Ion-Chain Dynamics in Polymer Electrolytes

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Abstract

Representing polyether-salt systems by chains of interacting coordination shells, defined by the cation and by its nearest ligands, we derive the interaction potential between closest shells – the inter-shells potential – in terms of two-electron polarization effects. Values are presented for monovalent-based crystalline poly(ethylene oxide), PEO, electrolytes. For the eutectic composition \(\text{PEO}_{12}\text{EuBr}_3\), the inter-shells energy is evaluated also by relating the empirical value of the nearest-ligands local-field potential with the variation of the \(\text{Eu}^{3+}\) concentration. Both methods give the same results.

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In spite of extensive work performed over the past two decades on polymer electrolytes modified by monovalent and multivalent cations, the interpretation of the abundant empirical results has been hindered by the lack of detailed knowledge of their ion-chain structures. Because polymer electrolytes present certain liquid-like features, with the polymer acting as an "immobile" solvent, the structural properties of these materials are predominantly determined by their local configuration in the vicinity of the cation, and depend on the number of complexed cations, that is, their structural features change with the number \( n \) of ether-oxygens in the polymer chain per cation. For crystalline monovalent-based poly(ethylene oxide), PEO, electrolytes, the ion-chain local configuration has been depicted as forming oxygen-lined helical turns, with the cation located within the polymer cavity, a configuration which has been confirmed by single crystal X-ray diffraction for a few salt-rich complexes. Following this idea, in this Letter, polyether-salt systems are represented by chains of interacting coordination shells, each of which is defined by a cation at its center and by its nearest ligands (ether-oxygens and, eventually, anions) at its boundary. In this model, the ion-chain local dynamics – which changes with the number of interacting shells, that is, with \( n \) – results jointly from each shell’s cation-nearest ligands interaction – the intra-shell interaction – and from the interaction between a given coordination shell and all the others in its immediate vicinity – the inter-shells interaction. (For crystalline electrolytes, these neighborhoods may be approximated to their unit cells). We here derive an expression for the inter-shells potential, \( V_{ss} \), between all nearest-shells, whose ligands are separated by an average inter-shells distance \( R_{ss} \), in terms of two-electron polarization effects, mediated by the ligands’ valence electrons (mainly the 2\( p \) oxygen electrons) of each interacting shell. For a given shell, we consider the polarization of one of its ligands located at \( \vec{R} \) from the cation (taken as the origin) by one of the valence electrons of the neighboring shells, at \( \vec{r}_1 \); one of the remaining electrons at \( \vec{r}_2 \) interacts with the multipole moments induced in the polarized ligand. Thus, we write for the interaction between a given coordination shell and all the others closest to it.
\[ V_{ss}^n = \sum_{ab\alpha} \sum_{k\beta m} F_n(abk) \frac{R^a C_{a+n,\alpha+m}^* (\hat{r}_1)}{(r_1)^{a+n+1}} \frac{R^b C_{b+n,\beta+m}^* (\hat{r}_2)}{(r_2)^{b+n+1}} \times \left( \begin{array}{ccc} b + n & a + n & k \\ -\beta - m & \alpha + m & -\alpha + \beta \end{array} \right) \frac{C_{k,\beta-\alpha}^* (\hat{R})}{}, \]  

(1)

where \( C_{\ell,q} = (4\pi/2\ell + 1)^{1/2} Y_{\ell,q} \) are spherical tensors, \( F_n(abk) \) - expressed in terms of 3-j symbols \( ( ) \) and of 6-j symbols \{ \} - is 

\[ F_n(abk) = (-\alpha_n e^2)(-1)^{n-m+\beta}(2k + 1) \begin{pmatrix} a & b & k \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} a & a+n & n \\ b+n & b & k \end{pmatrix} \frac{(2a+2n+1)(2b+2n+1)^{1/2}}{(2a+2n)} \left( \begin{array}{c} 2b+2n \\ 2a \end{array} \right) \left( \begin{array}{c} 2b+2n \\ 2a \end{array} \right)^{1/2}, \]

and \( \alpha_n \) is the nth multipole polarizability of the ligands. Taking only the dipolar contribution, assuming spherical symmetry in the space of the ligands valence electrons \( (k=0) \), \( r_1 = r_2 = R_{ss} + R \), and performing the sum over these electrons and over all the \( N \) ligands of valence \( Z_i \) at \( \bar{R}_i \), we write the inter-shells interaction as 

\[ V_{ss} = \frac{1}{2} \sum_i \alpha_i e^2 Z_i \sum_{a=0}^\infty (a + 1) \frac{R_{ss}^{2a}}{(R_i + R_{ss})^{2a+1}}. \]

(2)

Considering only the first two terms of the expansion \( (R_{ss} \gg R_i) \), and considering that all the ligands of each shell are at the same average distance \( \bar{R} \) from the cation, we have 

\[ V_{ss} = \frac{1}{2} \sum_i \frac{\alpha_i e^2 Z_i}{(R + R_{ss})^4} + \frac{2\bar{R}^2}{(R + R_{ss})^6}. \]

(3)

The application of Eq. (3) to polyether-salt systems requires the knowledge of the dipole polarizability \( \alpha_i \), the number of ligands \( N \), the cation-ligands average distance \( \bar{R} \), and the distance between closest shells \( R_{ss} \). These parameters have been determined, through single crystal X-ray diffraction, for a few crystalline monovalent-based PEO electrolytes [3,4], and the corresponding inter-shells potentials calculated from Eq. (3) are given in Table I. For PEO\(_3\)NaI, Wright [6] estimates the total interaction energy between the Na\(^+\) and I\(^-\) ions, and the 3EO polymer segments of neighboring helices as being \( \varepsilon (3EO-NaI-inter) \approx 20 - 30 \text{ kJ (mol of 3EO units)}^{-1} (\approx 1700 - 2500 \text{ cm}^{-1}) \), a value which is of the same order of magnitude as the one calculated in Table I.

For non-crystalline divalent polyether-salt complexes, the only local structural information is provided by extended X-ray absorption fine-structure measurements (EXAFS). These
results, which lie within a spherical domain of up to 6 Å of the target cation, besides giving the number \( N \) of ether-oxygens of the first coordination shell (the anions being further away from the cation), also furnish the average distances \( \bar{R} \) (some of which are referred to in Table III of Ref. [7]), but only a lower limit for \( R_{ss} + \bar{R} > 6 \) Å. The corresponding upper limits for \( V_{ss} \) are, for example, \( V_{ss} < 600 \text{ cm}^{-1} \) in PEO\(_n\)ZnI\(_2\) \((30 \geq n \geq 4)\), and \( V_{ss} < 900 \text{ cm}^{-1} \) in PEO\(_n\)ZnBr\(_2\) \((20 \geq n \geq 6)\).

Very little is known about the ion-chain structure of trivalent-base d polymer electrolytes. In particular, there are very few results for \( \bar{R} \) [4,5] (in this case, the anions are also supposed to be further away from the coordination cation), and none for \( R_{ss} \). Here, we evaluate \( R_{ss} \) in lanthanide-based electrolytes for the concentration for which the interaction between nearest shells does not yet modify the internal dynamics of each shell. That is, we determine the minimum inter-shells distance, \( R_{ss} = R_0 \), for which \( V_{ss} \) does not yet alter \( \bar{R} \). For this, following Morrison [9], we write the intra-shell potential \( V_s \), also due to two-electron polarization effects, as

\[
V_s = -\frac{1}{2} \sum_i \alpha_i e^2 Z_i \left( \frac{1}{R^4} + \frac{2\rho^2}{R^6} \right),
\]

where \( \rho \) is an ion-dependent, host-independent quantity, which corrects the Hartree-Fock expectation values of the even powers of the 4f electrons radial distances. Imposing a balance between the repulsive \( V_{ss} \), Eq. (3), and the attractive \( V_s \), Eq. (4), expressed by \( \frac{dV_{ss}}{dR}_{R=R_0} = \frac{dV_s}{dR}_{R=R} \), we get

\[
(\bar{R} + R_0)^7(\bar{R}^2 + 3\rho^2) + \bar{R}^7 R_0^2 + 2\bar{R}^8 R_0 + 4\bar{R}^9 = 0,
\]

from which, knowing \( \bar{R} \), the minimum inter-shells distance \( R_0 \) may be determined, and, therefore, from Eq. (3), also the associated lanthanide inter-shells potential. \( \bar{R} \) has been determined only for PEO\(_n\)EuBr\(_3\), for which the Eu\(^{3+}\) local surroundings were investigated by means of the observed \(^5\)D\(_{0-1} \rightarrow \(^7\)F\(_{0-4}\) emission lines. Taking the resulting value \( \bar{R} = 2.4 \) Å for \( 80 \geq n \geq 8 \) [4,5], and \( \rho^2 = 0.1666 \text{ Å}^2 \) [9] into Eq. (3), we get \( R_0 = 5.3 \) Å. Table II presents the results for the inter-shells potential for a number of europium-nearest oxygens
between 8 and 12, a value in accordance with both the determined $C_{2v}$ local symmetry group \cite{8,10}, generally associated with a coordination number around 8, and with a recent result on La$^{3+}$-based PEO electrolytes \cite{13}, which indicates between 9 and 10 oxygens surrounding the lanthanum ion.

Next, for the PEO$_n$EuBr$_3$ electrolytes, we represent the effect of the increase of the Eu$^{3+}$ concentration from $n = 80$ to $n = 5$ on the interaction potential between the europium and its surrounding oxygens – the intra-shell potential. As usual, we take this potential as the local-field interaction $V_{LF} = \sum_i \sum_{k,q} B_{k,q} C_{k,q}(\theta_i, \phi_i)$, with the spherical coordinates $(r_i, \theta_i, \phi_i)$ fixing the location of the Eu$^{3+}$ ith $4f$ electron, and $B_{k,q}$ ($k = 0, 2, 4, 6; -k \leq q \leq k$) being phenomenological parameters encompassing all the dynamics of Eu$^{3+}$ in the complex. Then, relating the dynamical part of $V_{LF}$ – the empirically determined $B_{k,q}$ – with the interaction energy between nearest shells – the inter-shells potential – we obtain, by an independent method, and for the PEO-EuBr$_3$ stablest concentration $n \approx 12$, the inter-shells interaction energy $\varepsilon$.

The emission spectra of these electrolytes present a series of sharp lines assigned to transitions between the Stark components of the $^5D_0$ and $^7F_{0-4}$ levels \cite{8,10,11}, of which the only transitions considered here are the dominant electric-dipole $^5D_0 \rightarrow ^7F_2$ and the magnetic-dipole $^5D_0 \rightarrow ^7F_1$ lines. The eigenvalues of the matrix elements of the local-field perturbation for the $^7F_{1,2}$ Stark sublevels are expressed in terms of the non-zero $B_{2,q}$ and $B_{4,q}$ parameters (the $k = 0$ term not being included, as it merely shifts the energetic configuration as a whole), and are fixed by the best fitting between the observed Stark energies and the calculated eigenvalues \cite{8,10,11}. Considering – as in Newman’s superposition model \cite{14} – that only the nearest ligands contribute significantly to the phenomenological intra-shell potential $V_{LF}$, the most relevant parameters are the $B_{4,q}$ (as the $k = 2$ terms relate to contributions beyond the first coordination shell). Since, for lanthanides complexes, the $B_{4,q}$ predicted by the point-charge model – in which the dynamical parameters depend on the angular distribution of the $4f$ electrons, on the ion-first neighbors distance, on the ligands valence, and on the number of cation-nearest neighbors – are in good agreement with the
corresponding empirical values, in the case of PEOₙEuBr₃ electrolytes, the effect of the increase of \( n \) on the intra-shell potential is represented expressing these \( B_{4,q} \) in terms of that model. These parameters change as the Eu\(^{3+} \) concentration increases from \( n = 80 \) to \( n = 5 \) [10,11]. Since, in this concentration range, neither \( \bar{R} \) nor \( N \) vary, the change of the phenomenological intra-shell potential \( V_{LF} \) must result from a modification of the ligands valence. The connection between the electrolyte global behavior – expressed by the ion’s concentration increase – and the local interaction within each coordination shell – expressed by the sum of all the \( B_{4,q} \) – must, therefore, be given by the changes in the ligands valence. In the model presented here of PEO-EuBr₃ electrolytes as chains of interacting luminescent shells – the number of which increases with the amount of complexed-Eu\(^{3+} \) –, the intra-shell potential \( V_{LF} \) (and, therefore, the ligands valence) must reflect the increase of the interaction between nearest shells with the decrease of the oxygen-cation ratio. For a europium concentration increase from \( n = 80 \) to \( n = 32 \), the coordination shells are spaced so far apart that they do not interact with each other. The existence of free PEO in this concentration range [12] indicates the coexistence of complexed and non-complexed ether-oxygens in the electrolytes. In the range \( 32 \geq n \geq 8 \), the number of luminescent shells present in the electrolytes is such that the distance between nearest shells decreases in such a way that the induced ligands valence charge of each shell also becomes smaller. This, in turn, is associated with a corresponding diminution of the intra-shell potential. Hence, in this concentration range, the inter-shells interaction begins to become relevant without yet altering the average Eu\(^{3+}\)-ligand oxygens distance. The constancy, between \( n = 80 \) and \( n = 8 \) of the mean radius \( \bar{R} \) of each coordination shell suggests that, as the concentration of Eu\(^{3+} \) increases, there should not be any significant modification of the internal dynamics of the shells. For \( n < 8 \), the electrostatic repulsion between nearest shells increases, their mutual interaction decreases, and the electrolytes are not found any more in their stablest phase – the eutectic concentration \( n \approx 12 \). This behavior of the intra-shell dynamics with the increase of \( n \) shows precisely the same trend as the observed dependence with \( n \) of the ratio between the \( ^5D_0 \rightarrow ^7F_2 \) and \( ^5D_0 \rightarrow ^7F_1 \) average intensities, \( I_{0-2}/I_{0-1} \).
which slowly diminishes between $80 \geq n \geq 12$, attains a minimum for $n \approx 12$, and sharply increases for $n < 12$. As it is well known that the relative intensities of the above two transitions (the only ones being considered here) are hypersensitive to the nature of the Eu$^{3+}$-ligand surroundings, the intra-shell potential $V_{LF}$ must, somehow, incorporate the ratio $I_{0-2}/I_{0-1}$. We define the strength of this local-field potential as $s_{LF}^2 \equiv (2k + 1)s_{k=4}^2$, where $s_{k=4}^2 = (2k + 1)^{-1}\sum_q (B_{4,q})^2$ is the corresponding Leavitt’s quadratic rotational invariant. We then propose that, in terms of this strength, the phenomenological potential is related to the Eu$^{3+}$ concentration by

$$s_{LF} = \left(\sum_q (B_{4,q})^2\right)^{1/2} = \varepsilon \left(1 - e^{1-n/n_0}\right)^2 \quad (6)$$

where $\varepsilon$ is the interaction energy between a given coordination shell and all the other shells closest to it, corresponding to the Eu$^{3+}$ stablest concentration $n_0$. 

(Here, the radial dependence of the $B_{4,q}$ is manifested on the variation of the cation concentration $n$ with the distance between nearest coordination shells.) Inserting into Eq. (6) the value for $s_{LF}$ obtained from the phenomenological $B_{4,q}$, we evaluate $\varepsilon$ and $n_0$ by the least squares fit (Fig. 3). The results obtained were $\varepsilon = 554.2 \text{ cm}^{-1}$ and $n_0 = 12.9$. This value for the Eu$^{3+}$ stablest concentration is precisely the one given by the morphological results (DSC, XRD, etc.) thus bearing out the relation proposed in Eq. (6).

In summary, representing polyether-salt systems by chains of interacting coordination shells, defined by the cation and its nearest ligands, we derive the interaction potential between a given coordination shell and all the others in its immediate surroundings in terms of two-electron polarization effects. The values obtained for monovalent-based crystalline PEO electrolytes are given in Table 4. For non-crystalline divalent electrolytes we are only able to estimate an upper limit for the inter-shells potential. For PEO-EuBr$_3$ electrolytes, we deal with this inter-shells potential in two separate ways, one involving the same two-electron polarization effects, and the other relating the empirical value of the nearest-ligands local-field potential with the variation of Eu$^{3+}$ concentration. The inter-shells interaction energy, $\varepsilon$, calculated by the the two-electron polarization potential is $\varepsilon = 520.3 \text{ cm}^{-1}$ for
10 nearest oxygens, and is \( \varepsilon = 572.4 \text{ cm}^{-1} \), for 11 oxygens. The value of \( \varepsilon \) evaluated by the phenomenological local-field potential is \( \varepsilon = 554.2 \text{ cm}^{-1} \) for the PEO-EuBr\(^{3+} \) stablest concentration \( n_0 \approx 12 \). The agreement between the two independent methods indicates that the concentration for which the inter-shells interaction does not yet alter the intra-shell dynamics is the stablest concentration \( (n \approx 12) \). In addition, this agreement also suggests that the screening effects of the non-complexed oxygens, included in the inter-shells potential, Eq. (3), are well accounted for by the dipole polarization, by the number of ligands, and by their valence. On the other hand, although, as previously referred to [7], the dependence of the intra-shell potential with the Eu\(^{3+}\)-ligands distance, Eq. (4), is essentially correct, the screening effects of the 5s and 5p shells is eventually over estimated. This may be due to the distance between two nearest shells being more than twice the europium-oxygens distance.

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FIGURES

FIG. 1. Dependence of the strength of the nearest-ligands local-field interaction $s_{LF}$ (cm$^{-1}$) on O/Eu ratio ($n$) for PEO$_n$EuBr$_3$ ($n=5,8,12,16,20,24,28,32,80$). Fitting parameter $\Delta = 40$ cm$^{-1}$. 
TABLES

TABLE I. Coordination number $N$, nearest cation-ligands average distance $\bar{R} (\text{Å})$, inter-shells distance $R_{ss} (\text{Å})$, and inter-shells potential $V_{ss} \text{ cm}^{-1}$, for a few monovalent-based PEO electrolytes.

|                | $N$ | $\bar{R}$ | $R_{ss}$ | $V_{ss}$ |
|----------------|-----|-----------|----------|----------|
| PEO$_3$NaI     | 5   | 2.71      | 2.98     | 1453.23  |
| PEO$_3$NaSCN   | 6   | 2.47      | 5.69     | 415.46   |
| PEO$_3$NaClO$_4$| 5   | 2.50      | 3.35     | 915.85   |
| PEO$_3$LiCF$_3$SO$_3$ | 5 | 2.10      | 4.41     | 526.65   |
| PEO$_4$KSCN    | 7   | 2.87      | 2.34     | 3742.49  |
| PEO$_4$NH$_4$SCN| 7  | 2.96      | 2.31     | 3638.94  |

Superscript:
a. 3 oxygen and 2 iodine ligands, $\alpha(O^{2-}) = 1.349 \text{ Å}^3$ and $\alpha(I^-) = 5.013 \text{ Å}^3$.
b. 4 oxygen and 2 nitrogen ligands, $\alpha(N^3-) = 2.684 \text{ Å}^3$.
c. 5 oxygen ligands.
d. 5 oxygen and 2 nitrogen ligands.

TABLE II. Inter-shells potential, $V_{ss} \text{ (cm}^{-1}\text{)}$, for a number of nearest oxygens $N$ between 8 and 12, $\bar{R} = 2.4 \text{ Å}$, and for $R_{ss} = R_0 = 5.3 \text{ Å}.$

| $N$ | 8    | 9    | 10   | 11   | 12   |
|-----|------|------|------|------|------|
| $V_{ss}$ | 416.3 | 468.4 | 520.3 | 572.4 | 624.4 |