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 reviewed 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 relaxation 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 measurements 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 described. The way new information is obtained from relaxation measurements on processes such as solvent-separation, ionic dissociation and aggregation 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 is to study this distribution as a function of the relevant parameters e.g. temperature, composition 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 information 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 belong to the realm of chemical kinetics. For a complete analysis of the interconversion processes of chemical species all the elementary steps should be analyzed for their dynamic behavior. 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 equilibrium state by a fast change in an intensive thermodynamic variable and the subsequent measurement 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. Irrespective of experimental difficulties frequency domain techniques - stationary relaxation methods - are to be preferred for their extreme sensitivity and accuracy, properties essentially 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 system. 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 equilibrium 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 information 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 chemical 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 atmosphere, 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 successful theoretical description of the effect can therefore only be obtained from the electrodiffusion treatment as carried out by Onsager. For the relative increase of dissociation rate of an ion pair under field conditions Onsager obtained the result:

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

with

\[
q = -\frac{e_1 e_2}{2Dk_B^2} \quad \text{and} \quad 2\beta = \frac{(e_1 u_1 - e_2 u_2)E}{(u_1 + u_2)k_BT}
\]

\(e_1\) and \(u_1\) is the charge, respectively the mechanical mobility of ion 1, D is the dielectric constant of the medium, \(k_B\) the Boltzmann constant and E the electric field strength, all expressed 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 higher than their thermal interaction with the surrounding medium. The reciprocal distance \(2\beta\) 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 \(2\beta\) 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 \(k_B E \cos \theta\), \(\theta\) being the angle between 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 frequency 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 dissociation:

\[
\frac{K_d(E)}{K_d(E=0)} = F(2\beta q)
\]

Or, specified for a uni-univalent electrolyte and retaining only the linear part of the function \(F(2\beta q)\):

\[
\delta \ln K_d \frac{\delta}{\delta E} = \frac{e_o^3}{2 Dk_B} \frac{2\beta q}{E}
\]

From this result we see that the field dissociation effect will be most pronounced in low polar 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 mostly measured as an increase in the conductance, or specific conductivity \(\sigma\), of the solution. Generally we can write:
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\[ \frac{1 - \alpha}{2 - \alpha} \frac{dK_D}{d\alpha} = \frac{\Delta \sigma}{\sigma} \]  

[4]

This result shows that the relative change in conductance is also most pronounced when the degree of ionic dissociation \( \alpha \) 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:

\[ \Delta G^\circ (E) = \Delta G^\circ (E=0) - \mu_{Bj} N e E \]  

[5]

or writing the Bjerrum dipole moment \( \mu_{Bj} \) as \( e_0 q \), we obtain for the dissociation equilibrium constant:

\[ K_D(E) = K_D(E=0) \exp \frac{e_0 q E}{k_B T} \]  

[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:

\[ A^+ B^- \xrightleftharpoons{k_r}{k_r} A^+ + B^- \]  

[7]

Considering the ions as hard spheres subjected to Brownian motion in a continuous medium with dielectric constant \( D \) and viscosity \( \eta \), and defining the ion pair as two ions at a distance \( \alpha \), which may be the distance of closest approach, i.e. the sum of the ionic radii, we can derive theoretical expressions for the rate of 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):

\[ k_r = \frac{8}{3} 10^{-3} \frac{N_o^2}{D_0 \eta} \]  

[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:

\[
k_d = \frac{2e^2}{\pi \eta a^4} \exp \left( -\frac{e^2}{\eta a Dk_BT} \right)
\]

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

\[
K_D = \frac{3 \cdot 10^{-3}}{4\pi a^3} \exp \left( -\frac{e^2}{\eta a Dk_BT} \right)
\]

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 \( \eta \) 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 \( \tau \) for the ionic equilibrium 7 is given by:

\[
\tau^{-1} = k_d + 2k_{\text{ion}}
\]

where \( C_{\text{ion}} \) 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. \( 2k_{\text{ion}} \). 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 \( \sigma = \sum n_i \) (\( n_i \) number of ions i per cm\(^3\)) the reciprocal relaxation time for equilibrium 7 becomes:

\[
\tau^{-1} = \frac{8\pi}{D} \left( \frac{e^2}{\eta a A^+} + \frac{e^2}{\eta a B^-} \right) = \frac{8\pi \sigma}{D}
\]

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 \( (c_0) \), we write for the reciprocal relaxation time of equilibrium 7, with the assumption of very low degree of dissociation:

\[
\tau^{-1} = (2k_{\text{ion}})^{1/2} c_0^{1/2} = 2(k_{\text{ion}})^{1/2} c_0^{1/2}
\]

From the concentration dependence of \( \tau^{-1} \), 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:

\[
2 A^+ B^- \xrightarrow{K_{\text{dim}}} (A^+ B^-)_2 \xrightarrow{k_d} A^+ + B^- A^+ B^- \xrightarrow{k_r} A^+ + B^- A^+ B^-
\]

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:
where \( c \) is the total concentration of ionic solute. In the second term we note a linear dependence 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 linear 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 continuum 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 favorable 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 essentially 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 equilibria. 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 analyzed 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) ferrite core transformer. Generator 2 is a low voltage (1-20 Vpp) sinusoidal oscillator synchronously locked on the square wave signal modulating the power oscillator. The sample cell contains, in a very symmetric arrangement, three electrodes two of which (E1 and E2) are connected to the high voltage transformer output terminals. Electrode E3 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 E3 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 E1 and E2 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 sinusoidal signal with a frequency equal to the modulation frequency. It is easy to see that this results in an intermediate signal containing a d.c. term-proportional to the modulation depth — which can be accurately measured. In the experimental set up the conducction modulation and the intermodulation products are generated in the same circuit. A sinusoidal generator (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 generator through the sample cell. As a consequence a number of electric charges are brought on capacitor C, a capacitor which effectively short circuits electrode E3 for a.c. signals. In the field off period the sample solution regains the normal low conductance and a "small" current 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 (VM) and to the relative conductance change of the solution (Δa/a), the modulation depth. Retaining only the square wave envelope of the high voltage, high frequency signal — neglecting 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%): 

\[ V_{\text{d.c.}} = \frac{\Delta a}{\sigma} \frac{V_M}{\pi} = g \left( \frac{\Delta a}{\sigma} \right) \text{Onsager} \cdot \frac{V_M}{\pi} \]  

[16]

where \( g \) is a correction factor taking into account the deviations of the experimental value of \( \frac{\Delta a}{\sigma} \) from the value calculated according to Onsager's theory. More specifically, \( g \) is a function of the high frequency within the pulses showing a rather complex dispersion with \( \omega_{HF} \).

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 modulation 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 vanishes 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 \( \omega_{PRF} \):

\[ V_{\text{d.c.}} = \frac{V_M}{\pi} \frac{\Delta a}{\sigma} \frac{1}{1 + \frac{\omega_{PRF}^2}{\tau^2}} = \frac{V_{\text{d.c. max}}}{1 + \frac{\omega_{PRF}^2}{\tau^2}} \]  

[17]

where \( V_{\text{d.c. max}} \) 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 dispersion equation. The relaxation time \( \tau \) 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 conductance 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 characteristic time constant which is directly related to the capacitance of C if the conductance of C is exactly known and 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,
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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](image_url)

**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, THF, and DMM-THF mixtures.

- Bu₄NPi in C₆H₆ / 25°C / 8.74×10⁻⁵ M, τ = 8.78×10⁻³ s.
- Bu₄NPi in C₆H₆ / 25°C / 1.52×10⁻⁴ M, τ = 2.20×10⁻³ s.
- Bu₄NPi in C₆H₆ / 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.
- FlCs in DMM/THF / 20°C / 7.21×10⁻⁴ M, τ = 1.11×10⁻⁵ s.
- FlCs in THF / -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 tetrabutylammoniumpicrate (TBA) 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 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 \( \alpha \) 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 \( \alpha \) 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>
<thead>
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<th>( D )</th>
<th>( \eta ) (mP)</th>
<th>( a ) (( \overline{A} ))</th>
<th>( 10^{-11} k_r ) (( 1 \overline{M}^{-1} s^{-1} ))</th>
<th>( 10 k_d ) (s(^{-1}))</th>
<th>( 10^{-11} k_r ) (from eq. 8)</th>
<th>( 10 k_d ) (from eq. 9)</th>
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<tr>
<td>3.22 (C)</td>
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<tr>
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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 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.

| \( T \), °C | \( [\text{THF}]^a \) = 0 M | \( [\text{THF}]^a \) = 0.43 M | \( [\text{THF}]^a \) = 0.94 M | \( [\text{THF}]^a \) = 1.38 M |
|---|---|---|---|
| \( k_d \) (10^{-11} s^{-1}) | \( k_r \) (10^{-11} s^{-1}) | \( k_d \) (10^{-11} s^{-1}) | \( k_r \) (10^{-11} 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 | 34.9 | 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.
However, closer inspection of the dissociation rate constants $k_d$ shows that their value increases with decreasing temperature, corresponding to a negative activation energy. This indicates that the dissociation step in the ionic dissociation process considered cannot be an elementary reaction step and strongly suggests that the ionic dissociation of F1Li 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 concentration of which is too small to be spectroscopically detectable. The experimental results may thus be interpreted in terms of the following reaction scheme:

$$\frac{F1^-}{Li^+} + n \text{THF} \underset{\text{(DEE)}}{\rightleftharpoons} \frac{F1^-}{Li^+}$$

where $F1^-/Li^+$ and $F1^-/Li^+$ denote a contact or tight and a DEE or THF separated ion pair, respectively, while $n$ represents the number of solvent molecules involved in the solvent separation. If we define $K_i$ as $[F1^-/Li^+]/[F1^-/Li^+]$, it is readily shown that

$$k_d = k_{ds} \frac{K_i}{1 + K_i}$$

and that consequently

$$E_d = E_{ds} + \frac{\Delta H_i}{1 + K_i}$$

or if $K_i \ll 1$ that $E_d = E_{ds} + \Delta H_i^*$. 

Figure 3
Dependence of reciprocal relaxation time on square root of solute concentration. Simple dissociation of ion pairs into free ions.
F1Li in DEE-THF mixture at 20°C with [THF] = 0.6 M (○).
TBAP in a 50% vol. chlorobenzene-benzene mixture (△), in a 40% chlorobenzene-benzene mixture (●), in a 30% chlorobenzene-benzene mixture (●), at 25°C.
Therefore, if the reaction of solvent—separation is exothermic, which it usually is, and if
ΔH‡ is greater in absolute value than Ead, it is easily seen that Ead will be negative.
The relaxation times measured pertain to the dissociation of the intermediately formed sol-
vent separated ion pairs. This leads to the conclusion that the preceding process of sol-
vent 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‡ 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‡ and the overall dissociation rate constant kds,
given in Table 2, we can derive a value for kds. The respective values are shown in table 3.

Table 3: K‡ and kds values at different temperatures and solvent composi-
tions for the ionic dissociation of FII in DEE—THF mixtures.

<table>
<thead>
<tr>
<th>[THF] =</th>
<th>[THF] =</th>
<th>[THF] =</th>
</tr>
</thead>
<tbody>
<tr>
<td>T, °C</td>
<td>0.43 M</td>
<td>0.94 M</td>
</tr>
<tr>
<td>10²K‡</td>
<td>kds</td>
<td>10²K‡</td>
</tr>
<tr>
<td>s⁻¹</td>
<td>s⁻¹</td>
<td>s⁻¹</td>
</tr>
<tr>
<td>+20</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>-20</td>
<td>(3.8)</td>
<td>(297)</td>
</tr>
<tr>
<td>-40</td>
<td>6.6</td>
<td>247</td>
</tr>
<tr>
<td>-55</td>
<td>10.7</td>
<td>195</td>
</tr>
</tbody>
</table>

Values of K‡ < 0.03 to 0.04 are of limited accuracy. These values and those of the corre-
spanding kds are therefore given between brackets.
In spite of some undesirable scatter kds 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 tempera-
ture for all THF concentrations used. This value compares favorably with the value a = 6.3Å
calculated by T.E. Hogen Esch and J. Smid for the solvent separated F1+,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 exis-
ting theories concerning the dynamics of ion pair formation and dissociation. The agreement
between experimental and theoretical values indicate that, once the intermediate THF separa-
ted 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 diethyl ether, 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 the interionic distance, similar to that in
the presence of THF, corresponds satisfactorily with the experimentally observed one. The oc-
currence of solvent separated species may therefore be characteristic of many more ionic disso-
ciation phenomena than hitherto assumed.
Essentially the same idea was recently expressed by Fuoss (18,19) when he presented a revi-
sed 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

\[ A^+ + B^- \rightleftharpoons (A^+ ... B^-) \rightleftharpoons A^+ B^- \]  [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 me-
dium 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 (F1−,Cs+) in dimethoxymethane (DMF),
the dielectric constant of which is only 2.66 at 20°C, and in mixtures of DMF with increasing
amounts of tetrahydrofuran (THF).
In electrolyte solutions, in which both triple ions of the two kinds are formed and associa-
tion of free ions to ion pairs takes place, the general conductance equation can be written
Ion pairing

as follows (20):

\[
\Lambda = \alpha \Lambda_0 + \gamma \Lambda_0^* \\
= \Lambda_0^{1/2} / C^{1/2} + \lambda_0^{1/2} K_d^{1/2} / K_t^{1/2}
\]

where \( \Lambda \) is the equivalent conductance, \( \alpha \) and \( \gamma \) are the fractions of free ions and triple ions, respectively, \( \Lambda_0 \) is the sum of the limiting conductances of free cations and free anions, \( \lambda_0 \) 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

\[
\Lambda = \Lambda_0^{1/2} / C^{1/2}
\]

and a plot of \( \log \Lambda \) 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

\[
\Lambda = \lambda_0^{1/2} K_d^{1/2} / K_t^{1/2}
\]

In such case \( \log \Lambda \) 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"Csi is only slightly dissociated into free ions and that important amounts of triple ions of both kinds viz. Fl2Cs" and FlCs4 are present. Indeed when \( \log \Lambda \) 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 \( T \) 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:

\[
\begin{align*}
\text{FlCs} + & \text{Fl}^+ + \text{FlCs}^+ \\
\text{Fl}_2\text{Cs}^- + \text{FlCs}^+ & \rightarrow 2 \text{FlCs} + \text{Fl}^+ + \text{Cs}^+ \\
\text{FlCs} + & \text{Cs}^+ + \text{Fl}_2\text{Cs}^- \\
\end{align*}
\]

[27]

In pure DMM and in mixtures with small amounts of THF, a linear relation is observed between \( T^{-1} \) 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 \( T^{-1} \) and \( C \) is observed, which is taken to correspond to the formation of triple ions from quadrupoles:

\[
2 \text{FlCs} \xrightarrow{K_{\text{Dim}}} (\text{FlCs})_2 \xrightarrow{K_d} \text{Fl}^+ + \text{FlCs}_2^+ \\
\text{or} \quad \xrightarrow{K_f} \text{Fl}_2\text{Cs}^+ + \text{Cs}^+ \quad \text{with} \quad K_d = \frac{k_d}{k_f}
\]

[28]
Figure 4
Dependence of log $\Lambda$ on log C for conductance of F1Cs in dimethoxymethane (DMM)-tetrahydrofuran (THF) mixtures.

When quadrupole formation is fast compared to the ionization, or when the electric field perturbation affects mainly the ionic dissociation process, the reciprocal relaxation time, provided the degree of dissociation is small, is given by

$$\tau^{-1} = k_d + 2 k_r (K_d K_{\text{dim}})^{1/2} C_0$$

[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 dimeric 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 reciprocal relaxation time.

Finally at still higher THF concentrations (D = 5.85) a linear relation between $\tau^{-1}$ 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 F1Li 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 $\tau^{-1}$ 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 concentration-, 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
Evolution of the concentration dependence of the reciprocal relaxation time for F1Cs in DMM-THF mixtures.

(*) 3/2 order dependence in pure DMM at 23°C; (o) in pure DMM at 13°C; (A) in pure DMM at 4.8°C.
In a mixture with [THF] = 6.19 M (A, △ and ●) a linear dependence on concentration of F1Cs is found. (A): 20°C; (O): 10°C; (△): 0°C.

The numerical estimate of $K_t$ from the conductance data treated according to the equation of Fuoss and Kraus (20)

$$\Lambda C^{1/2} = K_d^{1/2} \Lambda_o + (K_d^{1/2} \Lambda_o/K_t)(1 - \Lambda/\Lambda_o)C$$

indeed indicates that, except for the lowest THF concentrations and the highest salt concentrations 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 F1Li solutions in pure DEE clearly show deviations from the half order dependence of $\tau^{-1}$ on F1Li concentration reaching rapidly a stage of direct proportionality between $\tau^{-1}$ and F1Li concentration, as observed above for F1Cs in DMM-THF mixtures when the THF concentration was equal to 6.2 M as shown in eq. [27] and [28].

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