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# Solvent activities of the fluorinated solid polymer electrolyte/water system in fuel cells

Tae Hwan Kim, Young Chan Bae[*]

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

## Abstract

We modified the lattice fluid equation-of-state by the introducing Debye–Hückel equation. A thermodynamic model taking into account the specific interaction and ionic strength between the polymer and the solvent is proposed. The proposed model successfully predicts the vapor/liquid equilibria (VLE) of solvents and the solid polymer electrolyte (SPE). A generalized lattice fluid model is modified to describe the change of water activity in solid polymer electrolyte (SPE)/water systems. The calculated activity curves using the proposed model agree remarkably well with the experimental data.
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*Keywords:* Vapor–liquid equilibria; Lattice fluid model; Solid polymer electrolyte; Debye–Hückel theory

## 1. Introduction

A significant time generally elapses before any new technological development is fully exploited. The fuel cell, first demonstrated by Sir William Grove in 1839, has taken longer than most, despite the promise of clean and efficient power generation. However, there is a need to develop more people with knowledge of fuel cell technology. Today's engineers must deal with increasingly complex and non-ideal pure substances and mixtures, and with operating conditions involving extremes of temperature, pressure, concentration, ionic strength, etc. For many of these substances reliable experimental measurements at such conditions are time consuming and costly. Using the simulation method can solve these problems.

Perfluorosulfonic acid membranes are the objects of intense interest due to their potential use in fuel cells. Since du Pont showed that the presence of water in these membranes greatly enhances proton transport, considerable research has been directed toward the development of SPE having high ion conductivity as well as mechanical, thermal and chemical stability [1,2]. One important factor that can affect the performance of fuel cell is the hydration of SPEs [3,4]. Membranes can neither be too dry, in which case

the proton conductivity decreases nor too wet, in which case electrode flooding may result. To understand the above-mentioned phenomena of SPEs for the fuel cell application, a theoretical study is desirable. Investigating the manufacturing process of a fuel cell in common use, there is a pressure imposed on the SPE to improve the degree of uptake between electrolyte and fuel.

During the last half-century, there have been various theoretical and experimental approaches to investigate the structures and thermodynamic properties of polymers and their solvents. The first description of statistical thermodynamics of polymer solutions was proposed by Flory [5] and Huggins [6]. It is a rigid lattice model that ignores the free volume effect. Since then, various theories have been developed that allow for the possibility of volume changes. Prigigine [7] and Eyring et al. [8] presented a cell model theory that introduced a free volume by assuming a hard-sphere repulsive potential for the segments of the polymer chain moving in a square-well potential. Flory and Flory et al. [9,10] reported a modified version of this theory. The main difference was the replacement of the generalized Lennard–Jones potential by a van der Waals type potential. On the other hand, another quantitative theory taking the compressibility of both components into account has been developed by Sanchez and Lacombe [11–13]. This is similar to the Flory–Huggins theory, but a free volume term is introduced via vacant lattice sites. Based on this lattice fluid model, Panayitou [14] derived a modified molecular theory

* Corresponding author. Tel.: +82-222900529; fax: +82-222966280.
*E-mail address:* ycbae@hanyang.ac.kr (Y.C. Bae).

of r-mer fluid mixtures which takes into account the difference of the molecular shape. Membranes containing ions with multiple charges have larger effects on the activity of ions than membranes containing only singly charged ions. To express membrane ionic contributions in a way that takes this into account, Debye and Hückel were able to show that in solutions the activity coefficient of an ion species varies with charge number.

The purpose of this study is to modify the lattice fluid model to the polymer solvent systems by introducing the Debye–Hückel model as a function of the polymer ionic contribution. We examine a generalization lattice fluid model for water activities in fuel cell systems. If a membrane is contacted with an aqueous solution, the membrane will take up water and solutes. When the membrane with its dissolved water and solutes is considered as an aqueous solution, the fixed charge groups of the membrane are ordinary ions evenly distributed in the aqueous solution.

## 2. Model development

Two theoretical aspects are taken into account; the GLF model and Debye–Hückel theory. We assume that the solvent is a component in order to take account of a solvent effect of the free energy of mixing. We assume that the salt is component in order to take account of a salt effect of the free energy of mixing.

In this study, all expressions for the thermodynamic model framework are expressed in terms of a binary mixture of $N_1$ molecules of size $r_1$ and $N_2$ molecules of size $r_2$. The $r$-mer is a molecule that occupies $r$ sites on a lattice of coordination number $z$.

### 2.1. The free energy of mixing

In the generalization lattice-fluid (LF) model, free energy per molecule $G/rN$ as $f_E$, is given by

$$f_E = -\tilde{\rho}\varepsilon^* + \frac{Pv^*}{\tilde{\rho}} - TS \tag{1}$$

where $\varepsilon^*$ is the mixing interaction energy.

$$\varepsilon^*(\phi,T) = \tfrac{1}{2}z(\phi_1^2\varepsilon_{11} + 2\phi_1\phi_2 f_{12} + \phi_2^2\varepsilon_{22})$$
$$\equiv (\phi_1^2\varepsilon_{11}^* + 2\phi_1\phi_2 f_{12}^* + \phi_2^2\varepsilon_{22}^*) \tag{2}$$

$f_{12}$ is the free energy parameter that replaces the pure energetic parameter $\varepsilon_{12}$. It includes the specific interaction parameter $\delta\varepsilon/k$ and the entropy effect generated by the specific interaction. $f_{12}$ is defined as [16]

$$f_{12} = \varepsilon_{12} + \delta\varepsilon - kT\ln\left[\frac{1+q}{1+q\exp(-(\delta\varepsilon/kT))}\right] \tag{3}$$

Subscript 1 refers to 1-component (solvent) and subscript 2 refers to 2-component (polymer).

### 2.2. Chemical potential

The free energy of mixing is a minimum when

$$\left.\frac{\partial G}{\partial\tilde{v}}\right|_{T,P,\phi} = 0 \quad \text{or equivalently} \quad \left.\frac{\partial f_E}{\partial\tilde{\rho}}\right|_{T,P,\phi} = 0 \tag{4}$$

which yields the lattice fluid equation of state

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T}\left(\ln(1-\tilde{\rho}) + \left(1-\frac{1}{r}\right)\tilde{\rho}\right) = 0 \tag{5}$$

where

$$\beta = \frac{1}{kT}$$

and

$$v^* = \sum_i \phi_i v_i^* = \phi_1 v_1^* + \phi_2 v_2^*, \qquad \tilde{\rho} = \frac{\rho}{\rho^*},$$
$$\tilde{T} = \frac{T}{T^*} = \frac{kT}{\varepsilon^*}$$

### 2.3. Debye–Hückel theory

To take into account the ionic contribution between the segments of molecules, Debye and Hückel [15] showed that in dilute solutions the activity coefficient $\gamma_i$ of an ion species $i$ with a charge number of $z_i$ is given by

$$\log\gamma_i = -Az_i^2 I^{1/2} \tag{6}$$

where $I$ is the ionic strength and

$$A = \frac{1}{2.303}\left(\frac{2\pi N_A m_{\text{solv}}}{V}\right)^{1/2}\left(\frac{e^2}{4\pi\varepsilon_0\varepsilon_r kT}\right)^{3/2} \tag{7}$$

where $m_{\text{solv}}$ is the mass of solvent in volume $V$, $e^2$ is the unit charge $1.621\times10^{-19}$ C and $\varepsilon_r$ is the relative permittivity.

At higher ionic strength, the following empirical extension is often useful:

$$\log\gamma_i = \frac{Az_i I^{1/2}}{1+BI^{1/2}} \tag{8}$$

where $B$ presents the dependencies of the mean ionic activity coefficients of components on ionic strength for the extended Debye–Hückel theory.

### 2.4. The activity

The activity of a mixture is defined by

$$\mu_i = \mu_i^\circ RT\ln a_i \tag{9}$$

Thus, the activity $a_i$ is simply a means for expressing the chemical potential of a species on a mixture. In general, ion exchange membranes uptake water component. Thermodynamics gives this chemical phenomenon to activity.

In a binary mixture, the activity of solvent 1 in polymer 2 is

$$\ln a_1 = \frac{\mu_1 - \mu_1^\circ}{kT}$$

$$= \left(\frac{r_1}{kT}\right)\left[ -\tilde{\rho}\varepsilon^* + \frac{P\upsilon_1^*}{\tilde{\rho}} - \tilde{\rho}\phi_2\frac{\partial\varepsilon^*}{\partial\phi_1} + \tilde{\rho}\tilde{\varepsilon}_{11}^* - \frac{p\upsilon_1^*}{\tilde{\rho}_1} \right.$$

$$+ kT\left\{ \frac{1}{r_1}(\ln\phi_1 + \phi_2) - \frac{\phi_2}{r_2} + \frac{\ln\tilde{\rho}}{r_1} \right.$$

$$+ \frac{1-\tilde{\rho}}{\tilde{\rho}}\ln(1-\tilde{\rho}) - \frac{\ln-\tilde{\rho}_1}{r_1}$$

$$\left. -\frac{1-\tilde{\rho}_1}{\tilde{\rho}_1}\ln(1-\tilde{\rho}_1) \right\} - \frac{A(1-x_1)^{1/2}}{1+B(1-x_1)^{1/2}} + \ln x_1 \right]$$

$$(10)$$

## 3. Results and discussion

We employed the modified generalization lattice fluid model to predict water activities of perfluorosulfonic acid polymer electrolyte/water systems. The advantage of this model is its simplicity.

Fig. 1 shows basic structures of Nafion, Aciplex and Flemion. In SPE, the $HSO_3$ group added is ionically bonded, and so the end of the side chain is actually an $SO_3^-$ ion. The result of the presence of these $SO_3^-$ and $H^+$ ions is that there is a strong mutual attraction between the + and − ions from each molecule. Now, a key property of sulfonic acid is that it is highly hydrophilic—it attracts water. In SPE, this means we are creating hydrophilic regions within a generally hydrophobic substance. The hydrophilic regions around
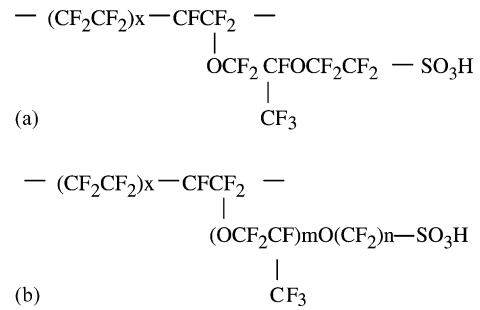
$$— (CF_2CF_2)x—CFCF_2 —$$
$$OCF_2\,CFOCF_2CF_2 — SO_3H$$
(a) $\qquad\qquad CF_3$

$$— (CF_2CF_2)x—CFCF_2 —$$
$$(OCF_2CF)mO(CF_2)n—SO_3H$$
(b) $\qquad\qquad CF_3$

Fig. 1. Repeating unit structures of perfluorinated proton exchange membrane with sulfonic acid functional groups. (a) Nafion ($x = 5$–11) (b) Aciplex and Flemion ($m = 0$ or 1, $n = 2$–5, $x = 1.5$–14).
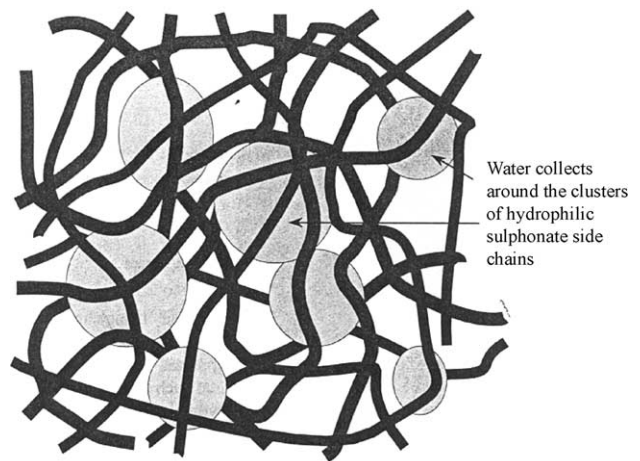


Fig. 2. Showing the structure of Nafion type membrane materials. Long chain molecules containing hydrated regions around the sulfonated side chains.
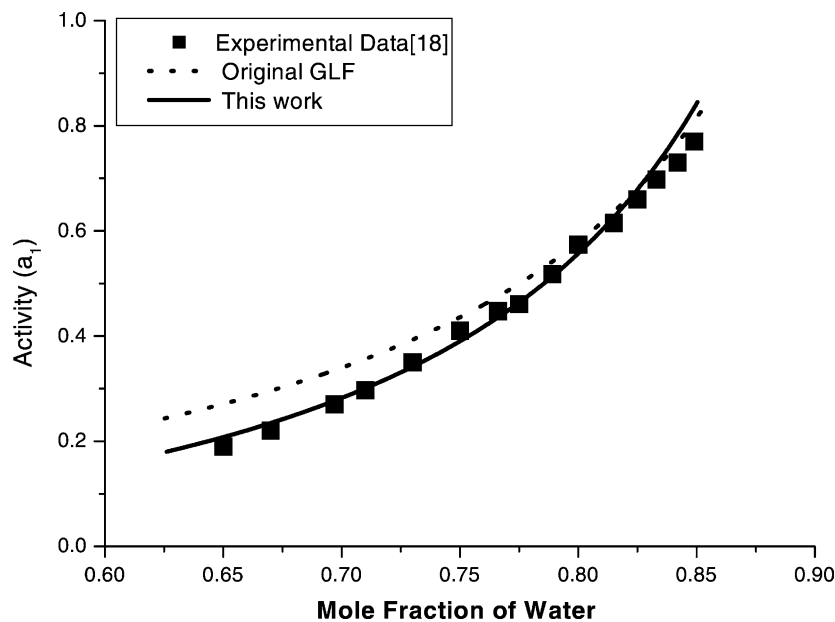


Fig. 3. Water activities for the Nafion (E.I. duPont de Nemours and Company)/water system at 353.15 K Nafion117 (EW = 1100). The solid line is calculated from this work. The other line is for the original generalization lattice fluid model. Solid squares are experimental data [18].
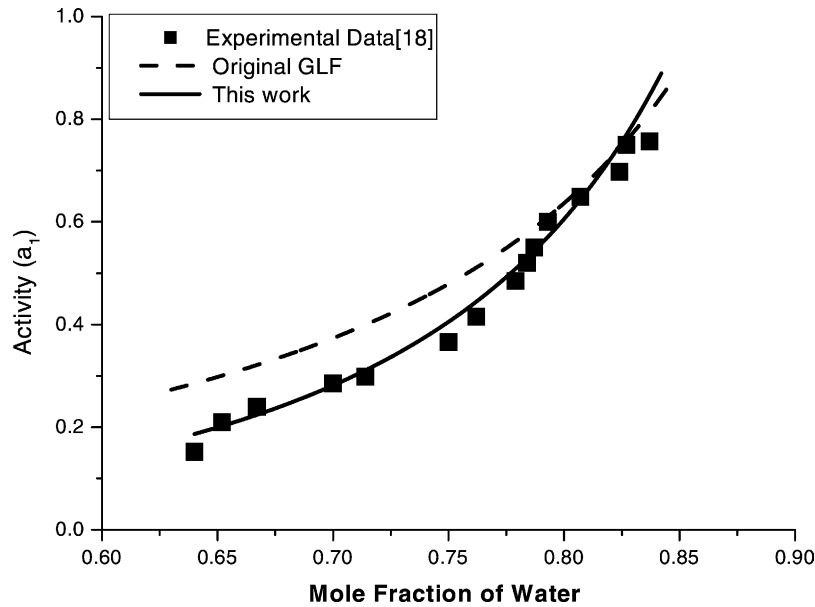
Fig. 4. Water activities for the Aciplex (Asahi Chemical Industry Co.)/water system at 353.15 K. Aciplex12 (EW = 1080). The solid line is calculated from this work. The other line is the generalization lattice fluid model. Solid squares are experimental data [18].

the cluster of sulfonated side chains can lead to the uptake of large quantities of water. Fig. 2 shows the micro-phase separated morphology [17]. Fig. 3 presents calculated water activities of Nafion117 (du Pont, EW = 1100) with experimental data reported by Hinatsu et al. [18] We compared original GLF with modified GLF (including ionic contribution). The each parameter values (subscript 1: solvent, subscript 2: polymer) of Nafion117/water system are $\varepsilon_{12}^* = -554.48$ K, $\delta\varepsilon = -14.53$ K and ionic parameter $B = 3.992$. These parameters are determined by fitting experimental data. The proposed model agrees well with

all regions. However, the GLF equation overestimates in the low water content region. Fig. 4 presents the water activities for Aciplex12 (Asahai Glass, EW = 980). The each parameter values are $\varepsilon_{12}^* = -566.39$ K, $\delta\varepsilon = -19.99$ K, and ionic parameter $B = 0.274$, respectively. Fig. 5 shows the activities for Flemion4 (Asahai Chemical, EW = 890). The parameter values are $\varepsilon_{12}^* = -577.58$ K, $\delta\varepsilon = -25.16$ K, and ionic parameter $B = -0.5836$.

The ultimate goal of this work is to improve fuel cell properties such as methanol crossover. As can be seen in these figures, the water activities increase as the equivalent
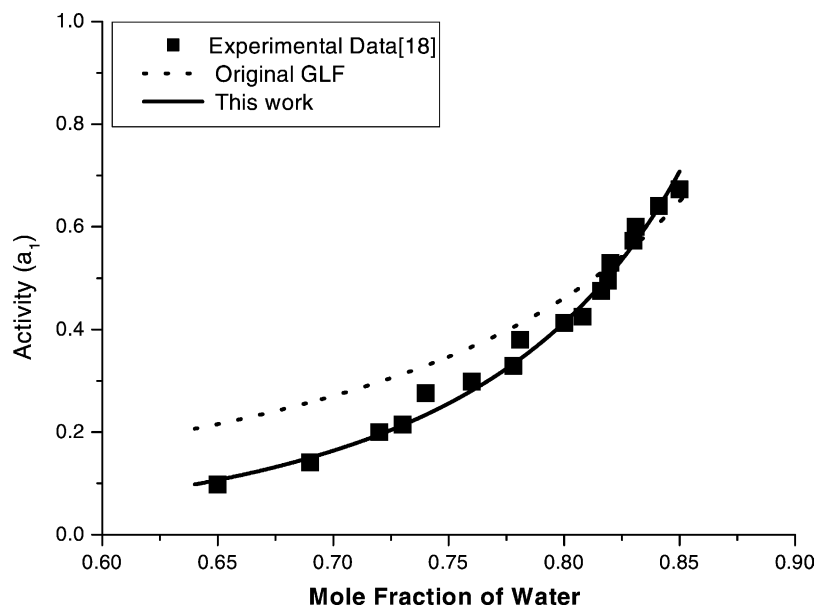


Fig. 5. Water activities for the Flemion (Asahai Glass)/water system at 353.15 K Flemion4 (EW = 890). The solid line is calculated from this work. The other line is for the generalization lattice fluid. Solid squares are experimental data [18].

weight of the polymer decreases, or in other words, as the number of exchange sites increases. The ionic strength plays a deceptive role in this system.

In this study, we determine interaction energy parameters and ionic parameters between perfluorosulfonic acid polymer electrolyte and the water component. The results obtained by the proposed model are expected to provide the appropriate operating conditions for fuel cells. They are important because cell performance can be adversely affected if the SPE is allowed to dry out (resulting in lower membrane conductivity) or if excess water is allowed then electrode flooding occurs (resulting in lower electrode performance). To characterize most common polymer electrolyte/fuel systems, more experimental data with different pressure systems are required.

In the context of ion exchange membrane fuel cells, the membrane activity is not the only issue. From the scientific viewpoint one must also consider aspects such as water transport through the membrane, chemical and mechanical stability, the ability to support electrochemistry, and the formation of low resistance interfaces with gas diffusion electrodes. From a technological viewpoint, processability, reproducibility, and cost must also be considered. In fuel cells, membranes operate under significant mechanical pressure that acts in opposition to the osmotic pressure. Nevertheless, these results should serve to help in understanding proton conductivity in PEMs and assist the design of PEMs with even lower ohmic resistance.

## 4. Conclusion

This work showed that activity in ion exchange membranes is determined by several factors. To describe the activity these of systems, we modified a generalization lattice fluid model. The model has a simplified and improved expression for the free energy of mixing for polymer/solvent systems that includes the combinatorial and vacant entropy contribution, the van der Waals energy contribution, and the ionic contribution. We compared calculated water activities of several commercial perfluorosulfonic membranes with experimental sorption data. The activity came under the influence of the ionic contribution. This model gives good agreement with experimental data.

## Acknowledgements

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