

Influence of preferential solvation on transport properties of electrolytes in mixed-solvent solutions

M. Chemla, J. M'Halla, M. Perie and P. Turq

Laboratoire d'Electrochimie (U.A. 430), Université Pierre et Marie Curie, Paris, France

Abstract - The use of radioactive isotopes of ions, of ^{14}C labelled molecules of solvents, and of tritiated water, makes it possible to follow the migration of all individual components in a mixed electrolyte solution.

Different kinds of experimental devices were perfected in order to determine the flux of each radioactive component as it migrated by several mechanisms such as : self-diffusion, mutual diffusion, ionic mobility under electric field, solvent drag by ion migration, etc...

Even if these results could be qualitatively interpreted in terms of ion-ion and ion-solvent interactions, the best formalism to represent this large number of experimental data was found to be within the framework of the formalism of irreversible thermodynamics so as to extract the phenomenological coefficients, since the flux of each species i can be written as :

$$J_i = - \sum_j l_{ij} \vec{\nabla}_{\mu_j} - \sum_n l_{in} \vec{\nabla}_{\mu_n}$$

where subscript j indicates an ionic species in the solution and subscript n is used for a neutral molecule of a solvent component.

This description of migration phenomena yields a symmetrical concept for solvation which appears as a reciprocal ion-solvent interaction. It follows, from the theorem of reciprocity, that the transport of solvent molecules by ions can be deduced from the flux of ions induced by the neutral components flow exerted by a gradient of solvent composition.

This method, called ion-solvent coupled transport, allows the quantitative determination of preferential solvation numbers. These agree very well with other properties such as those derived by NMR techniques or other transport data.

When compared to the values of ΔG° for transfer from water to the same mixed electrolyte solutions, useful conclusions are drawn concerning the distinction that must be made between the equilibrium solvation parameters and that obtained from transported solvent by ions in irreversible processes.

INTRODUCTION

As soon as the first natural radioisotopes have been discovered, they could be used for the study of transport properties of different materials, metals, ionic crystals and electrolyte solutions (1). Thereafter, the appearance of artificial radioactive isotopes of nearly all elements, together with the methods for the detection of stable isotopes, it has become possible to trace all the components of any solution.

Most of the transport properties studied with isotopic tracers were diffusion processes, using either labelled molecules for the neutral components of the solvents (2), or isotopic elements of the ions to follow the charged species of an electrolyte solution (3). Of course, these techniques are well adapted for the determination of self-diffusion constants which are useful to improve our knowledge of interaction and association phenomena in solutions (4) and for a comparison with systems where a gradient of chemical potential does exist (5).

In addition isotopic tracers are efficient tools for precise and reliable measurements of the transport properties in multicomponents systems since the radioactive properties permit an unambiguous identification of each species. Diffusion phenomena in multicomponent solutions (6) are subject to important coupling effects as described in the excellent book by CUSSLER (7). As an example, if we consider a gradient of concentration of a solute i , in an homogeneous mixed solvent, naively one could think that the flux of i species would obey the simple Fick's law. Instead, the real behaviour will be much more complicated, since this system results in unequal gradients of chemical potential for each component of the solvent. Then a flux of these components will take place following the linear relations of the Onsager phenomenological coefficients ; and, transiently the solvent will no longer remain homogeneous:

We shall now describe our own results and try to emphasize the role of specific ion-solvent interactions on coupling effects in diffusion phenomena.

DEFINITION OF PREFERENTIAL SOLVATION

Let us consider a solute i , generally a ionic species, in a binary aqueous-organic mixed solvent. A chemical model of solvation requires the knowledge of two numbers n_{iw} and n_{is} the numbers of water molecules and of solvent s respectively bound in the immediate surrounding of species i .

It is more convenient to define one relative solvation number. If C_w and C_s are the mean molarities of solvent components in the bulk of the liquid, the definition of preferential solvation was given by Strehlow (8) as the number n_i :

$$n_i = n_{iw} - \frac{C_w}{C_s} n_{is} \quad (1)$$

If the composition of the solvation shell is identical to that of the bulk ($n_{iw}/n_{is} = C_w/C_s$) then the number n_i of preferential solvation is equal to zero. A positive value of n_i means a preferential solvation by water molecules.

Alternatively we can define a coefficient n_i^s of preferential solvation by the component s :

$$n_i^s = n_{is} - \frac{C_s}{C_w} n_{iw} = - n_i \frac{C_s}{C_w} \quad (2)$$

This definition seems to be closely connected to the chemical concept of solvation, but it would be not too difficult to establish a correlation with a theoretical description based on statistical mechanics applying the Kirkwood-Buff theory to the distribution of solvent molecules around single ions (9). The number of molecules s associated with an ion i in dilute solutions is defined by the expression :

$$n_{is} = C_s \int_0^R (g_{is} - 1) 4\pi r^2 dr \quad (3)$$

where $g_{is}(r)$ is the radial distribution function ; the upper limit of integration R is large enough so as to reach the undisturbed bulk solvent while the probability of presence of another ion is negligible. In this concept the coefficient of preferential solvation, can be written as :

$$n_i = C_w \int_0^\infty (g_{iw} - g_{is}) 4\pi r^2 dr \quad (4)$$

Since $g_{iw} - g_{is}$ vanishes at a sufficiently long distance, the ∞ sign means that the integration limit is defined with the same conditions as R. A similar expression can be derived for n_i which also obeys eq. 2. This general definition of relative solvation applies equally to equilibrium solvation structure as to ion-solvent interaction in irreversible processes, in which case, n_{iw} and n_{is} indicate the respective numbers of solvent molecules carried with the migrating ion.

For this reason the experimental studies (10) of solvation can be divided into two classes :

The equilibrium distribution is roughly characterized by thermodynamic quantities such as the free energy of solvation or the free energy of transfer. But more valuable tools for obtaining insights into ion-solvent interactions are the spectroscopic techniques. The most widely used method is now N.M.R. which can detect either the resonance of an atom in the solvent or the resonance of the ion itself. The infra-red absorption spectra of the solvent molecules, which are under the influence of solvation interactions or of hydrogen bonding with ions, give useful information on the short range distribution in the immediate vicinity of ionic species.

The solvent transport in irreversible processes was examined very early in classical Hittorf experiments including the addition of an "inert" solute which was assumed to be not affected by the ions moving in the electric field and carrying their solvation shell (11). Later, Strehlow and Koepp (12) applied the Hittorf method to measure the preferential solvation of electrolytes in mixed solvents. The precision of the method was rather poor since the change in composition of the electrode compartments was small. The same result could be obtained by the measurement of emf using galvanic cells (13) with a liquid junction between two electrode compartments different in their solvent composition.

The aim of this paper is to present a new kind of experimental approach (14) to the solvation of individual ions. This is based on the study of the diffusion of electrolytes in a gradient of solvent composition. In this kind of experiment, the analysis of data must be carefully performed since we have to take into account the flux of all components of the solution. In the development of the interpretation, it appeared that the most suitable formalism was based on the phenomenological equations of the thermodynamics of irreversible processes. In fact, as a consequence of the reciprocity relations, one of the major ideas of the method is that, instead of studying the solvent drag by ions, it is easier to examine the transport of diluted ions by the flux of solvent.

We must also point out that the ion solvent interactions in irreversible processes include cross terms resulting from the "microscopic coupling" such as the ion solvent electrophoretic effect. This means that long range interactions are also taken into account. For this reason, it is obvious that the conclusions derived from these phenomena may be somewhat different from the solvation structure as deduced from thermodynamic properties.

SOLVENT PREFERENTIAL TRANSPORT IN A HITTORF CELL

The first systematic determination of preferential solvation in mixed solvents by the Hittorf method were undertaken by Strehlow and Koepp (8). The transport of ions in the electrode compartment is accompanied by a change of the composition of the solvent. For example, in the case of electrotransport of AgNO_3 in a water (w) - acetonitrile (s) mixed solvent, one can measure the increase Δ of the number of acetonitrile molecules per Faraday.

$$\Delta = N (x_s - x_s^0) \quad (5)$$

where N is the total number of solvent molecules in the section and x_s and x_s^0 are the final and initial mole fraction of component s; these are generally determined by chemical analysis using precise determinations of physical properties such as refractive index.

The observed Δ is a combination of the four numbers n_{+w} , n_{+s} , n_{-w} and n_{-s} , the respective numbers of water and acetonitrile molecules bounded to the cations Ag^+ and anions NO_3^- .

$$\Delta = x_w(t_{+n_{+s}} - t_{-n_{-s}}) - x_s(t_{+n_{+w}} - t_{-n_{-w}}) \quad (6)$$

where t_{+} and t_{-} are the transference numbers of ions as obtained in Hittorf method experiment.

Equation 5 can also be written as a symmetrical expression :

$$\Delta = x_w \Delta_s - x_s \Delta_w \quad (7)$$

where Δ_s and Δ_w represent the increase of s and w molecules in the electrode compartment and are correlated to the four individual numbers of solvation :

$$\Delta_s = t_{+n_{+s}} - t_{-n_{-s}} \quad \text{and} \quad \Delta_w = t_{+n_{+w}} - t_{-n_{-w}}$$

The determination of the individual n_{ik} values, requires several equations. Then these authors have determined the values of Δ through the whole range of the solvent composition. They indicated that, provided we accept "reasonable estimations" of the solvation numbers of Ag^+ and NO_3^- in pure water, and also in pure acetonitrile, and provided we accept the "reasonable assumption" that the individual n_{ik} numbers are monotonic functions of the solvent mole fraction, then the Δ values could be used to deduce the four individual solvation numbers.

While the method is really useful since it gives a "reasonable" picture of the variation of the four n_{ik} values, it is clearly far from being rigorous. In fact each measurement of Δ gives only one datum whereas four n_{ik} values are unknown. Moreover each new measurement of Δ , obtained by a change in solvent composition, introduces new unknown n_{ik} values.

In our laboratory, we also developed a technique, similar to that of Strehlow, so as to try to obtain the individual solvation numbers of ions. But instead of varying the solvent composition, we used a mixed electrolyte $\text{AgNO}_3\text{-NaNO}_3$ in different proportions. It seems worth to recall this technique, using radioactive compounds, which is the only method available for the determination of individual flux of each species in a mixed solvent or a mixed electrolyte system.

The experimental aspect of this method has been described in a previous publication (15). We only recall the peculiar design of the electrode compartments (Fig. 1). These are small containers which are connected to the main volume of the cell through a fine capillary which permits the migration of components into the compartment and prevents transport by convection. Moreover we have controlled the transport by diffusion which is quite negligible even if the corresponding correction is always taken into account.

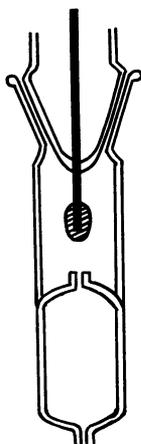


Fig. 1

The cell is filled with the solution under study, so that the chemical potential is homogeneous in the whole apparatus. But, the central compartment contains a small amount of labelled species whose transport is to be measured. In the given example, radioactive tritiated water is introduced, whereas acetonitrile is labelled with ^{14}C . Moreover radioactive ^{22}Na and ^{110}Ag permit a very precise measurement of cations transport numbers in any multicomponent solution.

When the electrical current is input, the labelled compounds enter the cathode compartment? An important feature is that the cathode itself is constituted of a second kind reversible electrode, e.g. Ag , AgCl or Ag_2O , so as to prevent any gas evolution during electrolysis. The volume of solution in the compartment is perfectly constant, except that a very small correction has to be made for the change of volume due to the electrode reaction.

At the end of the experiment which lasts about 30 min. the electrode compartments can easily be separated from the cell and introduced directly into a well-type crystal scintillation counter without any chemical handling. This is most convenient for γ -emitting radioisotopes, since it is possible, in some cases, to measure simultaneously the transport of several components, using the characteristics of the emitted radiation. In the case of soft β -rays, ^{14}C or ^3H the solution has to be collected and introduced into a special container for liquid scintillation counting.

This method has been applied to study the preferential solvation in a mixed solvent containing 5 % mole fraction of acetonitrile in water (16). First, the radioisotopes ^{110}Ag and ^{22}Na are used for the determination of the transport numbers of the three ionic components Ag^+ , Na^+ and NO_3^- which also can be expressed as J_i i.e. the flux of ions entering the compartment per unit time due to the applied current density. On the other hand the flux of wand s are measured under the same conditions ; this leads to the flux of solvent components referred to the same reference frame as for the flux of ions. We must point out that the data lack precision because the amount of transported solvent is very small.

According to the chemical model, which supposes that n_{is} molecules of solvent s move together with the ion i , the flux of s can be written as :

$$J_s = \sum n_{is} \cdot J_i \quad (8)$$

We encounter once more the problem of solving one equation containing several n_{is} parameters. For this reason, several experiments have been undertaken using different values of the ratio $\text{AgNO}_3/\text{NaNO}_3$ at constant ionic strength equal to 0.5 M. But this method was not expected to permit the resolution of the system, since, at first sight, the mobilities λ_i of ionic components should be nearly constant at constant ionic strength. Then the matrix formed by three lines such as :

$$|c_1\lambda_1 \quad c_2\lambda_2 \quad c_3\lambda_3|$$

would cancel out and the system would remain undetermined. However a slight variation of mobilities could be observed as shown in table I :

Table I : Mobilities of Ag^+ , Na^+ , NO_3^- in the mixed solvent :
95 H_2O , 5 ACN (mole %)

Electrolyte	λNO_3^-	λNa^+	λAg^+
AgNO_3 , .5 M	42.89		23.81
NaNO_3 , .5 M	46.55	31.75	
AgNO_3 , .25 M	44.81	31.49	23.20
+ NaNO_3 , .25 M			

Of course, the variations of the λ_i being small, the precision of the derived n_{ik} values is rather poor ; nevertheless, individual values of absolute solvation numbers, could be estimated as shown in table II. These are in fair agreement with the values proposed by Strehlow (8).

Table II : Transport solvation numbers of ions in the mixed solvent 95 H₂O, 5 ACN molar

Ion	n _{H₂O}	n _{ACN}	n _{H₂O}	n _{ACN}
Ag ⁺	8 ± 2	1.3 ± 0.2	~ 6	~ 1.6
Na ⁺	5 ± 1.5	0.1 ± 0.04		
NO ₃ ⁻	2.7 ± 1	0.1 ± 0.05	4	~ 0.2

Again, we must point out that all these results are strongly dependent on a "reasonable assumption" ; in fact, as already indicated, the mobilities of ions should be constant at first order in which case the system would be undetermined. As a consequence, if the observed variations of the λ_i could be assigned to ion-ion coulombic interactions only, such as relaxation or electrophoretic effects, then the numbers of solvation of Table II could be considered as fairly convincing results. On the other hand, if these variations of λ_i result partly from slight changes of solvation due to competing equilibria (17) then the significance of these results would be a matter of controversy.

Finally, a rigorous treatment of the experimental data should be restricted to the utilization of the coefficients of preferential solvation n_i (eq. 1). Indeed, the equation (6) can be rewritten as :

$$\Delta = x_w \left[t_+ (n_{+s} - \frac{x_s}{x_w} n_{+w}) - t_- (n_{-s} - \frac{x_s}{x_w} n_{-w}) \right] \quad (9)$$

$$= x_w (t_+ n'_+ - t_- n'_-)$$

Therefore the Washburn number is introduced, which, for a symmetrical 1-1 electrolyte, is written as :

$$W = n_+^H t_+ - n_-^H t_- \quad (10)$$

where n_+^H and n_-^H are the coefficients of preferential solvation of cation and anion, the affix H corresponds to the transport process of the Hittorf cell. The introduction of these relative numbers of solvation, reduces to two the number of parameters corresponding to a binary electrolyte in a mixed solvent solution.

INTRODUCTION OF THE PHENOMENOLOGICAL LINEAR EQUATIONS

The formalism of irreversible processes thermodynamics is more suitable for the description of transport processes in multicomponent solutions since it does not need any chemical model, all interactions being included in the coupling cross terms. The flux of ions is written :

$$\vec{J}_i = - \sum_j l_{ij} \vec{\nabla} \mu_j - \sum_n l_{in} \vec{\nabla} \mu_n \quad (11)$$

The signs i and j are used for ions (1 and 2 for cation and anion respectively), and the sign n for neutral molecules of solvent components s and w .

The flux of solvent s is given by :

$$J_s = - \sum_i l_{si} \vec{\nabla} \mu_i - \sum_n l_{sn} \vec{\nabla} \mu_n \quad (12)$$

All fluxes are referred to the center of mass.

These equations contain 16 parameters ; however taking into account (i) the Gibbs-Duhem theorem, (ii) the condition of fixity of the mass center and (iii) the theorem of Onsager, the number of independant l_{ij} parameters is reduced to six : of them, three concern the ion properties, one corresponds to the solvent-solvent coupling (interdiffusion), and only two are involved in ion-solvent interactions ; these two coefficients are directly linked to the relative numbers of solvation n_+ and n_- which appear as coefficients describing the irreversible process of coupled ion-solvent transport.

Using this formalism, the conditions existing in a Hittorf cell are summarized as follows :

$$\vec{\nabla} \mu_w = \vec{\nabla} \mu_s = 0 \quad \vec{\nabla} \mu_1 = - \vec{\nabla} \mu_2 = F \vec{\nabla} \phi \quad (13)$$

where ϕ is the external potential applied to the electrodes. As the flux of preferential solvation is equal to $J_w - C_w/C_s \cdot J_s$ the numbers of relative solvation of cation and anion are :

$$n_+^H = (l_{w1} - \frac{C_w}{C_s} \cdot l_{s1}) / \left\{ (l_{11} - \frac{C_1}{C_s} l_{s1}) - (l_{12} - \frac{C_1}{C_s} l_{s2}) \right\} \quad (14)$$

$$n_-^H = (l_{w2} - \frac{C_w}{C_s} l_{s2}) / \left\{ (l_{22} - \frac{C_2}{C_s} l_{s2}) - (l_{21} - \frac{C_2}{C_s} l_{s1}) \right\} \quad (15)$$

Now the measurement of the Washburn number using a Hittorf cell provides only one relationship between the two parameters n_+^H and n_-^H . Another kind of experiment is needed so as to resolve the system.

POTENTIAL OF A CONCENTRATION CELL WITH TRANSPORT OF SOLVENT

When a galvanic cell with mixed solvents includes a junction potential arising from a solvent concentration gradient, it has been shown (18) that the measured e.m.f. is a simple function of the preferential solvation numbers of the ions. For example, if the chemical potential of the electrolyte solute is maintained constant throughout the whole junction, the measured e.m.f. is simply proportional to the transport number Δ defined in eq. 6.

$$E = - \frac{\Delta}{F} \cdot \frac{1}{1 - x_2} \cdot (\mu_2'' - \mu_2') \quad (16)$$

where x_2 is the mean mole fraction of the solvent component s and $\mu_2'' - \mu_2'$ is the difference of the chemical potential of the same component in the extreme parts of the solution directly in contact with electrodes. The method has been thoroughly developed by Feakins (13), who could obtain a large number of experimental data leading to the Washburn number W_s referred to the solvent component s . The interest of the method is that the precision is excellent even at high dilution of the electrolyte. So the extrapolation to infinite dilution yields the limiting solvation parameters of the ions, noted W° , n_+° and n_-° . A large number of data have been obtained by Feakin's group at Dublin (19) and lead to important conclusions regarding the preferential solvation of nearly all univalent anions and cations in solutions containing various organic components such as ketones, alcohols, DMSO or Raffinose.

The diffusion potential of the liquid junction can also be expressed in terms of phenomenological coefficients as developed in a complete analysis by Miller (20) of diffusion in multicomponent solutions. In fact, using the flux equations (11) and (12), the condition of zero current gives the value of the junction potential :

$$F \vec{\nabla} \phi = - \sum_i \frac{t_i}{Z_i} \vec{\nabla} \mu_i - \frac{1}{\alpha} \sum_n t_n \vec{\nabla} \mu_n \quad (17)$$

where $\alpha = \sum_i Z_i Z_j l_{ij}$, t_i is the transport number of ion i and t_n is a convenient expression called the transport number of the solvent component :

$$t_i = \frac{1}{\alpha} \sum_j Z_i Z_j l_{ij} \quad t_n = \frac{1}{\alpha} \sum_i Z_i l_{in} \quad (18)$$

These expressions are used to derive the formulation of the Washburn number W in the case of a symmetrical Z -valent electrolyte.

$$W = \frac{Z^2}{\alpha} \left[\left(1_{+w} - \frac{C_w}{C_s} 1_{1s} \right) - \left(1_{2w} - \frac{C_w}{C_s} 1_{2s} \right) \right] \quad (19)$$

Since W is a simple linear combination of n_+ and n_- , the corresponding expressions for n_+ and n_- are obtained. We discover that these are identical to eqs. 14 and 15, except that each l_{ik} parameter is changed into l_{ki} . Then, according to the Onsager Reciprocity Relations, the data obtained with this junction cell e.m.f. are identical to those resulting from a Hittorf transport experiment. Then, this second kind of experiment is not available to provide a second relationship which is required for the determination of individual n_+ and n_- solvation numbers.

However, a great advantage of the e.m.f. method is that it can be extrapolated to very dilute concentration of ions. In this case, it has been demonstrated (21) that most of the cross coefficients cancel out (22) so that the expressions for n_+ and n_- are reduced to :

$$n_+^{\circ} = (1_{1w}^{\circ} - \frac{C_w}{C_s} 1_{1s}^{\circ}) / 1_{11}^{\circ} \quad (20)$$

$$n_-^{\circ} = (1_{2w}^{\circ} - \frac{C_w}{C_s} 1_{2s}^{\circ}) / 1_{22}^{\circ} \quad (21)$$

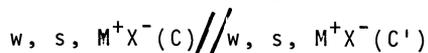
where the preferential solvation numbers n° and n° as well as the corresponding Washburn number W° represent the limiting solvation properties of dilute ions in a mixed solvent of a given composition.

COUPLED DIFFUSION PHENOMENA IN MIXED SOLVENTS

The general expression of phenomenological linear relationship eq. 11 indicates that, in a multicomponent system, all components undergo a transport process even if the "driving force" affects only one of them ; this is an illustration of macroscopic and microscopic coupling. Then two experimental situations can be considered depending whether the driving force is due to the gradient of chemical potential of the ionic solute or of the neutral solvent molecules.

a) Electrolyte concentration gradient

At this stage, it is interesting to describe the so-called "Erdey-Gruz proposed experiment" (23). The starting point is the remark that in the determination of Washburn number the anion and cation move in opposite directions. If now, the transport is due to chemical diffusion of a binary electrolyte in a homogeneous mixed solvent, the transport of solvent by ions would be in the same direction. Thus, a rough assumption would lead to the conclusion that the transported solvent should be $n_+ + n_-$ when the experiment is performed in a diffusion cell such as :



This conclusion is misleading for two reasons : (i) the gradient of electrolyte concentration changes the chemical potentials of the solvent components which induces a primary flux of these species as a consequence of macroscopic coupling (24). (ii) moreover, in such an experiment, the transport of solvent by ions is observable only if the concentration of electrolyte is high which increases the complexity of the process.

Since there is no net charge transport in diffusion process, it is more convenient to introduce μ_0 the chemical potential of the neutral electrolyte solute M^+, X^- , because the electrical contributions in $\tilde{\mu}_i$ cancel out :

$$\tilde{\nu}_{\mu_0} = \tilde{\nu}_{\mu_1}^{\nu} + \tilde{\nu}_{\mu_2}^{\nu} \quad (22)$$

In this case, according to the Gibbs-Duhem theorem, the chemical potentials of only two of the components of the ternary system are independent. Also, because of the limiting conditions, only two fluxes are independent. For example we can write, the flux of salt J_o and the flux J_s of s component.

$$\begin{aligned} \vec{J}_o &= -L_{oo} \vec{\nabla} \mu_o - L_{ow} \vec{\nabla} \mu_w \\ \vec{J}_s &= -L_{ss} \vec{\nabla} \mu_s - L_{sw} \vec{\nabla} \mu_w \end{aligned} \quad (23)$$

where the L_{ik} coefficient are derived from the l_{ik} used in the preceding calculations.

b) Flux of electrolyte induced by a solvent composition gradient

The principle of this new kind of experiment has been already described (25) and a thorough analysis of the phenomena together with a few examples of experimental results have been developed previously (24).

In the case of multicomponent diffusion, the linear phenomenological equations are moreoften converted into generalized Fick's equation (26).

$$\vec{J}_i = - \sum D_{ij} \vec{\nabla} C_j \quad (25)$$

where the D_{ij} diffusion coefficients are derived directly from the l_{ij} phenomenological parameters.

$$\vec{J}_o = -D_{oo} \vec{\nabla} C_o - D_{ow} \vec{\nabla} C_w \quad (26)$$

$$\vec{J}_s = -D_{ss} \vec{\nabla} C_s - D_{so} \vec{\nabla} C_o \quad (27)$$

This method has proved to be very useful, since the classical methods of measurements of diffusion constants using radioactive isotopes can be used without any modification, except the fact that the solvent composition is not homogeneous. In addition the radioactive tracers permit measurements in very dilute solutions of electrolyte. In this case we note that the usual diffusion constant of the electrolyte D is simply related to the self diffusion constants D_1 and D_2 of cation and anion respectively.

$$D = \frac{D_1 \cdot D_2}{D_1 + D_2} \quad (28)$$

If we restrict the treatment to the case where the concentration of s component is low enough so that the ratio $C_s/C_w \ll 1$, then it is possible to express each D_{ik} parameter in a simplified form :

$$D_{oo} = D \left[1 + (n_+ + n_-) \frac{\partial \ln f_+ f_w}{\partial C_o} \right] \quad (29)$$

$$D_{ss} = D_s + 2 C_o D \frac{\partial \ln f_+}{\partial C_s} \quad (30)$$

$$D_{so} = C_s D_s \frac{\partial \ln f_s}{\partial C_o} + 2 D (n_+ + n_-) \left(1 + \frac{\partial \ln f_+}{\partial C_o} \right) \quad (31)$$

Where f_+ , f_w and f_s are the activity coefficients of the corresponding components, referred to pure solvent. It is easy to recognize in each of these expressions that the generalized diffusion coefficients consist of two terms: the first is simply due to the gradient of chemical potential of the species itself ; the second is an additional contribution to the driving force arising from the influence of other components. For example, the first term in the coefficient D_{so} (eq. 31) includes the ratio $\partial \ln f_s / \partial C_o$ which is the main thermodynamic driving force due to the free energy of transfer $\partial G_s / \partial C_o$; this is called the macroscopic coupling term. The second part of eq. 31 containing n_+ and n_- arises from the ion-solvent interaction in the irreversible transport process, and represents the microscopic coupling contribution.

Note : It is interesting to point out that if the system is such that there is a preferential solvation of ions by the component s of the solvent, then the first term $\partial \ln f_s / \partial C_o$ is negative, whereas the parameters n_+ and n_- are generally expected to be positive. It follows that, in most cases, the microscop-

pic coupling effect due to the transport of solvent acts in the opposite direction to that of the driving force which arises from the free energy of solvation.

These equations clearly show that the determination of any one of the coupled diffusion coefficients, e.g. D_{s_0} , in a dilute solution, yields the sum $n_+^0 + n_-^0$, which, when combined with the Washburn number, allows the evaluation of n_+^0 and n_-^0 separately.

This last conclusion, when compared to the "proposed Erdey-Gruz experiment", means that, instead of studying the transport of solvent by ions, it is more fruitful to determine the transport of ions induced by a flux of solvent molecules. In fact, these two phenomena are equivalent in the frame of Onsager reciprocal relations.

THE EXPERIMENTAL PROCEDURE

The principle of the experimental procedure is to use a diffusion cell in which the flux of electrolyte, say Na^+Cl^- , is measured by the radioactive isotope ^{22}Na . Here, the radioactive labelling is particularly interesting, not only because it allows for a precise measurement of concentration without any chemical processing, but also adequate experimental precision is preserved even in very dilute solutions of electrolytes.

In practice, for the determination of the cross D_{ik} coefficients, the two compartments of the diffusion cell are filled with solutions whose ratio C_w/C_s are different, whereas, in order to simplify the treatment of data, the molar concentration of radioactive electrolyte is made identical in both parts of the cell.

Starting with these initial conditions, the sequence of observed phenomena is as follows :

(i) Transient regime : during a first period, whose duration is a few days in our experimental conditions, we observe of course the diffusion of solvent s in its own gradient of concentration ; but, simultaneously, a flux of electrolyte is also observed, as a result of the driving force due to the gradient of free energy of solvation. It is worth pointing out that, under these conditions, the electrolyte flows against its own gradient of concentration. The effect is rather large, since, starting from equal concentrations of salt, the transient difference in salt concentration may reach values as large as 10 %.

(ii) Steady evolution towards equilibrium : of course, after the gradient of C_0 has reached a maximum value, then all components of the solution undergo diffusion transport until the equilibrium situation corresponding to a completely homogeneous system. This stage also lasts a few days, so that the general shape of variation of concentration versus time is as shown on fig. 3.

Experiments for coupled diffusion process are carried out using the apparatus which was developed in our laboratory since more than 20 years (Fig. 2). Using species labelled as well with radioactive as with stable isotopes, the method was generally used for the determination of self-diffusion coefficients (27), and more recently for the study of diffusion in multicomponent systems (28)

The technique is based on the open-end capillary method proposed by Anderson and Saddington (29) and widely used by Mills (30). Each capillary tube is made of quartz glass, the inner diameter being of 1 mm to prevent convection in the liquid phase ; the end of the tube is sealed with a flat bottom so that the length of the capillary is measured with a precision of a few hundredths of a mm, the total length being equal to 3 cm.

The capillaries are filled with the solution generally labelled with radioactive isotopes. In each experiment a set of six capillaries fixed on a Teflon holder is immersed in a vessel whose volume is large compared to the inner content of the capillaries. This vessel is filled with a solution whose composition depends on the phenomenon under study. For example, in a self-diffusion coefficient measurement, the solutions inside the capillaries and the container are identical except that the sample within the capillaries is labelled with a radioactive tracer.

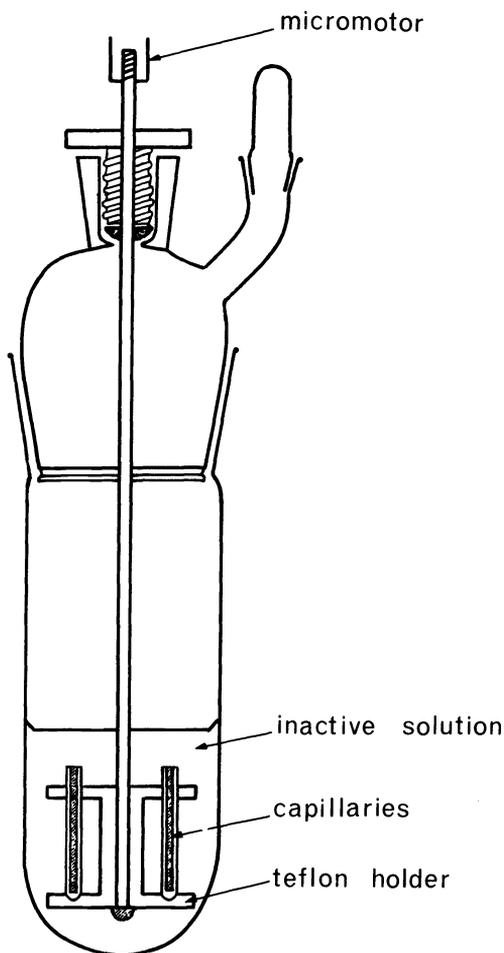


Fig. 2 The diffusion cell

COUPLED DIFFUSION DATA PROCESSING

A complete quantitative interpretation of the experimental results $g_i(t)$ is a hard piece of work which requires the knowledge and then the determination of many other properties of the system. The first problem is to find the solutions of a set of simultaneous differential equations such as :

$$\frac{\partial C_i}{\partial t} = \frac{\partial}{\partial x} \sum D_{ij} \frac{\partial C_j}{\partial x} \quad (33)$$

In our case the number of independent constituents is limited to two, which can be chosen as the electrolyte 0 and the solvent component s . These equations cannot find any analytical solutions since the D_{ij} coefficients are generally concentration dependent. It is then necessary to proceed with numerical techniques using the finite differences method. Moreover the unknown D_{ij} coefficients must be introduced using a polynomial function of solvent concentration with adjustable parameters. Finally, a try-and-error iteration technique is employed until the computed profile of concentration versus time gives the best fit to the experimental points (Fig. 3).

The adjustment of the parameters is made more reliable if a number of coefficients together with their concentration dependence are known from preliminary experiments. These are briefly listed below ; more details are given in recent publications (14) (24).

In the case of coupled diffusion under solvent composition gradient, both parts of the cell are filled with solutions which differ only in the ratio C_w/C_s , the molar concentration of radioactive salt being the same in the capillaries as in the container. Then, the whole cell is dipped in an oil bath whose temperature is maintained at $25^\circ \pm 0.002^\circ\text{C}$. Inside the cell, the set of capillaries undergoes a slow rotation movement which produces just enough stirring and avoids mouth effects on the diffusion out of the capillaries.

The size of the capillaries has been defined so as to permit a direct counting of their γ -ray intensities in a well-type crystal scintillation counter connected to an automatic sample changer and a γ -rays spectrometer built by Nuclear Chicago. This direct measurement of radiation intensity without any chemical handling, leads to the determination of the concentrations within the capillaries with an excellent accuracy. Finally the primary experimental result obtained in a diffusion run, is given as the ratio :

$$g_i(t) = (\bar{C}_i(t) - C_i^0)/C_i^0 \quad (32)$$

where C_i^0 is the initial concentration of the species i and $\bar{C}_i(t)$ is the average concentration inside the capillary at the end of the diffusion run whose duration t is about a few days.

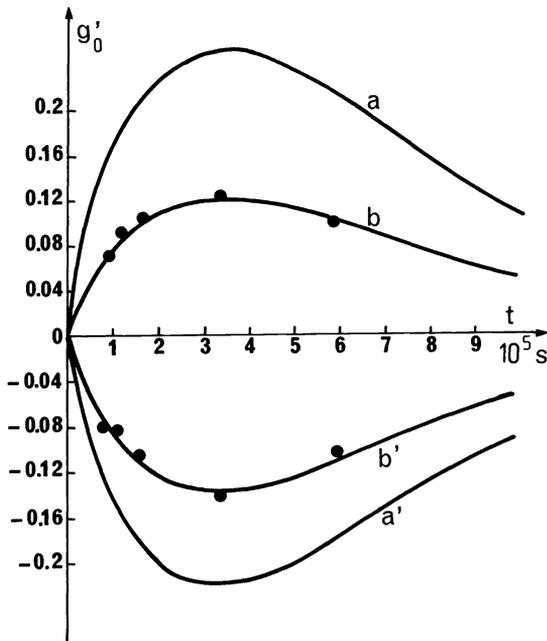


Fig. 3 : Transient variation of concentration (see text)

generally obtained from e.m.f. measurements (31), alternatively from high precision vapour pressure determinations (32).

(iii) Finally, other parameters such as the specific volume of the mixed solvent, the activity coefficients f_w and f_s as a function of X_s could easily be estimated from literature data. For example, the preferential solvation of Na^+Cl^- in a water-dioxane mixed solvent is determined after two kinds of experiments depending only on the initial conditions.

Diffusion "IN" : The capillaries are filled with an aqueous solution of NaCl 4.10^{-3}M whereas the central vessel contains the same concentration of NaCl in a 20 % Dioxane-Water mixed solvent.

Diffusion "OUT" : The capillaries are filled with a solution of NaCl 4.10^{-3}M in the mixed solvent and the central vessel contains an aqueous solution of NaCl 4.10^{-3}M .

In the first case, the electrolyte solute NaCl tends to concentrate inside the capillaries, then the $g_i(t)$ values are positive as represented by the dots of Fig. 3b. In the second case, the driving force tends to extract the NaCl out of the capillaries which corresponds to the dots of Fig. 3b'. The numerical calculation by the method of finite differences can be used to compute these variations of concentrations versus time. In our method of computation, the first step is the calculation of the predicted graph if the ions were not solvated and if the driving force was simply equal to the thermodynamic term $\partial G^\circ/\partial C_s$. The situation corresponds to a maximum effect on the transient concentration gradient (Fig. 3a and a'). As indicated, the microscopic coupling due to solvation always results in an attenuation of the transient effect. Several trials are then undertaken, with the introduction of increasing values of $n_+^\circ + n_-^\circ$ until the computed lines give an optimal fit to the experimental values (lines b and b' in Fig. 3).

In the case of Na^+Cl^- in a water-dioxane solvent, the best fit was obtained with the value $n_+^\circ + n_-^\circ = 14$. Then, from Feakin's result for the Washburn number found equal to 1.6 for Na^+Cl^- in the solvent of the same composition, we can deduce the individual preferential solvation numbers : $n_+^\circ = 10$ for Na^+ ion and $n_-^\circ = 4$ for Cl^- .

(i) The first factor which must be accounted for in these experiments is the dependence of the mobilities of species versus the solvent composition. For example the variation of the diffusion coefficient of the electrolyte has to be measured as a function of the component's concentration. This is obtained by preliminary determinations of self-diffusion constants using radioisotopes of ions in various mixed solvents.

(ii) The interdiffusion coefficient of components s and w , is conveniently measured with a Gouy interferometer over a wide range of composition, which gives a polynomial expression for the coefficient D_{ss} as a function of the molar fraction X_s of the s component.

(iii) The derivation of n_+° and n_-° from the cross coefficient of diffusion requires the very precise knowledge of the main thermodynamic driving force $\partial G^\circ/\partial X_s$. We could use a number of existing data,

This first result incites to introduce a first comment : in fact we find that the transport of water molecules by Na^+ ions in water-dioxane is much larger than the corresponding transport by Cl^- . However the standard free energy of transfert in the same solvent indicates a quite different preferential solvation effect , since within the usual extrathermodynamic assumptions, the value of $\partial G^\circ/\partial X_w$ is equal to $-13 \text{ kcal mol}^{-1}$ for Cl^- while it is nearly zero for Na^+ ion (23).

This apparent contradiction means that the contributions of water and dioxane molecules to the equilibrium solvation of Na^+ ions are nearly identical. But the water molecules are much more affected in the irreversible flow of these cations (13).

INDIVIDUAL SOLVATION NUMBERS AS OBTAINED BY THE COUPLED DIFFUSION METHOD

The above method has been applied to examine the behavior of various couples of ions in different mixed solvents. We were particularly interested in those ions which show very strong specific solvation and for which we could predict a large transient phenomenon.

For example, sodium tetraphenylborate is known to interact strongly with dioxane since the solvation free enthalpy $\partial G^\circ/\partial X_s$ is equal to $-60 \text{ kcal mol}^{-1}$ in a water-dioxane solvent (33). In this case, if there were no transport of solvent molecules by microscopic coupling with ions, one could expect a large transient increase of concentration which could be as large as 80 %.

Paradoxically, the observed transient effect was vanishingly small in this case. In order to eliminate all sources of errors, the measurements of concentrations were controlled by different techniques ; sodium ion was detected by γ -rays spectroscopy as well as by flame spectrophotometry ; the BPh_4^- ions concentration was checked up by U.V. spectroscopy. Finally, the quantitative analysis of the coupled diffusion data lead to a value of the preferential solvation number equal to -120 for the tetraphenylborate ion. This result demonstrates that the effect of the strong thermodynamic driving force is completely cancelled by the forces arising from the transported dioxane molecules. Such a conclusion is supported by a study of 0.5 M BPh_4^- in a water-dioxane solution using N.M.R. techniques, which indicates that, at this concentration, all the dioxane molecules are bound in the solvation shell of BPh_4^- ions (34).

It is now interesting to examine if correlations could be established between the numbers of preferential solvation obtained in transport phenomena with the usual thermodynamic data related to solvation properties. In general, the solvation of any compound in a solvent is characterized with reference to aqueous solutions by the free enthalpy of transfer $\Delta G_{w \rightarrow s}^\circ$ which is considered as a quantitative indication of solute-solvent interactions. In the case of electrolyte, an extrathermodynamic hypothesis is required to separate the ΔG° value into the respective contributions of anion and cation. Naturally the values of ΔG° for individual ions are strongly dependent on the extrathermodynamic assumption, nevertheless comparison of similar ions remains valid. In table III, we report the n° values of alkali metal and halide ions obtained with our measurements in a water-dioxane mixed solvent ; positive numbers imply a preferential solvation by water molecules. The table shows, for comparison, the individual ionic values of $\Delta G_i^\circ(w \rightarrow w+s)$ obtained in the same mixed solvent, using as the extrathermodynamic assumption, a calculated value of the free enthalpy of transfer for the proton (35) ; in this case, negative values are generally accepted as indicating preferential interactions with dioxane molecules.

Table III : Individual solvation parameters in 20 % Dioxane-Water mixed solvent.

	Li^+	Na^+	K^+	Rb^+	Cs^+	Cl^-	Br^-	I^-
n_i°	12.4	10	6.8	6.7	6.1	4	3.8	3
$\Delta G_i^\circ(w \rightarrow w+s)$: cal/mole ⁻¹	-350	-225	-190	-180	-260	+980	+790	+550

CONCLUSIONS

It is clear from Table III data that there is no simple correlation between solvation numbers obtained from transport phenomena and the thermodynamic properties represented by ΔG_i° values. Moreover we must emphasize that these two classes of solvation characteristics are quite dissimilar.

This apparent discrepancy is not really unexpected. In fact, the free enthalpy of transfer is not only an equilibrium property ; we must also recall that it is a quantity related to a variation of energy. For example, as suggested by Ben Naim (36), the energy balance is a result of all interaction terms, as well ion-solvent as solvent-solvent. As a consequence, $\Delta G^\circ < 0$ does not necessarily mean a change of solvation. In some cases, it may be simply a consequence of a strengthening of the local solvent structure.

On the other hand, the transported solvent seems to be more significant since these numbers obviously contain those molecules of solvent which are tightly bound in the immediate vicinity of the ions. Naturally, the experimental (37) results are also strongly influenced by long range solvent-solvent interactions. But, from theoretical considerations of relaxation and electroforetic terms of the l_{ik} cross coefficients, it is possible to reach an estimation of each of these contributions. It is clear from the preceding discussion that our method of coupled diffusion in a gradient of solvent composition yields an efficient new tool for the determination of ionic individual solvation properties.

REFERENCES

1. J. GROH and G. von HEVESY, *Ann. Physik.* 65, 216 (1920)
2. K.R. HARRIS, C.K.N. PUA and P.J. DUNLOP, *J. Phys. Chem.* 74, 3518 (1970)
3. R. MILLS and H.D. ELLERTON, *J. Phys. Chem.* 70, 4089 (1966)
4. L.A. WOOLF, *J. Chem. Phys.* 56, 2489 (1972)
5. H. MAGDELENAT, P. TURQ and M. CHEMLA *Biopolymers* 15, 175 (1976)
6. Y. OISHI, Y. KAMEI and A. NISHI, *J. Chem. Phys.* 57, 574 (1972)
7. K. NAKANISHI and S. KITAJIMA, *J. Phys. Chem.* 76, 2470 (1972)
8. E.L. CUSSLER, *Multicomponent Diffusion*, Elsevier Scientific Publishing Company, Amsterdam (1976)
9. H. STREHLOW and H.M. KOEP, *Z. Elektrochem.* 62, 373 (1958)
10. D.G. HALL, *Trans. Farad. Soc.* 67, 2516 (1971)
11. H. SCHNEIDER, in *Solute-Solvent Interactions*. J.F. COETZEE and C.D. RITCHIE Editors vol. 2, Marcel Dekker Inc. N.Y. (1976)
12. E.W. WASHBURN, *J. Amer. Chem. Soc.* 31, 322 (1906)
13. H. STREHLOW and H.M. KOEPP, *Z. Elektrochem. Ber. Bunsenges. Phys. Chem.* 62, 373 (1958)
14. D. FEAKINS, *J. Chem. Soc.* 5308 (1961)
15. J. M'HALLA, P. TURQ and M. CHEMLA, *J. Chem. Soc. Faraday Trans. I* 77, 465 (1981)
16. M. PERIE, J. PERIE and M. CHEMLA, *Electrochimica Acta* 19, 753 (1974)
17. M. PERIE and J. PERIE, *J. Chim. Phys.* 79, 499 (1982)
18. M. PERIE, J. PERIE and M. CHEMLA, *J. Solution Chem.* (in press)(1984)
19. C. WAGNER in *Advances in Electrochemistry and Electrochemical Engineering* vol. 4 pp. 1-46, Wiley Interscience, New York, (1966)
20. D. FEAKINS, R. O'NEIL and E. WAGHORNE, 8th International Conference on Non-Aqueous Solutions. *Pure and Appl. Chem.* 54, 2317 (1982)
21. D.G. MILLER, *J. Phys. Chem.* 63, 570 (1959)
22. H.G. HERTZ, *Ber. Bunsenges. Physik. Chem.* 81, 656 (1977)
23. L.A. WOOLF, *J. Phys. Chem.* 82, 959 (1978)
24. T. ERDEY-GRUZ, *Transport Phenomena in Aqueous Solutions* p ; 212 Adam Hilger, London (1974)
25. J. M'HALLA, Thesis, University of Paris, (1979)
26. J. M'HALLA and M. CHEMLA, *J. Chim. Phys.* 77, 407 (1980)
27. L. ONSAGER, *Ann. N.Y. Acad. Sci.* 45, 241 (1945)
28. P. TURQ, M. CHEMLA, H. LATROUS and J. M'HALLA, *J. Phys. Chem.* 81, 485 (1977)
29. J. M'HALLA, P. TURQ and M. CHEMLA, *J. Chem. Soc. Faraday Trans. I* 74, 2320 (1978)
30. J.S. ANDERSON and K. SADDINGTON, *J. Chem. Soc.* 5, 381 (1949)
31. R. MILLS, *J. Phys. Chem.* 63, 1873 (1959)
32. D. FEAKINS, B.E. HICKLEY, J.P. LORIMER and P.J. VOICE, *J. Chem. Soc. Faraday Trans. I* 71, 780 (1975)
33. C. TREINER, J.F. BOCQUET and M. CHEMLA, *J. Chim. Phys.* 70, 72 and 472 (1973)
34. J.C. RAT, S. VILLERMAUX and J.J. DELPUECH, *Bull. Soc. Chim.* p. 815 (1974)
35. J. M'HALLA, private communication.
36. D. BAX, C.L. DE LIGNY and A.G. REMIJNSE, *Rec. Trav. Chim.* 92, 374 (1973)
37. A. BEN NAIM, *J. Phys. Chem.* 82, 792 (1978)
38. R.L. KAY, D.F. EVANS and M.A. MATESICH in *Solute Solvent Interactions*, vol. 2, J.F. COETZEE and C.D. RITCHIE, eds., (Dekker, New York, 1976)