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Ionic conductivities of solid polymer electrolyte/salt systems in lithium battery: the pressure effect

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Abstract

A molecular thermodynamic model based on the Adam–Gibbs configurational entropy model and the modified double lattice model with the free volume effect is applied to interpret ionic conductivities of solid polymer electrolytes with various pressures. Quantitative descriptions according to the proposed model are in good agreement with experimental data for the given systems.

Our results show that an eutectic point moves toward higher T_m and lower weight fraction of salt, and the ionic conductivity significantly decreases with increasing system pressure.

Keywords: Solid polymer electrolyte; Melting point depression; Configurational entropy

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. Among them many direct applications are high-energy-density batteries, electrochromic display devices (ECD), and fuel cells [1–2].

Since the first empirical results related to the identification of a new group of electrolytes composed of polyethers and alkali metal salts were published [3–4], several characterization studies have been made [5]. However, most of those works were focused on the evaluation of ionic transport properties of polymer electrolytes and only a few investigations involved the characterization of their physicochemical properties have been made. For example, several PEO–zinc salt complexes have been characterized by thermo-optical analysis (TOA), differential scanning calorimetry (DSC), extended X-ray absorption fine structure (EXAFS), a.c. impedance measurements, transport number determinations, and Raman and IR spectroscopy [6–10].

Investigations of the manufacturing process of lithium polymer battery reveal that there is a pressure imposed on the SPE to improve the degree of contact between electrolyte and electrode. Physical properties of the compressed SPE systems would be totally different from those of the incompressed SPE systems. Therefore, it is desirable to develop a molecular thermodynamic model in the prediction of ionic conductivity for the compressed SPE system.

Gibbs et al. [11,12] developed the configurational entropy model for polymer properties, which has been discussed extensively by Goldstein [13]. Configurational entropy (or free volume) models can be expressed in the form of a Vogel–Tamman–Fulchur (VTF) equation [14–16], which is generally used for describing the dependence of conductivity on temperature. Sørensen and Jacobsen [17] developed a simple model that accounts quantitatively for the concentration dependence of the conductivity for the low purity type electrolyte. MacFarlane et al. [12,18] investigated the effect of plasticizer on the conductivity by using the Adam–Gibbs model combined with Flory's configurational entropy at the fixed temperature.

However, in previous studies of the conductivity of SPE, it is hard to find a theoretical consideration that can describe phase behavior and predict the pressure effect on the conductivity.

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In this study, based on the Adam–Gibbs configurational entropy model and the modified double lattice (MDL) model with free volume effect [19], we develop a new thermodynamic model taking into account the pressure effect on the ionic conductivities of the compressed SPE systems. In PEO/$ZnBr_2$ system, values of salt–salt and polymer–salt interaction energy parameters, which are obtained from the melting point depression data, are directly used to predict the change of ionic conductivity with various pressures.

2. Model development

In this study, to account for the pressure effect on ionic conductivities of SPE/salt systems, three theoretical aspects are taken into account. The first is the MDL model with the free-volume effect. The second is Flory's melting point depression of polymers and the third is Adam–Gibbs configurational entropy model.

2.1. Modified double lattice model

2.1.1. Primary lattice

Oh et al. [19] 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, $\tilde{\epsilon}$:

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

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

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

where ϵ_{11}, ϵ_{22} and ϵ_{12} are for the corresponding nearest-neighbor segment–segment interactions.

Universal constants

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 [19].

2.1.2. Secondary lattice

In Freed's theory [20,21], the solution of the Helmholtz energy of mixing for the Ising model is given by

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

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 oriented interaction. The expression is given by

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

where $\Delta A_{sec,ij}$ 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, $\delta\tilde{\epsilon}$ 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. [22,23] suggested. C_α is a universal constant. 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 [19].

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 $\epsilon_{ij} - \Delta A_{sec,ij}/N_{ij}$ in Eq. (2). Following the definition of $\tilde{\epsilon}$ in Eq. (3), if oriented interaction occurs in i–j segment–segment pairs, we replace $\tilde{\epsilon}$ by $\epsilon/kT + 2\,\Delta A_{sec,ij}/N_{ij}kT$ in Eq. (2). If oriented interaction occurs in i–i segment–segment pairs, $\tilde{\epsilon}$ is replaced by $\epsilon/kT - \Delta A_{sec,ii}/N_{ii}kT$.

2.2. MDL 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 [24,25]. 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.

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

For the second step [24], 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,

$$\frac{1}{r_\mathrm{a}} = \left(\frac{\phi_1}{r_1}\right) + \left(\frac{\phi_2}{r_2}\right) \quad (7)$$

$$\epsilon_{\mathrm{aa}} = \phi_1^2\epsilon_{11} + 2\phi_1\phi_2\epsilon_{12} + \phi_2^2\epsilon_{22} \quad (8)$$

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

$$\frac{\Delta A_{II}}{N_l kT} = \varphi_0 \ln \varphi_0 + \left(\frac{\varphi_\mathrm{a}}{r_\mathrm{a}}\right)\ln \varphi_\mathrm{a} + \chi^0_{\mathrm{OB}}\varphi_0\varphi_\mathrm{a} \quad (9)$$

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 $\tilde{\epsilon}_{II}$ are a new interaction parameter and a reduced energy defined by

$$\chi^0_{\mathrm{OB}} = C_\beta\left(\frac{1}{r_\mathrm{a}} - 1\right)^2 + \left(2 + \frac{1}{r_\mathrm{a}}\right)\tilde{\epsilon}_{II} - \left(\frac{1}{r_\mathrm{a}} - 1 + C_r\tilde{\epsilon}_{II}\right)\tilde{\epsilon}_{II}\varphi_\mathrm{a} + C_\gamma\tilde{\epsilon}^2_{II}\varphi^2_\mathrm{a} \quad (10)$$

$$\tilde{\epsilon}_{II} = \epsilon_{\mathrm{aa}}/kT \quad (11)$$

2.3. Equation of state

We obtain an equation of state from the Helmholtz energy of mixing for the expanded polymer solution. We defined a reduced temperature $\tilde{T}$, a reduced pressure $\tilde{P}$ and a reduced density $\tilde{\rho}$;

$$\tilde{T} = \tilde{\epsilon}^{-1}_{II} = kT/\epsilon_{\mathrm{aa}} \quad (12)$$

$$\tilde{P} = Pv^0/\epsilon_{\mathrm{aa}} \quad (13)$$

$$\tilde{\rho} = N_r v^0/V \quad (14)$$

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

$$v^0 = \sum_i \phi_i v^0_i = \phi_1 v^0_1 + \phi_2 v^0_2 \quad (15)$$

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

$$\tilde{\rho} = N_r/N_l = \varphi_\mathrm{a}, \quad 1 - \tilde{\rho} = \varphi_0 \quad (16)$$

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

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

Then, the reduced pressure becomes

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

$\tilde{A}_{r.I}$ (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.

$$\tilde{P} = \tilde{T}\left[-\ln(1-\tilde{\rho}) - \left(1 - \frac{1}{r_\mathrm{a}}\right)\tilde{\rho} - \left\{C_\beta\left(\frac{1}{r_\mathrm{a}} - 1\right)^2 + \left(2 + \frac{1}{r_\mathrm{a}}\right)\tilde{\epsilon}_{II} - \left(\frac{1}{r_\mathrm{a}} - 1 + C_r\tilde{\epsilon}_{II}\right)\tilde{\epsilon}_{II}(1-2\tilde{\rho})\right\}\tilde{\rho}^2 + C_r\tilde{\epsilon}^2_{II}(2-3\tilde{\rho})\tilde{\rho}^3\right] \quad (19)$$

2.4. The chemical potentials

Chemical potentials for the two components are calculated by

$$\mu_1 - \mu^0_1 = \left(\frac{\partial\Delta_{mix}A}{\partial N_1}\right)_{T,V,N_2} = r_1\left(\Delta f_E + \phi_2\frac{\mathrm{d}\Delta f_E}{\mathrm{d}\phi_1}\right) \quad (20)$$

$$\mu_2 - \mu^0_2 = \left(\frac{\partial\Delta_{mix}A}{\partial N_2}\right)_{T,V,N_1} = r_2\left(\Delta f_E - \phi_1\frac{\mathrm{d}\Delta f_E}{\mathrm{d}\phi_1}\right) \quad (21)$$

where

$$\Delta f_E = \Delta A_{(I+II)}/N_r \quad (22)$$

$$\frac{\mathrm{d}\Delta f_E}{\mathrm{d}\phi_1} = \frac{\partial\Delta f_E}{\partial\phi_1} + \frac{\partial\Delta f_E}{\partial\tilde{\rho}}\frac{\partial\tilde{\rho}}{\partial\phi_1} + \frac{\partial\Delta f_E}{\partial\tilde{\epsilon}_{II}}\frac{\partial\tilde{\epsilon}_{II}}{\partial\phi_1} + \frac{\partial\Delta f_E}{\partial r_\mathrm{a}} \times \frac{\partial r_\mathrm{a}}{\partial\phi_1} \quad (23)$$

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

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

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

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

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

2.5. 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 [26]

$$\mu_u^c - \mu_u^0 = \mu_u - \mu_u^0 \tag{28}$$

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:

$$\mu_u^c - \mu_u^0 = -\Delta H_u(1 - T/T_m^0) \tag{29}$$

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. The right-hand side of Eq. (28) can be restated as follows:

$$\mu_u - \mu_u^0 = \frac{V_u}{V_1}\frac{r_1}{r_2}\left(\frac{\partial \Delta_{mix}A}{\partial N_2}\right)_{T,V,N_1} \tag{30}$$

where V_1 and V_u are the molar volumes of the salt and of the repeating unit, respectively. By substituting Eqs. (29) and (30) into Eq. (28) and replacing T by $T_{m,2}$, the equilibrium melting temperature of mixture is given by

$$\frac{1}{T_{m,2}} - \frac{1}{T_{m,2}^0} = -\frac{1}{\Delta H_u T_{m,2}}\frac{V_u}{V_1}\frac{r_1}{r_2}\left(\frac{\partial \Delta_{mix}A}{\partial N_2}\right)_{T,V,N_1} \tag{31}$$

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

$$\frac{1}{T_{m,1}} - \frac{1}{T_{m,1}^0} = -\frac{1}{\Delta H_1 T_{m,1}}\left(\frac{\partial \Delta_{mix}A}{\partial N_1}\right)_{T,V,N_2} \tag{32}$$

2.6. Ionic conductivity

Adam and Gibbs [12] construct the partition function for fractions of the overall system that can or cannot undergo a configurational transition, and then evaluate the overall entropy in terms of the configurational entropy of oligomer subunit. For the probability of a mass-transporting cooperative rearrangement this yields:

$$\tilde{W} = A\exp\left[\frac{-\Delta E_P s_c^*}{kTS_c^{Total}}\right] \tag{33}$$

where A is a constant, ΔE_P is the potential energy hindering the cooperative rearrangement per monomer unit, s_c^* is a critical configurational entropy, and S_c^{Total} is the total molar configurational entropy at temperature T. To evaluate the temperature dependence of S_c^{Total}, we can write

$$S_c^{Total}(T) - S_c^{Total}(T_0) = \int_{T_0}^{T}\frac{\Delta C_p}{T}dT = \Delta C_p\ln(T/T_0) \tag{34}$$

with ΔC_p the difference in a specific heat between the equilibrium melt and the glass at $T_0[S_c^{Total}(T_0) = 0]$. From substituting Eq. (34) into Eq. (33), we obtain

$$\tilde{W} = A\exp\left[\frac{-\Delta E_P s_c^*}{kT\,\Delta C_p\ln(T/T_0)}\right] \tag{35}$$

From the assumption, $\ln(T/T_0) \approx (T - T_0)/T_0$ and

$T/T_0 \approx 1$, Eq. (35) can be written as the same form of the VTF[14–16] with $\bar{B} = \Delta E_P s_c^*/k\,\Delta C_p$.

$$\tilde{W} = \sigma(T) = A \exp\left[\frac{-\bar{B}}{T - T_0}\right] \tag{36}$$

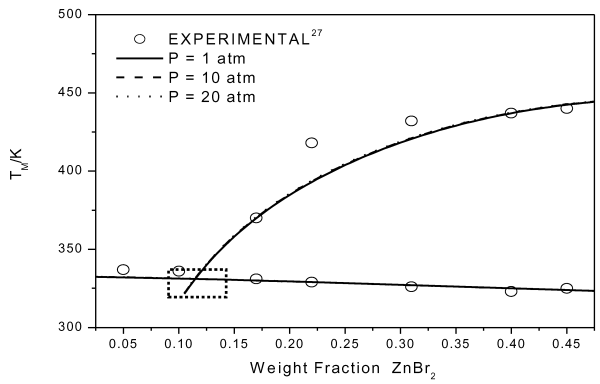
In this study, we introduce a confugurational entropy model as a function of isothermal composition. The primary exposition of theory is concerned with amorphous polymer/salt systems. To do so, we appeal to the MDL model treatment of polymer solutions [19]. The proposed configurational entropy of polymer/solvent system should be expressed as

$$S = S_{comb} + S_{vac} \tag{37}$$

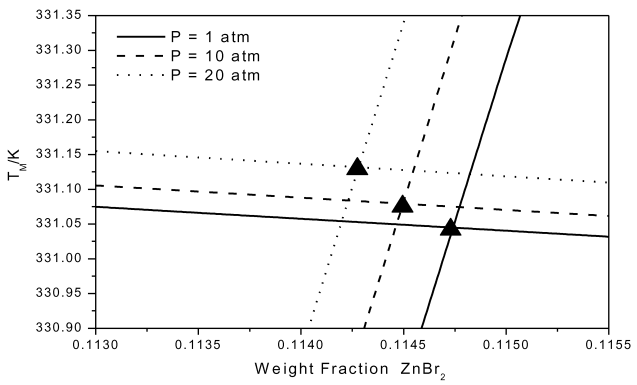
S_{comb} is a well-known combinatorial entropy of mixing in Eq. (1), and S_{vac} is an entropy of mixing holes in Eq. (9) and (16). There are

$$S_{comb} = -k\left[\frac{\phi_1}{r_1}\ln\phi_1 + \frac{\phi_2}{r_2}\ln\phi_2\right] \tag{38}$$

$$S_{vac} = -k\left[\frac{1-\tilde{\rho}}{\tilde{\rho}}\ln(1-\tilde{\rho}) + \frac{\ln\tilde{\rho}}{r}\right] \tag{39}$$



(a)



(b)

Fig. 1. (a) Phase diagram of PEO/$ZnBr_2$ system. The transition temperatures are obtained using TOA technique (○). The solid lines are calculated from the proposed model. (b) Enlarged the eutectic point region in Fig. 2(a), solid up-triangles are eutectic points computed by the proposed model with various pressure.

The mixing entropy does not take into account the difference between the salt cation and anion. In a SPE system, we consider a drop of chain flexibility with an increase of salt concentrations (i.e. the configurational entropy loss). Hence, the entropy introduced to correct a drop of chain flexibility is

$$S_{flex} = kf(\phi_1)\ln\frac{z-1}{e} \tag{40}$$

$$f(\phi_1) = \lambda_s\phi_1 \tag{41}$$

where λ_s is a degree of specific interaction between the salt ion and the base group of polymer, which is inversely proportional to temperature. $\lambda_s\phi_1$ is associated with the length of coordinated chain. The entropy, $k\ln[(z-1)/e]$, arises from the fact that the segment location relative to that of the immediate predecessor is not predetermined in the lattice. The total configurational entropy S_c^{Total} of the amorphous polymer/salt system is obtained by combining Eqs. (38)–(40).

$$S_c^{Total}/k = -\frac{\phi_1}{r_1}\ln\phi_1 - \frac{\phi_2}{r_2}\ln\phi_2 - \frac{1-\tilde{\rho}}{\tilde{\rho}}\ln(1-\tilde{\rho}) - \frac{\ln\tilde{\rho}}{r} + \lambda_s\phi_1\ln\frac{z-1}{e} \tag{42}$$

By substituting Eq. (42) and $s_c^* = k\ln 2$ [12,28] into Eq. (33), we obtain a configurational entropy model as a function of isothermal composition.

$$\tilde{W} = \sigma(\phi) = A\exp\left[\frac{-B'}{S_c^{Total}/k}\right] \tag{43}$$

where B' is defined

$$B' = \frac{\Delta E_P \ln 2}{kT\,\Delta C_p} \tag{44}$$

From Eqs. (42)–(44), we can describe the dependence of conductivity on salt composition and the chain length and calculate qualitatively the change of ionic conductivity with various pressure for the given systems.

3. Results and discussion

Fig. 1 shows the phase behavior of PEO/$ZnBr_2$ system.

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

	T_m^0 (K)	ΔH (J/mol)	MW (kg/mol)	Density (kg/m^3)	V ($\times 10^6$) (m^3/mol)
PEO	338	8284.32[a]	900[b] or 5000[c]	1210	36.60
$ZnBr_2$	667	10466.82	0.225	4200	53.60
ZnI_2	719	16677.13	0.319	4740	67.39

[a] 8284.32 J/unit.
[b] Kim et al.'s system [27].
[c] Yang and Farrington's system [6].

Open circles are experimental data from Kim et al. [27]. The polymer-rich liquidus curve and salt-rich curve are calculated from Eqs. (31) and (32). Densities of PEO and $ZnBr_2$ are taken as 1.21 and 4.2 g cm^{-3}, respectively. By substituting values of $P = 0$ atm, $\Delta H_1 = 10466.82$ J/mol, $r_1 = 1$, $r_2 = 13870$ and $T^0_{m,1} = 667.15$ K into Eq. (32), the best fit to the salt-rich liquidus curve (solid line in Fig. 1) is obtained. Adjustable model parameters are $\epsilon_{11}/k = 975.31$ K, $\epsilon_{12}/k = 918.54$ K, and $\delta\epsilon_{12}/k = 4844.06$ K. In this study, we obtained them from melting point temperature data of the given system (Table 1). Substituting the same adjustable model parameters with $\Delta H_u = 8284.32$ J/mol, $V_u = 36.6$ cm^3/mol, $V_1 = 53.6$ cm^3/mol and $T^0_{m,2} = 338.15$ K into Eq. (31) gives the solid line on the left-hand side of Fig. 1(a). As shown in Fig. 1(a), for $P = 0$ atm, the theoretical prediction (solid lines) not only gives an good agreement with the experimental data but also identifies the eutectic point at the intersection of two liquidus curves. Fig. 1(b) is the phase diagram enlarged the eutectic point region. Dashed ($P = 10$ atm) and dotted ($P = 20$ atm) lines in polymer-rich liquidus curve absolutely show that T_m increases with pressure. As shown in this figure, we expect that as the pressure increases, the eutectic point moves toward higher T_m and lower weight fraction of salt.

Figs. 2 and 3 represent conductivity data dependent on pressure at $T = 333$ *and* 353 K for PEO/$ZnBr_2$ systems, respectively. Open circles are experimental data from Kim et al. [28] Solid, dashed and dotted lines are calculated by the proposed model with $P = 0, 10, 20$ atm, respectively. By substituting values of $\epsilon_{11}/k = 975.31$ K, $\epsilon_{12}/k = 918.54$ K, and $\delta\epsilon_{12}/k = 4844.06$ K, and $z = 6$ into Eqs. (42)–(44), the best fit to conductivity data (the solid lines in Figs. 2 and 3) are obtained. Dashed ($P = 10$ atm) and dotted ($P = 20$ atm) lines in Figs. 2 and 3 show that the ionic conductivity decreases with increasing the pressure. Adjustable model parameters (A, B and λ_s) are listed in Table 2. The pre-

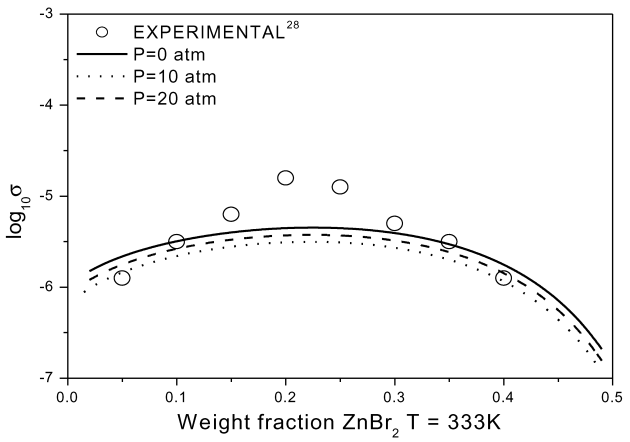


Fig. 2. The composition dependence of the conductivity at various pressures for the PEO/$ZnBr_2$ system. The conductivity was obtained using an a.c. impedance analysis (○) at $T = 333$ K. The solid, dashed and dotted lines are calculated by the proposed model with $P = 0$, 10, 20 atm, respectively.

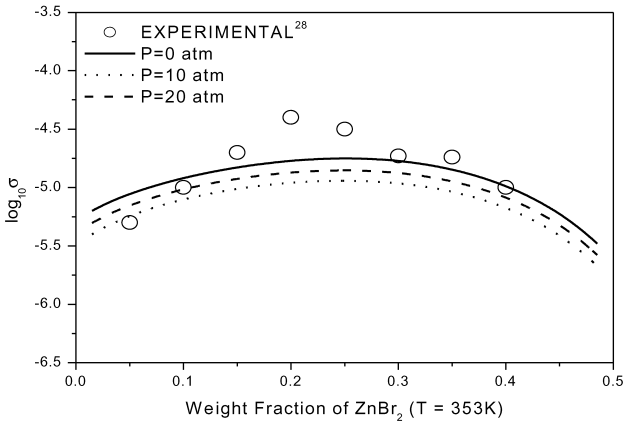


Fig. 3. The composition dependence of the conductivity at various pressures for the PEO/$ZnBr_2$ system. The conductivity was obtained using an a.c. impedance analysis (○) at $T = 353$ K. The solid, dashed and dotted lines are calculated by the proposed model with $P = 0$, 10, 20 atm, respectively.

exponential factor A is related to charge carriers such as Zn^{+2}, $ZnBr^{+1}$, $ZnBr_3^{-1}$, Br^{-1} and other ion clusters in the system, and decreases with the number of charge carriers. B' is related to the activation energy required to rearrange a small side-chain segment at a given salt concentration. Especially, at higher temperature, it is well known that strong ion associations occur and the entropy loss of salt ions follows. However, the entropy from the segmental movements of polymers offset the entropy loss from associations of salt ions. Consequently, we expect that the value of B' decreases with increasing temperature. Physically, B' is related to the potential energy hindering the cooperative rearrangement of the polymer/salt system. λ_s is the degree of specific interactions for the system. As the system temperature increases, values of the three parameters A, B' and λ_s are observed to decrease for the model systems as listed in Table 2.

Figs. 4 and 5 represent conductivity data with various pressures at $T = 333$ and 373 K for the PEO/ZnI_2 system, respectively. Open circles are experimental data from Yang

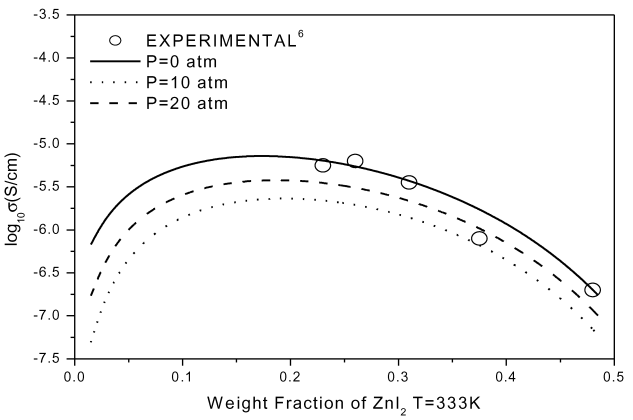


Fig. 4. The composition dependence of the conductivity at various pressures for the PEO/ZnI_2 system. The conductivity was obtained using an a.c. impedance analysis (○) at $T = 333$ K. The solid, dashed and dotted lines are calculated by the proposed model with $P = 0$, 10, 20 atm, respectively.

Table 2
Adjustable model parameters of given systems for the configurational entropy model

Polymer (MW_2)	Salt	T (K)	A	B'	λ_s	ϵ_{11}/k (K)	ϵ_{12}/k (K)	$\delta\epsilon_{12}$/k (K)
PEO (900)	$ZnBr_2$	333	0.85×10^{-3}	2.502	−2.651			
PEO (900)	$ZnBr_2$	353	0.72×10^{-3}	2.432	−2.351			
PEO (5000)	ZnI_2	333	0.58×10^{-3}	3.087	−0.561	355.42	186.79	301.78
PEO (5000)	ZnI_2	373	0.52×10^{-3}	2.799	−0.069	355.42	186.79	301.78

and Farrington [6]. Solid, dashed and dotted lines are calculated by the proposed model with $P = 0$, 10, 20 atm, respectively. As shown in Figs. 4 and 5, for $P = 0$ atm, the theoredical prediction (solid lines) gives a good agreement with experimental data. Dashed ($P = 10$ atm) and dotted ($P = 20$ atm) lines in Figs. 4 and 5 definitely show that ionic conductivity decreases with pressure. Adjustable model parameters are listed in Table 2. When the temperature was raised from 333 to 373 K, values of A, B' and $-\lambda_s$ decrease without losing physical meaning of each parameter.

4. Conclusion

In this study, we develop a thermodynamic model taking into account the pressure effect on the ionic conductivities of the compressed SPE systems. The proposed model based on the theory of melting point depression, the Adam–Gibbs configurational entropy model and MDL model with free volume effect is able to describe the compression dependence of the conductivity for the polymer/salt systems and agree fairly well with experimental data.

Our results show that an eutectic point moves toward higher T_m and lower weight fraction of salt and the ionic conductivity significantly decreases with increasing the pressure.

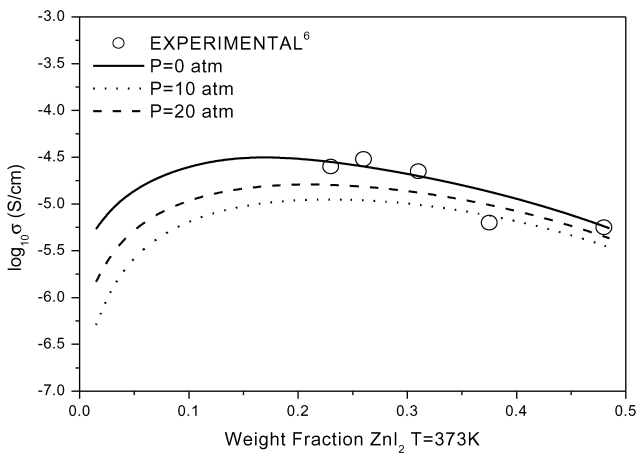


Fig. 5. The composition dependence of the conductivity at various pressures for the PEO/ZnI_2 system. The conductivity was obtained using an a.c. impedance analysis (○) at $T = 373$ K. The solid, dashed and dotted lines are calculated by the proposed model with $P = 0$, 10, 20 atm, respectively.

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