THE DYNAMICS OF ELECTRIC FIELD EFFECTS IN ION PAIRING PROCESSES

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Abstract - The theory of electric field effects in ionic systems is revie-
wed and their dynamic aspects related to chemical relaxation phenomena in
ionic equilibria. The theoretical descriptions are specified for organic,
low polar solvents.
A critical discussion is given of the field modulation technique, a new re-
laxation method based on the field dissociation effect and particularly
suited for the investigation of ionic equilibria in non aqueous media. The
domain of applicability of the method, the inherent limitations and some
remaining problems are treated. The value of chemical relaxation measure-
ments for the study of ion pairing phenomena is assessed from experimental
investigations. It is shown that the results obtained substantiate the
sphere in continuum model as a basic model for ionic interactions; ionic
processes in low polar media are well described from a diffusion treatment
for hard-sphere ions in a continuous medium.
The use of the field modulation technique in carbanion chemistry is des-
cribed. The way new information is obtained from relaxation measurements
on processes such as solvent-separation, ionic dissociation and aggrega-
tion is critically discussed.

INTRODUCTION

Ion pairing, triple ion formation, solvation phenomena, ionic aggregation ... are key processes
in the mechanistic description of a large class of organic reactions. A major tool for the
investigation of these processes are conductance measurements which yield information on the
distribution between ionic and non-conducting species. The common experimental approach are
to study this distribution as a function of the relevant parameters e.g. temperature, composi-
tion of the medium, concentration of polar solutes ... However, a major drawback of these
conductance techniques is their almost all or none response, i.e. only discriminating between
species with and without electric charge. While the conductance yields very accurate informa-
tion on the relative population of these states one would like to know the chemical *way* how
these species are interconverted. To answer the latter problem - which is mechanistically
the more important - information on the dynamic properties of dipolar or ionic intermediates,
eventually present at very low concentration, has a crucial importance. These questions be-
long to the realm of chemical kinetics. For a complete analysis of the interconversion pro-
cesses of chemical species all the elementary steps should be analyzed for their dynamic be-
havior. The rates of many elementary ionic processes are often very high and it is therefore
imperative in this kind of studies to apply chemical relaxation techniques.

All chemical relaxation techniques rely fundamentally on the perturbation of a chemical equili-
brium state by a fast change in an intensive thermodynamic variable and the subsequent measu-
rement of the adjustment of the system to the new equilibrium conditions. Both perturbation
and response detection can be carried out either in the time- or the frequency domain. Irres-
pective of experimental difficulties frequency domain techniques - stationary relaxation
methods - are to be preferred for their extreme sensitivity and accuracy, properties essen-
tially derived from inherent averaging in repetitive perturbations. Whatever the method used
the time course of adjustment to the external conditions - expressed by the relaxation time(s)-
depends on all the kinetic parameters describing the dynamic properties of the perturbed sys-
tem. In considering the application of chemical relaxation methods for the investigation of
ionic processes in non aqueous media the two essential aspects of relaxation techniques, i.e.
perturbation and detection of the subsequent response, should be clearly kept in mind.

In recent past one of us has developed a very sensitive stationary, i.e. in the frequency
domain, relaxation method for the investigation of ionic processes in media of low polarity
(1-3). In this technique the perturbing parameter is an electric field while the response of
the system is measured from the frequency dependent properties of the sample solution used as
an electric circuit element. In this paper we review this new method especially in view of
the application towards the study of organic reaction mechanism. The value of the technique

will be assessed from experimental investigations, some in the field of carbanion chemistry.
For a proper understanding of the methods used it is obligatory to have some knowledge of
electric field effects in chemical reactive systems and especially of the relation between
electric field strength and ionic equilibria.

ELECTRIC FIELD EFFECTS IN IONIC EQUILIBRIA

An equilibrium system tends to oppose a change in the external conditions governing its equi-
librium position - the famous theorem of Le Châtelier-Braun. In systems the energy of which
depends on the electric field density the field induces such an anisotropy as will reduce the
field density. At low field strength the system response is always linear and contains infor-
mation on density and translational, and/or rotational, properties of the species interacting
with the field. At high field strength the mobility becomes field dependent while in chemi-
cal reactive systems the density of interacting species increases due to an equilibrium shift.
These effects result in a gain in electrostatic stability at the expense of free energy of
the system. From these general arguments we infer the possibility of non linear effects in
chemical reactive systems when subjected to high electric fields. The nonlinear behavior of
ionic solutions at high electric field strength is indeed well known, as is the influence of
electric fields on dipolar equilibria.

Solutions of strong electrolytes show a small increase in conductance, which can be measured
as a deviation from Ohm's law, in high electric fields. After its discoverer this effect is
known as the first Wien effect (4). This nonlinear property of electrolyte solutions is
satisfactorily explained from the inability for the fast moving ions to build up an ionic at-
mosphere, resulting in an increase in mobility. The second Wien effect (5,6) is a much more
pronounced conductance increase in solutions of weak electrolytes subjected to high electric
fields. This effect is due to an enhanced rate of ion pair dissociation as conclusively
shown by Onsager (7); the effect is therefore also known as the field dissociation effect.
A thermodynamic approach to the field dissociation effect is not feasible because a system
containing free charges never reaches equilibrium in the presence of an electric field. A
successfull theoretical description of the effect can therefore only be obtained from the
electrodiffusion treatment as carried out by Onsager. For the relative increase of dissocia-
tion rate of an ion pair under field conditions Onsager obtained the result :

$$k_d(E)/k_d(E=0) \ = \ F(2\beta q) \ = \ 1 + 2\ \beta q \ + \ \frac{1}{3}\ (2\ \beta q)^2 \ + \ ... \qquad [1]$$

with

$$q \ = \ -\ \frac{e_1 e_2}{2Dk_B T} \qquad \text{and} \qquad 2\beta \ = \ \frac{|(e_1 u_1 - e_2 u_2)E|}{(u_1 + u_2)k_B T}$$

e_i and u_i is the charge, respectively the mechanical mobility of ion i, D is the dielectric
constant of the medium, k_B the Boltzmann constant and E the electric field strength, all ex-
pressed in cgs-units.
The parameter q is the Bjerrum distance, which has the physical meaning of the distance within
which the mutual electrostatic interaction energy of two oppositely charged ions becomes high-
er than their thermal interaction with the surrounding medium. The reciprocal distance 2β
depends on transport parameters and the absolute value of the field strength showing, apart
from the discontinuity at the origin, the linear relation between field dissociation effect
and field strength. For symmetrical electrolytes 2β becomes independent of the mobilities
and in that case $1/2\beta$ represents physically a distance at which two oppositely charged ions
form a dipole with an electrostatic stabilization energy $k_B T \cos\theta$, θ being the angle be-
tween the dipole and the field. It is also important to note that Onsager's theory neglects
shielding effects of the ionic atmosphere as well as all hydrodynamic interactions. Moreover
the theory is explicitly derived for constant electric fields; as yet no theory of the fre-
quency dependent properties of the field dissociation effect has been made.
Because the association rate for the ions is independent of the electric field, as proved
long ago by Langevin (8), we can write for the thermodynamic constant for ion pair disso-
ciation :

$$K_D(E) \ / \ K_D(E=0) \ = \ F\ (2\ \beta q) \qquad [2]$$

Or, specified for a uni-univalent electrolyte and retaining only the linear part of the func-
tion F(2 βq) :

$$\frac{\delta \ln K_D}{\delta |E|} \ = \ \frac{e_o^3}{2\ Dk_B^2 T^2} \qquad [3]$$

From this result we see that the field dissociation effect will be most pronounced in low po-
lar media. Moreover a numerical calculation shows that with rather modest electric fields a
measurable increase of a few percent in dissociation equilibrium constant can be obtained at
low dielectric constant. This increase in dissociation is most easily measured as an increase
in the conductance, or specific conductivity σ, of the solution. Generally we can write :

$$\frac{1 - \alpha}{2 - \alpha} \frac{dK_D}{K_D} = \frac{\Delta\sigma}{\sigma} \qquad [4]$$

This result shows that the relative change in conductance is also most pronounced when the degree of ionic dissociation α is very small, a situation usually met in media of low polarity. For a symmetrical electrolyte no parameters of transport theory appear in Onsager's result describing the field dissociation effect. It is therefore tempting to make a simple picture of the physical process responsible for the enhanced dissociation of an ion pair in field conditions. The species described as an ion pair in Onsager's theory is any configuration of two oppositely charged ions within the Bjerrum association sphere. The configuration with two ions in contact will have the highest probability in this association sphere while the state of two ions at the Bjerrum distance has only a fleeting existence. This state may indeed be considered as the transition state for the dissociation process because the probability for collapsing into an ion pair is for this configuration equal to the probability for separation into free ions. The facilitated dissociation of a symmetric ion pair can now be regarded as due to the reduction in electrostatic work needed to separate the "Bjerrum dipole" i.e. the dipole formed by the two ions at the Bjerrum distance, into free ions. Making the assumption of a fast rotation of the Bjerrum dipole towards energetically the most favorable orientation we can write for the standard free energy change for dissociation under field conditions :

$$\Delta G^\circ (E) = \Delta G^\circ (E=0) - \mu_{Bj} N_o E \qquad [5]$$

or writing the Bjerrum dipole moment μ_{Bj} as $e_o q$, we obtain for the dissociation equilibrium constant :

$$K_D(E) = K_D(E=0) \exp e_o q/k_B T \qquad [6]$$

which is, after expanding the exponential and retaining only the first term, exactly the linear part of Onsager's result. (The assumption of favorable orientation is somewhat an equivalent of using the absolute value of the field strength). Of course this picture is very elementary but we may obtain this way some insight in the frequency dependence of the field dissociation effect. We indeed conjecture that at alternating fields of high frequency the field dissociation will disappear as a consequence of the finite orientational mobility of the Bjerrum dipole, which is linked to the transport properties of the ions in the given medium.

CHEMICAL RELAXATION IN IONIC EQUILIBRIA

Electrolyte solution theories are predominantly occupied with ionic solutions in which only free ions and ion pairs - defined as ions in (electrostatic) contact - are present. These solutions are indeed the most simple systems in which the basic model, known as the sphere-in-continuum model, can be subjected to experimental test. It is therefore instructive to analyze the chemical relaxation of the ionization equilibria in these simple systems.
As shown by some elementary considerations, and substantiated by more elaborate interionic attraction theories, the single presence of simple ion pairing can be deduced from conductance measurements. For simple ion association the equivalent conductance is inversely proportional to the square root of total concentration of ionic solute. Deviations from this relation reveal the presence of higher aggregation, e.g. triple ion formation, which eventually leads to a situation where the equivalent conductance increases with total concentration of ionic solute. The physical reason behind these changing dependence of equivalent conductance upon concentration is simply related to a change in number of conducting species obtained from one ion pair.
In what we call the simple domain, i.e. the concentration region within which equivalent conductance is inversely proportional to total concentration, the distribution between ion pairs and free ions can formally be written as a dynamic equilibrium :

$$A^+B^- \underset{k_r}{\overset{k_d}{\rightleftarrows}} A^+ + B^- \qquad [7]$$

Considering the ions as hard spheres subjected to Brownian motion in a continuous medium with dielectric constant D and viscosity η, and defining the ion pair as two ions at a distance a, which may be the distance of closest approach, i.e. the sum of the ionic radii, we can derive theoretical expressions for ionic encounter and ion pair dissociation rate. The only dynamic process involved is the diffusion of the ions and the dissociation and recombination processes are therefore said to be diffusion controlled.
For the diffusion controlled recombination rate constant k_r we can write, according to Debye (9) :

$$k_r = \frac{8 \ 10^{-3}}{3} N_o e_o^2 \frac{1}{D \eta a} \qquad [8]$$

In writing this expression we assumed the ions to have equal radii, a being their sum, and an electrostatic interaction distance much larger than the contact distance a, a situation which is always realized in media of dielectric constants lower than 10. The term $10^{-3}N_0$ in eq.8 introduces the usual molar units for this bimolecular rate constant.

If no subsequent change occurs upon the formation of an ion pair the dissociation is a simple diffusion controlled separation process the rate constant of which is, according to Eigen (10) given by :

$$k_d = \frac{2}{\pi} \frac{e_o^2}{D\eta a^4} \exp - \frac{e_o^2}{Dk_BTa} \qquad [9]$$

The ratio of these two rate constants is the thermodynamic dissociation constant as given by Fuoss (11):

$$K_D = \frac{3 \; 10^3}{4\pi N_o a^3} \exp - \frac{e_o^2}{Dk_BTa} \qquad [10]$$

Considering the three previous equations it should be clear that for diffusion controlled association dissociation phenomena of ions in a medium of dielectric constant D and viscosity η the mere knowledge of the distance a allows a complete calculation of the static *and* dynamic behavior of the ion pairing processes. The value of a can in principle be obtained from conductance measurements.

The relaxation time τ for the ionic equilibrium 7 is given by :

$$\tau^{-1} = k_d + 2 k_r \bar{C}_{ion} \qquad [11]$$

where $\bar{C}_{ion}$ is the equilibrium concentration of either ionic species. A small degree of dissociation, as is most often the case in low polar media, means a very small k_d which can then usually be neglected vs. $2 k_r \bar{C}_{ion}$. Conductance, being essentially a measure of ionic concentration, allows the calculation of K_D and hence of a and it is therefore clear that the relaxation time for the ionization equilibrium can be derived from conductance measurements. This was shown by Langevin (8) in his investigation of ionic recombination processes in gases. Using Langevin's expressing for the recombination rate constant and noting that $\sigma = \Sigma_i n_i e_o^2 u_i$ (n_i number of ions i per cm^3) the reciprocal relaxation time for equilibrium 7 becomes:

$$\tau^{-1} = \frac{8\pi}{D} (e_o^2 u_A n_A + e_o^2 u_B n_B) = 8\pi \frac{\sigma}{D} \qquad [12]$$

From the foregoing theoretical considerations the importance of accurate measurements of relaxation in ionic solutions becomes clear. In first instance, the reciprocal relaxation time being a direct measure of ionic concentration, allows an independent test of the electrolyte solution theories. Secondly, and mechanistically of great importance, the dependence of the reciprocal relaxation time upon the total concentration of ionic solute contains generally information on the *way* the ionic species are generated. The values of the rate constants obtained, and their dependence on the intensive variables, will define whether the ionic processes are diffusion controlled.

Some examples may profitably illustrate the second point. Expressing the concentration of free ions as a function of total concentration of ionic solute (c_o), we write for the reciprocal relaxation time of equilibrium 7, with the assumption of very low degree of dissociation :

$$\tau^{-1} = (2 k_r K_D^{1/2})c_o^{1/2} = 2(k_r k_d)^{1/2} c_o^{1/2} \qquad [13]$$

From the concentration dependence of τ^{-1}, and knowing the degree of dissociation, the values of the recombination and dissociation rate constant are obtained and these values may be compared with the theoretical predictions.

An ionisation process which involves aggregation of ion pairs with a subsequent dissociation in charged species may obey a completely different expression for the reciprocal relaxation time. If we consider for example the formation of triple ions - the presence of which is revealed by conductance - as a result of the dissociation of an ion pair dimer :

$$2 \; A^+B^- \underset{K_{dim}}{\rightleftarrows} (A^+B^-)_2 \underset{k_r}{\overset{k_d}{\rightleftarrows}} A^+ + B^-A^+B^- \qquad [14]$$
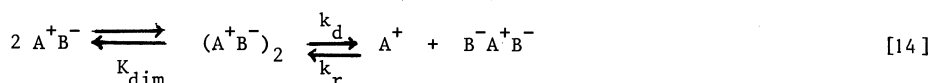
Depending on equilibrium position and equilibration rate of the dimerisation process different expressions for the relaxation time of the ion forming process apply. For example, if the dimerization is fast compared to the ionic dissociation we can write :

$$\tau^{-1} = k_d \frac{4\,K_{dim}c_o}{1 + 4K_{dim}c_o} + 2(k_r k_d K_{dim})^{1/2}c_o \qquad\qquad [15]$$

where c_o is the total concentration of ionic solute. In the second term we note a *linear* de-
pendence of the reciprocal relaxation time upon total concentration. Depending on the value
of the dimerisation constant the first term may, or may not, depend on concentration while
k_d, being the dissociation rate constant for the dimer, is not necessarily negligible. If
the dimerisation equilibrium is not perturbed by the electric field we may also obtain a li-
near relation between reciprocal relaxation time and total concentration.

In the case where aggregation becomes slow compared to the ionisation process we expect the
relaxation time to describe the dynamic properties of the aggregation equilibrium. Here we
may perhaps emphasize that even for these more complex situations the relaxation behavior
could in principle be derived from theoretical considerations based on the sphere in conti-
nuum model and using interionic distances obtained from conductance. However, when specific
solvation effects appear the sphere in continuum model becomes obviously inapplicable and only
the experimental investigation of the relaxation of the ionic equilibria will yield, in favo-
rable conditions, information on the dynamics of the solvation phenomena. If, for example,
the conversion of an externally solvated ion pair to a solvent separated ion pair is slow
compared to the dissociation into free ions the relaxation time for ionisation will essen-
tially be determined by the dynamics of this interconversion process.

THE FIELD MODULATION TECHNIQUE

In the field modulation technique the nonlinear behavior of an electrolytic resistance in high
electric fields is used to obtain information on the relaxation response of electrolytic equi-
libria. The advantages of electronic modulation and frequency conversion techniques are fully
exploited in this stationary relaxation method. Basically a solution of a weak electrolyte
is subjected to repetitive high frequency, high amplitude electric field pulses. The sample
is used as an electric, nonlinear circuit element the dynamic properties of which are analy-
zed from the frequency response. A detailed understanding of the method can be obtained from
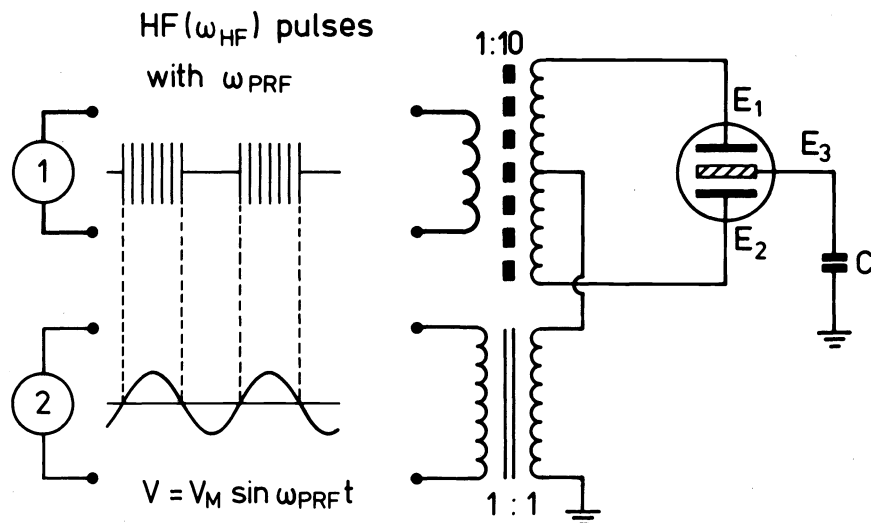a discussion of the schematic circuit given in figure 1.

Figure 1
Schematic circuit for the measurement of the field dissociation effect and
its dispersion. Generator 1 is a square wave (0.01-30 kHz) modulated high
frequency (0.1-1 MHz) high voltage (0.1-1 kVpp) driving a step up (1:10) fer-
rite core transformer. Generator 2 is a low voltage (1-20 Vpp) sinusoidal
oscillator synchronously locked on the square wave signal modulating the po-
wer oscillator. The sample cell contains, in a very symmetric arrangement,
three electrodes two of which (E_1 and E_2) are connected to the high voltage
transformer output terminals. Electrode E_3 is, over capacitor C (10pF-22nF),
grounded for a.c. signals. Electrode area is relatively uncritical while
the spacing between the HV electrodes and the center electrode E_3 is of the
order of 0.2-1 mm, depending on particular cell design. The center tap of
the high voltage transformer is connected, over an isolation transformer,
to oscillator 2.

A step up ferrite core transformer driven from a square wave modulated power oscillator
(oscillator 1) delivers a high voltage, high frequency signal to the HV-electrodes E_1 and E_2
of the sample cell. The sample is therefore subjected to square wave modulated high electric
fields which results, as a consequence of the field dissociation effect, in a modulation of
the conductance of the solution. The central concept of the field modulation technique is
the use of this conductance modulated sample as the load of a generator delivering a sinusoi-
dal signal with a frequency equal to the modulation frequency. It is easy to see that this
results in an intermodulation signal containing a d.c. term-proportional to the modulation
depth – which can be accurately measured. In the experimental set up the conductance modula-
tion and the intermodulation products are generated in the same circuit. A sinusoidal genera-
tor (generator 2) is therefore locked in frequency and phase to a square wave signal – the
main timing signal – also used to modulate the HV-HF power oscillator. The signal of this
low power sinusoidal generator is applied, over an isolation transformer, to the center tap
terminal of the high voltage transformer. In the field on period the sample conductance is
high, due to the field dissociation, and a "large" current flows from the sinusoidal genera-
tor through the sample cell. As a consequence a number of electric charges are brought on
capacitor C, a capacitor which effectively short circuits electrode E_3 for a.c. signals. In
the field off period the sample solution regains the normal low conductance and a "small" cur-
rent flows back, through the sample, to the sinusoidal generator or, otherwise stated, not
all the charges accumulated in capacitor C in the field on period can leave this capacitor
during the equally long field off period. We therefore observe, under stationary conditions,
a net amount of charge residing on capacitor C. Of course these charges can be measured, with
a high impedance voltmeter, as a d.c. voltage over capacitor C. It is intuitively clear that
the amplitude of this d.c. voltage is proportional to the amplitude of the sinusoidal signal
(V_M) and to the relative conductance change of the solution ($\Delta\sigma/\sigma$), the modulation depth.
Retaining only the square wave envelope of the high voltage, high frequency signal – neglec-
ting their internal, high frequency structure – a mathematical analysis (2) of the modulation
circuit gave for the d.c. voltage on capacitor C, assuming a small relative conductance change
(about 1%) :

$$V_{d.c.} = \frac{\Delta\sigma}{\sigma} \cdot \frac{V_M}{\pi} = g \left(\frac{\Delta\sigma}{\sigma}\right)_{Onsager} \cdot \frac{V_M}{\pi} \qquad [16]$$

where g is a correction factor taking into account the deviations of the experimental value
of $\Delta\sigma/\sigma$ from the value calculated according to Onsagers theory. More specifically, g is a
function of the high frequency within the pulses showing a rather complex dispersion with
ω_{HF}.

An important assumption in the foregoing discussion was the instantaneous character of the
response of the sample upon the perturbation. This assumption is valid as long as the pulse
duration is relatively long – at low pulse repetition frequencies – and the ionic equilibrium
changes are completely in phase with the perturbation. However, when the pulse repetition
frequency approaches the reciprocal relaxation time of the ionisation equilibrium the sample-
response will progressively lag behind the perturbation. As a result of this lag in response
the relative conductance change, or modulation depth, will become smaller lowering the modula-
tion efficiency. This is measured as a decrease of the d.c. voltage on capacitor C with an
increase of the pulse repetition frequency. Ultimately at pulse repetition frequencies much
higher than the reciprocal relaxation time of the ionisation equilibrium the d.c. signal va-
nishes completely. An analysis of the time dependent properties of the modulator circuit
yields for the d.c. voltage on capacitor C, as a function of pulse repetition frequency ω_{PRF}:

$$V_{d.c.} = \left(\frac{V_M}{\pi} \frac{\Delta\sigma}{\sigma}\right) \frac{1}{1 + \omega_{PRF}^2 \tau^2} = \frac{V_{d.c.\ max}}{1 + \omega_{PRF}^2 \tau^2} \qquad [17]$$

where $V_{d.c.\ max}$ is the d.c. signal measured at low pulse repetition frequency. Equation 17,
derived under the usual assumption of small perturbations, is recognized as a classical dis-
persion equation. The relaxation time τ obtained from this dispersion is the relaxation time
of the ionic dissociation equilibrium responsible for the field dissociation effect and is,
as previously shown, connected to the mechanism of ion formation.
A useful corollary of this technique is the possibility of a direct measurement of the con-
ductance of the sample solution. Indeed the d.c. signal on capacitor C does not appear, or
disappear, instantaneously but the charging of this capacitor is determined by a characteris-
tic time constant which yields, if the capacitance of C is exactly known, the cell resistance.
From a knowledge of the cell geometry, obtained from calibration measurements, the specific
conductivity is then easily derived. Moreover the high voltage, high frequency fields seems
to "clean" the electrodes avoiding the polarisation effects often encountered in conductance
measurements in solvents of low polarity.

A careful analysis of the potential of the field modulation method shows that a wide variety
of problems can be studied. Indeed the measuring principle has general applicability and
allows the investigation of the dynamics of processes underlying nonlinear behavior. Of
course the method is a stationary technique prohibiting the use of highly conducting systems,

e.g. aqueous solutions, due to an excessive heating under high electric fields. However the field modulation technique is successfully applied to the investigation of autoprotolysis in water (12) and solid acetic acid (13). Another illustrative example of the possibilities of these modulation methods is the study of photoconductive phenomena in solids where the conductance modulation is impressed by intensity modulated light (14).

A major remaining problem, connected to further developments in ionic solution theory, is the high frequency dependence of the field dissociation effect which vanishes even at low pulse repetition frequency upon increasing the high frequency within the pulses.

In figure 2 some typical dispersion curves are presented showing the very good accuracy with which the relaxation behavior of electrolyte solutions in low polar media can be investigated with the field modulation technique.
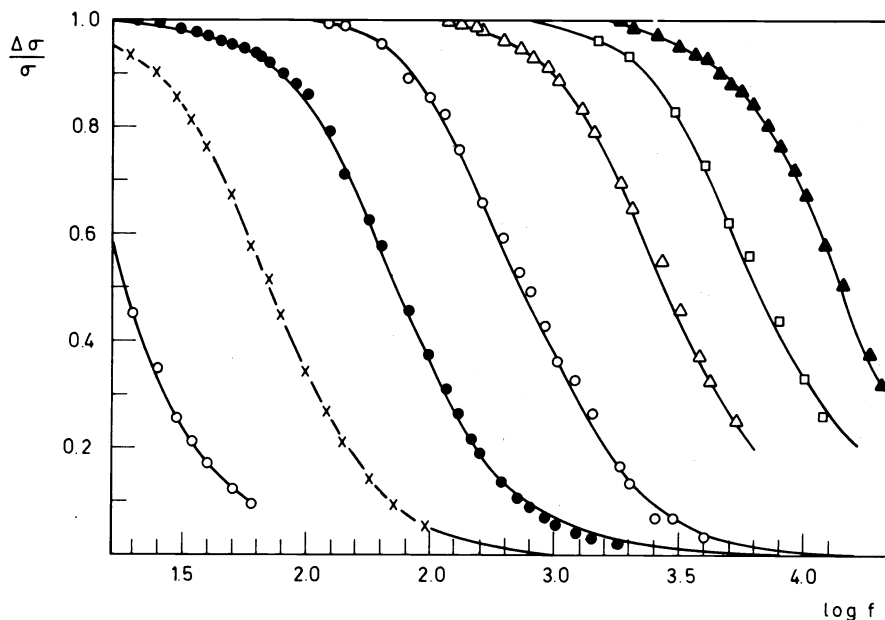

Figure 2
Dispersion of the field dissociation effect with the modulation frequency
for solutions of tetrabutylammoniumpicrate in benzene and of fluorenyl-
lithium in DEE-THF mixtures and of fluorenylcesium in DMM, THP, and DMM-THF
mixtures.

● Bu$_4$NPi in C$_6$H$_6$ / 25°C / 8.74 10^{-5}M, τ = 8.78 10^{-3} s.

x Bu$_4$NPi in C$_6$H$_6$ / 25°C / 1.52 10^{-4}M, τ = 2.20 10^{-3} s.

□ Bu$_4$NPi in C$_6$H$_6$ / 25°C / 3.60 10^{-3}M, τ = 2.28 10^{-5} s.

● FlCs in DMM / 22.9°C / 4.05 10^{-4} M, τ = 6.65 10^{-4}s.

x FlCs in DMM/THF / 20°C / 7.21 10^{-4}M, τ = 1.11 10^{-5}s.

○ FlCs in THP / -40°C / 8.23 10^{-5} M , τ = 2.03 10^{-4}s.

△ FlLi in DEE/THF / 20°C / 3.48 10^{-5}M, τ = 5.52 10^{-5}s.

EXPERIMENTAL RESULTS AND DISCUSSION

The verification of ionic solution theories for non aqueous media relies often upon conductance measurements of solutions of tetra-alkylammonium salts. In an initial application of the field modulation technique we investigated the chemical relaxation of tetrabutylammonium-picrate (TBAP) in diphenylether (15). At salt concentrations below 10^{-4}M this system is particularly simple as implied by conductance data and proven from the linear relation between reciprocal relaxation time and square root of total concentration. The main result obtained in this study is the remarkable agreement between the measured rate constants and the values calculated from theory, which identifies the ionic association dissociation processes as diffusion controlled phenomena. This conclusion is also corroborated from a study of the energetics of the ion pairing process (15,16). The experimental activation energies agree well with

values calculated from the temperature dependence of viscosity and from the electrostatic work done in separating the ions. However in these calculations we were forced to use a temperature dependent – or permittivity dependent, which may be the same phenomenon – interionic distance.

Electrolyte theories based on the sphere in continuum model are most criticized for the neglect of specific interactions between ions, or ion pairs and the medium. We therefore investigated the ionization of TBAP in mixed solvents, e.g. benzene-chlorobenzene and benzene-nitrobenzene mixtures. As clearly shown from the results in Table I the rate constants for recombination and dissociation are in good agreement with the values calculated from eq.7 and eq.8, using an interionic distance a obtained from conductance measurements. We may therefore conclude that even in these mixed solvents the ions are diffusing through a medium which is essentially continuous in the dielectric and viscous properties. The only experimental fact which hints to some specific interaction is the difference in interionic distance found in benzene-chlorobenzene mixtures vs. benzene-nitrobenzene mixtures. The change of a with dielectric constant may also be due to electrostatic interactions between ions, ion pairs and solvent dipoles.

Our main conclusion from the foregoing results is that, at sufficiently low concentration of ionic solute, the ion pairing process in a low polar medium is remarkably well described as a Brownian motion of hard sphere ions in a continuous medium. At increasing concentration of ionic solute, or decreasing polarity of the medium, deviations from the linearity between reciprocal relaxation time and square root of total concentration of ionic solute occur. These deviations, mirrored in the conductance behavior, are caused by the emergence of triple ions in solution. Although this complicates the interpretation of the relaxation phenomena it shows the great potential of the field modulation technique for the study of more complex ionic phenomena in low polar solvents.

Table I : Association dissociation dynamics of TBAP in mixtures of benzene-chlorobenzene (C) and benzene-nitrobenzene (N) at 25°C.

D	η mP	a Å	$10^{-11} k_r$ $M^{-1}s^{-1}$	$10\,k_d$ s^{-1}	$10^{-11} k_r$ from eq. 8	$10\,k_d$ from eq. 9
3.22 (C)	6.41	5.92	3.24	1.06	3.03	0.99
3.50 (C)	6.51	5.82	2.69	6.1	2.97	6.3
3.87 (C)	6.69	5.86	2.11	77.6	2.44	89.2
2.94 (N)	6.20	6.49	2.87	0.74	3.13	0.80
3.17 (N)	6.24	6.52	2.91	6.9	2.87	6.9
3.41 (N)	6.30	6.60	2.37	49.3	2.61	55.3

If in analogy with tetrabutylammonium picrate the relaxation behavior of fluorenyllithium (FlLi) is studied in pure diethylether (DEE) and in mixtures of DEE and increasing amounts of tetrahydrofuran (THF), the relaxation of the field dissociation effect is at first sight again very simple. Indeed, as shown in fig.2, the dispersion of the effect is described by a single Debye dispersion curve as in the case of the picrate, and equally a linear relation between reciprocal relaxation time and the square root of the total concentration, as predicted by eq.13 for a simple dissociation of an ion pair into free ions, is found in all experimental conditions. This is illustrated in fig.3 and the pertinent values of k_d and k_r are collected in table 2.

Table 2 : k_d and k_r values at different temperatures and solvent compositions for the association dissociation dynamics of FlLi in DEE-THF mixtures.[b]

T, °C	[THF][a] = 0		[THF][a] = 0.43 M		[THF][a] = 0.94 M		[THF][a] = 1.38 M	
	k_d s^{-1}	$10^{-11} k_r$ $M^{-1}s^{-1}$	k_d s^{-1}	$10^{-11} k_r$ $M^{-1}s^{-1}$	k_d s^{-1}	$10^{-11} k_r$ $M^{-1}s^{-1}$	k_r s^{-1}	$10^{-11} k_r$ $M^{-1}s^{-1}$
+20	0.73	12.2	2.86	5.71	10.25	4.29	28	2.69
0	0.92	8.44	5.89	3.65	17.0	3.03	41.6	2.12
-20	1.15	4.77	10.86	2.58	27.4	2.16	54.9	1.51
-40	1.45	3.25	15.28	1.72	39.5	1.53	83.9	0.98
-55	1.45	2.22	18.84	1.26	50.6	0.99	89.2	0.73

[a]concentrations are given at +20°C.

[b]The dissociation equilibrium constants K_d which are the ratios of k_d over k_r are not given in this Table. They were derived from conductance data and vary from 6.0x10^{-13}M in pure DEE at 20°C to 1.23x10^{-9}M in the presence of 1.38 M THF at -55°C.
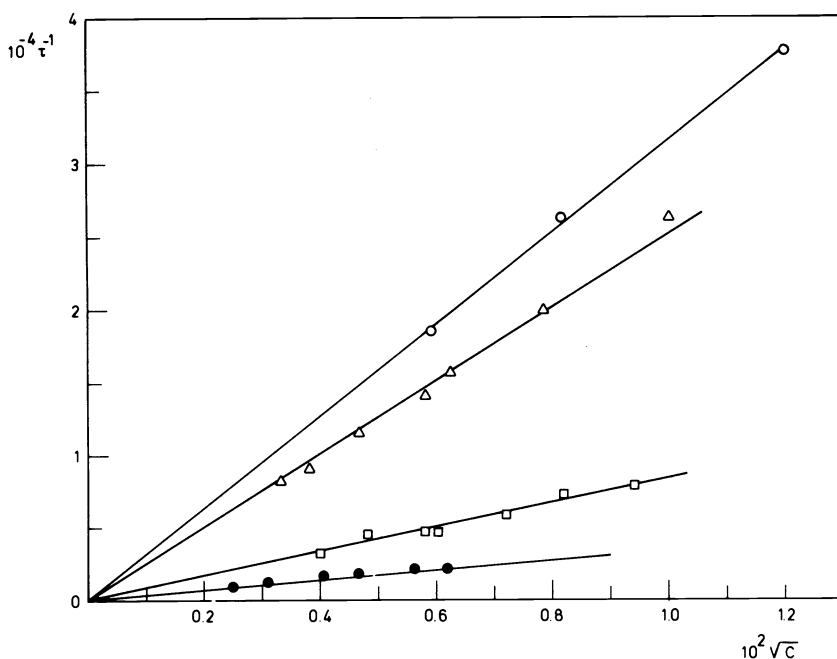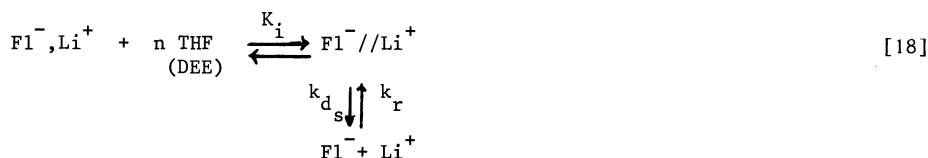
Figure 3
Dependence of reciprocal relaxation time on square root of solute concentra-
tion. Simple dissociation of ion pairs into free ions.
FlLi in DEE-THF mixture at 20°C with [THF] = 0.6 M (○)
TBAP in a 50% vol. chlorobenzene-benzene mixture (△), in a 40% chloroben-
zene-benzene mixture (□), in a 30% chlorobenzene-benzene mixture (●),
at 25°C.

However, closer inspection of the dissociation rate constants k_d shows that their value in-
creases with decreasing temperature, corresponding to a negative activation energy. This in-
dicates that the dissociation step in the ionic dissociation process considered cannot be an
elementary reaction step and strongly suggests that the ionic dissociation of Fl,Li even in
pure diethylether or in the presence of small amounts of THF, where no solvent separated ion
pairs could be detected spectroscopically, does not as represented in eq. 7 occur through
direct dissociation of the tight ion pairs, which are present in vast majority, but rather
via a small intermediate number of DEE- or THF separated ion pairs, respectively, the concen-
tration of which is too small to be spectroscopically detectable. The experimental results
may thus be interpreted in terms of the following reaction scheme :

$$\text{Fl}^-,\text{Li}^+ \;\; + \;\; \text{n THF} \;\;\xrightleftharpoons{K_i}\;\; \text{Fl}^-//\text{Li}^+ \qquad\qquad [18]$$
$$\text{(DEE)}$$
$$k_{d_s}\Big\downarrow\Big\uparrow k_r$$
$$\text{Fl}^- + \text{Li}^+$$

where Fl^-,Li^+ and $\text{Fl}^-//\text{Li}$ denote a contact or tight and a DEE or THF separated ion pair, res-
pectively, while n represents the number of solvent molecules involved in the solvent separa-
tion. If we define K_i^* as $[\text{Fl}^-//\text{Li}^+]/[\text{Fl}^-,\text{Li}^+]$, it is readily shown that

$$k_d \;=\; k_{d_s}\,\frac{K_i^*}{1 + K_i^*} \qquad\qquad [19]$$

and that consequently

$$E_{a_d} \;=\; E_{a_{ds}} \;+\; \frac{\Delta H_i^*}{1 + K_i^*} \qquad\qquad [20]$$

or if $K_i^* \ll 1$ that $E_{a_d} = E_{a_{ds}} + \Delta H_i^*$ $\qquad\qquad$ [21]

Therefore, if the reaction of solvent-separation is exothermic, which it usually is, and if ΔH_i^* is greater in absolute value than $E_{a_{ds}}$, it is easily seen that E_{a_d} will be negative. The relaxation times measured pertain to the dissociation of the intermediately formed solvent separated ion pairs. This leads to the conclusion that the preceeding process of solvent separation is fast or that the concentration of solvent separated or loose ion pairs is negligibly altered by the applied perturbation.

Results obtained at the higher THF concentrations and/or at the lower temperatures, when THF-separated ion pairs show up in the spectrum, enabling us to determine K_i^* from the intensities of the absorption maxima characteristic of both species (348 nm and 372 nm respectively) fully confirm the above given scheme. Indeed, knowing K_i^* and the overall dissociation rate constant k_d, given in Table 2, we can derive a value for k_{ds}. The respective values are shown in table 3.

Table 3 : K_i^* and k_{ds} values at different temperatures and solvent compositions for the ionic dissociation of FlLi in DEE-THF mixtures.

T, °C	[THF] = 0.43 M		[THF] = 0.94 M		[THF] = 1.38 M	
	$10^2 K_i^*$	k_{ds} s^{-1}	$10^2 K_i^*$	k_{ds} s^{-1}	$10^2 K_i^*$	k_{ds} s^{-1}
+20	–	–	–	–	5.4	547
0	–	–	4.7	379	8.2	549
-20	(3.8)	(297)	7.3	403	13.2	471
-40	6.6	247	12.5	355	22.9	450
-55	10.7	195	19.8	306	37.2	329

Values of $K_i^* < 0.03$ to 0.04 are of limited accuracy. These values and those of the corresponding k_{ds} are therefore given between brackets.

In spite of some undesirable scatter k_{ds} may satisfactorily be described in terms of the Eigen equation (9), derived for a simple diffusion controlled separation process, for an interionic distance a varying from 5.6 Å at 20°C to 5.2 Å at -55°C but nearly constant at each temperature for all THF concentrations used. This value compares favorably with the value $a = 6.3$Å calculated by T.E. Hogen Esch and J. Smid for the solvent separated Fl^-,Li^+ ion pair in pure THF (17). Moreover, if the interionic distance of the THF separated ion pair is accepted to be temperature dependent, the activation parameters of the formation and dissociation rate constants for the THF separated species are also found to be in full agreement with the existing theories concerning the dynamics of ion pair formation and dissociation. The agreement between experimental and theoretical values indicate that, once the intermediate THF separated ion-pair has been formed, its dissociation and its reformation by recombination of the free ions are processes mainly determined by diffusion.

If, as suggested by the negative activation energy of the overall dissociation rate constant, it is assumed that in pure diethylether, where no solvent separated species whatsoever can be detected spectrophotometrically, not even at the lowest temperatures, the dissociation occurs via a minute amount of intermediately formed solvent separated species, the recombination rate constant which may be calculated on the basis of an interionic distance, similar to that in the presence of THF, corresponds satisfactorily with the experimentally observed one. The occurrence of solvent separated species may therefore be characteristic of many more ionic dissociation phenomena then hitherto assumed.

Essentially the same idea was recently expressed by Fuoss (18,19) when he presented a revised theory according to which his original primitive model of ion association, which ignored completely all short range ion ion and ion solvent interactions had to be replaced by a two-step mechanism

$$A^+ + B^- \rightleftarrows (A^+...B^-) \rightleftarrows A^+B^- \qquad [22]$$

The first, which describes the formation and dissociation of solvent separated pairs $(A^+...B^-)$ represents the diffusion of an anion into and out of a sphere of radius R centered on the cation, R being the diameter of the Gurney cosphere, outside of which the solvent may be treated as a continuum. In the second step the anion and the cation, by site interchanges with solvent molecules inside the cosphere, eventually form a contact pair.

Some of the above mentioned complexities, which may arise with decreasing polarity of the medium or for very weakly dissociating electrolytes, when triple ions or possibly even higher ionic aggregates, such as quadrupoles, appear in the solution, are clearly exemplified by the conductance and relaxation behavior of fluorenylcesium (Fl^-,Cs^+) in dimethoxymethane (DMM), the dielectric constant of which is only 2.66 at 20°C, and in mixtures of DMM with increasing amounts of tetrahydrofuran (THF).

In electrolyte solutions, in which both triple ions of the two kinds are formed and association of free ions to ion pairs takes place, the general conductance equation can be written

as follows (20) :

$$\Lambda = \alpha \Lambda_o + \gamma \lambda_o \qquad\qquad [23]$$

$$= \Lambda_o K_d^{1/2} / C^{1/2} + \lambda_o C^{1/2} K_d^{1/2} / K_t \qquad [24]$$

where Λ is the equivalent conductance, α and γ are the fractions of free ions and triple ions, respectively, Λ_o is the sum of the limiting conductances of free cations and free anions, λ_o the sum of the limiting conductances of the triple ions, K_d and K_t are the dissociation constants of the ion pairs and the triple ions, respectively, and C is the electrolyte concentration. Under circumstances where triple ion formation is very small and where simple dissociation of ion pairs into free ions prevails, the second term of the right hand side of equation [24] can be neglected, and the conductance equation becomes

$$\Lambda = \Lambda_o K_d^{1/2} / C^{1/2} \qquad\qquad [25]$$

and a plot of log Λ versus log C should give a straight line with a slope of −0.5. When the contribution of the free ions to the total conductance is small compared to that of triple ions, the conductance equation becomes

$$\Lambda = \lambda_o C^{1/2} K_d^{1/2} / K_t \qquad\qquad [26]$$

In such case log Λ is again a linear function of log C but with slope equal to +0.5. The variation of the value of the slope between −0.5 and +0.5 reflects varying degrees of contribution of triple ions.
Conductance measurements carried out on Fl^-,Cs^+ in pure DMM as well as in DMM-THF mixtures indicate that Fl^-,Cs^+ is only slightly dissociated into free ions and that important amounts of triple ions of both kinds viz. Fl_2Cs^- and $FlCs_2^+$ are present. Indeed when log Λ is plotted as a function of log C, as represented in figure 4, a positive slope is obtained for the highest DMM concentrations, to go through a minimum and to reach the limiting slope of −0.5, characteristic of the simple dissociation, only when the amount of THF is progressively increased. Simultaneously relaxation measurements were also carried out on the different solutions. In the frequency domain, in which the measurements were carried out, (20−20,000 Hz) a single dispersion curve was obtained in all cases. From these curves the respective relaxation times τ were determined. In spite of the complexity of the system and the variety of the species present and although the analysis is complicated by the fact that a single dispersion is always found at all temperatures and solvent compositions, the field modulation technique still provides a powerful tool to unravel the detailed reaction mechanism. Indeed, information on the different mechanisms by which the ionic species, revealed by conductance, are generated, may be obtained from the detailed analysis of the functional dependence of the reciprocal relaxation time on the total concentration of ionic solute under different experimental conditions.
Thus, combination of the results of conductance with those of relaxation measurements permitted us to establish the following general reaction scheme :
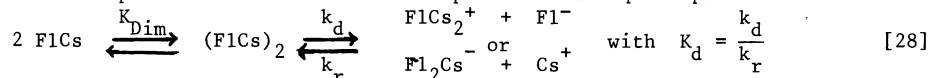

$$[27]$$
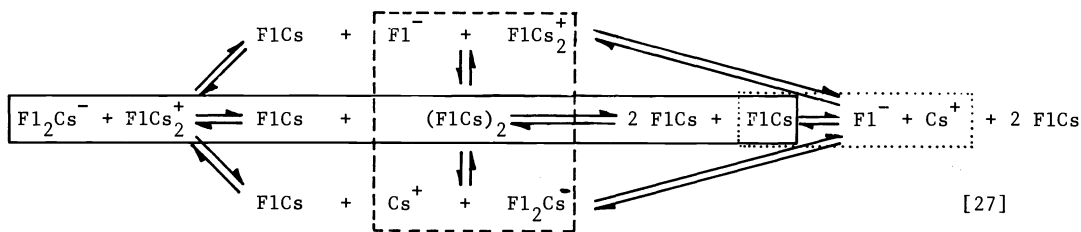
⬜ : pure DMM or DMM + small amounts of THF

⬜ : [THF] = 6.2 M

⬜ : [THF] = 7.7 M

In pure DMM and in mixtures with small amounts of THF, a linear relation is observed between τ^{-1} and $C^{3/2}$ as shown in figure 5. This can be explained by assuming that the relaxation times measured pertain to the formation of triple ions by the interaction between a dimeric and a free ion pair.
At higher THF concentrations (D = 5.16) a linear relation between τ^{-1} and C is observed, which is taken to correspond to the formation of triple ions from quadrupoles :

$$2\ FlCs \xrightleftharpoons[\,]{K_{Dim}} (FlCs)_2 \xrightleftharpoons[k_r]{k_d} \begin{array}{l} FlCs_2^+ + Fl^- \\ \text{or} \\ Fl_2Cs^- + Cs^+ \end{array} \quad \text{with}\ K_d = \frac{k_d}{k_r} \qquad [28]$$
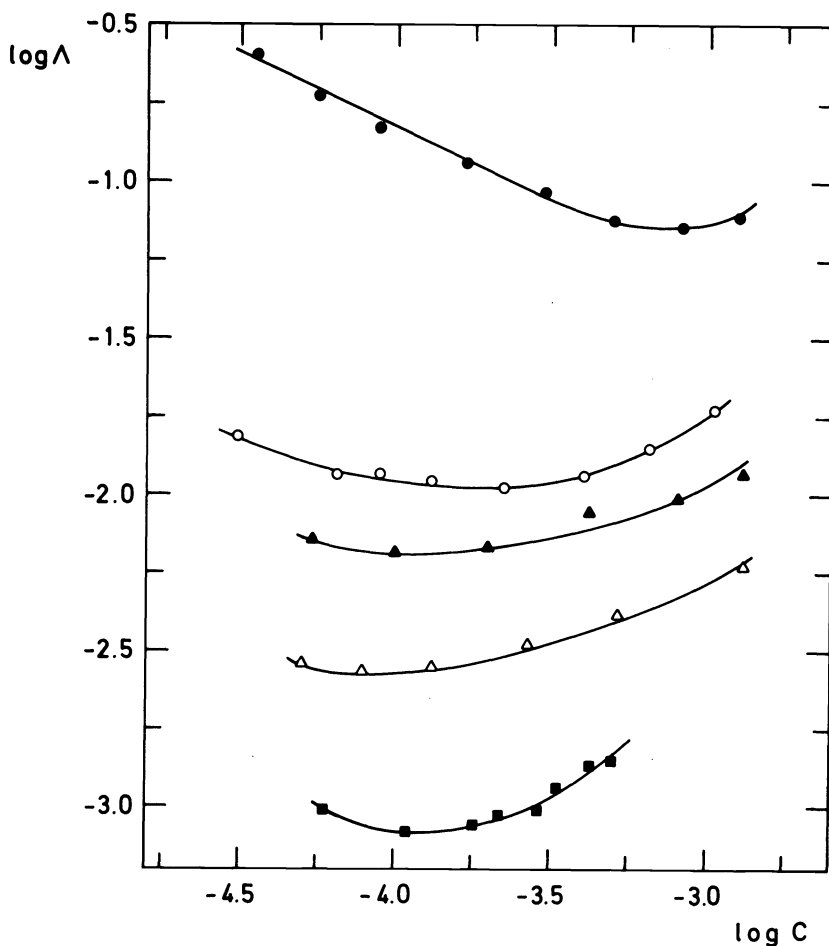
Figure 4
Dependence of log Λ on log C for conductance of F1Cs in dimethoxymethane
(DMM)-tetrahydrofuran (THF) mixtures.
(■) [THF] =.9 M, D = 2.91; (△) [THF] = 1.73 M, D = 3.36; (▲) [THF] = 2.9 M,
D = 3.68; (○) [THF] = 3.65 M, D = 4.04, (●) [THF] = 7.70, D = 5.85

When quadrupole formation is fast compared to the ionization, or when the electric field per-
turbation affects mainly the ionic dissociation process, the reciprocal relaxation time, pro-
vided the degree of dissociation is small, is given by

$$\tau^{-1} = k_d + 2 k_r (K_d K_{dim})^{1/2} C_o \qquad [29]$$

It should be emphasized that, in contrast to the media of low dielectric constant, where only
triple ions are formed, in this medium of higher dielectric constant not only triple ions but
also free ions appear in the solution through dissociation of a dimeric complex. These di-
meric species in the previous case and in this one may be present in very low concentration
but their intervention is indispensable to explain the concentration dependence of the reci-
procal relaxation time.
Finally at still higher THF concentrations (D = 5.85) a linear relation between τ^{-1} and $C^{1/2}$,
characteristic of the simple dissociation of ion pairs into free ions is found.
It is noteworthy at this point that in the previously treated case of F1,Li in DEE and in DEE-
THF mixtures, triple ions were also present, as revealed by conductance, yet, no deviation of
the half order dependence of τ^{-1} on the concentration of F1Li was observed. This means that
in spite of the occurrence of triple ions, the main ion generating process in the concentra-
tion-, solvent composition- and temperature range in which the data reported in table 2 were
obtained, is still the simple ionization of ion pairs into free ions and that the dispersion
of the field dissociation effect is therefore mainly due to the relaxation of this simple
ionization equilibrium, the contribution of the triple ions to the relaxation signal being
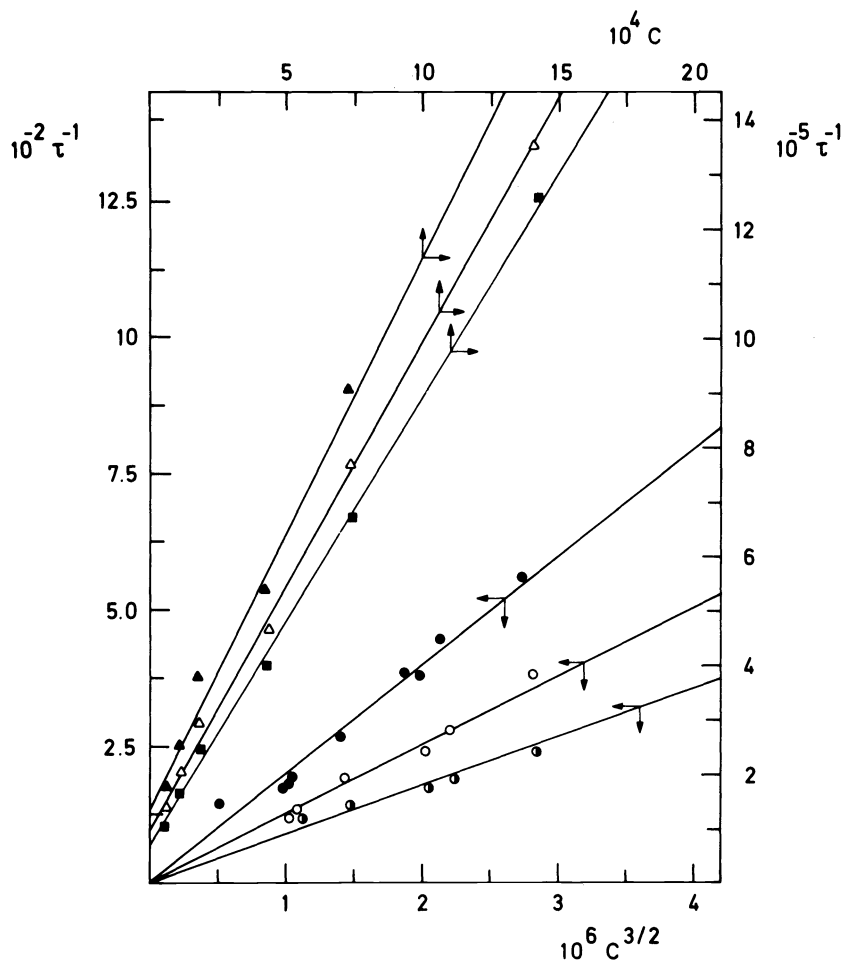
Figure 5
Evolution of the concentration dependence of the reciprocal relaxation time
for FlCs in DMM-THF mixtures.
(●) 3/2 order dependence in pure DMM at 23°C; (○) in pure DMM at 13°C;
(◐) in pure DMM at 4.8°C.
In a mixture with [THF] = 6.19 M (▲, △ and ■) a linear dependence on concen-
tration of FlCs is found. (▲) : 20°C; (△) : 10°C; (■) 0°C.

negligible compared to that of the free ions. The numerical estimate of K_t from the conduc-
tance data treated according to the equation of Fuoss and Kraus (20)

$$\Lambda \, c^{1/2} \;=\; K_d^{1/2} \, \Lambda_o \;+\; (K_d^{1/2} \, \lambda_o / K_t)(1 - \Lambda/\Lambda_o) c \hspace{3cm} [30]$$

indeed indicates that, except for the lowest THF concentrations and the highest salt concentra-
tions used, the concentration of free ions is distinctly higher than that of the triple ions.
This explanation is borne out by the fact that recent measurements (21) carried out on more
concentrated FlLi solutions in pure DEE clearly show deviations from the half order dependence
of τ^{-1} on FlLi concentration reaching rapidly a stage of direct proportionality between τ^{-1}
and FlLi concentration, as observed above for FlCs in DMM-THF mixtures when the THF concentra-
tion was equal to 6.2 M as shown in eq. [27] and [28].

ACKNOWLEDGMENTS

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