Supplementary data

Analyzing solubility and diffusion of solvents in novel hybrid materials of poly (vinyl alcohol)/γ-aminopropyltriethoxysilane by IGC

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Part A: Calculation of solubility properties

Determination of the solubility of a solute based on IGC method depends on the measurement of retention times, $t_R$ (min), of the solute flowing through a column packed with the polymer of interest. The $t_R$ is related to the specific retention volume, $V_g$ (cm$^3$/g), by

$$V_g = (t_R - t_M) F_0 \frac{273.2}{W_p T_{col}}$$

(1)

where $t_M$ (min) is the retention time of a ‘non-sorbed’ component (air in this study), $F_0$ (cm$^3$/min) is the flow rate of gas carrier, $W_p$ (g) is the mass of the polymer packed in the column, and $T_{col}$ (K) is the column temperature. $j$ is the pressure drop correction factor determined by

$$j = \frac{3 \left( \frac{P_{in}}{P_{out}} \right)^2 - 1}{2 \left( \frac{P_{in}}{P_{out}} \right)^3 - 1}$$

(2)

where $P_{in}$ and $P_{out}$ are the inlet and outlet pressures of the column, respectively.

Then, the value of various thermodynamic quantities can be obtained through $V_g$. Thus, infinite dilution activity coefficient $\Omega_i^\infty$ can be determined by

$$\ln \Omega_i^\infty = \ln \left( \frac{273.2 R}{V_g p_i^0 M_i} \right) - \frac{p_i^0}{RT_{col}} (B_1 - V_g)$$

(3)

where $p_i^0$ (pa) is the vapor pressure of a solute at temperature $T_{col}$, $M_i$ (g/mol) is the solute molecular mass,
$B_{11}$ is the second virial coefficient, and $V_1$ (cm$^3$/mol) is the solute molar volume. The second term in the right of this equation is the correction for non-ideality of the solute.

Based on the activity coefficient, the partial molar excess free energy of mixture at infinite dilution, $\Delta G_m$, can be calculated by

$$\Delta G_m = RT \ln \Omega_1^\infty$$  \hspace{1cm} (4)

The infinite dilution solubility coefficient, $S$, can be determined from the following equation by taking into account non-ideal gas behavior of vapor phase.

$$S = V_g \frac{\rho}{p_o} \exp \left[ (2B_{11} - V_1) \left( \frac{p_o}{RT} \right) \right]$$  \hspace{1cm} (5)

where $p_o$ is the standard pressure (1 atm), and $\rho$ (g/cm$^3$) is the density of polymer at temperature $T_{col}$.

The Flory–Huggins interaction parameter at infinite dilution $\chi_{12}^\infty$, which was used as a measure of the strength of interaction, is a guide in the prediction of the compatibility between a polymer and a solvent. And it can be obtained by the following equation related to $\Omega_1^\infty$

$$\chi_{12}^\infty = \ln \Omega_1^\infty - (1 - \frac{1}{r}) + \ln \frac{\rho_1}{\rho_2}$$  \hspace{1cm} (6)

where $r$ is the molar volume ratio of solute to polymer given by

$$r = \frac{\rho_1 M_2}{\rho_2 M_1}$$  \hspace{1cm} (7)

where, $\rho_1$ and $\rho_2$ is the density of solute and polymer (g/cm$^3$), $M_1$ and $M_2$ is the molecular weight of solute and polymer, respectively (g/mol).

**Part B: Calculation of diffusion properties**

According to Van Deemter’s model $^{33}$, infinite dilution diffusion coefficient $D^\infty$ is of the form
\[ D^m = \frac{8d_p^2}{\pi^2 C} \left[ \frac{k}{(1+k)^2} \right] \]  

where \( d_p \) (m) is the thickness of the polymer coated on the support material in the column, \( C \) is a parameter related to the column characteristics, \( k \) is the partition ratio given by

\[ k = \frac{t_R - t_M}{t_M} \]  

The thickness of the polymer coated on the support material \( d_p \) is calculated from the equation

\[ d_p = \frac{W_p \rho_d d_d}{3 \rho_p W_d} \]  

where \( \rho_p \) and \( \rho_d \) are the density of the polymer and the support material (g/cm\(^3\)), \( W_p \) is the mass of the polymer on the support material, \( W_d \) (g) and \( d_d \) (m) are the mass and the average diameter of the support material in the column, respectively.

From Plate theory \(^3\), the height equivalent to a theoretical plate \( H \) (m) is determined by

\[ H = A + \frac{B}{u} + Cu = L / n \]  

where \( u \) (m/s) is the linear velocity of carrier gas, \( L \) (m) is the length of column, \( A, B \) and \( C \) are constants independent of carrier gas flow rate, \( n \) is the number of theoretical plate determined by

\[ n = 5.54 \left( \frac{t_R}{W_{1/2}} \right)^2 \]  

where \( W_{1/2} \) (min) is the full peak width at half-maximum. \( u \) is calculated by

\[ u = j \frac{F_0 T_{col}}{a T_{flow}} \]  

where \( T_{flow} \) (K) is the temperature of the flowmeter, \( a \) (m\(^3\)/m) is the volume of gas-phase per unit length.

\( C \) is derived from equation (11) in conjunction with equations (12) and (13). The term \( B/u \) becomes small and can be negligible in relation to \( A + Cu \) at sufficiently high flow rates. Then the plot of \( H \) vs. \( u \) yields a straight line with slope \( C \).
Tables

Table S1 Parameters of the columns packed with the hybrid materials with various APTEOS contents

<table>
<thead>
<tr>
<th></th>
<th>PVA</th>
<th>PA-2.5</th>
<th>PA-5.0</th>
<th>PA-7.5</th>
<th>PA-10.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>$W_p$ (g)</td>
<td>0.472</td>
<td>0.397</td>
<td>0.401</td>
<td>0.431</td>
<td>0.422</td>
</tr>
<tr>
<td>$d_p$ (m)</td>
<td>4.36×10^{-6}</td>
<td>4.29×10^{-6}</td>
<td>4.24×10^{-6}</td>
<td>4.19×10^{-6}</td>
<td>4.16×10^{-6}</td>
</tr>
<tr>
<td>$\rho_p$ (g/cm$^3$)</td>
<td>1.325</td>
<td>1.347</td>
<td>1.361</td>
<td>1.378</td>
<td>1.391</td>
</tr>
</tbody>
</table>

$W_p$ (g) is the mass of the polymer packed in the column, $d_p$ (m) is the thickness of the polymer coated on the support material in the column, $\rho_p$ is the density of the PVA hybrid materials (g/cm$^3$).

Figures
Fig. S1 Effects of APTEOS content (a) and column temperature (b) on the partial molar excess free energy of mixture $\Delta G_m$ of hybrid material-solvent (1 water; 2 methanol; 3 ethanol; 4 isopropanol; 5 cyclohexane; 6 benzene)

Fig. S2 Temperature dependences of the solubility coefficients of solvents $S$ in PA-5.0 (1 water; 2 methanol; 3 ethanol; 4 isopropanol; 5 cyclohexane; 6 benzene)
**Fig. S3** Temperature dependences of the interaction parameters of PA-5.0-solvent pairs $\chi_{12}^\infty$ (1 water; 2 methanol; 3 ethanol; 4 isopropanol; 5 cyclohexane; 6 benzene)

**Fig. S4** Relationship of the height equivalent to a theoretical plate $H$ with the linear velocity of carrier gas $u$ in column PA-5.0 at 378.15 K (1 water; 2 methanol; 3 ethanol; 4 isopropanol; 5 cyclohexane; 6 benzene)
Fig. S5 Arrhenius plots for the infinite dilution diffusion coefficients of solvents in the hybrid materials PA-5.0 (1 water; 2 methanol; 3 ethanol; 4 isopropanol; 5 cyclohexane; 6 benzene)