# Lithium ion complexation kinetics by cyclic and acyclic polyethers

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Abstract - Results of the ultrasonic absorption relaxation and nuclear
magnetic resonance studies of the kinetics of alkali metal cation
complexation by macrocyclic ligands in a variety of nonaqueous solvents
are reviewed. The effects of a competition between low permittivity
solvent molecules, anions, and neutral macrocycles for the first
coordination sphere of the lithium cation are clearly evident. The
utility of the Eigen-Winkler reaction mechanism for describing the
ultrasonic absorption results is pointed out. When the same ultrasonic
techniques are used to explore the kinetics of lithium ion complexation by
acyclic polyethers such as poly(ethylene oxide) in acetonitrile a striking
insight emerges: The complexation kinetics reflect a localized cation-
polyether interaction that is independent of the length of the polyether
chain as one proceeds from triglyme to a poly(ethylene oxide) of 15,000
average molar weight. Extension of this result to similar lithium ion
complexation kinetic studies in neat liquid poly(ethylene oxides) is
discussed and possible applications of the results in developing an
understanding of polymeric electrolytes in lithium batteries is outlined.

## INTRODUCTION

Under favorable circumstances it is possible to detect the rapid, discrete steps by which a
$Li^+$ cation in a liquid solution is desolvated and is eventually encapsulated by a polyether
ligand. For the enthusiastic chemical kineticist such a study requires no external
justification. After we have considered the insights of a fundamental character emerging
from recent kinetic studies of lithium ion-polyether interactions in solutions we will,
however, also discuss a way in which this type of kinetic study can improve our
understanding of lithium battery electrolytes.

## ULTRASONIC ABSORPTION

The attenuation of high frequency sound waves in liquids can be measured by a variety of
experimental techniques that have been described in a comprehensive review by Stuehr
(ref. 1). Viscous losses and heat losses of the sound energy in liquids account for some of
the ultrasonic absorption, but dynamic chemical equilibria in liquids frequently make larger
contributions to the sound attenuation at resonant or relaxational frequencies, $f_r$,
characteristic of the particular chemical equilibria. Let f denote the frequency of sound
passing through the liquid ($s^{-1}$), $\alpha$ the attenuation constant ($cm^{-1}$), u the sound velocity
($cm\ s^{-1}$), B the background sound absorption ratio $(\alpha/f^2)_{f>>f_r}$, and $\mu$ the excess sound
absorption per wavelength given by

$$\mu = (\alpha - Bf^2)(u/f) \tag{1}$$

If a sample liquid contains two sound absorbing chemical equilibria with relaxation
frequencies $f_r \equiv f_I$ and $f_r \equiv f_{II}$ respectively, the sound absorption data can be fitted by either
one of the following functional forms:

$$\mu = 2\mu_I \frac{f/f_I}{1+(f/f_I)^2} + 2\mu_{II} \frac{f/f_{II}}{1+(f/f_{II})^2} \tag{2}$$

$$\frac{\alpha}{f^2} = A_I \frac{1}{1+(f/f_I)^2} + A_{II} \frac{1}{1+(f/f_{II})^2} + B \tag{3}$$

In the latter equation the relaxation amplitudes are $A_I = (2\mu_I/uf_I)$ and $A_{II} = (2\mu_{II}/uf_{II})$. Equation 2 gives rise to broad ultrasonic absorption peaks when $\mu$ is plotted on the vertical axis and log f is plotted on the horizontal axis. The superficial similarity of such a plot to an infrared spectrum makes the display of ultrasonic absorption data arising from eq. 2 the one usually preferred by chemists. The chemical kineticist can infer rate constants for chemical reactions directly from ultrasonic absorption data. For example, let us suppose that the chemical reaction

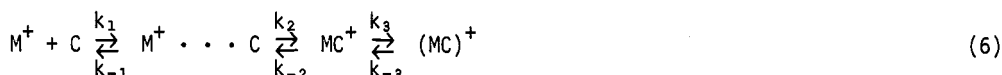$$A + B \underset{k_{-2}}{\overset{k_1}{\rightleftarrows}} C \tag{4}$$

gives rise to maximum sound absorption at a resonant frequency $f_r = (2\pi\tau)^{-1}$ where $\tau$ denotes the relaxation time. Then the familiar relaxation time $\tau$ yields (ref. 2) the rate constant from

$$\tau^{-1} = k_1([A] + [B]) + k_{-1} \tag{5}$$

Here [A] and [B] denote equilibrium concentrations of the species A and B. Advantages of ultrasonic absorption for kinetic studies that have kept this experimental method alive despite its comparatively great age include the following: 1) Chemical equilibria lacking chromophores can be investigated; 2) Fairly short relaxation times between about 2μs and 300 ps can be measured; and 3) Volume of activation data can be obtained without resorting to the use of high pressures. Disadvantages of the ultrasonic methods include the following: 1) Several different ultrasonic instruments are needed to cover the full 0.1 MHz to 500 MHz frequency range of interest; 2) Signals are weak necessitating high sample concentrations (typically >0.05 mol dm⁻³) and long signal averaging times; and 3) Sample equilibria must involve a net adiabatic (isoentropic) volume change $\Delta V_S = \Delta V_T - (\theta/\rho c_p)\Delta H$ where $\Delta V_T$ is the isothermal volume change, $\theta = \partial\ell nV/\partial T$ is the expansivity, $\rho$ is the density, $c_p$ is the specific heat, and $\Delta H$ is the enthalpy change of the relaxing process. Thus the observability by ultrasonic absorption of a relaxational process requires a finite $\Delta V_S$ that is an algebraic sum of $\Delta V_T$ and $\Delta H$ terms.

When ultrasonic absorption is used to study the reactions of alkali metal cations with the smaller crown ethers such as 12-crown-4, 15-crown-5 and 18-crown-6 in nonaqueous solvents two well separated relaxation times are frequently detected (ref. 3-12). The observed relaxations have always been fitted satisfactorily by the Eigen-Winkler reaction mechanism (ref. 13)

$$M^+ + C \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} M^+ \cdots C \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} MC^+ \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} (MC)^+ \tag{6}$$

where $M^+$ is the solvated metal cation, C denotes the crown ether, $M^+ \cdots C$ is the solvent-separated metal ion-crown ligand pair, $MC^+$ is a contact pair and $(MC)^+$ is the complex with the metal cation embedded in the crown ether cavity. The same model works well when other cations such as $Ba^{2+}$ (ref. 14), $Ag^+$ (ref. 11, 15) and $Tl^+$ (ref. 15) react with the simple crown ethers in nonaqueous liquid solutions. By varying the solvent donor number and permittivity and by varying the counter anion it can be shown that a vigorous competition between solvent molecules, anions and neutral macrocycles exists for positions in the first coordination sphere of the metal cation (ref. 12). This result contrasts sharply with the very useful generalization (ref. 16) for Main Group metal cations in aqueous solutions that the rate limiting step in the reaction of such a cation and a ligand is the loss of a comparatively tightly bound water molecule from the first coordination sphere of the metal cation.

Some other interesting generalizations emerge from ultrasonic absorption studies of macrocycles in nonaqueous solutions. Hanging a side chain on the ring increases the complexity of the ultrasonic spectrum but does not have a dramatic impact on the mechanism of metal cation binding (ref. 17). In the absence of metal cations and when the side chain is terminated by a carboxyl group one sees an ultrasonic spectrum in dimethylformamide solutions suggesting the formation of dimers of the macrocycle (ref. 18). In the absence of metal cations the bicyclic cryptants such as cryptand 222 also have interesting ultrasonic absorption spectra in nonaqueous solutions (ref. 19) indicating a rapid conformational change involving inversion of the ring nitrogen atoms. Since stopped-flow techniques have characterized the comparatively slow complexation of metal cations by cryptands (ref. 20), it would be reasonable to expect that the ultrasonic absorption spectrum of a solution of metal ions and 222 cryptand would provide no new kinetic information. The counter intuitive experimental ultrasonic spectrum (ref. 21) clearly indicates an intramolecular rearrangement

of the 222 cryptate on a rapid time scale with the metal cation bound to the cryptand throughout the conformational change that probably involves inversion of the ring nitrogen atoms. When long alkyl chains are hung on these ring nitrogen atoms as in Kryptofix 22-DD, rotation of the ring nitrogen atoms becomes much slower because of the drag imposed by the $C_{10}H_{21}$ chains (ref. 22).

## NUCLEAR MAGNETIC RESONANCE RESULTS

A great many more kinetic studies of alkali metal cation-macrocycle solutions have been carried out with nuclear magnetic resonance techniques than will probably ever be completed by the more laborious ultrasonic absorption methods. Some NMR studies point to the dissociative mechanism

$$M^+ + C \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} (M^+_,C) \tag{7}$$

as the major reaction in some metal cation-crown ether solutions. An example is sodium ion and dibenzo-18-crown-6 dissolved in dimethoxyethane (ref. 23).

Schmidt and Popov (ref. 24) were the first to report a bimolecular interchange mechanism

$$M^{+*} + (M^+_,C) \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} M^+ + (M^{+*}_,C) \tag{8}$$

based on their NMR study of a $KAsF_6$ plus 18-crown-6 solution in 1,3-dioxolane. A great many subsequent NMR studies have confirmed the preeminence of the bimolecular interchange mechanism, particularly in the case of larger crown ethers such as dibenzo-24-crown-8 (ref. 25, 26). The dissociative mechanism of eq. 7 is detected only when the concentration of the sodium cation is very low (ref. 26). Stöver and Detellier (ref. 27) have explored the effect of various anions on the exchange kinetics in the mechanism of eq. 8. The contrast in perceptions of crown ether complexation kinetics arising from ultrasonic absorption and NMR experiments is interesting. On the basis of ultrasonic and infrared data we have ventured a tentative explanation for the discrepancy (ref. 12). We have observed a dependence of the amplitude of the ultrasonic absorption spectrum upon the nature of the anion as well as the anion concentration at a fixed concentration of sodium cation and 18-crown-6 concentration. We therefore wonder whether the bimolecular exchange mechanism of eq. 8 is just a reflection of an anion versus crown ether competition for a site in the first coordination sphere of the cation

$$MC^+ + X^- \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} MX + C \tag{9}$$
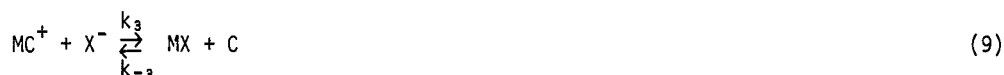
where $X^-$ denotes the anion. If this is true, the observability of the dissociative mechanism, eq. 7, depends not so much on having a low concentration of the cation (ref. 26) as it does on having a low concentration of the anion. Said another way, decomplexation of the cation is solvent-assisted when the cation is not associated with the anion as is usually true in solvents of high relative permittivity. However, decomplexation may be anion-assisted in lower permittivity solvents where the cation exists mainly in pairs, MX. In intermediate situations, both reaction pathways will be present, and the reaction of eq. 9 will dominate when there is a high concentration of anions.

## ACYCLIC POLYETHERS

Crown ethers have been found (ref. 28) to improve the electrical conductivity of solid polymer electrolytes that might be used in lithium batteries. However, there is another way that the above kinetic studies make much closer contact with the practical world of lithium batteries. Poly(ethylene oxide) [hereafter referred to as PEO] has been the prototypical polymer used in studies of lithium battery solid electrolytes. The same $-CH_2CH_2O-$ moiety that appears in the crown ethers is the building-block of PEO. Thus it is hardly surprising that PEO has a high affinity for alkali metal cations just as crown ethers do.

The polymer electrolyte field has been reviewed recently by Cowie and Cree (ref. 29). X-ray studies (ref. 30) of PEO in the solid state revealed a helical structure with a periodicity of seven oxygen atoms over a distance of 1.93 nm which changed upon stretching the polymer. Early interpretations (ref. 31) of conductance measurements suggested helix formation and cation migration within helical tunnels as being prerequisites for the mechanism of ionic transport. Later (ref. 32) it was proposed that the major part of the conduction occurs in the amorphous region of the polymer with the cation migrating by an interchain rather than

by an intrachain mechanism within the helical tunnel. In another treatment (ref. 33) it is assumed that all the transport processes are controlled by the local segmental mobility of the polymer host. An ion is capable of jumping from one site to a neighboring site if the latter site is available and vacant. This in turn depends on the dynamics of the chain segmental motion. The relaxation time of the segmental motion of the polymer chain has been determined (ref. 34) by measurement of dielectric relaxation at microwave frequencies.

There are a number of questions about electrical conductivity in solid polymer electrolytes that remain to be answered: For example, what is the rate of cation wrapping when the cation is coordinated by the polymer chain? Is the process a two stage process with an initial "contact" by one of the oxygen atoms of the polymer chain followed by the complete wrapping of the cation? Conversely, what is the mechanism of cation unwrapping when the cation is "leaving" a coordinating polymer chain? Is the rate of cation migration in the amorphous phase dependent on the segmental motion of the chains, as current theories predict? Can one change systematically the identity of the anion and find evidence for change in the rate of complexation of the cation by the polymer? If the anion forms a stable ion-pair with the cation, will a new relaxation be observed that is attributable to dipolar rotation of the pair? Our first steps in the field of kinetics of complexation by acyclic polymers have been guided by our interest in these questions.

## ULTRASONIC ABSORPTION IN LIQUID SOLUTIONS OF PEO

Ultrasonic absorption spectra have been determined (ref. 35) for acetonitrile solutions variously containing $LiClO_4$, $LiAsF_6$, triglyme and PEO. Triglyme is acyclic and has the formula $CH_3(OCH_2CH_2)_3OCH_3$. It superficially resembles cyclic 12-crown-4 in the number of carbon atoms and ether linkages each molecule contains. Ultrasonic relaxations measured in solutions containing 15,000 average mole weight PEO had substantially larger amplitudes than the relaxations found in solutions of triglyme. However, the relaxation times found in triglyme and in PEO solutions are independent of molecular chain length. Thus there appears to be a localized lithium ion-polyether interaction that we have called the "ether moiety effect." Ultrasonic absorption studies are presently underway with lithium salts and other short polyethers such as tetraglyme and triethylene glycol dissolved in acetonitrile to determine the generality of this surprising observation.

Another way to explore the kinetics of the PEO-salt systems is to replace the lithium salts with sodium salts. In acetonitrile (relative permittivity $\varepsilon = 36.0$ and donor number DN = 14) with $NaClO_4$ and tetraglyme at a molar ratio R = [TG]/[$NaClO_4$] = 1 (where TG denotes tetraglyme) an ultrasonic absorption spectrum is obtained that can be interpreted in terms of two Debye relaxations. Qualitatively, the concentration dependence of the relaxation times is similar to that found for $LiClO_4$ plus triglyme in acetonitrile at 25°C. The existence of three molecular configurations as in eq. 6, i.e., a solvent separated pair, contact pair, and inclusive complex, is supported by the infrared spectrum in the 800 to 900 $cm^{-1}$ frequency range. The tetraglyme spectral envelope in this wavenumber region splits into three Gaussian bands. In contrast to the ultrasonic data for $Li^+$ + PEO at R = [-$CH_2CH_2O$-]/[$M^+$] = 4, the slower of the two ultrasonic relaxations of $Na^+$ + PEO of average molar mass M = 2,000 and at R = 5 shifts to much lower frequencies than those that characterize the $Na^+$ + tetraglyme system in acetonitrile at 25°C.

Dimethylformamide (DMF) has almost the same $\varepsilon$ as $CH_3CN$ but has a much larger DN. When DMF is the solvent for $Na^+$ + tetraglyme the faster ultrasonic relaxation process is the only one detected. The same is true for $Na^+$ + PEO with an average molar mass ranging from 400 to 2000 and with R = 5 at 25°C. However, the forward and reverse rate constants for the formation of the $Na^+$ + PEO contact pair in DMF are smaller than the corresponding rate constants for the $Na^+$ + tetraglyme contact pair. The infrared spectra in the 800 to 900 $cm^{-1}$ region show no evidence of an alteration of the polyether band. This result suggests that little if any of the (NaTG)$^+$ inclusive species forms.

The kinetics of complexation of $Na^+$ with the acyclic tetraglyme and $Na^+$ with the corresponding cyclic polyether 15-crown-5 have been determined in DMF at 25°C. For 15-crown-5 the ultrasonic relaxation envelope can be deconvoluted into two Debye relaxation processes whereas only one relaxation (as noted above) is seen with $Na^+$ + tetraglyme. This suggests the existence of the inclusive complex (Na15C5)$^+$ reflecting a greater affinity of the 15-crown-5 macrocycle than of tetraglyme for the $Na^+$ cation. A significant splitting of the infrared spectral envelope of 15-crown-5 in the 800 to 900 $cm^{-1}$ range when $Na^+$ is added to R = 1 in DMF supports the above interpretation.

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## NOTE ADDED IN PROOF

NMR experiments [ A. Delville, H.D.H. Stover and C. Detellier, J. Am. Chem. Soc. 109, 7293-7301 (1987)] appear to disprove the anion assisted mechanism of decomplexation [our eq.9] in the case of $NaPF_6$ interacting with a crown ether in nitromethane.