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Ionic conductivities of solid polymer electrolyte/salt systems: Group-contribution method

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Abstract

We establish a new group-contribution model based on the Nernst–Einstein equation in which the diffusion coefficient is derived from the modified double-lattice (MDL) model and the Debye–Hückel (DH) theory. The model includes the combinatorial energy contribution that is responsible for the revised Flory–Huggins entropy of mixing, the van der Waals energy contribution from dispersion, and the polar force and the specific energy contribution from hydrogen bonding.

The Nernst–Einstein equation takes into account the mobility of the salt and the motion of the polymer host. To describe the segmental motion of the polymer chain, which is the well known conduction mechanism for solid polymer electrolyte (SPE) systems, the effective co-ordinated unit parameter is introduced.

Our results show that good agreement is obtained upon comparison with experimental data of various PEO and salt systems in the interested ranges.
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Keywords: Group-contribution method; Ionic conductivity; Solid polymer electrolyte; Debye–Hückel theory; Nernst–Einstein equation

1. Introduction

Solid polymer electrolytes (SPEs), formed by dissolving salts in a polymer matrix, have long received extensive attention because of their potential for achieving high ionic conductivities. Their many direct applications are high-energy-density batteries, electrochromic display devices (ECD), and fuel cells [1–5].

Solid polymer electrolytes have improved safety for lithium battery compared to liquid electrolytes, but they are known to result with insufficient performance, especially due to low ionic conductivity. Researches on the electrochemical applications of SPEs have, therefore, focused on the ionic conductivity for each complex.

To increase the ionic conductivities of SPE, the polymer should have both low T_g and low crystallinity. Reibel et al. [6] described ionic conductivities of PEO/lithium bis(4-nitrophenylsulfonyl)imide (LiNPSI), and PEO/lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) systems as polymer electrolytes. Sreekanth et al. [7] reported an application of PEO complexes with $NaNO_3$ salt as an electrochemical cell. Andreev and Bruce [8] investigated the structure-conductivity relation of PEO/$LiAsF_6$ in the analogous phase. Reddy and Chu [9] also reported the structure-conductivity relation of PEO with potassium ionic salt. Historically, for the quantitative study of the ionic conduction, Gibbs and co-workers [10,11] developed the configurational entropy model for polymer properties, which has been discussed extensively by Goldstein [12]. Configurational entropy (or free volume) models can be expressed in the form of a Vogel–Tamman–Fulchur (VTF) equation [13–15], which is generally used for describing the dependence of conductivity on temperature. SØrensen

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and Jacobsen [16] developed a simple model that accounts quantitatively for the concentration dependence of the conductivity for the low purity type electrolyte. MacFarlane et al. [17] investigated the effect of plasticizer on the conductivity by using the Adam–Gibbs model combined with Flory's configurational entropy at the fixed temperature.

Recently, Kim and Bae [18,19] developed configurational entropy model for conductivities of SPEs that can express the composition dependence of the given systems based both on the Adam and Gibbs conductivity model and on the Flory's entropy model. To take into account the pressure effect on the ionic conductivities of the compressed SPE systems, Ahn and Bae [20,21] and Choi and Bae [22] extended Kim's configurational entropy model. It is important that the salt effect must be taken into account in the ionic conductivity model because the ionic conduction is worked by the mobility of salt as well as the segmental motion of polymer.

The purpose of this work is to overcome the shortcomings of the previous models by taking into account the salt effect in the conductivity model using a group-contribution method.

Group-contribution method is very efficient tool to describe thermodynamic properties of polymer solution because it utilizes exiting phase equilibrium data when predicting phase behaviors of given systems of which data are not plentiful. The ultimate goal of the group-contribution method lies in its ability to predict physical properties for systems which are not included in the experimental data, that is the set of data uses to determine the parameters. The basic idea is starting from that whereas the chemical compounds of interest in chemical technology are numerous, the number of functional groups which constitute those compounds is, however, much smaller. Thermodynamic properties of a fluid then can be calculated as sum of contributions made by the functional groups. However, any group-contribution method is necessarily approximate as the contribution of given group in one molecule is not necessarily the same as that in another molecule.

To describe the ionic conductivity of the given systems, we employ the diffusion coefficient for which the driving force is based on a gradient of chemical potential.

To account for the effect of both salt and polymer concurrently, the sum of each chemical potential is differentiated with concentration. Since the conduction mechanism in SPE is correlated with segmental motion of polymer chain, the effective co-ordination between salt and polymer units is taken into account.

Each chemical potential is calculated from Flory's melting point depression theory [23] combined with the modified double-lattice (MDL) theory and the Debye–Hückel (DH) theory extended by Guggenheim. Combination of the derived diffusion coefficient equation with Nernst–Einstein relationship yields the final conductivity equation.

In this work, we develop a new group-contribution model taking into account interactions between different species (salt). It describes ionic conductivities of number of SPE/Li and sodium salt systems at various temperatures and compositions.

2. Model description

Three theoretical aspects are taken into account: the lattice notation of a Debye–Hückel type function proposed by Guggenheim [25,26], modified double-lattice model [24] and Flory's melting point depression concept [23].

In this study, the expression for the Helmholtz energy of mixing for binary polymer solutions is defined as a sum of two contributions.

The total molar Gibbs energy of mixing $\Delta G_{\text{mix}}^{\text{Total}}$ is assumed to consist of an extended Debye–Hückel theory and modified double-lattice theory:

$$\frac{\Delta G_{\text{mix}}^{\text{Total}}}{RT} = \frac{\Delta G_{\text{mix}}^{\text{MDL}}}{RT} + \frac{\Delta G_{\text{mix}}^{\text{DH}}}{RT} \tag{1}$$

where $\Delta G_{\text{mix}}^{\text{MDL}}/RT$ is the Helmholtz energy of modified double-lattice model; $\Delta G_{\text{mix}}^{\text{DH}}/RT$, the Helmholtz energy of Debye–Hückel model; R, the gas constant and T is the absolute temperature.

2.1. Modified double-lattice model

2.1.1. Primary lattice

Oh and Bae [24] proposed a new Helmholtz energy of mixing as the form of Flory–Huggins theory. The expression is given by:

$$\frac{\Delta A}{N_{\text{r}}kT} = \left(\frac{\phi_1}{r_1}\right)\ln\phi_1 + \left(\frac{\phi_2}{r_2}\right)\ln\phi_2 + \chi_{\text{OB}}\phi_1\phi_2 \tag{2}$$

where N_{r} is the total number of lattice sites; k, the Boltzmann's constant and r_i is the number of segments per molecule i. χ_{OB} is a new interaction parameter and functions of r_i and $\tilde{\varepsilon}$ and is given by:

$$\chi_{\text{OB}} = C_\beta\left(\frac{1}{r_2} - \frac{1}{r_1}\right)^2 + \left(2 + \frac{1}{r_2}\right)\tilde{\varepsilon} - \left(\frac{1}{r_2} - \frac{1}{r_1} + C_\gamma\tilde{\varepsilon}\right)\tilde{\varepsilon}\phi_2 + C_\gamma\tilde{\varepsilon}^2\phi_2^2 \tag{3}$$

$\tilde{\varepsilon}$ is a reduced interaction parameter given by:

$$\tilde{\varepsilon} = \frac{\varepsilon}{kT} = \frac{(\varepsilon_{11} + \varepsilon_{22} - 2\varepsilon_{12})}{kT} \tag{4}$$

where ε_{11}, ε_{22} and ε_{12} are for the corresponding nearest-neighbor segment–segment interactions. Parameters C_β and C_γ are universal constants. These constants are not adjustable parameters and are determined by comparing with Madden et al.'s Monte–Carlo simulation data ($r_1 = 1$ and $r_2 = 100$). The best fitting values of C_β and C_γ are 0.1415 and 1.7985, respectively [24].

2.1.2. Secondary lattice

In Freed's theory [27,28], the solution of the Helmholtz energy of mixing for the Ising model is given by:

$$\frac{\Delta A}{N_r kT} = x_1 \ln x_1 + x_2 \ln x_2 + \frac{z\tilde{\varepsilon} x_1 x_2}{2} - \frac{z\tilde{\varepsilon}^2 x_1^2 x_2^2}{4} + \cdots \tag{5}$$

where z is the coordination number and x_i is the mole fraction of the component i.

To obtain an analytical expression for the secondary lattice, we defined a new Helmholtz energy of mixing as the fractional form to improve the mathematical approximation defect by revising Eq. (5). This secondary lattice is introduced as a perturbation to account for the oriented interaction. The expression is given by:

$$\frac{\Delta A_{\mathrm{sec},ij}}{N_{ij}kT} = \frac{2}{z}\left[\eta \ln \eta + (1-\eta) \ \ln(1-\eta) + \frac{zC_\alpha \delta\tilde{\varepsilon}_{ij}(1-\eta)\eta}{1 + C_\alpha \delta\tilde{\varepsilon}_{ij}(1-\eta)\eta}\right] \tag{6}$$

where $\Delta A_{\mathrm{sec},ij}$ is the Helmholtz energy of mixing of the secondary lattice for i–j segment–segment pair; N_{ij}, the number of i–j pairs, $\delta\tilde{\varepsilon}$, the reduced energy parameter contributed by the oriented interactions and η is the surface fraction permitting oriented interactions. For simplicity, η is arbitrarily set to 0.3 as Hu and co-workers [29,30] suggested. C_α is also not an adjustable parameter and is determined by comparing with Panagiotopolous et al.'s Gibbs-ensemble Monte–Carlo simulation data of Ising lattice. The best fitting value of C_α is 0.4880 [24].

2.1.3. Incorporation of secondary lattice into primary lattice

To incorporate a secondary lattice, we replace ε_{ij} by $\varepsilon_{ij} - \Delta A_{\mathrm{sec},ij}/N_{ij}$ in Eq. (4). If oriented interaction occurs in the i–j segment–segment pairs, we replace $\tilde{\varepsilon}$ by $\varepsilon/kT + 2(\Delta A_{\mathrm{sec},ij}/N_{ij}kT)$ in Eq. (5). If oriented interaction occurs in the i–i segment–segment pairs, we replace $\tilde{\varepsilon}$ by $\varepsilon/kT - \Delta A_{\mathrm{sec},ii}/N_{ii}kT$. In this study, we assume the oriented interaction occurs in the i–i, j–j and i–j segment–segment pairs. We replace $\tilde{\varepsilon}$ by:

$$\varepsilon_{12} = (\varepsilon_{11}^* + \varepsilon_{22}^* - 2\varepsilon_{12}^*) + \left(-\frac{\Delta A_{\mathrm{sec},11}}{N_{11}} - \frac{\Delta A_{\mathrm{sec},22}}{N_{22}} + \frac{2\Delta A_{\mathrm{sec},12}}{N_{12}}\right) \tag{7}$$

where ε_{11}^*, ε_{22}^* and ε_{12}^* are van der Waals energy interaction parameters. $\Delta A_{\mathrm{sec},11}$, $\Delta A_{\mathrm{sec},22}$ and $\Delta A_{\mathrm{sec},12}$ are the additional Helmholtz functions for the corresponding secondary lattice. Eq. (7) then becomes:

$$\tilde{\varepsilon} = \frac{\varepsilon_{11}^* + \varepsilon_{22}^* - 2\varepsilon_{12}^*}{kT} - 2C_\alpha(1-\eta)\eta\left[\frac{\delta\varepsilon_{11}/kT}{1 + C_\alpha(\delta\varepsilon_{11}/kT)(1-\eta)\eta} + \frac{\delta\varepsilon_{22}/kT}{1 + C_\alpha(\delta\varepsilon_{22}/kT)(1-\eta)\eta} - \frac{2\delta\varepsilon_{12}/kT}{1 + C_\alpha(\delta\varepsilon_{12}/kT)(1-\eta)\eta}\right] \tag{8}$$

To correlate MDL model to melting point depression theory, we require chemical potentials of components 1 and 2. The definition of chemical potential is:

$$\frac{\Delta\mu_i}{kT} = \frac{\partial(\Delta A/kT)}{\partial N_i} \tag{9}$$

The final expression for the chemical potential can be written as:

$$\begin{aligned}\frac{\Delta\mu_1}{kT} &= \ln(1-\phi_2) - r_1\left(\frac{1}{r_2} - \frac{1}{r_1}\right)\phi_2 \\ &\quad + r_1\left[C_\beta\left(\frac{1}{r_2} - \frac{1}{r_1}\right)^2 + \left(\left(\frac{1}{r_2} - \frac{1}{r_1}\right) + C_\gamma\tilde{\varepsilon}\right)\tilde{\varepsilon} \right. \\ &\quad \left. + \left(2 + \frac{1}{r_2}\right)\tilde{\varepsilon}\right]\phi_2^2 \\ &\quad - 2r_1\left[\left(\left(\frac{1}{r_2} - \frac{1}{r_1}\right) + C_\gamma\tilde{\varepsilon}\right)\tilde{\varepsilon} + C_\gamma\tilde{\varepsilon}^2\right]\phi_2^3 \\ &\quad + 3r_1 C_\gamma \tilde{\varepsilon}^2 \phi_2^4\end{aligned} \tag{10}$$

and

$$\begin{aligned}\frac{\Delta\mu_2}{kT} &= \ln\phi_2 + r_2\left[\left(\frac{1}{r_2} - \frac{1}{r_1}\right) + C_\beta\left(\frac{1}{r_2} - \frac{1}{r_1}\right)^2 \right. \\ &\quad \left. + \left(2 + \frac{1}{r_2}\right)\tilde{\varepsilon}\right] - r_2\left[\left(\frac{1}{r_2} - \frac{1}{r_1}\right) \right. \\ &\quad \left. + 2\left(\left(\frac{1}{r_2} - \frac{1}{r_1}\right) + C_\gamma\tilde{\varepsilon}\right)\tilde{\varepsilon} + 2C_\beta\left(\frac{1}{r_2} - \frac{1}{r_1}\right)^2 \right. \\ &\quad \left. + 2\left(2 + \frac{1}{r_2}\right)\tilde{\varepsilon}\right]\phi_2 \\ &\quad + r_2\left[4\left(\left(\frac{1}{r_2} - \frac{1}{r_1}\right) + C_\gamma\tilde{\varepsilon}\right)\tilde{\varepsilon} + \left(2 + \frac{1}{r_2}\right)\tilde{\varepsilon} \right. \\ &\quad \left. + C_\beta\left(\frac{1}{r_2} - \frac{1}{r_1}\right)^2 + 3C_\gamma\tilde{\varepsilon}^2\right]\phi_2^2 \\ &\quad - r_2\left[6C_\gamma\tilde{\varepsilon}^2 + 2\left(\left(\frac{1}{r_2} - \frac{1}{r_1}\right) + C_\gamma\tilde{\varepsilon}\right)\tilde{\varepsilon}\right]\phi_2^3 \\ &\quad + 3r_2 C_\gamma \tilde{\varepsilon}^2 \phi_2^4\end{aligned} \tag{11}$$

where ϕ_i is the segment fraction of component i, $\phi_i = N_i r_i / N_r$ and $N_r = \sum_i^m N_i r_i$ is the total number of segments in the system and r_i is the segment number of components 1 (salt) and 2 (polymer).

2.2. A lattice notation of an extended Debye–Hückel theory

For a binary polymer/salt system at solute molality m (mol kg^{-1}polymer), Guggenheim's expression for the molar Gibbs energy of mixing $\Delta G_{\text{mix}}^{\text{DH}}$could be rewritten in the framework of lattice theory as follows [25,26]:

$$\frac{\Delta G_{\text{mix}}^{\text{Total}}}{RT} = \frac{\phi_1}{r_1 vm}\left[-\frac{4}{3}AI^{3/2}\tau(I^{1/2})\right] \tag{12}$$

$$\tau(x) = \frac{3}{x^3}\left[\ln(1+x) - x + \frac{x^2}{2}\right] \tag{13}$$

where ϕ_1 is the segment fraction of the salt ion, r_1 (=1), the number of segments per salt ion, $v(= v_{\text{M}} + v_{\text{X}}$; where v_{M} and v_{X} are the number of M and X ions per salt, respectively), the number of ions per salt and I is the ionic strength. A is the usual Debye–Hückel coefficient. In this study we fix $A = 0.068$ (assumed to be independent of temperature) as an optimization factor for polymer/salt systems. This small value implies that ion–ion interactions in a polymer/salt system are relatively small (for example, calculated percentage at molality of salt ≈0.1 mol kg^{-1}in PEO/$LiCF_3SO_3$ system: ions = 2%; pairs = 71%; and triples = 27%) [1]. For a binary polymer/salt system containing 1 kg of polymer and v_{M} moles of salt ion, ϕ_1, ϕ_2 and I are defined by:

$$\phi_1 = \frac{r_1 vm}{(r_1 vm + r_2 1000)/M} = \frac{r_1 N_1}{r_1 N_1 + r_2 N_2},$$
$$\phi_2 = 1 - \phi_1 \tag{14}$$

$$I = \frac{1}{2}mv\,|z_{\text{M}} z_{\text{X}}| = \frac{1}{2}\left[\frac{(r_2\phi_1 1000)/M}{r_1\phi_2}\right]|z_{\text{M}} z_{\text{X}}| \tag{15}$$

where M is the molecular weight of polymer in g mol^{-1} (i.e. $M = 900{,}000$ g mol^{-1}). N_1, N_2, z_{M}, z_{X} and r_2 are the number of moles of salt ion and polymer, the valences of M and X ions and the number of segments per polymer, respectively. The chemical potentials are given by:

$$\frac{\Delta\mu_1^{\text{DH}}}{RT} = \frac{1}{RT}\left(\frac{\partial(r_1N_1 + r_2N_2)\Delta G_{\text{mix}}^{\text{DH}}}{\partial N_1}\right)$$
$$= -\frac{v}{1000}\left(\frac{A\,|z_{\text{M}} z_{\text{X}}|\,I^{1/2}}{1 + I^{1/2}}\right) \tag{16}$$

$$\frac{\Delta\mu_2^{\text{DH}}}{RT} = \frac{1}{RT}\left(\frac{\partial(r_1N_1 + r_2N_2)\Delta G_{\text{mix}}^{\text{DH}}}{\partial N_1}\right)$$
$$= \frac{M}{1000}\left(\frac{2}{3}AI^{3/2}\sigma(I^{1/2})\right) \tag{17}$$

$$\sigma(x) = \frac{3}{x^3}\left[1 + x - \left(\frac{1}{1+x}\right) - 2\ln(1+x)\right] \tag{18}$$

2.3. van der Waals energy contribution

The energy parameter ε_{ij}^* in Eq. (19) is due to van der Waals forces (dispersion and polar forces). For a pure-component i, ε_{ii}^* can be estimated using the square of the pure-component van der Waals solubility parameter of Hansen (Barton) [31], which is the sum of a dispersion contribution and a polar contribution: $\delta_{\text{vdw}}^2 = \delta_{\text{d}}^2 + \delta_{\text{p}}^2$.

$$\delta_{\text{vdw},i}^2 = \frac{3N_{\text{A}}\varepsilon_{ii}^* r_i}{V_{mi}} \tag{19}$$

where N_{A} is the Avogadro number and where δ_{vdw}^2 and V_{mi} are at 25 °C. For a pure-component, the effect of temperature on ε_{ii}^* is given by:

$$\varepsilon_{ii} = \phi_{s_1}\varepsilon_1 + \phi_{s_2}\varepsilon_2 \tag{20}$$

$$\varepsilon_{jj}^* = \frac{\varepsilon_{ii}^+}{V_{mi}} \tag{21}$$

where V_{mi} depends on temperature. The temperature-independent parameter ε_{ii}^+ can be estimated by:

$$\varepsilon_{ii}^+ = \frac{\delta_{\text{vdw}}{}^2 V_{mi}^2, \quad (25°C)}{3N_{\text{A}} r_i} \tag{22}$$

$$r_i = \frac{V_{mi(\text{vdw})}}{15.17 \times 10^{-6}\ \text{m}^3\ \text{mol}^{-1}} \tag{23}$$

The constant 15.17×10^{-6} m^3 mol^{-1} is the molar hard-core volumes of a CH_2 group. In our model, the group-contribution concept is considered to calculate the chain length contrary to that of the existing modified double-lattice model.

The cross interaction van der Waals energy parameter ε_{ij}^* is estimated by the geometric mean of the corresponding pure-component parameters:

$$\varepsilon_{ij}^* = \sqrt{\varepsilon_{ii}^*\varepsilon_{jj}^*} \tag{24}$$

Cross specific energy parameter $\delta\tilde{\varepsilon}_{ij}$ is calculated from pair-interaction group parameters:

$$\frac{\delta\varepsilon_{ij}}{k} = \sum_{m=1}^{N_{\text{s}}}\sum_{n=1}^{N_{\text{p}}}\phi_m\phi_n g_{mn} \tag{25}$$

where N_{s} and N_{p} are number of groups in solvents and polymers, respectively. ϕ_m and ϕ_n are volume fractions of group m in a solvent and that of group n in a polymer, respectively; and g_{mn} are pair interaction parameters between group m in a solvent and group n in a polymer. To improve the accuracy of prediction, we assume that a functional group in a polymer is different from that in a solvent. In this study, they are estimated by fitting experimental solid–liquid equilibria data of polymer solutions.

2.4. Ionic conductivity

For binary diffusion in gases or liquids, the generalized Fick's equation for heat and mass is as follows [32]:

$$J_A^* = -cD_{AB}\left[x_A\nabla \ln a_A + \frac{1}{cRT}[(\phi_A - \omega_A)\nabla p - \rho\omega_A\omega_B(g_A - g_B)] + k_T\nabla \ln T\right] \quad (26)$$

This equation represents that the thermodynamics of irreversible processes dictates using the activity gradient as the driving force for concentration diffusion. This requires a diffusion coefficient different from Fick's first law. When the pressure-, thermal-, and forced-diffusion terms are dropped, Eq. (26) for binary electrolyte is simplified by:

$$J_s^* = -D^*C_s\nabla \ln a_s \quad (27)$$

where D^*, C_s and a_s are self-diffusion coefficient, concentration and activity of salt, respectively. This equation may be rewritten by making use of the fact that the activity is a function of concentration to obtain:

$$J_s^* = -D^*C_s\left(\frac{\mathrm{d}\ \ln a_s}{\mathrm{d}\ C_s}\right)\nabla C_s \quad (28)$$

when comparing Eq. (28) with the original Fick's equation, $J_s^* = -D_s\nabla C_s$, this is related to the measured diffusion coefficient D_s (based on a concentration driving force) by [32]:

$$D_s = D^*\left(\frac{\mathrm{d}\ \ln a_s}{\mathrm{d}\ \ln c_s}\right) \quad (29)$$

where D^* characterizes the component mobility in the absence of any interactions in the given system [33]. This may be rewritten by the fact that the activity is related to the chemical potential by $\ln a = \Delta\mu/RT$

$$D_s = D^*C_s\frac{\mathrm{d}(\Delta\mu_s/RT)}{\mathrm{d}C_s} \quad (30)$$

The transport of cations in solvent-free polymer electrolytes differs from that of systems based on molecular liquids or low molar mass polymers. In the latter systems, ions can move together with their co-ordinated solvent, but in the case of high molecular weight polymers the centre of gravity of the chain cannot be moved significant distances. For electrolytes using high molecular weight polymers, cation transport does not only occur in conjunction with polymer diffusion but lithium ion transport also occurs as a result of segmental motion [34]. Since cations move across co-ordinating sites which are made up of the acid–base interactions between solvent and solute molecules, diffusion of cation must be taken into account with effective co-ordinated polymer units. To express this co-ordinating effect in the conductivity model, the chemical potential in Eq. (30) is replaced by the sum of chemical potentials of salt and effective co-ordinating polymer units, which is given by:

$$D_s = D^*C_s\frac{\mathrm{d}(\Delta\mu_{eff}/RT)}{\mathrm{d}C_s},$$
$$\frac{\Delta\mu_{eff}}{RT} = \frac{\Delta\mu_s}{RT} + \lambda_{eff}\frac{\Delta\mu_u}{RT} \quad (31)$$

where λ_{eff} are the effective co-ordinated units of polymer. A mathematical form of $\lambda_0 e^{\omega C_s}$ is adopted for λ_{eff} based on the exponentially lowering coordinating units, where λ_0 and ω are adjustable model parameters, respectively.

This in turn yields, using the Nernst–Einstein relationship for multi-component system, the conductivity equation for SPE having the form as:

$$\sigma = \frac{F^2}{RT}\sum_i z_i^2 v_i D_i C_i \quad (32)$$

where F is a Faraday constant. Since we assume that the phase at the given condition is binary system of polymer and salt, the moving object is salt itself instead of cation. If the charge effect of each ion remains for the ion interactions, this assumption brings Eq. (32) in a simple form:

$$\sigma = \frac{F^2C_s}{RT}D_s\sum_i z_i^2 \quad (33)$$

Substituting Eq. (30) into Eq. (33) gives the final ionic conductivity equation for SPE systems:

$$\sigma = \frac{F^2C_s}{RT}D^*C_s\frac{\mathrm{d}(\Delta\mu_s/RT + \lambda_0 e^{\omega C_s}(\Delta\mu_u/RT))}{\mathrm{d}C_s}\sum_i z_i^2 \quad (34)$$

where the chemical potentials are given by:

$$\begin{aligned}\frac{\Delta\mu_s}{RT} = \Bigg(&-\frac{v}{1000}\left(\frac{A\,|z_M z_X|\,I^{1/2}}{1+I^{1/2}}\right) \\ &+ \ln(1-\phi_2) - r_1\left(\frac{1}{r_2}-\frac{1}{r_1}\right)\phi_2 \\ &+ r_1\left[C_\beta\left(\frac{1}{r_2}-\frac{1}{r_1}\right)^2 + \left(\left(\frac{1}{r_2}-\frac{1}{r_1}\right) + C_\gamma\tilde{\varepsilon}\right)\tilde{\varepsilon}\right. \\ &\left. + \left(2+\frac{1}{r_2}\right)\tilde{\varepsilon}\right]\phi_2^2 \\ &- 2r_1\left[\left(\left(\frac{1}{r_2}-\frac{1}{r_1}\right) + C_\gamma\tilde{\varepsilon}\right)\tilde{\varepsilon} + C_\gamma\tilde{\varepsilon}^2\right]\phi_2^3 \\ &+ 3r_1C_\gamma\tilde{\varepsilon}^2\phi_2^4\Bigg)\end{aligned} \quad (35)$$

and

$$\begin{aligned}\frac{\Delta\mu_u}{RT} = &\frac{V_u}{V_1}\frac{r_1}{r_2}\left(\frac{M}{1000}\left(\frac{2}{3}AI^{3/2}\sigma(I^{1/2})\right)\right) + \ln\phi_2 \\ &+ r_2\left[\left(\frac{1}{r_2}-\frac{1}{r_1}\right) + C_\beta\left(\frac{1}{r_2}-\frac{1}{r_1}\right)^2 + \left(2+\frac{1}{r_2}\right)\tilde{\varepsilon}\right]\end{aligned}$$

$$
\begin{aligned}
&- r_2\left[\left(\frac{1}{r_2}-\frac{1}{r_1}\right)+2\left(\left(\frac{1}{r_2}-\frac{1}{r_1}\right)+C_\gamma\tilde{\varepsilon}\right)\tilde{\varepsilon}\right.\\
&\left.+2C_\beta\left(\frac{1}{r_2}-\frac{1}{r_1}\right)^2+2\left(2+\frac{1}{r_2}\right)\tilde{\varepsilon}\right]\phi_2\\
&+r_2\left[4\left(\left(\frac{1}{r_2}-\frac{1}{r_1}\right)+C_\gamma\tilde{\varepsilon}\right)\tilde{\varepsilon}+\left(2+\frac{1}{r_2}\right)\tilde{\varepsilon}\right.\\
&\left.+C_\beta\left(\frac{1}{r_2}-\frac{1}{r_1}\right)^2+3C_\gamma\tilde{\varepsilon}^2\right]\phi_2^2\\
&-r_2\left[6C_\gamma\tilde{\varepsilon}^2+2\left(\left(\frac{1}{r_2}-\frac{1}{r_1}\right)+C_\gamma\tilde{\varepsilon}\right)\tilde{\varepsilon}\right]\phi_2^3\\
&\left.+\ 3r_2C_\gamma\tilde{\varepsilon}^2\phi_2^4\right) \qquad (36)
\end{aligned}
$$

3. Results and discussion

We establish a new group-contribution model based on the Nernst–Einstein equation in which the diffusion coefficient is derived from the modified double-lattice model and the Debye–Hückel theory with $A = 0.068$. The new model employs the secondary lattice concept to take into account an oriented interaction. The advantage of this model follows from its simplicity.

In this work, most of parameters are calculated from pure-component properties, either from experimental data or from published estimation methods. To establish the group-contribution method, the most significant role is to determine the cross-pair interaction between polymer and salt segments.

In energy parameters of polymer/salt systems, ions can move together with their co-ordinated solvent, but in the case of high molecular weight polymers the centre of gravity of the chain cannot be moved significant distances. For electrolytes using high molecular weight polymers, cation transport does not only occur in conjunction with polymer diffusion but lithium ion transport also occurs as a result of segmental motion [34]. Since cations move across co-ordinating sites that are made up of the acid–base interactions between solvent and solute molecules, diffusion of cation must be taken into account with effective co-ordinated polymer units.

Table 2
Diffusion and co-ordinated unit parameters for PEO/salt systems

	T (K)	D^* (cm^2 s^{-1})	λ_0	ω (cm^3 mol^{-1})
PEO/$LiAsF_6$	338	2.85×10^{-7}	15.713	−275.247
	358	6.23×10^{-7}	18.527	−212.359
	378	1.24×10^{-6}	17.677	−192.672
	398	2.21×10^{-6}	13.163	−157.232
PEO/$LiClO_4$	338	5.3×10^{-8}	12.612	−387.425
	358	2.5×10^{-7}	9.252	−326.247
	378	4.0×10^{-7}	8.347	−276.437
	398	8.0×10^{-7}	6.403	−245.623
PEO/$NACF_3SO_3$	358	8.2×10^{-8}	18.527	−175.241

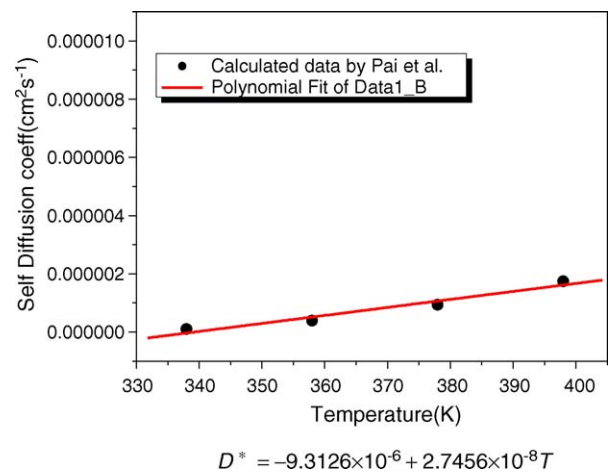

Fig. 1. The calculated value of diffusion coefficient (D^*) plotted against T. $D^* = -9.3126 \times 10^{-6} + 2.7456 \times 10^{-8}T$.

Table 1 gives physical properties of each component such as melting temperature, heat of fusion, molecular weight, density, and molar volume [35].

We assume that λ_0 and ω are co-ordinating unit parameters. D^* is a diffusion coefficient dependent on temperature and is obtained from elsewhere [37]. These parameters (λ_0, ω and D^*) are reported for the co-ordinating effect at various temperatures (Table 2). Pai and Bae have [37] set these parameters constant.

We employ the same assumption as Pai and Bae [37]. These parameters (λ_0, ω and D^*), however, are not adjustable parameters but universal parameters dependant on temperature. In Figs. 1–3, calculated values of λ_0, ω and D^* are

Table 1
Physical properties of PEO and salts

	T_m^0 (K)	ΔH (J mol^{-1})	M.W. (g mol^{-1})	Density (g cm^{-3})	V_u (cm^3 mol^{-1})
PEO	338.15	6798.00[a]	5000000	1.21	36.6
	338.15	8284.32[a]	900000	1.21	36.6
$NaCF_3SO_3$	527.15	10433.72	172.06	1.13	36.0
$LiClO_4$	509.15	14600.00	106.39	2.43	43.8
$LiAsF_6$	525.63	57188.20	195.85	2.65	73.9

[a] J unit^{-1}.

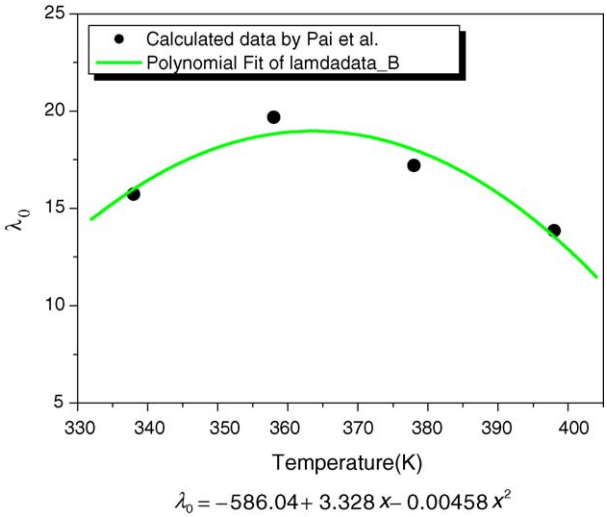

Fig. 2. The calculated value of co-ordinating units parameters (λ_0) plotted against T. $\lambda_0 = -586.04 + 3.328x - 0.00458x^2$.

compared with experimentally determined values calculated by Pai and Bae. To simply correlate with simulation data, λ_0, ω and D^* are suggested as follow:

$$D^* = -9.31 \times 10^{-6} + 2.75 \times 10^{-8}T \quad (37)$$

$$\omega = 17988.91 - 98.87T + 0.13T^2 \quad (38)$$

$$\lambda_0 = -586.04 + 3.33T - 0.00458T^2 \quad (39)$$

These Eqs. (37)–(39) provide a simple and accurate the expression for predicting ionic conductivity.

Fig. 4 shows ionic conductivities of PEO/$NaCF_3SO_3$ system. The dark circles are experimental data reported by Ma et al. [36] and the lines are calculated by the proposed model. To differentiate chemical potential with concentration, the

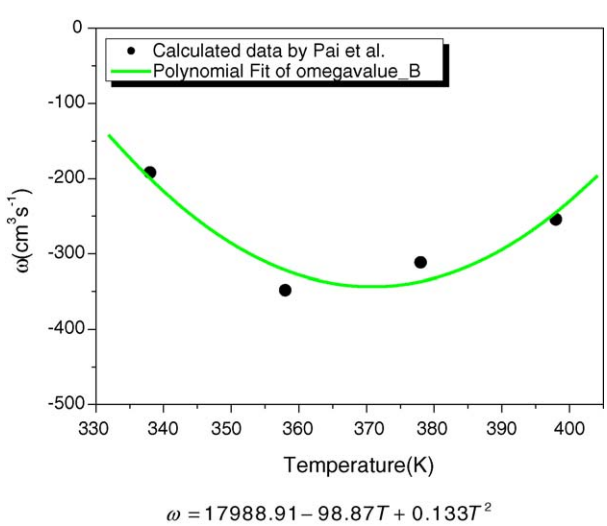

Fig. 3. The calculated value of co-ordinating units parameters (ω) plotted against T. $\omega = 17988.91 - 98.87T + 0.133T^2$.

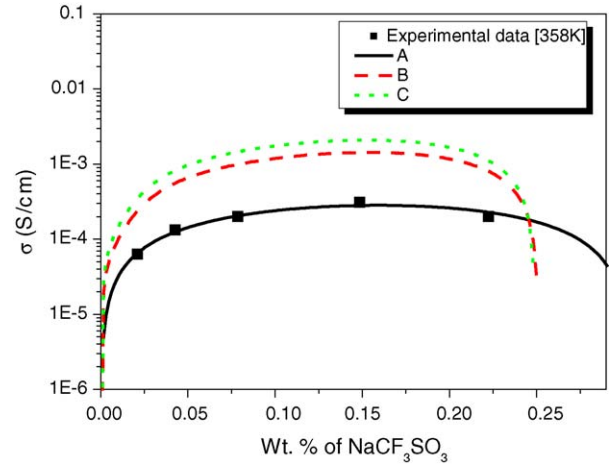

Fig. 4. Ionic conductivity as a function of weight% of $NaCF_3SO_3$ at 358.15 K. (A) The solid line is calculated from D^*, an adjustable model parameter and λ_0 and ω are calculated by Eqs. (38) and (39); (B) the dashed line is calculated with fixed D^* at 3.5×10^{-7} and λ_0 and ω are calculated by using Eqs. (38) and (39); and (C) the dotted line is calculated from the final ionic conductivity equation (Eq. (34)) using Eqs. (37)–(39) for the given systems. The dark circles are experimental data reported by Hu et al. [30], and the lines are calculated values using the proposed model.

salt concentration is calculated from the salt mass fraction as follows:

$$C_1 = \frac{\rho_1 w_1}{M_1} \quad (40)$$

where w_1 is the weight fraction of salt. We set $\eta = 0.3$ and $z = 6$ as suggested by Hu et al. [29]. The density of salt, ρ_1, then is given by:

$$\frac{1}{\rho_1} = \frac{1}{\rho_2^0} + w_1\left(\frac{V_1}{M_1} - \frac{1}{\rho_2^0}\right) \quad (41)$$

where ρ_2^0 is the density of PEO.

In Fig. 4, each line is calculated based on the different cases of λ_0, ω and D^* parameters. The dotted line is calculated from the final ionic conductivity equation (Eq. (34)) using Eqs. (37)–(39) for the given systems. Dashed line is calculated with fixed D^* at 3.5×10^{-7}. λ_0 and ω are calculated by using Eqs. (38) and (39), respectively. Results show that these two cases slightly overestimate ionic conductivities of the given system. The significance of such disagreement is difficult to assess because D^* especially is very sensitive to the given system and also is very dependant on temperature. When we set D^* is an adjustable model parameter and λ_0 and ω are calculated by Eqs. (38) and (39), respectively, we obtain the best fitting line (solid line in Fig. 4).

Figs. 5 and 6 show ionic conductivities of PEO/$LiClO_4$ and PEO/$LiAsF_6$ systems in which the experimental data are reported by Robitallie and Fauteux [38]. These figures are also calculated by the ionic conductivity equation (Eq. (34)) with Eqs. (37)–(39). Dotted, dashed and solid lines are also

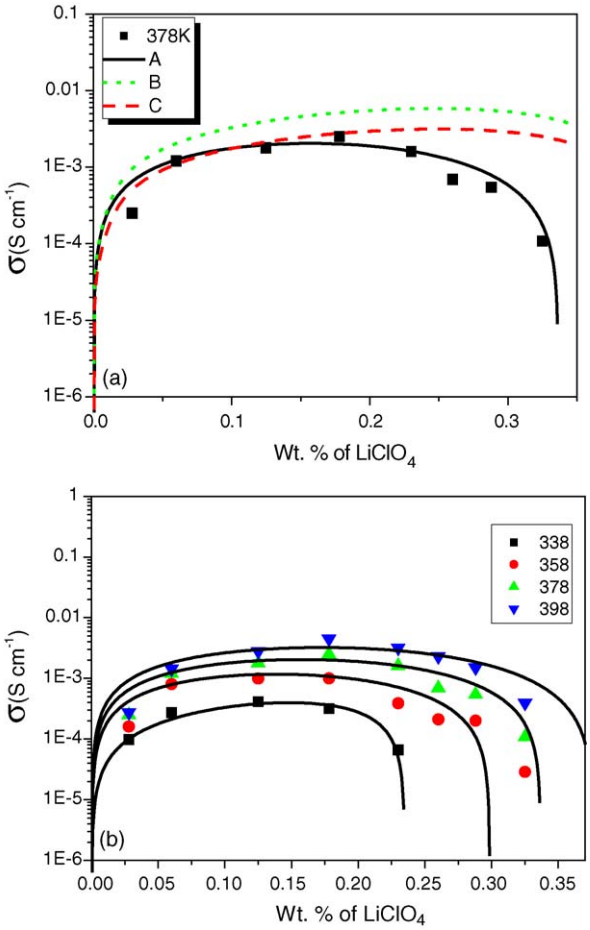

Fig. 5. (a) Ionic conductivity as a function of weight% of $LiClO_4$ at 378.15 K. (A) The solid line is calculated from D^*, an adjustable model parameter and λ_0 and ω are calculated by Eqs. (38) and (39); (B) the dashed line is calculated with fixed D^* at 3.5×10^{-7} and λ_0 and ω are calculated by using Eqs. (38) and (39); and (C) the dotted line is calculated from the final ionic conductivity equation (Eq. (34)) using Eqs. (37)–(39) for the given systems. (b) Ionic conductivity of PEO/$LiClO_4$ system. Experimental data are reported by Barton [31] and the lines are calculated by the proposed model.

evaluated by the same procedure as in Fig. 4 with previously obtained group interaction energy parameters (see Table 3.) with no additional group interaction parameters. As shown in Figs. 5(b) and 6(b), the fitted values agree fairly well with the experimental data.

Table 3
Group interaction parameter g_{mn} (k)

Salts	Polymer (PEO)	
	CH_2	O
Li	−386.47	−762.45
CF_3SO_3	869.91	240.719
Na	−3518.75	−3483.71
AsF_6	235.05	−495.72
ClO_4	1243.33	−257.99

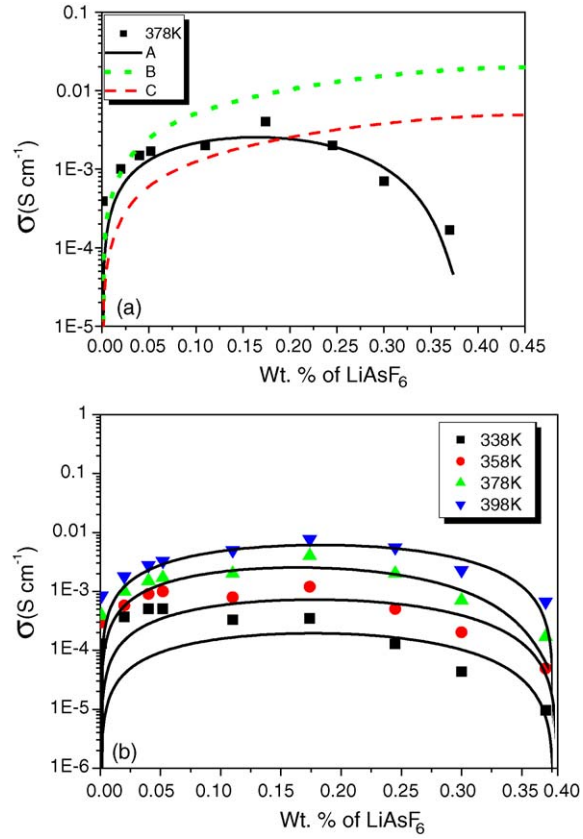

Fig. 6. (a) Ionic conductivity as a function of weight% of $LiAsF_6$ at 378.15 K. (A) The solid line is calculated from D^*, an adjustable model parameter and λ_0 and ω are calculated by Eqs. (38) and (39); (B) the dashed line is calculated with fixed D^* at 3.5×10^{-7} and λ_0 and ω are calculated by using Eqs. (38) and (39); and (C) the dotted line is calculated from the final ionic conductivity equation (Eq. (34)) using Eqs. (37)–(39) for the given systems. (b) Ionic conductivity of PEO/$LiAsF_6$ system. Experimental data are reported by Barton [31] and the lines are calculated by the proposed model.

4. Conclusion

We establish a new group-contribution model based on the Nernst–Einstein equation in which the diffusion coefficient is derived from modified double-lattice model and the Debye–Hückel theory with $A = 0.068$. The proposed model gives a simplified and improved expression for the ionic conductivity for polymer/salt systems that includes the van der Waals energy contribution. The ultimate goal of this work is to describe ionic conductivity of SPE/salts system using the group-contribution method.

When D^* is determined by Eq. (37), calculated values are slightly overestimated experimentally observed ionic conductivities of the given system. The significance of such disagreement is difficult to assess because D^* especially is very sensitive to given system and also is very dependant on temperature. When we set D^* be an adjustable model parameter and λ_0 and ω are calculated by Eqs. (38) and (39), respectively, the best fitting results are obtained.

To characterize most common SPE/salt system, more experimental data are required to obtain numerous group parameters for other electrolyte systems, and then to extend the group-contribution method to a larger variety of systems.

Acknowledgements

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