



**HAL**  
open science

## Thermal diffusion in (LiCl, RH<sub>2</sub>O)

Jean Colombani, J. Bert, J. Dupuy-Philon

► **To cite this version:**

Jean Colombani, J. Bert, J. Dupuy-Philon. Thermal diffusion in (LiCl, RH<sub>2</sub>O). The Journal of Chemical Physics, 1999, 110 (17), pp.8622-8627. 10.1063/1.478769 . hal-03461877

**HAL Id: hal-03461877**

**<https://hal.science/hal-03461877v1>**

Submitted on 17 May 2022

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

## Thermal diffusion in (LiCl, RH<sub>2</sub>O)

J. Colombani, J. Bert, and J. Dupuy-Philon

*Département de Physique des Matériaux (CNRS UMR 5586), Université Claude Bernard, Lyon 1, 43, Boulevard du 11 Novembre 1918, F-69622 Lyon-Villeurbanne, France*

(Received 19 November 1998; accepted 3 February 1999)

By means of an accurate investigation of the hydrodynamical behavior of the studied liquid, we have been able to perform interdiffusion and pure Soret effect measurements in (LiCl, RH<sub>2</sub>O) with  $R$  ranging from 6 to 100 and temperature from  $-60$  to  $0$  °C. The interdiffusion coefficient corrected by a thermodynamic factor shows a characteristic evolution with concentration, which is a straightforward consequence of the role of the ions in this direct transport phenomenon. The Soret coefficient has revealed itself to be strongly negative, to increase with temperature, and to exhibit a sharp minimum with concentration. By comparison with measurements in other aqueous alkali chlorides, these results have contradicted the existing theory: negative Soret coefficients do not seem to be associated with poorly organized water. Furthermore, the extremum in the medium concentration range is likely to be related to the polarizing influence of the alkali ions on the outer hydration shells. © 1999 American Institute of Physics. [S0021-9606(99)50817-9]

### I. INTRODUCTION

The existence of a matter flux in a thermally inhomogeneous mixture has been referred to as thermal diffusion, or Soret effect in condensed matter. The strength of the phenomenon is determined by the Soret coefficient  $S_T$ , proportional to the ratio of the resulting steady concentration gradient and the applied temperature gradient.<sup>1</sup>

The interest in this secondary coefficient has been reinforced for some 10 years by theoretical as well as industrial considerations. The former include fluctuation hydrodynamics<sup>2</sup> and statistical mechanics.<sup>3</sup> The latter deal with new separation techniques<sup>4</sup> or hydrocarbons distributions in petroleum reservoirs.<sup>5</sup>

But from our standpoint, the main significance of the study of thermal diffusion lies elsewhere. This phenomenon has revealed itself as being a very sensitive probe of molecular interactions.<sup>6</sup> Corresponding to a nonequilibrium cross effect, the interpretation of the variations of the Soret coefficient appeals to subtle models of atomic organization. This is particularly true for aqueous electrolytic solutions.<sup>7</sup>

But accurate and reproducible measurements of Soret coefficients have turned out to be hard to obtain. Convective motions are very likely to disturb the diffusion process. They may be due to hydrodynamic instabilities<sup>8</sup> or to small parasitic temperature gradients.<sup>9</sup>

To avoid these disturbances, we had stated in a previous work that two conditions were compulsory to get reliable Soret measurements.<sup>10</sup> First, the complete stability diagram of the studied liquid mixture must be precisely determined in the conditions of the experiments, in order to identify the feasibility domains of the Soret measurements. Second, the absence of local motions in the fluid must be controlled during the whole experiments. With this aim, after the pioneering work of Sanchez *et al.*,<sup>11</sup> we have performed Soret coefficient determinations in concentrated aqueous lithium chloride (LiCl, RH<sub>2</sub>O), where  $R$  is the number of moles of

water per mole of salt, by the use of a holographic interferometry technique, which fulfills the two conditions mentioned above. It also gives the opportunity to derive the interdiffusion coefficient  $D$  of the mixture from the kinetics of the experiment.

The choice of the system is accounted for by its high viscosity (it is a vitrifying liquid), and by the fact that its structure and transport properties are well known and can guide the discussion on the thermodiffusive properties.<sup>12,13</sup> Liquids with standard viscosity ( $\sim 1$  cPo) are very difficult to maintain in a diffusive regime on earth and microgravity measurements are often needed.<sup>14</sup> But we must notice the recent appearance of promising new techniques.<sup>15-17</sup> One of them<sup>17</sup> has in particular enlightened the problem of the discrepant values of  $S_T$  of organic mixtures obtained by various techniques.

The feasibility of our procedure has been proved; it can now be used to deepen our understanding of the transport properties of aqueous alkali chlorides, by enlarging the temperature and concentration ranges of the measurements and linking them to our knowledge of the molecular organization of these liquids.

The remainder of the paper is organized as follows. Section II summarizes the experimental apparatus and procedure. Sections III and IV present the interdiffusion and thermal diffusion results, the microscopic origin of which is discussed in Sec. V. Section VI is a conclusion.

### II. PROCEDURE

The complete experimental device and procedure are described elsewhere.<sup>10</sup> As a summary, holointerferometry mainly differs from classical interferometry in the fact that a reference system is not needed: the initial state of the system is recorded on a so-called reference hologram. Interference fringes then materialize isotherms or isomass fractions,

TABLE I. The three phases of the procedure.

Phase	$\Delta T$	$\Delta x$	Description
1	increasing	0 (considered constant)	search of the thermal convection threshold
2	$\Delta T^{\text{th}}$	increasing (from 0 to $\Delta x^{\text{th}}$ )	thermal diffusion
3	increasing	$\Delta x^{\text{th}}$ (considered constant)	search of the thermosolutal convection threshold

which permits one to measure temperature and concentration evolutions in the sample and, at the same time, to visualize the appearance of convection.

The sample is contained in a rectangular cell of interior dimensions 30 mm (diffusion length)  $\times$  10 mm (optical pathlength)  $\times$  10 mm, which is inserted in a cryostatic device, the temperature of which ranges from  $-100$  to  $+40$  °C. This setup permits one to submit the liquid to a uniform vertical thermal gradient. The entire device takes place on a vibration free holographic bench.

From a mechanical point of view, the large viscosity of our liquid enables us to follow a very convenient procedure. Owing to this property, the concentration relaxation time  $\tau_{\text{conc}}$  is much greater than the temperature one  $\tau_{\text{temp}}$ . The ratio of both quantities is given by the Lewis number  $Le = \tau_{\text{temp}}/\tau_{\text{conc}} = D/D_T \sim 10^{-3}$ ,  $D_T$  being the thermal diffusivity. In this condition, during a hydrodynamical study lasting a few hours, for which the convection threshold is searched for by increasing the temperature difference  $\Delta T$  between the upper and lower ends of the cell, the concentration distribution is regarded as remaining constant. So the hydrodynamic instabilities in the liquid are investigated for constant Soret-induced concentration differences  $\Delta x^{\text{th}}$  between the top and bottom of the cell.

With these assumptions, the stability diagram of the system can be drawn in the  $(Ra_s, Ra_t)$  plane.  $Ra_s$  is a dimensionless  $\Delta x$  (solutal Rayleigh number) and  $Ra_t$  a dimensionless  $\Delta T$  (thermal Rayleigh number):

$$Ra_t = \frac{\alpha g h^3 \Delta T}{\nu D_T} \quad \text{and} \quad Ra_s = \frac{\beta g h^3 \Delta x}{\nu D}. \quad (1)$$

Here,  $\alpha$  and  $\beta$  are the dependence coefficients of the density on temperature and concentration,  $g$  is the acceleration due to gravity,  $h$  the diffusion length (height of the cell), and  $\nu$  the kinematic viscosity. Conventionally,  $Ra_t$  is positive when heating from below and  $Ra_s$  is positive when the denser component migrates downwards. The three phases of the procedure are summarized in Table I.

The investigation of this diagram (Fig. 1) takes place in the field of the study of free convection in binary liquid mixtures exhibiting a Soret effect and will not be developed here. But according to our purpose, from this sketch we can learn the critical value of  $Ra_t$  (and subsequently  $\Delta T$ ) under which the Soret experiment must be performed. When  $\Delta T^{\text{th}} < \Delta T^{\text{crit}}$  is imposed to the cell, a concentration difference  $\Delta x$  progressively settles in the mixture. During the diffusion (bold arrow on the diagram), we can be ensured to remain in the diffusive regime. Indeed, the appearing  $\Delta x$  stabilizes the mixture, the heaviest component migrating towards the bot-

tom of the cell. So, provided that no local convection loop be created in the liquid, this procedure permits reliable values of the interdiffusion and Soret coefficients:

$$D = \frac{h^2}{\pi^2 \tau_{\text{diff}}} \quad \text{and} \quad S_T = \frac{1}{x(1-x)} \frac{\Delta x_{\infty}}{\Delta T^{\text{th}}}, \quad (2)$$

with  $\tau_{\text{diff}}$  time constant of the thermal diffusion,  $x$  initial mixture concentration, and  $\Delta x_{\infty}$  stationary concentration difference. The mole fraction  $x$  is preferred to the mass fraction  $c$  for easier comparison with the literature values. Conventionally,  $S_T$  is positive if the denser component migrates towards the cold end of the cell.

Our aim being an enlargement of the experimental conditions, the knowledge of the limits of the concentration and temperature ranges is needed. Optical measurement methods are especially designed for concentrated solutions: in the case of high dilution, the Soret-induced concentration evolution does not yield significant enough variations of the index of refraction. For (LiCl,  $RH_2O$ ), we have assessed that holography measurements are ineffective for  $R \geq 150$ .

Considering temperature, the upper limit is the consequence of hydrodynamical considerations. At constant  $\Delta T$ , increasing temperature gives rise to an enhancement of  $Ra_t$  (through the decrease of the viscosity). So all the compositions of the homogeneous mixture exceed the thermal convection critical value  $Ra_t^{\text{crit}} = 1.7 \times 10^5$  in the vicinity of  $0$  °C, which makes pure Soret effect measurements impossible. The lower limit can be ascribed to two factors. In the vicinity of  $R=6$ , the liquid is easily vitrifying and the temperature can be considerably lowered without crystallization, but the molecular motions are then progressively frozen-in and diffusion time constants become too large (up to one year). For  $R \geq 7$ , the possibility of entering the metastable phase is lim-

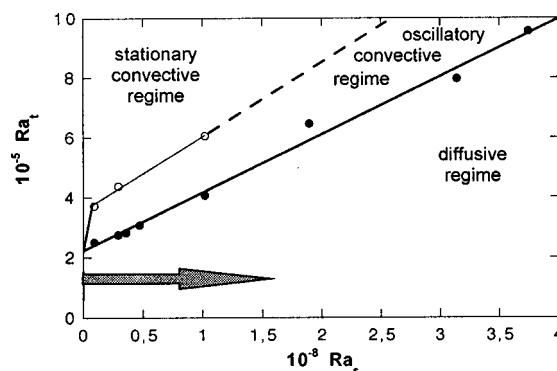


FIG. 1. Stability diagram  $(Ra_s, Ra_t)$  of a binary mixture submitted to temperature and concentration gradients in a 3:1:1 geometry for impermeable, rigid, and conducting boundary conditions.

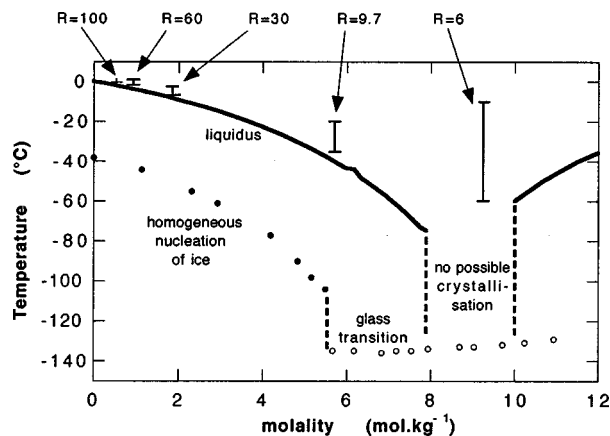


FIG. 2. Equilibrium<sup>31</sup> and out-of-equilibrium<sup>32</sup> phase diagram of (LiCl, water). The temperature of homogeneous nucleation of ice<sup>33</sup> and the investigated mixtures are also displayed.

ited by the crystallization of ice, a few degrees under the liquidus curve (see the phase diagram on Fig. 2).

With these experimental conditions, we have performed the following measurements of the transport properties of our aqueous electrolyte.

### III. INTERDIFFUSION

Our values of the interdiffusion coefficient of (LiCl,  $\text{RH}_2\text{O}$ ) at several temperatures and concentrations are given in Table II. Despite the usefulness of such low temperature measurements in the study of the glass transition of this system, these results are the first ones under the  $0^\circ\text{C}$  temperature.

Such a direct transport property is strongly related to the molecular mobility in the system. Like viscosity, this diffusion phenomenon is for example tremendously affected by the approach of the glass transition, the molecular dynamics being progressively frozen-in.

TABLE II. Interdiffusion  $D$  and Soret  $S_T$  coefficients of (LiCl,  $\text{RH}_2\text{O}$ ) for several temperatures and concentrations.

$R$	$m$ (mol·kg <sup>-1</sup> )	$T$ (°C)	$D$ ( $10^{-10}$ m <sup>2</sup> ·s <sup>-1</sup> )	$S_T$ ( $10^{-3}$ K <sup>-1</sup> )
6	9.25	-59.9	0.66	-2.12
		-43.4	1.38	-1.72
		-29.1	2.43	-1.26
		-20.0	3.92	-1.23
		-10.0	4.44	-1.04
9.7	5.72	-35.5	1.76	-3.78
		-33.6	2.33	-3.84
		-29.5	2.25	-3.54
		-23.4	2.42	-3.06
		-20.3	3.13	-2.73
30	1.85	-7.1	5.93	-3.76
		-3.0	5.81	-3.64
60	0.93	-0.9	5.72	-4.54
		1.4	5.84	-4.57
100	0.56	-0.5	7.79	-7.57

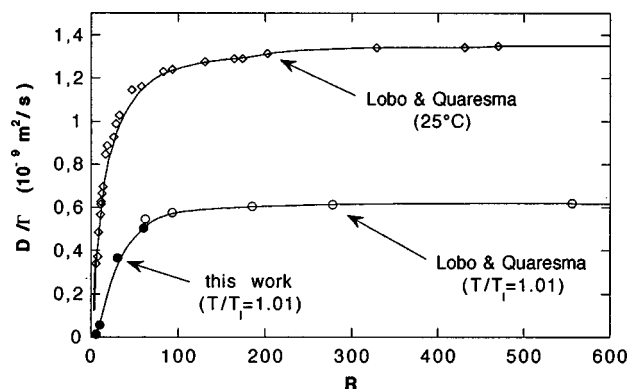


FIG. 3. Corrected values  $D/\Gamma$  of the interdiffusion coefficient of (LiCl,  $\text{RH}_2\text{O}$ ) as a function of  $R$ .

Thus, two data processings are useful to emphasize the significant mechanisms. First, the sensitivity to the interactions between the species is expressed through the influence of the mixture ideality. Hence, to get rid of this dependence,  $D$  is usually corrected by a thermodynamic factor  $\Gamma = 1 + \partial \ln \gamma / \partial \ln m$ ,  $\gamma$  being the activity coefficient and  $m$  the mixture molality.<sup>18</sup> Second, in order to distinguish the respective influence of temperature and concentration on the diffusion, the various mixtures are preferred to be compared at equivalent temperatures  $T/T_{\text{reference}}$ . We have chosen  $T_l$ , the liquidus temperature, as the reference temperature which amounts to equalize the thermal energy for the different mixtures, i.e., to take the phase diagram into account (Fig. 2). Though of slight influence, this treatment is necessary for a proper analysis.

Figure 3 displays our  $D/\Gamma$  measurements of (LiCl,  $\text{RH}_2\text{O}$ ) as well as the literature ones for  $T/T_l = 1.01$ . The values of  $\Gamma$  are derived from data of Lobo and Quaresma's handbook.<sup>19</sup> The high dilution and ambient temperature values of  $D$  are from the same source. As a first comment, the agreement between the high and low concentration values is a new proof of the reliability of our procedure. However, experimental data of  $\gamma$  below  $0^\circ\text{C}$  would be of great interest for computing more precise values of  $D/\Gamma$ , thus avoiding extrapolations.

Literature values of  $D/\Gamma$  at constant temperature  $T = 25^\circ\text{C}$  are also displayed, which infer the noncrucial character of the absolute ( $T$ ) or relative ( $T/T_l$ ) temperature choice of representation in the case of this transport phenomenon. The temperature influence appears to be of secondary part here.

Besides these minor remarks, the main feature of these curves is the existence of a transition domain in the medium concentration range ( $R \approx 100$ , i.e.,  $m \approx 0.5$  mol·kg<sup>-1</sup>). Below this threshold,  $D/\Gamma$  exhibits a rise and above it, a plateau. This kind of behavior has already been observed once and can be interpreted as follows.<sup>20</sup> Starting from the infinite dilution regime ( $R \sim \infty$ ) and progressively decreasing  $R$  leads to a gradual growth of the part of the salt in the solution structure. But what is striking is the total lack of consequence of this growth on the behavior of  $D/\Gamma$ , which remains approximately constant down to  $R \approx 100$ .

In this way, it can be stated that the slight modification

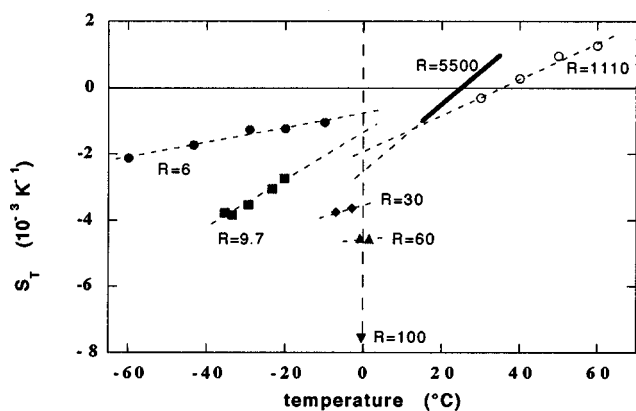


FIG. 4. Soret coefficient of (LiCl,  $\text{RH}_2\text{O}$ ) for several values of  $R$  against temperature. The literature values are from Alexander<sup>22</sup> ( $R=1110$ ) and from Wood and Hawksworth<sup>21</sup> ( $R=5550$ ).

of the H bond network of water induced by the ions down to  $R \approx 100$  has no incidence on the global transport properties. If  $R$  is still decreased, the influence of the ions on the organization of the liquid becomes significant and the self-diffusion of  $\text{Li}^+$  rapidly prevails over the interdiffusion behavior.<sup>20</sup>

Keeping these direct diffusion results in mind, we can now face our cross diffusion measurements.

#### IV. SORET EFFECT

The values of the Soret coefficient of (LiCl,  $\text{RH}_2\text{O}$ ) performed in the same temperature and concentration conditions as the interdiffusion measurements are listed in Table II. These values are displayed against temperature on Fig. 4. The  $\Gamma$  correction and the  $T/T_l$  renormalization are of no use for this cross phenomenon, highlighting no characteristic behavior (for example see below Fig. 6). We have added on this graph the only other Soret experiments as a function of temperature on (LiCl, water): Wood and Hawksworth's conductimetric measurements<sup>21</sup> and Alexander's thermogravitational diffusion results.<sup>22</sup> Two first inferences may be drawn from these curves:

- On the one hand, opposite to previous measurements<sup>23</sup> and statements,<sup>24</sup> aqueous lithium chloride is not characterized by a small thermodiffusive power with regard to the other aqueous alkali chlorides. The strength of the effect in the medium concentration range—one of the largest ever measured in such systems—especially contradicts this idea and justifies the enlarging of the field of the experimental conditions we have undertaken.
- On the other hand, the slow increase of  $S_T$  with temperature is consistent with most previous reported work in aqueous alkali halides.<sup>21,22,25,26</sup>

The wide variation of  $S_T$  against  $R$  has led us to draw its evolution as a function of the concentration. But this attempt has to be carefully considered, because it has needed extrapolations, which are always delicate operations. First, we have chosen the 0 °C temperature (needing the smallest ex-

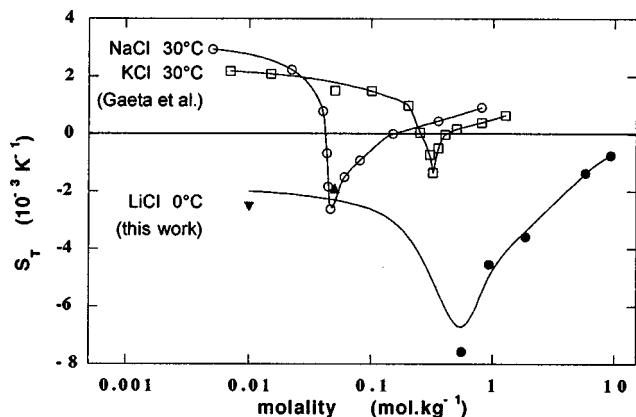


FIG. 5. Soret coefficient of aqueous LiCl, NaCl, and KCl as a function of the molality.

trapolations), and second, a molality representation (the most used concentration unit in the literature). Figure 5 displays LiCl results at 0 °C as well as Gaeta *et al.*'s results of thermogravitational diffusion on NaCl and KCl at 30 °C.<sup>27</sup> The following trends may be noticed:

- Aqueous LiCl exhibits a sharp minimum, in the same way that aqueous NaCl and KCl, but relatively deeper. This minimum is located in the medium concentration range.
- Particularly looking at the NaCl and KCl results, the curves exhibit a plateau at high dilution and a steep decrease down to the minimum at medium concentration.
- The LiCl curve is characterized by a shift towards the negative values of  $S_T$ . As a consequence, the Soret effect is nearly always negative in LiCl solutions, when it changes sign twice in NaCl and KCl solutions when the concentration increases. This shift cannot be attributed to the temperature difference of 30 °C between the two experiments. Indeed, Gaeta *et al.* report that when temperature is decreased, the minima of the  $S_T=f(m)$  curves of the NaCl and KCl solutions increase, which still accentuates the discrepancy with the LiCl curve.

We want now to emphasize the similarity between two features of the interdiffusion and thermal diffusion curves, displayed on the same graph in a  $R$  representation on Fig. 6: the existence of a plateau at high dilution (large  $R$ ) and a rapid evolution with  $R$  at high concentration (small  $R$ ). But this similarity is failing in the medium concentration range where the Soret effect behavior is much more catastrophic than the interdiffusion one. So these two phenomena are unlikely to originate in the same molecular mechanisms over the whole range of concentration. More precisely, thermal diffusion, being a cross phenomenon, appeals to the energetic bases of mass transport, evidencing therefore other aspects of molecular interactions that direct diffusion.

In order to elucidate the mechanisms accounting for such behaviors, we will now consider the microscopic scale of thermal diffusion.

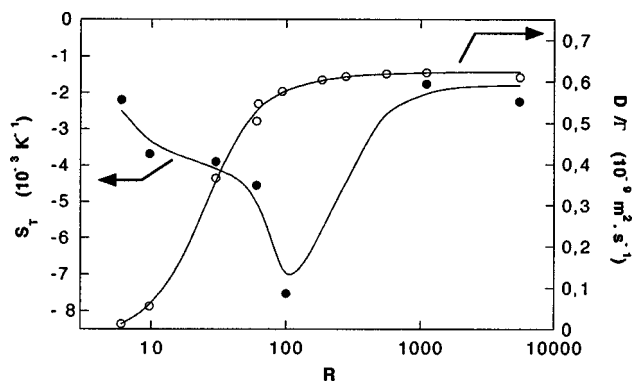


FIG. 6.  $S_T$  and  $D/T$  of (LiCl,  $\text{RH}_2\text{O}$ ) at reduced temperature  $T/T_l = 1.01$  as a function of  $R$ .

## V. DISCUSSION

Among the very few theories attempting to interpret the Soret effect, one dealing with the inversion of the effect with temperature has already been discussed.<sup>10</sup> Another one, that can be called the Chanu–Gaeta model,<sup>27,7</sup> based on the Franck and Wen's model of aqueous electrolytic solutions,<sup>28,29</sup> can be summarized as follows. Stating that entropic considerations are the cornerstones of the understanding of cross diffusion phenomena, this model assesses that if the organization of the water molecules solvating an ion is more ordered than the organization of molecules in pure water, the arrival of a migrating ion in a pure water region yields a local decrease of entropy. This process corresponds to a heat liberation and leads the ions to diffuse towards the cold wall (i.e.,  $S_T > 0$ ), in order to contend with the heat flux due to the thermal gradient.

In the high dilution range, the water organization prevails, characterized by a high number of hydrogen bonds, leading to a mostly tetrahedral structure. In the high concentration range, the ionic organization prevails, characterized by ion–dipole interactions with a more spherical structure, yielded by the Coulombic atmosphere of the ions, and by incipient indirect ion–ion interactions.

Both these states amount to a high level of order in the water molecules arrangement. For this reason, they correspond to positive values of  $S_T$  in the KCl and NaCl cases. In the medium concentration range, the competition between these two types of structure, which are not consistent with each other, leads to an increased disorder in the water molecules, according to Chanu and Gaeta. The minimum of the  $S_T = f(m)$  curve, corresponding to a positive to negative evolution of  $S_T$ , originates in this structure-breaking mechanism.

We are now going to experience the compatibility of this theory with our new aqueous LiCl results. Recent structural investigations of the (LiCl,  $6\text{H}_2\text{O}$ ) system<sup>12</sup> and *ab initio* computations<sup>30</sup> have considerably strengthened the following early idea<sup>28</sup> about  $\text{Li}^+$ : the reduced electron cloud of this ion gives rise to a very strong electrostatic field in its neighborhood, drastically acting on the water molecules around. Among the alkali ions,  $\text{Li}^+$  is thereby the strongest structure maker, using Frank and Wen's term. In the case of a highly polar solvent like water, this polarizing effect explains, in

(LiCl,  $6\text{H}_2\text{O}$ ), the progressive recreation of the H bond network, characteristic of pure water when temperature is decreased, leading to the supercooling and vitrification of the liquid.<sup>12</sup>

According to the Chanu–Gaeta model, all these properties imply for aqueous LiCl positive values of  $S_T$ . Nevertheless, the experimental results dismiss this expectation, (LiCl,  $\text{RH}_2\text{O}$ ) exhibiting much more negative values of  $S_T$  than aqueous NaCl and KCl. As the model turns out to be discrepant with the measurements, a new analysis seems to be necessary.

The consequence of the existence of a thermal gradient in a fluid is the modification of the dynamical state of its species: the vibrational entropy becomes larger at the hot end than at the cold end. According to Prigogine's theorem of nonequilibrium thermodynamics,<sup>1</sup> a steady state amounts to a minimum of the entropy source strength. Therefore, if the trend of the solute in an aqueous solution is to reduce the local entropy (structure maker), it will thus diffuse towards the hot wall, to contend with the effect of the temperature and to make the entropy source strength minimum, and  $S_T$  will be negative. According to these assumptions, a structure-making ionic mechanism therefore leads to negative values of  $S_T$ , instead of positive values with Chanu–Gaeta's hypotheses. This relates the large Coulombic influence of  $\text{Li}^+$  on water, compared with  $\text{Na}^+$  and  $\text{K}^+$ , to its strongly negative thermodiffusive character, in particular at high dilution where it exhibits a negative plateau when the other ions show a positive one.

Though the two models are based on the same mechanism, Chanu and Gaeta consider it during the transient regime, what seems to us tentative. So we consider the entropy heat transfer at the steady-state, where the nonequilibrium laws are better considered.

Following these assumptions, the medium concentration domain, being the most negative in  $S_T$ , should be associated with the most ordered configuration of the solvent. And the high concentration range should correspond to a poorly ordered liquid,  $S_T$  being positive for the three salts. But these two structural considerations are clearly known to be wrong. This evidences the deficiency of a too macroscopic view of these phenomena.

Trying to lay out a molecular picture of the above-mentioned structure-making mechanism in  $\text{Li}^+$  at high dilution, that  $\text{Na}^+$  and  $\text{K}^+$  do not seem to experience, the relevant feature is very likely to be the polarizing influence of the ions on the second and following hydration shells. Indeed, this polarizing effect is strong enough to encourage the pure water structure (by enhancing the spatial charge separation of the water molecules) in the outer shells. If this orientational influence is thus the basis of the negative values of  $S_T$ , the medium concentration range—where no more free water exists—could be the state where the ratio of water molecules under the polarizing influence of the ions is the largest and then  $S_T$  should be the most negative. This polarizing effect may thus be the energetic molecular mechanism mentioned in the last section, hidden in isothermal diffusion by the direct Coulombic and H bonds processes.

The high concentration range is however still in ques-

tion. The similarity between the behaviors of the three salts can easily be ascribed to the vanishing of the outer hydration shells and then of the polarizing effect of the three ions. But the origin of the positive sign of the Soret coefficient has to be searched for in the difference of the first shell organizations of the different anions and cations.

What is also still questionable among many problems is the way places with entropic evolutions become heat sources or sinks. Furthermore, the essentially *vibrational* entropy modification due to the temperature gradient is contended with by the *configurational* entropy evolution due to the matter flux and this process has still to be deepened.

## VI. CONCLUSION

We have presented in this paper pure Soret measurements in aqueous lithium chloride with the broadest temperature and concentration range available. We have thus been able to attempt a theoretical explanation of the behavior of thermal diffusion in salt solutions.

Macroscopically, the negative sign of  $S_T$  seems to originate in the structure-making character of the solute on the solvent. In the case of aqueous alkali chlorides, the main microscopic feature has appeared to be the electrostatic influence of the alkali ion on water molecules, especially the polarizing effect in the outer hydration shells. But experimental structural results are being missed and numerical simulations could be of great interest to validate our assumptions.

Facing the reduced field of earth measurements, this study has also facilitated the specifications of the indispensable microgravity experiments by highlighting some pressing questions.

<sup>1</sup>S. de Groot and P. Mazur, *Non-equilibrium Thermodynamics* (North Holland, Amsterdam, 1962).

<sup>2</sup>P. Segrè, R. Gammon, and J. Sengers, *Phys. Rev. E* **47**, 1026 (1993).

<sup>3</sup>S. Yi and R. Rowley, *J. Chem. Phys.* **87**, 7214 (1987).

<sup>4</sup>J. Giddings, *Science* **260**, 1456 (1993).

<sup>5</sup>B. Faissat and F. Montel, *Entropie* **198–199**, 107 (1996).

<sup>6</sup>V. Backlund, J. Dupuy, S. Gustafsson, and A. Lunden, *Z. Naturforsch. A* **22**, 471 (1967).

<sup>7</sup>J. Chanu, *Adv. Chem. Phys.* **13**, 349 (1967).

<sup>8</sup>M. Velarde and R. Schechter, *Chem. Phys. Lett.* **12**, 312 (1971).

<sup>9</sup>D. Henry and B. Roux, *J. Fluid Mech.* **195**, 175 (1988).

<sup>10</sup>J. Colombani, H. Dez, J. Bert, and J. Dupuy-Philon, *Phys. Rev. E* **58**, 3202 (1998).

<sup>11</sup>V. Sanchez, C. Durou, and J. Mahenc, *C. R. Seances Acad. Sci., Ser. C* **277**, 663 (1973).

<sup>12</sup>B. Prével, J. Jal, J. Dupuy-Philon, and A. Soper, *J. Chem. Phys.* **103**, 1886 (1995).

<sup>13</sup>P. O. Maurin, N. Asahi, J. Kawamura, T. Kaniyama, Y. Nakamura, JF. Jal, and J. Dupuy-Philon, *Ber. Bunsenges. Phys. Chem.* **102**, 152 (1998).

<sup>14</sup>J. Bert and J. Dupuy-Philon, *J. Phys.: Condens. Matter* **9**, 11045 (1997).

<sup>15</sup>P. Kolodner, H. Williams, and C. Moe, *J. Chem. Phys.* **88**, 6512 (1988).

<sup>16</sup>W. Köhler and B. Müller, *J. Chem. Phys.* **103**, 4367 (1995).

<sup>17</sup>K. Zhang, M. Briggs, R. Gammon, and J. Sengers, *J. Chem. Phys.* **104**, 6881 (1996).

<sup>18</sup>H. Tyrell and K. Harris, *Diffusion in Liquids* (Butterworths, London, 1984).

<sup>19</sup>V. Lobo and J. Quaresma, *Physical sciences Data 41, Handbook of Electrolyte Solutions, Part B* (Elsevier, Amsterdam, 1989).

<sup>20</sup>A. Aouizerat-Elarby, H. Dez, B. Prevel, JF. Jal, J. Bert, and J. Dupuy-Philon (unpublished).

<sup>21</sup>C. Wood and W. Hawksworth, *J. South African Chem. Inst.* **24**, 170 (1971).

<sup>22</sup>K. Alexander, *Z. Phys. Chem. (Leipzig)* **203**, 213 (1954).

<sup>23</sup>P. Snowdon and J. Turner, *Trans. Faraday Soc.* **56**, 1409 (1960).

<sup>24</sup>J. Lin, W. Taylor, W. Rutherford, and J. Millat, in *Measurement of Transport Properties of Fluids*, edited by W. A. Wakeman, A. Nagashima, and J. V. Sengers (Blackwell Scientific, Oxford, 1991), pp. 321–387.

<sup>25</sup>L. Longworth, *J. Phys. Chem.* **61**, 1557 (1957).

<sup>26</sup>D. Caldwell, *J. Phys. Chem.* **77**, 2004 (1973).

<sup>27</sup>F. Gaeta, G. Perna, G. Scala, and F. Bellucci, *J. Phys. Chem.* **86**, 2967 (1982).

<sup>28</sup>H. Franck and W.-Y. Wen, *Discuss. Faraday Soc.* **24**, 133 (1957).

<sup>29</sup>W.-Y. Wen, *Water and Aqueous Solutions* (Wiley, New York, 1972).

<sup>30</sup>E. Glendening and D. Feller, *J. Phys. Chem.* **99**, 3060 (1995).

<sup>31</sup>R. Cohen-Adad and J. Lorimer, *Solubility Data Series, Alkali Metal and Ammonium Chlorides in Water and Heavy Water (Binary Systems)* (Perгамon Press, Oxford, 1991), Vol. 47.

<sup>32</sup>P. Claudy, J. Lettofé, J. Counioux, and R. Cohen-Adad, *J. Therm. Anal.* **29**, 423 (1984).

<sup>33</sup>C. Angell, E. Sare, J. Donnelly, and D. McFarlane, *J. Phys. Chem.* **85**, 1461 (1981).