

Short communication

## Water activities of polymeric membrane/water systems in fuel cells

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### Abstract

A new equation of state (EOS) is established to describe water activities of polymeric membrane/water systems in fuel cell. It is developed based on the modified perturbed hard-sphere-chain (PHSC) EOS by introducing a new perturbation equation that is obtained from the generalized Lennard-Jones (GLJ) potential function based on a statistical–mechanical relationship. Experimentally observed water activities of polymeric electrolyte/water systems are interpreted by the proposed model. The values calculated from the proposed model are in a good agreement with the experimental data for given systems.

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### 1. Introduction

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. Since DuPont showed that perfluorosulfonic acid ion-exchange membranes have significant ionic conductivities and can be used in the fuel cell, considerable research has been directed toward the development of polymer electrolytes having high ion conductivity as well as mechanical, thermal, and chemical stability. One important factor that can affect the performance of fuel cell is the hydration of perfluorosulfonic acid membranes [1–5]. Membranes can neither be too dry, in which case the proton conductivity decreases nor too wet, in which case electrode flooding may result. To solve the above-mentioned problem of solid polymer electrolyte (SPE) for fuel cell application, a general thermodynamic model to be able to predict phase equilibria for these systems reliably is required. During the last half-century, there are various theoretical and experimental approaches to investigate the structures and thermodynamic properties of polymers and their solvents.

EOS is very efficient tool to understand properties of polymer solutions. Molecular-based thermodynamic models for describing vapor–liquid equilibria (VLE) can be divided into four categories, each corresponding to a particular statistical mechanical framework: incompressible-lattice models, generalized van der Waals partition-function theories, compressible-lattice models, and off-lattice (continuous-space) models of chain fluids.

Among several kinds of equations, the cubic equation of state is the simplest type, which is capable of representing both liquid and vapor phases. Unfortunately, simple cubic EOS is only applicable to the calculation of fluid phase equilibria in simple systems. Dickman and Hall [6] were the first to present an EOS for hard-sphere chains. They obtained the pressure through the formulation of chain-segment insertion probabilities in a manner analogous to that used to derive the lattice-based Flory–Huggins theory. Later, Honnell and Hall [7] derived a new EOS utilizing the Carnahan–Starling equation [8] and the Tildesley–Streeter [9] dimer equation. These equations have been tested against computer-simulation results for hard-sphere chains [10] and their binary mixtures [11,12] also extended the above equation to include square-well chains where non-bonded segments interact through a square-well intermolecular potential.

In general, hard-sphere chains can provide a useful reference system for representing a simple model of polymers [13]. Chiew

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solved the Percus-Yevick integral EOS coupled with chain connectivity for mixtures of hard-sphere chains analytically. However, as Chiew used different radial distribution functions in bonding term and non-bonding term [13], Chiew's equation did not show the relation between the bonding and non-bonding terms.

Song et al. [13] proposed PHSC EOS for the purpose of calculating phase equilibria in solutions including solvents and polymers by generalizing Chiew's equation through reformulating the radial distribution functions of hard-sphere mixtures at contact in both the bonding and non-bonding terms. It gives us very useful information in investigating properties of fluids, including mixtures of chain-like molecules. It contains all the information about substances and any equilibrium property can be obtained from any one of the fundamental equations of state by applying the appropriate thermodynamic relations.

This model has three parameters characterizing normal fluids including polymers: the number of single hard spheres per chain molecule (segment number)  $r$ , the separation distance between segment centers (segment size)  $\sigma$ , and the segment-pair interaction energy  $\varepsilon/k$ .

In this work, we employed the reference equation for hard spheres proposed by Hu et al. [14]. To describe the attractive forces between hard spheres, the square-well (SW) fluid model has been extensively studied until recently because it is useful as the first approximation to the understanding of properties of real fluids with spherically shaped molecules. In fact, properties of real fluids can be approximated by those of an SW fluid (SWF) with suitably chosen potential depth and range. Moreover, thermodynamic properties of an SWF are easier to determine theoretically than those of other fluids having more complicated potentials. This, in particular, is the case for perturbation theories, from which thermodynamic properties of SWFs can be obtained analytically [15–17]. However, the SW model appears to be a rather crude approximation of a real fluid. To obtain thermodynamic properties of a real fluid from those of a fluid with a model potential, we used the GLJ potential model established by Kim and Bae [18].

Thermodynamic properties investigated in this study are water activities of SPE/water systems. We develop a new thermodynamic framework based on a MPHSC model wherein proposed by Hu et al. [14] and Kim and Bae [18] into the reference term and accounts for the attractive force as a perturbation term. We also calculate the water activity by proposed model and GLJ potential in PEM fuel cell.

## 2. Model development

### 2.1. PHSC EOS

Derivation of EOS for mixtures follows a rigorous first order statistical-mechanical perturbation theory based on a mixture of hard-sphere chains as the reference system, and closely parallels that for pure fluids. Only the main steps need to be presented.

The van der Waals-type equation of state has the general form of

$$\frac{P}{\rho kT} = \left( \frac{P}{\rho kT} \right)_{\text{ref}} + \left( \frac{P}{\rho kT} \right)_{\text{pert}} \quad (1)$$

In this work, we employ the reference equation proposed by Hu et al. [14]

$$\left( \frac{P}{\rho kT} \right)_{\text{ref}} = \frac{1 + \alpha\eta + \beta\eta^2 - \gamma\eta^3}{(1 - \eta)^3} \quad (2)$$

where  $P$  is the pressure,  $\rho = N/V$  the number density ( $N$  is the number of molecules and  $V$  is the volume), and  $k$  is the Boltzmann constant and  $\alpha$ ,  $\beta$ ,  $\gamma$  parameters are as follows:

$$\alpha = r \left( 1 + \frac{r-1}{r} a_2 + \frac{r-1}{r} \frac{r-2}{r} a_3 \right) \quad (3)$$

$$\beta = r \left( 1 + \frac{r-1}{r} b_2 + \frac{r-1}{r} \frac{r-2}{r} b_3 \right) \quad (4)$$

$$\gamma = r \left( 1 + \frac{r-1}{r} c_2 + \frac{r-1}{r} \frac{r-2}{r} c_3 \right) \quad (5)$$

$a_2 = 0.45696$ ,  $b_2 = 2.10386$ ,  $c_2 = 1.75503$ ,  $a_3 = -0.74745$ ,  $b_3 = 3.49695$ ,  $c_3 = 4.83207$ , where  $\eta$  is defined as the packing fraction given by

$$\eta = \frac{rb\rho}{4} \quad (6)$$

where  $b$  reflect the second virial coefficient of hard spheres

$$b = \frac{2\pi}{3} \sigma^3 \quad (7)$$

In Eq. (1), the perturbation term, which accounts for the attractive force, can be generally expressed as below.

$$\left( \frac{P}{\rho kT} \right)_{\text{pert}} = \frac{\rho U}{2kT} \quad (8)$$

where  $U$  is the perturbation energy that can be obtained from the following relationship:

$$U = 4\pi \int W(r)r^2 dr \quad (9)$$

where  $W(r)$  is the pair potential function.

The GLJ potential function has the form of [18],

$$W(r) = \begin{cases} \infty & (0 < r < \sigma) \\ -\varepsilon & \left( \sigma < r < \frac{2\sigma}{A(\tilde{T})} \right) \\ \frac{\varepsilon}{1 - A(\tilde{T}) \left( \frac{r}{\sigma} \right)} & \left( \frac{2\sigma}{A(\tilde{T})} < r < \lambda\sigma \right) \\ 0 & (r > \lambda\sigma) \end{cases} \quad (10)$$

where  $r$  is the center-to-center distance between two adjacent molecules,  $\sigma$  the diameter,  $\varepsilon$  the minimum potential energy,  $\tilde{T} = kT/\varepsilon$  the reduced temperature with Boltzmann constant  $k$ , and  $A(\tilde{T})$  is the temperature-dependent parameter that is determined from the computer-simulation data for the compressibility factor.

Combining Eq. (8) with Eq. (9) yields the perturbation equation as follows:

$$\left(\frac{P}{\rho kT}\right)_{\text{pert}} = \frac{12\eta}{\tilde{T}} \left[ -\frac{8}{3A^3} - \frac{1}{A} \left\{ \frac{\ln(A\lambda - 1)}{A^2} + \frac{\lambda^2}{2} + \frac{\lambda}{A} - \frac{4}{A^2} \right\} + \frac{1}{3} \right] \quad (11)$$

Then the final form of EOS can be written as

$$\frac{P}{\rho kT} = \frac{1 + \alpha\eta + \beta\eta^2 - \gamma\eta^3}{(1 - \eta)^3} + \frac{12\eta}{\tilde{T}} \left[ -\frac{8}{3A^3} - \frac{1}{A} \left\{ \frac{\ln(A\lambda - 1)}{A^2} + \frac{\lambda^2}{2} + \frac{\lambda}{A} - \frac{4}{A^2} \right\} + \frac{1}{3} \right] \quad (12)$$

The EOS for the mixture is obtained by extending Eq. (12) directly

$$\frac{P}{\rho kT} = \left[ \frac{1 + 3(BE/F) - (E^3/F^2)}{1 - \eta} + \frac{3(BE/F)\eta - (E^3/F^2)}{(1 - \eta)^2} + \frac{2(E^3/F^2)}{(1 - \eta)^3} \right] + \sum_{i,j=1}^m x_i x_j r_i r_j \left( \frac{12\eta}{\tilde{T}} \right) \times \left[ -\frac{8}{3A^3} - \frac{1}{A} \left\{ \frac{\ln(A\lambda - 1)}{A^2} + \frac{\lambda^2}{2} + \frac{\lambda}{A} - \frac{4}{A^2} \right\} + \frac{1}{3} \right] \quad (13)$$

where  $x_i = N_i/N$  is the mole fraction of molecule  $i$  and  $r_i$  is the number of hard spheres and  $B, E, F$  are given by,

$$B = \frac{\sum_{i=1}^m N_i r_i \sigma_i}{\sum_{i=1}^m N_i r_i}, \quad E = \frac{\sum_{i=1}^m N_i r_i \sigma_i^2}{\sum_{i=1}^m N_i r_i}, \quad F = \frac{\sum_{i=1}^m N_i r_i \sigma_i^3}{\sum_{i=1}^m N_i r_i} \quad (14)$$

and  $\eta$  is given by

$$\eta = \frac{\rho}{4} \sum_i x_i r_i b_i \quad (15)$$

The additivity of hard-sphere diameters allows the expression for  $b_{ij}$  as follows:

$$b_{ij} = \frac{2\pi}{3} \sigma_{ij}^3 \quad (16)$$

The pair potential between unlike segments  $\epsilon_{ij}$  and size parameter  $\sigma_{ij}$  can be determined by

$$\epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}} \quad (17)$$

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \quad (18)$$

To transform the number basis to segment basis equations, more useful variables should be introduced for polymer mixtures. These variables are segment density,  $\rho_r = N_r/V$ , and segment fraction  $\phi_i = N_i r_i / N_r$ , where  $N_r$  is the total number of segments in the system with volume  $V$ .

$$N_r = \sum_i^m N_i r_i \quad (19)$$

In these terms, the final form of the new equation of state is

$$\frac{P}{\rho kT} = \left[ \frac{1 + 3(BE/F) - (E^3/F^2)}{1 - \eta} + \frac{3(BE/F)\eta - (E^3/F^2)}{(1 - \eta)^2} + \frac{2E^3/F^2}{(1 - \eta)^3} \right] + \sum_{i,j=1}^m \phi_i \phi_j \left( \frac{12\eta}{\tilde{T}} \right) \times \left[ -\frac{8}{3A^3} - \frac{1}{A} \left\{ \frac{\ln(A\lambda - 1)}{A^2} + \frac{\lambda^2}{2} + \frac{\lambda}{A} - \frac{4}{A^2} \right\} + \frac{1}{3} \right]. \quad (20)$$

### 2.2. Thermodynamic functions

The Helmholtz energy can be calculated from the pressure-explicit EOS [19]

$$\frac{A}{N_r kT} = \sum_i^m \frac{\phi_i}{r_i} \frac{A_i^0}{N_r kT} + \int_0^{\rho_r} \left( \frac{P}{\rho_r kT} - \frac{N}{N_r} \right) \frac{d\rho_r}{\rho_r} + \sum_i^m \frac{\phi_i}{r_i} \ln \left( \frac{\phi_i}{r_i} \rho_r kT \right) \quad (21)$$

$$\frac{\Delta A}{NkT} = \left[ \frac{3(BE/F) - (E^3/F^2)}{1 - \eta} + \frac{E^3/F^2}{(1 - \eta)^2} + \left( \frac{E^3}{F^2} - 1 \right) \ln(1 - \eta) \right] + \sum_{i,j=1}^m \phi_i \phi_j \left( \frac{12\eta}{\tilde{T}} \right) \times \left[ -\frac{8}{3A^3} - \frac{1}{A} \left\{ \frac{\ln(A\lambda - 1)}{A^2} + \frac{\lambda^2}{2} + \frac{\lambda}{A} - \frac{4}{A^2} \right\} + \frac{1}{3} \right]. \quad (22)$$

### 2.3. Chemical potentials

The chemical potential is defined as:

$$\mu_k = \left( \frac{\partial A}{\partial N_k} \right)_{T,V,N_{i \neq k}} \quad \text{or} \quad \frac{\Delta \mu_k}{kT} = \frac{\partial}{\partial \eta} \left( \eta \frac{\Delta A}{NkT} \right)_{T,V,N_{i \neq k}} \quad (23)$$

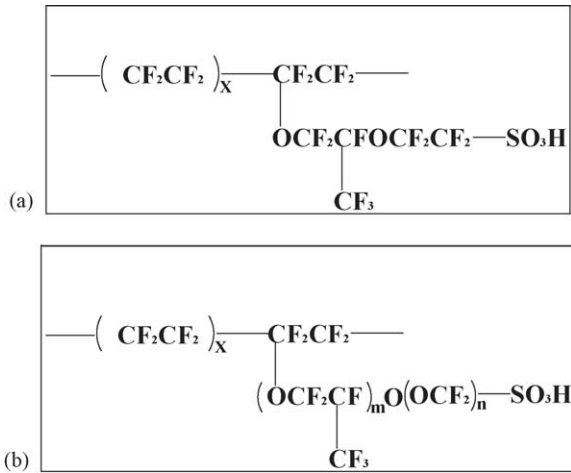


Fig. 1. Repeat unit structures of perfluorinated proton exchange membrane with sulfonic acid functional groups. (a) Nafion ( $x=5\text{--}11$ ) and (b) Flemion ( $m=0$  or  $1$ ,  $n=2\text{--}5$ ,  $x=1.5\text{--}14$ ).

and activity can be obtained as

$$\ln a = \left[ \frac{3(BE/F)\eta^3 - (E^3/F^2 + BE/F)\eta^2 + (E^3/F^2 + 6BE/F)\eta - (E^3/F^2)}{(1-\eta)^2} + \frac{(E^3/F^2)(1+\eta)}{(1-\eta)^3} + \left( \frac{E^3}{F^2} - 1 \right) \ln(1-\eta) - \left( \frac{E^3}{F^2} - 1 \right) \frac{\eta}{1-\eta} \right] + \sum_{i,j=1}^m \phi_i \phi_j \left[ \frac{24\eta}{\tilde{T}} \left\{ -\frac{8}{3A^3} - \frac{1}{A} \left( \frac{\ln(A\lambda - 1)}{A^2} + \frac{\lambda^2}{2} + \frac{\lambda}{A} - \frac{4}{A^2} \right) + \frac{1}{3} \right\} \right]. \quad (24)$$

### 3. Results and discussion

We developed a new thermodynamic frame work based on combining the reference model by Hu et al. [14] and the perturbation model by Kim and Bae [18] to describe water activities of perfluorosulfonic acid polymer electrolyte systems—Nafion and Flemion. Their structures are illustrated in Fig. 1.

The model has three characteristic parameters: the number of single hard spheres per chain molecule  $r$ , the segment size  $\sigma$  and the non-bonded segment-pair interaction energy  $\varepsilon$ . For  $i$  component (water) and  $j$  component (polymer), the pure component parameters for polymers ( $r_j$ ,  $\sigma_j$ ,  $\varepsilon_j$ ) and mixture parameters ( $r_{ij}$ ,  $\sigma_{ij}$ ,  $\varepsilon_{ij}$ ) are obtained by fitting simulation results.

In Fig. 2, the solid and dotted lines are calculated from the proposed model and MPHSC equation, respectively [20]. In the entire density region, MPHSC EOS shows slight deviations from the experimental data, however our model shows good agreement with the data. The obtained characteristic parameters for water are  $r_{\text{water}} = 1.75$ ,  $\sigma_{\text{water}} = 2.81$ ,  $\varepsilon_{\text{water}}/k = 680.2$ .

Figs. 3a, b, 4a, b, and 5a represent calculated water activities of Nafion 117, 125 (DuPont, EW = 1100, 1200), Flemion 4, 12 (Asahi Glass, EW = 890, 920), and Aciflex 4 (Asahi Chemical, EW = 980), respectively. Dark squares are experimental data reported by Hinatsu et al. [21]. The solid and dotted lines are calculated by the proposed model and MPHSC equation, respec-

Table 1  
Lists of characteristic parameters for the proposed model

Polymer	Characteristic parameters		
	$r$	$\sigma$	$\varepsilon/k$
Nafion 117/water	2735.2	9.8	1540
Nafion 125/water	2682	10.82	1585
Flemion 4/water	4326	10.20	1610
Flemion 12/water	2745	8.84	1442
Aciflex 4/water	2725	10.40	2400

tively. The values of the three characteristic parameters are listed in Table 1.

All results show that the water activities increase as the equivalent weight of the polymer decreases, or in other words, as the number of exchange sites increases. The calculated curves for the different polymer electrolytes show the same trends because all the commercial SPEs have similar chemical structures (as shown in Fig. 1).

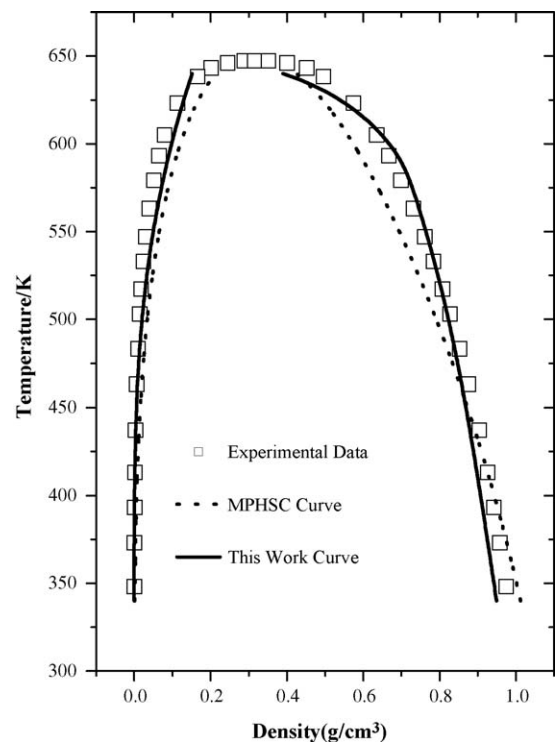


Fig. 2. Vapor/liquid equilibrium experimental data for water. The solid line and dotted line are calculated by this work and the modified PHSC. Open squares are experimental data [20].

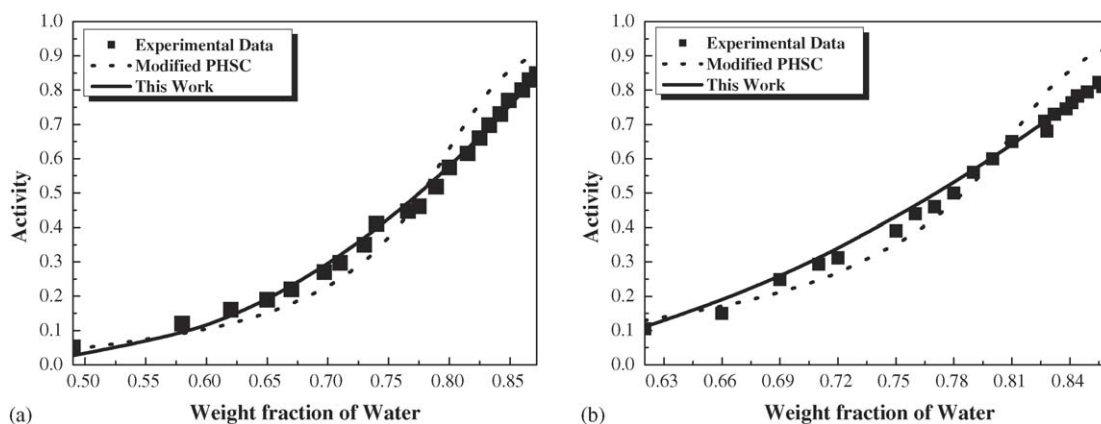


Fig. 3. Water activities for the Nafion (E.I. DuPont de Nemours and Company)/water system at 353.15 K. (a) Nafion 117 (EW = 1100) and (b) Nafion 125 (EW = 1200). The solid line is calculated from this work. The dotted line is calculated from modified PHSC. Dark squares are experimental data [21].

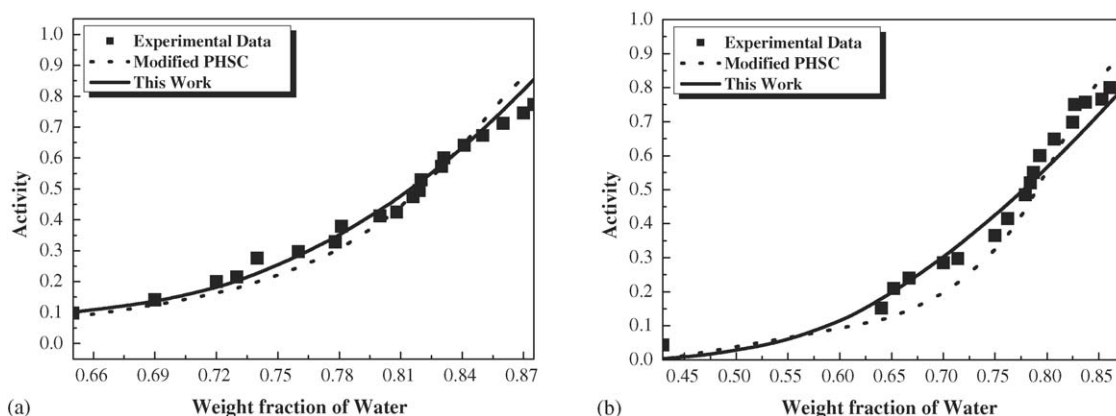


Fig. 4. Water activities for the Flemion (Asahi Glass)/water system at 353.15 K: (a) Flemion 4 (EW = 890) and (b) Flemion 12 (EW = 920). The solid line is calculated from this work. The dotted line is calculated from modified PHSC. Dark squares are experimental data [21].

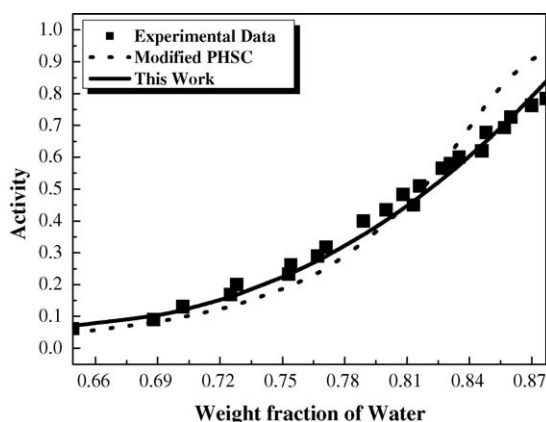


Fig. 5. Water activities for the Aciplex-4 (EW = 980) (Asahi Chemical Industry Co.)/water system at 353.15 K. The solid line is calculated from this work. The dotted line is calculated from modified PHSC. Dark squares are experimental data [21].

#### 4. Conclusion

In this study, we propose a new thermodynamic model based on the MPHSC for SPE/water mixtures by introducing a new perturbation equation that is obtained from the generalized Lennard-Jones (GLJ) potential function based

on a statistical–mechanical relationship. The proposed model includes the short-range interaction contribution and the long-range interaction contribution which depends on temperature. The characteristic parameters are calculated from the experimental data so that we are able to predict the water activities of fluorinated solid polymer electrolyte/water systems.

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