

# Solubility and Diffusivity Measurements in Nitrogen–Poly(vinyl acetate) and Nitrogen–Toluene–Poly(vinyl acetate) Systems with the Differential Pressure Decay Technique

Reza Pourdarvish, Ronald P. Danner, J. Larry Duda

*Center for the Study of Polymeric Systems, Department of Chemical Engineering, Pennsylvania State University, University Park, Pennsylvania 16802*

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**ABSTRACT:** In creating thin films of polymers by solution processing, a common problem is the undesirable formation of bubbles during the drying process. Practical experience shows that bubbles can be created well below the boiling point of the solvent. Also, it has been observed that the degassing of the polymer solutions results in reduced bubble formation, and this indicates a relationship between the presence of air and bubble formation. This work is based on the hypothesis that if the solubility of air in the polymer solution increases with the solvent concentration, then the solution can become supersaturated with air as the concentration of the solvent is reduced during the drying process. To test this hypothesis, knowledge of the thermodynamics of the mixture is required. This study concentrated on the system of poly(vinyl acetate), toluene,

and nitrogen. A thermodynamic model to predict phase behavior of this system was developed. The solubility of nitrogen in poly(vinyl acetate) and poly(vinyl acetate)–toluene as a function of the toluene composition over wide ranges of temperatures and pressures was measured with the pressure decay technique. The group-contribution lattice–fluid equation of state was employed to correlate the thermodynamic behavior of the binary and ternary systems. In addition, experiments were conducted to measure the diffusion coefficients of the nitrogen in poly(vinyl acetate). © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 1407–1413, 2008

**Key words:** diffusion; gas permeation; phase behavior; solution properties; thermodynamics

## INTRODUCTION

In the drying of a polymer solution in a convective oven, bubbles can be created in the film. The vapor pressure of the volatile solvent is one of the reasons for bubble nucleation in the polymer–solvent mixture. During the drying process, however, bubbles can also develop and grow well below the boiling point of the solvent. This indicates another mechanism exists for bubble formation.

This project was initiated on the premise that the supersaturation of air (oxygen and nitrogen) in a polymer solution during drying can lead to bubble or blister defects in the resulting coating. The system of poly(vinyl acetate) (PVAc), toluene, and nitrogen was chosen as a test system.

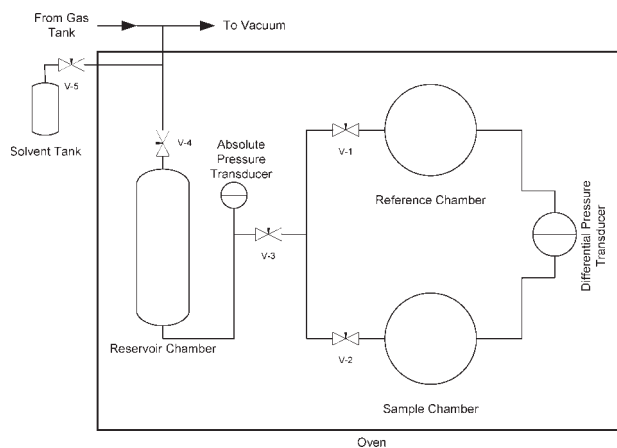
The first step was to determine the vapor–liquid equilibria of the binary and ternary mixtures. The pressure decay method was used to measure the solubility and diffusivity in the PVAc–toluene–nitrogen systems at various temperatures, pressures, and sol-

vent concentrations. With these data, an equation of state model was developed to correlate the nitrogen and toluene solubilities in the polymer.

The pressure decay method is based on the change in pressure of a sealed chamber that contains polymer and gas. As the gas is absorbed into the polymer, the pressure decreases in the chamber, and the pressure drop is recorded as a function of time. The pressure is converted to the mass uptake in the polymer with an equation of state. At equilibrium, the total change of pressure reflects the solubility of gas in the polymer. Monitoring the rate of uptake and using Fick's second law of diffusion provides an evaluation of the binary mutual diffusion coefficient.

Newitt and Weale<sup>1</sup> in 1948 first measured the solubility of gases in a polymer–solvent system using the pressure decay technique. In 1963, Lundberg et al.<sup>2</sup> modified the pressure decay technique to measure both the diffusivity and solubility, but they had a problem in obtaining the initial gas density. Koros and Paul<sup>3</sup> in 1976 introduced a dual-chamber method for polymer–gas systems. They improved the pressure decay method by using a reservoir chamber with known pressure, volume, and temperature to find the initial gas density.

Correspondence to: R. P. Danner (rpd@psu.edu).



**Figure 1** Diagram of the pressure decay apparatus in a forced-air convection oven.

For solvents that have significant solubility in a polymer, the change in absolute pressure can be monitored. In the case of a gas that has very low solubility in the polymer, as nitrogen does, the use of a differential pressure decay method is needed. This approach increases the accuracy of data by measuring the difference in pressure between a reference chamber and a sample chamber that are initially at the same pressure. In this study, a differential pressure decay apparatus was constructed to measure solubility and diffusivity data over wide ranges of pressures and temperatures.

## EXPERIMENTAL

### Apparatus

A diagram of the differential pressure decay apparatus is shown in Figure 1. This apparatus included three main parts: a reservoir, a reference chamber, and a sample chamber, all of which were stainless steel. The design of the sample and reference chambers incorporated minimum headspace and reduction of potential leak sources. The absolute pressure transducer (PO53H series, UE Trans-Metric, Watertown, MA) was operated at pressures up to 13.8 MPa and temperatures up to 500 K. This transducer measured the absolute pressure in the reservoir chamber. The differential pressure transducer (OMEGA, Inc., Stamford, CT) measured the pressure difference between the sample and reference chambers and operated at pressures up to 6.9 MPa and temperatures up to 350 K. Two thermocouple sensors that were mounted inside the caps of the chambers monitored the temperature in the headspace of both the sample and reference chambers.

All parts of the apparatus were placed in a forced-air convection oven. This oven included four 400-W heating strips and two circulation fans. The temperature was controlled by a microprocessor-based pro-

portional-integral-derivative (PID) controller using an Omega RTD thermocouple sensor. A vacuum system was used to degas the system. For binary measurements, the gas (e.g., nitrogen) was brought to the desired pressure in the reservoir. For ternary measurements, the solvent tank, which was maintained at a controlled temperature, was connected to the reservoir chamber to establish the solvent equilibrium vapor pressure in the reservoir. The temperature, absolute pressure, and differential pressure were acquired with a data acquisition system.

Experiments were conducted first by degassing of the sample for several hours (depending on the thickness of the polymer) to remove any residual gases in the sample at the temperature of the experiment (valves 1–4 were open; see Fig. 1). Then, upon the closing of valve 3, the gas of interest flowed into the reservoir chamber to the desired pressure. After a steady temperature was achieved, opening valve 3 allowed the gas to expand into the sample and reference chambers, and data acquisition was started. After a short interval, valves 1 and 2 were closed. The differential and absolute pressure transducers determined the pressure in the sample chamber as a function of time. When equilibrium was reached, data acquisition ceased, and this completed the experiment. The experimental procedure for the ternary system was more complicated and is described in detail in a later section.

### Materials

In this study, the solubility and diffusivity of nitrogen and carbon dioxide were measured in PVAc. Ultrahigh-purity-grade nitrogen (99.9995%) and Coleman-grade carbon dioxide (99.9%) were used. The samples were PVAc with a molecular weight of 90,000 g/mol, which was solvent-cast into flat disks with toluene.

### Data analysis

#### Diffusion coefficient measurement

The data acquisition compiled the temperature and differential pressure versus time. The volumes of the chambers were obtained by the measurement of the amount of gas expanded from a known capsule volume.<sup>4</sup> Subtracting the volume of the sample at the experimental temperature from the volume of the sample chamber resulted in the volume of headspace. The sample volume was determined from its mass and density. The Benedict–Webb–Rubin (BWR) equation of state<sup>5</sup> was used to calculate the mass of gas in the headspace at any time:

$$P = \frac{RT}{v} + \left( B_0 RT - A_0 - \frac{C_0}{T_2} \right) \frac{1}{v^2} + (bRT - a) \frac{1}{v^3} + \frac{a\alpha}{v^6} + \frac{c}{T^2 v^3} \left[ \left( 1 + \frac{\gamma}{v^2} \right) \exp \left( -\frac{\gamma}{v^2} \right) \right] \quad (1)$$

**TABLE I**  
**BWR Parameters for Nitrogen and Carbon Dioxide<sup>6</sup>**

BWR parameter	Nitrogen	Carbon dioxide
$A_0$	120,835.5	277,379.8
$B_0$	$4.579973 \times 10^{-2}$	$4.991091 \times 10^{-2}$
$C_0$	596,737,100	$140,408 \times 10^5$
$a$	1,509.846	13,863.44
$b$	$1.981615 \times 10^{-3}$	$4.12407 \times 10^{-3}$
$c$	55,536,280	$151,165 \times 10^4$
$\alpha$	$2.91564 \times 10^{-4}$	$8.46675 \times 10^{-5}$
$\gamma$	$7.500286 \times 10^{-3}$	$5.393795 \times 10^{-3}$

Pressures are presented in pascals, volumes are presented in cubic meters per killimole, and temperatures are presented in kelvins.

where  $P$ ,  $T$ , and  $v$  are the pressure, temperature, and molar volume of the gas, respectively. The parameters  $a$ ,  $b$ ,  $c$ ,  $A_0$ ,  $B_0$ ,  $C_0$ ,  $\alpha$ , and  $\gamma$  are empirical constants found from the correlation of pressure–volume–temperature data. The parameters of the BWR equation for nitrogen and carbon dioxide are given in Table I.

The diffusion coefficient can be found by the fitting of the experimental mass uptake curve to the theoretical model. The Fickian one-dimensional species continuity equation for diffusion through a slab with constant thickness is

$$\frac{\partial \rho}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial \rho}{\partial x} \right) \quad (2)$$

where  $\rho$  is the mass concentration of the gas in the polymer,  $D$  is the mutual diffusion coefficient,  $x$  is the direction of diffusion, and  $t$  is the time. In this research, the temperature was above the glass-transition temperature, and the mutual diffusion coefficient was assumed to be constant. Because of the low solubility of the gases in this study, the concentration in the gas phase (i.e., the pressure) can be considered to be constant and the polymer swelling to be negligible. The initial and boundary conditions are as follows:

$$\rho = 0 \quad 0 \leq x \leq L \quad t = 0 \quad (3)$$

$$\rho = \rho^* \quad x = L \quad t > 0 \quad (4)$$

$$\frac{\partial \rho}{\partial x} = 0 \quad x = 0 \quad t > 0 \quad (5)$$

where  $L$  is the film thickness and  $\rho^*$  is the mass concentration of the gas at equilibrium in the polymer. An analytical solution using these conditions was given by Crank:<sup>6</sup>

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(\frac{-D(2n+1)^2 \pi^2 t}{L^2}\right) \quad (6)$$

where  $M_t$  is the total mass of gas uptake in the polymer at any time  $t$  and  $M_\infty$  is the mass of gas uptake in the polymer at equilibrium. A regression program was used to obtain the mutual diffusion coefficients by minimization of the deviation between the equation and the experiment over the entire range of data.

### Solubility measurement

The uptake curve yielded the solubility of the gas in the polymer at equilibrium:

$$S = \frac{M_\infty}{M_p + M_\infty} \quad (7)$$

where solubility  $S$  is the weight fraction of gas in the polymer and  $M_p$  is the mass of the polymer sample.

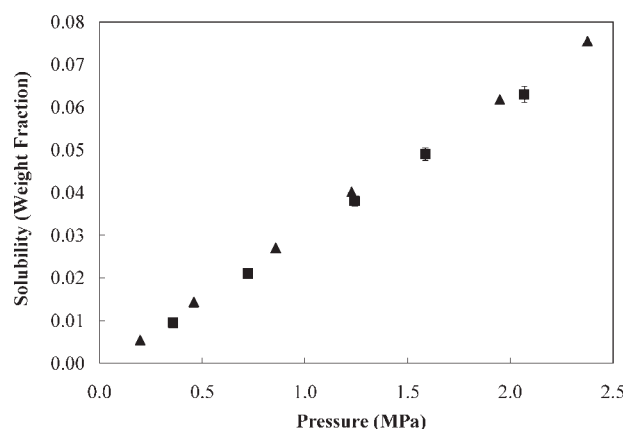
### Panayiotou and Vera equation of state

The Panayiotou–Vera equation of state, based on lattice–fluid theory,<sup>7</sup> was used to correlate the solubility data:

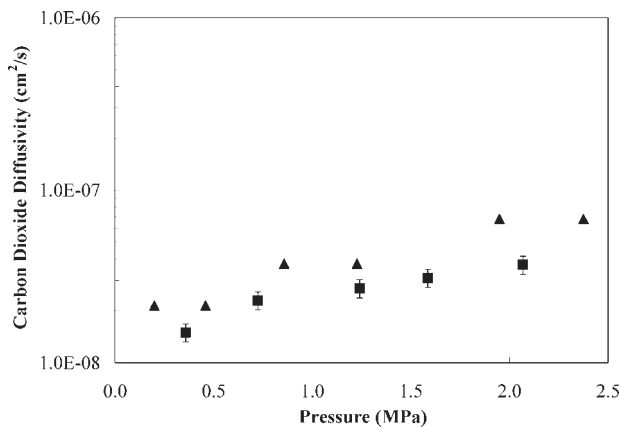
$$\frac{\tilde{P}}{\tilde{T}} = \ln\left(\frac{\tilde{v}}{\tilde{v}-1}\right) + \frac{z}{2} \ln\left(\frac{\tilde{v} + (q/r) - 1}{\tilde{v}}\right) - \frac{\theta^2}{\tilde{T}} \quad (8)$$

$q$  is the surface area parameter,  $r$  is the number of occupied lattice sites,  $z$  is the coordination number (=10), and  $\theta$  is the molecular surface area fraction. Where  $\tilde{T}$ ,  $\tilde{P}$ , and  $\tilde{v}$  are the reduced temperature, pressure, and molar volume, respectively. To apply this equation of state, it is necessary to determine two pure-component parameters— $\varepsilon_{ii}$ , the interaction energy between like molecules, and  $v_i^*$ , the hard core volume of molecule  $i$ —and a binary interaction term between each pair of molecules ( $k_{ij}$ ).

Lee and Danner<sup>8</sup> developed groups to predict the parameters in the Panayiotou–Vera equation: the group-contribution lattice–fluid equation of state



**Figure 2** Solubility of carbon dioxide in PVAc at 313 K. (■) The pressure decay data are compared with (▲) the magnetic suspension balance technique of Sato et al.<sup>9</sup>



**Figure 3** Diffusion coefficients of carbon dioxide in PVAc at 313 K. (■) The pressure decay data are compared with (▲) the magnetic suspension balance technique of Sato et al.<sup>9</sup>

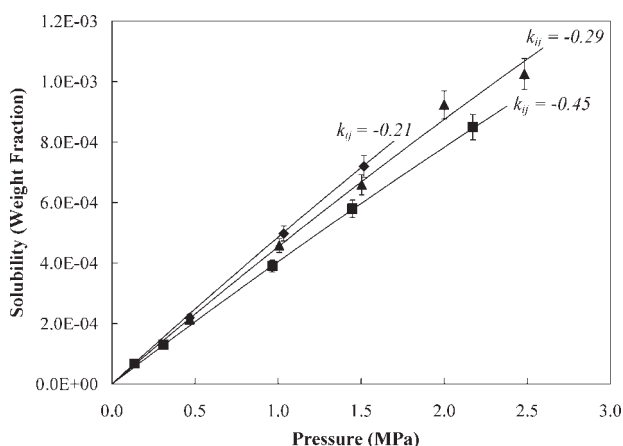
(GCLF-EoS). The two pure-component parameters are calculated as follows:

$$\varepsilon_{ii} = \sum_k \sum_m \Theta_k^{(i)} \Theta_m^{(i)} (e_{kk} e_{mm})^{1/2} \quad (9)$$

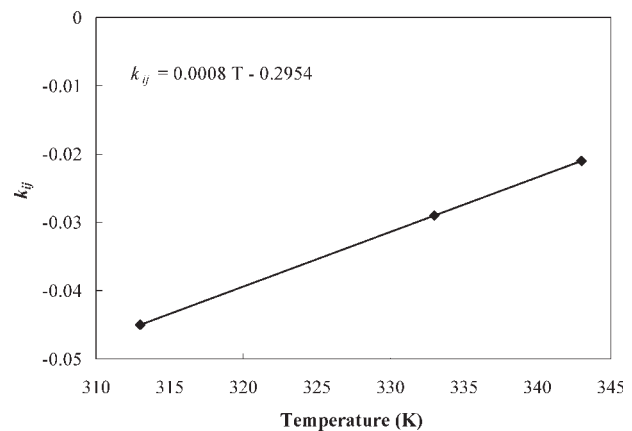
$$v_i^* = \sum_k n_k^{(i)} R_k \quad (10)$$

where  $\Theta_k^{(i)}$  is the group surface area fraction and  $n_k^{(i)}$  is the number of group  $k$  in component  $i$ .  $e_{kk}$  and  $R_k$  are the interaction energy and reference volume parameters of group  $k$ , respectively, and were determined by regression of the experimental vapor pressure and saturated liquid data. These parameters are quadratic functions of temperature.

In this work, the GCLF-EoS was used to correlate the vapor–liquid equilibria of the nitrogen–PVAc and toluene–PVAc binary systems and the nitrogen–



**Figure 4** Solubility data for the nitrogen–PVAc system at (■) 313, (▲) 333, and (◆) 343 K. The lines are for the GCLF-EoS fits.



**Figure 5** Temperature dependence of interaction parameter  $k_{ij}$  for the nitrogen–PVAc system.

toluene–PVAc ternary system. The  $k_{ij}$  parameters were not predicted from the groups but rather were determined by regression of the experimental data.

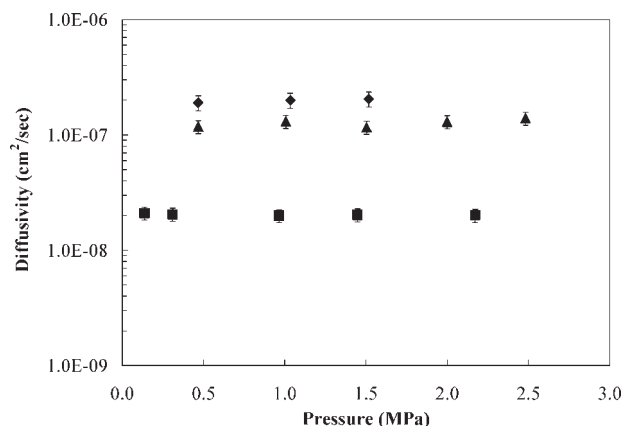
## RESULTS AND DISCUSSION

Experimental solubility and diffusivity for carbon dioxide in PVAc over ranges of temperatures and pressures were obtained to compare the pressure decay method with existing techniques in the literature. Figures 2 and 3 compare experimental data obtained in this study by pressure decay with those reported by Sato et al.<sup>9</sup> using a magnetic suspension balance. The comparison indicates excellent agreement between the two sets of data for solubility. The diffusion coefficient data obtained by the pressure decay technique, however, were slightly lower overall than those obtained from the magnetic suspension balance. This is most likely a result of the sensitivity of the diffusion coefficient to the thickness of the sample.

**TABLE II**  
GCLF-EoS Parameters  $\varepsilon_{ii}$  and  $v_i^*$

Temperature (313 K)	Nitrogen	PVAc
313 K		
— $\varepsilon_{ii}$ (J/mol)	368.94	1129.2
— $v_i^*$ (m <sup>3</sup> /kmol)	$6.819 \times 10^{-5}$	0.7695
— $k_{ij}$		−0.045
333 K		
— $\varepsilon_{ii}$ (J/mol)	402.45	1131.3
— $v_i^*$ (m <sup>3</sup> /kmol)	$7.260 \times 10^{-5}$	0.7700
— $k_{ij}$		−0.029
343 K		
— $\varepsilon_{ii}$ (J/mol)	420.0	1133.4
— $v_i^*$ (m <sup>3</sup> /kmol)	$4.490 \times 10^{-5}$	0.7698
— $k_{ij}$		−0.021

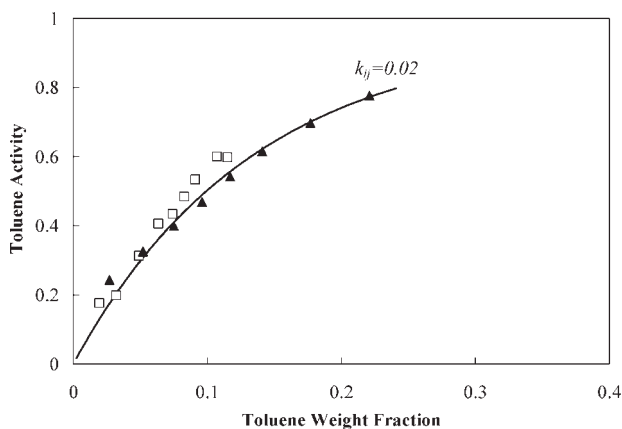
Interaction parameter  $k_{ij}$  was found by fitting.



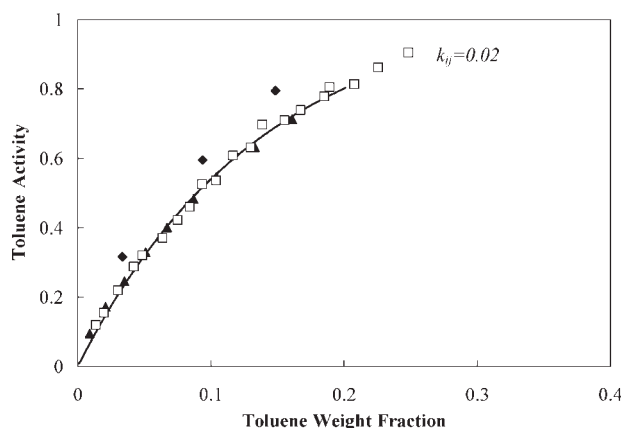
**Figure 6** Mutual diffusion coefficients in the nitrogen-PVAc system at (■) 313, (▲) 333, and (◆) 343 K.

### Phase equilibria in the PVAc–nitrogen system

The experimental solubility data for nitrogen in PVAc at 313, 333, and 343 K as a function of pressure are shown in Figure 4. Note that these solubilities are in the range of  $10^{-3}$  to  $10^{-4}$  weight fractions. The binary interaction parameters ( $k_{ij}$ ), obtained by the fitting of the experimental data with the GCLF-EoS, are negative for the nitrogen-PVAc system. These negative values do not have any physical meaning. Figure 5 shows that there is a linear relationship between  $k_{ij}$  and temperature. This linearity can be useful for the interpolation and extrapolation of solubility with temperature. Sato and coworkers<sup>9,10</sup> correlated the experimental solubility of carbon dioxide in PVAc and polystyrene using the Sanchez-Lacombe equation of state. They obtained negative interaction parameters also. The experimental data show that unlike most gases, the solubility of nitrogen increases as the temperature increases.



**Figure 7** Activity data for the PVAc-toluene system at 313 K. The solid line shows the GCLF-EoS correlation. Experimental data were collected with different techniques: (□) the magnetic suspension balance technique<sup>12</sup> and (▲) the quartz sorption technique.<sup>13</sup>



**Figure 8** Activity data for the PVAc-toluene system at 333 K. The solid line shows the GCLF-EoS correlation. Experimental data were collected with different techniques: (◆) the gravimetric sorption technique,<sup>11</sup> (□) the magnetic suspension balance technique,<sup>12</sup> and (▲) the quartz sorption technique.<sup>13</sup>

As shown in Figure 4, the GCLF-EoS gave very good correlations with the experimental data for the nitrogen-PVAc system. The interaction parameters were independent of the nitrogen concentration and only a function of temperature. Table II lists the group-contribution parameters of the GCLF-EoS at 313, 333, and 343 K.

The mutual diffusivity coefficients for the nitrogen-PVAc system at different temperatures and pressures are shown in Figure 6. In this system, the diffusivity data were independent of the gas concentration. This result was expected because the temperatures of the experiments were above the glass transition, the solubility data of nitrogen in PVAc were very low, and there was a lot of free volume in PVAc for the small gas molecules.

### Phase equilibria in the PVAc-toluene system

Experimental data from a variety of techniques have been reported in the literature for the PVAc-toluene system: gravimetric sorption (Hou<sup>11</sup>), magnetic suspension balance (Mamaliga and Schabel<sup>12</sup>), and pie-

**TABLE III**  
GCLF-EoS Parameters  $\epsilon_{ii}$  and  $v_i^*$

Temperature	Toluene	PVAc
313 K		
— $\epsilon_{ii}$ (J/mol)	993.3	1129.2
— $v_i^*$ (m <sup>3</sup> /kmol)	$9.743 \times 10^{-5}$	0.7695
— $k_{ij}$		0.02
333 K		
— $\epsilon_{ii}$ (J/mol)	993.72	1131.3
— $v_i^*$ (m <sup>3</sup> /kmol)	$9.781 \times 10^{-5}$	0.7700
— $k_{ij}$		0.02

Interaction parameter  $k_{ij}$  was found by fitting.

TABLE IV  
Procedure for the Determination of  $k_{ij}$  for Nitrogen–Toluene

Step 1	Use GCLF-EoS to determine the pressure of toluene in the toluene–PVAc binary mixture with the fixed toluene concentration in the liquid phase
Step 2	Make an initial guess for $k_{ij}$ of nitrogen–toluene (usually 0)
Step 3	Use this value of $k_{ij}$ to determine the partial pressure of toluene and solubilities with the fixed toluene concentration when the toluene–PVAc mixture is pressurized with nitrogen
Step 4	Determine the enhancement of toluene pressure in the gas phase ( $\Delta P_{\text{Toluene}}$ ) from differences between the pressures of toluene in steps 3 and 1
Step 5	Obtain the actual nitrogen pressure drop due to absorption in the mixture from $\Delta P_{\text{N}_2} = \Delta P_{\text{Exp}} - \Delta P_{\text{Toluene}}$
Step 6	Estimate the solubility of nitrogen with $\Delta P_{\text{N}_2}$ in the BWR equation of state
Step 7	Calculate the error between solubilities determined in steps 3 and 6
Step 8	Adjust $k_{ij}$ for nitrogen–toluene and return to step 3

zoelectric–quartz sorption (Wimbawa et al.<sup>13</sup>). Figures 7 and 8 illustrate the capability of the GCLF-EoS to correlate the activity of toluene in PVAc at 313 and 333 K. Binary interaction parameter  $k_{ij}$  was determined to be 0.02 for both temperatures. The GCLF-EoS provided excellent correlations of the data.  $k_{ij}$  was found to be independent of the temperature and concentration. Table III lists the group-contribution parameters of the GCLF-EoS for the toluene–PVAc system at 313 and 333 K. All parameters are essentially independent of the temperature.

#### Phase equilibria in the PVAc–toluene–nitrogen system

The experimental procedure used to measure the solubility data of nitrogen in the PVAc–toluene–nitrogen ternary system was different than that used in the binary system. First, the sample was degassed for several hours, and the solvent chamber was kept at a fixed temperature and activity to achieve the desired liquid phase composition. Then, valve 5 was opened (valves 1–4 were opened). Therefore, the solvent was introduced into the polymer, which had been coated on several pans until equilibrium was reached. After the polymer phase was fixed with a certain solvent concentration, valves 3 and 5 were closed, and all solvent was evacuated from the reservoir chamber. The second step was to introduce nitrogen with the desired pressure to the reservoir chamber. Then, valve 3 was opened, and nitrogen expanded to the sample and reference chamber. After a short interval, valves 1 and 2 were closed, and the experiment began. However, because the nitrogen absorbing into the polymer solution during the transient stage of the experiment could influence the solubility of the solvent, the gas phase pressure change was due to a complex coupling of gas absorption and a redistribution of the solvent between the polymer solution and the gas phase. Consequently, the transient stage of the experiment could not be used to obtain accurate diffusivity data. Also, the measurement of the solubility of nitrogen in the ternary system had to be corrected.

The partial pressure of toluene in the experiment increases because of the high pressure of nitrogen on top of the PVAc–toluene solution. This means that, during the experiment, nitrogen diffuses in and toluene diffuses out. Thus, the change in pressure from data acquisition is not the actual change of pressure of nitrogen and should be corrected as follows:

$$\Delta P_{\text{N}_2} = \Delta P_{\text{Exp}} + \Delta P_{\text{Toluene}} \quad (11)$$

where  $\Delta P_{\text{Exp}}$  is the change of pressure in the experiment obtained from data acquisition and  $\Delta P_{\text{Toluene}}$  is the change of pressure of toluene due to the influence of nitrogen in the polymer phase. The GCLF-EoS correlation was used to estimate  $\Delta P_{\text{Toluene}}$ . This required knowledge of all interaction parameters. As described earlier, these were determined for nitrogen–PVAc and toluene–PVAc. However,  $k_{ij}$  for nitrogen–toluene was unknown. An iterative procedure was adopted to determine an optimized value of this parameter and hence the solubility of nitrogen in the mixture. Table IV shows this iterative procedure. Steps 2–6 are repeated until the GCLF-EoS solubility

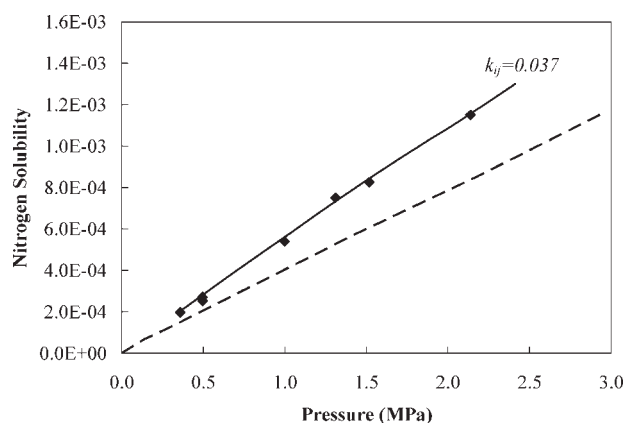
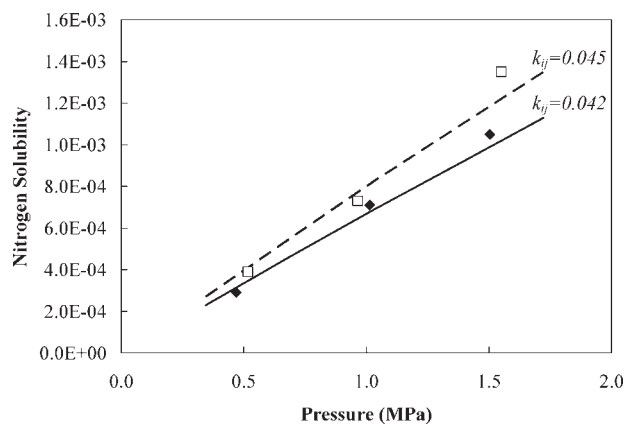


Figure 9 Pressure decay data of nitrogen in the PVAc–toluene mixture at 313 K when the concentration of toluene in the liquid phase was 20 wt %. The solid line is the GCLF-EoS correlation. The dashed line is the solubility of nitrogen in pure PVAc.



**Figure 10** Solubility data of nitrogen in the PVAc-toluene mixture at 333 and 343 K when the concentration of toluene in the liquid phase was 18 wt %. The solid and dashed lines are the GCLF-EoS correlations. The experimental data from the pressure decay technique at (◆) 333 and (□) 343 K are given.

matches the experimental solubility data. The interaction parameter of toluene-nitrogen was determined to be 0.037.

Figure 9 shows the solubility of nitrogen in the PVAc-toluene-nitrogen system at 313 K when the weight fraction of toluene in the liquid phase was fixed at 20 wt %. This figure compares the ternary experimental data with the GCLF-EoS correlation and the experimental data for the PVAc-nitrogen binary system.

The solubility of nitrogen in the toluene-PVAc system when the toluene concentration was fixed at 18 wt % at 333 and 343 K is shown in Figure 10. The binary interaction parameters for nitrogen-toluene were obtained with the iterative procedure. These values were 0.042 and 0.045 at 333 and 343 K, respectively. The GCLF-EoS provided good correlations of the experimental data.

## CONCLUSIONS

The pressure decay technique was used to obtain the solubility of nitrogen in PVAc and in the PVAc-toluene system. Solubility and diffusivity data of nitrogen in PVAc and solubility data of nitrogen in the PVAc-toluene system were obtained at 313, 333, and 343 K over a wide range of pressures. The GCLF-EoS, based on the Panayiotou-Vera equation of state, provided excellent correlation with experimental solubility data as a function of temperature and pressure. The correlated GCLF-EoS could be used to predict the phase behavior of this mixture. In particular, it could be used to analyze if and when supersaturation of the nitrogen might occur during the drying of a PVAc film. This will be applied in a future publication.

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