

A non-ergodic thermodynamics based not on concentrations but on time fractions. Application to conductance problems of solutions of lithium salts in ethers

Pierre Huyskens, Marcel Van Beylen and Hilde Verheyden

University of Leuven, Department of Chemistry, Celestijnenlaan 200F,
B-3001 Heverlee, Belgium.

ABSTRACT

Hydrogen bonds or strong dipole-dipole interactions lead to the formation of transient chain-association in solution. The interaction has a given molar energy: ΔH_{bond} . In an open chain as for instance in alcohols $\text{O-H}\cdots\text{O-H}\cdots\text{O-H}\cdots\text{O-H}\cdots\text{O-H}$, only the completely inserted molecules are in possession of this energy during the whole time they are inserted. The head and the tail are transient forms during the life-time of which ΔH_{bond} is transferred from the medium to the molecule or vice-versa. In the ensemble at a given time they have no definite energy and their concentrations cannot be calculated by means of a Boltzmann equation. But in a time schedule they can be considered half of the time as possessing ΔH_{bond} and half of the time as free. The classical Guldberg and Waage equilibrium expression using concentrations has to be replaced by another one where time fractions γ appear. In an alcohol the time fraction γ during which the molecule escapes from H-bonding and becomes vaporizable is given by the equation $(1-\gamma)/\gamma = K_A C_{\text{alcohol}}$. The new equations derived from these principles allow to predict correctly the vapor pressures of the alcohols and the solubilities of foreign substances in these solvents and provide a completely new quantitative explanation for the hydrophobicity of alkanes.

Non-ergodic association also occurs between ion pairs as LiCl in moderately polar solvents as tetrahydrofuran THF ($\epsilon^{293} = 7.53$) or tetrahydropyran THP ($\epsilon^{293} = 5.71$), which can form open dimers LiClLiCl or higher associates in these solvents. The formation of these dimers is accompanied by the appearance in the solution of triple anions and cations between which there exists via the neutral dimer a perpetual exchange of a LiCl molecule according to:



The triple ions formed in this way cannot be considered as separated thermodynamic entities and do not follow the Guldberg and Waage equilibrium expression. The LiCl group which they have in common is sometimes involved in a positive ion and sometimes in a negative one. Only in the neutral dimer it may be considered as in possession of the insertion bond.

On the other hand LiCl may also be involved in a dissociation where the Li^+ ion becomes specifically solvated by the ether, giving:



However this specific solvation is incompatible with the formation of triple ions because it would prevent the oscillation of LiCl between the triple ions.

As a consequence one has to distinguish in the time schedule of a given LiCl a fraction of the time ξ° during which it dissociates in an anion and a solvated cation, and the fraction of the time $(1-\xi^\circ)$ during which it is involved in a dimerization process and where triple ions can be formed. One has:

$$(1-\xi^\circ)/\xi^\circ = K^{\text{ass}} (K^{\text{d}})^{-1/2} C_{\text{LiCl}}^{3/2}$$

where K^{ass} is the non-ergodic constant governing the association of the ion pairs and K^{d} the classical dissociation constant, C_{LiCl} being the concentration of the salt. The quantitative equations based on this theory allow to explain the peculiarities of the conductance of LiCl solutions and the paradoxical effects of the addition of LiCl on the conductivity of Polystyryl $^-\text{Li}^+$ solutions and on the kinetics of the anionic polymerization.

Transient phenomena which perturb the nature of solutes play a dominant role in a lot of physical characteristics of the solutions but also in the intervention of the solute in chemical reactions. For instance, the electrical conductance of a solution of polystyryl cesium in THF is due to the temporary dissociation of a molecule of the solute in separate ions:



In the same way the intervention of PStCs in the anionic polymerization of styrene is also

governed by the temporary dissociation and thus to the chance γ that an entity PStCs has to form PSt⁻ single anions.

For both conductivity and reactivity, the influence of the electrolyte is related to its formal concentration C by means of a chance factor γ :

$$\begin{aligned}\kappa &= L C \gamma \\ k_{\text{react}} &= k_{\text{react}}^{\circ} C \gamma\end{aligned}$$

L and k_{react}° being proportionality factors.

Both electrical conductivity and polymerization concern events which take place in the time, and therefore it is evident that γ appearing in these equations is, in principle, the chance in the time.

One may also consider the chance to find a PSt⁻ ion at a given time in the ensemble, which will be denoted by α .

$$[\text{PSt}^-] = \alpha C$$

For most scientists the ergodic principle which postulates that ensemble fractions and time fractions are equal, is considered as an absolute dogma. They will consider the distinction between γ and α as redundant. For them the conductivity and reactivity equations are:

$$\begin{aligned}\kappa &= L [\text{PSt}^-] \\ k_{\text{react}} &= k_{\text{react}}^{\circ} [\text{PSt}^-]\end{aligned}$$

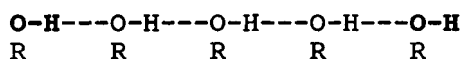
As a matter of fact, in the present case the ergodic principle holds.

But this is not always the case. Let us for instance consider Li⁺ and Cl⁻ ions colliding in the gas phase. During the time of the collision they form an ion pair. In the ensemble we will count them among the associated entities. However, during the time of the collision, these ions which will spontaneously dissociate (because they cannot lose the energy in absence of a third body collision) preserve their share in the conductivity which remains the same as when they are moving freely in the gas. In a time schedule the collision time does not decrease γ . In this case α and γ are thus not equal.

This example demonstrates that the ergodic principle is not absolute.

We have discovered a much more common occurrence of non-ergodicity in the liquid phase. As a matter of fact heads or tails of transient open association chains are always non-ergodic.

Hydrogen bonds or strong dipole-dipole interactions lead to the formation of such transient chain-association in solution. The interaction has a given molar energy: ΔH_{bond} . In an open chain as for instance in alcohols:



only the completely inserted molecules are in possession of this energy during the whole time they are inserted. The head and the tail are transient forms during the life-time of which ΔH_{bond} is transferred from the medium to the molecule or vice-versa. Thus, for the end and the tail there is only one ΔH_{bond} available. This means that during the half of the time they have to be considered in the ensemble as located next to the remainder of the

chain, but not bonded to it, just as the two ions in the collision complex considered above. During this half of the time the energy of the insertion bond is compensated by kinetic energy coming from the surrounding.

This revolutionary point of view is completely supported by the experimental facts: In the pure alcohols, the concentration of the tails of the chains can be determined by infrared spectrometry. The proportion is of the order of 1 % at room temperature. This is also the proportion of the heads. The proportion α_{OH} of alcohol molecules free of bonding at the left and at the right is therefore only 0.01%.

When we compare the vapor pressure of an alcohol with that of the homomorphous ether, the first one is of the order of 1% of the second one. This is due to the H-bonds. We can thus conclude that the chance γ in the time for a given molecule to escape from H-bonding in the liquid is 1 %.

These results are reconcilable with the non-ergodic equation:

$$\gamma = \frac{1}{2} \alpha_{\text{-OH}} + \frac{1}{2} \alpha_{\text{OH-}} + \alpha_{\text{OH}}$$

(bonded at the left) (bonded at the right) (free at both sides)

The non-ergodic thermodynamics of the "Mobile order" leads to the following equation governing the time fraction γ :

$$\gamma = 1 / (1 + K^a C_A)$$

where K^a is the non-ergodic association constant and C_A the formal concentration of the alcohol. As expected, the constants for all the primary alcohols are of the same order of magnitude. They were determined by comparing the vapor pressures of the alcohol and those of the homomorphous hydrocarbon or ether. They are given in Table 1.

Table 1

Vapor pressures p/hectopascal of primary alcohols and of the homomorphous hydrocarbons and ethers at 25°C. Deduced value of the time fraction γ during which the alcohol molecule escapes from the effect of H-bonding and is able to evaporate. Concentration $C_A/\text{mol dm}^3$ of the pure alcohol. Non-ergodic association constant $K^a/\text{dm}^3\text{mol}^{-1}$

	P_{Alcohol}	$P_{\text{Hydrocarbon}}$	P_{Ether}	γ	C_A	K^a
Ethanol	79.7	9410	6500	0.010	17.0	6 ± 1
1-Propanol	27.5	2426	1970	0.012	13.3	6 ± 1
1-Butanol	8.2	684	712	0.012	10.9	7 ± 1
1-Pentanol	3.1	209	289	0.013	9.2	8 ± 2

A similar non-ergodic behavior can be expected for the association of electrolytes as LiCl in solvents as THF.

However, in this case, the association has unexpected consequences for the conductivity. In the dimer we can consider the central molecule as "inserted" :

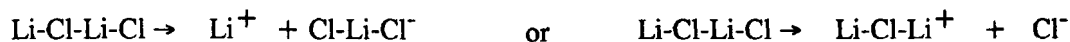


This dimer regularly *disassociates* in monomolecules:



and the insertion bond disappears.

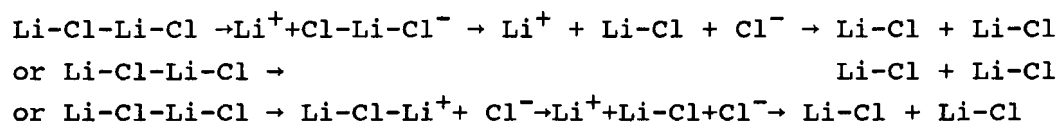
But the dimer can also sometimes be broken either at the left or at the right, giving triple anions or cations:



In this case the insertion bond does not disappear but according to the ideas above, it is active half of the time in the triple anion, and necessarily the other half of the time in the triple cation.

This means that these triple ions are to be considered half of the time as having the mobility of the single ions.

Regularly the bond in the triple ions is broken. The single ions can recombine. This means that there are three ways for a dimer to "disassociate": the "neutral" one, and two equivalent "ionic" ones :



During the time where LiCl is involved in an association equilibrium, the ions which occasionally participate to this equilibrium are prevented to become specifically solvated by ligands or by the solvent.

As a matter of fact the solvation of Li^+ by THF giving $\text{Li}(\text{S}_4)^+$ would disturb the equilibrium, by pumping Li^+ entities needed to insure the dimerization equilibrium.

Specific solvation and dimerization are thus incompatible and have to share the time of a given LiCl molecule. As a consequence one has to distinguish in the time schedule of a given LiCl a fraction of the time ξ° during which it dissociates in an anion and a solvated cation, and the fraction of the time $(1-\xi^\circ)$ during which it is involved in a dimerization process and where, occasionally, triple ions can be formed. These time fractions are ruled by the non-ergodic equation:

$$(1-\xi^\circ)/\xi^\circ = K^{ass} (K^d)^{-1/2} C_{\text{LiCl}}^{3/2}$$

where K^{ass} is the non-ergodic constant governing the association of the ion pairs and K^d the classical dissociation constant, C_{LiCl} being the concentration of the salt.

The quantitative equations based on this theory allow to explain the peculiarities of the conductance of LiCl solutions.

Let us for instance compare the conductances of PStLi and LiCl solutions in THF. The ionic radii of PSt^- and Cl^- being very similar ($r_{\text{PSt}^-} = 1.87 \cdot 10^{-8}$ cm, $r_{\text{Cl}^-} = 1.81 \cdot 10^{-8}$ cm) one expects an high similitude of the curves of k^2 versus the concentration of the electrolyte.

As shown in figure 1, this is absolutely not the case. The conductivity of the PStLi solutions is two orders of magnitude larger.

Furthermore, there is a fundamental difference in the shape. We see that for PStLi the function is practically linear. This means that the formation of triple anions is negligible.

But, as seen in the extended scale used in fig.2, for LiCl the functions exhibit a quadratic term, indicating the formation of triple ions.

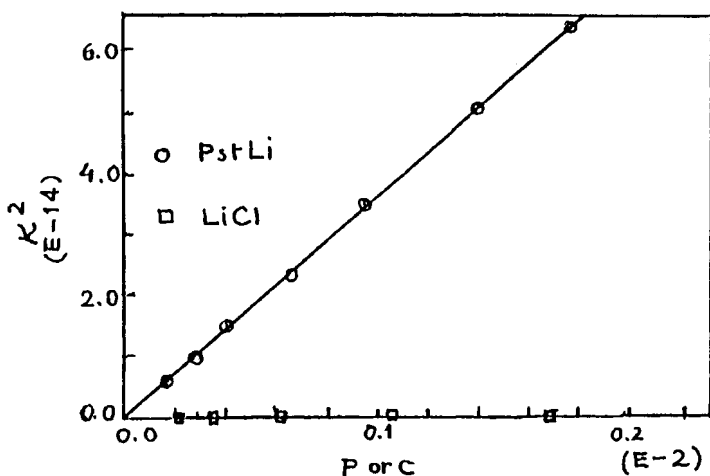


Fig.1 Square of the specific conductance $\kappa^2 / 10^{-14} \text{ s}^2 \text{ cm}^{-2}$ as a function of the concentration $P/10^{-3} \text{ mol dm}^{-3}$ of polystyryllithium and concentration $C/10^{-3} \text{ mol dm}^{-3}$ of LiCl at -20°C in THF

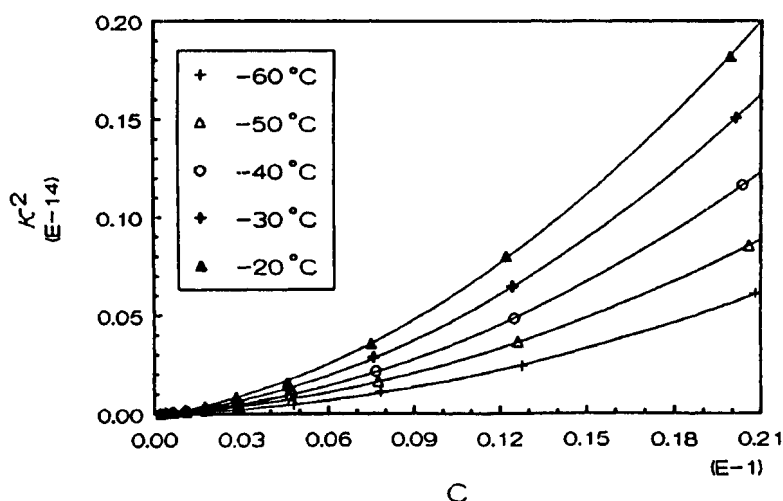


Fig.2 Square of the specific conductance $\kappa^2 / 10^{-14} \text{ s}^2 \text{ cm}^{-2}$ as a function of the concentration $C/10^{-1} \text{ mol dm}^{-3}$ of LiCl at several temperatures in THF. (Notice the scale difference in the abscissa)

The large values of the PStLi systems can be attributed to the formation of specifically solvated cations of the $\text{Li}(\text{THF})_4$ type. For LiCl such solvation apparently does not occur. It is absolutely impossible to explain this phenomenon by classical treatments based on the Guldberg and Waage equations.

However, the non-ergodic formation of triple anions which accompanies the dimerization or higher association explains both the dramatic reduction of the conductivity and the shape of the curves.

A still more spectacular effect can also be explained by this new theory. It concerns the influence of LiCl on the conductivity of the PStLi solutions. As already told, the conductivities of the LiCl solutions are negligible compared to that of the PStLi solutions at the same concentration.

Therefore one does not expect a large effect on the conductivity upon addition of LiCl to the last solutions.

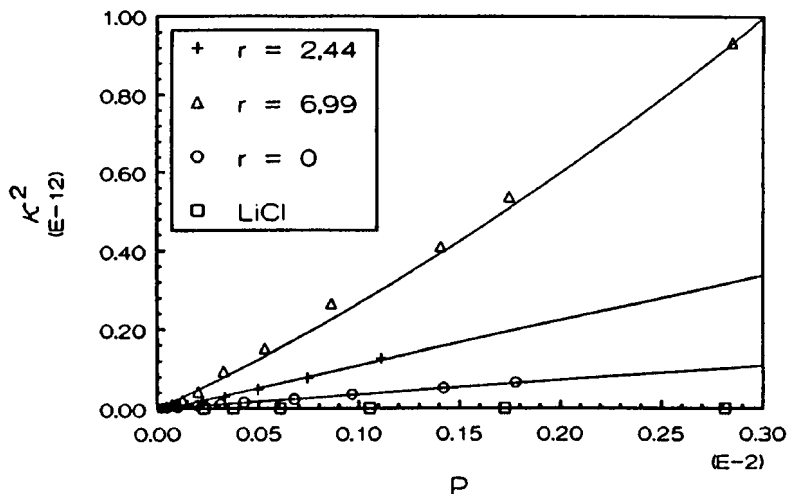
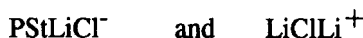


Fig.3 Square of the specific conductance $\kappa^2 / 10^{-12} \text{ S}^2 \text{ cm}^{-2}$ as a function of the concentration $P / 10^{-2} \text{ mol dm}^{-3}$ of polystyryllithium upon addition of various ratio's r of LiCl at -20°C in THF. The points on the abscissa refer to the concentration $C / 10^{-2} \text{ mol dm}^{-3}$ of pure LiCl.

The opposite is observed. As seen in fig.3 the addition of LiCl increases the square on the conductivity approximately in the same ratio as that of the added electrolyte.

This can by no means be explained by the formation of classical mixed triple anions PStLiCl^- with a concentration ruled by the Fuoss equation.

However, the effect is quantitatively described by the formation of *non-ergodic couples of triple ions*:



where the insertion bond is shared in the time by both the cation and the anion.

These triple ions are related to the replacement of an LiCl by a PStLi in the neutral LiClLiCl dimers:



The liberated LiCl has no longer the obligation to participate in the dimerization. As a consequence the fraction of time ξ during which it can dissociate in Li^+ ions able to undergo specific solvation giving $\text{Li}(\text{THF})_4^+$ ions increases. This explains the spectacular increase of the conductivity of the solutions. The quantitative treatment leads to the calculated curves in fig.3.

Another effect which can also be explained by the non-ergodicity of the dissociation is the paradoxical influence of LiCl on the kinetics of the polymerization. In the concentration range of 10^{-5} mol dm^3 of PStLi the addition of LiCl reduces the polymerization rate. On the contrary, in the concentration range of 10^{-3} mol dm^3 of PStLi the addition of LiCl increases the reactivity. At low concentration, the major effect of LiCl is to reduce the concentration of the reactive PSt^- single ions; at higher concentration the formation of non-ergodic triple anions ClLiPSt^- , which have during the half of the time the reactivity of the single anions, becomes predominant.