

Phase Behaviors of Solid Polymer Electrolytes/Salt System in Lithium Secondary Battery by Group-Contribution Method: Applicability of the Extended Debye-Hückel Theory

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ABSTRACT: A new group-contribution model based on both the modified double-lattice theory and the Debye-Hückel theory extended by Guggenheim theory is developed to interpret the phase behaviors of solid polymer electrolyte/salt systems at various temperatures and compositions. The model includes a 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 specific energy

contribution from hydrogen bonding. Quantitative description according to the proposed model is in good agreement with the experimentally observed transition temperatures of the given systems. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 2884–2890, 2008

Key words: melting point depression; solid polymer electrolyte; group contribution; Debye-Hückel theory; lithium battery

INTRODUCTION

Polymer electrolyte, i.e., the ionic conductors resulting from the complexation of porous polymers with low-lattice energy salts, has been the subject of many studies. Most recent research and development activities have been focused on the identification of solid polymer electrolytes (SPE) with sufficiently high ionic conductivity to allow the operation of solid-state Li batteries at ambient temperature with rates similar to those of their liquid electrolyte-based counterpart. SPE has been proposed for a wide variety of extremely demanding applications, such as electric vehicle, start-light-ignition, and portable electronic and personal communication.^{1–3}

Since the concept of a SPE was first proposed by Wright,⁴ a global interest has especially been focused on polymer electrolyte batteries because of their high energy density, safety, and flexibility in fabrication. One of the properties of SPE is the ionic conductivity that explains how well lithium cations are transported in the electrolyte.

A 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 that, although the chemical compounds of interest in chemical technology are numerous, the number of functional groups constituting these compounds is, however, much smaller. The thermodynamic properties of a fluid can then be calculated as a 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 of another molecule. The fundamental assumption of the 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 the other groups within that molecule.

Extension of the group-contribution idea to polymer solutions have been proposed previously by Oishi and Prausnitz,⁵ with later variations by Holten-Andersen and Fredenslund,^{6,7} Chen et al.,⁸ Elbro et al.,⁹ Kontogeorgis et al.,¹⁰ and Bogdanic and Fredenslund.¹¹ 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

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theory of Flory¹² and Huggins¹³ with variations (e.g., Guggenheim,¹⁴ Orifino and Flory,¹⁵ Koningsveld et al.,¹⁶). However, it is well known that the Flory-Huggins theory is based on severe simplifying assumptions, which have been overcome in the much-improved lattice-cluster theory of Freed and coworkers^{17,18}. Freed's theory is mathematically complicated. However, the results can be well approximated using a mathematical simplification introduced by Hu et al.¹⁹⁻²¹. Recently, Helmholtz energy of mixing has been reported by Chang et al.²² to describe the phase equilibria of various polymer solutions over the entire concentration and for various temperatures. Hu et al.²³ presented the group-contribution method including a revised Flory-Huggins entropy, a series expression for excess internal energy, and a double lattice model to account for specific interactions.

In this study, we combine the modified double lattice model²⁴ and the extended Debye-Hückel theory developed by Guggenheim and Turgeon.^{25,26} The advantage of the extended Debye-Hückel theory is its simplicity in calculating liquidus curves in the phase diagram of the binary polymer/salt systems, where systems containing salt cation and polymer repeating unit with multiple charges have a great effect on the activity of ions when compared with electrolyte containing only singly charged ions. The purpose of this study is to apply the modified double lattice model to the SPE/Salt systems by employing the extended Debye-Hückel theory^{25,26} as a function of the polymer ionic contribution.

We examine a generalization of the modified double lattice model for phase behaviors in lithium secondary battery systems. If an electrolyte is contacted with an aqueous system, the electrolyte will take up PEO and Li salts. PEO is capable of dissolving large concentrations of ionic salts because of the strong salt ion-polymer interactions that overcome the lattice energies of the salts. The extended Debye-Hückel theory^{25,26} assumes that salts dissociate completely and the consequential increase in the ion-ion interactions should be corrected in an optimization factor that is chosen to be universal for all polymer/salt systems.

MODEL DEVELOPMENT

Four theoretical aspects are taken into account: the lattice notation of a Debye-Hückel type function proposed by Guggenheim and Turgeon,^{25,26} modified double lattice model,²⁴ and Flory's melting point depression concept.²⁷

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

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

where R is the gas constant and T is the absolute temperature.

Modified double lattice model

Primary lattice

Oh and Bae²⁴ proposed a new Helmholtz energy of mixing as the form of Flory-Huggins theory. The expression is given by

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

where N_r is the total number of lattice sites and k is the Boltzmann's constant. r_i is the number of segments per molecule i . χ_{OB} is a new interaction parameter and function of r_i , $\tilde{\epsilon}$:

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

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

$$\tilde{\epsilon} = \epsilon/kT = (\epsilon_{11} + \epsilon_{22} - 2\epsilon_{12})/kT, \tag{4}$$

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

Secondary lattice

In Freed's theory,^{28,29} the solution of the Helmholtz energy of mixing for the Ising model is given by

$$\frac{\Delta A}{N_r kT} = x_1 \ln x_1 + x_2 \ln x_2 + \frac{z\tilde{\epsilon}x_1x_2}{2} - \frac{z\tilde{\epsilon}^2x_1^2x_2^2}{4} + \dots, \tag{5}$$

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

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

where $\Delta A_{\text{sec},ij}$ is the Helmholtz energy of mixing of the secondary lattice for $i - j$ segment-segment pair, N_{ij} is the number of $i - j$ pairs, $\delta \tilde{\varepsilon}$ is 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 et al.^{19,30} suggested. C_α is also not an adjustable parameter and is determined by comparing with Panagiotopoulos et al.'s Gibbs-Ensemble Monte-Carlo simulation data of Ising lattice. The best fitting value of C_α is 0.4880.²⁴

Incorporation of secondary lattice into primary lattice

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

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

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

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

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

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

The final expression for the chemical potential can be written as

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

and

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

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).

Lattice notation of an extended Debye-Hückel theory

For a binary polymer/salt system at solute molality m (mol/kg 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}:

$$\frac{\Delta G_{\text{mix}}^{\text{Total}}}{RT} = \frac{\Phi_1}{r_1 v m} \left[-\frac{4}{3} A I^{3/2} \tau(I^{1/2}) \right], \quad (12)$$

where

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

where Φ_1 is the segment fraction of the salt ion, $r_1 (=1)$ is the number of segments per salt ion, $v (=v_M + v_X; v_M$ and v_X are the number of M and X ions, per salt, respectively) is 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 in PEO/LiCF₃SO₃ system: ions = 2%; pairs = 71%; triples = 27%.¹ For a binary polymer/salt system containing 1 kg of polymer and v_M moles of salt ion, ϕ_1 and I are defined by

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

$$I = \frac{1}{2} m v |z_M z_X| = \frac{1}{2} \left[\frac{r_2 \phi_1 1000/M}{r_1 \phi_2} \right] |z_M z_X|, \quad (15)$$

where M is the molecular weight of polymer in g/mol (i.e., $M = 900,000$ g/mol). 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

$$\begin{aligned} \frac{\Delta\mu_1^{\text{DH}}}{RT} &= \frac{1}{RT} \left(\frac{\partial(r_1 N_1 + r_2 N_2) \Delta G_{\text{mix}}^{\text{DH}}}{\partial N_2} \right) \\ &= -\frac{v}{1000} \left(\frac{A |z_M z_X| I^{1/2}}{1 + I^{1/2}} \right), \quad (16) \end{aligned}$$

$$\begin{aligned} \frac{\Delta\mu_2^{\text{DH}}}{RT} &= \frac{1}{RT} \left(\frac{\partial(r_1 N_1 + r_2 N_2) \Delta G_{\text{mix}}^{\text{DH}}}{\partial N_2} \right) \\ &= \frac{M}{1000} \left(\frac{2}{3} A I^{3/2} \sigma(I^{1/2}) \right), \quad (17) \end{aligned}$$

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

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: $\delta_{vdw}^2 = \delta_d^2 + \delta_p^2$.

$$\delta_{vdw,i}^2 = \frac{3N_A \epsilon_{ii}^* r_i}{V_{mi}}, \quad (19)$$

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

$$\epsilon_{ii} = \Phi_{s_1} \epsilon_1 + \Phi_{s_2} \epsilon_2, \quad (20)$$

$$\epsilon_{jj}^* = \frac{\epsilon_{ii}^+}{V_{mi}}, \quad (21)$$

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

$$\epsilon_{ii}^+ = \frac{\delta_{vdw}^2 V_{mi}^2 (25^\circ\text{C})}{3N_A r_i}, \quad (22)$$

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

The constant $15.17 \times \text{m}^3/\text{mol}$ is the molar hard-core volumes of a CH₂ 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

$$\epsilon_{ij}^* = \sqrt{\epsilon_{ii}^* \epsilon_{jj}^*}. \quad (24)$$

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

$$\frac{\delta\epsilon_{ij}}{k} = \sum_{m=1}^{N_s} \sum_{n=1}^{N_p} \phi_m \phi_n g_{mn}, \quad (25)$$

where N_s and N_p are the 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 solid-liquid equilibria data of polymer solutions.

The melting point depression theory

To determine the parameters from phase diagrams, Flory's melting point depression theory is used. In a semicrystalline system, the condition of equilibrium between a crystalline polymer and the polymer unit in the solution may be described as follows³²:

$$\mu_u^c - \mu_u^0 = \mu_u - \mu_u^0, \quad (26)$$

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-handed side is expected as follows:

$$\mu_u^c - \mu_u^0 = -\Delta H_u(1 - T/T_m^0), \quad (27)$$

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-handed side of eq. (26) can be restated as follows:

$$\mu_u - \mu_u^0 = \frac{V_u r_1}{V_1 r_2} \left(\frac{\partial \Delta A}{\partial N_2} \right)_{T,V,N_1}, \quad (28)$$

where V_1 and V_u are the molar volumes of the salt and of the repeating unit, respectively. By substituting eqs. (27) and (28) into eq. (26) and replacing T by $T_{m,2}$, the equilibrium melting temperature of mixture is given by

$$\frac{1}{T_{m,2}} - \frac{1}{T_{m,2}^0} = -\frac{k}{\Delta H_u} \frac{V_u r_1}{V_1 r_2} \left(\frac{\mu_2 - \mu_2^0}{kT_{m,2}} \right), \quad (29)$$

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

$$\frac{1}{T_{m,1}} - \frac{1}{T_{m,1}^0} = -\frac{k}{\Delta H_1} \left(\frac{\mu_1 - \mu_1^0}{kT_{m,1}} \right). \quad (30)$$

Correlating eqs. (29) and (30) to the present work gives

$$\begin{aligned} \frac{1}{T_{m,2}} - \frac{1}{T_{m,2}^0} = & -\frac{k}{\Delta H_u} \frac{V_u r_1}{V_1 r_2} \left(\frac{M}{1000} \left(\frac{2}{3} A I^{3/2} \sigma \left(I^{1/2} \right) \right) \right) \\ & + \ln \phi_2 + r_2 \left[\left(\frac{1}{r_2} - \frac{1}{r_1} \right) + C_\beta \left(\frac{1}{r_2} - \frac{1}{r_1} \right)^2 + \left(2 + \frac{1}{r_2} \right) \varepsilon\% \right] \\ & - r_2 \left[\left(\frac{1}{r_2} - \frac{1}{r_1} \right) + 2 \left(\left(\frac{1}{r_2} - \frac{1}{r_1} \right) + C_\gamma \varepsilon\% \right) \varepsilon\% \right. \\ & \quad \left. + 2C_\beta \left(\frac{1}{r_2} - \frac{1}{r_1} \right)^2 + 2 \left(2 + \frac{1}{r_2} \right) \varepsilon\% \right] \phi_2 \\ & + r_2 \left[4 \left(\left(\frac{1}{r_2} - \frac{1}{r_1} \right) + C_\gamma \varepsilon\% \right) \varepsilon\% + \left(2 + \frac{1}{r_2} \right) \varepsilon\% \right. \\ & \quad \left. + C_\beta \left(\frac{1}{r_2} - \frac{1}{r_1} \right)^2 + 3C_\gamma \varepsilon^2\% \right] \phi_2^2 \\ & - r_2 \left[6C_\gamma \varepsilon^2\% + 2 \left(\left(\frac{1}{r_2} - \frac{1}{r_1} \right) + C_\gamma \varepsilon\% \right) \varepsilon\% \right] \phi_2^3 \\ & \quad \left. + 3r_2 C_\gamma \varepsilon^2\% \phi_2^4 \right] \quad (31) \end{aligned}$$

and

TABLE I

List of Melting Temperature, Heat of Fusion, Molecular Weight, Density, and Molar Volume for Each Sample

	T_m^0 (K)	ΔH (J/mol)	MW (g/mol)	Density (g/cm ³)	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	10433.718	172.06	1.13	108.8
NaI	933	23,600	149.89	3.667	65.7
LiCF ₃ SO ₃	499.29	10516.48	156.01	2.69	52.66

^a 8284.32 J unit⁻¹.

$$\begin{aligned} \frac{1}{T_{m,1}} - \frac{1}{T_{m,1}^0} = & -\frac{k}{\Delta H_1} \left(-\frac{v}{1000} \left(\frac{A|z_M z_X| I^{1/2}}{1 + I^{1/2}} \right) + \ln(1 - \phi_2) \right) \\ & - r_1 \left(\frac{1}{r_2} - \frac{1}{r_1} \right) \phi_2 + r_1 \left[C_\beta \left(\frac{1}{r_2} - \frac{1}{r_1} \right)^2 + \left(\left(\frac{1}{r_2} - \frac{1}{r_1} \right) \right. \right. \\ & \quad \left. \left. + C_\gamma \varepsilon\% \right) \varepsilon\% + \left(2 + \frac{1}{r_2} \right) \varepsilon\% \right] \phi_2^2 - 2r_1 \left[\left(\left(\frac{1}{r_2} - \frac{1}{r_1} \right) \right. \right. \\ & \quad \left. \left. + C_\gamma \varepsilon\% \right) \varepsilon\% + C_\gamma \varepsilon^2\% \right] \phi_2^3 + 3r_1 C_\gamma \varepsilon^2\% \phi_2^4 \quad (32) \end{aligned}$$

RESULTS AND DISCUSSION

We have developed a new group-contribution model to describe phase behaviors for polymer/salt systems. 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 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.

Table I gives physical properties of each component such as melting temperature, heat of fusion, molecular weight, density, and molar volume.³³ The densities of PEO and LiCF₃SO₃ are 1.21 and 2.69 g/cm³, respectively. We let the number of the salt segment, r_1 , be a unity and calculate the number of the polymer units, r_2 , using specific volumes v_1 and v_2 for solvent and polymer, respectively,

$$r_2 = \frac{M_2 v_2}{M_1 v_1} \quad (33)$$

where M_1 and M_2 are molecular masses for salt and polymer, respectively. By substituting values of $r_1 = 1$, $r_2 = 12824.99$, and $T_{m,1}^0 = 499.29$ K into eq. (32), the best fit to the salt-rich liquidous curve (solid line in Fig. 1) is obtained. The solid lines were

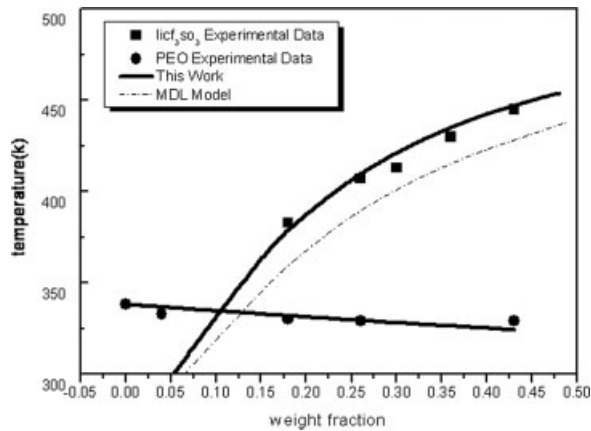


Figure 1 Phase diagram for the PEO/LiCF₃SO₃ system. The dark squares and dark circles are experimental melting point data reported by Minier et al.³³ The solid lines are calculated by the proposed model and dotted lines are calculated by the MDL model.

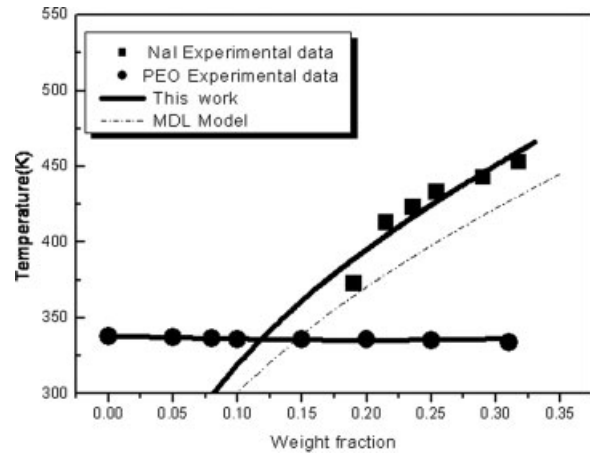


Figure 2 Phase diagram for the PEO/NaI system. The dark squares and dark circles are experimental melting point data.³⁴ The solid lines are calculated by the proposed model and dotted lines are calculated by the MDL model.

predicted by the proposed model with A [the usual Debye-Hückel coefficient shown in eq. (12)] = 0.068. The dotted lines were calculated in the case of $A = 0$. We set $\eta = 0.3$ and $z = 6$ as suggested by Hu et al.³⁰ These are generally accepted as reasonable values in many researches. Group-interaction parameters, $g_{mn}(k)$, are listed in Table II for corresponding functional group pairs.

The phase behaviors of PEO/LiCF₃SO₃ systems are given in Figure 1. Dark squares are experimental data for the salt-rich phase and dark circles for the polymer-rich phase reported by Minier et al.,³³ respectively. The solid line is the calculated coexistence curve by the MDL-Debye-Hückel (MDL-DH) model, and the dotted line is by the original MDL. The polymer-rich liquidus curve is calculated from eq. (31), and the salt-rich curve is calculated from eq. (32).

Figure 2 shows the phase behavior of PEO/NaI system. The densities of PEO and NaI are 1.21 and 3.667 g/cm³, respectively. The solid lines are calculated by the proposed model with $A = 0.068$. The dotted lines are calculated in the case of $A = 0$.

By substituting values of $\Delta H_1 = 23,600$ J/mol, $r_1 = 1$, $r_2 = 20,147$, and $T_{m,1}^0 = 933$ K into eq. (32), the best fit to the salt-rich liquidous curve is obtained. Adjustable model parameters are listed in Table II.

TABLE II
Group-Interaction Parameter $g_{mn}(k)$

Salts	Polymer (PEO)	
	CH ₂	O
Li	-163.77465	-900.23556
CF ₃ SO ₃	-150.66725	198.46362
Na	-451.76044	188.00657
I	-400.05931	178.67928

Substituting the same adjustable model parameters with $\Delta H_u = 8284.32$ J/mol, $V_u = 36.6$ cm³/mol, $V_1 = 65.7$ cm³/mol, and $T_{m,2}^0 = 338.15$ K into eq. (31), the solid lines are predicted by the MDL-DH model with $A = 0.068$. The dotted lines are calculated in the case of $A = 0$.

Figures 3 and 4 represent phase behaviors of PEO/LiI and PEO/NaCF₃SO₃ systems, respectively. All solid lines are calculated by using previously obtained group interaction energy parameters (Table II) with no additional model parameters. Dark squares and circles are experimental data reported by Kim et al.^{34,35} The solid line is the calculated coexistence curve by the MDL-DH model with $A = 0.068$, and the dotted line is calculated in the case of $A = 0$. It is clear that the MDL-DH model gives better description of experimental data than those of the MDL model for the given systems.

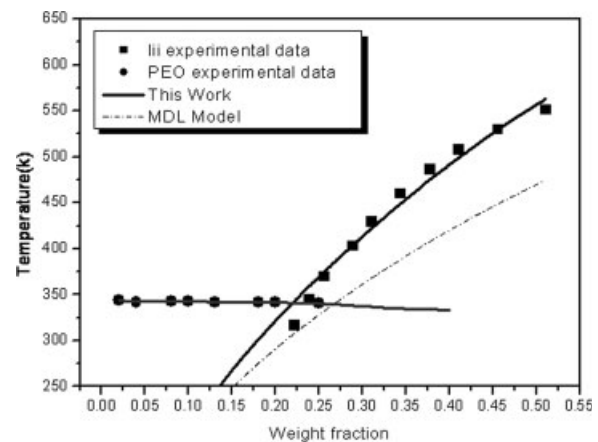


Figure 3 Phase diagram for the PEO/LiI system. The dark squares and dark circles are experimental melting point data.³⁴ The solid lines are calculated by the proposed model and dotted lines are calculated by the MDL model.

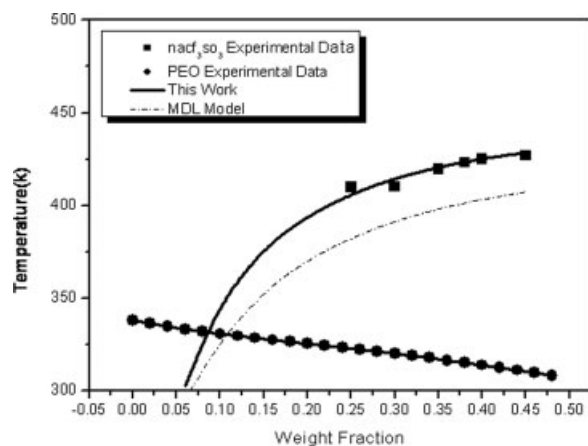


Figure 4 Phase diagram for the PEO/NaCF₃SO₃ system. The dark squares and dark circles are experimental melting point data reported by Kim and Bae.³⁵ The solid lines are calculated by the proposed model and dotted lines are calculated by the MDL model.

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

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.

CONCLUSIONS

We have developed a new thermodynamic framework extended to the group contribution method to describe phase behaviors of number of SPE/Li salt systems. The model is based on the theory of melting point depression and MDL-DH model that takes into account the ionic interaction. The proposed model has a simplified and improved expression for the Helmholtz energy of mixing for polymer/salt systems that includes the van der Waals energy contribution.

The ultimate goal of this work is to describe phase behaviors of SPE/Salts system using the group-contribution method. Our results show that the MDL-DH model gives better description of experimental data than those of the MDL model for the given systems, specifically near the eutectic point. The results obtained by the proposed model are expected to provide the appropriate operating conditions for lithium secondary battery.

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