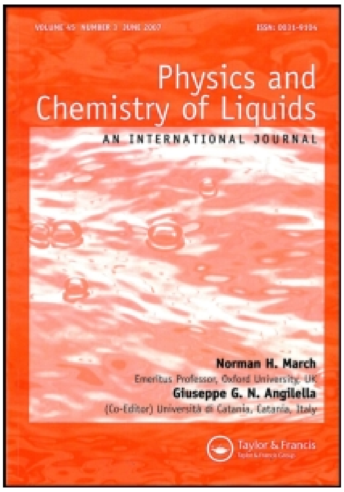

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Diffusion Processes in Multicomponent Systems

I NMR Investigations of a LiCl Solution

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The diffusion coefficients of both the proton and the cation are measured by means of a spin-echo technique in a solution of LiCl at various temperatures and concentrations. The aim of the present work is to obtain experimental values for the diffusion coefficients defined from a microscopic point of view. In a next paper the diffusive behaviour of the same system will be investigated from a macroscopic behaviour.

However the NMR results, reported here, show some interesting peculiarities in itself, that can be discussed from a rather general point of view, in the frame of structural properties of electrolytic solutions.

1 INTRODUCTION

In the last years an increasing attention has been given to a lot of investigations concerning the liquid state, both from a theoretical and an experimental point of view. Mainly, as far as electrolytic solutions are concerned, a large number of experimental results, performed with various techniques, are at present available. A rather general picture of this kind of systems arise, in terms of structural properties. It seems in fact well established that in its liquid state the system tends to reproduce the structural arrangement characteristic of the corresponding hydrated crystals. In other words, in the solutions there exists a local order, whose range, although not infinite as in the case of a crystal, is long enough to allow a solid-like behaviour as far as many physical properties are concerned.

We want to recall some recent results belonging to this argument, namely:

i) Exafs investigations of electrolytic solutions[1,2,3] that allow the evaluation of coordination numbers as well as of the interionic distances;

ii) Raman spectroscopy[4,5] in which modes characteristic of the solid are founded, and the low-frequency part of the spectra can be fully described in terms of a projected density of states, like in a disordered solid;

iii) Infrared absorption spectra of polar and non-polar liquids, showing peaks that can be directly compared with lattice modes resolved in the corresponding solids.[6]

These results are only a part of the numerous available works in this field, some of which are quoted in the above-mentioned papers.

According to the new "structural" point of view, also the dynamical properties of fluids have been revised, although all the implications of the existence of a local order are, at present, not fully explored, especially as far as the "hydrodynamic" region is concerned.

In fact, while for large k and ω a solid-like description in terms of collective excitations (acoustical and optical phonons, as well as "transverse" modes) can be usefully employed, the $\omega \to 0$ behaviour does not have any direct correspondence in the solid state, although it is reasonable that the local order in the liquids again plays a noticeable role.

Let us mention, as an example, the various models proposed for the diffusion processes (jump-diffusion[7] rattling,[8] itinerant oscillator[9] and so on).

In any case one is concerned with some kind of coupling between modes characteristic of an ordered, solid-like system and hydrodynamic modes. Let us mention, as an example, a paper of Rahaman,[8] in which through a simulation experiment, a strong correlation between local structure and diffusion processes is found.

From such a point of view, in addition, a possible "non-locality" both in time and space of the transport coefficients will play a role of paramount importance. As a consequence the experimental procedures themselves would influence the results. For instance, in a conducibility measurement performed at nonzero frequency, polar modes would give a contribution, through the displacement current: as a consequence the ionic mobility could be overestimated. Moreover experimental result of this kind cannot be longer compared with results obtained, e.g. in a tracer diffusion experiment. In turn the latter can give results somewhat different from those obtained in a quasi-elastic light scattering measurement, and so on.

In order to give some experimental insight into this problem, we try to study diffusion processes, in an electrolytic solution by using different techniques, in order to compare the various results. In the present paper we refer the results obtained by the use of an NMR technique in a solution of LiCl at various temperatures and concentrations. In a next paper[10] the same solution will be investigated from a macroscopic point of view, in presence of large concentration gradients, by means of an optical technique.

It is to be noted that, as far as diffusion processes are concerned, we are also faced with additional problems that are briefly discussed in the next section.

The third section is devoted to the experimental technique as well as to the experimental results. In the last section a short preliminary discussion of the experimental data is carried out.

2 DIFFUSION PROCESSES AND DIFFUSION COEFFICIENTS IN A MULTICOMPONENT SYSTEM

The aim of this section is not to give a theoretical analysis of the concerned matter, but simply to review briefly the present "status of art", putting in evidence some circumstances that, in our opinion, are not still fully clarified.

The concept of diffusion coefficient, needs some care when used in connection with a multicomponent system. In principle one has to distinguish between:

a) the diffusive behaviour of any single component in the system, the concentration diffusion, and an overall mass diffusion;

b) a "macroscopic" definition of diffusion coefficients, in terms of Fick's equations and a "microscopic" definition in terms of correlation functions.

The latter definition amounts to postulate a proportionality between the mean square displacement $\langle R_A^2 \rangle$ of a tagged particles and time, in the limit of long times:

$$\lim_{t \to \infty} \langle R_A^2 \rangle = 6 D_A t \tag{2.1}$$

Being D_A the diffusion coefficient of species A. Because $\langle R_A^2 \rangle$ can easily be obtained through the velocity autocorrelation function $\phi_A(t)$:

$$\langle R_A^2 \rangle = 2 \int_0^t (t - \tau) \phi_A(\tau)\, \mathrm{d}\tau \tag{2.2}$$

it follows at once

$$D_A = \tfrac{1}{3} \int_0^\infty \phi_A(t)\, \mathrm{d}t \tag{2.3}$$

With such a procedure it is easy to define unambiguously as many diffusion coefficients as many different components are present in the fluid. The effects of interactions between different species are, obviously, implicitly contained in the behaviour of the velocity autocorrelation functions.

On the contrary, from a macroscopic point of view one is concerned with an ensemble of coupled diffusion equations (see, e.g. De Groot[11]):

$$\mathbf{J}_A = \sum_{B-1}^{n-1} D_{AB}(\mathbf{X}_B - \mathbf{X}_n) \qquad (A = 1, \ldots, n-1) \tag{2.4}$$

where the flux $\mathbf{J}_A$ is referred to a centre-of-mass frame of reference, and (in an isothermal process) the generalized forces $\mathbf{X}_A$ are given by

$$\mathbf{X}_A = -\operatorname{grad} \mu_A \tag{2.5}$$

μ_A being the chemical potential of species A.

It is easy to show that (apart from the simple case of two components) a unique diffusion coefficient related to a specific component cannot be longer recovered. It does not seem reasonable in fact to simply identify the diagonal components D_{AA} with the D_A defined in Eq. (2.1). In fact in Eqs (2.4) the interaction between different components is explicitly taken into account through the various coefficients D_{AB}.

In addition, Eqs (2.4) refers, as mentioned above, to a centre-of-mass frame of reference. Again such a circumstance prevents a direct identification with the microscopically defined coefficients of diffusion.

On the other hand, if one assumes that a diffusive equation holds for each single component:

$$\frac{\partial \rho_i}{\partial t} = D_i \Delta \rho_i \tag{2.6}$$

(where ρ_i is the number density of the ith species) then it is easy to show that the concentration (expressed e.g. as the fraction $r_i = \rho_i/\sum \rho_i$) does not obey a diffusive equation. For example, in a two components system, provided that each component obeys Eq. (2.6), one finds for the concentration:

$$\frac{\partial r}{\partial t} = [(1-r)D_1 + rD_2]\,\Delta r + \frac{r(1-r)}{\rho}(D_1 - D_2)\,\Delta\rho + 2\frac{[(1-r)D_1 + rD_2]}{\rho} \cdot \operatorname{grad} \rho \cdot \operatorname{grad} r \tag{2.7}$$

where $r = \rho_1/\rho$ and $\rho = \rho_1 + \rho_2$. Only if one makes the assumption $\rho = \cos t$, Eq. (2.7) reduces to a diffusive one, with an "effective" diffusion coefficient D^*, given by

$$D^* = (1-r)D_1 + rD_2$$

The implication of Eq. (2.7) will be fully discussed in Ref. 10.

3 EXPERIMENTAL PROCEDURE AND RESULTS

The self diffusion coefficients D_i has been measured in aqueous solutions of LiCl as a function of both concentration and temperature.

Measurements are performed by a standard spin-echo NMR technique, using, as usual, a $90° - \tau - 180°$ sequence. The amplitude of the spin-echo $A(t)$ was recorded as a function of the applied gradient G of the magnetic field (the gradient being constant along the sample), the measured values being fitted with the equation:[12]

$$A(t) = A_0 \exp\left[\frac{-t}{T_2} - \frac{\gamma^2 G^2 D t^3}{12}\right] \qquad (3.1)$$

where γ is the gyromagnetic ratio, $t = 2\tau$ and T_2 is the spin-spin relaxation time.

Such a procedure implies that the involved physical quantity is the mean displacement of a tagged nucleus in the time t. As a consequence one is concerned with a "microscopic" diffusion coefficient, Eq. (2.1).

We measured the self diffusion coefficient of both water (i.e. of the protons) and Li^+, using an RF of 25 MHz, the magnetic field being 5.87 KG in the first case and 15.1 KG in the second one.

The various solutions are prepared by dilution of a mother solution at the saturation concentration (46% by weight). We use high purity (research grade) reagents and doubly distilled water.

Each measurement is repeated several times, the goodness of each run being estimated from the goodness of the fit with Eq. (3.1).

In Figure 1 we report the experimental results obtained for different concentrations, as a function of temperature both for the proton and lithium.

In Figure 2 the diffusion coefficient of the proton is reported as a function of the concentration, together with the values obtained for pure water. The latter are in very good agreement with literature data,[13] thus certifying the affidability of the experimental procedure.

The following circumstances can be shown:

i) the diffusion coefficient of the Li^+ turns out to be at least an order of magnitude smaller than that of water. Such a result is in contrast with an indication available in literature,[14] according to which the self diffusion coefficient of Li^+ was estimated from conductivity measurements to be 1.03×10^{-5} cm.^{2}/sec, at 25°C.

In our opinion such a circumstance is related to the impossibility of comparison between results obtained with different techniques, as mentioned in Section 1. In fact the spin-echo method actually measures a physical displacement over a distance that in our experimental conditions can be

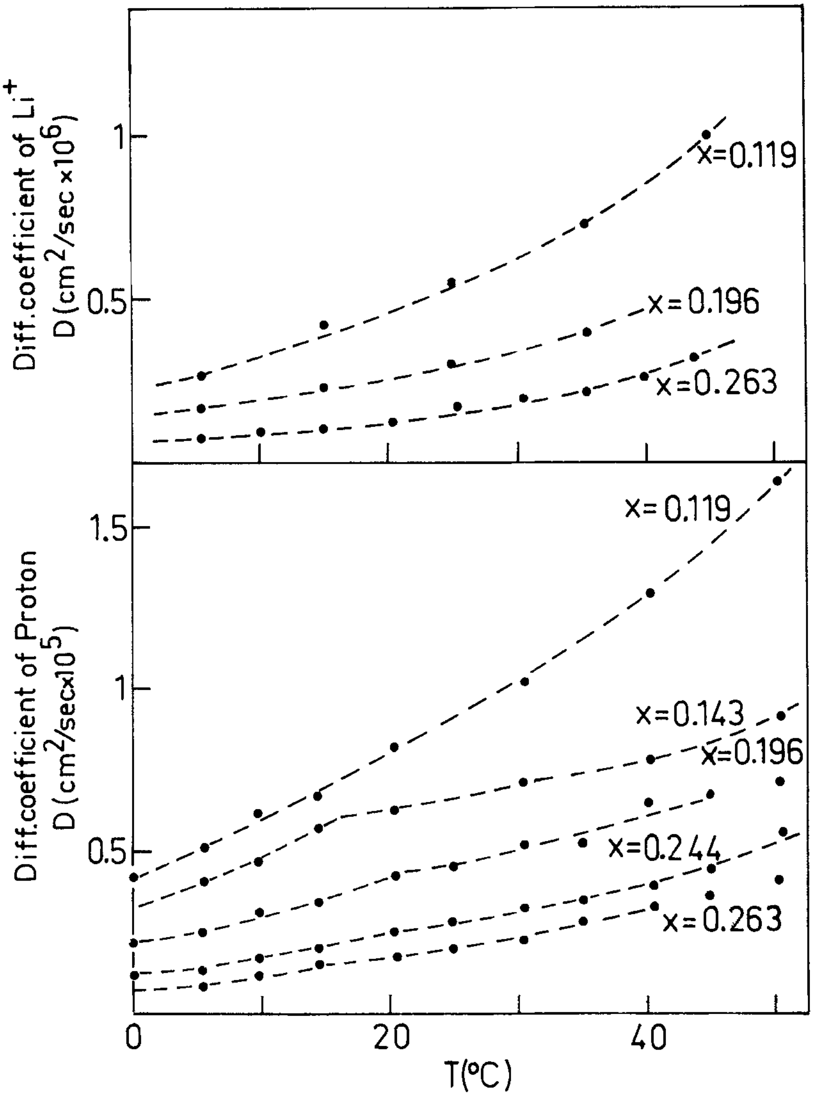

FIGURE 1 Self-diffusion coefficients for water (proton) and Li$^+$. The concentrations are indicated as molar fractions.

estimated to be of some microns. On the contrary in a conductivity measurement small displacement of some Angstrom around an equilibrium position can also contribute to the A-C current, like a displacement (polarization) current.

ii) There is a peculiar concentration, between 0.12 and 0.14 molar fraction in which some break seems to take place. This effect, more evident in the plot

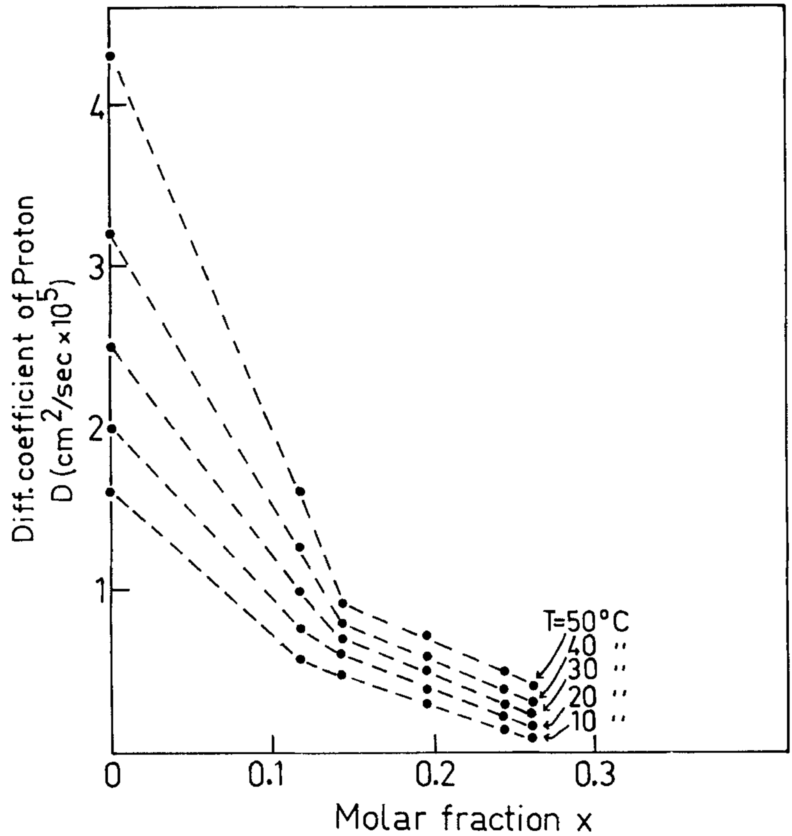

FIGURE 2 Self-diffusion coefficient of water as a function of concentration for different temperatures.

of Figure 2, concerns mainly the self-diffusion coefficient of water, and becomes evident at temperatures higher than 20°C.

It is to be noted that the concentration of 0.125 molar fraction corresponds to the composition of the eutectic. In addition, the temperature of 19.4°C is a transition temperature in the phase diagram of the LiCl solution.[15] We shall return later to this subject.

4 DISCUSSION OF EXPERIMENTAL RESULTS

The fundamental purpose of the present work, as discussed in Section 1, is the comparison between the diffusive behaviour of a multicomponent fluid system, tested with different experimental procedures. Such a discussion will be fully developed in Ref. 10.

However, some comments concerning the present results can be made, in order to give some insight concerning the behaviour of the LiCl aqueous solutions.

The obtained values for the diffusion coefficients can be plotted in an Arrhenius plot (see Figures 3 and 4) and an "activation energy" for the diffusion processes can be obtained.

In the case of pure water ($X = 0$ in Figure 3) the diffusion coefficient actually behaves according to an Arrhenius type law. The activation energy turns out to be 4.7 Kcal/mole. Such a value is characteristic of water[16] and

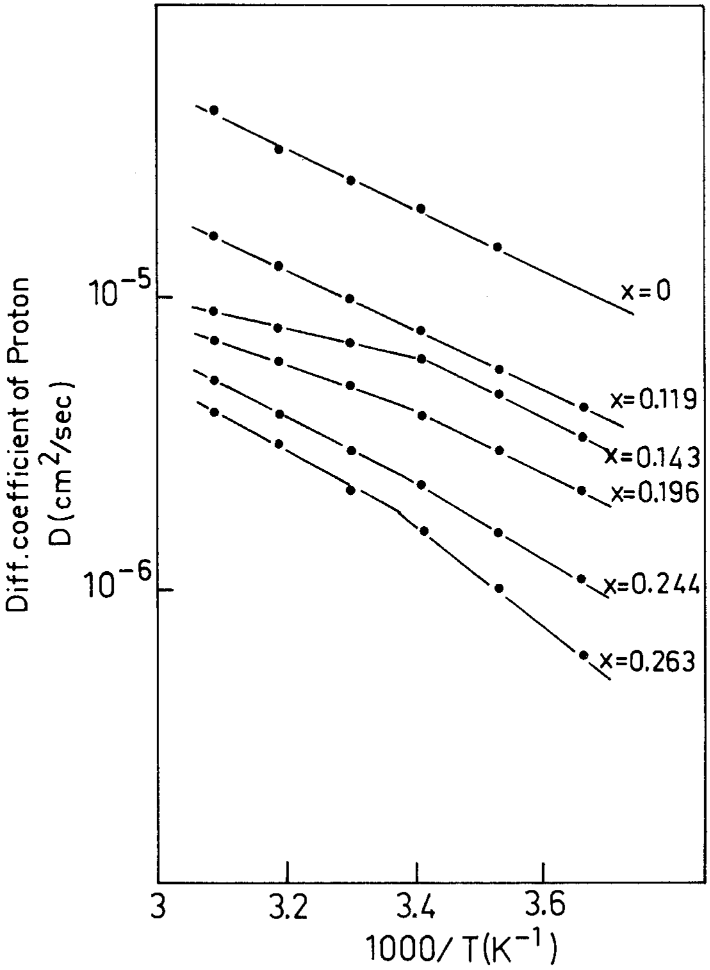

FIGURE 3 Arrhenius plot of diffusion coefficient of water for various concentrations.

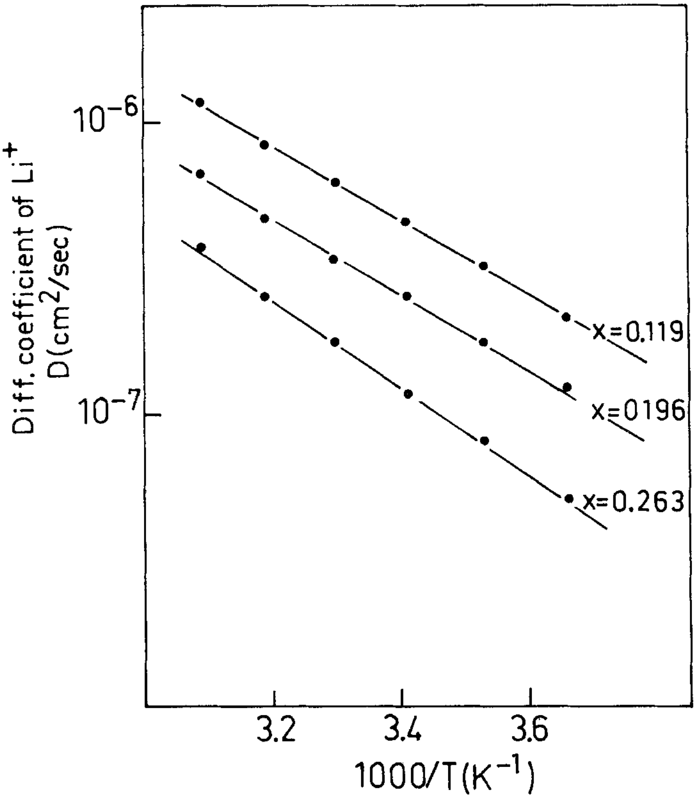

FIGURE 4 Arrhenius plot of diffusion coefficient of Li^+, for various concentrations.

can be favourably compared with the energy of the hydrogen bond. In fact there is some ambiguity in the evaluation of such an energy, depending on the involved physical phenomenon. In literature values ranging from 2.3 to 5 Kcal/mole are reported,[17] the latter value being related to a "strong" definition. Alternatively, one can assume that the breaking of two hydrogen bonds is needed in order to allow a molecule to flow.

The addition of salt to water up to a concentration of 0.12 molar fraction lowers the values of diffusion coefficient, but leaves the activation energy unchanged. At concentration higher than 0.14 molar fraction, however, the behaviour of the diffusion coefficient of water no longer obeys a simple Arrhenius type law. It is possible to fit the data of Figure 3 with two straight lines, obtaining two different activation energies for the same composition. The change takes place around a temperature of 20°C, as mentioned above.

In Figure 5 we plot the activation energy as a function of concentration. It can be seen that, while for temperatures lower than 20°C a continuous

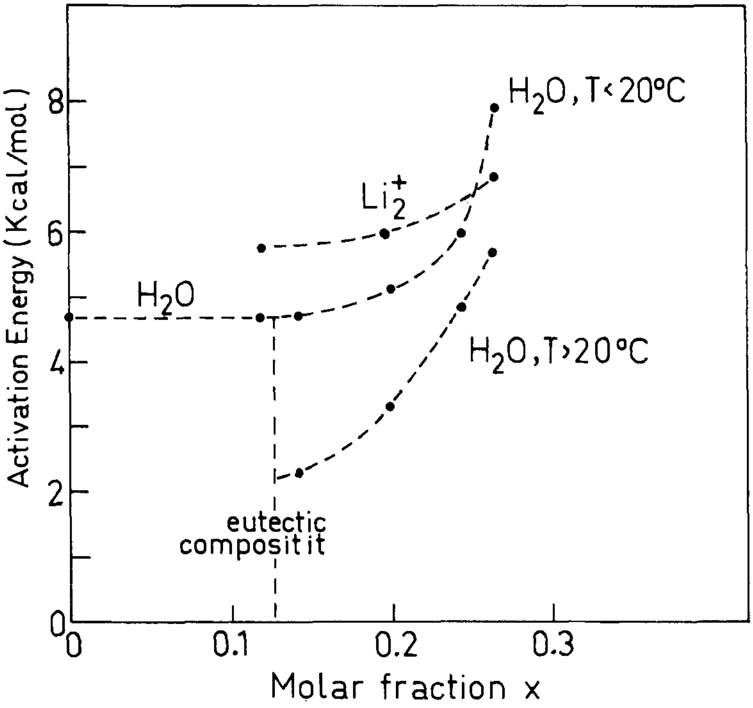

FIGURE 5 Activation energy of the diffusion coefficients as a function of temperature.

behaviour is found, for temperatures higher than 20°C a discontinuity takes place at a concentration corresponding to the eutectic composition.

Such a circumstance suggests that, for temperature higher than 20°C, a structural change takes place in the solution when the concentration becomes larger than the value of the eutectic.

Taking into account the values of the activation energy at the breaking point (about 4.7 Kcal/mol for $T < 20°C$ and about 2.3 Kcal/mol for $T > 20°C$) one could suggest that for temperatures higher than 20°C the effect of the dissolved salt gives rise to a structural variation, as far as water is concerned, so that the breaking of only one hydrogen bond is enough to allow the water molecules to flow.

As mentioned above,[15] the phase diagram of the LiCl solution shows a transition temperature, $T = 19.4°C$, that separate a mono-hydrated from a bi-hydrated solid phase. Actually such a transition takes place at the saturation concentration, while from our measurements the discontinuity in the activation energy takes place starting from the eutectic concentration.

It seems, therefore that, at least for concentration higher than the eutectic one, also in the liquid phase the solution has a memory of the structural properties belonging to the corresponding solid phase at the same temperature. Such a behaviour is a quite common feature of electrolytic solutions. From such a point of view our present results give further confirmation to the local-order structural model sketched in Section 1.[1–6]

However it is not clear, at present, why such a memory effect becomes relevant only for concentrations larger than the eutectic one. Perhaps it is worthwhile to note that at the eutectic concentration the system behaves in a sense, like a chemical compound rather than a usual solution. Further research are in progress in order to clarify this point.

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