Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Polymer 47 (2006) 211–217
polymer
www.elsevier.com/locate/polymer

Phase behaviors of solid polymer electrolytes/salt system in lithium secondary battery by group-contribution method: The pressure effect

Jae Ho Joo, Young Chan Bae *, Yang Kook Sun

Division of Chemical Engineering and Molecular Thermodynamics Laboratory, Hanyang University, Seoul 133-791, South Korea[1]

Received 2 October 2004; received in revised form 1 November 2005; accepted 10 November 2005
Available online 23 November 2005

Abstract

A new group-contribution model based on the modified double-lattice theory with the free volume effect is developed and applied to describe phase-behaviors of solid polymer electrolyte/salt system with various pressures. The proposed group-contribution model includes the van der Waals energy contribution from dispersion and polar forces.

Our result show that an eutectic point moves toward higher T_m and lower weight fraction of salt with increasing pressure. Quantitative description according to the proposed model is in good agreement with the experimentally observed transition temperature of a given system.

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

1. Introduction

Since Fenton et al. [1] and Armand et al. [2] showed that solid polymer electrolytes (SPE) consisting of poly(ethylene oxide) (PEO) and an alkali metal salt have significant ionic conductivities and can be used in all solid-state electrochemical batteries, considerable research has been directed toward the development of polymer electrolytes having high ionic conductivity at room temperature.

To increase the ionic conductivities of SPE, the polymer should have both low T_g and low crystallinity. Reibel et al. [3] 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. [4] reported an application of PEO complexed with $NaNO_3$ salt as an electro chemical cell. Andreev et al. [5] reported the structure–conductivity relation of PEO/$LiAsF_6$ in the analogous phase. Reddy et al. [6] also reported the structure–conductivity relation of PEO with potassium ionic salt.

Investigations of the manufacturing process of lithium polymer battery in common use, there is a pressure imposed on the SPE to improve the degree of contact between electrolyte and electrode. The physical properties of the compressed SPE system would be totally different from those of the uncompressed SPE system. Further, when plasticized SPE is used, the effect will be even greater. However, for engineering design, it is often necessary to estimate liquidous curves in polymer solutions. Because experimental data for such solutions are not plentiful, it is desirable to use a group-contribution method.

Group-contribution model is a 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. 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.

---

* Corresponding author. Tel.: +82 2 2220 0529; fax: +82 2 2296 0568.
E-mail address: ycbae@hanyang.ac.kr (Y.C. Bae).

[1] http://www.inchem.hanyang.ac.kr/lab/mtl/

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.11.022

Extension of the group-contribution idea to polymer solutions have been proposed previously by Oishi and Prausnitz [7], with later variations by Holten-Andersen and Fredenslund [8,9], Chen et al. [10], Elbro et al. [11], Kontogeogis et al. [12], and Bogdanic and Fredenslund [13]. Those 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 [14], and Huggins [15] with variations (e.g. Guggenheim [16], Orifino and Flory [17], Koningsveld et al. [18]). 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 co-workers [19,20]. Freed's theory is mathematically complicated. The results, however, can be well approximated using a mathematical simplification introduced by Hu et al. [21–23]. They 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 [24,25].

In this work, we propose a new thermodynamic frame work extended to the group contribution method taking into account interactions between different species (salt) to describe phase behaviors of number of SPE/Li salt systems with various pressures.

To describe the pressure effect of the given systems, we extend the modified double lattice model [26] for polymer solution to the equation of state model. We then combined it with the theory of melting point depression [27].

2. Model development

Two theoretical aspects are taken into account; one is the modified double lattice model with the free-volume effect and the other is Flory's melting point depression of polymers, which well describes the effect of diluents, copolymerized units, and end groups on the melting point when the concentration of each is low [27]. We assume that the salt is a particle to consider a salt effect of the free energy of mixing.

2.1. Modified double lattice model

2.1.1. Primary lattice

Oh et al. [28] proposed a new Helmholtz energy of mixing as the form of Flory–Huggins theory. The expression is given by

$$\frac{\Delta A}{N_r kT} = \left(\frac{\phi_1}{r_1}\right)\ln\phi_1 + \left(\frac{\phi_2}{r_2}\right)\ln\phi_2 + \chi_{OB}\phi_1\phi_2 \tag{1}$$

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, $\tilde{\varepsilon}$:

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

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

$$\tilde{\varepsilon} = \varepsilon/kT = (\varepsilon_{11}+\varepsilon_{22}-2\varepsilon_{12})/kT \tag{3}$$

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 [28].

2.1.2. Secondary lattice

In Freed's theory [29,30], the solution of the Helmholtz energy of mixing for the Ising model is given by

$$\frac{\Delta A}{N_r kT} = x_1\ln x_1 + x_2\ln x_2 + \frac{z\tilde{\varepsilon}x_1x_2}{2} - \frac{z\tilde{\varepsilon}^2x_1^2x_2^2}{4} + \cdots \tag{4}$$

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. (4). This secondary lattice is introduced as a perturbation to account for the oriented interaction. The expression is given by

$$\frac{\Delta A_{\mathrm{sec},ij}}{N_{ij}kT} = \frac{2}{z}\left[\eta\ln\eta + (1-\eta)\ln(1-\eta) + \frac{zC_\alpha\delta\tilde{\varepsilon}_{ij}(1-\eta)\eta}{1+C_\alpha\delta\tilde{\varepsilon}_{ij}(1-\eta)\eta}\right] \tag{5}$$

where $\Delta A_{\mathrm{sec},ij}$ is the Helmholtz energy of mixing of the secondary lattice for i–j segment–segment pair and 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. [31,32] suggested. C_α also is 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 [28].

2.1.3. Incorporation of secondary lattice into primary lattice

To account for the oriented interaction, the secondary lattice contribution is a perturbation to the primary lattice. To incorporate a secondary lattice, we replace ε_{ij} by $\varepsilon_{ij}-\Delta A_{\mathrm{sec},ij}/N_{ij}$ in Eq. (2). Following the definition of $\tilde{\varepsilon}$ in Eq. (3), if oriented interaction occurs in i–j segment–segment pairs, we replace $\tilde{\varepsilon}$ by $\varepsilon/kT+\Delta 2A_{\mathrm{sec},ij}/N_{ij}kT$ in Eq. (2). If oriented interaction occurs in i–i segment–segment pairs, $\tilde{\varepsilon}$ is replaced by $\varepsilon/kT-\Delta A_{\mathrm{sec},ij}/N_{ij}kT$.

2.2. Lattice model with hole

To account for free-volume effects of the MDL model, which is an incompressible model, we follow an approach outlined in principle by Kleintjens [33,34]. In this approach, the lattice is made up of occupied and vacant lattice sites (molecules and holes, respectively), and on a rigid lattice densities can be varied by adjustment of the concentration of holes.

2.2.1. Helmholtz energy of mixing

We design two-step process to expand a close-packed polymer solution to volume V at temperature T and pressure P. For the first step, close-packed pure components are mixed to form a close-packed polymer solution N_1 molecules of solvent 1 and N_2 molecules of polymer 2. In this step, Eq. (1) is directly used to express the contribution to the Helmholtz function of mixing.

$$\tilde{A}_{\mathrm{r.I}} = \frac{\Delta A_{\mathrm{I}}}{N_{\mathrm{r}}kT} = \left(\frac{\phi_1}{r_1}\right)\ln\phi_1 + \left(\frac{\phi_2}{r_2}\right)\ln\phi_2 + \chi_{\mathrm{OB}}\phi_1\phi_2 \tag{6}$$

For the second step [33], the close-packed polymer solution considered to be a pseudo-pure substance is mixed with N_0 molecules of holes 0 to form an expanded polymer solution with volume V at T and P. In this step, the close-packed polymer solution is a pseudo-pure substance a, its average chain length r_a and its energy parameter ε_{aa} are estimated by the following mixing rules:

$$\frac{1}{r_a} = \left(\frac{\phi_1}{r_1}\right) + \left(\frac{\phi_2}{r_2}\right) \tag{7}$$

$$\varepsilon_{aa} = \phi_1^2\varepsilon_{11} + 2\phi_1\phi_2\varepsilon_{12} + \phi_2^2\varepsilon_{22} \tag{8}$$

The contribution of the second step to the Helmholtz energy of mixing is again expressed by Eq. (6)

$$\frac{\Delta A_{\mathrm{II}}}{N_{\mathrm{l}}kT} = \varphi_0\ln\varphi_0 + \left(\frac{\varphi_a}{r_a}\right)\ln\varphi_a + \chi^0_{\mathrm{OB}}\varphi_0\varphi_a \tag{9}$$

where N_{l} is the total number of sites including holes, ϕ_0 and ϕ_a are volume fractions of holes and of the pseudo substance, respectively, while ϕ is the volume fraction for close-packed lattice: χ^0_{OB} and $\tilde{\varepsilon}_{\mathrm{II}}$ are a new interaction parameter and a reduced energy defined by

$$\chi^0_{\mathrm{OB}} = C_\beta\left(\frac{1}{r_a}-1\right)^2 + \left(2+\frac{1}{r_a}\right)\tilde{\varepsilon}_{\mathrm{II}} - \left(\frac{1}{r_a}-1+C_{\mathrm{r}}\tilde{\varepsilon}_{\mathrm{II}}\right)\tilde{\varepsilon}_{\mathrm{II}}\varphi_a + C_\gamma\tilde{\varepsilon}^2_{\mathrm{II}}\varphi_a^2 \tag{10}$$

$$\tilde{\varepsilon}_{II} = \varepsilon_{aa}/kT \tag{11}$$

2.3. Equation of state

We obtain an equation of state from the Helmholtz energy of mixing of polymer solution considering the free volume effect. A reduced temperature $\tilde{T}$, a reduced pressure $\tilde{P}$ and a reduced density $\tilde{\rho}$ are given;

$$\tilde{T} = \tilde{\varepsilon}_{\mathrm{II}}^{-1} = kT/\varepsilon_{aa} \tag{12}$$

$$\tilde{P} = Pv^0/\varepsilon_{aa} \tag{13}$$

$$\tilde{\rho} = N_{\mathrm{r}}v^0/V \tag{14}$$

where v^0 is the hard-core volume of one site or one segment calculated by:

$$v^0 = \sum_i \phi_i v_i^0 = \phi_1 v_1^0 + \phi_2 v_2^0 \tag{15}$$

The reduced density $\tilde{\rho}$ is related to the volume fraction by:

$$\tilde{\rho} = N_{\mathrm{r}}/N_{\mathrm{l}} = \varphi_a, \qquad 1-\tilde{\rho} = \varphi_0 \tag{16}$$

Upon the substitution of those reduced variables into Eq. (10), we obtain the reduced Helmholtz energy of mixing for the second step.

$$\tilde{A}_{\mathrm{r.II}} = \frac{\Delta A_{\mathrm{II}}}{N_{\mathrm{r}}kT} = \tilde{T}\left[\tilde{\rho}^{-1}(1-\tilde{\rho})\ln(1-\tilde{\rho}) + \left(\frac{1}{r_a}\right)\ln\tilde{\rho} + \chi^0_{\mathrm{OB}}(1-\tilde{\rho})\right] \tag{17}$$

The reduced pressure becomes

$$\tilde{P} = \tilde{\rho}^2\left(\frac{\partial\tilde{A}_{\mathrm{r,II}}}{\partial\tilde{\rho}}\right)_{\tilde{T}\phi} \tag{18}$$

$\tilde{A}_{r.I}$ (Eq. (6)) for the first step is independent of density due to the closed-packing, therefore it makes no contribution to the pressure. Substitution of Eq. (17) into Eq. (18) gives an equation of state for polymer solutions.

$$\tilde{P} = \tilde{T}\Bigg[-\ln(1-\tilde{\rho}) - \left(1-\frac{1}{r_a}\right)\tilde{\rho} - \left\{C_\beta\left(\frac{1}{r_a}-1\right)^2 + \left(2+\frac{1}{r_a}\right)\tilde{\varepsilon}_{\mathrm{II}} - \left(\frac{1}{r_a}-1+C_{\mathrm{r}}\tilde{\varepsilon}_{\mathrm{II}}\right)\tilde{\varepsilon}_{\mathrm{II}}(1-2\tilde{\rho})\right\}\tilde{\rho}^2 + C_{\mathrm{r}}\tilde{\varepsilon}_{\mathrm{II}}(2-3\tilde{\rho})\tilde{\rho}^3\Bigg] \tag{19}$$

2.4. The chemical potentials

Chemical potentials for the two components are calculated by

$$\mu_1 - \mu_1^0 = \left(\frac{\partial\Delta_{\mathrm{mix}}A}{\partial N_1}\right)_{T,V,N_2} = r_1\left(\Delta f_E + \phi_2\frac{\mathrm{d}\Delta f_{\mathrm{E}}}{\mathrm{d}\phi_1}\right) \tag{20}$$

$$\mu_2 - \mu_2^0 = \left(\frac{\partial\Delta_{\mathrm{mix}}A}{\partial N_2}\right)_{T,V,N_1} = r_2\left(\Delta f_{\mathrm{E}} - \phi_1\frac{\mathrm{d}\Delta f_{\mathrm{E}}}{\mathrm{d}\phi_1}\right) \tag{21}$$

where

$$\Delta f_{\mathrm{E}} = \Delta A_{(\mathrm{I+II})}/N_{\mathrm{r}} \tag{22}$$

$$\frac{\mathrm{d}\Delta f_{\mathrm{E}}}{\mathrm{d}\phi_1} = \frac{\partial\Delta f_{\mathrm{E}}}{\partial\phi_1} + \frac{\partial\Delta f_{\mathrm{E}}}{\partial\tilde{\rho}}\frac{\partial\tilde{\rho}}{\partial\phi_1} + \frac{\partial\Delta f_{\mathrm{E}}}{\partial\tilde{\varepsilon}_{\mathrm{II}}}\frac{\partial\tilde{\varepsilon}_{\mathrm{II}}}{\partial\phi_1} + \frac{\partial\Delta f_{\mathrm{E}}}{\partial r_a}\frac{\partial r_a}{\partial\phi_1} \tag{23}$$

and the terms in Eq. (23) are given by

$$\frac{\partial \Delta f_E}{\partial \phi_1} = kT\left[\frac{1}{r_1}\ln \phi_1 + \frac{1}{r_1} - \frac{1}{r_2}\ln \phi_2 - \frac{1}{r_2} + \left\{C_\beta\left(\frac{1}{r_2} - \frac{1}{r_1}\right)^2 + \left(2 + \frac{1}{r_2}\right)\tilde{\varepsilon}\right\}(1-2\phi_1) - \left(\frac{1}{r_2} - \frac{1}{r_1} + C_\gamma\tilde{\varepsilon}\right) \times \tilde{\varepsilon}(1-3\phi_1)\phi_2 + C_\gamma\tilde{\varepsilon}^2(1-4\phi_1)\phi_2^2\right] \tag{24}$$

$$\frac{\partial \Delta f_E}{\partial \tilde{\rho}}\frac{\partial \tilde{\rho}}{\partial \phi_1} = \tilde{T}kT\left[-\frac{1}{\tilde{\rho}^2}\ln(1-\tilde{\rho}) - \frac{1}{\tilde{\rho}} + \frac{1}{r_a\tilde{\rho}} - \left\{C_\beta\left(\frac{1}{r_a} - 1\right)^2 + \left(2 + \frac{1}{r_a}\right)\tilde{\varepsilon}_{\mathrm{II}} + \left(\frac{1}{r_a} - 1 + C_\gamma\tilde{\varepsilon}_{\mathrm{II}}\right)\tilde{\varepsilon}_{\mathrm{II}}(1-2\tilde{\rho}) - C_\gamma\tilde{\varepsilon}_{\mathrm{II}}^2(2-3\tilde{\rho})\tilde{\rho}\right\}\right]\left[\frac{(1-\tilde{\rho})\tilde{\rho}}{\phi_2}\right] \tag{25}$$

$$\frac{\partial \Delta f_E}{\partial \tilde{\varepsilon}_{\mathrm{II}}}\frac{\partial \tilde{\varepsilon}_{\mathrm{II}}}{\partial \phi_1} = 2\left[\left\{-\frac{(1-\tilde{\rho})}{\tilde{\rho}}\ln(1-\tilde{\rho}) - \frac{1}{r_a}\ln\tilde{\rho}\right\}\tilde{\varepsilon}_{\mathrm{II}}^{-2} + \left\{-C_\beta\left(\frac{1}{r_a} - 1\right)^2\tilde{\varepsilon}_{\mathrm{II}}^{-2} - C_\gamma\tilde{\varepsilon}_{\mathrm{II}}\tilde{\rho}(1-\tilde{\rho})\right\}(1-\tilde{\rho})\right] \times [\phi_1\varepsilon_{11} + (1-2\phi_1)\varepsilon_{12} - \phi_2\varepsilon_{22}] \tag{26}$$

$$\frac{\partial \Delta f_E}{\partial r_a}\frac{\partial r_a}{\partial \phi_1} = \tilde{T}kT\left[-\ln\tilde{\rho} + \left\{2C_\beta\left(1 - \frac{1}{r_a}\right) - \tilde{\varepsilon}_{\mathrm{II}} + \tilde{\varepsilon}_{\mathrm{II}}\tilde{\rho}\right\} \times (1-\tilde{\rho})\right]\left[\left(\frac{1}{r_2} - \frac{1}{r_1}\right)\right] \tag{27}$$

2.5. van der Waals energy contribution

The energy parameter ε_{ij}^* in Eq. (28) 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) [35], which is the sum of a dispersion contribution and a polar contribution: $\delta_{\mathrm{vdw}}^2 = \delta_{\mathrm{d}}^2 + \delta_{\mathrm{p}}^2$.

$$\delta_{\mathrm{vdw},i}^2 = \frac{3N_A\varepsilon_{ii}^* r_i}{V_{\mathrm{m}i}} \tag{28}$$

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

$$\varepsilon_{ii} = \Phi_{s_1}\varepsilon_1 + \Phi_{s_2}\varepsilon_2 \tag{29}$$

$$\varepsilon_{jj}^* = \frac{\varepsilon_{ii}^+}{V_{\mathrm{m}i}} \tag{30}$$

where $V_{\mathrm{m}i}$ depends on temperature. The temperature-independent parameter ε_{ii}^+ can be estimated by

$$\varepsilon_{ii}^+ = \frac{\delta_{\mathrm{vdw}}^2 V_{\mathrm{m}i}^2(25\ ^\circ\mathrm{C})}{3N_A r_i} \tag{31}$$

$$r_i = \frac{V_{\mathrm{m}i(\mathrm{vdw})}}{15.17 \times 10^{-6}\ \mathrm{m}^3\ \mathrm{mol}^{-1}} \tag{32}$$

The constant $15.17 \times 10^{-6}\ \mathrm{m}^3\ \mathrm{mol}^{-1}$ 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:

$$\varepsilon_{ij}^* = \sqrt{\varepsilon_{ii}^*\varepsilon_{jj}^*} \tag{33}$$

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

$$\frac{\delta\varepsilon_{ij}}{k} = \sum_{m=1}^{N_s}\sum_{n=1}^{N_p}\phi_m\phi_n g_{mn} \tag{34}$$

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 solid–liquid equilibria data of polymer solutions.

2.6. Theory of the melting point depression

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 [36]

$$\mu_{\mathrm{u}}^{\mathrm{c}} - \mu_{\mathrm{u}}^0 = \mu_{\mathrm{u}} - \mu_{\mathrm{u}}^0 \tag{35}$$

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

$$\mu_{\mathrm{u}}^{\mathrm{c}} - \mu_{\mathrm{u}}^0 = -\Delta H_{\mathrm{u}}(1 - T/T_{\mathrm{m}}^0) \tag{36}$$

where ΔH_{u} is the heat of fusion per segment unit, T and T_{m}^0 are melting temperature of the species in a mixture and of the pure phases, respectively (Table 1). The right-hand side of Eq. (35)

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

	T_{m}^0 (K)	ΔH (J mol^{-1})	MW (g mol^{-1})	Density (g cm^{-3})	v_{u} ($\mathrm{cm}^3\ \mathrm{mol}^{-1}$)
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}.

can be restated as follows:

$$\mu_u - \mu_u^0 = \frac{V_u}{V_1}\frac{r_1}{r_2}\left(\frac{\partial \Delta_{\text{mix}} A}{\partial N_2}\right)_{T,V,N_1} \tag{37}$$

where V_1 and V_u are the molar volumes of the salt and of the repeating unit, respectively. By substituting Eqs. (36) and (37) into Eq. (35) and replacing T by $T_{m,2}$, the equilibrium melting temperature of mixture is given by:

$$\frac{1}{T_{m,2}} - \frac{1}{T_{m,2}^0} = -\frac{1}{\Delta H_u T_{m,2}}\frac{V_u}{V_1}\frac{r_1}{r_2}\left(\frac{\partial \Delta_{\text{mix}} A}{\partial N_2}\right)_{T,V,N_1} \tag{38}$$

The subscripts 1, 2 and u refer to the salt, the polymer, and polymer segment unit, respectively. Similarly, we obtain:

$$\frac{1}{T_{m,1}} - \frac{1}{T_{m,1}^0} = -\frac{1}{\Delta H_1 T_{m,1}}\left(\frac{\partial \Delta_{\text{mix}} A}{\partial N_1}\right)_{T,V,N_2} \tag{39}$$

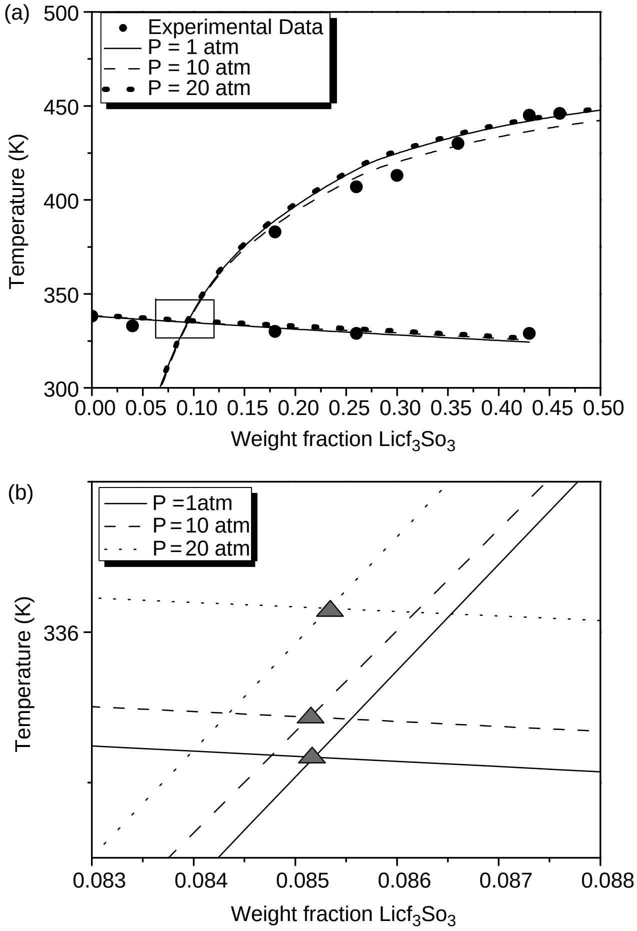

Fig. 1. (a) Phase diagram of PEO–LICF$_3$SO$_3$ system. The transition temperatures were obtains using thermo-optical analysis technique. The solid lines, dashed lines and dotted lines were calculated by the proposed model with $P=1$, 10, 20 atm, respectively. (b) Phase diagram which enlarges the eutectic points region in (a), the solid up-triangles are the eutectic points computed by the proposed model.

3. Results and discussion

The success of a group-contribution method depends primarily on the molecular-thermodynamic model. We establish the thermodynamic model to describe phase behavior of SPE/salt system with various pressures. We employ the secondary lattice concept to take into account an oriented interaction. Our proposed model has six pair-interaction parameters to characterize the group interaction (g_{mn}). Fig. 1 shows the phase behavior of PEO–LICF$_3$SO$_3$ system. Dark circles are experimental data from Kim et al. [34]. The polymer-rich liquidous curve is calculated from Eq. (38) and the salt-rich curve is calculated from Eq. (39). The densities of PEO and LICF$_3$SO$_3$ are 1.21 and 2.69 g/cm^3, respectively. Solid, dashed and dotted lines are predicted by the proposed model with $P=1$, 10, 20 atm, respectively. By substituting values of $\Delta H_1=10{,}516.48$ J/mol, $r_1=1$, $r_2=12{,}824.99$ and $T_{m,1}^0=499.29$ K into Eq. (39), the best fit to the salt-rich liquidous curves are obtained. Adjustable model parameters are represented in Table 2. Substituting the same adjustable model parameters with $\Delta H_u=8284.32$ J/mol, $V_u=36.6$ cm^3/mol, $V_1=52.66$ cm^3/mol and $T_{m,2}^0=338.15$ K into Eq. (38), the polymer-rich liquidous curve are obtained. As shown in Fig. 1(a), the theoretical prediction (solid lines) not only gives a good agreement with the experimental data, but also identifies the eutectic point at the intersection of the two liquidous curves. Fig. 1(b) shows the enlarged eutectic points region.

Fig. 2 shows the phase behavior of PEO–NaI system. In Fig. 2(a), solid, dashed and dotted lines are calculated by the proposed model with $P=1$, 10, 20 atm, respectively. 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. (39), the best fit to the salt-rich liquidous curves are obtained. Fig. 2(b) shows the enlarged eutectic points region. Adjustable model parameters also are represented in Table 2. Substituting the same adjustable model parameters with $\Delta H_u=8284.32$ J/mol, $V_u=36.6$ cm^3/mol,

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

Salts	Polymer (PEO)	
	CH$_2$	O
1 atm		
Li	−2968.80	6305.04
CF$_3$SO$_3$	−9858.56	−3150.40
Na	−5844.07	17,133.71
I	−11,803.50	9234.38
10 atm		
Li	−295.34	192.32
CF$_3$SO$_3$	−119.87	132.03
Na	−2528.16	6455.33
I	−13,041.6	−3539.20
20 atm		
Li	271.39	167.26
CF$_3$SO$_3$	170.84	405.94
Na	−9135.30	−2181.41
I	−10,532.13	17,861.29

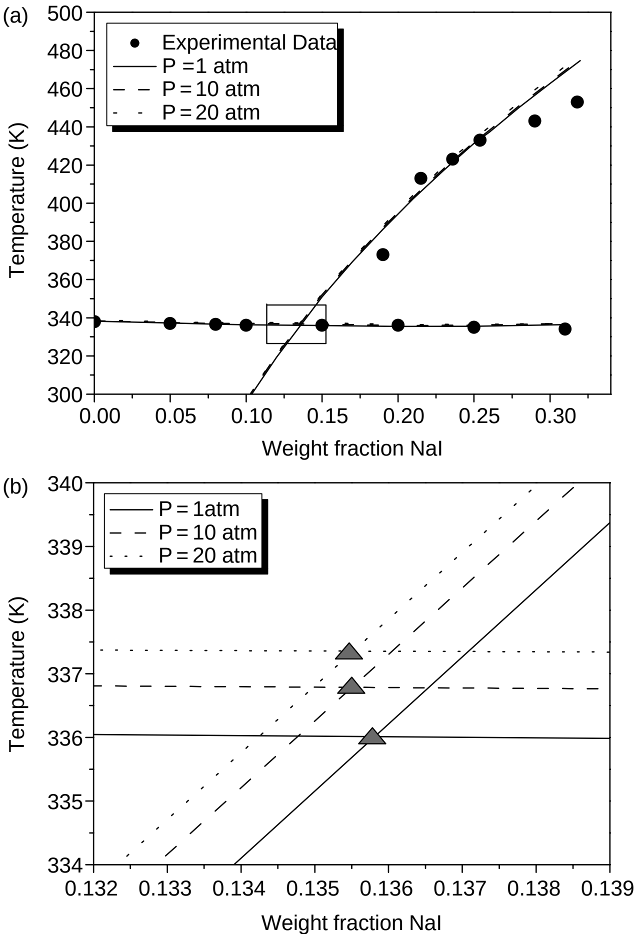

Fig. 2. (a) Phase diagram of PEO–NaI system. The transition temperatures were obtained using thermo-optical analysis technique. The solid lines, dashed lines and dotted lines were calculated by the proposed model with $P=1$, 10, 20 atm, respectively. (b) Phase diagram which enlarges the eutectic points region in (a), the solid up-triangles are the eutectic points computed by the proposed model.

$V_1 = 65.7\ \mathrm{cm}^3/\mathrm{mol}$ and $T^0_{\mathrm{m},2} = 338.15\ \mathrm{K}$ into Eq. (38), the polymer-rich liquidous curve are obtained with various pressures.

In Figs. 3(a) and 4(a), solid lines are calculated by using previously obtained interaction energy parameters with no additional adjustable model parameters. Solid, dashed and dotted lines are predicted by the proposed model with $P=1$, 10, 20 atm, respectively. Figs. 3(b) and 4(b) gives the enlarged eutectic points region. As shown in these figure, calculated values with no additional model parameter agree fairly well with experimental data for the given systems. Dark circles are experimental data for the salt rich phase and for the polymer rich phase reported by Kim and Bae [37].

In order to characterize most common SPE/salt system, more experimental data, however, 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.

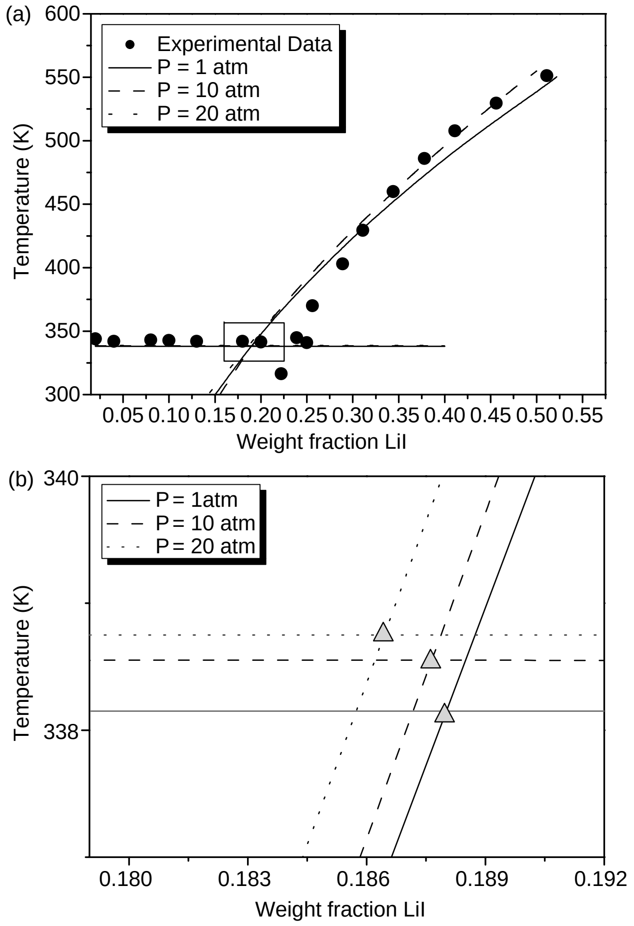

Fig. 3. (a) Phase diagram of PEO–LiI system. The transition temperatures were obtains using thermo-optical analysis technique. The solid lines, dashed lines and dotted lines were calculated by the proposed model with $P=1$, 10, 20 atm, respectively. (b) Phase diagram which enlarges the eutectic points region in (a), the solid up-triangles are the eutectic points computed by the proposed model.

4. Conclusion

We have developed the group contribution method taking into account pair-interactions between different species (salts) to describe phase behaviors of number of SPE/Li salt systems with various pressures.

To describe the pressure effect of the given systems, we extend the group-contribution method and the modified double lattice model for polymer solution to the equation of state model. 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. We determined six pair-interaction energy parameters between solid polymer electrolyte and salt groups. We then combined it with the theory of melting point depression. The 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 and taking into account the compression effect agrees fairly well with experimental data.

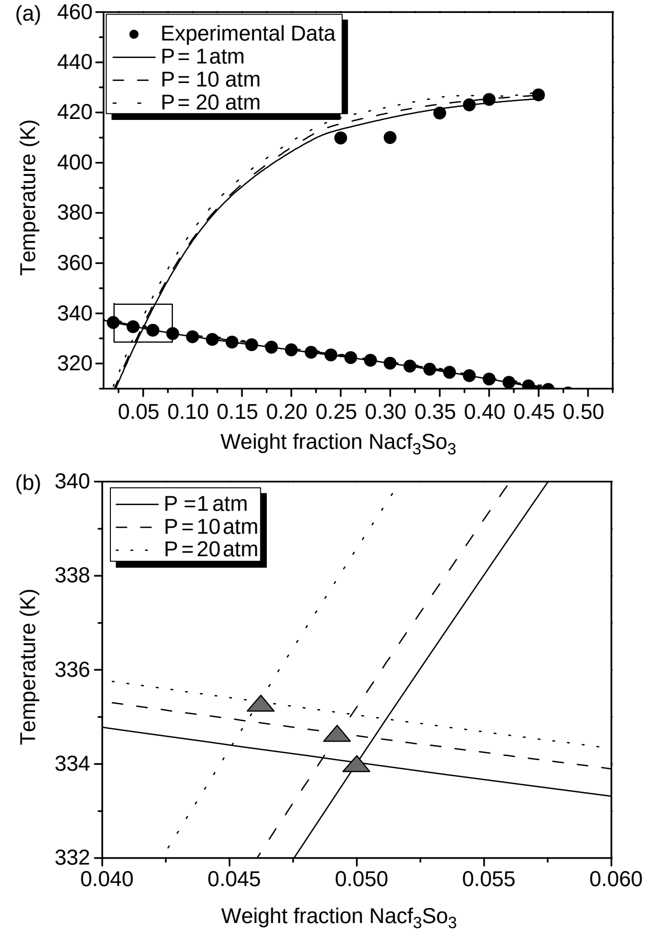

Fig. 4. (a) Phase diagram of PEO–NaCF$_3$SO$_3$ system. The transition temperatures were obtains using thermo-optical analysis technique. The solid lines, dashed lines and dotted lines were calculated by the proposed model with $P = 1$, 10, 20 atm, respectively. (b) Phase diagram which enlarges the eutectic points region in (a), the solid up-triangles are the eutectic points computed by the proposed model.

Our results obtained by the proposed model are expected to provide the appropriate operating conditions for lithium secondary battery and eutectic point.

Acknowledgements

This work is supported in part by the Ministry of Information & Communication of Korea (‘Support Project of University Information Technology Research Center’ supervised by IITA).

References

[1] Fenton BE, Parker JM, Wright PV. Polymer 1973;14:589.
[2] Armand M, Chabagno JM, Duclot M. In: Vashishta P, Mundy JN, Shenoy GK, editors. Fast ion transport in solids. Amsterdam: North-Holland; 1979. p. 131.
[3] Reibel L, Bayoudh S, Baudry P, Matstre H. Electrochim Acta 1998;43:1171.
[4] Sreekanth T, Reddy MJ, Ramalingaiah S, Subba Rao UV. J Power Sources 1999;79:105.
[5] Andreev YG, Bruce PG. Electrochim Acta 2000;45:1417.
[6] Reddy MJ, Chu PP. Electrochim Acta 2002;47:1189.
[7] Oishi T, Prausnitz JM. Ind Eng Chem Process Des Dev 1978;17:333–9.
[8] Holten-Andersen J, Fredenslund A, Rasmussen P, Carvoli G. Fluid Phase Equilibria 1986;29:357–64.
[9] Holten-Andersen J, Rasmussen P, Fredenslund A. Ind Eng Chem Res 1987;26:1382–90.
[10] Chen F, Fredenslund A, Rasmussen P. Ind Eng Chem Res 1990;29:875–82.
[11] Elbro HS, Fredenslund A, Rasmussen P. Macromolecules 1990;23:4707–14.
[12] Kontogeogis G, Fredenslund A, Tassios DP. Ind Eng Chem Res 1993;32:362–72.
[13] Bogdanic G, Fredenslund A. Ind Eng Chem Res 1994;33:1331–40.
[14] Flory PJ. Disc Faraday Soc 1970;49:7–29.
[15] Huggins ML. J Phys Chem 1942;46:151–8.
[16] Guggenheim EA. Mixtures. Oxford: Clarendon Press; 1952.
[17] Orifino TA, Flory PJ. J Chem Phys 1957;26:1067–76.
[18] Koningsveld R, Kleintjens LA, Schultz AR. Macromolecules 1971;4:637–41.
[19] Bewendi MG, Freed KF. J Chem Phys 1988;88:2741–56.
[20] Dudowicz J, Freed KF. Macromolecules 1991;24:5076–91.
[21] Hu Y, Liu H, Soane DS, Prausnitz JM. Fluid Phase Equilibria 1991;67:65–86.
[22] Hu Y, Ying X, Wu DT, Prausnitz JM. Fluid Phase Equilibria 1993;83:289–300.
[23] Hu Y, Liu H, Shi Y. Fluid Phase Equilibria 1996;117:100–6.
[24] Chang BH, Bae YC. Polymer 2002;43:6627–34.
[25] Hu Y, Zhou H, Liu H, Wu DT, Prausnitz JM. Fluid Phase Equilibria 1997;134(1–2):43–54.
[26] Oh JS, Bae YC. Polymer 1998;39:1149.
[27] Flory PJ. Principles of polymer chemistry. Ithaca, NY: Cornell University Press; 1953 p. 568.
[28] Oh JS, Bae YC. Polymer 1997;39(5):1145.
[29] Freed KF. J Phys A: Math Gen 1985;18:871.
[30] Bawendi MG, Freed KF, Mohanty U. J Chem Phys 1988;87:5534.
[31] Hu Y, Lambert SM, Soane DS, Prausnitz JM. Macromolecules 1991;24:4356.
[32] Hu Y, Liu H, Soane DS, Prausnitz JM. Fluid Phase Equilibria 1991;67:65.
[33] Kleintjens LA. Fluid Phase Equilibria 1989;33:289.
[34] Kleintjens LA, Koningsveld R. Colloid Polym Sci 1980;711:258.
[35] Barton AFM. CRC handbook of solubility parameter and other cohesion parameters. 2nd ed. Boca Raton, FL: CRC Press; 1991 p. 4356.
[36] Flory PJ. Principles of polymer chemistry. Ithaca, NY: Cornell University Press; 1953.
[37] Kim JY, Bae YC. Polymer 1999;40:1979.