Diffusion Processes in Multicomponent Systems II Macroscopic Investigation of a LiCI Solution

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Diffusion Processes in Multicomponent Systems

II   Macroscopic Investigation of a LiCl Solution

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The macroscopic diffusive behaviour of a solution of LiCl is investigated by an optical technique. The time evolution of a macroscopic concentration gradient is detected. The main goal of the present work is to compare the obtained results with the microscopic values of diffusion coefficients of both salt and water, previously found in an NMR measurement.

It is shown that, even in the case of large gradients, a linear relationship between flux and forces exists, provided that a new phenomenon, macroscopic in character, is properly taken into account.

In such a case the diffusion coefficients found in the NMR measurements also describe the macroscopic behaviour.

1   INTRODUCTION

In a previous paper,[1] hereafter referred to as (I), the diffusion coefficients of both water (proton) and cation Li^+ has been measured by means of a spin echo NMR technique, in a LiCl solution, at various temperatures and concentrations. In this kind of measurements the self-diffusion coefficients are measured in an equilibrium situation, the system being investigated from a microscopic point of view.

In fact the obtained values for the diffusion coefficient are to be related to the mean square displacement of a tagged nucleus, as pointed out in (I).

In the present paper we study the same system from a macroscopic point of view. A macroscopic gradient of concentration is artificially induced in the sample, and the evolution towards the equilibrium is experimentally studied. The aim of such an investigation is the comparison between microscopic and macroscopic behaviour. In particular we want to test the possibility that the

same coefficients, found in the NMR measurements, can be used to describe
the non-equilibrium macroscopic evolution of the system.

As far as the theoretical elaboration of a model is concerned, we will treat
the solution as a two-component system, namely water and dissolved salt, the
diffusive behaviour of the latter being identified with that of the Li^+ cation.
Such a simplifying assumption means disregarding charge fluctuations, i.e. we
assume that, at least in the macroscopic behaviour implied in this measure-
ment, the charge neutrality is assured. In addition, as we shall see in the
sequel, the macroscopic behaviour of the solution is mainly determined by
the diffusive properties of water molecules, because of the large value of the
diffusion coefficient of water, compared with that of the Li^+.

We will show that the same diffusion coefficients found in the NMR
investigation can be used to describe the macroscopic behaviour of the
solution, provided that an additional phenomenon, macroscopic in char-
acter, is properly taken into account. The latter refers to a change in the local
density of the system, induced by the large difference between the diffusion
coefficient of water and of solute. The corresponding density gradient is
smeared out by a "compensation" flux, whose effect, ultimately, results in the
fact that the larger diffusion coefficient (in our case, namely that of water) is,
in a sense, also transferred to the second component.

2 EXPERIMENTAL PROCEDURE AND RESULTS

As far as sample preparation is concerned, the procedure is the same as the
one described in (I). In the present measurement, an optical cell is half-filled
with saturated solution (concentration of 46% by weight); then the remaining
part of the cell is filled, with great care, with doubly distilled water.

Saturated solution and pure water remain well separated because of the
large difference in their densities, the separation meniscus being clearly
visible. In the course of time, a macroscopic diffusion process takes place, and
its evolution, both in space and time, is experimentally detected. The cell has
a thickness of 0.1 cm and height of 2 cm. A thin laser beam is allowed to pass
through the sample. Owing to the presence of gradients of both concentration
and density, a gradient of the refractive index also occurs in the sample, so
that the beam is bent, the angle of bending being proportional to the gradient
of the refractive index. The position (height) of the cell with respect to the
incoming beam can be continuously changed, so that the gradients can be
revealed along the entire height of the sample, as a function of time.

In a first experiment the time evolution of the gradient was detected at the
constant height of 1 cm, i.e. at one-half of the total height, that is the position
in which at $t = 0$ the separation between saturated solution and pure water
occurs.

Within the approximation of a constant diffusion coefficient, the analytical solution of Fick's equation evaluated at this point, becomes very simple to handle, as we shall see in the next section. In such a way a first indication of the actual behaviour of the system can be obtained (see Section 3 and Figure 3).

In a second experiment the behaviour of the gradient of the refractive index was detected along the entire length of the sample as a function of time. In Figure 1 we report the experimental results of such an experiment, showing the gradients as a function of position at fixed time values, up to 50,000 sec., after the sample preparation.

Some preliminary considerations can be made:

i) the behaviour of the gradients is not symmetrical around the centre of the sample, as one would expect in the hypothesis of a simple diffusion equation, characterized by constant diffusion coefficients (see Section 3)

ii) One can consider the following quantity:

$$\int_0^l (\text{grad } n)\, dx = n(l) - n(0) \tag{1}$$

where l is the length of the sample and n the refractive index. Such a quantity can be plotted as a function of time (see Figure 2).
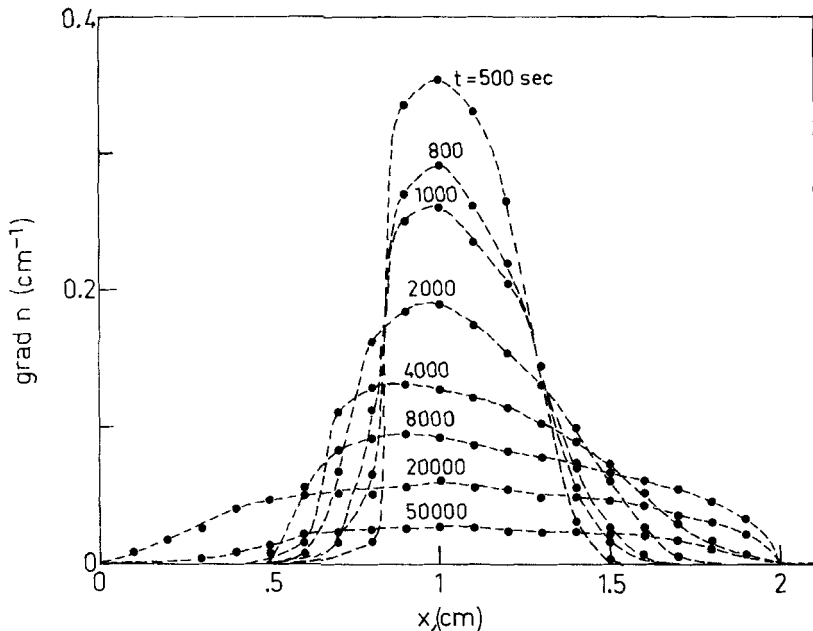

FIGURE 1   Gradients of the refractive index along the sample, after various time intervals after preparation.
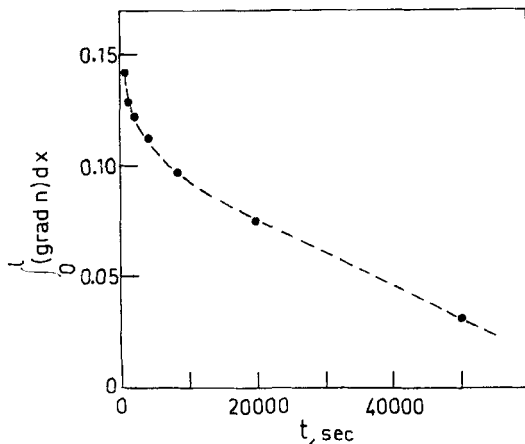
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FIGURE 2   Difference between refractive index at the top and bottom of the sample as a function of time (See Eq. (1)).

One would expect such a quantity to stay constant until the gradients do not become sizeable at the lower and upper edge of the sample, i.e. at least for 4000 sec. On the contrary, the experimental values of Eq. (1) start to decrease very quickly almost immediately after the sample preparation. As we shall see in the next section, such a circumstance turns out to be very important for the interpretation of experimental results.

3   DISCUSSION OF EXPERIMENTAL DATA AND THEORETICAL MODELS

The simplest model that one can try to use, consists of the assumption that the concentration $c(x, t)$, expressed as weight fraction of the solute, obeys a diffusion equation of the kind

$$\frac{1}{D} \frac{\partial c}{\partial t} = \frac{\partial^2 c}{\partial x^2} \tag{2}$$

where D is an overall diffusion coefficient, and the coordinate x spans the height of the sample.

Equation (2) can be analytically solved, provided that D is constant. With the appropriate boundary conditions the solution takes the form of a series:

$$c(x, t) = \frac{C_0}{2} + \frac{2C_0}{\pi} \sum_{n=0}^{\infty} (-1)^n \cdot \frac{\cos(2n + 1) \frac{\pi}{l} x}{(2n + 1)} \exp\left[\frac{(2n + 1)\pi}{l}\right]^2 Dt \tag{3}$$

where, in our case, $C_0 = 0.46$ is the saturation concentration, and $1 = 2$ cm the length of the sample. The concentration gradient $(\partial c/\partial x)$ can be calculated from Eq. (3). The latter, evaluated at $x = l/2$, assumes a very simple form:

$$\left(\frac{\partial c}{\partial x}\right)_{x=l/2} = C_0 \sqrt{\frac{\pi}{Dt}} \qquad (4)$$

The comparison with experimental data requires the knowledge of the refractive index as a function of concentration. We use literature data.[2]

A comparison with experimental results is shown in Figure 3, in which the experimental points are plotted as a function of $1/\sqrt{t}$. The following considerations can be made:

i) the slope of a straight line that best fits the experimental data furnishes a value $D = 5 \times 10^{-4}$ cm^2/sec. i.e. 25 times larger than the maximum value of the diffusion coefficient of water ($D = 2 \times 10^{-5}$ cm^2/sec.) found in (I) with the NMR technique.

ii) The deviations of experimental points from a straight line, although not very large, show a systematic rather than a random behaviour.
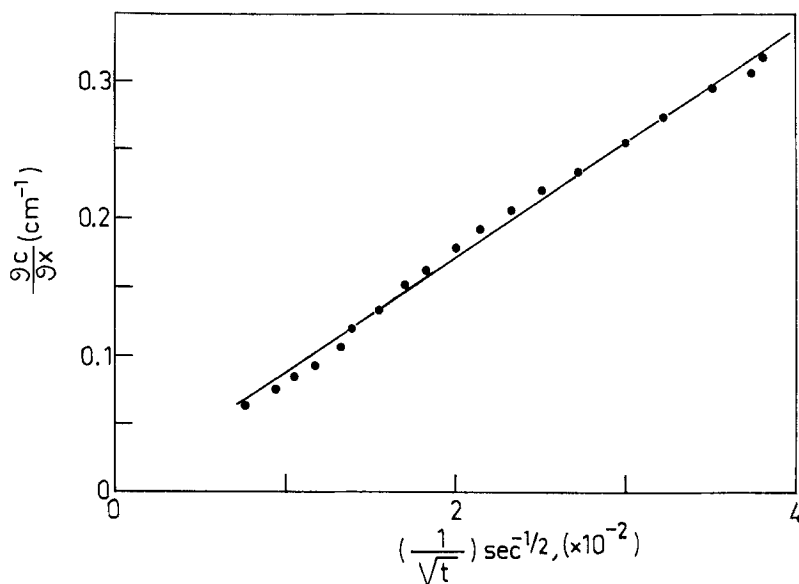

FIGURE 3   Theoretical behaviour of the concentration gradient at half the height of the sample as a function of $1/\sqrt{t}$ (continuous line). Dots refer to experimental data.

iii) According to Eq. (3), the concentration gradient turns out to be symmetric, for any value of t, around the middle point $x = \frac{1}{2}$. On the contrary, experimental results (see Figure 1) show a marked asymmetry.

iv) The quantity $C(0) - C(1)$ can be calculated from Eq. (3) and plotted as a function of the product Dt (see Figure 4). A comparison with the data of Figure 2 shows a marked difference, mainly in the initial behaviour. In addition the value that should be attributed to the diffusion coefficient D in Figure 4, in order to make comparable the decrease of calculated and experimental values, again turns out to be much larger than the NMR values found in (I).

All these circumstances show that the simple model described in Eq. (2) cannot explain, even qualitatively, the experimental results.

Let us now suppose that in the solution, each component (water and salt) obeys a diffusion equation, with its own diffusion coefficient.

We write:

$$c = \frac{\rho_1}{\rho_1 + \rho_2} = \frac{\rho_1}{\rho} \tag{5}$$

where the concentration c is expressed as weight fraction of solute, ρ_1 and ρ_2 being the partial density of salt and water respectively and $\rho = \rho_1 + \rho_2$ is the total density. From Eq. (5), the temporal variation of the concentration can be expressed as:

$$\frac{\partial c}{\partial t} = \frac{1}{\rho}\left[(1-c)\frac{\partial \rho_1}{\partial t} - c\,\frac{\partial \rho_2}{\partial t}\right] \tag{6}$$
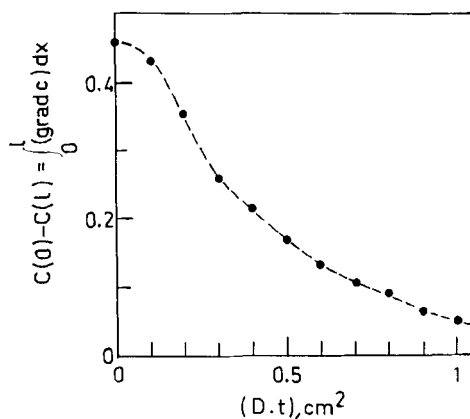

FIGURE 4   Difference between concentrations index at the top and bottom of the sample as a function of Dt, calculated according to Eq. (2).

On the other hand each component must obey to a continuity equation:

$$\frac{\partial \rho_1}{\partial t} = -\text{div } \mathbf{J}_1$$

$$\frac{\partial \rho_2}{\partial t} = -\text{div } \mathbf{J}_2 \tag{7}$$

where $\mathbf{J}_1$ and $\mathbf{J}_2$ are the fluxes of the two components, that, according to our hypothesis obey the diffusion equations:

$$\mathbf{J}_1 = -D_1 \text{ grad } \rho_1$$

$$\mathbf{J}_2 = -D_2 \text{ grad } \rho_2 \tag{8}$$

Moreover, because $\rho_1 = \rho c$ and $\rho_2 = \rho(1 - c)$, the gradients in Eq. (8) can be expressed in terms of gradients of concentration and density. Inserting the results in Eq. (6) one gets:

$$\frac{\partial c}{\partial t} = [(1 - c)D_1 + cD_2] \Delta c + \frac{1}{\rho}\frac{d\rho}{dc} c(1 - c)(D_1 - D_2) \Delta c$$

$$+ \left\{ (1 - c)D_1 \frac{d}{dc}\left(c \frac{d\rho}{dc} + \rho \right) - cD_2 \frac{d}{dc}\left[(1 - c)\frac{d\rho}{dc} - \rho \right] \right\}(\text{grad } c)^2 \tag{9}$$

In order to obtain Eq. (9) we suppose that $\rho = \rho(c)$ so that grad $\rho = d\rho/dc \cdot \text{grad}.c$. We shall return later to such a question.

An interesting feature of Eq. (9) is the presence of an "effective" diffusion coefficient

$$D_{\text{eff}} = (1 - c)D_1 + cD_2 \tag{10}$$

Indeed, in the case in which the difference between the diffusion coefficients and/or between the densities of the two components could be neglected, and for small enough values of the concentration gradient, Eq. (9) reduces again to Eq. (2) with a diffusion coefficient given by Eq. (10).

Actually an expression like Eq. (10) can be formally obtained in the case of a conformal mixture of two equal-mass components.[3]

In our case, however, we have shown that Eq. (2) cannot explain the experimental behaviour, so that we are forced to retain all the terms in Eq. (9).

Equation (9) is nonlinear, and cannot be solved analytically. In addition we know that the diffusion coefficients D_1 and D_2 are not constant, being functions of concentration as shown from the NMR measurements.

Such a circumstance would result in the appearance in Eq. (9) of additional terms of the (grad.D grad.c) kind.

However Eq. (9) can be solved numerically, using the variable values of the diffusion coefficients (corresponding to the actual values of the concentration) experimentally found in the NMR measurements.

Such a numerical calculation has been carried out, the values of the density as a function of concentration being taken from literature.[4] The following results arise:

i) The allowance of a variability for the diffusion coefficients gives rise to the correct asymmetry in the concentration gradients profile, experimentally found (see Figure 1).

ii) the time scale, theoretically evaluated from the numerical solution of Eq. (9) through the calculation of the quantity $C(0) - C(1)$ as a function of time, again turns out to be much larger than the experimental behaviour of Figure 2.

The latter circumstance could suggest that the values of the diffusion coefficients given by the NMR measurements, cannot be used to describe macroscopic fluxes, as those implied in the present measurements. However there is a deeper inconsistency that is inherent in the formulation of Eq. (9).

4   EXCESS DENSITY AND "COMPENSATION FLUX"

In the previous section we suppose that the density of the solution depends only on the concentration, $\rho = \rho(c)$. In such a case, however, ρ_1, and ρ_2 cannot be considered as independent variables any longer. As a consequence Eq. (9) could be rewritten in terms of either ρ_1 or ρ_2 solely. It is clear, however, that, depending on the choice of ρ_1 or ρ_2 (and therefore of D_1 or D_2), two different time scales will be obtained.

The inconsistency originates from the fact that the uniqueness of the function $\rho = \rho(c)$ arises only for equilibrium states. Let us consider, as an example, a small volume element, in which the concentration is higher than that of the surrounding medium. Then an incoming water flux and an outcoming salt flux take place, the former being larger than the latter, due to the different values of the diffusion coefficients. After a short time interval both concentration and density in the considered volume element are changed, but the density *does not* correspond to the equilibrium value at that concentration. Such an excess density, in turn, will give rise to a flux of solution (i.e. of both components) that must be properly taken into account.

In order to do this, we write:

$$\rho = \rho_0 + \delta\rho \tag{11}$$

where $\rho_0 = \rho_0(c)$ is the equilibrium value, i.e. the value corresponding to the local concentration, while ρ is the actual value of the density.

As a consequence the gradients of the partial densities can be written:

$$\text{grad } \rho_1 = \left(\rho + c \frac{d\rho_0}{dc} \right) \text{grad } c + c \text{ grad}(\delta\rho)$$

$$\text{grad } \rho_2 = \left(-\rho + (1 - c) \frac{d\rho_0}{dc} \right) \text{grad } c + (1 - c) \text{ grad}(\delta\rho) \qquad (12)$$

As far as the fluxes $\mathbf{J}_1$ and $\mathbf{J}_2$ are concerned, one must distinguish between a contribution driven by grad c characterized by the diffusion coefficients D_1 and D_2 respectively, and a contribution driven by grad$(\delta\rho)$. As far as the latter is concerned, it is reasonable to assume that a unique and constant diffusion coefficient, D, characterizes such a contribution. In fact the excess density will give rise to a hydrodynamic flux that involves the liquid as a whole, like a pressure gradient.

It is possible to elaborate a calculus procedure that simulates the physical diffusion processes described above. The "sample" is partitioned in N small enough volume elements V_i, and suitable initial conditions are assigned to them ($C_i = 0.46$ for $i = 1$ to $N/2$, $C_i = 0$ for $i = N/2 + 1$ to N, and $\rho_i = \rho_0$ is calculated according to the literature data).[4] Initially $(\delta\rho)_i$ is obviously zero. Then the concentration gradient is calculated as finite difference between neighbouring volume elements and the corresponding fluxes $\mathbf{J}_1$, $\mathbf{J}_2$ are also calculated using the proper values of D_1 and D_2 (taken from the NMR measurements).

The fluxes change the values of the partial densities ρ_1 and ρ_2. After a small enough time interval the latter can be calculated, as well as the new values of concentration $c = \rho_1/(\rho_1 + \rho_2)$, density $\rho = \rho_1 + \rho_2$ and excess density $\delta\rho = \rho - \rho_0$, being $\rho_0(c_i)$ the equilibrium value corresponding to the actual value of concentration. The procedure is repeated, taking into account that from the second step onwards the gradients of $\delta\rho$ contribute to the fluxes, through a single diffusion coefficient D.

After a suitable number of steps the gradient of the refractive index can be calculated along the sample, and compared with experimental results. A comparison can also be made for the quantity $n(0) - n(1)$.

It is quite obvious that the results strongly depend on the (constant) value attributed to D.

If D is much smaller than D_2 (the diffusion coefficient of water), one practically obtains the same results furnished by Eq. (9). In such a case, in fact, the role played by the excess density $\delta\rho$ becomes negligible, and one describes an unphysical process in which the partial density of water goes quickly to the equilibrium, due to the larger value of D_2, giving rise to enormous values of local excess density. The partial density of salt, and therefore the concentration, goes to equilibrium much slowly, due to the smaller value of D_1.

On the contrary, for values of D larger than D_2 the excess density is quickly smeared off. In a sense the large flux of water "pulls out" the solution as a whole, so that, ultimately, the flux of the salt also turns out to be determined by the D_2 values rather than by its own coefficient D_1.

It can be shown that assuming a value of 10^{-4} cm^2/sec for D, the experimental results are reproduced with great accuracy. An increase of D beyond such a value no longer appreciably changes the results.

In Figure 5 we show the profile of the gradient of the refractive index, calculated by the above mentioned procedure. The refractive index $n(c_1\rho_0)$ is calculated according to the literature data[2] at the equilibrium density, the excess density being taken into account according to $n(\rho) = n(\rho_0) \cdot \rho/\rho_0$.

A comparison with the experimental data of Figure 1 shows that not only the shape of the curves and their time evolution are well reproduced, but also the numerical values theoretically calculated turn out to be equal to the experimental values. If one takes into account the entirely different physical situation and experimental methods which Figure 1 (equilibrium state, NMR measurements, literature data) and Figure 5 (macroscopic fluxes, measure of refractive index) refer to, the above mentioned agreement is, in our opinion, a strong support for the validity of our model.

Another comparison can be made showing the calculated quantity $n(0) - n(1)$ as a function of time (Figure 6). Again the experimental data (see Figure
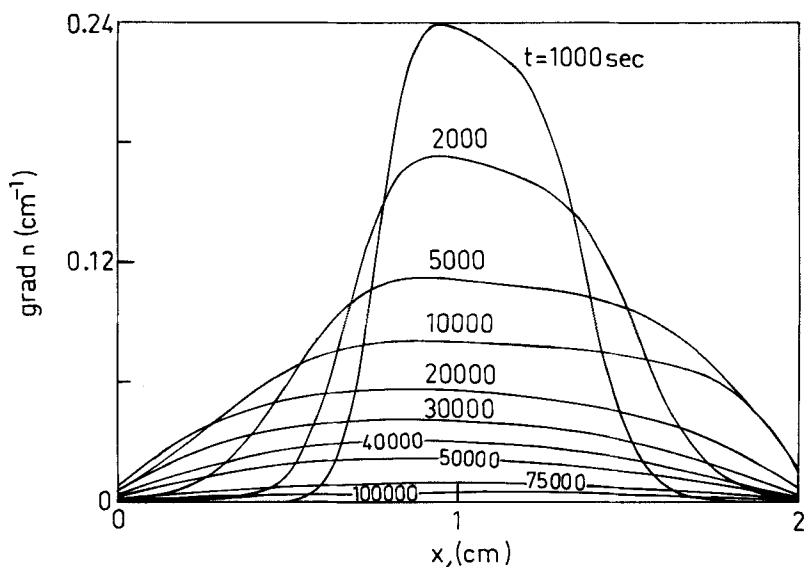

FIGURE 5   Gradients of refractive index along the sample at various time intervals after preparation, calculate according to the procedure described in Section 4.
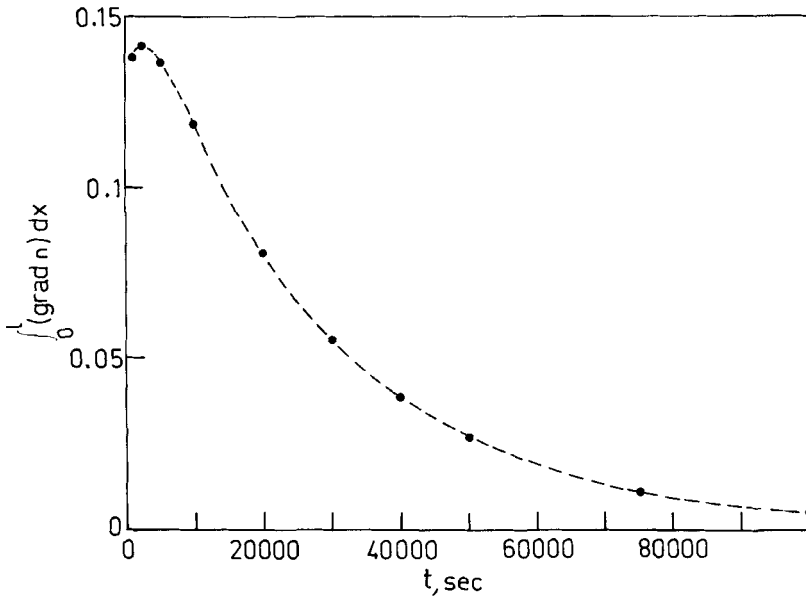
FIGURE 6   Difference between refractive index at the top and bottom of the sample as a function of time, calculated according to the procedure described in Section 4.

2) are well reproduced as far as both time scale and numerical values are concerned. Actually there are some differences regarding the short time behaviour. However such a circumstance can be easily understood if one takes into account that in the theoretically calculated values one starts with a "step" initial condition (the concentration gradient at $t = 0$ being a delta-function). Obviously in the experimental observation this is not true, because of some unavoidable initial mixing between saturated solution and pure water, that takes place despite the great care with which the sample is prepared.

5   CONCLUDING REMARKS

As mentioned in Section 1, the aim of the present work is to make a comparison between microscopic and macroscopic behaviour of the same system, as far as diffusion processes are concerned.

The conclusion that can be drawn from our investigation can be summarized as follows:

i) Microscopic (NMR) measurements, where the equilibrium concentration fluctuations are concerned, show that the diffusion coefficients are different for the various components.

Moreover they depend on the concentration, suggesting a collective behaviour of the system.

ii) As a consequence a diffusion process cannot be described by a simple Fick equation (Eq. (2)), because, in any case, one is concerned with differential equations with variable coefficients.

iii) The macroscopic behaviour, concerned with macroscopic values of gradient and fluxes, can again be described through linear relationship between fluxes and forces, provided that the local excess density, arising from the difference between the diffusion coefficients, is properly smeared out by a suitable flux. In such a case, however, the "microscopic" values of the diffusion coefficients also describe the macroscopic process correctly.

iv) The effect of the flux that arises from the excess density ultimately results in the circumstance that the component characterized by the lower value of the diffusion coefficient flows at nearly the same rate as the faster one. This is because the faster component pulls-out the solution, at the actual concentration, therefore forcing the salt to leave out the regions of higher concentration.

There is a problem that arises from the above mentioned circumstances. The NMR measurements actually detect the mean square displacement of selected nuclei in a given time interval, irrespective of the specific process that originates the displacement itself. Therefore one would expect an apparent diffusion coefficient of the salt, nearly equal to that of water, to be measured in the NMR experiment.

In other words, we can ask why the flux originated by the excess density that involves the salt as well as the water does not influence the NMR measurements.

A tentative answer could be as follows: NMR measurements refer to a system in an equilibrium state. The equilibrium state is characterized by a well defined spectrum of fluctuations both in the density and concentration.

The circumstance that, in such conditions, the two components show different diffusion coefficients would suggest that the density fluctuations are strictly correlated to the concentration fluctuations, in such a way that the regression of a concentration fluctuation towards equilibrium also implies the regression of the correlated density fluctuation. On the contrary, in the macroscopic case, the initial status can be considered as characterized by an enormous concentration fluctuation, while density corresponds to the equilibrium value (at the local concentration) along the entire sample.

More research is in progress in order to obtain a deeper insight on such a question.

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