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Molecular thermodynamics approach for phase behaviors of solid polymer electrolytes/salt system in lithium secondary battery on the nonrandom mixing effect: Applicability of the group-contribution method

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Abstract

A new group-contribution model based on the lattice model is developed to interpret phase behaviors of solid polymer electrolyte/salt systems on the nonrandom mixing effect. 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.

Lattice model gives a starting point for a theoretical description of thermodynamic properties of polymer solution systems. The proposed model in this study improves the configurational energy of mixing and correlates energy of mixing term including the effect of nonrandom mixing on the configurational thermodynamic properties of a binary mixture with experimental data.

Our results show that good agreement is obtained upon comparison with experimental data of various PEO and salt systems in the interested ranges.

Keywords: Melting point depression; Solid polymer electrolyte; Group contribution

1. Introduction

Solid polymer electrolytes, formed by dissolving salts in a polymer matrix, have been receiving a considerable attention as solid electrolyte materials in the advanced applications such as high energy density batteries, electrochromic devices and chemical sensors, etc. Since the concept of a solid polymer electrolyte was first proposed by Wright et al. [6], global interest has especially focused on lithium polymer electrolyte batteries because of their high energy density, safety, and the flexibility in both their shapes and production processes. A large number of studies to date have been carried out on poly(ethylene oxide) (PEO) containing lithium salts.

Since David Fenton and crystallographer John Parker [8] examined on semi-crystalline polyethylene oxide (PEO)–alkali salt complexes of simple structure having alkali salts in high concentrations throughout both crystalline and amorphous components, solid polymer electrolytes (SPE) have been widely studied and expected to be excellent composites because of their electrochemical processability, high energy density, and flexibility.

Group-contribution model is a very efficient tool to describe thermodynamic properties of polymer solution because it utilizes existing phase equilibrium data when predicting phase behaviors of given systems of which data are not plentiful. 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 can then be calculated as the sum of contributions made by the

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functional groups. However, any group-contribution method is necessarily an approximate as the contribution of a given group in one molecule is not necessarily the same as that in another molecule. The fundamental assumption of group-contribution method is additivity. This assumption is valid only when the contribution made by one group in a given molecule is not affected by the nature of other groups within that molecule.

Extension of the group-contribution idea to polymer solutions has been proposed previously by Oishi and Prausnitz [9], with later variations by Holten-Andersen et al. [10,11], Chen et al. [12], Elbro et al. [13], Kontogeogis et al. [14], and Bogdanic and Fredenslund [15]. These methods are based on the UNIFAC correlation which is often successful for estimating phase equilibria in mixtures containing ordinary (nonpolymer) liquids.

The fundamental basis for existing group-contribution methods for polymer solutions is the lattice theory of Flory [16] and Huggins [17] with variations (e.g. Guggenheim [18], Orifino and Flory [19], Koningsveld et al. [20]). However, it is well known that the Flory–Huggins theory is based on severe simplifying assumptions which have happily been overcome in the much-improved lattice-cluster theory of Freed and coworkers [21,22]. Freed's theory is mathematically complicated. However, the results can be well approximated using a mathematical simplification introduced by Hu et al. [23–25]. Recently, Helmholtz energy of mixing has been reported by Chang and Bae [26] to describe the phase equilibria of various polymer solutions over the entire concentration and for various temperatures. And Hu et al. [27] presented the group-contribution method including a revised Flory–Huggins entropy, a series of expression for excess internal energy and a double lattice model to account for specific interactions.

This work is to employ the lattice model which gives a starting point for a theoretical description of thermodynamic properties of polymer/salt systems, and the configurational Helmholtz energy is obtained upon combining the Gibbs–Helmholtz equation with Guggenheim's athermal entropy of mixing as a boundary condition [5,28]. Classical models, such as the Flory–Huggins model [1–4] and the quasi-chemical model [5], are existing configurational energy of mixing models, in which the residual terms are truncated resulting in significant errors on the prediction of the property for polymer solution systems.

The purpose of this work is to propose a new Helmholtz energy of mixing expression to improve the configurational energy of mixing and a group-contribution model, in which the configurational energy of mixing term includes the effect of nonrandom mixing on the configurational thermodynamic properties of a binary mixture and is extended to predict the chemical potentials using the six adjustable parameters obtained from phase behavior calculations for various solid polymer electrolyte/salt systems, and with various solid polymer electrolyte/salt systems.

2. Model development

In this section, we derive the Helmholtz energy of mixing to describe the phase behaviors of solid polymer electrolyte/salt systems. To take the oriented interaction into account, the secondary lattice concept [23,29], which is a perturbation to a fixed reference system (i.e. the Helmholtz energy of mixing for the ordinary polymer solutions), is introduced. Finally, chemical potential equation for phase-behavior description is derived from the Helmholtz energy of mixing.

2.1. Internal and Helmholtz energies of mixing

The energy of mixing related to the number of nearest-neighbor pairs is given by

$$\frac{\Delta_{\text{mix}}U}{N_\text{r}\varepsilon} = \frac{1}{2}\frac{N_{12}}{N_\text{r}} \tag{1}$$

where N_{12} and N_r are the total number of 1–2 pair contacts and total lattice sites, respectively, and ε is the interchange energy defined by Eq. (2)

$$\varepsilon = \varepsilon_{11} + \varepsilon_{22} - 2\varepsilon_{12} \tag{2}$$

where ε_{ij} is the i–j nearest-neighbor interaction energy. The Helmholtz energy of mixing ($\Delta_{\text{mix}}A$) is obtained by integrating the Gibbs–Helmholtz equation using the Guggenheim's athermal entropy of mixing [30] as a boundary condition:

$$\frac{\Delta_{\text{mix}}A}{N_\text{r}kT} = \left(\frac{\Delta_{\text{mix}}A}{N_\text{r}kT}\right)_{1/\tilde{T}=0} + \int_0^{1/\tilde{T}} \frac{\Delta_{\text{mix}}U}{N_\text{r}\varepsilon}\,\partial\left(\frac{1}{\tilde{\tilde{T}}}\right) \tag{3}$$

$$\left(\frac{\Delta_{\text{mix}}A}{N_\text{r}kT}\right)_{1/\tilde{T}=0} = \frac{\phi_1}{r_1}\ln\phi_1 + \frac{\phi_2}{r_2}\ln\phi_2 + \frac{z}{2}\left[\phi_1\frac{q_1}{r_1}\ln\frac{\theta_1}{\phi_1} + \phi_2\frac{q_2}{r_2}\ln\frac{\theta_2}{\phi_2}\right] \tag{4}$$

A dimensionless temperature is defined by $\tilde{T} = kT/\varepsilon(\tilde{\varepsilon}^{-1})$, where T is an absolute temperature and k is a Boltzmann's constant. r_i, ϕ_i and θ_i are the relative molar volume, volume fraction, and surface fraction of component i, respectively. ϕ_i and θ_i are defined by Eqs. (5) and (6), respectively, as

$$\phi_i = \frac{N_i r_i}{N_1 r_1 + N_2 r_2} \tag{5}$$

$$\theta_i = \frac{N_i q_i}{N_1 q_1 + N_2 q_2} \tag{6}$$

where q_i is the surface area parameter as defined by

$$z q_i = r_i(z-2) + 2 \tag{7}$$

where z is the lattice coordination number. A simple cubic lattice is used in this study ($z = 6$).

The mathematical form to correlate energy of mixing with Monte-Carlo simulation data [31], which give the values of N_{12} taking nonrandom mixing into account, is given by

$$\frac{2\Delta_{\text{mix}}U}{N_\text{r}\varepsilon} = \phi_1\phi_2\left[\frac{B'}{1 - A'(\phi_2 - \phi_1)}\right] \tag{8}$$

where

$$A' = a_0 + a_1[\exp(\tilde{\varepsilon}) - 1] \tag{9}$$

$$B' = b_0 + b_1[\exp(\tilde{\varepsilon}) - 1] \tag{10}$$

Parameters, a_0, a_1, b_0 and b_1 depend on the polymer chain lengths. The following equations are obtained from Monte-Carlo simulations

$$a_0 = 0.00012 + \frac{0.22999(r_2 - 1)}{1 + 1.37129(r_2 - 1)} \tag{11}$$

$$a_1 = -0.01717 + \frac{0.02160(r_2 - 1)}{1 + 0.09642(r_2 - 1)} \tag{12}$$

$$b_0 = 5.79880 - \frac{1.45604(r_2 - 1)}{1 + 1.83417(r_2 - 1)} \tag{13}$$

$$b_1 = -1.42112 - \frac{0.16059(r_2 - 1)}{1 - 1.34296(r_2 - 1)} \tag{14}$$

The determining procedures for Eqs. (11)–(14) are described elsewhere [32].

A simple lattice model expression for $\Delta_{\text{mix}}A$ is given by Eq. (15) from Eqs. (3) and (8).

$$\frac{\Delta_{\text{mix}}A}{N_r kT} = \left(\frac{\Delta_{\text{mix}}A}{N_r kT}\right)_{1/\tilde{T}=0} + \frac{1}{2}\phi_1\phi_2\left[C\tilde{\varepsilon} - \frac{B}{a_1(2\phi_2 - 1)} \times \ln\left\{1 - \frac{a_1(2\phi_2 - 1)}{1 - a_0(2\phi_2 - 1)}\{\exp(\tilde{\varepsilon}) - 1\}\right\}\right] \tag{15}$$

where

$$B = \frac{(a_1 b_0 - a_0 b_1)(2\phi_2 - 1) + b_1}{1 + (a_1 - a_0)(2\phi_2 - 1)}; \quad C = \frac{b_0 - b_1}{1 + (a_1 - a_0)(2\phi_2 - 1)} \tag{16}$$

2.2. Oriented interaction term

In Freed's theory [33–39], $\Delta_{\text{mix}}A$ of two monomers is given by

$$\Delta_{\text{mix}}A/N_r kT = x_1 \ln x_1 + x_2 \ln x_2 + z\tilde{\varepsilon}x_1x_2/2 - z\tilde{\varepsilon}^2x_1^2x_2^2/4 + \cdots \tag{17}$$

where z is the coordination number and x_i is the mole fraction of the component i. To obtain an analytical expression of the secondary lattice, Oh and Bae [40] defined a new expression for $\Delta_{\text{mix}}A$, replacing x by η and $\tilde{\varepsilon}$ by $\delta\tilde{\varepsilon}$ in Eq. (17). Their expression is given by

$$\frac{\Delta A_{\text{sec},ij}}{N_{ij}kT} = \frac{2}{z}\left[\eta \ln \eta + (1 - \eta)\ln(1 - \eta) + \frac{zC_\alpha \delta\tilde{\varepsilon}_{ij}(1 - \eta)\eta}{1 + C_\alpha \delta\tilde{\varepsilon}_{ij}(1 - \eta)\eta}\right] \tag{18}$$

where $\Delta A_{\text{sec},ij}$ is the Helmholtz energy of mixing for the secondary lattice for an i–j segment–segment pair and N_{ij} is the number of i–j pairs; η is the surface fraction permitting oriented interactions. In general, η is different for different components. The calculation results are not sensitive to η. For simplicity, we arbitrarily set η to 0.3 following Hu et al. [23,29] within a reasonable range from 0.3 to 0.5. C_α is a universal constant equal to 0.4881. $\delta\tilde{\varepsilon}_{ij}\left(\delta\varepsilon_{ij}/kT\right)$ is the reduced energy parameter contributed by the oriented interactions of i–j pairs such as hydrogen bonding, donor–acceptor electron transfer or dipole–dipole interaction except London dispersion force. If the secondary lattice is regarded as an independent one, $\delta\varepsilon_{ij}$ is separated into two parts [5] for the system with strongly oriented interactions between two components,

$$\delta\varepsilon_{ij} = \delta\varepsilon_{ij}^H - \delta\varepsilon_{ij}^S T \tag{19}$$

where $\delta\varepsilon_{ij}^H$ and $\delta\varepsilon_{ij}^S$ are enthalpic and entropic energy contributions for the oriented interactions, respectively. Two parameters represent the enthalpic disadvantage, $\delta\varepsilon_{ij}^H$, and the entropic advantage, $\delta\varepsilon_{ij}^S$, for $\delta\varepsilon_{ij}$ when system temperature increases. To incorporate a secondary lattice with $\Delta_{\text{mix}}A$ in Eq. (15), ε_{ij} is replaced by $\varepsilon_{ij} - \Delta A_{\text{sec},ij}/N_{ij}$. Following the definition of $\tilde{\varepsilon}$ in Eqs. (2) and (3), if an oriented interaction occurs in an i–j segment–segment pair, we replace $\tilde{\varepsilon}$ in Eq. (15) by $\varepsilon/kT + 2\Delta A_{\text{sec},ij}/N_{ij}kT$. If oriented interaction occurs in an i–i segment–segment pair, $\tilde{\varepsilon}$ is replaced by $\varepsilon/kT - \Delta A_{\text{sec},ii}/N_{ii}kT$.

2.3. van der Waals energy contribution

The energy parameter ε_{ii}^* in Eq. (20) 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) [41], which is the sum of a dispersion contribution and a polar contribution: $\delta_{\text{vdW}}^2 = \delta_{\text{d}}^2 + \delta_{\text{p}}^2$.

$$\delta_{\text{vdW},i}^2 = \frac{3N_{\text{A}}\varepsilon_{ii}^* r_i}{V_{mi}} \tag{20}$$

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

$$\varepsilon_{ii} = \boldsymbol{\Phi}_{\text{s}_1}\varepsilon_1 + \boldsymbol{\Phi}_{\text{s}_2}\varepsilon_2 \tag{21}$$

$$\varepsilon_{jj}^* = \frac{\varepsilon_{ii}^+}{V_{mi}} \tag{22}$$

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

$$\varepsilon_{ii}^+ = \frac{\delta_{\text{vdW}}^2 V_{mi}^2(25\ ^\circ\text{C})}{3N_{\text{A}}r_i} \tag{23}$$

$$r_i = \frac{V_{mi(\text{vdW})}}{15.17 \times 10^{-6}\ \text{m}^3\ \text{mol}^{-1}} \tag{24}$$

The constant 15.17×10^{-6} m^3 mol^{-1} is the molar hard-core volume 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

$$\varepsilon_{ij}^* = \sqrt{\varepsilon_{ii}^* \varepsilon_{jj}^*} \tag{25}$$

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

$$\frac{\delta\varepsilon_{ij}}{k} = \sum_{m=1}^{N_s} \sum_{n=1}^{N_p} \phi_m \phi_n g_{mn} \tag{26}$$

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; 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 phase-behavior data of solid polymer electrolyte/salt systems.

2.4. Solvent activity

If the solvent of a binary polymer solution is designated as component 1, the solvent activity can be derived from Eq. (15):

$$\begin{aligned}\ln a_1 = \left(\frac{\Delta_{\text{mix}}\mu}{N_r kT}\right) = \ln\phi_1 + \left(1 - \frac{r_1}{r_2}\right)\phi_2 + \frac{z}{2}\bigg[q_1 \ln\frac{\theta_1}{\phi_1} \\ +(\theta_1 - \phi_2)q_1 + \frac{r_1\phi_2}{r_2\phi_1}(\phi_1 - \theta_1)q_2\bigg] \\ +r_1\phi_2^2 I + r_1\phi_2^2\phi_1\left(\frac{\partial I}{\partial\phi_1}\right)\end{aligned} \tag{27}$$

$$\begin{aligned}I = \frac{1}{2}\phi_1\phi_2\bigg[C\tilde{\varepsilon} - \frac{B}{a_1(2\phi_2 - 1)} \\ \times \ln\left\{1 - \frac{a_1(2\phi_2 - 1)}{1 - a_0(2\phi_2 - 1)}\{\exp(\tilde{\varepsilon}) - 1\}\right\}\bigg]\end{aligned} \tag{28}$$

where V_{mi} and $V_{mi(\text{vdW})}$ are the molar volume and the van der Waals volume of component i, respectively. V_{mi} is a function of temperature; however, $V_{mi(\text{vdW})}$ is a constant. V_{mi} and $V_{mi(\text{vdW})}$ are estimated by the van Krevelen group-contribution method [42]. The molar volume of solvents is estimated by the modified Racett equation [43] for accuracy.

The final expression for the chemical potential can be written as

$$\begin{aligned}\Delta\mu_1 &= \left(\frac{\partial\Delta_{\text{mix}}A}{\partial N_1}\right)_{T,N_2} \\ &= \ln(1 - \phi_2) + \phi_2\left(1 - \frac{r_1}{r_2}\right) \\ &\quad + \frac{z}{2}\left[q_1 \ln\frac{\theta_1}{\phi_1} + q_1(\theta_2 - \phi_2) + q_2\frac{r_1\phi_2}{r_2\phi_1}(\phi_1 - \theta_1)\right] \\ &\quad + r_1\phi_2^2 Y + r_1\phi_2^2\phi_1\left(\frac{\partial Y}{\partial\phi_1}\right)\end{aligned} \tag{29}$$

$$\begin{aligned}\Delta\mu_2 &= \left(\frac{\partial\Delta_{\text{mix}}A}{\partial N_2}\right)_{T,N_2} \\ &= \ln\phi_2 + (1 - \phi_2)\left(1 - \frac{r_2}{r_1}\right) \\ &\quad + \frac{z}{2}\left[q_2 \ln\frac{\theta_2}{\phi_2} + q_2(\theta_1 - \phi_2) + q_1\frac{r_2\phi_1}{r_1\phi_2}(\phi_2 - \theta_2)\right] \\ &\quad + r_2\phi_1^2 Y + r_2\phi_1^2\phi_2\left(\frac{\partial Y}{\partial\phi_2}\right)\end{aligned} \tag{30}$$

$$Y = \frac{1}{2}\left[B\tilde{\varepsilon} - \frac{A}{a_1(2\phi_2 - 1)} \times \ln\left\{1 - \frac{a_1(2\phi_2 - 1)}{1 - a_0(2\phi_2 - 1)}\{\exp(\tilde{\varepsilon}) - 1\}\right\}\right] \tag{31}$$

2.5. The melting point depression theory

To determine the parameters from phase diagrams, Flory's melting point depression theory is used. In a semi-crystalline system, the condition of equilibrium between a crystalline polymer and the polymer unit in the solution may be described as follows [44]:

$$\mu_u^c - \mu_u^0 = \mu_u - \mu_u^0 \tag{32}$$

where μ_u^c, μ_u and μ_u^0 are chemical potentials of crystalline polymer segment unit, liquid (amorphous) polymer segment unit and chemical potential in standard state, respectively. Now the formal difference of appearing on the left-hand side is expected as follows:

$$\mu_u^c - \mu_u^0 = -\Delta H_u\left(1 - T/T_m^0\right) \tag{33}$$

where ΔH_u is the heat of fusion per segment unit, T_m and T_m^0 are melting point temperatures of the species in a mixture and a pure phase, respectively. The right-hand side of Eq. (32) can be restated as follows:

$$\mu_u - \mu_u^0 = \frac{V_u}{V_1}\frac{r_1}{r_2}\left(\frac{\partial\Delta A}{\partial N_2}\right)_{T,V,N_1} \tag{34}$$

where V_1 and V_u are the molar volumes of the salt and of the repeating unit, respectively. By substituting Eqs. (33) and (34) into Eq. (32) and replacing T by $T_{m,2}$, the equilibrium melting temperature of mixture is given by

$$\frac{1}{T_{m,2}} - \frac{1}{T_{m,2}^0} = -\frac{k}{\Delta H_u}\frac{V_u}{V_1}\frac{r_1}{r_2}\left(\frac{\mu_2 - \mu_2^0}{kT_{m,2}}\right) \tag{35}$$

The subscripts 1, 2 and u refer to the salt, the polymer, and polymer segment unit, respectively. Similarly, we obtain for salt (component 1)

$$\frac{1}{T_{\mathrm{m},1}}-\frac{1}{T^0_{\mathrm{m},1}}=-\frac{k}{\Delta H_1}\left(\frac{\mu_1-\mu_1^0}{kT_{\mathrm{m},1}}\right) \tag{36}$$

Correlating Eqs. (35) and (36) to the present work gives

$$\frac{1}{T_{\mathrm{m},2}}-\frac{1}{T^0_{\mathrm{m},2}}=-\frac{k}{\Delta H_\mathrm{u}}\frac{V_\mathrm{u}}{V_1}\frac{r_1}{r_2}\left(\ln\phi_2+(1-\phi_2)\left(1-\frac{r_2}{r_1}\right)\right) +\frac{z}{2}\left[q_2\ln\frac{\theta_2}{\phi_2}+q_2(\theta_1-\phi_2)+q_1\frac{r_2\phi_1}{r_1\phi_2}(\phi_2-\theta_2)\right] +r_2\phi_1^2Y+r_2\phi_1^2\phi_2\left(\frac{\partial Y}{\partial\phi_2}\right) \tag{37}$$

$$\frac{\partial Y}{\partial\phi_2}=\frac{1}{2}\left\{C'\tilde{\varepsilon}-\left(\frac{B}{a_1(2\phi_2-1)}\right)'\times L-\left(\frac{B}{a_1(2\phi_2-1)}\right)\times L'\right\}$$

and

$$\frac{1}{T_{\mathrm{m},1}}-\frac{1}{T^0_{\mathrm{m},1}}=-\frac{k}{\Delta H_1}\left(\ln(1-\phi_2)+\phi_2\left(1-\frac{r_1}{r_2}\right)\right) +\frac{z}{2}\left[q_1\ln\frac{\theta_1}{\phi_1}+q_1(\theta_2-\phi_2)+q_2\frac{r_1\phi_2}{r_2\phi_1}(\phi_1-\theta_1)\right] +r_1\phi_2^2Y+r_1\phi_2^2\phi_1\left(\frac{\partial Y}{\partial\phi_1}\right) \tag{38}$$

$$\frac{\partial Y}{\partial\phi_1}=-\frac{1}{2}\left\{C'\tilde{\varepsilon}-\left(\frac{B}{a_1(2\phi_2-1)}\right)'\times L-\left(\frac{B}{a_1(2\phi_2-1)}\right)\times L'\right\}$$

3. Results and discussion

We have developed a new group-contribution model to describe phase behaviors for polymer/salt systems. To take the oriented interaction into account, the secondary lattice concept [23,29], which is a perturbation to a fixed reference system (i.e. the Helmholtz energy of mixing for the ordinary polymer solutions), is introduced.

The proposed model gives a new expression for the configurational energy of mixing.

To correlate the energy of mixing term including the effect of nonrandom mixing on the configurational thermodynamic properties of a binary mixture with simulation data, we use Monte-Carlo simulation data [28].

In this work, most of the 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.

Fig. 1 shows the phase behavior of PEO/LiCF$_3$SO$_3$ systems. Dark squares are experimental data for the salt-rich phase and dark circles for the polymer rich phase reported by Minier et al. [45]. The solid line is the calculated coexistence curve by the proposed model and the dotted line is by the original modified double lattice model (MDL).

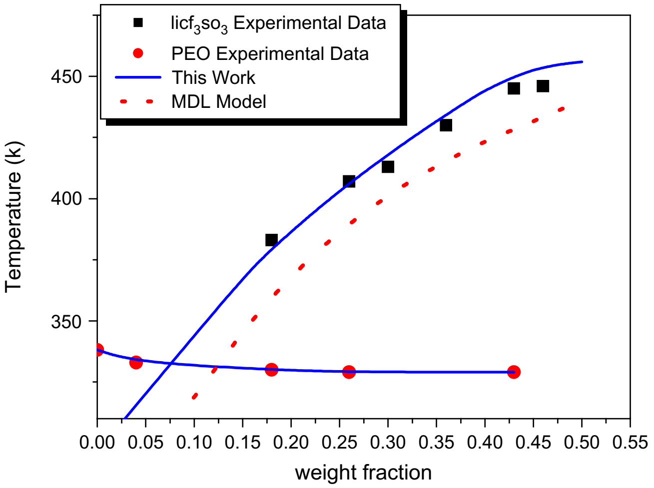

Fig. 1. Phase diagram for the PEO/LiCF$_3$SO$_3$ system. The dark squares and dark circles are experimental melting point data reported by Minier et al. [45]. The solid lines are calculated by the proposed model and dotted lines are calculated by the MDL model.

Table 1 gives the physical properties of each component such as melting temperature, heat of fusion, molecular weight, density, and molar volume [45]. The densities of PEO and LICF$_3$SO$_3$ are 1.21 and 2.69 g/cm^3, respectively. We let the number of the salt segment, r_1, be a unity and calculated the number of the polymer units, r_2, using specific volumes v_1 and v_2 for solvent and polymer, respectively:

$$r_2=\frac{M_2v_2}{M_1v_1} \tag{39}$$

where M_1 and M_2 are molecular masses for salt and polymer, respectively. By substituting values of $r_1=1$, $r_2=12{,}824.99$ and $T^0_{\mathrm{m},1}=499.29$ K into Eqs. (37) and (38) the best fit to the polymer and salt-rich liquidous curve (solid line in Fig. 1) is obtained.

These are generally accepted as reasonable values in many researches. Group-interaction parameters, g_{mn} (k), are listed in Table 2 for corresponding functional group pairs.

Fig. 2 shows the phase behavior of PEO/NaI system. The densities of PEO and NaI systems are 1.21 and 3.667 g/cm^3, respectively. By substituting values of $\Delta H_1 = 23{,}600$ J/mol, $r_1=1$, $r_2=20{,}147$ and $T^0_{\mathrm{m},1} = 933$ K into Eq. (38), the best fit to the salt-rich liquidous curve is obtained. Adjustable model

Table 1
List of melting temperature, heat of fusion, molecular weight, density, and molar volume for each sample

Sample	T^0_m (K)	ΔH (J/mol)	MW (g/mol)	Density (g/cm)	v_u (cm^3/mol)
PEO	338.15	8284.32[a]	900,000	1.21	36.60
LiI	719	14,600	133.84	4.06	55.3
NaCF$_3$SO$_3$	527.15	10,433.718	172.06	1.13	108.8
NaI	933	23,600	149.89	3.667	65.7
LiCF$_3$SO$_3$	499.29	10,516.48	156.01	2.69	52.66

[a] 8284.32 J unit^{-1}.

Table 2
Group-interaction parameter g_{mn} (k)

Salts	Polymer (PEO)	
	CH_2	O
Li	182.74	198.68
CF_3SO_3	−36.22	100.63
Na	198.66	43.50
I	−95.38	−111.48

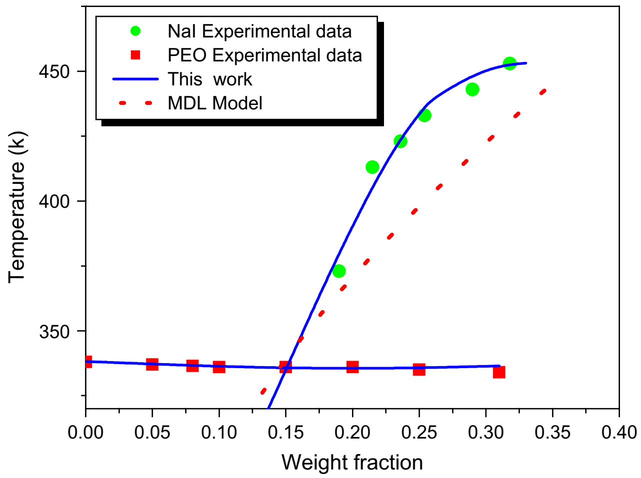

Fig. 2. Phase diagram for the PEO/NaI system. The dark squares and dark circles are experimental melting point data [46]. The solid lines are calculated by the proposed model and dotted lines are calculated by the MDL model.

parameters are listed in Table 2. Substituting the same adjustable model parameters with $\Delta H_u = 8284.32$ J/mol, $V_u = 36.6$ cm^3/mol, $V_1 = 65.7$ cm^3/mol and $T^0_{m,2} = 338.15$ K into Eq. (37), the solid lines are the best fit to the polymer and salt-rich liquidous curve (solid line in Fig. 2) by proposed model, and the dotted line is by the original modified double lattice model (MDL).

Figs. 3 and 4 represent phase behaviors of PEO/LiI and PEO/$NaCF_3SO_3$ systems, respectively. All solid lines are calculated by using previously obtained group-interaction energy parameters (Table 2) with no additional adjustable model parameters. Dark squares and circles are experimental data reported by Kim et al. [47]. The solid line is the calculated coexistence curve by the proposed model, and the dotted line is by the original modified double lattice model (MDL).

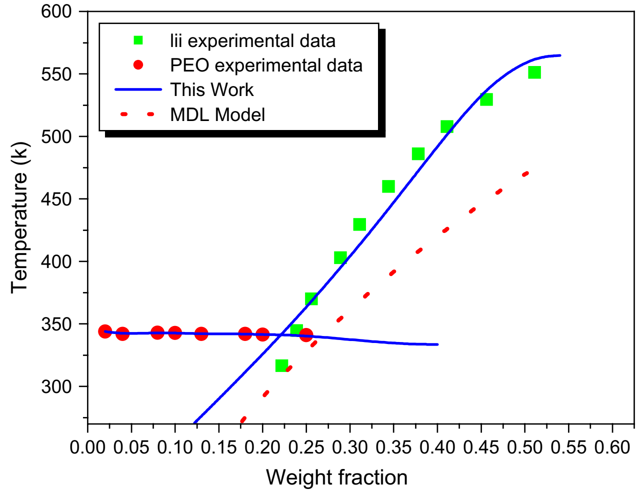

Fig. 3. Phase diagram for the PEO/LiI system. The dark squares and dark circles are experimental melting point data [46]. The solid lines are calculated by the proposed model and dotted lines are calculated by the MDL model.

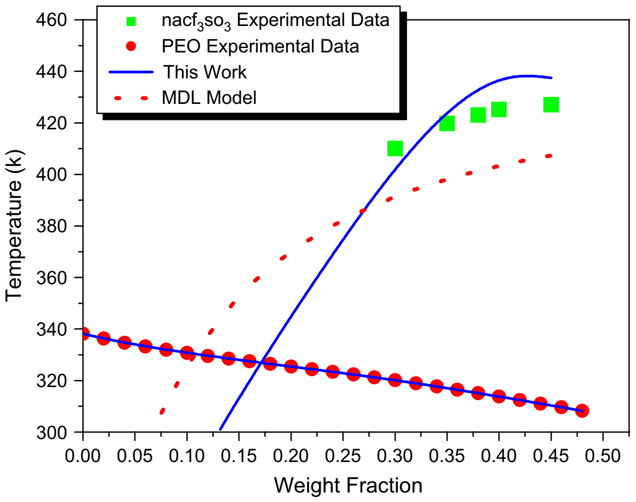

Fig. 4. Phase diagram for the PEO/$NaCF_3SO_3$ system. The dark squares and dark circles are experimental melting point data reported Kim et al. [47]. The solid lines are calculated by the proposed model and dotted lines are calculated by the MDL model.

It is clear that the lattice model gives good agreement with experimental data.

In this study, we determined group-interaction energy parameters and ionic parameters between solid polymer electrolyte and salt groups. The results obtained by the proposed model are expected to provide the appropriate operating conditions for lithium secondary battery.

To characterize the 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.

4. Conclusion

A new group-contribution model based on the lattice model is developed to interpret phase behaviors of solid polymer electrolyte/salt systems on the nonrandom mixing effect. We derive the Helmholtz energy of mixing to describe the phase behaviors of solid polymer electrolyte/salt systems using previously determined interaction energy parameters with no adjustable model parameters of the calculated curves and experimental results were compared.

The proposed model has a simplified and improved expression for the Helmholtz energy of mixing for polymer/salt systems and gives good agreement with the experimental data.

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