# Phase Equilibria for Water–Methanol Mixtures in Perfluorosulfonic-Acid Membranes

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*A new apparatus was constructed for precise measurements of water–methanol uptake compositions in a membrane. Uptake concentrations of methanol and water in a Nafion 117 membrane were measured as a function of methanol mole fraction in a liquid-methanol–water mixture for the temperature range 298 to 333 K. Also, uptake concentrations of methanol and water were determined for a second-cycle uptake run. All methanol–water compositions were determined by gas chromatography. The results were quantitatively described by either one of two thermodynamically consistent equations derived from models for the Gibbs energy of the system.*

## Introduction

Ion-exchange membranes have found uses in many electrochemical devices, including batteries, electrochemical sensors/ reactors, and fuel cells. (Dorfner, 1991). Renewed attention has been given to low-temperature polymer electrolyte fuel cells (PEFCs) that use perfluorosulfonated membranes such as Nafion as electrolyte and hydrogen as the input fuel for providing high-energy efficiency combined with low pollution. Therefore, these types of fuel cells are of particular interest for portable power sources and vehicular applications. Because a reservoir of hydrogen causes storage and space problems, hydrogen could be derived from onboard reformation systems using a primary fuel, such as, methanol. However, the additional reformer system presents problems of space, complexity, cost, and overall system efficiency. Direct methanol fuel cells (DMFCs) using polymerelectrolyte membranes could provide an attractive alternative to indirect methanol fuel cells (Ren et al., 1996). Unfortunately, perfluorosulfornated membranes are quite permeable to methanol, leading to methanol crossover to the oxygen/air cathode. This causes losses in terms of lost fuel and depolarization at the cathode. Furthermore, for operating a PEFC, a major concern is to maintain adequate water content of the persulfonate membrane, because a dry membrane lowers conductivity, while excessive amounts of water could impede transport within the electrode structure (cathode flooding). Previous investigations (Skou et al., 1997; Nandan et al., 1992; Gates and Newman, 2000) have shown that the presence of methanol as a second component inside the membrane changes the solubility properties of these ionomers.

Since research on Nafion polymers has focused mostly on the needs of the chlor-alkali industry and of the $H_2$-PEFC, there is a lack of data on the properties of these membranes under typical liquid-feed DMFC operating conditions. Little work on the uptake of methanol-water solutions in Nafion has been reported in the literature (Skou et al., 1997; Nandan et al., 1992; Gates and Newman, 2000). Because these data have discrepancies, further studies are necessary. In this work, we report new experimental data followed by a correlation of the pertinent Gibbs energy.

## Experimental Design and Procedure

Although the liquid uptake of methanol–water mixtures in Nafion has not been extensively reported in the literature (Skou et al., 1997; Nandan et al., 1992; Gates and Newman, 2000), some experimental data are available for the liquid uptake of water in Nafion (Hinatsu et al., 1994; Morris and Sun, 1993; Zawodzinski et al., 1993). However, liquid-uptake measurements are not standardized and are performed differently with widely varying results.

Our major concern is to measure the methanol–water equilibrium in perfluorosulfonate membranes as precisely as possible. Therefore, the experimental apparatus used by Gates (1998) (similar to those most investigators use to measure the uptake of liquid solutions in a membrane) cannot be used and required modification. In previous work, the composition of the sorbents was determined by a separation

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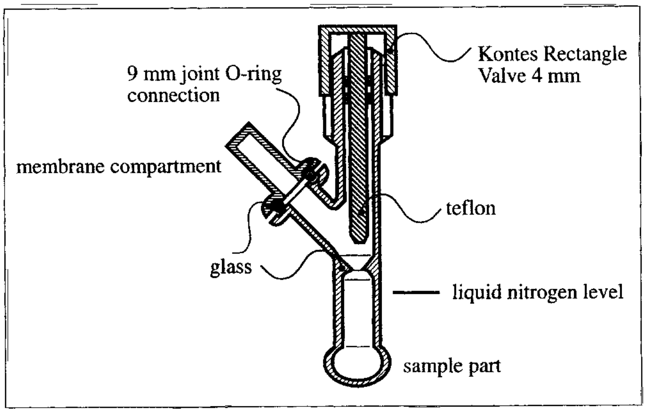

**Figure 1. Membrane containment for heating and weighing; the total volume is 9.6 mL.**

caused by a combination of a thermal gradient and a pressure gradient, condensing the evaporated solutes, and afterwards analyzing the composition of the condensate. For precise determination of the methanol–water equilibrium in Nafion, however, it is necessary to evaporate and to condense all of the solutes. Unfortunately, complete recovery cannot be achieved due to losses to the vacuum system (Gates, 1998). Therefore, a new apparatus had to be developed. The new experimental procedure meets the following conditions: (1) the apparatus must be a closed system, and (2) the effects of Schroeder's paradox must be minimized (Gates, 1998).

Figure 1 shows a diagram of the newly developed solute-recovery apparatus. We modified the experimental procedure used by Skou et al. (1997) and Gates (1998) by splitting the entire process into two steps and by avoiding the vacuum system: Inside a glove box, the membrane was removed from the equilibrating solution, the surface of the membrane was carefully dried, and finally, the membrane was transferred into the heating apparatus, as shown in Figure 1. The glove box contains a saturated nitrogen atmosphere to minimize the effects of solute evaporation and absorption during the surface-drying and transfer processes. The nitrogen atmosphere is saturated with a methanol–water mixture comparable to that with which the membrane is equilibrated.

The heating apparatus, shown in Figure 1, is constructed of a rectangle valve (Kontes 4 mm) with a glass bulb blown on one side; the other side is welded together with a joint O-ring connection (9 mm). The weight of the membrane is now determined as the weight difference between the weight of the apparatus with the membrane and without. This allows us to minimize the amount of solute evaporation while weighing the membrane.

Each membrane was pretreated before use. "As received" Nafrion 117 was boiled in 3% $H_2O_2$ to remove impurities on the surface, washed in boiling deionized water, followed by boiling in 0.5 M $H_2SO_4$, and finally, again rinsing in deionized boiling water. In each step, the membranes were boiled for at least 1 h. This pretreatment is used by most investigators (Ren et al., 1996; Skou et al., 1997; Gates and Newman, 2000; Morris and Sun, 1993). The pretreated membrane was allowed to equilibrate for at least 24 h in a large excess (300 mL) of a water–methanol mixture of a given composition within the range from pure water to pure methanol.

To obtain reliable data, the following experimental procedure was used: To eliminate any impurities inside the apparatus, it was rinsed with acetone and afterwards dried at 160° C for at least 1 h. After it was tightly sealed, and while it was hot, it was allowed to equilibrate at room conditions. As soon as the weight of the apparatus was constant, the total weight and the weight of the lower compartment of the apparatus (sample part) were determined by an analytical mass balance (Sartorius analytical balance LA200S). Meanwhile, a saturated atmosphere was established in the glove box by bubbling nitrogen through a solution of composition equal to that soaking the membrane. Within the saturated nitrogen atmosphere, the membrane was removed from the liquid, blotted gently dry with filter paper to remove droplets on the surface of the membrane, and transferred into the upper part of the heating apparatus (membrane compartment). Surface drying and transfer of the membrane were carried out as quickly as possible. After the membrane compartment was tightly sealed to the apparatus using a clamp connection, it was weighed again. To obtain reliable results, the outside of the apparatus was cleaned and the apparatus was allowed to equilibrate with the environment every time before the weight was determined; the apparatus was handled only with disposable rubber gloves (clean-room approved). To induce separation, the membrane compartment of the apparatus was held at 333 K and after 1 h raised to 378 K. This temperature was held for another 2 h. Meanwhile the sample part was kept in a liquid-nitrogen bath at 77 K.

After 3 h, while the membrane remained at 378 K and the sample part at 77 K, the latter was isolated from the membrane by closing the valve of the apparatus. To avoid errors in the weighing procedure, we allowed the apparatus to equilibrate again with the environment. To ensure that the apparatus has equilibrated with the environment, the whole apparatus was weighed, and the weight was compared to that before heating. Next, the membrane was removed from the apparatus, and its dry weight was determined. The weight difference of the lower compartment before and after separation yields the total weight of the recovered solutes. To obtain a reference weight of the membrane (Zawodzinski et al., 1993), it was heated under vacuum at 378 K for 24 h; the membrane's weight was then determined. Samples of the solution and of the recovered solutes were analyzed by gas chromatography (HP5890 Series II) to determine their compositions. To avoid evaporation of the recovered solutes while performing the GC analysis, a septum was placed over the joint O-ring connection of the apparatus after disconnecting the membrane compartment. After the valve of the apparatus was opened, a sample of the recovered solutes was withdrawn using a microliter syringe (Hamilton Gastight) with a long needle.

Second-cycle data were obtained in the same way as in the first-cycle uptake data; after pretreating the membranes again according to the pretreatment procedure described before, the membranes were treated as in the first-cycle uptake measurements.

## Results and Discussion

Different membrane pieces are used for each first-cycle measurement. For the second-cycle uptake, the membrane

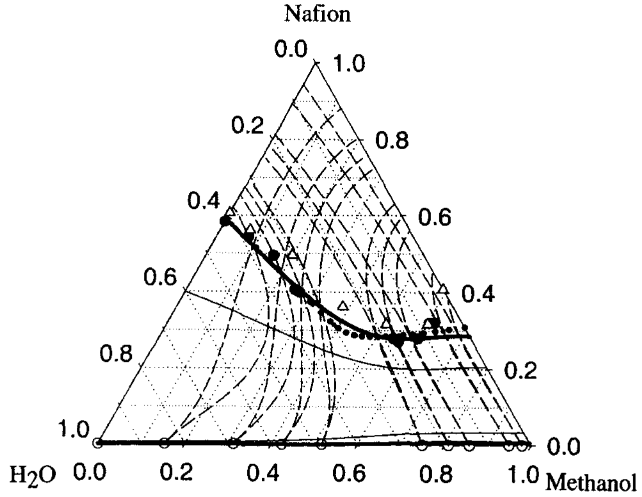

**Figure 2. Ternary diagram (in volume fractions, $z_i$) from first-cycle uptake measurements for the methanol–water–Nafion equilibrium at 333 K.**

Lines represent the fit obtained by the modified Wohl expansion (Eq. 5): thick solid lines are equilibrium curves; thin solid lines show loci of methanol or water of the spinodal points, and dashed lines show lines of constant activity, both derived from Eq. 5. The dotted line is the fit of the expansion using molalities (Eq. 9). The filled circles show the experimentally determined composition of the membrane phase in equilibrium with the liquid phase (unfilled circles). The unfilled triangles are experimental data from Gates (1998).

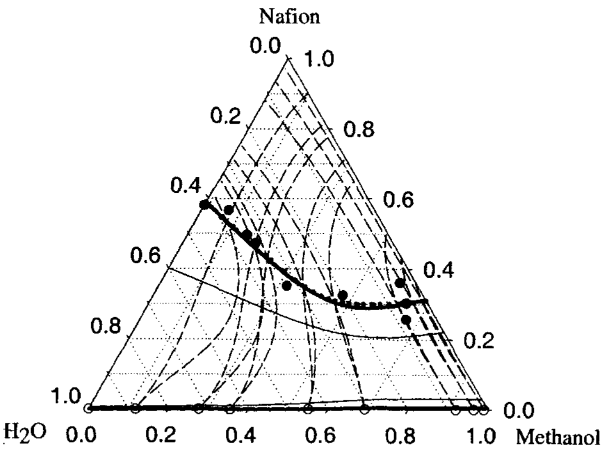

**Figure 3. Ternary diagram (in volume fractions, $z_i$) from second-cycle uptake measurements for the methanol–water–Nafion equilibrium at 333 K.**

Lines represent the fit obtained by the modified Wohl expansion (Eq. 5): thick solid lines are the equilibrium curves; thin solid lines show loci of methanol or water of the spinodal points, and dashed lines show lines of constant activity, both derived from Eq. 5. The dotted line is the fit of the expansion using molalities (Eq. 9). The filled circles show the experimentally determined composition of the membrane phase in equilibrium with the liquid phase (unfilled circles).

samples (after pretreating) used to measure the uptake of methanol and water were the same as those used to determine the first-cycle uptake at the same temperature. To ensure that different pieces of Nafion 117 membrane show similar uptake behavior in the first-cycle uptake when soaked in the same solution, we measured the uptake of several membrane samples. We found that the uptake behavior of these membranes showed closely similar compositions within a range of ±3%. Therefore, we believe that we can use different pieces of membrane to measure the uptake of solutes in Nafion.

Figures 2 and 3 show first- and second-cycle uptake data at 333 K, giving the results at the highest temperature measured that is close to that for industrial operation. Second-cycle uptake data are recorded to determine how membrane properties change with length of cycling and temperature treatment. Figure 2 also shows experimental results of Gates (1998), included for comparison. Temperature accuracy is ±1 K. Because literature uptake data for methanol–water mixtures in Nafion are only available at 298 K, Figure 4 shows first-cycle uptake data at 298 K together with literature data (Skou et al., 1997; Nandan et al., 1992).

### *Thermodynamics of multicomponent solutions in membranes*

The general condition of a system at phase equilibrium is equality of the chemical potential $\mu_i$ for each component $i$ that is simultaneously present in each phase. Activity $a_i$ is related to chemical potential $\mu_i$ through $\mu_i - \mu_i^o = \Re T \ln a_i$ where the superscript $o$ refers to the standard state. Therefore, prediction of the solute uptake of the polymer-electrolyte membrane could be achieved by knowing the activities of water and methanol as functions of composition, temperature, and pressure of the solution. For water–methanol mix-

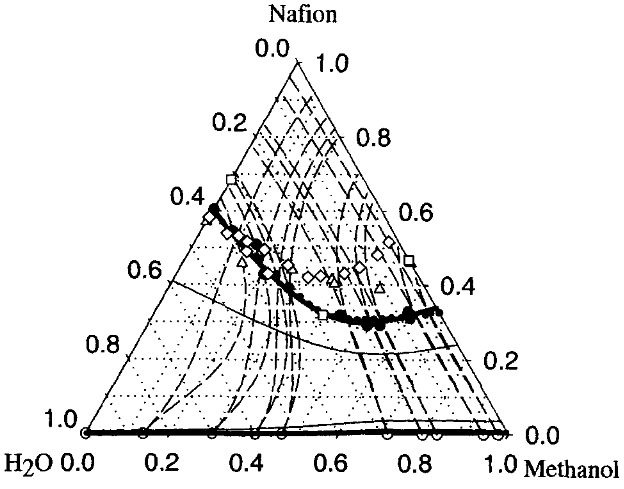

**Figure 4. Ternary diagram (in volume fractions, $z_i$) from first-cycle uptake measurements for the methanol–water–Nafion equilibrium at 298 K.**

Lines represent the fit obtained by the modified Wohl expansion (Eq. 5): thick solid lines are the equilibrium curves; thin solid lines show loci of methanol or water of the spinodal points, and dashed lines show lines of constant activity, both derived from Eq. 5. The dotted line is the fit of the expansion using molalities (Eq. 9). The filled circles show the experimentally determined composition of the membrane phase in equilibrium with the liquid phase (unfilled circles). The unfilled triangles are experimental data from Gates (1998), the unfilled squares are data from Nandan et al. (1992), and the unfilled diamonds are data from Skou et al. (1997).

tures, these functions can be estimated from vapor–liquid equilibrium data found in the literature (Gmehling and Onken, 1977; Hirata et al., 1975), as described by Gates and Newman (2000).

*Modified Wohl Expansion.* Similar to Gates (1998), we use a modified form of the Wohl expansion (the original form of the Wohl expansion uses $x_i$ instead of $z_i$ in the logarithmic term; however, $z_i$ can be independent of the molar masses assumed for the components, a desirable feature when describing polymer solutions) (Wohl, 1946) to describe our phase-equilibrium data:

$$G = \sum_i n_i \mu_i^o + \Re T \sum_i n_i \ln z_i + \frac{1}{2} \sum_i \sum_j A_{ij} n_i q_i z_j + \frac{1}{3} \sum_i \sum_j \sum_k B_{ijk} n_i q_i z_j z_k, \quad (1)$$

with

$$z_i = \frac{x_i q_i}{\sum_l x_l q_l}, \quad (2)$$

where $G$ is the Gibbs energy of a phase, either the liquid phase or the membrane phase, $\mu_i^o$ is the standard-state chemical potential of component $i$, $n_i$ is the number of moles of component $i$, and $x_i$ is the mole fraction of component $i$ in the phase of interest. The $q_i$, $A_{ij}$, and $B_{ijk}$ are fitting parameters that depend on temperature and pressure; the effect of pressure is ignored here. These fitting parameters are for the ternary system; they are the same in both phases. In this work, parameter $q_i$ (values for $q_i$ ar given in Table 1) is set equal to the molar volume of component $i$. The $q_i$ ($= \tilde{M}_i/\rho_i$) are calculated from experimental volumetric data when available; here $\tilde{M}_i$ is molecular or equivalent weight, and $\rho_i$ is density of component $i$. The densities of methanol at 313 and 333 K were estimated by the Hankin-Brobst-Thomson correlation using parameters given by Reid et al. (1987). Because density data for Nafion ($\rho = 1.896$ kg/m$^3$) are available only at 298 K (Nandan et al., 1992), we kept the $q$-value for Nafion constant. The equivalent weight for Nafion is 1100 g/mol.

Equation 1 is a model for the total Gibbs energy $G$ that includes correction terms to account for nonidealities. Therefore, any equation derived from Eq. 1 is thermodynamically consistent. An extensive discussion of Eq. 1 is given elsewhere (Gates and Newman, 2000).

For a ternary system at fixed temperature, seven parameters must be obtained: three $A_{ij}$ and four $B_{ijk}$. Six of them can be evaluated from binary data alone; $B_{123}$, however, requires information on the ternary mixture. Unfortunately, we can obtain only two constants from binary equilibria, because Nafion shows a discontinuity in its uptake behavior between vapor and liquid (Heintz and Stephen, 1994; Gates and Newman, 2000), known in the literature as Schroeder's paradox (Schroeder, 1903). While the origin of this paradox remains unclear, it has often been observed.

**Table 1. Calculated Values of $q_i$**

| Temp. (K) | $q_{\mathrm{MeOH}}$ (cm$^3$/mol) | $q_{\mathrm{H_2O}}$ (cm$^3$/mol) | $q_{\mathrm{Nafion}}$ (cm$^3$/mol) |
|---|---|---|---|
| 298 | 40.77 | 18.07 | 580.2 |
| 313 | 41.70 | 18.16 | 580.2 |
| 333 | 43.04 | 18.32 | 580.2 |

By differentiating Eq. 1 with respect to $n_\alpha$, the chemical potential of component $\alpha$ is

$$\begin{aligned} \mu_\alpha = \mu_\alpha^\circ + \Re T \ln z_\alpha + \Re T \left[ 1 - q_\alpha \frac{\Sigma_j n_j}{\Sigma_l n_l q_l} \right] \\ + \frac{1}{2} q_\alpha \left[ \sum_j A_{\alpha j} z_j + \sum_i A_{i\alpha} z_i + \sum_i \sum_j A_{ij} z_i z_j \right] \\ + \frac{1}{3} q_\alpha \left[ \sum_i \sum_j B_{ij\alpha} z_i z_j + \sum_i \sum_k B_{i\alpha k} z_i z_k + \sum_j \sum_k B_{\alpha jk} z_j z_k \right. \\ \left. - 2 \sum_i \sum_j \sum_k B_{ijk} z_i z_j z_k \right]. \quad (3) \end{aligned}$$

The activity $a_\alpha$ is defined by

$$\mu_\alpha = \mu_\alpha^\circ + \Re T \ln a_\alpha, \quad (4)$$

where $\mu_\alpha^\circ$ is the standard-state chemical potential of component $\alpha$. We set $\mu_\alpha^\circ$ for the membrane phase equal to that for the liquid phase. Equation 3 gives the chemical potential of component $\alpha$ in either phase at the composition $z$ corresponding to the phase.

From Eqs. 3 and 4, the activity coefficient, defined by $\gamma_\alpha = a_\alpha / z_\alpha$, is given by

$$\begin{aligned} \ln \gamma_\alpha = \frac{\Sigma_j n_j (q_j - q_\alpha)}{\Sigma_l n_l q_l} \\ + \frac{1}{2} \frac{q_\alpha}{\Re T} \left[ \sum_j A_{\alpha j} z_j + \sum_i A_{i\alpha} z_i + \sum_i \sum_j A_{ij} z_i z_j \right] \\ + \frac{1}{3} \frac{q_\alpha}{\Re T} \left[ \sum_i \sum_j B_{ij\alpha} z_i z_j + \sum_i \sum_k B_{i\alpha k} z_i z_k \right. \\ \left. + \sum_j \sum_k B_{\alpha jk} z_j z_k - 2 \sum_i \sum_j \sum_k B_{ijk} z_i z_j z_k \right]. \quad (5) \end{aligned}$$

Equation 5 gives the activity coefficient of component $\alpha$ in either phase at the composition $z$ corresponding to that phase. Because we set the standard-state chemical potential of component $\alpha$ in the membrane phase equal to that in the liquid phase, the equation for the liquid–membrane equilibrium becomes

$$z_\alpha^L \gamma_\alpha^L = z_\alpha^S \gamma_\alpha^S, \quad (6)$$

where superscripts $S$ and $L$ refer, respectively to solid (membrane) and to liquid.

*Expansion for Gibbs Energy Using Molalities.* A different, thermodynamically consistent correlation equation was developed by Meyers (1998), giving special attention to the charge on the membrane. Because the derivation is general, Meyer's model can be used to describe the uptake of any species in a

**Table 2. Fitting Parameters of the Expansion Using Molalities**

| Temperature/ Parameters | 1st Cycle | | | 2nd Cycle | | |
|---|---|---|---|---|---|---|
| | 298 K | 313 K | 333 K | 298 K | 313 K | 333 K |
| $E_{11}$ | −13 | −13 | −13 | −13 | −13 | −13 |
| $E_{12}$ | −10 | −8 | −9.5 | −9 | −8.5 | −10 |
| $E_{22}$ | 10 | 12 | 10 | 10 | 10 | 10 |
| $\lambda_1^\theta/\lambda_1^o$ | 85 | 85 | 85 | 85 | 85 | 85 |
| $\lambda_2^\theta/\lambda_2^o$ | 22 | 22 | 22 | 26 | 26 | 26 |

charged membrane, and is applicable as a special case to the uncharged species considered here.

Similar to the equation given by Edwards et al. (1975), we write

$$\frac{G}{\Re T} = n_m \ln(\lambda_m^o) + \sum_{j \neq m} n_j\left[\ln\left(m_j \lambda_j^\theta\right) - 1\right] + \left(n_m \tilde{M}_m\right) \sum_{i \neq m} \sum_{j \neq m} E_{ij} m_i m_j, \quad (7)$$

where $n_j$ is the number of moles of component $j$; $\lambda_m^o$ represents the absolute activity of the pure solvent (membrane) at the system temperature and pressure; $m_j$ is the molality of component $j$; $\lambda_j^\theta$ is the standard-state absolute activity of the solute; $\tilde{M}_m$ is the equivalent weight of the membrane; and the $E_{ij}$ are fitting parameters. Subscript $m$ denotes the component membrane.

Equation 7 contains no Debye-Hückel contribution from electrostatic interactions. As pointed out by Meyers (1998), we can neglect these Debye-Hückel terms because of the large ionic strength of the membrane. The ideal-solution contribution to the Gibbs energy provides the first two terms on the right of Eq. 7. The last term in Eq. 7 is a nonideality correction to the chemical potentials of the solutes. Since $n_i m_j$ is equal to $n_j m_i$, we can set $E_{ij} = E_{ji}$ without loss of generality. For a system with $N$ solutes, there are $\frac{1}{2}N(N+1)$ independent $E_{ij}$.

Differentiating Eq. 7 with respect to $n_\alpha$ gives the chemical potential of component $\alpha$. For the membrane

$$\frac{\mu_m}{\Re T} = \frac{\partial}{\partial n_m}\left(\frac{G}{\Re T}\right) = \ln(\lambda_m^o) - \tilde{M}_m \sum_{i=1}^{N} m_i - \tilde{M}_m \sum_{i=1}^{N} \sum_{j=1}^{N} E_{ij} m_i m_j, \quad (8)$$

and for a solute

$$\frac{\mu_\alpha}{\Re T} = \frac{\partial}{\partial n_\alpha}\left(\frac{G}{\Re T}\right) = \ln\left(m_\alpha \lambda_\alpha^\theta\right) + 2\sum_{j=1}^{N} E_{ij} m_j. \quad (9)$$

Equation 9 is used to describe the measured uptake composition in Nafion.

For a ternary system, Eq. 9 requires five fitting parameters: three $E_{ij}$ parameters ($E_{11}$, $E_{12}$, and $E_{22}$) and two ratios of the standard-state absolute activities of the membrane and of the liquid-phase solutes ($\lambda_1^\theta/\lambda_1^o$ and $\lambda_2^\theta/\lambda_2^o$). The expansion using molalities is not used to describe the liquid phase. The solubility of the membrane in the liquid is neglected, in contrast to the modified Wohl expansion. Table 2 indicates that parameters obtained by fitting Eq. 9 to our phase-equilibrium data for first- and second-cycle uptake are constant over the whole temperature range.

*Discussion and Data Correlation.* For fitting Gibbs-energy parameters to the uptake data, we present the data in a manner different from the usual one where solute molecules per sulfonic acid site are plotted vs. mole fraction, with the assumption of negligible solubility of the membrane in the liquid solution. Here, we consider the membrane as a component of a ternary system. Therefore, we show the data in a triangular diagram for better illustration. Figures 2, 3, and 4 show the fit of the modified Wohl expansion (solid line), Eq. 5, and the fit obtained from the expansion using molalities (dotted line), Eq. 9; measured data, are also shown. In addition, these figures show lines of constant activity (dashed lines), derived from the modified Wohl expansion; these lines provide the composition of the liquid phase that is in equilibrium with the wet membrane. The equilibrium compositions are found from the modified Wohl expansion, where both of the constant-activity lines from the liquid solution intersect in the ternary region of the triangular diagram. The intersection points are plotted in Figures 2, 3, and 4 as two equilibrium curves (thick solid lines). The upper equilibrium curve corresponds to ternary equilibrium when the solutes are absorbed in the membrane. The equilibrium line that runs along the water–methanol base line shows the equilibrium predicted if the membrane is considered to be soluble in the liquid phase. The offset of the calculated intersection points compared with our ternary phase-equilibrium data may be due to slightly imperfect fit.

The region of unconditional instability in the ternary system was calculated using the modified Wohl expansion. This region is enveloped by spinodal points defined as extrema of activities of two components, while the third is held constant. In Figures 2, 3, and 4 the loci of these points are represented by the thin solid lines.

Different from the expansion using molalities, the modified Wohl expansion uses information from binary vapor–liquid equilibrium data. Parameters $A_{12}$ and $B_{112}$ were determined by fitting binary vapor–liquid data found in the literature (Gmehling and Onken, 1977; Hirata et al., 1975) and correlated with the temperature (Figure 5); the binary fit

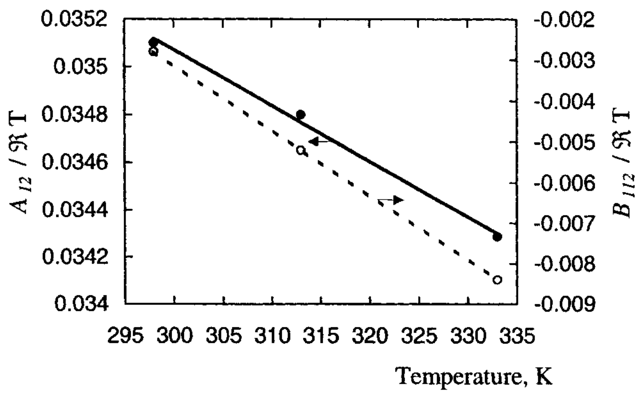

**Figure 5. Correlation of $A_{12}$ and $B_{112}$ with temperature.**

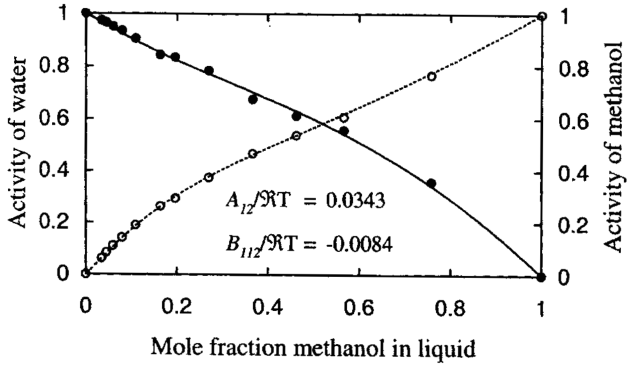

**Figure 6. Vapor-liquid equilibrium activity fit for water (1) – methanol (2) at 333 K; the data are from Hirata et al. (1975). Points are experimental; lines are calculated.**

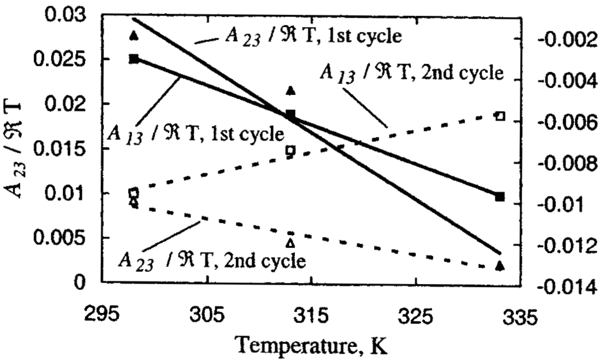

**Figure 7. Effect of temperature on the *A* parameters of the modified Wohl expansion for first- and second-cycle uptake.**

at 333 K is shown in Figure 6. While $A_{12}$ and $B_{112}$ represent the methanol–water binary equilibrium, $A_{13}$ and $B_{113}$ represent the water–membrane binary equilibrium, and $A_{23}$ and $B_{223}$ determine the methanol—membrane binary equilibrium. Parameter $B_{123}$ is the only ternary parameter. Because of Schroeder's paradox, we can obtain only two of the parameters, $A_{12}$ and $B_{112}$, by fitting to binary data. By adjusting the remaining five parameters of Eq. 5 to ternary data, however, our degrees of freedom are restricted because of the pairwise interdependence of the parameters. If $A_{13}$ is changed, $B_{113}$ can be changed to compensate and to yield the same binary point; parameters $A_{23}$ and $B_{223}$ behave in a similar manner. The values obtained for the $A$'s and $B$'s are given in Table 3; they correlate well with temperature, as shown in Figures 7 and 8. All parameters of the modified Wohl expansion can be correlated well with simple linear equations given in Table 4. On the other hand, parameters of the expansion using molalities, obtained by fitting Eq. 9 to our ternary phase-equilibrium data, are constant over the whole temperature range, as shown in Table 2. The parameters of Eq. 9 are summarized in Table 2 for first- and second-cycle uptake for all three temperatures.

As shown in Figures 2, 3, and 4, both Eqs. 5 and 9 can reasonably be adjusted to ternary methanol-water-Nafion data. The quantity and accuracy of our experimental data do not permit us to favor either one of the two expansions. While the parameters of both equations are not assigned any physical meaning, the modified Wohl expansion provides us with information on the region of instability of the ternary system and allows us to calculate the equilibrium curve we expect if the membrane were soluble in the liquid phase. Both models describe our ternary phase-equilibrium data adequately, and neither equation can fit the data better than the other. The parameters of the modified Wohl expansion correlate well with temperature, and the model can cover the entire composition range. However, the model based on molalities has the advantage that its parameters are constant over the entire temperature range. Both models have the same number of parameters that must be estimated from experimental ternary phase-equilibrium data. When using binary vapor–liquid equilibria, five parameters must be estimated from ternary phase equilibria for the modified Wohl expansion as well as for the molality equation.

**Table 3. Fitting Parameters of the Modified Wohl Expansion**

| Temperature/ Parameters | 1st Cycle | | | 2nd Cycle | | |
|---|---|---|---|---|---|---|
| | 298 K | 313 K | 333 K | 298 K | 313 K | 333 K |
| $A_{12}/\Re T$ | 0.0351 | 0.0348 | 0.0343 | 0.0351 | 0.0348 | 0.0343 |
| $A_{13}/\Re T$ | 0.025 | 0.019 | 0.01 | 0.01 | 0.015 | 0.019 |
| $A_{23}/\Re T$ | −0.002 | −0.0046 | −0.013 | −0.01 | −0.012 | −0.013 |
| $B_{112}/\Re T$ | −0.0028 | −0.0052 | −0.0084 | −0.0028 | −0.0052 | −0.0084 |
| $B_{113}/\Re T$ | 0.044 | 0.052 | 0.062 | 0.0642 | 0.057 | 0.048 |
| $B_{223}/\Re T$ | 0.014 | 0.0165 | 0.018 | 0.022 | 0.021 | 0.019 |
| $B_{123}/\Re T$ | 0.004 | 0.0085 | 0.009 | 0.018 | 0.012 | 0.012 |

As shown in Figure 9, for these experimental studies, typical recoveries are usually better than 95%. If 100% represents the total amount of weight decrease between the wet membrane and the dry membrane, the squares in Figure 9 represent the weight loss of the membrane at the end of the first 3-h heating at 378 K compared to the total weight loss

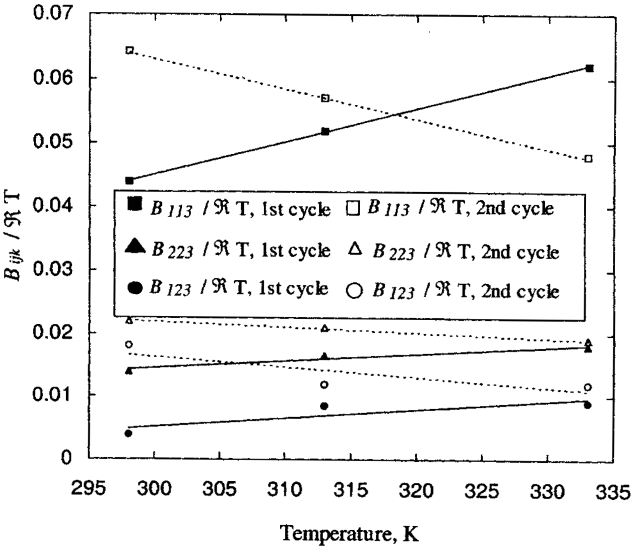

**Figure 8. Effect of temperature on the *B* parameters of the modified Wohl expansion for first- and second-cycle uptake.**

**Table 4. Equations for $A$ and $B$ of the Modified Wohl Expansion Correlated with Temperature**

| Parameter | Equation |
|---|---|
| $A_{13}/\Re T$, 1st cycle | $= -0.0004T + 0.1532$ |
| $A_{13}/\Re T$, 2nd cycle | $= 0.0003T - 0.0653$ |
| $A_{23}/\Re T$, 1st cycle | $= -0.0003T + 0.0942$ |
| $A_{23}/\Re T$, 2nd cycle | $= -8 \cdot 10^{-5}T + 0.0147$ |
| $B_{113}/\Re T$, 1st cycle | $= 0.0005T - 0.1089$ |
| $B_{113}/\Re T$, 2nd cycle | $= -0.0005T + 0.2018$ |
| $B_{223}/\Re T$, 1st cycle | $= 0.0001T - 0.0191$ |
| $B_{223}/\Re T$, 2nd cycle | $= -9 \cdot 10^{-5}T + 0.0479$ |
| $B_{123}/\Re T$, 1st cycle | $= 0.0001T - 0.0358$ |
| $B_{123}/\Re T$, 2nd cycle | $= -0.0002T + 0.065$ |

*Note:* Temperature $T$ is in K.

after an additional 24 h at 378 K; the dots represent the weight of the recovered, condensed solutes (again compared to the total weight loss of the membrane). Figure 9 also shows that almost all of the solutes, typically better than 99%, were evaporated (squares) and that at the end of the 3-h recovery period nearly complete condensation of the vaporized solutes (indicated by the closeness of the squares to the dots) was achieved. Recoveries above 100% are due to weighing errors. Because we assume that the concentration of the uncollected liquid is the same as that collected, we use the weight fraction of methanol and water obtained from the analysis to determine the membrane-phase composition.

Compared with literature data (Gates, 1998; Nandan et al., 1992; Skou et al., 1997), in general, a higher uptake of methanol and water in Nafion could be measured, as shown in Figures 2 and 4. In a triangular diagram our ternary phase equilibria show a shift toward higher solute concentrations in Nafion, as indicated in Figure 2 [compared with the work of Gates (1998) at 333 K, for the first cycle uptake] and Figure 4 [compared with literature data (Skou et al., 1997; Nandan et al., 1992; Gates, 1998)]. In other words, we measured more adsorption of solutes in Nafion due to smaller solute loss in the experiment. Therefore, we believe that our experimental method yields a more accurate measurement of the phase equilibria for water–methanol mixtures in a perfluorosulfonic acid membrane. Consistent with other investigators (Nandan et al., 1992; Gates, 1998), Figure 10 shows that Nafion absorbs more mass in the presence of methanol. At a methanol mole fraction of about 0.65 in the liquid solution, the uptake in Nafion reaches a maximum.

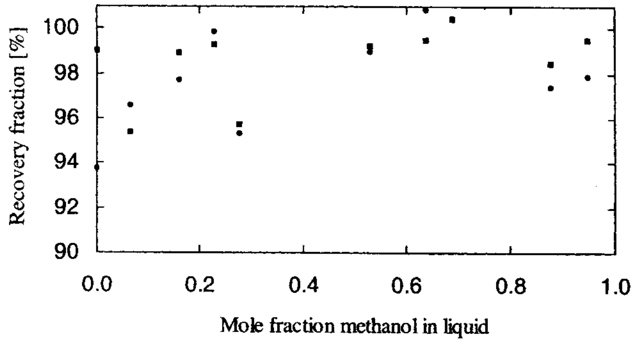

**Figure 9. Recovery fractions of first-cycle-uptake measurements at 298 K.**

The squares show the weight loss of the membrane at the end of the first 3-h heating (compared to the total weight loss after an additional 24 h at 378 K), and the dots represent the weight of recovered, condensed solvents (again compared to the total weight loss of the membrane).

Starting from the maximum, however, production of dimethylether (DME) was observed. Two molecules of methanol produce one molecule of water and one molecule of DME. Thus, the observed maximum in solute uptake in Nafion may be influenced by the appearance of DME. Our use of two-stage heating avoids (as much as practicable) conversion to DME, because DME formation over Nafion strongly depends on temperature (Nunan et al., 1993). While temperature ramping minimized the amount of DME, it could not be eliminated entirely. Accurate measurement of the amount of DME produced could not be obtained because of the volatility of DME. While the septum used for the GC analysis was intended to prevent impurities from the environment, it could not withstand the gas pressure of DME. Therefore, the data presented in Figures 2, 3 and 4 are less accurate for (liquid-phase) methanol mole fractions above 0.65, because at this methanol mole fraction, the presence of DME was first observed. As pointed out by Nunan et al. (1993) DME formation over Nafion is also a strong function of methanol partial pressure. It is likely that above (liquid-phase) 0.65 methanol mole fraction, the measured compositions of the ternary phase equilibria for methanol are slightly too low and for water slightly too high.

Our measurements are subject to some experimental errors due, first, to the assumption that the composition of the recovered liquid is equal to that of the liquid phase absorbed by the membrane, and second, to small analytical errors in measuring compositions and masses.

Drying the membrane's surface is intended to remove surface droplets that would influence the experimental results toward a higher uptake mass and toward the composition of the equilibrating liquid solution. However, drying the surface of the membrane might also lower the uptake of solutes. Squeezing the membrane while surface drying might cause the membrane to lose some of its uptake. Although we dried the surface of the membrane under a nitrogen atmosphere saturated with a methanol–water mixture of the same composition, the membrane loses water and methanol due to Schroeder's paradox. Evaporation of the solutes is higher for methanol because it has a boiling point well below that of

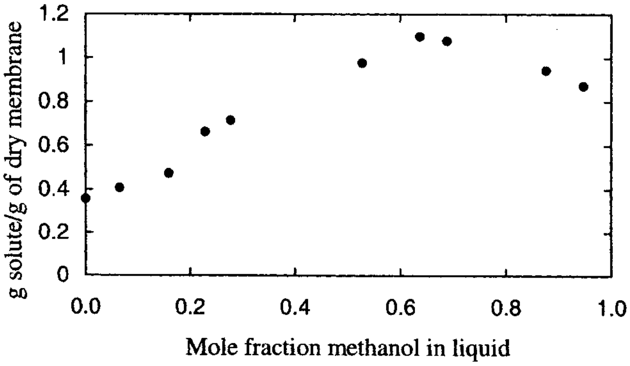

**Figure 10. First-cycle-solute uptake in Nafion 117 for the entire composition range at 298 K.**

water. This preferential evaporation would reduce the measured mass of solutes and influence the experimental data toward a leaner methanol content. While these errors are small, there is no obvious way to estimate them quantitatively.

## Conclusions

The major purpose of this work is to develop a new method for reliable measurement of the uptake of methanol–water solutions in an ion-exchange resin. The new method was demonstrated by measuring the uptake of methanol and water in a Nafion 117 membrane at 298, 313, and 333 K. In addition, the uptake of methanol and water solutions in Nafion in a second cycle was measured. The uptake data are quantitatively described by either of two equations derived from two models for the Gibbs energy of the system, thereby ensuring thermodynamic consistency. The uptake of pure water in Nafion is in the range $z_{H_2O} = 0.40$ at 298 K to $z_{H_2O} = 0.42$ at 333 K. Consistent with reports by previous investigators, we noted an increase in solute solubility in Nafion when methanol is present in the liquid phase. The decrease of the uptake curves at high methanol content in the equilibrating solution may be due to production of dimethyl ether. We could show that, by using surface drying, by minimizing evaporation while weighing the membrane, and by achieving separation exclusively with a thermal gradient, we can obtain better solvent recoveries that yield improved uptake compositions, different from those determined by earlier investigators (Skou et al., 1997; Nandan et al., 1992; Gates and Newman, 2000). A significant temperature dependence of mixed-solvent uptake was not observed, consistent with published water-uptake data reported (Hinatsu et al., 1994).

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## Notation

$a_i$ = activity of component $i$
$A_{ij}$ = parameter of the modified Wohl equation, J/mol
$B_{ijk}$ = parameter of the modified Wohl equation, J/mol
$C$ = number of components
$E_{ij}$ = parameter of the expansion for the Gibbs energy using molalities, kg/mol
$G$ = Gibbs energy, J
$m_i$ = molality of component $i$, mol/kg
$M_i$ = molecular weight of component $i$, g/mol
$M_m$ = equivalent weight of the membrane, g/mol
$n_i$ = number of moles of component $i$, mol
$q_i$ = molar volume of component $i$, cm$^3$/mol
$S$ = number of solutes
$T$ = absolute temperature, K
$x_i$ = mole fraction of component $i$ in the liquid phase
$z_i$ = effective volume fraction defined by Eq. 2
$\Re$ = universal gas constant, 8.3143 J/(mol·K)

### *Greek letters*

$\lambda_i$ = numbers of solute molecules of component $i$ per sulfonic acid site
$\lambda_j^\theta$ = standard-state absolute activity of component $j$, kg/mol
$\lambda_m^o$ = absolute activity of the pure solvent
$\gamma_i$ = activity coefficient of component $i$
$\mu_i$ = chemical potential of component $i$, J/mol
$\rho_i$ = density of component $i$, g/cm$^3$

### *Superscripts and subscripts*

$S$ = membrane phase
$L$ = liquid phase
$o$ = standard state
$m$ = component membrane
$\alpha$ = component $\alpha$

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