Configurational Entropy Effect for Conductivities of Solid Polymer Electrolytes

JUNG YONG KIM, YOUNG CHAN BAE

Department of Industrial Chemistry and Molecular Thermodynamics Laboratory, Hanyang University, Seoul 133-791 Korea

ABSTRACT: Poly(itaconic acid) esters with oligo(ethylene oxide) side chains can form amorphous solid solutions with $LiClO_4$ and $NaClO_4$. Many research groups have examined AC ionic conductivities of these polymer/salt mixtures as a function of side-chain length and salt concentration. We propose a model to interpret these experimental data based on a configurational entropy consisting of three kinds of entropy such as a mixing of polymer and salt ions, a disorientation of polymers, and a drop of chain flexibility (or increase of T_g) with salt concentrations. Quantitative description according to the proposed model is presented. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1891–1897, 1999

Key words: solid polymer electrolyte; configurational entropy; composition dependence; conductivity

INTRODUCTION

Since Fenton et al.[1] and Armand et al.[2] showed that solid polymer electrolyte (SPE) has a significant ionic conductivity and can be used in all solid-state electrochemical batteries, several procedures for preparation of highly conducting ($\sigma \geq 10^{-3}$ Scm^{-1}) SPE films are reported elsewhere.[3–12] The most significant theoretical constructs have been based on continuum quasithermodynamic theories, notably the free volume[13] and the configurational entropy models.[14,15] More microscopic theories are introduced, such as percolation models.[16,17] Based on these two theoretical approaches (quasithermodynamic and microscopic), SPE conductivity results can be interpreted. In this study, we limit our discussion to a quasithermodynamic approach.

The free-volume theory provides a useful method of describing transport phenomena in polymer/salt and polymer/solvent systems.[13,18–21] Doolittle[18] found empirically the relationship between the viscosity of hydrocarbon liquids and the free volume. Cohen and Turnbull[13] derived a theory about the molecular transport regulated by the free volume. Their basic assumption is that diffusion is not activated (i.e., ignore energy effect), but rather occurs as a result of the redistribution of the free volume within the liquid. Then, numerous investigators have modified the free-volume models.[19–21] For example, Miyamoto and Shibayama[19] considered jump energy and dissociation energy as well as free volume. Duda and Vrentas[20,21] extensively studied the free-volume theory. They considered the combined effects of energy and free volume.

Gibbs et al.[14,15] developed the configurational entropy model for polymer properties, which has been discussed clearly by Goldstein.[22] Configurational entropy (or free volume) models can be expressed in the form of a Vogel–Tamman–Fulchur (VTF) equation,[23–25] which is generally used

for describing the dependence of conductivity on temperature. Angell and Bressel[26] rationalized the composition dependence of transport properties on the basis of the VTF equation. However, as is true of the free-volume model, the configurational entropy model attempts to discuss the properties not of the polymer/salt complex but of the polymer itself.[17]

In this study, based on both the Adam–Gibbs configurational entropy model[15] and the Flory's configurational entropy[27] in a lattice treatment, we propose a new configurational entropy model and compare our model with experimental data reported by Cowie et al.[28] The model systems are Poly(itaconic acid) esters with three or seven oligo(ethylene oxide) side chains [polymer code: PDMEO(3)I, PDMEO(7)I, respectively]. The salts used are $NaClO_4$ and $LiClO_4$. The proposed model takes into account the properties of a polymer/salt complex from short-range specific interactions between the salt ion and the base group (oxygen) in the polymer. The proposed configurational entorpy model consists of three contributions: a mixing of the polymer and salt ion (or salt), and the disorientation of polymer due to a number of segments in polymer molecules, and a drop of chain flexibility with increase of salt concentrations. We quantitatively present conductivities of solid polymer electrolytes dependent on the salt concentration and the chain length for amorphous polymer/salt systems.

MODEL DEVELOPMENT

Continuum quasithermodynamic theories such as the free volume and the configurational entropy models have been considered for the interpretation of the conductivity behavior of solid polymer electrolytes as a function of stoichiometry and temperature.

THE FREE VOLUME MODELS

Doolittle's empirical relation between the fluidity of simple hydrocarbons and their free volume (v_f) is as follows:[18]

$$\phi = A \, \exp[-bv_0/v_f] \tag{1}$$

where A and b are constants and v_0 is the van der Waals volume of the molecule.

As with the same form of Doolittle's eq. (1), Cohen and Turnbull[13] developed a relation between the diffusion constant D in a liquid of hard spheres and the free volume. This derivation is based on the concept that the statistical redistribution of the free volume occasionally opens up voids large enough for a diffusive displacement. The relation is:

$$D = A \, \exp[-\gamma v^*/v_f] \tag{2}$$

where $A \, (=ga^*u)$ is a proportionality factor that is related to a geometric factor (g), the molecular diameter (a^*), and the gas kinetic velocity (u). γ is a numerical factor between 0.5 and 1.0 that is introduced to correct for the overlap of the free volume. v^* is the minimum required volume of the void. To test the applicability of eq. (2) to real liquids, Cohen and Turnbull assume that the free volume is equivalent to the total thermal expansion at constant pressure. Then

$$v_f = v_0\left\{ \exp\left[\int_{T_0}^{T} \alpha \, dT \right] - 1 \right\} = \alpha \bar{v}_m (T - T_0) \tag{3}$$

where α is the thermal expansion coefficient, $\bar{v}_m$ is the mean value of the molecular volume (v_0), T is temperature, and T_0 is the temperature at which the free volume disappears. Substituting eq. (3) into eq. (2) gives

$$D = ga^*u \, \exp\left[\frac{-\gamma v^*}{\bar{v}_m \alpha (T - T_0)} \right] \tag{4}$$

From the Nernst-Einstein relationship $\sigma = (nq^2/k_BT)D$ between conductivity (σ) and diffusivity (D), where n is the carrier concentration, q is the carrier charge, and k_B is the Boltzmann constant, eq. (4) results in the VTF form:[17,23–25]

$$\sigma(T) = A \, \exp\left[\frac{-B}{T - T_0} \right] \tag{5}$$

where A and B are constants.

THE CONFIGURATIONAL ENTROPY MODELS

Adam and Gibbs[15] construct the partition function for the 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:

$$\bar{W} = A \ \exp\left[\frac{-\Delta\mu s_c^*}{k_B T S_c^{\text{Total}}}\right] \qquad (6)$$

where A is constant, $\Delta\mu$ 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

$$S_C^{\text{Total}}(T) - S_C^{\text{Total}}(T_0) = \int_{T_0}^{T} \frac{\Delta C_p}{T} \, dT = \Delta C_p \ln(T/T_0) \tag{7}$$

with ΔC_p the difference in a specific heat between the equilibrium melt and the glass at $T_0 [S_c^{\text{Total}}(T_0) = 0]$. From substituting eq. (7) into eq. (6), we obtain

$$\bar{W} = A \ \exp\left[\frac{-\Delta\mu s_c^*}{k_B T \Delta C_p \ln(T/T_0)}\right] \qquad (8)$$

From the assumption, $\ln(T/T_0) \approx (T - T_0)/T_0$ and $T/T_0 \approx 1$, eq. (8) can be written as the same form of the VTF eq. (5) with $\bar{B} = \Delta\mu s_c^*/k_B\Delta C_p$.

$$\bar{W} = \sigma(T) = A \ \exp\left[\frac{-\bar{B}}{T - T_0}\right] \qquad (9)$$

In this study, we develop a new configurational entropy model as a function of isothermal composition. The primary exposition of theory is concerned with amorphous polymer/salt systems. Then, we extend our model to semicrystalline polymer/salt systems. To do so, we appeal to Flory's lattice treatment of polymer solutions.[27] At the outset, the molar entropy corresponding to a number of different arrangements of the polymer and the salt ion in mixing will be

$$S_1 = -k\left[\frac{\phi_1}{r_1} \ln \ \phi_1 + \frac{\phi_2}{r_2} \ln \ \phi_2\right] \qquad (10)$$

where ϕ_1, ϕ_2, r_1, and r_2 are the volume fractions and relative molar volumes of components 1 and 2, respectively, r_2 is defined by

$$r_2 = \frac{v_2 \text{MW}_2}{v_1 \text{MW}_1} \qquad (11)$$

where v_1, v_2, MW_1, and MW_2 are specific volumes of salt and polymer, and molecular weights of salt and polymer, respectively; $r_1 = 1$ for the salt ion. The mixing entropy does not take into account the difference between the salt cation and the salt anion.

The disorientation of polymer contributes to the entropy amounting to

$$S_2 = k\left[\frac{\phi_2}{r_2} (r_2 - 1)\ln \frac{z-1}{e}\right] \qquad (12)$$

where z is the lattice coordination number from 6 to 12, we take it as 6 in this study. Flory proposed that the configurational entropy of amorphous polymer/solvent system (or amorphous polymer/salt system) should be expressed as $S_1 + S_2$. However, in a solid polymer electrolyte system we should consider a drop of chain flexibility (or increase of T_g) with an increase of salt concentrations (i.e., the configurational entropy loss). Hence, the entropy introduced to correct for a drop of chain flexibility will be

$$S_3 = k_B f(\phi_1)\ln \frac{z-1}{e} \qquad (13)$$

$$f(\phi_1) = \lambda_s \phi_1 \qquad (14)$$

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 $k_B \ln[(z-1)/e]$ arises from the fact that the segment location relative to that of the immediate predecessor is not predetermined in the lattice.

The total molar configurational entropy S_c^{Total} of the amorphous polymer/salt system is obtained by combining eqs. (10), (12), and (13).

$$S_c^{\text{Total}}/k_B = -\frac{\phi_1}{r_1} \ln \ \phi_1 - \frac{\phi_2}{r_2} \ln \ \phi_2$$
$$+ \frac{\phi_2}{r_2}(r_2 - 1)\ln \frac{z-1}{e} + \lambda_s \phi_1 \ln \frac{z-1}{e} \qquad (15)$$

If we consider the semicrystalline polymer/salt system, we should take into account the deduction of $S_4 = k_B f(\phi_c) \ln(z - 1/e)$, where ϕ_c is the volume fraction of the crystalline unit in the polymer.

By substituting eq. (15), and $s_c^* = k_B \ln 2$ into eq. (6), we obtain a new configurational entropy model as a function of isothermal composition.

$$\bar{W} = \sigma(\phi) = A \exp\left[\frac{-B'}{S_c^{\text{Total}}/k_B}\right] \qquad (16)$$

where constant B' is defined by

$$B' = \frac{\Delta\mu \ln 2}{k_B T} \qquad (17)$$

If we do not consider the S_3 contribution to the total configurational entropy (i.e., consider only Flory's configurational entropy), eq. (6) is reduced to

$$\bar{W} = \sigma(\phi) = A \exp\left(\frac{B'}{(S_1 + S_2)/k_B}\right) \qquad (18)$$

From eqs. (15)–(17), we can describe the dependence of conductivity on salt composition and the chain length and predict the maximum of the conductivity for amorphous polymer/salt systems.

RESULTS AND DISCUSSION

Figure 1 shows a configurational entropy as a function of salt concentration at $T = 403$ K and $\lambda_s = -1.06$ for the PDMEO(7)I/NaClO$_4$ system. The properties of the chosen model systems are listed in Table I. Mixing entropy [S_1: dotted line calculated from eq. (10)] shows a maximum at the volume fraction of salt ≈ 0.4. Disorientation of polymer [S_2: dashed line calculated from eq. (12)]
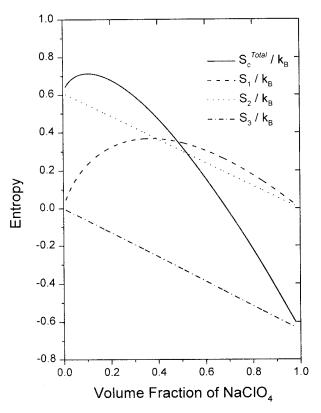

Figure 1 The configurational entropy as a function of salt concentrations at $T = 403$ K and $\lambda_s = -1.06$ for the PDMEO(7)I/NaClO$_4$ system. Solid line (S_c^{Total}) is a total molar entropy. The dotted line (S_1) is a mixing entropy. The dashed line (S_2) is a disorientation of the polymer. The dot-dashed line (S_3) is a drop of chain flexibility with raising salt concentration.

decreases monotonically with NaClO$_4$ composition. By adding more salt, a drop of chain flexibility [S_3: dot-dashed line calculated from eqs. (13) and (14)] increases. Total molar configurational entropy [S_c^{Total}: solid line calculated from eq. (15)] has a maximum of entropy at the volume fraction of salt ≈ 0.1, and approaches zero when the volume fraction of salt reaches 0.68, where conductivity also is approximately zero.

Table I   List of Molecular Weight, Density, Molar Volume, Degree of Polymerization, and Glass Transition Temperatures for a Model System[28]

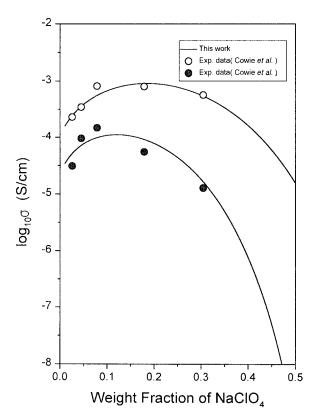| System	MW g/mol	Density g/cm^3	Molar Volume cm^3/mol	DP_n	T_g K
PDMEO(3)I	44,000	1.1	40,000	104	218
PDMEO(7)I	37,000	1.1	33,636	47	213
NaClO$_4$	122.44	2.50	48.99	—	—
LiClO$_4$	106.39	2.42	43.96	—	—

Figure 2 The conductivity dependence on salt concentrations at $T = 353$ and 403 K for the PDMEO(3)I/NaClO$_4$ system. Open circle (at 403 K) and dark circle (at 353 K) are measured by an AC conductivity meter (1.59 kHz).[28] Solid lines are calculated by eqs.(15), (16), and (17).

Figure 2 shows the conductivity dependence on salt concentrations at $T = 353$ and 403 K for the PDMEO(3)I/NaClO$_4$ system. The open circle (at 403 K) and dark circle (at 353 K) are measured by an AC conductivity meter (1.59 Hz).[28] Solid lines are calculated from the proposed model. The density of PDMEO(3)I is 1.1 gcm^{-3}, which is calculated by the group contribution method.[29] The density of NaClO$_4$ is 2.499 gcm^{-3}. By substituting

values of 44,000 (MW$_2$), 122.44 (MW$_1$), $r_1 = 1$, $r_2 = 688.99$, and $z = 6$ into eqs. (15)–(17), the best fit to the curvature of the conductivity plots (the solid line in Fig. 2) was obtained. Adjustable model parameters (A, B', and λ) are listed in Table II. The preexponential factor A is regarded as being inversely proportional to charge carriers in the system and decreases as the number of charge carriers increases. As the temperature of the system increases, A is observed to decrease from 7370 to 4240 for the model systems. B' decreases from 12.2 to 10.7, with raising temperatures from 353 to 403 K, which can be explained in terms of $\Delta\mu$, the activation energy required to rearrange a small side-chain segment at a given salt concentration. As the temperature increases, $\Delta\mu$ decreases as expected. The degree of specific interactions $(-\lambda_s)$ also decreases from 2.07 to 1.03 when the temperature was raised from 353 to 403 K, which explains that there is a small entropy loss with increasing salt concentrations at high temperature. When more salt is added to the system, the short-range specific interactions between the salt ions and the polymer or solvating base groups [oxygen in PDMEO(3)I] of the polymer leading to the loose complex formation, raise the T_g and make the segmental motion more difficult. Angell[30] proposed that the maximum in conductivity be caused by two competing effects. At first, there is a buildup of charge carriers as more salt is added, but this is eventually offset by the increase in T_g. Therefore, the consequential reduction in chain mobility impedes an ion movement. As the temperature increases, the chains become more mobile and the maximum point moves to a higher salt concentration. These phenomena are shown in Figure 2, and the proposed model predicts a maximum of conductivity at weight fraction of salt ≈ 0.12 (at 353 K) and 0.21(at 403 K), respectively.

Figure 3 shows the conductivity dependence on salt concentrations at $T = 403$ K for PDMEO(7)I/

Table II List of Adjustable Model Parameters of Given Systems for the Configurational Entropy Model

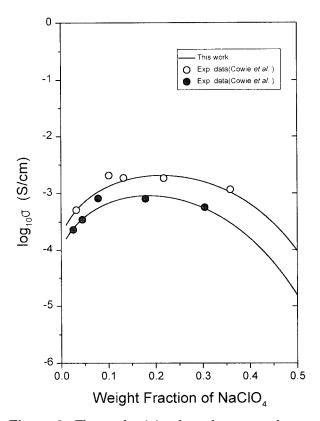| Polymer Code	Salt	T (K)	A	B'	λ_s
PDMEO(3)I	NaClO$_4$	403	0.424×10^4	0.107×10^2	-0.103×10^1
PDMEO(3)I	NaClO$_4$	353	0.737×10^4	0.122×10^2	-0.207×10^1
PDMEO(7)I	NaClO$_4$	403	0.354×10^4	0.102×10^2	-0.106×10^1
PDMEO(3)I	LiClO$_4$	353	0.104×10^6	0.138×10^2	-0.222×10^1
PDMEO(7)I	LiClO$_4$	353	0.162×10^5	0.118×10^2	-0.195×10^1

Figure 3 The conductivity dependence on salt concentrations at $T = 403$ K for the PDMEO(7)I/NaClO$_4$ system and the PDMEO(3)I/NaClO$_4$ system. Open circles for the PDMEO(7)I/NaClO$_4$ system and dark circles for the PDMEO(3)I/NaClO$_4$ system are measured by an AC conductivity meter (1.59 kHz).[28] Solid lines are calculated by eqs. (15), (16), and (17).

NaClO$_4$ and PDMEO(3)I/NaClO$_4$ systems. As shown in Figure 3, the conductivity of the PDMEO(7)I/NaClO$_4$ system is higher than that of the PDMEO(3)I/NaClO$_4$ system. This is consistent with the analysis of three adjustable model parameters: $A = 3540$, $B' = 10.2$, and $\lambda_s = -10.6$ for the PDMEO(7)I/NaClO$_4$ system, and $A = 4240$, $B' = 10.7$, and $\lambda_s = -10.3$ for the PDMEO(3)I/NaClO$_4$ system, respectively.

Figure 4 shows the conductivity dependence on salt concentrations at $T = 353$ K for the PDMEO(7)I/LiClO$_4$ and PDMEO(3)I/LiClO$_4$ systems. Open and dark circles are experimental data.[28] The solid line is calculated from the proposed model. Model parameters are listed in Table II. The conductivity of the PDMEO(3)I/LiClO$_4$ system is lower than that of the PDMEO(7)I/LiClO$_4$ system. The proposed model describes very well the conductivity behavior of the PDMEO(7)I/LiClO$_4$ and PDMEO(3)I/LiClO$_4$ systems, includ-

ing the maximum of conductivity at the weight fraction of salt ≈ 0.14 and 0.1, respectively.

In this study, we tried to explain the conductivity of polymer/salt system by using the configurational entropy distribution. The proposed model gives a good agreement with experimental data.

CONCLUSIONS

A new configurational entropy model composed of S_1 (the mixing of polymer and salt ion), S_2 (the disorientation of polymer), and S_3 (a drop of chain flexibility with increasing salt concentrations) describes very well the amorphous polymer/salt systems including the maximum conductivity. Model parameters, A (inversely proportional to charge carriers), B' (activation energy), and $-\lambda_s$ (degree of specific interaction), decrease with increasing
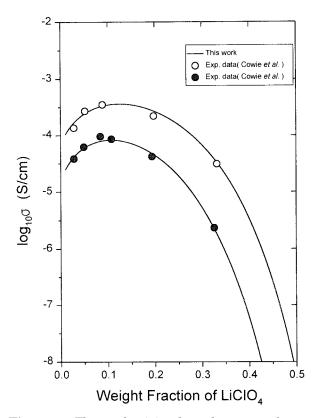

Figure 4 The conductivity dependence on salt concentrations at $T = 353$ K for the PDMEO(7)I/LiClO$_4$ system and the PDMEO(3)I/LiClO$_4$ system. Open circles for the PDMEO(7)I/NaClO$_4$ system and dark circles for the PDMEO(3)I/NaClO$_4$ system are measured by an AC conductivity meter (1.59 kHz).[28] Solid lines are calculated by eqs. (15), (16), and (17).

temperature. These three adjustable model parameters are sufficient for elucidating the conductivity behavior of chosen model systems without losing the physical meaning of the model parameters. Our proposed model has some theoretical bases. Its advantage follows its simplicity: a simple algebraic form with three model parameters appears to be suitable for representing the conductivity of polymer/salt system.

REFERENCES

1. Fenton, B. E.; Parker, J. M.; Write, P. V. Polymer 1973, 14, 589.
2. Armand, M.; Chabagno, J. M.; Duclot, M. In Fast Ion Transport in Solids; Vashishta, P.; Mundy, J. N.; Shenoy, G. K., Eds.; North-Holland: Amsterdam, 1979, p. 131.
3. Plocharski, J.; Wieczorek, W. Solid State Ionics 1988, 28, 979.
4. Kaplan, M. L.; Reitman, E. A.; Cava, R. J. Polymer 1989, 30, 504.
5. Abraham, K. M.; Alamgir, M. J Electrochem Soc 1990, 137, 1657.
6. Przyluski, J.; Such, K.; Wycislik, H.; Wieczorek, W.; Florianczyk, Z. Synthet Met 1990, 35, 241.
7. Hug, R.; Farrington, G. C.; Koksbang, R.; Tonder, P. E. Solid State Ionics 1992, 57, 277.
8. Nagasubramanian, G.; Attia, A. I.; Halpert, G.; Peled, E. Solid State Ionics 1993, 67, 51.
9. Munichandraiah, N.; Scanlon, L. G.; Marsh, R. A.; Kumar, B.; Sircar, A. K. J Appl Electrochem 1994, 24, 1066.
10. Xue, R.; Huang, H.; Huang, X.; Chen, L. Solid State Ionics 1994, 74, 133.
11. Munichandraiah, N.; Scanlon, L. G.; Marsh, R. A.; Kumar, B.; Sircar, A. K. J Appl Electrochem 1995, 25, 875.
12. Kumar, B.; Scanlon, L. G. J Power Sources 1994, 52, 261.
13. Cohen, M. H.; Turnbull, D. J Chem Phys 1959, 31, 1164.
14. Gibbs, J. H.; Di Marzio, E. A. J Chem Phys 1958, 28, 373.
15. Adam, G.; Gibbs, J. H. J Chem Phys 1965, 43, 139.
16. Druger, S. D.; Nitzan, A.; Ratner, M. A. J Chem Phys 1983, 79, 3133.
17. Ratner, M. In Polymer Electrolytes Reviews—1; MacCallum, J. R.; Vincent, C. A., eds.; Elsevier: London, 1987.
18. Doolittle, A. K. J Appl Phys 1951, 22, 1471.
19. Miyamoto, T.; Shibayama, K. J Appl Phys 1973, 44, 5372.
20. Duda, J. L.; Vrentas, J. S.; Ju, S. T.; Liu, H. T. AIChE J 1982, 28, 297.
21. Vrentas, J. S.; Vrentas, C. M. Macromolecules 1993, 26, 1277.
22. Goldstein, M. J Phys Chem 1973, 77, 667.
23. Vogel, H. Phys Z 1921, 22, 645.
24. Tamman, G.; Hesse, W. Z Anorg Allg Chem 1926, 156, 245.
25. Fulcher, J. S. J Am Ceram Soc 1925, 8, 339.
26. Angell, C. A.; Bressel, R. D. J Phys Chem 1972, 76, 3244.
27. Flory, P. J. In Principles of Polymer Chemistry; Cornell University Press: Ithaca, NY, 1953.
28. Cowie, J. M. G.; Martin, A. C. Polymer 1991, 32, 2411.
29. Van Krevelen, D. W. In Properties of Polymer; Elsevier: New York, 1990, p. 87.
30. Angell, C. A. Solid State Ionics 1983, 9–10, 3.