Nanosecond Molecular Dynamics and Vibrational Spectra of Li⁺-Chain-Polyethers in Acetonitrile

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University of Utah
Department of Chemistry
Salt Lake City, UT 84112

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Lithium Arsenic Hexafluoride

Ultrasonic relaxation spectra in the 1-500 MHz frequency range for LiC₆O₂ or Li₂AsF₆ (0.03 to 0.1 M) added to open chain polyethers (triglyme) in molar ratio R=1, or added to poly-(ethylene oxide) in molar ratio RPEO = [(CH₂)₂(CH₂O)];[Li⁺] = 4, in the solvent acetonitrile at 25°C are reported. The spectra were interpreted by the sum of two Debye relaxation processes. The remarkable finding is that the relaxation times are independent of the chain length in going from triglyme at R=1 to a poly(ethylene oxide) of 15,000 average molar weight at RPEO = 4. The observed processes appear to reflect a localized cation-polyether interaction (here dubbed the “ether moiety effect”). The relaxations are interpreted by an Eigen-Winkler mechanism in which a cation-ether contact is followed by the polyether chain wrapping around the Li⁺ ion. Specific effects in the ultrasonic absorption amplitudes differentiating the spectra of triglyme from the polyether spectra are reported.
Infrared spectra between 800 and 900 cm\(^{-1}\) of the same systems show cation-ether vibrations due to cage effects. The infrared spectral envelopes of both the polyethers alone and the polyether added to Li\(^{+}\) are deconvoluted by three Gaussian-Lorentzian bands. For triglyme a weak band at 879 cm\(^{-1}\) is strongly enhanced in absorbance and shifted to 870 cm\(^{-1}\) when Li\(^{+}\) is present. This band is attributed to wrapping of the polyether glyme around the cation. Since no significant infrared band enhancement is observed for poly(ethylene oxide) in acetonitrile, it is possible that the same configuration is hindered for long polyether chains.

Ultrasonic and infrared spectra for the cyclic polyether 12-crown-4 in the presence of Li\(^{+}\) in acetonitrile are reported for comparison. For 12C4 + Li\(^{+}\), the ultrasonic spectrum can be interpreted by the sum of two Debye relaxation processes. The first at lower frequencies has a lower relaxation frequency (by a factor of 5) than the one present in triglyme. This may reflect the more rigid ring structure of 12C4 opposing the entrance of the cation and thus altering (enthalpically or entropically) the activation free energy of the complexation process. The infrared spectrum of 12C4 in the 800-900 cm\(^{-1}\) region can be deconvoluted by four Gaussian-Lorentzian bands, two of which dominate the absorbance. Addition of Li\(^{+}\) in molar ratio \(R = [\text{macrocycle}]/[\text{Li}^{+}]\) = 0.5 shifts dramatically both the position and relative intensity of the infrared bands of the crown-ether.
Nanosecond molecular dynamics and vibrational spectra of Li⁺-chain-polyethers in acetonitrile

by

J. Eschmann, J. Strasser, M. Xu, Y. Okamoto, Edward M. Eyring
and S. Petrucci*

Weber Research Institute, Polytechnic University,
Long Island Center, Route 110, Farmingdale, NY 11735, and
Department of Chemistry, University of Utah,
Salt Lake City, UT 84112

Abstract

Ultrasonic relaxation spectra in the 1-500 MHz frequency range for LiClO₄ or LiAsF₆ (0.03 to ~1 M) added to open chain polyethers (triglyme) in molar ratio R=1, or added to poly(ethylene oxide) in molar ratio R_{PBO} = \left[\frac{[-CH₂-CH₂-O-]}{[Li⁺]}\right] = 4, in the solvent acetonitrile at 25°C are reported. The spectra were interpreted by the sum of two Debye relaxation processes. The remarkable finding is that the relaxation times are independent of the chain length in going from triglyme at R=1 to a poly(ethylene oxide) of 15,000 average molar weight at R_{PBO} = 4. The observed processes appear to reflect a localized cation-polyether interaction (here dubbed the "ether moiety effect"). The relaxations are interpreted by an Eigen-Winkler mechanism in which a cation-ether contact is followed by the polyether chain wrapping around the Li⁺ ion. Specific effects in the ultrasonic absorption amplitudes differentiating the spectra of triglyme from the polyether spectra are reported.
Infrared spectra between 800 and 900 cm\(^{-1}\) of the same systems show cation-ether vibrations due to cage effects. The infrared spectral envelopes of both the polyethers alone and the polyether added to Li\(^+\) are deconvoluted by three Gaussian-Lorentzian bands. For triglyme a weak band at 879 cm\(^{-1}\) is strongly enhanced in absorbance and shifted to 870 cm\(^{-1}\) when Li\(^+\) is present. This band is attributed to wrapping of the polyether glyme around the cation. Since no significant infrared band enhancement is observed for poly(ethylene oxide) in acetonitrile, it is possible that the same configuration is hindered for long polyether chains.

Ultrasonic and infrared spectra for the cyclic polyether 12-crown-4 in the presence of Li\(^+\) in acetonitrile are reported for comparison. For 12C4 + Li\(^+\), the ultrasonic spectrum can be interpreted by the sum of two Debye relaxation processes. The first at lower frequencies has a lower relaxation frequency (by a factor of \(\sim 5\)) than the one present in triglyme. This may reflect the more rigid ring structure of 12C4 opposing the entrance of the cation and thus altering (enthalpically or entropically) the activation free energy of the complexation process. The infrared spectrum of 12C4 in the 800-900 cm\(^{-1}\) region can be deconvoluted by four Gaussian-Lorentzian bands, two of which dominate the absorbance. Addition of Li\(^+\) in molar ratio \(R = \frac{[\text{macrocycle}]}{[\text{Li}^+]} = 0.5\) shifts dramatically both the position and relative intensity of the infrared bands of the crown-ether.
Introduction

The mechanism of complexation of cyclic polyethers with alkali ions in aqueous and nonaqueous solutions has been studied extensively by ultrasonic, NMR and stopped flow techniques. In media of relatively high permittivity (where anion competition for the first coordination shell of the cation is negligible) the Eigen-Winkler mechanism:\(^2\)

\[
\begin{align*}
&k_0 \quad k_1 \quad k_2 \\
&k_0 \quad k_1 \quad k_2
\end{align*}
\]

appears to rationalize successfully most of the kinetic data. The present paper extends this kinetic research to open chain polyethers and to polymers. Justifications for such a study include the wish to understand the "macrocyclic effect"\(^3\) (namely the ring effect, whether enthalpic or entropic) on the rate of ion complexation. Elongating the open polyether chain yields data relevant both to biological systems and to new, thin film, polymeric battery electrolytes.

Ultrasonic relaxation techniques,\(^4\) covering the 1-500 MHz frequency range (0.3 ns to 160 ns), have proven to be particularly suitable tools for this kinetic investigation.

Infrared (IR) spectra have been obtained in the 800 to 900 cm\(^{-1}\) region because polyethers in the presence of cations have shown Raman absorption bands which were ascribed\(^5\) to the cation vibrating in an ethereal solvation-cage. Since Li\(^+\) vibrates against a solvent cage at ~400 cm\(^{-1}\),\(^6\) the bands at 800-900 cm\(^{-1}\) are similar in nature to the far-IR bands now appearing in the IR spectrum for polyether-ligands.
Experimental

The equipment and procedures for the ultrasonic and IR work have been described elsewhere.\(^1\) LiClO\(_4\) (Aldrich) and LiAsF\(_6\) (Agri. Chem. Co.) were dried at 70°C in vacuo for several hours to constant weight. Acetonitrile (Aldrich, gold label) was distilled over P\(_2\)O\(_5\) after refluxing the liquid for a few hours. Triglyme (Aldrich) was distilled in vacuo in an all Pyrex column without grease on the joints. Poly(ethylene oxide) (MW ~ 15,000) was prepared in Dr. Okamoto’s laboratory. It was dried in vacuo to constant weight at room temperature before use. Solutions of electrolytes and polyethers were prepared by weight, bringing the solution to volume in volumetric flasks with distilled acetonitrile, after dissolving the solute in the same solvent. Contact with the atmosphere during preparation of the solutions and filling of the cells was kept to a minimum (~ 30 seconds overall).

For polymeric solutions the (-CH\(_2\)-CH\(_2\)-O-) moiety was the "molar mass unit." Hence solutions reported as R\(_{PEO}\) = 4 have a composition [(-CH\(_2\)-CH\(_2\)-O-)]/[LiX] = 4 where X denotes the anion. A solution of triglyme [CH\(_3\)(-O-CH\(_2\)-CH\(_2\))\(_3\)-OCH\(_3\)]/[LiX] = 1 is equivalent to a polymer solution at R\(_{PEO}\) = 4 that can be depicted as (-CH\(_2\)-CH\(_2\)-O-\(_4\))/LiX with the same oxygen atom to Li\(^+\) ratio.
Results and Calculations

a) Ultrasonic Relaxation Kinetics

Figures 1A and 1B are representative ultrasonic absorption spectra of LiClO$_4$ + Triglyme and LiClO$_4$ + PEO, respectively, in acetonitrile at 25°C. The ultrasonic spectra are expressed in terms of the function $\mu$, the excess sound absorption per wavelength,$^4$

$$\mu = \alpha_{\text{exc}} \lambda = (\alpha - Bf^2) \frac{u}{f} \quad (1)$$

where the wavelength $\lambda = \frac{\mu}{f}$ with $u$ denoting the sound velocity and $f$ the frequency. Here $\alpha$ is the sound attenuation coefficient at the frequency $f$.

$B$ is the value of $\frac{3}{f^2}$ at frequencies much higher than the relaxation frequency(ies) of the process(es) under study.

The solid line in these ultrasonic absorption spectra is $\mu$ evaluated as the sum of two Debye relaxation processes$^3$

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

with $\mu_I$ and $\mu_{II}$ the maximum excess sound absorptions per wavelength at the respective relaxation frequencies $f_I$ and $f_{II}$. The insets of Figs. 1A and 1B report the tail of the relaxation processes expressed by $a/f^2$ vs $f$ where the solid line is eq. 2 rearranged$^3$ to read
\[ \frac{a}{f^2} = \frac{A_I}{1+(f/f_I)^2} + \frac{A_{II}}{1+(f/f_{II})^2} + B \]  

(3)

with \( A_I = 2\mu_I/f_I u \) and \( A_{II} = 2\mu_{II}/f_{II} u \). Table I (microfilm edition) reports the parameters \( \mu_I, f_I, \mu_{II}, f_{II}, B \) and the sound velocity \( u \). These five parameters were calculated by a computer-graphic fit of eqs. 2 and 3 to the experimental values \( a/f^2 \) and \( \mu \) vs. \( f \) data. Estimated average errors are \( \pm 5\% \) for the \( \mu \) values, \( \pm 2 \text{ MHz} \) for the \( f_I, f_{II} \) values, and \( \pm 1 \times 10^{-17} \text{ cm}^{-1} \text{ s}^2 \) for \( B \) while the sound velocities are affected by an experimental average error of \( \pm 1\% \).

Figures 2A and 2B report the values of \( u \) and of \( B \) vs concentration for the various systems investigated. Specific effects appear for \( u \) depending on the electrolyte and independent of the polyethers. On the other hand, \( B \) values seem to show specificity for both anion and polyether with increasing concentration. Apparently, the electrolyte influences the adiabatic compressibility \( \beta_s = \frac{1}{\rho u^2} \) through the sound velocity \( u \) where \( \rho \equiv \text{density} \).

Both the shear viscosity \( \eta_s \) and the bulk compressional viscosity \( \eta_v \) of the liquids are affected by the polyethers and the anions

\[ \frac{a}{f^2} = \frac{2\pi}{\rho u^3} \left( \frac{4}{3} \eta_s + \eta_v \right) \]  

(4)
since the value of $\frac{f}{f_2^2}f_{II} >> f_{I}, f_{II}$
and anion concentrations.

Figure 3A reports the inverse of the relaxation times for the "fast" process, $\tau_{I}^{-1} = 2\pi f_{I}$, plotted vs. the concentration of the electrolyte. The significant features of this plot are a leveling to a plateau of the $\tau_{I}^{-1}$ values with increasing concentration and the independence of the results of the nature of the ligand (triglyme or POE) as well as of the type of anion present (ClO$_4^-$ or AsF$_6^-$). A solution containing either of the electrolytes alone or either of the polyethers alone does not show any ultrasonic relaxation. Thus the observed effect is due to the interaction of Li$^+$ with the polyethers. This interaction is local in the sense that each Li$^+$ interacts with a local section of the PEO (one or more oxygens of the four available per Li$^+$ atom) and ignores the next segment + Li$^+$ interaction. We have chosen to call this the "ether moiety effect". This would explain the equality of the ultrasonic results for Li$^+$ + PEO with those for Li$^+$ + TG (TG $\equiv$ triglyme) in the solvent acetonitrile.

Figure 3B is a plot of $\tau_{II}^{-1} = 2\pi f_{II}$ for the "slow" process vs. the concentration of the electrolyte. The same qualitative behavior as for $\tau_{I}^{-1}$ vs. concentration is observed with the data tending asymptotically toward a constant value at high concentration and showing independence of
the nature of either the polyether or anion within experimental error (except for two points at 0.1 and 0.5 M). Hence the same general conclusions reached for the "fast" process also apply here.

On the basis of the above observations, we propose a mechanism of the Eigen-Winkler type\textsuperscript{2} wherein Li\textsuperscript{+} and the polyether (or a segment of it in the case of PEO) approach each other, presumably by a diffusion controlled process, followed by a first encounter involving partial desolvation of Li\textsuperscript{+} ion and contact with one oxygen atom of the polyether. This process is then followed by the polyether wrapping around the completely desolvated Li\textsuperscript{+} ion. This sequence of events can be represented by the scheme:

\[
\text{Li}^+ + \text{TG} \xrightarrow{k_0} \text{Li}^+ \ldots \text{TG} \xrightarrow{k_1} \text{LiTG}^+ \xrightarrow{k_2} \text{(LiTG)}^+ \quad (5)
\]

which at high concentrations, when [Li\textsuperscript{+}] and [TG] become relatively very small, is reduced to a pseudo first-order scheme

\[
\text{Li}^+ \ldots \text{TG} \xrightarrow{k_1} \text{LiTG}^+ \xrightarrow{k_2} \text{(LiTG)}^+ \quad (6)
\]

that is observed experimentally.

In the above mechanisms, TG can be replaced by a segment of PEO. Also, Li\textsuperscript{+}...TG represents a solvent separated species, whereas LiTG\textsuperscript{+} and (LiTG)\textsuperscript{+} symbolize the contact and the "wrapped" complex respectively. From scheme (5), following Eigen and Tamm,\textsuperscript{8} it follows that for the "fast" process:
\[ \tau^{-1} = k_1 \frac{\theta}{\theta + K_0} + k_{-1} = k_1 \phi + k_{-1} \]  \hspace{1cm} (7)

with \( \theta \approx 2\sigma C \) where \( \sigma \) is the degree of dissociation of the complex \((LiT_G)^+\).

Thus the observed "fast" relaxation corresponds to the second step of scheme (5) coupled to the one with \( K_0 = \frac{k_{-0}}{k_0} \), the inverse of the equilibrium constant of the first step. At high enough concentration, one can predict that \( \theta >> K_0 \) and \( \phi + 1 \) giving

\[ \tau^{-1} = k_1 + k_{-1} \]  \hspace{1cm} (8)

whereas as \( C \to 0 \) \( \tau_1^{-1} = k_{-1} \)  \hspace{1cm} (9)

Condition (8) is achieved experimentally, as shown in Fig. 3A, giving \( \tau_1^{-1} = k_1 + k_{-1} = 6.3 \times 10^8 \text{ s}^{-1} \). Taking the data at \( C < 0.15 \text{ M} \) for \( Li^+ + PEO \), namely \( \tau^{-1} \times 10^{-8} \text{ (s}^{-1}) = 2.83, 3.46, 4.40 \) and 5.66 for \( C = 0.05, 0.076, 0.10 \) and 0.15 M respectively, by linear regression one obtains the determination coefficient \( r^2 = 0.993 \), intercept \( I = 1.4 \times 10^8 \), and slope \( S = 2.88 \times 10^9 \). Thus for the first step of scheme (6): \( k_{-1} = 1.4 \times 10^8 \text{ s}^{-1} \), \( k_1 = 4.9 \times 10^8 \text{ s}^{-1} \) and \( K_1 = (k_1/k_{-1}) = 3.5 \). From scheme (5), following Eigen and Tamm, one can write for the "slow" process:

\[ \tau_{II}^{-1} = k_2 \frac{\phi}{\phi + k_{-1}} + k_{-2} \]  \hspace{1cm} (10)
where $K_{-1} = (3.5)^{-1} = 0.29$.

At high enough concentrations, one can have the condition $\phi = 1$, and:

$$\frac{\phi}{\phi + K_{-1}} = \frac{1}{1.3} = 0.77.$$ 

Therefore $\tau_{II}^{-1} = 0.77 k_2 + k_{-2} \sim 1.2 \times 10^7 \text{ s}^{-1}$ as taken from the asymptotic value of $\tau_{II}^{-1}$ (Fig. 3B). Also, from the data for Li$^+$ + PEO at $C \leq 0.20$,

namely $\tau_{II}^{-1} \times 10^7(\text{s}^{-1}) = 1.76$, $2.51$, $4.40$, $4.71$, $5.65$ at the concentrations $C = 0.05$, $0.076$, $0.10$, $0.15$, $0.20$ (mol/dm$^3$) respectively, by linear regressions, one obtains $r^2 = 0.88$, intercept $I = 9.1 \times 10^6$, and slope $S = 2.5 \times 10^8$.

Thus for the slow step of scheme (6): $k_{-2} = 9 \times 10^6 \text{ s}^{-1}$, $k_2 = (10.4 - 0.9)10^7/0.77 \sim 1.2 \times 10^7 \text{ s}^{-1}$ and $K_2 = (k_2/k_{-2}) = 13$.

The overall formation constant $K_L$ is related to the formation constants of the various steps by:

$$K_L = K_0(1 + K_1 + K_1K_2),$$

leading in this case to the numerical result: $(K_L/K_0) = 1 + K_1 + K_1K_2 = 50$.

From these calculations it follows that forward and reverse rate constants and equilibrium constants of scheme (6) are independent of the length of the
poly(ethylene oxide) chains at an oxygen to Li\(^+\) ratio = 4 in the solvent CH\(_3\)CN.

Examination of the values of \(\mu_I\) and \(\mu_{II}\) reported in Table I further illuminates the situation. Figure 4A is a plot of \(\mu_I\), the excess sound absorption coefficient per wavelength, for the "fast" process plotted vs. the concentration of electrolyte. The data show a strong dependence on the nature of the polyether ligand.

Following Eigen and Tamm,\(^8\) scheme (5) can be rewritten as

\[
\begin{align*}
\text{Li}^+ + \text{PEO} & \rightleftharpoons C_0 \quad \text{Li}^+ \ldots \text{PEO} \rightleftharpoons C_1 \quad \text{LiPEO}^+ \rightleftharpoons C_2 \\
& \rightleftharpoons (\text{LiPEO})^+ C_3
\end{align*}
\] (12)

where PEO denotes here the segment of the polymer reacting with a particular Li\(^+\) ion.

From the above, \(C = C_0 + C_1 + C_2 + C_3 \sim C_1 + C_2 + C_3\), neglecting \(C_0\) (\(C_0 \ll C_1, C_2, C_3\)). Then:

\[
\mu_I = \frac{\pi \Delta V_I^2}{2\beta g} \frac{1}{RT} \frac{1}{[\frac{1}{C_1} + \frac{1}{C_2}]} = \frac{\pi \Delta V_I^2}{2\beta g} \frac{1}{RT} \Gamma_I^{-1}.
\] (13)

The calculation of \(C_1, C_2, C_3\), and hence of \(\Gamma_I^{-1}\) has been done by using the relations: \(C \sim C_1 + C_2 + C_3\), \(K_1 = (C_2/C_1) = 3.5\) and \(K_2 = (C_3/C_2) = 13.5\).

Figure 5A is a plot of \(\mu_I\) vs. \(\Gamma_I^{-1}\) data for LiClO\(_4\) + PEO and LiAsF\(_6\) + PEO for \(C \leq 0.5\) M. Linear regression, giving 50% statistical weight to the
origin, gives \( r^2 = 0.994 \), an intercept \( I = 6.9 \times 10^{-5} \), and a slope \( S = 942.2 \) from which, given \( \beta_s = \left( \rho u^2 \right)^{-1} = \left[ 0.777 \times (1.279 \times 10^5)^2 \right]^{-1} = 78.6 \times 10^{-12} \), it follows that

\[
\Delta V_I = \left[ \frac{28}{\pi} \frac{RT}{S} \right]^{1/2} = 34.2 \text{ cm}^3/\text{mole}.
\]

The \( \mu_I \) data in the plot of \( \mu_I \) vs. \( C \) for Li\(^+\) + TG appear to be too small in value to attempt a correlation with \( \Gamma^{-1}_I \), requiring a slope to evaluate \( \Delta V_I \).

Figure 4B is a plot of \( \mu_{II} \) vs. \( C \), (the excess sound absorption per wavelength for the "slow" process vs. concentration) for all the systems investigated. One notices (as for the corresponding plot of \( \mu_I \) vs \( C \)) a saturation or tendency to saturation of \( \mu_{II} \) with \( C \), thereafter \( \mu_{II} \) becoming independent of \( C \). In addition, whereas all the data of LiClO\(_4\) + TG, LiClO\(_4\) + PEO and LiAsF\(_6\) + TG seem to fall on a common line, the data for LiAsF\(_6\) + PEO diverge, and they follow their own saturation trend. This anion specificity, for longer chain polyethers, will be investigated later.

For the moment we will focus on the data for Li\(^+\) + PEO (LiClO\(_4\) + PEO) at \( C \leq 0.32 \text{ M} \). Following Eigen and Tamm,\(^8\) for process (6):

\[
\mu_{II} = \frac{28}{\beta_s} \frac{RT}{\Gamma_{II}^{-1}} \frac{\Delta V_{II}^2}{\left[ C_1 + C_2 + C_3 \right]^1} = \frac{28}{\beta_s} \frac{RT}{\Gamma_{II}^{-1}} \Delta V_{II}^2
\]

(14)
Figure 5B reports the data for $v_{II}$ plotted vs. the calculated $F_{II}^{-1}$. Linear regression applied to the linear portion of the plot of the LiClO$_4$ + PEO data for $C < 0.32$ M, assigning 50% statistical weight to the origin, gives $r^2 = 0.98$, an intercept $I_{II} = 6.1 \times 10^{-5}$, and a slope $S_{II} = 144$, from which it follows that

$$\Delta v_{II} = \left[ \frac{28R}{S_{II}} \right] \frac{1}{2} = 13.4 \text{ cm}^3/\text{mole}.$$

b) Infrared Spectra

Figure 6A is the infrared spectrum in the 800-900 cm$^{-1}$ region of triglyme 0.6 M in acetonitrile. The spectral envelope can be deconvoluted by three Gaussian-Lorentzian semiempirical product functions$^9$ (dashed lines):

$$A_j = A_j^0 \left[ \exp \left( -\frac{(\tilde{\nu} - \tilde{\nu}_j^0)^2}{2\sigma_j^2} \right) \right] \left[ 1 + \frac{(\tilde{\nu} - \tilde{\nu}_j^0)^2}{\sigma_j^2} \right]^{-1}$$

where $A_j^0$ is the absorbance at the peak of the band centered at the wavenumber $\tilde{\nu}_j^0$, $\tilde{\nu}$ is the wavenumber (cm$^{-1}$) and $\sigma_j^2$ is the variance, with the standard error $\sigma_j = \frac{(\Delta \tilde{\nu}_{1/2})_j}{1.46}$. $(\Delta \tilde{\nu}_{1/2})_j$ is the width of the function at $A_j^0/2$. 

Addition of either 0.6 M LiClO$_4$ or 0.6 M LiAsF$_6$ (Figs. 6B and 6C) in molar ratio R=1 causes a shift of the spectrum to lower wavenumbers and strong enhancement of the higher frequency band, which now appears at 870 cm$^{-1}$.

Previous workers$^5$ noted a similar appearance of bands at 800-900 cm$^{-1}$ upon addition of alkali ions to polyethers including macrocycles. These bands were attributed$^5$ to vibration of the ion inside an ethereal wrap-around cage similar to the far infrared spectra of alkali vibrating against a solvent cage$^6$ (~400 cm$^{-1}$ for Li$^+$).

A similar interpretation is given here to the band at 870 cm$^{-1}$ for Li$^+$ + triglyme. The normalized absorbances at unit cell length $A^0_j/l$ for triglyme and Li$^+$ + triglyme are reported in Figs. 7A and 7B. The band at 870 cm$^{-1}$ (with an amplitude independent of the nature of the anion) is shown in Fig. 7B to be very much enhanced with respect to the one at 874 cm$^{-1}$ for pure triglyme in CH$_3$CN. Thus for Li$^+$ + triglyme there is structural evidence that correlates nicely with the dynamic spectra produced by ultrasonic relaxation techniques.

The situation is not so straightforward when the infrared spectra of PEO and of Li$^+$ + PEO are considered. Figures 8A, 8B and 8C report the infrared spectral profiles of the digitized spectra for PEO, LiClO$_4$ + PEO
and LiAsF$_6$ + PEO, respectively, in the 800-900 cm$^{-1}$ region. Again, three Gaussian-Lorentzian functions (dashed lines) can describe the spectra (solid lines in Figs. 8A, 8B, and 8C). However, in the present case, no strong enhancement of bands occurs with the exception of a modest increase of the band at 811-813 cm$^{-1}$ which appears also to be anion dependent.

Figures 9A, 9B, and 9C compare the normalized absorbances $A_j^0/l$ per unit length of cell for the three bands for PEO alone and for the two electrolyte solutions. Consistent with the above observations, the electrolyte does seem to depress the value of $A_j^0/l$ for the two upper bands at ~864 and 845 cm$^{-1}$. Evidently, for long chain polyethers, the structural configuration that causes the appearance of a new or enhanced band when Li$^+$ is present does not form. Thus, in this respect there is no correspondence between the information deduced from ultrasonic absorption spectra (very similar for TG and PEO) and the information derived from the infrared spectra.

All the parameters required for the deconvolution of the spectral envelopes by eq. 15 are reported in Table II (microfilm edition).

c) **Comparison with macrocycle - lithium ion interactions in solutions of LiClO$_4$ + 12C4 in acetonitrile.**

A comparison of the above results, gathered on Li$^+$ interacting with triglyme, with corresponding information for Li$^+$ interacting with the cyclic macrocycle 12C4 could conceivably illuminate both systems. 12-crown-4 is
the macrocycle that corresponds to the acyclic triglyme since both have four oxygen atom electron donors per molecule:

Figure 10A is the ultrasonic absorption spectrum of LiCtO₄ 0.3 M + 12C₄ 0.3 M in acetonitrile at 25°C plotted as μ vs f. Two Debye relaxation processes adequately describe the spectrum. Whereas the upper relaxation has a frequency comparable to that reported above for LiCtO₄ + TG, the lower relaxation frequency for LiCtO₄ + 12C₄ is about 5 times smaller at C = 0.3 M than the corresponding relaxation frequency for LiCtO₄ + TG in acetonitrile.

Assuming either scheme 5 or 6 also applies for the Li⁺ + 12C₄ system, the qualitative conclusion to be drawn is that the free energy of activation barrier ΔG°, for the "slow" process, is greater for 12C₄ than that for the triglyme. It remains to be established whether this difference has an enthalpic or entropic origin, although the rigidity of the 12C₄ polyether ring compared to the flexible TG, would appear to play a leading role in the relative ease of cation encapsulation. The fitted parameters μ_I, f_I, μ_II, f_II, B and the sound velocity u for LiCtO₄ 0.3 M + 12C₄ 0.3 M in acetonitrile at 25°C, are reported in Table I (microfilm edition).
Figure 10B is a representative infrared spectrum in the 800-900 cm\(^{-1}\) region for 12C4 in the solvent acetonitrile, expressed in absorbance \(A\) vs. wavenumber \(\tilde{\nu}(\text{cm}^{-1})\). The spectral envelope has been deconvoluted into three Gaussian-Lorentzian product functions, eq. 15. From Fig. 10B it is evident that the two bands centered at \(\tilde{\nu}_o = 851 \text{ cm}^{-1}\) and \(\tilde{\nu}_o = 844 \text{ cm}^{-1}\) are the dominant components of the spectral envelope. A third band centered at \(\tilde{\nu}_o = 833 \text{ cm}^{-1}\) is invisible at \(C = 0.2 \text{ M}\), but becomes evident at higher concentrations. A fourth satellite band appears at \(\tilde{\nu}_o = 815 \text{ cm}^{-1}\). These results may indicate the presence of two predominant conformers in solution associated with \(\tilde{\nu}_o = 851\) and \(\tilde{\nu}_o = 844 \text{ cm}^{-1}\), respectively. For all the macrocyclic systems investigated, the parameters \(\tilde{\nu}_j\), \(A^0_j\) \((\Delta\tilde{\nu}_{1/2})_j\) and calibrated cell lengths are reported in Table II (microfilm edition).

Figure 11A reports the absorbances \(A_j^0\), normalized by the cells lengths \(l\), as functions of the total concentration of the crown ether in CH\(_3\)CN. The solid lines, in Fig. 11A, have been calculated by fitting cubic polynomials \((A_j^0/l) = a + bC + \gamma C^2 + \delta C^3\) to the \((A_j^0/l)\) vs. concentration \(C\) data. The parameters \(a, b, \gamma\) and \(\delta\) are reported in Table II (microfilm edition), together with the determination coefficients \(r^2\).

Qualitative similarities and differences between the spectra of 12C4 and those of triglyme and of PEO in CH\(_3\)CN should be noted. The spectral
profiles of all of the three species at low concentrations are interpretable by three Gaussian-Lorentzian bands, although both the positions $\nu_j^0$ and the spectral absorbances $A_j^0$ are different for the three different species.

Figure 10C shows a representative digitized infrared spectrum of LiClO$_4$ + 12C4 in the 800-900 cm$^{-1}$ region in molar ratio $R = \frac{[12C4]}{[LiClO_4]} = 0.50$. Below this value of the ratio the spectral profile remained constant (at the same concentration of 12C4), a sign of saturation of the crown ether by the cation Li$^+$. Figure 10C shows a dramatic change in the wavenumber, number of bands, and the relative absorbance $A_j^0$ of both of the two major bands of 12C4 in acetonitrile (Fig. 10B). The relative shift in absorbance of the bands suggests the predominance of one configuration when Li$^+$ is present, probably that with the Li$^+$ cation imbedded in the cavity of 12C4.

Table II displays the results in terms of the parameters $\bar{\nu}_j^0$, $A_j^0$ and $(\Delta \nu_{1/2})$, for the deconvoluted infrared spectra of LiClO$_4$ + 12C4 at molar ratio $R = 0.5$ in acetonitrile. Figure 11B reports the normalized absorbances $A_j^0/\bar{A}$ vs. concentration for LiClO$_4$ + 12C4 at $R = 0.5$ in acetonitrile. As in the case of Li$^+$ + TG, presented above, unambiguous evidence for the interaction between Li$^+$ and the polyether 12C4 is seen.
here, possibly of the same nature, namely Li$^+$ vibrating against the ethereal cage of the cyclic cavity.

d) **Influence of the polymer chain length on the ultrasonic relaxation spectra and on the IR spectra.**

The changes of $\mu_I$ from triglyme to PEO (15,000) as shown in Fig. 4A were of interest. Also the changes in $\mu_{II}$ shown for LiAsF$_6$ + PEO, with respect to the other systems (Fig. 4B), clearly indicate an anion effect as mentioned above. To clarify this result we have recorded ultrasonic spectra of LiAsF$_6$ 0.50 M + tetraglyme 0.50 M and of LiAsF$_6$ + PEO of average molar mass 400, 1000, 2000 in molar ratio $R = \frac{[(-\text{CH}_2-\text{CH}_2{-}\text{O}-)]}{[\text{Li}^+]} = 4$ in acetonitrile at 25°C.

The spectra were interpreted by the sum of two Debye relaxation processes. The parameters for the fit, namely $\mu_I$, $f_I$, $\mu_{II}$, $f_{II}$, B and the sound velocity $u$ are reported in Table III (microfilm edition). The most salient effect associated with chain length is reported in Fig. 12 where $\mu_I$ and $\mu_{II}$ are replotted vs. average molar mass.

It can be seen that $\mu_I$ increases from the value in triglyme to the value for PEO (15,000), the larger initial increase occurring for $R < 1000$. Similarly, the values of $\mu_{II}$ decrease rapidly for $R < 1000$ and reach a plateau. Whereas the first effect for $\mu_I$ is associated with the chain
length of the polymer, the second effect for $\mu_{II}$ is also dependent on the anion, the effect of decreasing $\mu_{II}$ with increasing $\bar{M}$ not being present for LiClO$_4$. As the relaxation frequencies, the rate constants and the equilibrium constants are not affected by either chain length or anion, the above effects seem to be linked to $\Delta V_I$ and $\Delta V_{II}$, namely to the isoentropic volume changes of reaction. The specific molecular mechanisms of this behavior are not apparent at the present time. The anion dependence of $\mu_{II}$ may reflect some steric hindrance to the complete wrapping of the polyether chain about the cation (due to the presence of the anion AsF$_6^-$), which increases rapidly with increasing polyether chain length. Notice, in fact, from Fig. 4B, that the effect of $\mu_{II}$ diverging from the common behavior is specific for LiAsF$_6$ in PEO; hence it is an anion effect associated with the length of the polyether chain.

An effect also dependent on the chain length is detectable from the IR spectra of the same systems in the 910-780 cm$^{-1}$ region. Table IV (microfilm edition) reports the infrared parameters for the systems tetracyglyme 0.5 M + LiAsF$_6$ 0.50 M in acetonitrile and for the systems LiAsF$_6$ 0.5 M + poly(ethylene oxide) polymers of average molar masses 400, 1000, and 2000 respectively in acetonitrile. The composition of these mixtures corresponds to a molar ratio $R = [(-\text{CH}_2=\text{CH}_2-\text{O-})]/[\text{Li}^+] = 4$. Except for the system
tetraglyme 0.5 M + LiAsF₆ 0.5 M, the spectral envelopes have been deconvoluted by three Gaussian-Lorentzian product functions.

Table IV (microfilm edition) reports also the parameters related to the IR spectra of the polyethers alone in CH₃CN at the same concentrations as studied for the systems containing LiAsF₆ and in the 910-780 cm⁻¹ range. Three Gaussian-Lorentzian product functions suffice to describe the spectral profiles.

Figure 13 reports the most salient information from the above spectra, namely the decrease in the normalized absorbance for the band appearing in the range 860-880 cm⁻¹ (for the various systems investigated) vs. the molar mass \( \bar{M} \) of the polyethers. The rapid decrease in \( (A_2^0/l) \) with \( \bar{M} \), when Li⁺ is present, resembles the behavior of \( \mu_{\text{II}} \) as a function of \( \bar{M} \) (Fig. 12). It is possible that both \( \mu_{\text{II}} \) and \( A_2^0/l \) reflect the increasing difficulty, by increasing \( \bar{M} \), of forming a given coordinated structure around Li⁺. This would cause a decrease in absorbance and in \( \mu_{\text{II}} \) (through \( \Delta V_{\text{II}} \)) for the IR band and ultrasonic spectrum, respectively.

The other main relevant feature of the IR spectra is the appearance of a new band for LiAsF₆ 0.5 M + tetraglyme 0.5 M in acetonitrile at \( \tilde{\nu}^0 = 837 \) cm⁻¹ (termed arbitrarily \( \tilde{\nu}_4^0 \)). The new band is sizeable (Fig. 14); its absorbance is comparable to the band at \( \tilde{\nu}_3^0 = 869 \) cm⁻¹, which is the one
enhanced by Li⁺ when added to the polyethers (Fig. 13). It is possible that for tetruglyme, as the oxygen to Li⁺ ratio is 5 instead of 4 (as for the other systems) a different coordination symmetry is being formed.

Acknowledgments

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References


Glossary of Figures

Fig. 1  A. Representative ultrasonic spectrum in the form of excess ultrasonic absorption per wavelength $\mu$ vs. the frequency $f$ for LiClO$_4$ + Triglyme at $R = 1$ in acetonitrile at 25°C.

B. Representative ultrasonic spectrum in the form $\mu$ vs. $f$ for LiClO$_4$ + PEO at an oxygen to Li$^+$ molar ratio $R_{\text{PEO}} = 4$ in acetonitrile at 25°C.

Fig. 2  A. Values of the sound velocity $u$ vs. concentration of electrolyte $C$ for all systems investigated in acetonitrile at 25°C.

B. Value of the ratio $B = \left(\frac{a}{f^2}\right)_{f\gg f_I,f_{II}}$ vs. concentration $C$ for all the systems investigated in acetonitrile at 25°C.

Fig. 3  A. Inverse of the relaxation time of the "fast" process $\tau_{I}^{-1}$ vs. the concentration of electrolyte for all the systems investigated in acetonitrile at 25°C.

B. Inverse of the relaxation time of the "slow" process $\tau_{II}^{-1}$ vs. the concentration of electrolyte for all the systems investigated in acetonitrile at 25°C.

Fig. 4  A. Excess sound absorption coefficient for wavelength $\mu_I$ for the "fast" process vs. concentration of electrolyte for all the systems investigated in CH$_3$CN at 25°C.
B. Plot of $u_{II}$ for the "slow" process vs. $C$ for all the systems investigated in CH$_3$CN at 25°C.

Fig. 5
A. Plot of $u_{I}$ vs. $r_{I}^{-1}$ for LiClO$_4$ + PEO at molar ratio $R = 4$ and $C \leq 0.5$ M in acetonitrile at 25°C.

B. Plot of $u_{II}$ vs. $r_{II}^{-1}$ for LiClO$_4$ + PEO at $R = 4.0$ and $C \leq 0.32$ M in acetonitrile at 25°C.

Fig. 6
A. Digitized infrared spectrum [Absorbance vs. $\tilde{v}$ (cm$^{-1}$)] of triglyme 0.6 M in acetonitrile in the 800-900 cm$^{-1}$ region.

B. Digitized absorbances vs. wavenumber for LiClO$_4$ 0.6 M + Triglyme 0.6 M in acetonitrile in the 800-900 cm$^{-1}$ region.

C. Digitized absorbance vs. wavenumber for LiAsF$_6$ 0.6 M + Triglyme 0.6 M in acetonitrile in the 800-900 cm$^{-1}$ region.

Fig. 7
A. Normalized absorbances per unit cell length $A_{j}^0/\xi$ vs. concentration for the deconvoluted spectrum (expressed by the three bands) of triglyme in CH$_3$CN.

B. Normalized absorbance per unit cell length $A_{j}^0/\xi$ vs. concentration for LiClO$_4$ or LiAsF$_6$ + Triglyme at $R = 1$ in acetonitrile.
Fig. 8.  
A. Digitized infrared spectrum in the 800-900 cm\(^{-1}\) region for PEO of molar unit (-CH\(_2\)-CH\(_2\)-O-)\(_4\) 0.4 M in acetonitrile.

B. Digitized infrared spectrum in the 800-900 cm\(^{-1}\) region for LiClO\(_4\) + PEO at molar ratio R [oxygen]/[Li\(^+\)] = 4 in acetonitrile.

C. Digitized infrared spectrum in the 800-900 cm\(^{-1}\) region for LiAsF\(_6\) + PEO at molar ratio R [oxygen]/[Li\(^+\)] = 4 in acetonitrile.

Fig. 9 A,B,C  
Normalized absorbances A\(_j^0/l\) per unit cell length of the three bands of PEO and of PEO + Lithium salts in acetonitrile.

Fig. 10  
A. Ultrasonic spectrum of LiClO\(_4\) 0.3 M + 12C\(_4\) 0.3 M in acetonitrile at 25\(^\circ\) C.

B. Representative digitized spectrum of 12C\(_4\) in acetonitrile in the 800-900 cm\(^{-1}\) region.

C. Representative digitized spectrum of LiClO\(_4\) + 12C\(_4\) at R = \([12C_4]/[LiClO_4]\) = 0.5 in acetonitrile in the 800-900 cm\(^{-1}\) region.

Fig. 11  
A. Normalized absorbance A\(_j^0/l\) vs. concentration for the 12C\(_4\) in acetonitrile.
B. Normalized absorbance $A_j^0/1$ vs. concentration for $\text{LiClO}_4 + 12\text{C}_4$ at $R = 0.5$ in acetonitrile.

Fig. 12 Dependence of $\mu_1$ and of $\mu_{II}$ on the average molar mass $\bar{M}$ of the polyether for $\text{LiAsF}_6 0.5 \text{ M} + \text{polyether}$ in acetonitrile.

Fig. 13 Dependence of the normalized absorbance $A_3^0/1$ upon average molar mass $\bar{M}$ of the polyether for $\text{LiAsF}_6 + \text{polyethers}$ and for polyethers in acetonitrile.

Fig. 14 Deconvoluted infrared spectral envelope of the digitized spectrum of the system $\text{LiAsF}_6 0.50 \text{ M} + \text{tetraglyme} 0.50 \text{ M}$ in $\text{CH}_3\text{CN}$. The dashed Gaussian-Lorentzian component centered at $\nu^0 = 837 \text{ cm}^{-1}$ is specific for the tetraglyme + Li$^+$ solution.
$\mu_I = 110 \times 10^{-5}$
$\mu_I = 400 \times 10^{-5}$
$f_I = 90 \text{MHz}$
$f_I = 12 \text{MHz}$
$B = 60 \times 10^{-17} \text{cm}^{-1} \text{s}^{-2}$
$u = 1.300 \times 10^5 \text{cm}^{-1}$

Ultrasonic relaxation spectrum
$\text{LiClO}_4 0.32 \text{M} + \text{triglyme} 0.32 \text{M}$
in CH$_3$CN; $T = 25^\circ \text{C}$.

$\mu_I = 500 \times 10^{-5}$
$f_I = 100 \text{MHz}$
$\mu_I = 350 \times 10^{-5}$
$f_I = 12 \text{MHz}$
$B = 53 \times 10^{-17} \text{cm}^{-1} \text{s}^{-2}$
$u = 1.288 \times 10^5 \text{cm} \text{s}^{-1}$
Sound velocities vs. electrolyte concentration for Li$^+$+PEO and Li$^+$+TG systems in CH$_3$CN; $t$=25°C.

- LiClO$_4$+PEO; $R$=4.0
- LiAsF$_6$+PEO; $R$=4.0
- LiClO$_4$+TG; $R$=4.0
- LiAsF$_6$+TG; $R$=4.0

Background sound absorption parameter B vs. electrolyte concentration for Li$^+$+PEO and Li$^+$+TG systems in CH$_3$CN; $t$=25°C.
Reciprocal of the "fast" relaxation time vs. concentration for Li\(^+\)+polyethers in CH\(_3\)CN; \(t=25^\circ C\)

Reciprocal of the "slow" relaxation time vs. concentration for Li\(^+\)+polyethers in CH\(_3\)CN; \(t=25^\circ C\)
$\mu_1$ vs. concentration for Li$^+$-polyethers in CH$_3$CN; $t=25^\circ$C

$\mu_2$ vs. concentration for Li$^+$-polyethers in CH$_3$CN; $t=25^\circ$C
\( \mu_1 \) vs. \( \Gamma_1^{-1} \) for Li\( \text{ClO}_4 \) + PEO and for LiAs\( \text{F}_6 \) + PEO in CH\( _3 \)CN; \( t=25^\circ \text{C} \)

- PEO + Li\( \text{ClO}_4 \)
- PEO + LiAs\( \text{F}_6 \)

\( \mu_2 \) vs. \( \Gamma_2^{-1} \) for Li\( \text{ClO}_4 \) and for Li\( \text{ClO}_4 \) + PEO and +TG in CH\( _3 \)CN; \( t=25^\circ \text{C} \)

- PEO + Li\( \text{ClO}_4 \)
- TG + Li\( \text{ClO}_4 \)
- PEO + LiAs\( \text{F}_6 \)
- TG + LiAs\( \text{F}_6 \)
Infrared spectral envelope of Triglyme 0.604M in the solvent CH$_3$CN

Infrared spectral envelope of LiC/CO$_4$ 0.603M + Triglyme 0.603M in the solvent CH$_3$CN

Infrared spectral envelope of LiAsF$_6$ 0.613M + Triglyme 0.61M in the solvent CH$_3$CN
Normalized maximum absorbance per unit length of the deconvoluted 790-910 cm\(^{-1}\) envelope of triglyme in the solvent CH\(_3\)CN

\[ \bar{\nu}^0 = 853\text{cm}^{-1} \]

\[ \bar{\nu}^0 = 879\text{cm}^{-1} \]

\[ \bar{\nu}^0 = 818\text{cm}^{-1} \]

Normalized maximum absorbance per unit length of the deconvoluted 790-910 cm\(^{-1}\) envelope of triglyme added to LiClO\(_4\) or LiAsF\(_6\) at molar ratio R=1.0 in the solvent CH\(_3\)CN

\[ \bar{\nu}^0 = 844\text{cm}^{-1} \]

\[ \bar{\nu}^0 = 870\text{cm}^{-1} \]

\[ \bar{\nu}^0 = 813\text{cm}^{-1} \]
Infrared Spectral envelope of PEO of formula unit (CH₂₋₋₂-O)₄ 0.40M in the solvent CH₃CN

Infrared spectral envelope of LiClO₄ 0.509M + PEO in molar ratio R=4 in the solvent CH₃CN

Infrared spectral envelope of LiAsF₆ 0.500 M + PEO in molar ratio R = 4 in the solvent CH₃CN
Normalized absorbance $A^o/l$ for the deconvoluted band at $\bar{\nu}=812-815$ cm$^{-1}$ for PEO($\bullet$), PEO+LiClO$_4$ (○) and PEO+LiAsF$_6$ (△) at $R=4.0$ in acetonitrile.

Normalized absorbance $A^o/l$ for the deconvoluted band at $\bar{\nu}=844$ cm$^{-1}$ for PEO($\bullet$), PEO+LiClO$_4$ (○) and PEO+LiAsF$_6$ (△) at $R=4.0$ in acetonitrile.

Normalized absorbance $A^o/l$ for the deconvoluted band at $\bar{\nu}=864$ cm$^{-1}$ for PEO($\bullet$), PEO+LiClO$_4$ (○) and PEO+LiAsF$_6$ (△) at $R=4.0$ in acetonitrile.
Digitized infrared spectrum of the macrocycle 12-crown-4 0.20M in acetonitrile.

Digitized infrared spectrum of LiClO₄ 0.603M + 12C4 0.30M in CH₃CN
Normalized maximum absorbance per unit cell length vs. molar concentration C of the macrocycle 12-crown-4 in acetonitrile

(A)

- ○ = 852 cm\(^{-1}\) band
- □ = 844 cm\(^{-1}\) band
- ■ = 833 cm\(^{-1}\) band
- △ = 815 cm\(^{-1}\) band

Normalized maximum absorbance per unit cell length vs. molar concentration C of the macrocycle 12-crown-4 + LiClO\(_4\) in CH\(_3\)CN

(B)
Dependence of $\mu_I$ $\bigcirc$ and of $\mu_{II}$ $\bullet$ on the average molar mass $\bar{M}$ of the polyether for LiAsF$_6$ 0.5M+polyethers in acetonitrile
$t=25^\circ$C

($\bigcirc$ $\mu_I$ $\bigcirc$ $\mu_{II}$ for LiAsF$_6$ 0.6M+triglyme 0.6M)
Dependence of the normalized absorbance $A_\lambda / \lambda$ upon average molar mass $M$ of the polyethers for LiAsF$_6$-polyether mixtures (O) and for polyethers in acetonitrile.

"3" denotes the band appearing in the 860-880 cm$^{-1}$ range for the systems studied.
Infrared spectral envelope of
LiAsF$_6$ 0.50M+tetraglyme
0.50M in CH$_3$CN
Table I. Ultrasonic parameters $\mu_1$, $f_I$, $\mu_{II}$, $f_{II}$, B and sound velocity $u$ for all the concentrations investigated of the systems LiClO$_4$ or LiAsF$_6$ + Triglyme and LiClO$_4$ or LiAsF$_6$ + polyethylene oxide (at $R_{PEO} = 4.0$ with $R_{PEO} = [\text{-CH}_2\text{-CH}_2\text{-O-}]/[\text{Li}^+]$) in the solvent CH$_3$CN at 25°C.

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### Microfilm Edition

#### Table II

Infrared parameters $\tilde{v}_j$, $A_j^o$, $(\Delta \tilde{v})_j$ (J = 1, 2, 3) for the three Gaussian-Lorentzian bands used to deconvolute the spectral envelope of TG, LiClO$_4$ + TG (R=1) LiAsF$_6$ + TG (R=1), of PEO, LiClO$_4$ + PEO (R$_{PEO}$ = 4.0) and LiAsF$_6$ + PEO (R$_{PEO}$ = 4.0) and of the macrocycle 12C$_4$, LiClO$_4$ + 12C$_4$ in the solvent acetonitrile. Also reported are the IR cell lengths $l$ and, for each system, the normalized absorbances $A_j^o/l$ (to unit cell length) vs concentration functions$^a$

<table>
<thead>
<tr>
<th>C</th>
<th>$v_1^o$</th>
<th>$A_1^o$</th>
<th>$(\Delta \tilde{v})_1^o$</th>
<th>$v_2^o$</th>
<th>$A_2^o$</th>
<th>$(\Delta \tilde{v})_2^o$</th>
<th>$v_3^o$</th>
<th>$A_3^o$</th>
<th>$(\Delta \tilde{v})_3^o$</th>
<th>$l_{cell}$</th>
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<tbody>
<tr>
<td>(M)</td>
<td>(cm$^{-1}$)</td>
<td></td>
<td>(cm$^{-1}$)</td>
<td></td>
<td>(cm$^{-1}$)</td>
<td></td>
<td>(cm$^{-1}$)</td>
<td></td>
<td>(cm$^{-1}$)</td>
<td></td>
</tr>
<tr>
<td>System:</td>
<td>Triglyme in CH$_3$CN</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>1.00</td>
<td>818.5</td>
<td>0.025</td>
<td>30</td>
<td>852.5</td>
<td>0.328</td>
<td>23.5</td>
<td>878.5</td>
<td>0.045</td>
<td>18.5</td>
<td>0.469</td>
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<td>0.908</td>
<td>818</td>
<td>0.030</td>
<td>30</td>
<td>853</td>
<td>0.285</td>
<td>25</td>
<td>880</td>
<td>0.040</td>
<td>18</td>
<td>0.501</td>
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<td>0.802</td>
<td>818</td>
<td>0.019</td>
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<td>853</td>
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<td>0.023</td>
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<td>0.016</td>
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<td>0.467</td>
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<td>0.297</td>
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<td>880</td>
<td>0.014</td>
<td>18</td>
<td>0.462</td>
</tr>
</tbody>
</table>

$\frac{1}{l} A_j^o = 0.246 + 64.7 C \quad r^2 = 0.989 \quad ^a$

$\frac{1}{l} A_j^o = -0.056 + 5.59 C \quad r^2 = 0.943 \quad ^a$

$\frac{1}{l} A_j^o = -0.032 + 8.83 C \quad r^2 = 0.987 \quad ^a$

---

a) Least squares performed giving 50% statistical weight to the intercepts.
<table>
<thead>
<tr>
<th>CLIX</th>
<th>CTG</th>
<th>v^-1</th>
<th>A_1^o</th>
<th>(Δν^1/2)</th>
<th>v_2^-1</th>
<th>A_2^o</th>
<th>(Δν^1/2)</th>
<th>v_3^-1</th>
<th>A_3^o</th>
<th>(Δν^1/2)</th>
<th>l cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>(M)</td>
<td>(M)</td>
<td>(cm^-1)</td>
<td></td>
<td>(cm^-1)</td>
<td></td>
<td>(cm^-1)</td>
<td>(cm^-1)</td>
<td>(cm^-1)</td>
<td></td>
<td>(cm^-1)</td>
<td>cm x 10^2</td>
</tr>
</tbody>
</table>

**System:** LiClO_4 + Triglyme in acetonitrile R = 1.0

| 0.900 | 0.901 | 813   | 0.022 | 16 | 843.5 | 0.310 | 14 | 870 | 0.240 | 14 | 0.447 |
| 0.804 | 0.804 | 813   | 0.019 | 16 | 843.5 | 0.265 | 15.5 | 870 | 0.210 | 14 | 0.448 |
| 0.698 | 0.693 | 812   | 0.016 | 16 | 843.5 | 0.235 | 15.5 | 870 | 0.185 | 13.5 | 0.445 |
| 0.603 | 0.603 | 813   | 0.011 | 15 | 843   | 0.220 | 15   | 870 | 0.170 | 14   | 0.510 |
| 0.503 | 0.503 | 813   | 0.012 | 16 | 843.5 | 0.175 | 15   | 870 | 0.140 | 14   | 0.463 |
| 0.407 | 0.412 | 813   | 0.009 | 16 | 844   | 0.150 | 15   | 870 | 0.110 | 14   | 0.501 |
| 0.299 | 0.299 | 813   | 0.006 | 16 | 844   | 0.095 | 15.5 | 870.5 | 0.074 | 16 | 0.467 |

**System:** LiAsF_6 + Triglyme in acetonitrile R = 1.0

| 0.810 | 0.812 | 815.5 | 0.040 | 16.8 | 843.6 | 0.300 | 13.6 | 870 | 0.220 | 12.9 | 0.470 |
| 0.613 | 0.610 | 815.5 | 0.032 | 16.8 | 843.5 | 0.230 | 15.5 | 870 | 0.165 | 13.5 | 0.478 |
| 0.406 | 0.407 | 816   | 0.008 | 20   | 843.8 | 0.063 | 12.5 | 870 | 0.048 | 12.3 | 0.201 |

\[
\frac{1}{l} A^o_{813} = -0.061 + 5.1 \ C, \quad r^2 = 0.974 \ b
\]
\[
\frac{1}{l} A^o_{844} = -0.200 + 75.65 \ C, \quad r^2 = 0.999 \ b
\]
\[
\frac{1}{l} A^o_{870} = -0.252 + 58.41 \ C, \quad r^2 = 0.998 \ b
\]

b) Least squares performed on LiClO_4 + Triglyme data of \( A^o_{l} \), giving 50% statistical weight to the intercepts.
Table II (continued)

<table>
<thead>
<tr>
<th>System: PEO in CH₂CN</th>
<th>( C_{\text{PEO}} )</th>
<th>( l_{\text{cell}} \times 10^2 )</th>
<th>( v_1 )</th>
<th>( A_1^0 )</th>
<th>( (\Delta v_1/2)_1 )</th>
<th>( v_2^0 )</th>
<th>( A_2^0 )</th>
<th>( (\Delta v_1/2)_2 )</th>
<th>( v_3^0 )</th>
<th>( A_3^0 )</th>
<th>( (\Delta v_1/2)_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(M)</td>
<td>(cm)</td>
<td>(cm⁻¹)</td>
<td></td>
<td>(cm⁻¹)</td>
<td></td>
<td>(cm⁻¹)</td>
<td></td>
<td>(cm⁻¹)</td>
<td></td>
<td>(cm⁻¹)</td>
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</tr>
<tr>
<td>0.900</td>
<td>0.417</td>
<td>810</td>
<td>0.016</td>
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<td>845</td>
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<td>29</td>
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<td>0.048</td>
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<td>0.120</td>
<td>27</td>
<td>865</td>
<td>0.050</td>
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<tr>
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<td>26</td>
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<td>0.089</td>
<td>26</td>
<td>862</td>
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<td>21</td>
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<tr>
<td>0.600</td>
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<td>845</td>
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<td>26</td>
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<td>27</td>
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<td>0.006</td>
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<td>0.053</td>
<td>25</td>
<td>864</td>
<td>0.030</td>
<td>25</td>
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<td>0.043</td>
<td>25</td>
<td>865</td>
<td>0.024</td>
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</table>

\[ \frac{1}{L} A^0_{811} = -0.036 + 3.76 C \quad r^2 = 0.927 \ a \]

\[ \frac{1}{L} A^0_{844} = -0.13 + 32.6 C \quad r^2 = 0.992 \ a \]

\[ \frac{1}{L} A^0_{864} = 0.23 + 13.50 C \quad r^2 = 0.975 \ a \]

\( c \) The concentration \( C_{\text{PEO}} \) is expressed as the molarity of the moiety \((-\text{O-CH}_2-\text{CH}_2-)_{4}\) of formal molar mass = 
\[ 4 \times 44.054 = 176.22 \text{ grams.} \]
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Table II (continued)

<table>
<thead>
<tr>
<th>System: LiClO₄ + PEO in CH₃CN</th>
<th>C_LIX</th>
<th>R_PEO</th>
<th>ν₀</th>
<th>A₁₀</th>
<th>(Δν₁/₂)₁</th>
<th>ν₂₀</th>
<th>A₂₀</th>
<th>(Δν₁/₂)₂</th>
<th>ν₃₀</th>
<th>A₃₀</th>
<th>(Δν₁/₂)₃</th>
<th>k_{cell} x10², cm</th>
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<tbody>
<tr>
<td>(M)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>0.710</td>
<td>4.0</td>
<td>812</td>
<td>0.017</td>
<td>18</td>
<td>843</td>
<td>0.087</td>
<td>28</td>
<td>862</td>
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<tr>
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<td>4.0</td>
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<td>17</td>
<td>843</td>
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<td>28</td>
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<td>844.3</td>
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<td>812</td>
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<td>15</td>
<td>843.5</td>
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<td>862</td>
<td>0.012</td>
<td>23</td>
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<tr>
<td>System: LiAsF₆ + PEO in CH₃CN</td>
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<tr>
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<td>844</td>
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<td>0.034</td>
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<td>844</td>
<td>0.077</td>
<td>28</td>
<td>864</td>
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<td>4.0</td>
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<td>15</td>
<td>844.5</td>
<td>0.063</td>
<td>26</td>
<td>864</td>
<td>0.017</td>
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<td>0.460</td>
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\[
\begin{align*}
\frac{1}{l} A^0_{812-815} &= -0.346 + 10.03 \ C \\
\frac{1}{l} A^0_{844} &= -0.120 + 27.3 \ C \\
\frac{1}{l} A^0_{864} &= -0.025 + 8.02 \ C
\end{align*}
\]

r² = 0.78₅ d
r² = 0.997 d
r² = 0.947 d

d) least squares applied to both LiClO₄ + PEO and LiAsF₆ + PEO data giving 50% statistical weight to the intercept.
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Table II (continued)

**System**: $^{12}$C$_4$ in CH$_3$CN

<table>
<thead>
<tr>
<th>C$_{12}$C$_4$</th>
<th>$\nu_0$</th>
<th>A$_1^o$</th>
<th>($\Delta \nu_{142}$)$_1$</th>
<th>$\nu_2^o$</th>
<th>A$_2^o$</th>
<th>($\Delta \nu_{142}$)$_2$</th>
<th>$\nu_3^o$</th>
<th>A$_3^o$</th>
<th>($\Delta \nu_{142}$)$_3$</th>
<th>$\nu_4^o$</th>
<th>A$_4^o$</th>
<th>($\Delta \nu_{142}$)$_4$</th>
<th>$\lambda$ cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(M) (cm$^{-1}$)</td>
<td>(cm$^{-1}$)</td>
<td>(cm$^{-1}$)</td>
<td>(cm$^{-1}$)</td>
<td>(cm$^{-1}$)</td>
<td>(cm$^{-1}$)</td>
<td>(cm$^{-1}$)</td>
<td>(cm$^{-1}$)</td>
<td>(cm$^{-1}$)</td>
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<td>(cm$^{-1}$)</td>
<td>(cm$^{-1}$)</td>
<td>(cm$^{-1}$)</td>
<td>(cm$^{-1}$)</td>
</tr>
<tr>
<td>0.601</td>
<td>815</td>
<td>0.014</td>
<td>6</td>
<td>832.3</td>
<td>0.012</td>
<td>7</td>
<td>843.6</td>
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<td>6.25</td>
<td>850.8</td>
<td>0.246</td>
<td>9.7</td>
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<tr>
<td>0.493</td>
<td>815</td>
<td>0.013</td>
<td>6</td>
<td>833.3</td>
<td>0.009</td>
<td>6</td>
<td>843.8</td>
<td>0.144</td>
<td>7.8</td>
<td>851.4</td>
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<td>9.1</td>
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<td>6</td>
<td>833.3</td>
<td>0.008</td>
<td>6</td>
<td>844</td>
<td>0.125</td>
<td>7.9</td>
<td>851.5</td>
<td>0.146</td>
<td>9.6</td>
<td>0.504</td>
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<td>836</td>
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<td>6.5</td>
<td>844</td>
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<td>851.3</td>
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<td>9.2</td>
<td>0.451</td>
</tr>
<tr>
<td>0.201</td>
<td>815</td>
<td>0.003</td>
<td>6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>844</td>
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<td>7.9</td>
<td>851.6</td>
<td>0.070</td>
<td>8.6</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>844</td>
<td>0.040</td>
<td>6.8</td>
<td>851.5</td>
<td>0.045</td>
<td>7.2</td>
<td>0.487</td>
</tr>
</tbody>
</table>

1. \( \frac{1}{k} A_{815}^o = -0.0048 - 1.884 \, C + 32.32 \, C^2 - 34.24 \, C^3, \quad r^2 = 0.992^e \)

2. \( \frac{1}{k} A_{844}^o = 0.0404 + 76.75 \, C - 74.11 \, C^2 + 92.37 \, C^3, \quad r^2 = 0.998^e \)

3. \( \frac{1}{k} A_{851}^o = 0.0323 + 82.82 \, C - 74.78 \, C^2 + 144.5 \, C^3, \quad r^2 = 0.998^e \)

---

e) The band centered at \( \nu_0^o = 833 \) cm$^{-1}$ is visible only for C > 0.20 M. Hence the \((A_3^o/k)\) data have not been fitted by interpolation functions.
<table>
<thead>
<tr>
<th>System: LiClO₄ + 12C₄ in CH₃CN</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁₂C₄</td>
</tr>
<tr>
<td>(M)</td>
</tr>
<tr>
<td>0.304</td>
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<tr>
<td>0.252</td>
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<tr>
<td>0.200</td>
</tr>
<tr>
<td>0.161</td>
</tr>
<tr>
<td>0.0978</td>
</tr>
<tr>
<td>0.051</td>
</tr>
</tbody>
</table>

\[
\frac{1}{l} A^{o} = -0.0274 + 16.904 C + 78.429 C^2 - 331.0 C^3, \quad r^2 = 0.921^a
\]

\[
\frac{1}{l} A^{o} = -0.0065 + 138.98 C, \quad r^2 = 0.9941^a
\]
Table III. Ultrasonic parameters $\nu_I$, $f_I$, $\nu_{II}$, $f_{II}$, $B$ and sound velocity $u$ for the concentrations 0.5 M of LiAsF$_6$ + Tetraglyme molar ratio (Tetraglyme/LiClO$_4$) = 1 and of 0.5 M LiAsF$_6^-$ + PEO, 400, 1000, 2000 at $R = \left[ -(\text{CH}_2-\text{CH}_2-0-) \right] / [\text{Li}^+] = 4$ in the solvent CH$_3$CN at 25°C.

<table>
<thead>
<tr>
<th>C LiAsF$_6$ (M)</th>
<th>R</th>
<th>$\nu_I \times 10^5$</th>
<th>$f_I$ (MHz)</th>
<th>$\nu_{II} \times 10^5$</th>
<th>$f_{II}$ (MHz)</th>
<th>$B \times 10^{17}$ (cm$^{-1}$ s$^2$)</th>
<th>$u \times 10^{-5}$</th>
<th>Ligand</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>C = 0.50</td>
<td>250</td>
<td>100</td>
<td>330</td>
<td>12</td>
<td>52</td>
<td>1.272</td>
<td>Tetragl.</td>
</tr>
<tr>
<td>0.50</td>
<td>4.0</td>
<td>400</td>
<td>100</td>
<td>170</td>
<td>16</td>
<td>52</td>
<td>1.268</td>
<td>PEO (400)</td>
</tr>
<tr>
<td>0.50</td>
<td>4.0</td>
<td>450</td>
<td>80</td>
<td>200</td>
<td>15</td>
<td>62</td>
<td>1.281</td>
<td>PEO (1000)</td>
</tr>
<tr>
<td>0.50</td>
<td>4.0</td>
<td>500</td>
<td>90</td>
<td>200</td>
<td>15</td>
<td>63</td>
<td>1.265</td>
<td>PEO (2000)</td>
</tr>
</tbody>
</table>
Table IV. Infrared parameters $\tilde{v}_j^0$, $A_j^0$, $(\Delta \tilde{v}_j)_{1/2}$ (j=1,2,3,4) for LiAsF$_6$ 0.50 M + tetracylame 0.50 M and (j = 1, 2, 3) for LiAsF$_6$ 0.50 M + PEO (400), PEO (1,000), PEO (2000) at R = [-O-CH$_2$-CH$_2$-]/[Li] = 4 in acetonitrile. Same parameters for Tetracylame and the PEO of molar masses 400, 1000, 2000 in CH$_3$CN. The spectral envelopes have been deconvoluted into four Gaussian-Lorentzian product functions for LiAsF$_6$ + Tetracylame and into three Gaussian-Lorentzian products functions for LiAsF$_6$ + PEO of the above average molar masses.

<table>
<thead>
<tr>
<th>System: Tetracylame 0.50 + LiAsF$_6$ 0.50 in CH$_3$CN</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tilde{v}_1^0$</td>
</tr>
<tr>
<td>(cm$^{-1}$)</td>
</tr>
<tr>
<td>815</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$A_3^0$</th>
<th>$(\Delta \tilde{v}<em>3)</em>{1/2}$</th>
<th>$t_{cell} \times 10^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(cm$^{-1}$)</td>
<td>(cm$^{-1}$)</td>
</tr>
<tr>
<td>0.075</td>
<td>14</td>
<td>0.425</td>
</tr>
<tr>
<td>System: PEO (400) + LiAsF$_6$ 0.50 M, R = 4.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>---------------------------------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>813  0.019  16  843  0.077  25  862.5  0.045  22  0.449</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>System: PEO (1000) + LiAsF$_6$ 0.50 M; R = 4.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>814  0.022  20  842.5  0.068  26  862.5  0.030  22  0.457</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>System: PEO (2000) + LiAsF$_6$ 0.50 M; R = 4.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>814  0.023  20  843  0.06  27  862.5  0.022  21  0.457</td>
</tr>
</tbody>
</table>
Table IV (cont.)

<table>
<thead>
<tr>
<th>$\nu^o_1$ (cm$^{-1}$)</th>
<th>$A^o_1$</th>
<th>$\frac{\Delta \nu^o_1}{2}$ (cm$^{-1}$)</th>
<th>$\nu^o_2$ (cm$^{-1}$)</th>
<th>$A^o_2$</th>
<th>$\frac{\Delta \nu^o_2}{2}$ (cm$^{-1}$)</th>
<th>$\nu^o_3$ (cm$^{-1}$)</th>
<th>$A^o_3$</th>
<th>$\frac{\Delta \nu^o_3}{2}$ (cm$^{-1}$)</th>
<th>$l_{cell} \times 10^2$ (cm)</th>
</tr>
</thead>
</table>

**System: Tetracycline 0.50 M in CH$_3$CN**

| 819 | 0.011 | 30 | 851 | 0.155 | 27 | 874 | 0.018 | 16 | 0.432 |

**System: PEO (400) 0.502 M$^a$ in CH$_3$CN**

| 819 | 0.008 | 30 | 851 | 0.11 | 27 | 871 | 0.008 | 20 | 0.463 |

**System: PEO (1000) 0.505 M$^a$ in CH$_3$CN**

| 815.5 | 0.009 | 20 | 846.5 | 0.074 | 27 | 864 | 0.028 | 22 | 0.422 |

**System: PEO (2000) 0.503 M$^a$ in CH$_3$CN**

| 813 | 0.007 | 20 | 845 | 0.071 | 27 | 864 | 0.029 | 22 | 0.452 |

---

*a) The term molarity (M) here is intended as the weight of polymer in gram divided by the mass of the molecular unit (-O-CH$_2$-CH$_2$-)$_4$ per dm$^3$ of solution.*