PROPERTIES OF NON-AQUEOUS ELECTROLYTE SOLUTIONS IN THE MICROWAVE
AND FAR INFRARED REGION

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Abstract - The microwave properties of electrolyte solutions in non-aqueous
solvents consist mainly in an excess dielectric polarization and absorption
which is interpreted in terms of ionic processes. Some information about
solvatation can also be derived from these properties. In the far infrared
region, tetraalkylammonium salts exhibit an absorption which can yield
information about the interionic potential. FIR spectra of alkali metal
salts have also be obtained ; they show the presence of an absorption which
is not the well known cation band.

INTRODUCTION

The frequency range we are dealing with extends up to about 15×10^{12} Hz ($500 \ cm^{-1}$ in usual
units). Far infrared (FIR) can be considered as starting at 3×10^{11} Hz ($10 \ cm^{-1}$). The micro-
wave region corresponds to lower frequencies. In fact, different words are used because the
technics differ ; microwaves are associated with coaxial lines and wave guides, FIR with
optical devices such as interferometers and spectrometers. In any case we are interested in
the response of matter to an electric field. For a molecular liquid (the solvent of an
electrolyte solution), this response is mainly that of a dipole. The relaxing part of its
motion - the dielectric properties of the liquid - can be detected by microwave measurements.
The FIR response is related to inertial effects, and libration of the dipole. This descrip-
tion is quite schematic and other effects do appear, either related to the molecule itself
or to cooperative processes. Nevertheless, the energy loss is roughly proportional to the
square of the dipole moment all over the frequency range dealt with in this paper. As a
consequence, in an electrolyte solution, a positive effect of the solute is likely to be
evidenced more easily in a solvent with a low dielectric constant, a condition which implies
not too high a dipole moment.

The description of the ionic processes which contribute the response to an electric field is
not so easy as that of molecular processes. They can be nearly the same if the solute is in
the form of aggregates with a permanent dipole moment, such as ion pairs. However, even in
that case, it is necessary to keep in mind that the very existence of such aggregates is an
assumption which can be a starting point of the interpretation : a dielectric and/or FIR
spectrum analogous to that of molecules cannot prove the existence of entities with a dipole
moment because other mechanisms can yield the same response. For instance, the ions themselves
can contribute a relaxing polarization without the existence of any polar species, this
effect being associated with a frequency dependent conductivity. In the FIR region, other
effects specific to the ions can be evidenced.

The present paper is presented in two parts. The first one (microwave properties) deals with
the dielectric properties of electrolyte solutions in the frame of a model for salt asso-
ciation which tries and takes into account both complex permittivity and conductivity data.
The second part (FIR properties) deals with two classes of problems : excess absorption of
tetraalkylammonium salts in weakly polar solvents, and the consequence which can be derived
from FIR measurements upon ionic association - alkali metal salts which, apart from the
well-known "cation-band" absorption, exhibit another absorption at lower frequencies, which
is not yet interpreted. In both parts, a special attention is given to the solvent response.

MICROWAVE PROPERTIES

The complex permittivity $\varepsilon = \varepsilon' - i\varepsilon''$ ($i^2 = -1$) of an electrolyte solution is plotted, in fig. 1, in the complex plane (ε', ε''). The data refer to lithium perchlorate in a mixed solvent, tetrahydrofuran (THF) + benzene. The example (Ref.1) has been chosen because it is typical of what can be observed in an electrolyte solution. No maximum of ε'' does appear unless this quantity is corrected for a conductivity loss $\sigma/\omega\varepsilon_o$ where σ is the zero frequency (static) conductivity, ω the angular frequency and ε_o a constant which depends on the units. Then, if some conclusions are to be drawn from the data, the corrected complex permittivity $\varepsilon - \sigma/i\omega\varepsilon_o$ has to be splitted into two quantities, one of which ($\varepsilon_m(\omega)$) originates in the reorientation of the solvent molecules, the other one ($\Delta\varepsilon(\omega)$) in the motion of the solute particles, apart from the contribution of σ. The observed permittivity thus is given by :

$$\varepsilon = \varepsilon' - i\varepsilon'' = \varepsilon_m(\omega) + \Delta\varepsilon(\omega) + \sigma/i\omega\,\varepsilon_o \qquad (1)$$

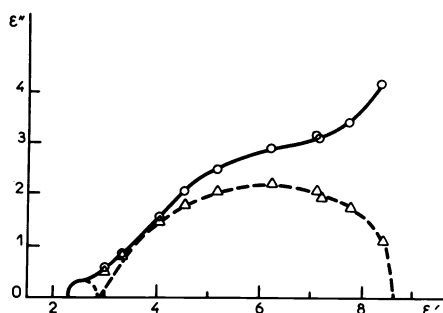Fig. 1   LiClO$_4$(0.6 M) in THF (3M)+benzene. The leftmost point corresponds to 0.14 GHz, the rightmost to 35 GHz. Raw data (o) and data corrected for a constant conductivity loss (Δ). The half circle on the left corresponds to the contribution on the solvent $\varepsilon_m(\omega)$, the skewed arc on the right to the contribution of the solute $\Delta\varepsilon(\omega)$.

The last two terms of the right hand side could have been written $\sigma(\omega)/i\omega\varepsilon_o$ in terms of a complex conductivity $\sigma(\omega)$. But it is more important to notice that any splitting up of ε is arbitrary to some extent. From a theoretical view point, we neglect cross effects between the motion of the solvent particles and that of the solute particles, unless we put them either in $\varepsilon_m(\omega)$ or in $\Delta\varepsilon(\omega)$. From an experimental view point, only one physical quantity is observed, namely the electrical current response of the material to an applied electric field; and experiment cannot decide which part of this response originates in the solvent, which part in the solute. Fortunately, in some cases, the time-scales where something happens are different enough for such a splitting up to be justified on an empirical basis. In the present paper, we shall mainly insist on cases where, as in fig. 1, the ionic contribution is clearly evidenced by experiment. These cases are met where the dielectric constant of the solvent is low enough (typically less than 10) and the salt concentration high enough (0.1 to 1 mole/1) . These conditions are very far from those where any theory of electrolyte solutions is available, and models have to be used to a large extent.

In a previous paper (Ref. 2), we had discussed the possibility of deriving $\Delta\varepsilon(\omega)$ from a time correlation function $\phi(t)$ involving the positions of the ions, and called this a dielectric approach. If $\underset{\sim}{M}(t)$ is the electrical moment of a given volume V of solution, $\Delta\varepsilon(\omega)$ is given by:

$$\Delta\varepsilon(\omega) = \frac{1}{3kTV} \int_0^\infty e^{-i\omega t}\,\phi(t)dt$$

$$\phi(t) = \langle \underset{\sim}{M}(o)\,\underset{\sim}{M}(t) \rangle \qquad (2)$$

Doing so is justified if $\phi(t)$ goes to zero when t goes to infinity. A necessary condition is the absence of conductivity. There are different ways for this approximation to hold, which we have previously described (Ref. 3). The static conductivity has to be studied by another model, more or less related to that used for the ionic relaxation $\Delta\varepsilon(\omega)$. Another approach, more satisfying from a theoretical view point, would be to build a model for a frequency dependent conductivity :

$$\sigma(\omega) = \sigma + i\omega\varepsilon_o\,\Delta\varepsilon(\omega) \qquad (3)$$

Recent advances have been performed in this way by Justice and Ebeling (Ref.4),but the concentration range is limited and the data such as those given in fig.1 still have to be interpreted in terms of dielectric models based on eq.2. In the past (Ref.5), we had proposed to start from the assumption that the ions were moving according to a Brownian linear motion, randomly
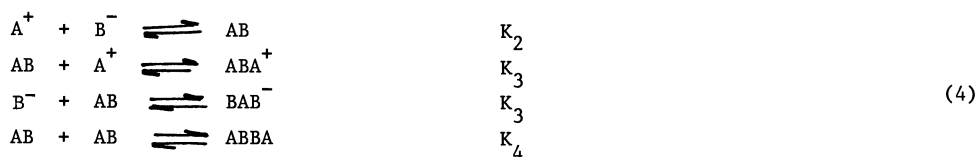
interrupted by collisions with other ions or the solvent particles. Three parameters were
necessary to describe this motion, namely a diffusion coefficient, a collision frequency and
the mean time for the position of an ion at time t to be uncorrelated with its position at
time zero. The model could fit the relaxation data of many systems. In some cases, the first
two parameters could be compared with independent evaluations, but the main interest of the
model was to demonstrate that a polarization, and a relaxation of this polarization could be
ascribed to the presence of the ions, without any permanent dipole moment of ionic origin.
The same data could of course be reproduced by other dielectric models. Farber and Petrucci
(Ref.6) analysed our own data on LiClO$_4$/THF solutions with a model of ion pairs with a defini-
te dipole moment; another element was necessary to explain the "skewed arc" character of the
(ε', ε'') plot of $\Delta\varepsilon(\omega)$ and they used Glarum's theory(Ref.7)which states that such diagrams can
be given by a mechanism where a dipole relaxes instantly upon the arrival of a diffusing
defect. For the systems studied, the defects were the ion-pairs themselves. Just as in the
older model, the ionic relaxation was described by a process involving diffusion and colli-
sion of particles. Unfortunately Glarum's theory is built on a one-dimensional model, so that
the conclusions of Farber and Petrucci remainded qualitative. It is nevertheless a good
starting point to go further, using the extension of Glarum's theory to three dimensions by
Hunt and Powles (Ref.8),and,more recently Bordewijk (Ref.9). We have just improved this model
(Ref. 10), taking into account the finite size of the defects and of the dipole. As explained
below, only two parameters –instead of three– are necessary to describe the motion of the
solute particles. Moreover, the parameters can be compared with parameters able to describe
the variations of the equivalent (static) conductivity Λ with concentration. We shall first
present some data of this kind, in the same concentration range as the dielectric relaxation
data. We shall then deal with the model for the reorientation of the ion pairs, and finally
with the perturbation in the reorientation of the solvent molecules which can be attributed
to the presence of the ions.

Experimental
The complex permittivity is measured (Ref. 11) by a coaxial line technique below 3 GHz, with
waveguide interferometers at 9.34 and 34.7 GHz (3 and 0.8 cm wavelength). Additional measu-
rements at 124 GHz (0.24 cm wavelength) have been performed with a Michelson interferometer,
analogous with that described in the FIR section of this paper, but with a variable length
of liquid in front of the moving mirror so that both ε' and ε'' can be determined (Ref. 12).
Conductivity measurements (Ref. 10) have been performed between 1000 Hz and 20 kHz with
usual techniques, with a coaxial cell and a capacitive bridge for very low conductivities,
below 20 x 10^{-6} ohm^{-1} cm^{-1}.

Static conductivity
In Fig. 2, the equivalent conductivity Λ is plotted against the concentration c for sodium
perchlorate solutions in dimethoxyethane (DME). According to   Fuoss and Kraus (Ref. 13)
theory, the minimum in the curve indicates the existence of triple ions. The downwards curva-
ture could indicate the presence of quadrupoles. Along these lines a series of chemical equi-
libria between single ions (A$^+$ and B$^-$), ion pairs (AB) and higher order aggregrates (ABA$^+$,
BAB$^-$, ABBA) can be written as

$$
\begin{array}{llr}
A^+ + B^- \rightleftharpoons AB & & K_2 \\
AB + A^+ \rightleftharpoons ABA^+ & & K_3 \\
B^- + AB \rightleftharpoons BAB^- & & K_3 \qquad\qquad (4)\\
AB + AB \rightleftharpoons ABBA & & K_4
\end{array}
$$

The concentrations $\alpha_1 c$, $\alpha_2 c$, $\alpha_3 c$, $\alpha_4 c$ of each species ($0 < \alpha_i < 1$) can be deduced from the
following set of equations :

$$
\begin{array}{ll}
\alpha_1 + \alpha_2 + 3\alpha_3 + 2\alpha_4 = 1 & \qquad \alpha_2/\alpha_1^2 = K_2 c \\
& \qquad\qquad\qquad\qquad\qquad (5)\\
\alpha_3 / \alpha_1 \alpha_2 = K_3 c & \qquad \alpha_4/\alpha_2^2 = K_4 c
\end{array}
$$

where the activity coefficients have been chosen as equal to 1. This is a kind of zero order
approximation, and the same can be done about the equivalent conductivities of the conduc-
ting species, taking Λ_o for the single ions, $\Lambda_o/3$ for the triple ions, so that :

$$
\Lambda = \alpha_1 \Lambda_o + \alpha_3 \Lambda_o / 3 \qquad\qquad\qquad (6)
$$

It would be naïve to consider this approximation as a good one, but no sophisticated formula
can apply for so low a solvent permittivity and so high a concentration range. For instance,
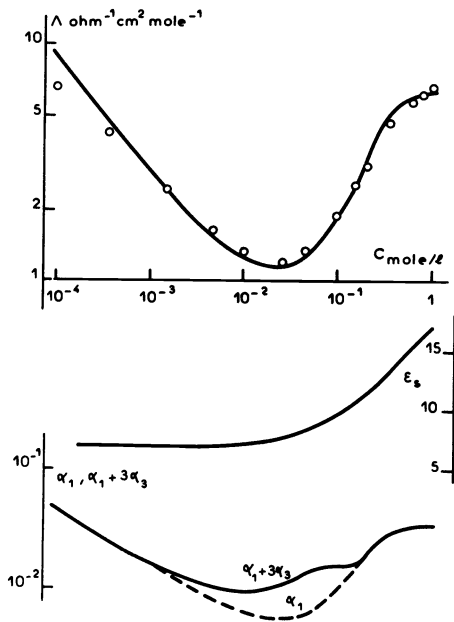the Fuoss-Onsager limiting law(Ref.14) yields negative Λ values. The Λ(c) curve can then be

Fig. 2   Na ClO$_4$ in DME ; ε_s is the dielectric constant of the solution $\alpha_1 c$ and $\alpha_3 c$ the concentration of single and triple ions.

reproduced by eq. 5 and 6 with only three parameters, namely K_2, K_3, K_4. The next step in such a study is to try and relate the equilibrium constants to specific parameters at the microscopic level. K_2 and K_3 can be related, for instance to the closest distance of approach a_2 between an anion and a cation, a similar distance a_3 being introduced for K_3 (Ref. 13). In the revised form proposed by Jagodinski and Petrucci (Ref. 15) they read :

$$K_2 = (4 \pi N_A a_2^3 / 3000) \exp (e^2 / a_2 \varepsilon_s kT - 1/2)$$

$$K_3 = (\pi N_A a_3^3 / 1000) \exp (e^2 / 2a_3 \varepsilon_s kT - 3/2)$$

(7)

The parameters thus become a_2, a_3 and K_4. The last idea we can introduce in this model is that K_2 and K_3 depend on the dielectric constant of the solution, ε_s, instead of that of the solvent, as usually assumed. As shown in fig. 2, (middle part) the difference is rather academic at c lower than 10^{-2} mole/1, but is not at higher c values. This proposal had been made by Cavell (Ref. 16) for K_2, in a slightly different form, in order to interpret the increase of Λ with c without introducing triple ions. The full line in the Λ vs c plot of fig. 2 has been obtained with eqs. 5, 6, 7 using the ε_s values of the solutions deduced from the dielectric relaxation data as a zero frequency extrapolation of ε'. The best fit values of a_2, a_3 and K_4 given in table I, along with values for other systems, have been obtained by minimizing the sum of the squares of the deviations between computed and experimental

Table 1.   Association parameters from conductivity data

System	c range mole 1^{-1}		a_2 A°	a_3 A°	K_4 mole^{-1}1
LiClO$_4$/THF	10^{-4}	$-$ 0.8	3.97	3.98	151
LiClO$_4$/EA*	0.5×10^{-3}	$-$ 1	3.93	5.30	17.4
LiClO$_4$/DME	0.4×10^{-4}	$-$ 0.2	4.70	11.0	8.8
NaClO$_4$/DME	10^{-4}	$-$ 1	4.70	11.8	7.7

*
   EA stands for ethyl acetate

values of Λ. Since Λ is far from a linear function of the parameters, the numerical minimization has been performed by the algorithm of Nelder and Mead(Ref.17). The Λ_0 value was evaluated by the Walden rule (Ref. 14), starting from 156.1 ohm^{-1} cm^2 mole^{-1} for LiClO$_4$ (Ref. 15) and 167.7 ohm^{-1}cm^{2}mole^{-1} for Na ClO$_4$ (Ref. 18) in THF. In fig. 2 (bottom), α_1 is plotted vs c,

showing that the relative concentration of single ions α_1 increases at high concentration because of the increase in the dielectric constant of the medium around the ions. But the overall fraction of the salt in the form of conductive species, $\alpha_1 + 3\alpha_3$, always remains very small, less than 0.5%. This is probably the main argument in favour of the "dielectric model" which follows, where the whole solute is assumed to be in the form of ion-pairs .

Ionic relaxation

The purpose of the model is to give $\Delta\varepsilon(\omega)$ an analytical formulation through the time corre-lation function $\phi(t)$ and eq. 2. The solute is assumed to be in the form of ion pairs which bear a permanent dipole moment μ_a. They reorient with a relaxation time τ'_o which is associa-ted to the radius a_o of a rotating sphere through the Debye equation :

$$\tau'_o = 4\pi\eta \, a_o^3 / kT \tag{8}$$

where η is the viscosity of the medium. The ion-pairs also have a translational motion with a diffusion coefficient D which can be related to the same sphere radius a_o through the Stokes-Einstein equation :

$$D = kT / 6\pi\eta \, a_o \tag{9}$$

Following Clarum's theory, the normalized correlation function reads :

$$\phi(t) = < \underline{M}(o) \, \underline{M}(t) > / < \underline{M}^2(o) > = [1 - P(t)] \exp(-t/\tau_o) \tag{10}$$

where τ_o is the macroscopic relaxation time related to the microscopic one by the Powles-Glarum equation (Ref. 19, 20). :

$$\tau_o = [3\varepsilon_s / (2\varepsilon_s + \varepsilon_m)] \, \tau'_o \tag{11}$$

In this equation, ε_m is the zero frequency limit of the solvent contribution $\varepsilon_m(\omega)$. Eq. 2, namely the relation between $\Delta\varepsilon(\omega)$ and $\phi(t)$, should be more sophisticated if eq. 11 were to be written on a strict theoretical basis (Ref. 20) ; but the latter is merely used as an empi-rical improvement, so that we retain the simple form of eq. 2 for the relation between $\Delta\varepsilon(\omega)$ and $\phi(t)$. The exponential relaxation of an ion-pair is perturbed by collisions of defects ; upon such a collision, the dipole relaxes instantly (Ref. 7). In the present case, the defect is also an ion pair. The three-dimensional model of Hunt and Powles (Ref.8) introduces a characteristic distance R such that the instantaneous relaxation of the dipole occurs as soon as the distance between two ion-pairs becomes smaller than R. In their model, the distance of a defect to a dipole could actually be smaller than R, but we assumed it could not, so that R is also the closest distance of approach of two ion pairs. Since the calcula-tion of P(t) involves the probability for the nearest defect to be at a given distance of the dipole, we had to prescribe the impossibility for this distance to be smaller than R ; as a consequence, the expression of $\Delta\varepsilon(\omega)$ is not exactly that of Hunt and Powles, but has to be calculated through the following set of equations :

$$\Delta\varepsilon(\omega) = \frac{\varepsilon_s - \varepsilon_m}{1 + i\omega\tau_o} \left\{ 1 + i\omega\tau_o \int_o^\infty 3r\,(x + r) \exp[-(x+r)^3 + r^3 - \lambda x]\,dx \right\} \tag{12}$$

$$r = R/l_o \qquad (4\pi/3) \, \rho \, l_o^3 \, g(R) = 1$$

$$\lambda^2 = (1_o^2 / D\tau_o) \, (1 + i\omega\tau_o)$$

where ρ is the numerical density of ion-pairs and g(R) the radial distribution function of hard spheres of diameter R, at contact. In the Percus-Yevik approximation (Ref. 21) :

$$g(R) = (1 + \xi/2) / (1 - \xi)^2$$

$$\xi = (\pi/6) \, \rho R^3 \tag{13}$$

The details of the calculations leading to eq.12 are given in Ref.10, as well as an alternative treatment using the derivation of Bordewijk(Ref.9)instead of that of Hunt and Powles (Ref.8) in the estimation of P(t). Fitting the parameters or the model to various data allow them to be perfectly reproduced within error limits (see for instance Ref. 10, and also Ref.23 for more recent results). In fig. 3 and 4, a_o and R are compared with the closest distance of approach a_2 of an anion and a cation, as given by conductivity (table 1). When fitting a_o and R, we have to fit also ε_s and ε_m, the zero frequency limit of the overall permittivity and of the solvent contribution $\varepsilon_m(\omega)$. We shall discuss the last point later, in the section about the solvent relaxation. In fig. 3, it can be seen that a_o is not very far from a_2 for Li ClO_4 solutions in THF and ethyl acetate. It corresponds to the picture (bottom of fig. 3) of an ion pair which rotates and diffuses as the sphere of radius a_o circumscribed to two smaller spheres of diameter a_2 which represent the anion and the cation. In the case of DME solutions, a_o is definitely smaller than a_2 ; it can be ascribed to a difference in the
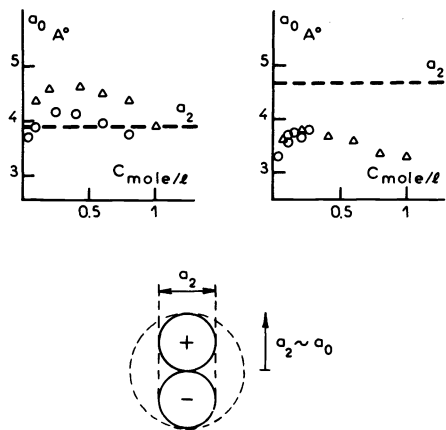
Fig. 3   Radius a_0 of the equivalent sphere representing an ion pair in diffusion and/or rotation. Left : Li ClO$_4$ solutions in THF (o) and ethyl acetate (Δ). Right : Li ClO$_4$(o) and Na ClO$_4$ (Δ) solutions in DME. Bottom : picture of an ion pair.
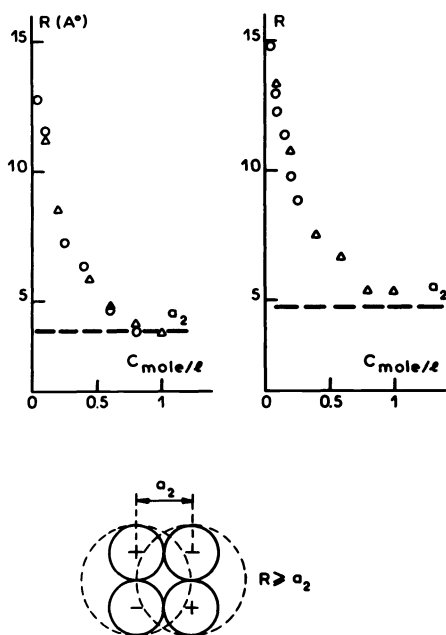

Fig. 4   Closest distance of approach R of two ion pairs. Left : Li ClO$_4$ solutions in THF (o) and ethyl acetate (Δ). Right : Li ClO$_4$ (o) and Na ClO$_4$ (Δ) solutions in DME. Bottom : picture of two ion pairs in close contact.

solvation process which can also be evidenced by the discussion of the solvent contribution to the relaxation data, as it will be seen below. The parameter R is not so well determined by experiment as a_0 is. It can be explained by the fact that R is rather related to the shape of the relaxation diagram ($\Delta\varepsilon(\omega)$) in the complex plane, see Fig. 1) whereas a_0 is directly related to a characteristic time. Nevertheless it can be seen that R has this property that it is always greater than or equal to a_2. If we retain again the picture of small spheres of diameter a_2 for the ions, the situation R = a_2 is shown in fig. 4 (bottom)

R being the closest distance of approach of two ion pairs whose ions are in the same plane.

Figure 5 shows, for the same systems, the apparent dipole moments of the ion pairs. We use the word "apparent" because they are calculated under the assumption that there is no correlation in the orientation of neighbouring ion pairs, and that the whole solute is in the form of ion pairs (neglecting the fact that quadrupole ions, with unknown dipole moments,
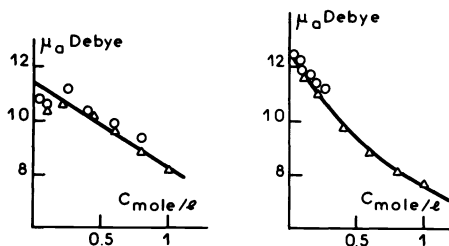

Fig. 5   Apparent dipole moment. Left : Li ClO$_4$ solutions in THF (o) and ethyl acetate (Δ). Right : Li ClO$_4$ (o) and Na ClO$_4$ (Δ) solutions in DME.

may exist). The formula used is that of Fröhlich-Kirkwood (Ref.24) applied to a mixture of dipoles μ (solvent) and μ_a (ion pairs) :

$$\frac{(\varepsilon_s - \varepsilon_\infty)(2\varepsilon_s + \varepsilon_\infty)}{9\,\varepsilon_s} = \frac{4\pi}{9kT}\,(\rho_m\,g\mu^2 + \rho\mu_a^2)\,\left(\frac{\varepsilon_\infty + 2}{3}\right)^2 \tag{14}$$

where ε_∞ is the infinite frequency limit of the permittivity and g the Kirkwood correlation factor for the solvent molecules. The first term of the right hand side can be rewritten with the same formula applied to the solvent, as :

$$\frac{(\varepsilon_m - \varepsilon_\infty)(2\,\varepsilon_m + \varepsilon_\infty)}{9\,\varepsilon_m} = \frac{4\pi}{9kT}\,\rho_m\,g\mu^2\left(\frac{\varepsilon_\infty + 2}{3}\right)^2 \tag{15}$$

The apparent dipole moment μ_a can be extrapolated to zero concentration, so as to give an actual dipole moment in a given solvent. In the case of Li ClO$_4$ in THF and ethyl acetate, the value thus found is (11.4 ± 0.4) Debye. It is higher than the value given in a previous paper (Ref. 10), (10.5 ± 0.5) Debye, where the model of ionic relaxation had been used with the condition $R < 2\ a_0$, which has been dropped in the present work. Both values, which do not differ from more than 10%, are close to the value 10.3 ± 0.3 Debye, recently given for Li ClO$_4$ in less polar solvents (Ref. 25). If we turn to the model consisting of two charges ± e separated by a distance a_2, the dipole moment should be about 19 Debye with a_2 given in table 1. In fact, it is necessary to take into account the polarizability α_+ and α_- of the ions, using for instance the Böttcher formula (Ref. 26)

$$\mu_a = e\ a_2\ \frac{1 + (\alpha_+ + \alpha_-)\,/\,a_2^{\,3} - 8\,\alpha_+\alpha_-\,/\,a_2^{\,6}}{1 - 4\,\alpha_+\alpha_-\,/\,a_2^{\,6}} \tag{16}$$

Chosing $\alpha(ClO_4^-) = 5{,}30 \times 10^{-24}$ cm^3 (Ref. 25), α_+ has to be taken as 13×10^{-24} cm^3, far larger than $\alpha(Li^+)$, to get $\mu_a = 11.4$ Debye. This can be interpreted as indicating that Li$^+$ is solvated. However this conclusion cannot be but qualitative, because eq. 16 hardly applies better than a crude approximation in that case. The same calculations can be performed for Li ClO$_4$ and Na ClO$_4$ in DME, where the values found for μ_a are 12.5 and 12.2 Debye, extrapolated to zero concentration. The corresponding α_+ values, calculated with $a_2 = 4.7 \times 10^{-3}$ cm, are about 32×10^{-24} cm^3. It can be qualitatively understood as Li$^+$ being more solvated in DME than in the other solvents.

The model of ionic relaxation has been used for several other systems, particularly with solutions of Bu$_4$ NBr (where Bu stands for n-butyl) (Ref. 10). The conductivity of this salt in acetone, and acetone + CCl$_4$ mixtures, in a wide concentration range, leads to $a_2 = 5.13$ Å. The ionic relaxation model applies to a series of solutions in the previous solvents, and also THF + benzene, THF + carbon tetrachloride and non polar solvents. In the latter, there is no dipole relaxation of the solvent molecules and the data can be analysed with $\varepsilon_m(\omega) \equiv \varepsilon_\infty$, this parameter being fitted. In these analyses, the further assumption $R = 2\ a_0$ has been found suitable. It is interesting that it is possible, for these systems, to have a good experimental determination of ε_∞ and that this quantity can be related to the overall (low frequency) polarizability of the ions through the simple assumption that it simply adds to the polarizability of the solvent, so that it is possible to write

$$\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} - \frac{d - Mc}{d_0}\ \frac{\varepsilon_{\infty_0} - 1}{\varepsilon_{\infty_0} + 2} = \frac{4\pi}{3}\,N_A\,\alpha\,c \tag{17}$$

where d and d$_0$ are the densities of the solution and of the solvent, ε_{∞_0} the dielectric constant of the latter (2.274 for C$_6$H$_6$, 2.228 for CCl$_4$), M the molecular mass of the solute, c its concentration and α its polarizability. As shown in fig. 6, the left-hand side of eq.17 is a linear function of c and the slope corresponds to $\alpha = 52.9 \times 10^{-24}$ cm^3. Since $\alpha(Br^-)$ is known to be 4.85×10^{-24} cm^3 and $a_2 = 5.13 \times 10^{-8}$ cm as previously said, we have everything to calculate μ with eq. 16, and 12.0 Debye is obtained. This value is in remarkable agreement with the 12.2 Debye independently found by Bauge and Smith from dielectric measurements at very low concentrations (Ref. 27).
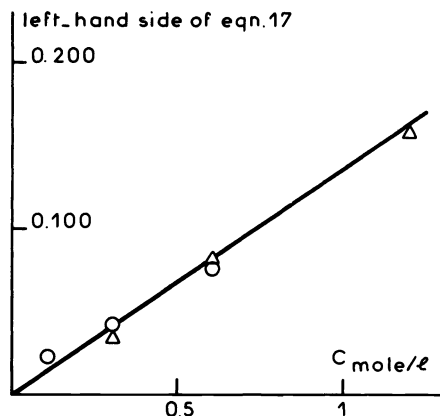
left_hand side of eqn.17

Fig. 6   Polarizability of Bu_4 NBr
calculated from ε_∞ in solutions of
benzene (o) and carbon tetrachloride (Δ),
through eq. 17.

Solvent relaxation

The perturbation of the solvent relaxation $\varepsilon_m(\omega)$ in the presence of salt had been observed
for a long time in the dielectric behaviour of aqueous electrolyte solutions. This topic was
reviewed by Hasted(Ref.28)and Pottel(Ref.29)some years ago.The real part of the permittivity,
ε', decreases with increasing salt concentration at every frequency used. The data are gene-
rally analysed without taking into account any positive contribution of the ions as we have
just discussed (in other words, $\Delta\varepsilon(\omega)$ is set to   zero   in eq. 1). Such an assumption
can be justified, in many cases, by the high permittivity of the solvents and by the fact
that the frequencies used are high enough. Moreover, association is not likely to occur to
such an extent as in the solutions studied in the present work. The main effect deduced from
the data is thus a decrease in ε_m, when compared to the dielectric constant ε_{m_o} of pure
solvents. Other systems of high dielectric constant solvents have been studied, and the same
effect is observed. For instance Barthel and al.(Ref.30) found a decrease in ε_m as high as
100 units for a 1 mole/l Li NO_3 solution in N-methylformamide (ε_{m_o} = 182). The relaxation
time of the solvents is also observed to change in the presence of salt, but it sometimes
increases, sometimes decreases, and very often does not change more than 20% at concentra-
tions less than 1 mole/l (Ref. 3). In the case of low dielectric constant solvents, the
details in the change of $\varepsilon_m(\omega)$ are hidden to a large extend by the amount of ionic relaxation,
as   can be seen on fig. 1. For that reason, the first step in the analysis is to consider
that the only parameter which changes is ε_m, so that we write

$$(\varepsilon_m(\omega) - \varepsilon_\infty) / (\varepsilon_{m_o}(\omega) - \varepsilon_\infty) = (\varepsilon_m - \varepsilon_\infty) / (\varepsilon_{m_o} - \varepsilon_\infty) \tag{18}$$

The subscript zero refers to pure solvent, ε_m is the zero frequency limit of $\varepsilon_m(\omega)$, the
complex permittivity. Such an approximation holds for Li ClO_4 solutions in THF and ethyl
acetate. It can be interpreted as follows : among the ρ_o molecules of solvent present in
a solution, only

$$\rho_m = \rho_{mo} - qc \tag{19}$$

of them reorient under the influence of the field. Around each cation (ClO_4^- being considered
as not solvated) q of them are tightly bound in such a way that the overall dipole moment of
the aggregate is zero. The value of ρ_m can be deduced from ε_m through the Fröhlich-Kirkwood
formula already quoted as eq. 15, hence q. The variations of q with c are shown in fig. 7
(left). When extrapolated to infinite dilution, q can be considered as a solvation number.
In the present case, the value of 6 is acceptable for such a model. In the case of DME, if
the calculations are made with eq. 18 for $\varepsilon_m(\omega)$, the values of q at the lowest concentrations
are higher than 30 (Ref. 23) : so high values are unrealistic for a model of rigidly bound
molecules in the absence of association between the solvent molecules. For that reason, we
dropped the assumption that the solvating molecules do not reorient and we assumed them to
rotate with a relaxation time τ_p, so that we write :

$$\varepsilon_m(\omega) = \varepsilon_p(\omega) + \Delta\varepsilon_m / (1 + i\omega\,\tau_p)$$

$$\varepsilon_m = \varepsilon_p + \Delta\varepsilon_m \equiv \varepsilon_{mo} \tag{20}$$

$$(\varepsilon_p(\omega) - \varepsilon_\infty) / (\varepsilon_{mo}(\omega) - \varepsilon_\infty) = (\varepsilon_p - \varepsilon_\infty) / (\varepsilon_{mo} - \varepsilon_\infty)$$

The meaning of these parameters, and the difference with eq. 18 are given in fig. 7 (bottom).
The Fröhlich-Kirkwood formula (Ref.15)is then used with ε_p instead of ε_m in order to calculate
ρ_m and q. The q values thus found are shown in fig. 7 (right) and it can be seen that the
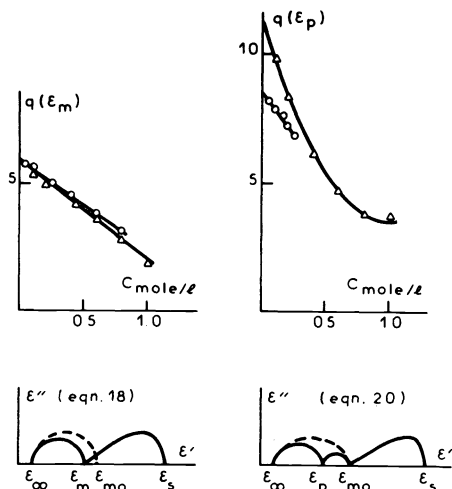solvation numbers are 9 for Li^+, 11 for Na^+. It remains to be explained why DME does not

Fig. 7   Solvation numbers.
Left : Li^+ in THF (o) and ethyl acetate
           (Δ)
Right : Li^+(o) and Na^+(Δ) in DME

behave as other solvents, but the solvation numbers thus found are then acceptable. The fact that the solvation sheath is not so rigid in DME could qualitatively explain why the ion pair rotates and diffuses more rapidly than predicted by the conductivity measurements, insofar as the value found for a_o is lower than a_2. We thus find another link between dielectric and conductivity measurements.

FAR INFRARED PROPERTIES

Though molecular liquids have been intensively studied by FIR spectroscopy many years ago (Ref. 31 and 32), there are only a few investigations on aqueous (Ref. 33) and non aqueous electrolyte solutions in the submillimeter region (Ref. 34 to 38). Most works on ionic solutions were performed at shorter wavelengths. This situation was mainly due to experimental difficulties to measure large absorption coefficients of liquids in this spectral region by means of the available spectrometer. Pioneer works on liquids were undertaken with the aim to examine the high frequency part of the dielectric relaxation (Ref. 39, 40). In the case of non aqueous electrolyte solutions, about which we are concerned here, preliminary investigations started many years ago in two ways : (i) a study of the response of tetraalkylammonium salts in benzene solutions (Ref. 34) ; (ii) a study of the "cation-band" (Ref. 41, 42). For the first case, the observed absorption was attributed to ionic vibrating aggregates. For the second one, it was firstly assumed to arise from ion-pair vibration (Ref. 41) and, then, from the solvated cation vibration (Ref. 42, 43).

In what follows, a survey of the FIR investigations on electrolyte solutions will be given for alkali metal salts and for tetraalkylammonium salts, with the emphasis upon ionic interactions. Beforehand, the present understanding of the FIR response of molecular liquids will be summarized, after a few comments about FIR spectroscopy.

FIR spectroscopy

Most devices are designed for the power absorption coefficient α to be measured. It is defined by Lambert's law: $\alpha = (1/l)\log P_o/P$ where l is the optical path length, P_o the incident power and P the transmitted power. It is related to the complex relative dielectric permittivity ε by :

$$\alpha = 4 \pi \bar{\nu} (\varepsilon'/2)^{1/2} \{(1 + (\varepsilon''/\varepsilon')^2)^{1/2} - 1\}^{1/2} = 2 \pi \bar{\nu} \varepsilon'' / n$$

where n is the real part of the complex refractive index of the material at the wavenumber $\bar{\nu}$. It is noteworthy that if the loss factor ε'' contains a conductivity term $\sigma/\omega\varepsilon_o$, the corresponding absorption α is proportional to the conductivity σ.

The absorption coefficient α can be measured by means of a grating spectrometer or a Michelson Fourier transform interferometer. The latter is more efficient at wavenumbers below 250 cm^{-1} and is now largely used (Ref. 44). A schematic diagram of such a device is given in Fig. 8. A broad band source (mercury lamp) is used to illuminate the interferometer. Compared to wavelength selective systems, the whole energy emitted by the source and transmitted by optical components and sample reaches the detector. Two inter-coherent beams are formed by means of a beam-splitter. One of these is reflected by a moving mirror introducing a phase delay. Interference takes place in the recombined emergent beam. The latter passes through the sample and falls onto the Golay detector. The output signal, recorded *vs* path difference, is the Fourier transform of the spectral energy distribution of the light reaching the

detector ; $\alpha(\bar{\nu})$ is obtained by recording interferograms with and without sample and rationing energy at every wavenumber. A lock-in detection is used, the light beam being modulated either
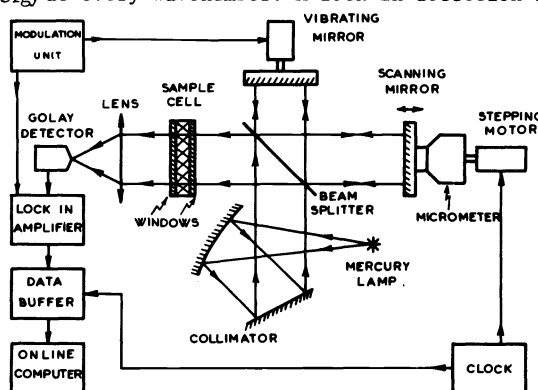

Fig. 8   Schematic diagram of a Fourier transform interferometer.

in amplitude by a chopper, or in phase by a vibrating mirror. A computer is needed to perform Fourier transforms.

However, severe limitations exist due to the available sources and detectors. For transmission measurements, a very short cell thickness must be used in the case of strongly absorbing liquids, as polar ones, and the precision drastically decreases when absorption increases. For instance, the precision on the amplitude is not better than 10 % when absorption reaches about 100 Neper cm^{-1}. Such a situation corresponds to most organic solvents. As far as a single liquid is concerned, this precision may be considered as acceptable. More accurate spectra can be obtained by studying the response of polar molecules diluted with non polar ones, this procedure being largely used in the literature. The problem is different when studying electrolyte solutions in polar solvents. Such a study implies a comparison of the solution spectrum with that of the pure solvent, in order to evidence salt effects. This difficulty has been recently overcome by use of new powerful FIR sources. They are wave-guided molecular lasers pumped by a high power IR laser. Taking advantage of the Stark effect for tuning energy levels, it is possible to obtain a large number of discrete lines in the range 20 - 185 cm^{-1} (Ref. 45). The resolution is about 5 to 10 cm^{-1}, which is sufficient for spectroscopy of liquids. Then more accurate α measurements can be performed by a transmission method (Ref. 46).

The laser spectrometer we have built (Ref. 46) for studies of electrolyte solutions is shown in fig. 9. The cell is a commercially available, continuously variable path length cell with polyethylene windows. Fluctuations of the FIR output power are eliminated by means of a differential detection. The signal emerging from the sample is detected and then electrically compensated by a variable gain G audioamplifier. Log G depends linearly on the thickness of the liquid with a slope α.
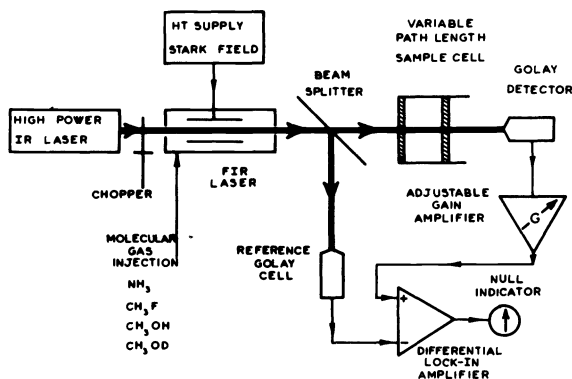

Fig. 9   FIR laser spectrometer

Solvents

Dipolar liquids exhibit a very important absorption which presents a maximum in the range 30 - 100 cm^{-1} for most liquids. It is now well established that this broad band absorption is the high frequency part of a profile extending from zero to THz frequencies (Ref. 47). This profile is a measure of the rotational motion of the polar molecules in the condensed state of matter. The observed behaviour is illustrated in fig. 10 for chlorobenzene, a well studied liquid, and for a few other organic liquids commonly used as solvents for electrolytes : propylene carbonate (PC), 1,2-dimethoxyethane (DME) and tetrahydrofuran (THF). Below 10 cm^{-1}, the absorption coefficient values are calculated from dielectric permittivity measurements. The vertical arrows in Fig. 10 indicate the frequency for which the loss factor ε'' is maximum. In the lower part of the microwave region, α practically varies as the square frequency, as shown in fig. 10 below 0.3 cm^{-1}. Above 1 cm^{-1} α approximately varies as the

square root of $\bar{v}$, up to its maximum. Afterwards, it drastically decreases.
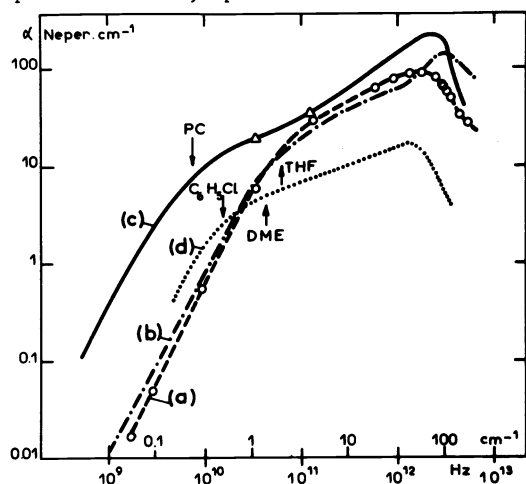

Fig. 10   Absorption spectrum vs frequency, at 298 K, plotted in logarithmic scales :
(a) tetrahydrofuran : data from Ref. 1,36,66.
(b) 1,2-dimethoxyethane : data from Ref. 23,46,67.
(c) Propylene carbonate : data from Ref. 68 and unpublished results.
(d) chlorobenzene : data from Ref. 46 and 69.

The arrows indicate the frequency for which the loss factor ε'' is maximum.

The analytical expressions which are usually used to represent the dielectric relaxation do not reproduce FIR data because they predict for α, either a (Debye) plateau or an increase when the dielectric relaxation time is "distributed". For instance, Fig. 11 illustrates the observed FIR absorption spectrum of THF in linear scales for α and the frequency. In this representation, the FIR response is magnified. The Debye plateau, calculated from dielectric relaxation data (Ref. 1), is equal to 44 Neper cm^{-1}, far below the observed maximum at 90 Neper cm^{-1}. It is clearly seen that both essential experimental facts are not accounted for by extrapolating the dielectric spectrum towards high frequencies : the return to the transparency in the visible region and the excess absorption defined by comparison with
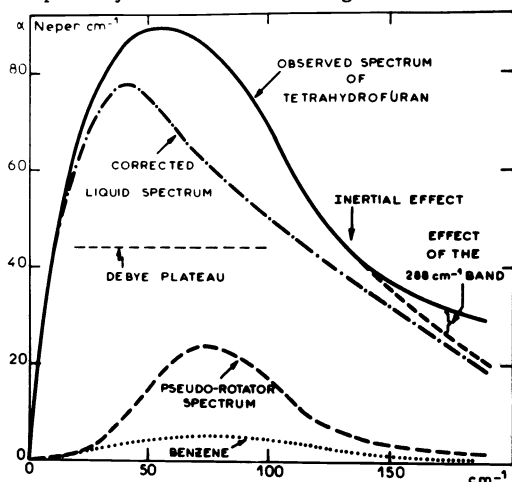

Fig. 11   FIR responses of tetrahydrofuran (from Ref. 6) and benzene (from Ref. 30) at 298 K. The observed spectrum of THF has been slightly corrected above 150 cm^{-1} because of an internal vibration band at 288 cm^{-1}. The other curves are discussed in the text.

the Debye plateau. The first point has been elucidated many years ago (Ref. 48). Inertial effects on the rotational motion of molecules were successfully invoked to explain the decrease of α. For a symmetrical top molecule, Leroy and Constant derived an expression for $\alpha(\bar{v})$ including inertia of molecules. Both low and high-frequency parts of the α spectrum were well described. In their formulation, two characteristic times were introduced such as :

$$\tau_d \cdot \tau_i = I / 2 k T \tag{21}$$

where τ_d is the dielectric relaxation time, τ_i the characteristic time for inertial effect defined as the correlation time for the angular velocity. To illustrate this, let us consider the case of THF, for which $\tau_d = 2.53 \times 10^{-12}s$ (Ref. 1). Because of the lower symmetry of the THF molecule, a reduced inertia moment I_r must be considered to apply in the above relation. I_r is an average moment, weighted by the dipole vector components in the molecular frame ; it is equal to 0.825×10^{-45} kgm^2 for THF, after Ref. 49. A value of $3.9 \times 10^{-14}s$ is found for τ_i. It corresponds to 135 cm^{-1}, in the high frequency part of the α spectrum, for α values lower than the Debye plateau (fig. 11).

The origin of the excess absorption has given rise to a number of works (see for instance Ref. 32, 47, 49 and references cited herein). The basic physical idea was to assume that each molecule undergoes rotational librations *i.e.* angular oscillations with a characteristic resonance frequency, in the cage formed by its neighbours. In this class of models, the most famous is the so-called itinerant oscillator model, initially proposed by Hill(Ref.50) and extended by several authors (Ref. 47). Two Langevin-type equations, including inertial effects, are required to describe both motions of the rotator and the cage. This model gives a good qualitative description of the α spectrum but is not able to fit the data accurately. Compared to the dielectric relaxation, the explanation of the FIR absorption is much more primitive at the present time.

Additional difficulties may arise because of other effects possibly contributing   to the FIR absorption. The first one is the coupling between libration and low frequency deformation of molecules. An example is given by the THF molecule. For a five membered ring, it is known that a FIR absorption occurs due to pseudo-rotation in the gas phase (Ref. 51). A first attempt has been made recently to estimate the intensity of this absorption in the liquid state, by scaling gas phase absorption data up to the liquid density (Ref. 32). Keeping in mind the high level of approximation, already outlined in Ref. 32, we extrapolate the estimated pseudo-rotator spectrum for a dilute solution to the density of the pure THF. The result is illustrated in Fig.11. According to Ref.32, this result may be considered as a maximum for this effect. Substracting it from the observed spectrum of pure THF, a corrected liquid spectrum is obtained. The apparent librational peak position is shifted by $20 cm^{-1}$ and the maximum of α is lowered by 13 Neper cm^{-1}. Another effect is a possibly induced absorption. It has been demonstrated that such an effect constitutes the origin of FIR absorption for non polar liquids (Ref. 52). As an example, absorption of benzene is shown in Fig. 11, reaching 5.2 Neper cm^{-1} at $80 cm^{-1}$. It arises from quadrupolar interactions. As far as we know, the spectral contribution of induced absorption has not been evaluated for polar liquids. Thus no correction can be attempted for THF. But for molecules similar to benzene, such an effect may well be expected with an order of magnitude similar to the benzene absorption. Applied to chlorobenzene, this correction would be large, since for this liquid the absorption is always lower than 17 Neper cm^{-1}.

To complete this survey on liquids, two comments have to be made. Firstly, it must be noticed that induced absorption spectra for non polar liquids can be accurately described by means of the Evans and Davies formalism for the orientational correlation function (Ref. 53). Secondly, for a predominantly rotational molecular motion, the Gordon sum rule yields the integrated intensity $A = \int_{band} \alpha(\bar{\nu}) \, d\bar{\nu}$ to be proportional to μ^2/I where μ is the dipole moment and I the average inertia moment (Ref. 54). It has been found that the product $A.I.\mu^2$ was approximately a constant for molecules of the same class (Ref. 55). Inversely, the Gordon rule may be used as a criterion to estimate the rotational part of a FIR band due to entities bearing an electrical moment μ.

From the above considerations, it can be concluded that it is still difficult to analyse the FIR response of any non-diluted polar liquid in terms of molecular dynamics. Further progress will be made firstly in the case of very simple liquids with this disadvantage that they are scarcely good solvents for ionic salts.

Electrolyte solutions

We have just seen that for molecular liquids, FIR absorption originates mainly from rotational motion, combined eventually with low frequency vibration modes. The rotational contribution occurs below $200 cm^{-1}$ and is conditioned by a cage effect. In the presence of ions, additional effects may be expected because of ion-ion and ion-solvent interactions, each one depending on the nature of the solvent and ions. For that reason, the case of alkali metal salts will be distinguished from that of tetraalkylammonium salts. For the former, solvation is the predominant phenomenon. For the latter, their ability to dissolve into weakly or non polar solvents favours ionic interactions.

Alkali metal salts

For this family of ionic solutions, numerous investigations were undertaken about the so-called "cation-band". These studies will not be discussed in detail here because they are covered in a review by Popov (Ref.43). The cation band is a strong, broad band which could not be assigned to the solvent or the solute. The frequency of the maximum mainly depends on the mass of the cation. For alkali cations, it ranges from about $400 cm^{-1}$ for Li^+ to about $110 cm^{-1}$ for Cs^+. The effect of the anion has been found more pronounced in the case of a weakly polar solvent, for instance THF, than for a highly polar one as dimethylsulfoxide. For Li^+, the frequency dispersion reaches $40 cm^{-1}$ in THF , depending on the anion (Ref. 42). From the observed behaviour in THF, it has been firstly suggested that the origin lays in anion-cation vibrations (Ref. 42). Further investigations in other solvents or systems such as crystals, glasses (Ref. 56), crown-ethers (Ref. 57) suggested that the cation

band mainly arose from cation-solvent vibrations, more or less influenced by the anion. In
the following, we give the general lines of a simple model for the short range ion-solvent
interactions, able to simulate the observed cation band frequencies.

Schematically, we can assume that the band position depends on three factors : the geometric
configuration of the solvation shell, the moving mass, the ion-solvent interaction energy.
From studies on solids or crown-ether complexes, with oxygen donor atoms, evidences were
found to assign the cation band to vibrations of cation-oxygen coordination polyhedra
(Ref. 58). Normal vibration calculations can be performed with the model of an asymmetric
stretching vibration of the metal-oxygen polyhedron. We restrict here to the simplest geo-
metric case for which the vibrating system is the M^+ ... O cation-oxygen band only. The ion-
solvent potential energy U_{M-O} may be represented by :

$$U_{M-O}(r) = \frac{e^2}{4\pi \, \varepsilon_o} \left(\frac{b}{r^n} - \frac{z\gamma}{r} \right) \tag{22}$$

where the oxygen atom is assumed to have a negative charge $(-\gamma e)$, with $0 < \gamma < 1$, the cation a
positive charge $(+ze)$. For oscillations to occur, the repulsive term b/r^n is required. The
equilibrium distance r_o between centers of M^+ and O is defined by setting the first deriva-
tive of energy to zero. The force constant k_{M-O} governing the vibration is given by the
second derivative of energy, taken for $r = r_o$. The vibration frequency $\bar{\nu}_{cation}$ is then given
by :

$$\bar{\nu}_{cation} = \frac{e\sqrt{z}}{4\pi c\sqrt{\pi \varepsilon_o}} \times [\gamma(n-1) / r_o^3 \cdot m^*]^{1/2} \tag{23}$$

where m^* is the reduced mass of the diatomic oscillator and c the light velocity. Let us
consider the series of monovalent $(z=1)$ cations : Li^+, Na^+, K^+, Rb^+, Cs^+. The distances
M^+ ... O are deduced from the Li^+ ... O distance (taken as 2Å) by adding the difference
between the ionic radii of M^+ and Li^+. The observed frequencies are well accounted for if
$\sqrt{\gamma}(n-1) = 1.2$ (Fig. 12). This condition is reasonably satisfied for instance by setting
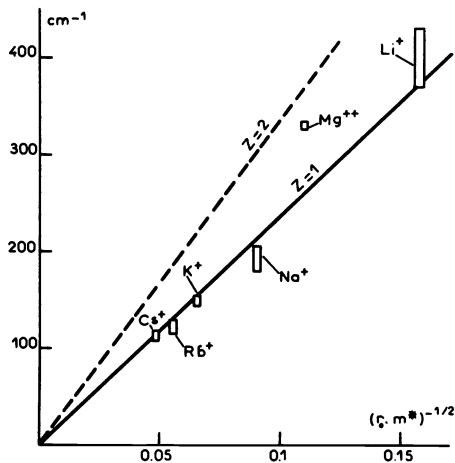$n = 7$, which yields a charge – 0.24 e on oxygen atom of the hypothetic solvent.

Fig. 12   Cation band position vs
the quantity $(r_o.m^*)^{-1/2}$; r_o and m^* are
defined in the text. Units are : r_o in
10^{-10}m, m^* in 10^{-3} kg/mole. Full line :
monovalent cations ; dotted line :
divalent cations.
Rectangles represent the observed
dispersion of data on anions and solvents

For a divalent cation, as Mg^{++}, the effect of the charge is to introduce a $\sqrt{2}$ factor in the
expression of $\bar{\nu}_{cation}$. As shown in fig. 12, our model yields 370 cm^{-1} for the Mg^{++} band
frequency, not far from literature data (Ref. 59 to 61).

The solvation cation band could be not the only effect observable in the FIR region and, for
the first time, an investigation has been recently undertaken in the low end of the spectrum,
in the vicinity of the FIR libration band of polar solvents (Ref. 36). A powerful source
– a laser – was necessary because measurements of both solvent and solution absorptions had
to be more accurate that usually. Lithium salts have been chosen in order to avoid an unde-
sirable overlap with the solvated cation band, just discussed above. The data obtained with
THF and LiClO$_4$ solutions in THF are shown in Fig. 13. For the more concentrated solution
(0.8 mol dm^{-3}), the absorption is significantly higher than that of THF. The excess absorption
defined as the difference between the solution and solvent spectra, presents a maximum around
110 cm^{-1}. Similar excess absorptions exist for LiClO$_4$ solutions in binary mixtures THF/C$_6$H$_6$
and PC/C$_6$H$_6$. The salt effect has been verified to be proportional to the salt concentration.
It reaches 25 Neper cm^{-1} per 1 mole dm^{-3} of LiClO$_4$ (at 110 cm^{-1}). No significant difference
can be detected by changing the ClO$_4^-$ anion into Cl$^-$. The small number of systems which can

be studied makes it difficult to assign an origin to the effect.The non visible effect of the anion mass does not seem in favour of ion pair vibrations. Furthermore, the amplitude is much smaller than that observed for ionic vibrations of tetraalkylammonium salts (see later). Another possible origin, not still established, could be an induced effect in THF molecule by the electric field of ions. In any case, sufficient data are still lacking for an interpretation to be given now.
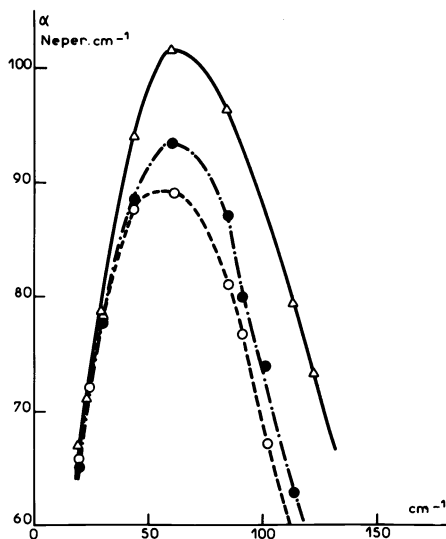

Fig. 13   FIR spectra of $LiClO_4$ solutions in THF. Symbols refer the laser data from Ref 36 and 46.
THF (o) ; 0.25 M $LiClO_4$: (o) ;
0.8 M $LiClO_4$: (Δ) .
Concentrations in molar units.

Tetraalkylammonium salts

In this section, we are dealing with tetraalkylammonium halides (R_4NX).Cations such as R_4N^+ are large in comparison with the alkali ions and no solvation shell due to linked solvent molecules has to be taken into account in solution at least in a first approximation. Most of them are very soluble in weakly absorbing solvents such as benzene,carbon tetrachloride,chloroform or THF.For solutions in these solvents,a broad,strong and asymmetrical absorption band is observed(Fig.14a).The maximum absorption per $mol.dm^{-3}$of salt is about 90 Neper cm^{-1}(at 110 cm^{-1})for Bu_4NCl and about 75 Neper cm^{-1}(at 80 cm^{-1})for Bu_4NBr or Pr_4NBr. Let us assume this band to arise from libration of ion pairs, characterized by a permanent dipole moment of, say, 11 D. The inertia moment with respect to an axis perpendicular to the dipole moment axis may be estimated $\sim$ 150 x 10^{-46} $kg.m^2$ for Bu_4NCl. From the Gordon sum rule, for most polar liquids, the quantity $\alpha_{max}/(N\mu^2/I)$ is equal to 1 to 2. This empirical criterion applied
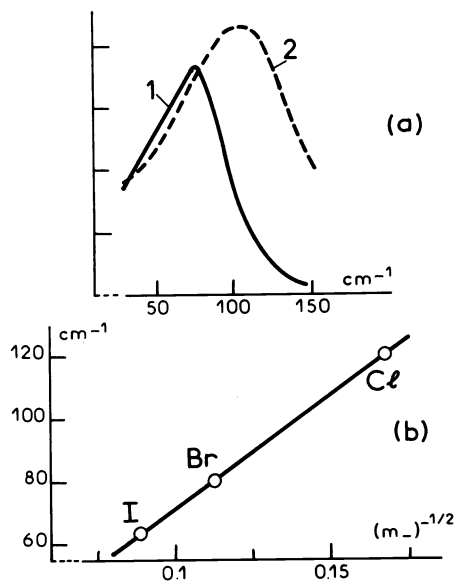

Fig. 14   Tetraalkylammonium halides.

(a) Absorption spectra (in absorbance units) at 298 K of : Pr_4 NBr in chloroform (1), Bu_4 NCl in a 5% v/v acetone-CCl_4 mixture (2).

(b) Dependence of the absorption maximum on the anion mass m.

to ion pairs will predict a α_{max} value of 20 to 40 Neper cm^{-1}per mole of salt,much lower than the actual absorption.The situation is similar for the other salts,bromide or iodide.Further-more, an important feature is that the frequency $\bar{\nu}_L$ corresponding to the absorption maximum mainly depends on the anion, the cation being much heavier. As shown in Fig. 14b, the picture of the harmonic oscillator is well verified : the quantity $\bar{\nu}_L{}^2.m_-$ is a constant, m_- being the anion mass. These facts, associated to the lack of solvent and salt concentration depen-dence, suggest that $\bar{\nu}_L$ is related to vibration.

If $u_L(r)$ is the interionic potential energy in solution, $\bar{\nu}_L$ is calculated from m_{+-}, the redu-ced mass anion-cation, and from a force constant k_L. This latter is given by the second deri-vative of $u_L(r)$ with respect to the anion-cation distance r and taken for the equilibrium distance in the pair r_L. In recent papers (Ref. 62, 63), we have shown that for tetraalkylam-monium salts, a realistic interionic potential could be derived from properties of the solid. The proposed form was :

$$u_{ij}(r_{ij}) = \frac{1}{4\pi\varepsilon_o} \left[\frac{e_i e_j}{r_{ij}} - \frac{(\alpha_i + \alpha_j)e^2}{2\,r_{ij}^4} - \frac{c_{ij}\,e^2}{r_{ij}^6} + \frac{be^2}{r_{ij}^n} \right] \qquad (24)$$

where r_{ij} is the distance between the ions i and j,having a charge e_i or e_j,and polarizabili-ties α_i and α_j respectively.The $r^{-4}$and r^{-6}terms can be estimated from literature data. The soft repulsive b/r^n term must necessarily be introduced for an ion-ion vibration to exist. The b coefficient is deduced from the equilibrium condition for the crystal, n being chosen *a priori*. It depends on the crystal structure, especially through the shortest anion-cation distance and the number of first neighbours (Ref. 64). A first approximation for the series of tetraalkylammonium halides was obtained by assuming ions to be identical and distributed on a body-centered cubic arrangement (Ref. 63). A more refined potential has been derived for tetrapropylammonium bromide by considering the true structure. For this salt, the set of parameters was : n = 9 ; c = 86.2 x 10^{-50} m^5 ; α = 15.0 x 10^{-30} m^3 ; b = 7.20 x 10^{-76} m^8 ; the shortest anion-cation distance in the lattice : 4.94 x 10^{-10} m ; all ions being identical (Ref. 63). This direct anion-cation potential, $u_{+-}(r)$, is able to predict an ion-pair vibra-tion frequency very close to the experimental one. This good agreement has been obtained with the assumption that any solvent effect in the interionic potential gives negligible contributions into both the first and second derivatives of the potential energy.

It is interesting to use this soft ionic potential to calculate the association constant K_A in the Bjerrum sense. It is defined (Ref. 64) by :

$$K_A = \frac{1-\alpha}{\alpha^2 c} = 4\pi\,N_A \times 10^3 \int_o^q r^2 . \exp\left[\frac{-\bar{u}(r)}{kT} \right] dr \qquad (25)$$

To here c is the salt concentration in mol.dm^{-3}and $\bar{u}(r)$ represents the potential of mean force between two ions. The calculated values for the association constant K_A are illustrated in Fig. 15 as a function of the solvent dielectric constant, in the case of Pr$_4$NBr. Two cases have been considered. The first corresponds to the restricted primitive model (curve "b"), with a = 6.48 Å for the closest distance of approach anion-cation (Ref. 65). This potential
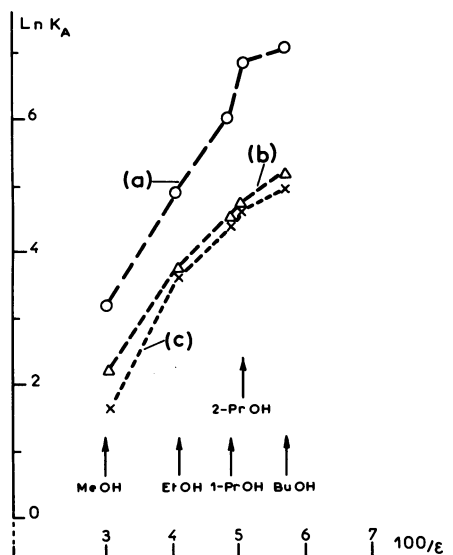

Fig. 15   Ionic association constant for Pr$_4$NBr as a function of the dielectric constant.
(a) from conductivity data
(b) primitive model with a = 6.48 Å ;
(c) soft interionic potential elabo-rated from FIR data.

is unable to yield vibrational motion. The second case is relative to the soft potential $u_{ij}(r)$ defined above, the solvent acting only by its dielectric constant ε (curve (c)). Both models yield very similar values for K_A, which are far below the K_A values deduced from conductivity data (curve (a)). This result suggests that a contribution is lacking in the potential of mean force which could be the short range ion-solvent forces (Ref. 64), *ie* :

$$\bar{u}\,(r_{ij}) \;=\; u_{ij}\,(r_{ij}) + u_{SR}\,(r_{ij})$$

Then, the association constant would become the product of two factors, one originating from the direct interionic potential, the other from the short range ion-solvent potential.

To summarize, the short range ion-solvent contribution cannot be neglected for K_A calculations but seems not significant to interpret FIR ion pair frequencies. It is concluded that $u_{SR}(r)$ does not contribute markedly to the curvature of the potential of mean force which governs the ion pair vibration. Inversely, a refined description for the short range ion-ion potential is not needed to calculate an association constant.

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