authors have calculations of D_{OF} and D_{PIKAL} for hundreds of electrolytes which we may give to anyone.

7. Diffusion in polymers

With a double objective of supplying important data to those working in the degradation and stabilization of polymers at the request of the Russian Academy of Sciences, and studying the mechanism of diffusion within the narrow channels of a spongy polymer, we undertook the task of adapting our cell to the study of diffusion of an electrolyte imbibed in a polymer. Figures and tables in references [22, 23, 24, 37, 38] show the experimental procedures and results obatined. They show a D lower that what we have measured in "free diffusion" (e.g. 1.938 and 1.845 X 10^{-9} m^2 s^{-1} for 0.01 M and 0.1 M KCl, respectively), but we were surprised that it is not much lower, as we expected once the diffusion path should be much larger.

Our interpretation is that the ions move so much in contact with the polymer surface that it plays some sort of a role in accelerating their movement down the concentration gradient.

In "free diffusion" the "Brownian movements" are equal in all directions. If there is a net flow of matter from an elemental cube of volume dv at concentration c to an adjacent elemental cube of volume dv' at a smaller concentration c', it is because there will be more particles going from dv to dv' than the reverse. But, obviously, this net flow of matter from dv to dv' is very slow. The walls of the container are too far away to play a significant role, even in a glass capillary 2.5 mm in diameter as is our previous case.

Now in the polymer, its surface may play a significant role. Interaction with the walls is now significant because any ion is close to them. Polymer-solvent and polymer-solute interactions are certainly strong and may be such that the end result is to speed up the flow of matter from an elemental cube of volume dv to the adjacent dv' down the gradient concentration. An equilibrium is established between adsorved ionic species A^+_{ads} and A^+_{free}

$$A^+_{ads} \Longleftrightarrow A^+_{free}$$

As the surface down the concentration gradient is freer from A^+_{ads}, this equilibrium may rapidly move ==> in volume dv and rapidly move <== in the adjacent dv' so that the net movement of A^+ down the wall is much faster than in similar conditions in free diffusion.

8. The mechanism of diffusion in solid electrolytes

The study of ionic conductivity in the crystal structure of $RbAg_4I_5$ in the microwave range [36] give interesting results concerning the mechanism of diffusion in solid electrolytes. In fact, we found that elementary steps of translational diffusion occur in a time scale faster than in other materials previously studied by K. Funke and others from the W. Jost school (at the University of Gottingen, where we did this research). Our study lead us to the conclusion that a structure like $RbAg_4I_5$ has moving Ag^+ ions which will go with less friction than in any previously studied cases.

9. Testing theories concerning diffusion in electrolyte solutions

References [5, 6, 7, 8, 16, 18, 39, 40] show experimental data from diffusion experiments in several electrolytes in aqueous solutions and curves drawn in the basis of models previously indicated, calculated with what we believe is the most reliable data, according to procedures previously discussed.

Because our system could go to lower concentrations than Harned's cell, we proved, see [5], that in the case of HCl, we should account for the inclusion of the electrophoretic term when applying Onsager-Fuoss treatment. We also show that the theory is applicable in "simple" electrolytes as HCl or KCl but, in fact, as previously said, no model is adequate when we go to higher concentrations or electrolytes of a more complex ionic structure.

Now that we have a substantial amount of data on isothermal diffusion coefficients, we plan to further explore the field of thermal diffusion when parameters like heats of transport and entropy of transport may show characteristics not easily detectable by other thermodynamic properties. As previously said with thermal diffusion we have already shown that polyelectrolytes with n monomer units contribute additively to the total heat of transport of the electrolyte, that is they move as if they were a collection of units moving together.

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MICROELECTRODES ON METALLIC IMPLANTS DEGRADATION, ELECTRODEPOSITION AND SURFACE TREATMENT STUDIES ¶

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Abstract

Despite the high success rate with the use of stainless steel and titanium materials in orthopaedic and dentistry for hard tissue replacement, repair and augmentation procedures, it became apparent that biodegradation of these implants did occur. In order to investigate the systemic effects of corrosion products released from these metallic implants, *in vitro* and *in vivo* studies were undertaken. The results of these studies revels that significant levels of metal species are released into the biological tissues. The properties and advantages of microelectrodes makes them useful tools for quantification and characterisation of released metal species either by performing *in vitro* or *in vivo* studies. Microelectrodes are also used to evaluate the surface modification and mineralization processes that occurs at the implants surface. The goal of these studies is to develop a selective microelectrode which should be able to monitor the species involved in the biodegradation and mineralization processes.

Introduction

Metals have been extensively used in orthopaedic and dental applications as biomedical implant materials for a variety of external support an augmentation procedures. Their use in human and veterinary surgery as hard tissue replacement materials enjoys a long and successful history and has becoming a worldwide routine procedure. Actually, at least two thirds of the population of the developed countries are or were portable of permanent or temporary implants. For instance, just in the

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