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Ionic conductivities of perfluorosulfonic acid membrane by group contribution method

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ABSTRACT

A new group contribution model based on a modified double lattice (MDL) theory is developed and applied to describe the ionic conductivities of perfluorosulfonic acid (PFSA) membrane/water systems. The proposed model includes a combinatorial energy contribution that consists of the revised Flory–Huggins entropy of mixing, the van der Waals energy from dispersion, polar force and specific energy contributions. We investigated six groups used for PFSA membranes and changed the configuration of polymer, which was calculated separately. To obtain good mechanical properties of PFSA membranes, the specific polymer configuration was optimized. As a result, shorter CF_2CF_2 groups in polymer backbone chain and in the side chain lead to a higher ionic conductivity, as does a single CF_2CFCF_3O group in the side chain. Quantitative description according to the proposed model is in good agreement with experimentally observed physical property for a given system.

1. Introduction

Since PFSA membranes were introduced as a novel class of ionic conductor having physical and chemical stability, there has been a notable increase in research in polymer electrolytes resulting from the combined efforts of both electrochemists and polymer scientists. PFSA membranes in aqueous solutions have been carefully investigated, therefore, these have the immense advantage of castability, allowing the fabrication of thin and highly ion conducting but impervious structures that have found applications in fuel cell technology. The conductivity of the PFSA membrane increases dramatically on exposure to moisture because the counterions are shielded from the backbone charge by hydration, and thus the membrane behaves as a simple ionomer in an aqueous solution A qualitative approach to predicting PFSA membrane physical properties in an aqueous solution using a general thermodynamic model to be able to reliably predict the PFSA membrane/water behavior for these systems is required.

The most widely used and best known of the excess Gibbs energy group contribution models is the UNIFAC (UNIQUAC functional group activity coefficient) [1]. Oishi and Prausnitz [2] modified the UNIFAC model by providing a free volume contribution suggested by Prigogine–Flory–Patterson theory for polymer solutions to consider the compressibility and change in density upon isothermal mixing. Hu et al. [3] presented a group contribution method including revised Flory–Huggins entropy, a series expression for excess internal energy and a double lattice model to account for specific interactions. Jones et al. [4] studied equations of state based on a lattice-statistics approach and used Guggenheim's quasi-chemical approximation to describe the non-randomness in the mixture due to the energetic interactions between the molecules. Peters et al. [5] revised the group contribution equation of state (GC-EOS) used to predict the phase behavior of binary systems of ionic liquids within the homologous families of 1-alkyl-3-methylimidazolium hexafluorophosphate and tetrafluoroborate with CO_2. Passarello et al. [6] introduced a group contribution method for pure compound parameters proposed by Tamouza et al. [7], which has been extended for the calculation of vapor pressures and saturated liquid volumes of polyaromatic hydrocarbons (PAHs). Rarey et al. [8] extended the subsequent physical property methods to enable the prediction of vapor pressure data with special attention to the low-pressure region. The molecular structure of the compound and a reference point, usually the normal boiling point, are the only required inputs, and the method enables the estimation of vapor pressure at other temperatures by group contribution. Galindo et al. [9], using a GC-EOS approach, postulated that the molecules are formed from fused heteronuclear spherical segments, each of which represents a distinct chemical functional group. The different

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segments were characterized by size and attractive energy (well-depth and range) parameters, and a shape factor parameter which describes the contribution that each segment makes to the overall molecular properties. Jones et al. [10] predicted the nonlinear mechanical properties of a highly cross-linked thermosetting polymer as a function of temperature, strain, and strain rate. The model is extended from the Group-Interaction Model (GIM) that was originally developed for linear amorphous thermoplastics.

In this work, we propose a modified double lattice (MDL) model combined with the group contribution method and Debye–Hückel (DH) theory to predict the group dependence of the polymer electrolyte's ionic conductivity. We also suggest an optimized configuration and group dependencies for the ionic conductivity of the polymer/water system. It is assumed that all systems in our calculation are at equilibrium from a macroscopic viewpoint.

2. Model development

2.1. MDL model with DH theory

The total molar Gibbs energy of mixing ($\Delta G_{\text{mix}}^{\text{Total}}$) is assumed to consist of an MDL model and extended DH theory,

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

2.1.1. MDL model

2.1.1.1. Primary lattice. Oh and Bae [11] proposed expressing the Helmholtz energy of mixing in terms of the Flory–Huggins theory as

$$\frac{\Delta A}{N_r kT} = \left(\frac{\varphi_1}{r_1}\right)\ln \phi_1 + \left(\frac{\varphi_2}{r_2}\right)\ln \varphi_2 + \chi_{\text{OB}}\varphi_1\varphi_2 \tag{2}$$

where r_i is the number of segments per molecule I, and φ_i is the volume fraction of component i. The subscripts 1 and 2 refer to the solvent and polymer, respectively. The χ_{OB} parameter of Eq. (2), a new interaction parameter, is a function of r_i and $\tilde{\varepsilon}$ and is given by:

$$\begin{aligned}\chi_{\text{OB}} = {} & C_\beta\left(\frac{1}{r_2}-\frac{1}{r_1}\right)^2 + \left(2+\frac{1}{r_2}\right)\tilde{\varepsilon} - \left(\frac{1}{r_2}-\frac{1}{r_1}+C_\gamma\tilde{\varepsilon}\right)\tilde{\varepsilon}\varphi_2 \\ & + C_\gamma\tilde{\varepsilon}^2\varphi_2^2\end{aligned} \tag{3}$$

where C_β and C_γ are universal constants. These constants were determined by using Madden et al.'s Monte-Carlo simulation data [12]. The calculated universal constants values are $C_\beta = 0.1415$ and $C_\gamma = 1.7986$.

$\tilde{\varepsilon}$ is a reduced interaction energy parameter,

$$\tilde{\varepsilon} = \frac{\varepsilon}{kT} = \frac{\varepsilon_{11}+\varepsilon_{22}-2\varepsilon_{12}}{kT} \tag{4}$$

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

2.1.1.2. Secondary lattice. To solve the mathematical approximation defect and to reduce the number of parameters, a new Helmoltz energy of mixing is defined in fractional form [11]. The expression is given by

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

where $\Delta A_{\text{sec},ij}$ is the Helmholtz energy of mixing of the secondary lattice for the *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 of permitted oriented interactions. For simplicity, we arbitrarily set η to 0.3 as suggested by Hu et al. [13]. C_α is a universal constant and can be found using Panagiotopolous et al.'s Gibbs-ensemble Monte-Carlo simulation data of the Ising lattice [14]. The best-fit value of $C_\alpha = 0.4881$ [11].

2.1.1.3. Incorporation of secondary lattice into primary lattice. To improve accuracy, we have incorporated a secondary lattice by replacing ε_{ij} with $\varepsilon_{ij} - (\Delta A_{\text{sec},ij}/N_{ij})$. If oriented interaction occurs in the *i–j* segment–segment pairs, then we replace $\tilde{\varepsilon}$ with $(\varepsilon/kT) + 2(\Delta A_{\text{sec},ij}/N_{ij}kT)$. Thus,

$$\varepsilon_{12} = \left(\varepsilon_{11}^{*}+\varepsilon_{22}^{*}-2\varepsilon_{12}^{*}\right) + \left(-\frac{\Delta A_{\text{sec},11}}{N_{11}} - \frac{\Delta A_{\text{sec},22}}{N_{22}} + \frac{2\Delta A_{\text{sec},12}}{N_{12}}\right) \tag{6}$$

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

2.1.2. Extended Debye–Hückel (DH) theory

For a binary polymer/solvent 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 [15, 16] as follows:

$$\frac{\Delta G_{\text{mix}}^{\text{DH}}}{RT} = \frac{\varphi_1}{r_1 \nu m}\left[-\frac{4}{3}AI^{3/2}\tau\left(I^{1/2}\right)\right] \tag{7}$$

and

$$\tau(x) = \frac{3}{x^3}\left[\ln(1+x) - x + \frac{x^2}{2}\right] \tag{8}$$

where φ_1 is a segment fraction of the solvent ion, r_1 is the number of segments per salt ion, $\nu = \nu_{\text{M}} + \nu_{\text{X}}$ (where ν_{M} and ν_{X} are the number of M and X ions per salt, respectively), A is the usual Debye–Hückel coefficient, and I is ionic strength. We fix the Debye–Hückel coefficient at 0.003 as an optimization factor for polymer/solvent system [24].

For a binary polymer/solvent system containing 1 kg of polymer and νm moles of solvent ions, $\varphi 1$, $\varphi 2$ and I are defined by:

$$\varphi_1 = \frac{r_1\nu m}{r_1\nu m + r_2 1000/M} = \frac{r_1 N_1}{r_1 N_1 + r_2 N_2}, \varphi_2 = 1 - \varphi_1 \tag{9}$$

$$I = \frac{1}{2}m\nu|z_{\text{M}}z_{\text{X}}| = \frac{1}{2}\left[\frac{r_2\varphi_1 1000/M}{r_1\varphi_2}\right]|z_{\text{M}}z_{\text{X}}| \tag{10}$$

where M is the molecular weight of polymer in g/mol (i.e., $M = 500{,}000$ g/mol). N_1, N_2, z_{M}, z_{X} and r_2 are the number of moles of salt ions and polymer, the valences of M and X ions, and the number of segments per polymer, respectively.

The chemical potential derived from the Debye–Hückel Gibbs energy of mixing is:

$$\frac{\Delta\mu_1^{\text{DH}}}{RT} = \frac{1}{RT}\left(\frac{\partial(r_1N_1+r_2N_2)\Delta G_{\text{mix}}^{\text{DH}}}{\partial N_1}\right) = -\frac{\nu}{1000}\left(\frac{A|z_{\text{M}}z_{\text{X}}|I^{1/2}}{1+I^{1/2}}\right) \tag{11}$$

$$\begin{aligned}\frac{\Delta\mu_2^{\text{DH}}}{RT} &= \frac{1}{RT}\left(\frac{\partial(r_1N_1+r_2N_2)\Delta G_{\text{mix}}^{\text{DH}}}{\partial N_2}\right) \\ &= \frac{M}{1000}\left(\frac{2}{3}AI^{3/2}\rho(I^{1/2})\right)\end{aligned} \tag{12}$$

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

2.1.3. van der Waals energy contribution

The energy parameter ε^*_{ij} in Eq. (4) 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) [17], which is the sum of a dispersion contribution and a polar contribution:

$$\delta^2_{\mathrm{vdw}} = \delta^2_d + \delta^2_p, \delta^2_{\mathrm{vdw},i} = \frac{3N_{\mathrm{A}}\varepsilon^*_{ii}r_i}{V_{\mathrm{mi}}} \tag{14}$$

where N_{A} is the Avogadro number and δ^2_{vdw} and V_{mi} are taken at 25 °C. For a pure component which is affected by temperature ε^*_{ii} is defined by

$$\varepsilon^*_{ii} = \frac{\varepsilon^+_{ii}}{V_{\mathrm{mi}}} \tag{15}$$

where $\{V_{\mathrm{mi}}(T)\}$ depends on the temperature. The temperature-independent parameter ε^+_{ii} can be estimated by

$$\varepsilon^+_{ii} = \frac{\delta^2_{\mathrm{vdw}}V^2_{\mathrm{mi}}(25\ ^\circ\mathrm{C})}{3N_{\mathrm{A}}r_i} \tag{16}$$

$$r_i = \frac{V_{\mathrm{mi}(vdw)}}{15.17 \times 10^{-6}\ \mathrm{m}^3\ \mathrm{mol}^{-1}} \tag{17}$$

where $15.17 \times 10^{-6}\ \mathrm{m}^3/\mathrm{mol}$ is the molar hardcore volume of a CH_2 group. The cross interaction van der Waals energy parameter, ε^*_{ij}, is estimated by the geometric mean of the corresponding pure-component parameters as

$$\varepsilon^*_{ij} = \sqrt{\varepsilon^*_{ii}\varepsilon^*_{jj}} \tag{18}$$

2.1.4. Specific energy contribution

Hilderbrand parameters are calculated using group molar volumes [18]. This method requires knowledge of the chemical structure, without the molar volume (or density), but it is applicable only at 25 °C.

$$\delta = -\left(\frac{U}{V}\right)^{1/2} = -\left(\frac{\sum\limits_z {}^zU}{\sum\limits_z {}^zV}\right)^{1/2} \tag{19}$$

Hansen and Beerbower have assumed that hydrogen-bonding cohesive energy is additive, i.e.,

$$\delta_h = \left(\sum_z -\frac{{}^zU_h}{V}\right)^{\frac{1}{2}} \tag{20}$$

In this paper, we use Hansen's hydrogen-bonding solubility parameter for obtaining the pure-component parameter $\delta\varepsilon_{ij}$, as

$$\Delta U_{\mathrm{sec},ii}(25\ ^\circ\mathrm{C}) = -\delta^2_h V_{\mathrm{mi}}(25\ ^\circ\mathrm{C}) \tag{21}$$

For the temperature dependence of $\Delta U_{\mathrm{sec},ii}$, we assume that

$$\Delta U_{\mathrm{sec},ii} = \frac{\Delta U^+_{\mathrm{sec},ii}}{V_{\mathrm{mi}}} \tag{22}$$

where $\Delta U^+_{\mathrm{sec},ii}$ is independent of temperature and

$$\Delta U_{\mathrm{sec},ii(T)} = -\frac{\delta^2_h V^2_{\mathrm{mi}}(25\ ^\circ\mathrm{C})}{V_{\mathrm{mi}}(T)} \tag{23}$$

For a pure component i, inserting the above into the thermodynamic relation $[\partial(\Delta A/T)/\partial(1/T)] = \Delta U$, we have

$$\frac{\Delta U_{\mathrm{sec},ii}}{k} = \frac{N_i r_i z C_\alpha(1-\eta)\eta\left(\frac{\delta\varepsilon_{ii}}{k}\right)}{\left[1 + C_\alpha\frac{\delta\varepsilon_{ii}}{kT}(1-\eta)\eta\right]^2} \tag{24}$$

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

$$\frac{\delta\varepsilon_{ij}}{k} = \sum_{m=1}^{N_{\mathrm{s}}}\sum_{n=1}^{N_{\mathrm{p}}}\varphi_m\varphi_n g_{mn} \tag{25}$$

where N_{s} and N_{p} are the number of groups in the solvents and polymers, respectively, and φ_m and φ_n are the volume fractions of group m in a solvent and group n in a polymer, respectively. Finally, g_{mn} are pair-interaction parameters between group m in a solvent and group n in a polymer. $\tilde{\varepsilon}$ is calculated using the group contribution method to characterize the interaction of each set of groups between polymer electrolyte and solvent.

$$\tilde{\varepsilon} = \frac{\varepsilon^*_{11} + \varepsilon^*_{22} - 2\varepsilon^*_{12}}{kT} - 2C_\alpha(1-\eta)\eta\left[\frac{\frac{\delta\varepsilon_{11}}{kT}}{1 + C_\alpha\frac{\delta\varepsilon_{11}}{kT}(1-\eta)\eta} + \frac{\frac{\delta\varepsilon_{22}}{kT}}{1 + C_\alpha\frac{\delta\varepsilon_{22}}{kT}(1-\eta)\eta} - \frac{2\frac{\delta\varepsilon_{12}}{kT}}{1 + C_\alpha\frac{\delta\varepsilon_{12}}{kT}(1-\eta)\eta}\right] \tag{26}$$

By summarizing the chemical potential of MDL with DH theory, the polymer and solvent chemical potentials are derived. The chemical potential of the solvent is

$$\begin{aligned}\frac{\Delta\mu_1}{RT} = {} & \ln(1-\varphi_2) - r_1\left(\frac{1}{r_2} - \frac{1}{r_1}\right)\varphi_2 + r1\left[C_\beta\left(\frac{1}{r_2} - \frac{1}{r_1}\right)^2\right. \\ & \left. + \left\{\left(\frac{1}{r_2} - \frac{1}{r_1}\right) + C_\gamma\tilde{\varepsilon}\right\}\tilde{\varepsilon} + \left(2 + \frac{1}{r_2}\right)\tilde{\varepsilon}\right]\varphi^2_2 \\ & -2r_1\left[\left\{\left(\frac{1}{r_2} - \frac{1}{r_1}\right) + C_\gamma\tilde{\varepsilon}\right\}\tilde{\varepsilon} + C_\gamma\tilde{\varepsilon}^2\right]\varphi^3_2 + 3r_1C_\gamma\tilde{\varepsilon}^2\varphi^4_2 \\ & + \left[-\frac{\nu}{1000}\left(\frac{A|z_{\mathrm{M}}z_{\mathrm{X}}|I^{1/2}}{1 + I^{1/2}}\right)\right]\end{aligned} \tag{27}$$

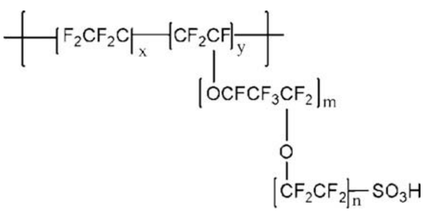

Fig. 1. Configuration of PFSA membrane. We have set an initial value of 1 for all cases except $x = 6$.

Table 1
Number of groups in Nafion as our initial set of *x*, *y*, *m* and *n*.

Number of groups						
H_2O	$(CF_2CF_2)_x$	$(CF_2CF)_y$	$(CF_2CF_3CFO)_m$	O	$(CF_2CF_2)_n$	SO_3H
1	6	1	1	1	1	1

while the chemical potential of polymer is

$$\begin{aligned}\frac{\Delta\mu_2}{RT} = {} & \ln\varphi_2 - r_1\Bigl[\Bigl(\frac{1}{r_2}-\frac{1}{r_1}\Bigr)+C_\beta\Bigl(\frac{1}{r_2}-\frac{1}{r_1}\Bigr)^2+\Bigl(2+\frac{1}{r_2}\Bigr)\tilde{\varepsilon}\Bigr] \\ & -r_2\Bigl[\Bigl(\frac{1}{r_2}-\frac{1}{r_1}\Bigr)+2\Bigl\{\Bigl(\frac{1}{r_2}-\frac{1}{r_1}\Bigr)+C_\gamma\tilde{\varepsilon}\Bigr\}\tilde{\varepsilon} \\ & +2C_\beta\Bigl(\frac{1}{r_2}-\frac{1}{r_1}\Bigr)^2+2\Bigl(2+\frac{1}{r_2}\Bigr)\tilde{\varepsilon}\Bigr]\varphi_2 r_2\Bigl[4\Bigl\{\Bigl(\frac{1}{r_2}-\frac{1}{r_1}\Bigr) \\ & +C_\gamma\tilde{\varepsilon}\Bigr\}\tilde{\varepsilon}+3C_\gamma\tilde{\varepsilon}^2\Bigr]\varphi_2^2-r_2\Bigl[2\Bigl\{\Bigl(\frac{1}{r_2}-\frac{1}{r_1}\Bigr)+C_\gamma\tilde{\varepsilon}\Bigr\}\tilde{\varepsilon} \\ & +6C_\gamma\tilde{\varepsilon}^2\Bigr]\varphi_2^3+3r_2C_\gamma\tilde{\varepsilon}^2\varphi_2^4+\Bigl[\frac{M}{1000}\Bigl(\frac{2}{3}AI^{3/2}\rho\bigl(I^{1/2}\bigr)\Bigr)\Bigr] \qquad (28)\end{aligned}$$

2.2. Ionic conductivity

Pai et al. [19] developed an ionic conductivity equation using a generalized Fick's equation for the diffusivity of a solvent in polymer and the Nernst–Einstein equation. To express the correspondence between diffusion coefficient and chemical potential, they combined those relations in the conductivity model [19,20]. Their final ionic conductivity equation is [21]

$$\sigma = \frac{F^2C_s}{RT}D^*C_s\frac{\mathrm{d}\left(\frac{\Delta\mu_s}{RT}+\lambda_0 e^{\omega C_s}\frac{\Delta\mu_u}{RT}\right)}{\mathrm{d}C_s}\sum_i z_i^2 \qquad (29)$$

A mathematical form of $\lambda_0 e^{\omega C_s}$ is used that is based on the exponentially decreasing coordinating units, where λ_0 and ω are the adjustable model parameters. The self-diffusion coefficient D^* characterizes the component mobility in the absence of any interactions in the system [20]. While C_s denotes concentration, z_i is the ion number of component *i*, *F* is the Faraday constant, *R* is the gas constant, and *T* is temperature.

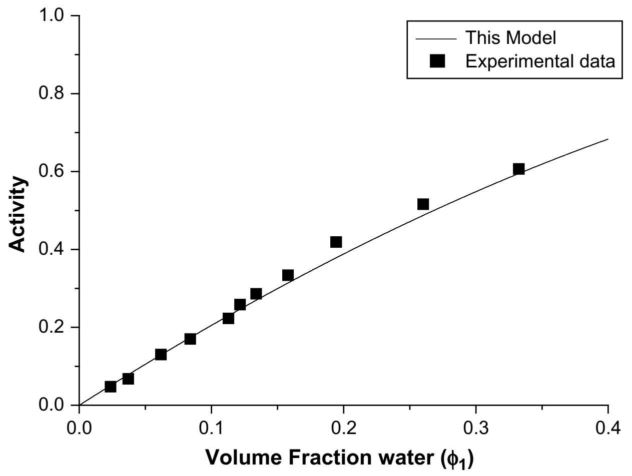

Fig. 2. Water activity of PFSA membrane (Nafion 117, EW = 1100)/solvent system at 353.15 K. The filled squares are the experimental data of Hinatsu [22] and the solid line is our calculated data.

Table 2
Group-interaction parameters: g_{mn} (K).

Solvent	Polymer					
	$(CF_2CF_2)_x$	$(CF_2CF)_y$	$(CF_2CF_3CFO)_m$	O	$(CF_2CF_2)_n$	SO_3H
H_2O	g_{11}	g_{21}	g_{31}	g_{41}	g_{51}	g_{61}
Parameters						
ε/k (K)	g_{11} (K)	g_{21} (K)	g_{31} (K)	g_{41} (K)	g_{51} (K)	g_{61} (K)
609.613	8866.67	−12534.5	4212.69	−150828	51187.8	18613.3

3. Results and discussion

We studied the group dependences for physical properties: in particular, the ionic conductivity of the PFSA membrane/water system. Fig. 1 represents a schematic of a PFSA membrane and its applicable configuration. The standard configuration of this membrane is provided in Fig. 1, where the "*x*" is set to 6 and the other values are 1. The number of groups is shown in Table 1.

We employed the secondary lattice concept to take into oriented interaction into account. On the secondary lattice, the group contribution method was used to appropriately understand the ionic conductivity, which depends on the membrane structure and group parameters. First, to determine the group parameters in Eq. (25), we calculated the water activity of a Nafion 117 (EW = 1100)/water system, which is shown in Fig. 2. Our models fit well with the experimental data of Hinatsu [22]. The group parameter values for the membrane were $g_{11} = 8866.67$ K, $g_{21} = -12534.5$ K, $g_{31} = 4212.69$ K, $g_{41} = -150828$ K, $g_{51} = 51187.8$ K, and $g_{61} = 18613.3$ K listed in Table 2. These parameters were adjusted at a temperature of 353.15 K using experimental data. The cross interaction van der Waals energy parameter, ε_{ij}^*, was estimated using the square of the pure-component van der Waals solubility parameter of Hansen (Barton) [17].

Fig. 3 shows the ionic conductivity of the PFSA membrane. Eq. (29) includes the chemical potentials of the polymer and solvent consisting of the van der Waals energy parameter (from the

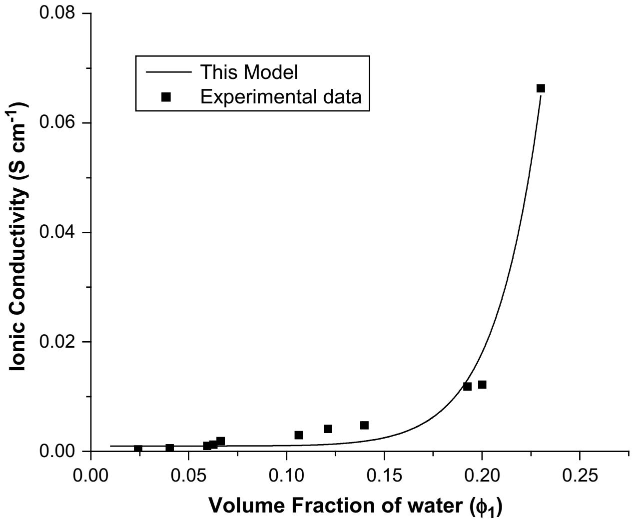

Fig. 3. Ionic conductivity of PFSA membrane (Nafion 117, EW = 1100) vs. volume fraction of solvent at 353.15 K. The filled squares are the experimental data of Anantaraman [23] and the solid line is our calculated data.

Table 3
Ionic conductivity parameters.

Ionic conductivity parameters		
D^* (cm^2/s)	λ_0 (–)	ω (cm^3/mol)
3.47×10^{-10}	3.18×10^{-6}	39.48

primary lattice equation) and group parameters (from the secondary lattice equation), which are no longer adjustable parameters. The ionic conductivity value is greatly increased at a water volume fraction range over 0.15. Our model agrees well with experimental data from Anantaraman et al. [23]. They boiled the Nafion 117 (1100 g/mol of equivalent weight) membrane in 30% nitric acid for 30 min for pretreatment and measured the impedance under differential relative humidity 0–100%. The parameters obtained for the ionic conductivity are listed in Table 3.

The temperature dependencies of the ionic conductivities are shown in Fig. 4, where we calculated dependence with respect to the volume fraction of the water at three values: 0.15, 0.2 and 0.23. Fig. 4 shows that, for temperatures less than 378 K, ionic conductivities increase with temperature. However, for temperatures higher than 378 K, ionic conductivities decrease.

The purpose of this work was to predict the physical properties for a given system with the ultimate goal of developing a group contribution method that can predict the best configuration of the membrane. Fig. 5 illustrates calculations of the conductivity with respect to different group numbers of g_{11}; the number of g_{11} groups connected to the main chain of the system reflects changes in chain length. For values of g_{11} in the range of 5–6, the ionic conductivity of the system is relatively constant. When the number increases up to 7, the ionic conductivity falls to the same level of the volume fraction of water. In particular, the shortest chain group, where $x = 5$, shows the highest value compared to other chain groups with large deviations. From a microscopic point of view, the sulfonic acid sites (side chain) can be seen as being in the hydrophilic phase, while the perfluorinated sites (main chain) can be seen as being in the hydrophobic phase. This could explain the occurrence of phase separation in the PFSA membrane/water system corresponding to a membrane equilibrated with vapor, which results in structuring of the hydrophilic phase as an inverted micelle. This is the cluster-network model first proposed by Hsu and Gierke [25]. The short chain groups of CF_2CF_2, where $x = 5$, cause the repeat unit to have low hydrophobicity, because water sorption by these short chains is more effective than water sorption by long chain groups. At the different values of ionic conductivity at a different chain length, the short main chain groups are responsible for the high ionic conductivity rather than the long main chain groups. In addition, Fig. 6, which shows how conductivity depends on the group number of g_{21}, provides the same conclusion as that of g_{11} in Fig. 5. Considering that the g_{11} and g_{21} numbers affect the main chain length of the repeat unit of the configuration, we conclude that as the main chain length becomes longer in the repeat unit, the ionic conductivity of the system definitely decreases. The influence of g_{31} on the conductivity shows another significant result wherein the dependence of the ionic conductivity of the system represents a different trend than that seen previously, as shown in Fig. 7. If the g_{31} does not exist in the repeat unit, the side chain of perfluorosulfonic acid membrane becomes short and causes the low flexibility of the side chain. From a microscopic viewpoint, the physical model of perfluorosulfonic acid membrane of Kreuer [26] can explain our group contribution model. They divided the three parts of hydrated membrane into microscopic phase separation, main chain, sulfonic site and water with hydronium ions. The g_{31} is comparable with the sulfonic site which contains the substituted

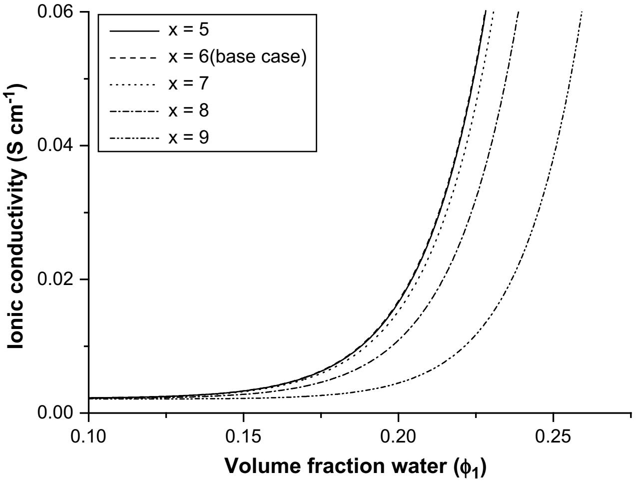

Fig. 5. Variation of ionic conductivity with CF_2CF_2 (g_{11}) group value ($T = 353.15$ K), where the value of g_{11} is taken from Fig. 1.

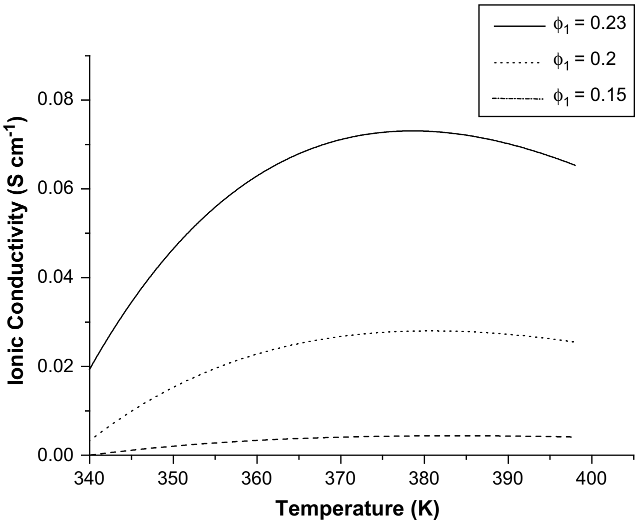

Fig. 4. Temperature dependence of ionic conductivities varies with volume fraction. We calculated the volume fraction of solvent at three points ($\varphi_1 = 0.15$, 0.2, 0.23).

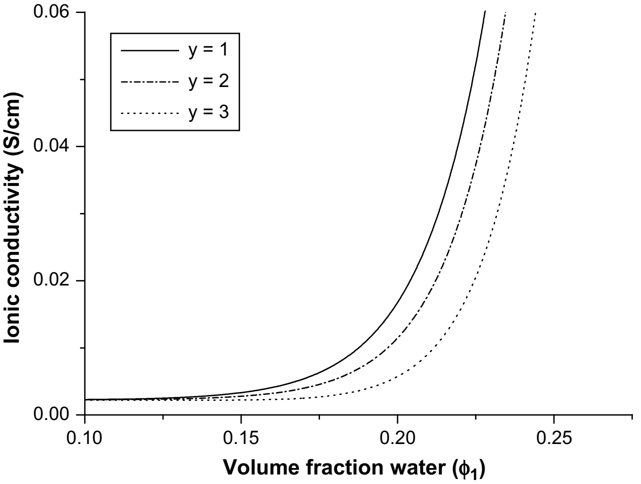

Fig. 6. Variation of ionic conductivity with CF_2CF (g_{21}) group value ($T = 353.15$ K), where the value of g_{21} is taken from Fig. 1.

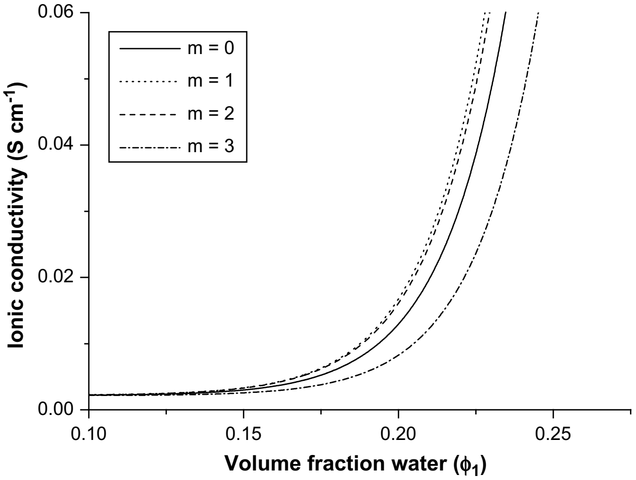

Fig. 7. Variation of ionic conductivity with CF_2CFCF_3O (g_{31}) group value ($T = 353.15$ K), where the value of g_{31} is taken from Fig. 1.

trifluoromethane and is connected to the main chain by oxygen. If this g_{31} is not exists, the sulfonic site becomes short and the action radius of the anions located at the end of the chain is decrease. Unfortunately, the substituted trifluoromethane and the oxygen stiffen the sulfonic site chain. This might affect the chain flexibility, the group number for g_{31} reached the limits of increase for good ionic conductivity. At the group number $m = 0$, the ionic conductivity value was less than that of $m = 1$ or $m = 2$. When the number "m" increases up to 3, the ionic conductivity decreases below that of m at 0. This shows that the best configuration of the system depends on group numbers of "m". For good mechanical properties, ionic conductivity should not be increasing or decreasing. In Fig. 8, the accuracy of the ionic conductivity with different values of 'm' is represented for group numbers of g_{31}. Precise values for the changes in the group number m are as follows: '0' is 0.0486(S/cm), '1' is 0.0661(S/cm), '2' is 0.0617(S/cm), and '3' is 0.0297(S/cm). We suggest that '1' is the best choice of 'm' for the system. The g_{51} group, which is the same configuration as g_{11} but having a different position from the repeat unit, shows a similar result for the ionic conductivity. There is no substituted molecules or oxygen groups in g_{51}, chain will more flexible and increasing the occupancy of sulfonic site between main chain and water phase. If the number of "n" grows larger, the conductivity of the system decreases in Fig. 9.

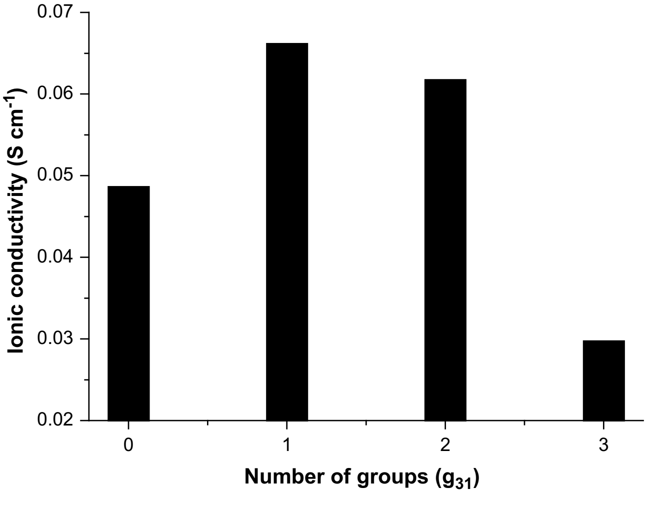

Fig. 8. Ionic conductivity values for different group numbers of g_{31}.

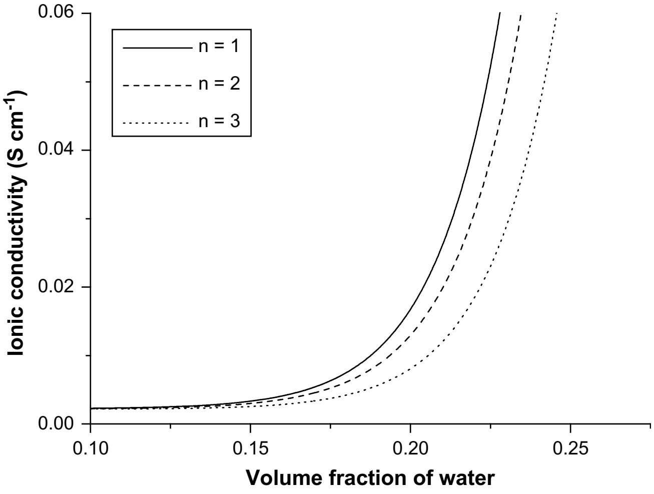

Fig. 9. Variation of ionic conductivity with CF_2CF_2 (g_{51}) group value ($T = 353$ K), where the value of g_{51} is taken from Fig. 1.

In conclusion, for good mechanical properties of PFSA membranes, the backbone chain length of the repeat unit should be short, the substituted perfluorosulfonic chain group should be short and the 'm' value of group g_{31} should be 1.

4. Conclusion

In this study, we proposed a modified double lattice (MDL) model combined with the group contribution method and DH theory to predict the group dependence of the ionic conductivity for PFSA membranes. Our model agrees well with experimental data used to determine the parameters. A significant contribution in our study is the calculation of the group dependences for the ionic conductivity of the PFSA membrane/water system. We changed several group numbers of units in the polymer. Short groups of CF_2CF_2 in the polymer backbone and in the side chain show a higher ionic conductivity than long CF_2CF_2 groups in the backbone chain and side chain. In particular, the CF_2CFCF_3O group in the side chain shows an interesting result. One CF_2CFCF_3O group represents higher ionic conductivity than zero, two or three CF_2CFCF_3O groups. As a result, we suggest that the optimized group numbers for these systems are as follows: short CF_2CF_2 groups in backbone and side chain, and a single group in the CF_2CFCF_3O side chain.

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References

[1] Fredenslund A, Jones RL, Prausnitz JM. AIChE J 1977;21:1086.
[2] Oishi T, Prausnitz JM. Ind Eng Chem 1978;17:333.
[3] Hu Y, Zhou H, Liu H, Wu DT, Prausnitz JM. Fluid Phase Equilibr 1997;134:43.
[4] Jones AT, Derawi S, Danner RP, Duda JL. Fluid Phase Equilibr 2007;259:116.
[5] Breure B, Bottini SB, Witkamp GJ, Peters CJ. J Phys Chem B 2007;111:14265.
[6] Huynha DN, Benamira M, Passarello JP, Tobaly P, Hemptinne JC. Fluid Phase Equilibr 2007;254:60.
[7] Tamouza S, Passarello JP, Tobaly P, Hemptinne JC. J Power Sources 2001;101:275.
[8] Nannoolala Y, Rarey J, Ramjugernatha D. Fluid Phase Equilibr 2008;269:117.
[9] Lymperiadis A, Adjiman CS, Jackson G, Galindo A. Fluid Phase Equilibr 2008;274:85.
[10] Foreman JP, Porter D, Behzadi S, Jones FR. Polymer 2008;49:5588.

[11] Oh JS, Bae YC. Polymer 1998;39:1149.
[12] Madden WG, Pesci AI, Freed KF. Macromolecules 1990;23:1181.
[13] Hu Y, Lambert SM, Soane DS, Prausnitz JM. Macromolecules 1991;24:4356.
[14] Panagiotopolous AZ, Quirke N, Sapleton M, Tildersley DJ. Mol Phys 1988;63:527.
[15] Guggenheim EA. Philos Mag A 1935;19:588.
[16] Guggenheim EA, Turgeon TJ. Trans Faraday Soc 1955;51:747.
[17] Barton AFM. CRC handbook of solubility parameter and other cohesion parameters. 2nd ed. CRC Press; 1991. p. 4356.
[18] van Krevelen DW. Properties of polymers. 3rd ed. Elsevier; 1990.
[19] Pai SJ, Sun YK, Bae YC. Polymer 2005;46:3111.
[20] Gray FM. Polymer electrolytes. The Royal Society of Chemistry; 1997. p. 104.
[21] Springer TE, Zawodzinski TA, Gottesfeld S. J Electrochem Soc 1991;138:2334.
[22] Hinatsu JT. J Electrochem Soc 1994;141:1493.
[23] Anantaraman AV. J Electroanal Chem 1996;414:115.
[24] Pitzer KS. J Phys Chem 1973;77(2):268.
[25] Hsu WY, Gierke TD. J Membr Sci 1983;13:307.
[26] Kreuer KD. J Membr Sci 2001;185:29.