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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

$$V_g = (t_R - t_M) j F_0 \frac{273.2}{W_p T_{col}} \tag{1}$$

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

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

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 Ω_1^∞ can be determined by

$$\ln \Omega_1^\infty = \ln\left(\frac{273.2R}{V_g p_1^o M_1}\right) - \frac{p_1^o}{RT_{col}}(B_{11} - V_1) \tag{3}$$

where p_1^o (pa) is the vapor pressure of a solute at temperature T_{col}, M_1 (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, ΔG_m, can be calculated by

$$\Delta G_m = RT \ln \Omega_1^\infty \tag{4}$$

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

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

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

The Flory–Huggins interaction parameter at infinite dilution χ_{12}^∞, 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 Ω_1^∞

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

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

$$r = \frac{\rho_1 M_2}{\rho_2 M_1} \tag{7}$$

where, ρ_1 and ρ_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^∞ is of the form

$$D^{\infty} = \frac{8d_p^2}{\pi^2 C}\left[\frac{k}{(1+k)^2}\right] \tag{8}$$

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

$$k = \frac{t_R - t_M}{t_M} \tag{9}$$

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

$$d_p = \frac{W_p \rho_d d_d}{3\rho_p W_d} \tag{10}$$

where ρ_p and ρ_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 [33], the height equivalent to a theoretical plate H (m) is determined by

$$H = A + \frac{B}{u} + Cu = L/n \tag{11}$$

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

$$n = 5.54\left(\frac{t_R}{W_{1/2}}\right)^2 \tag{12}$$

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

$$u = j\frac{F_0}{a}\frac{T_{col}}{T_{flow}} \tag{13}$$

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*.

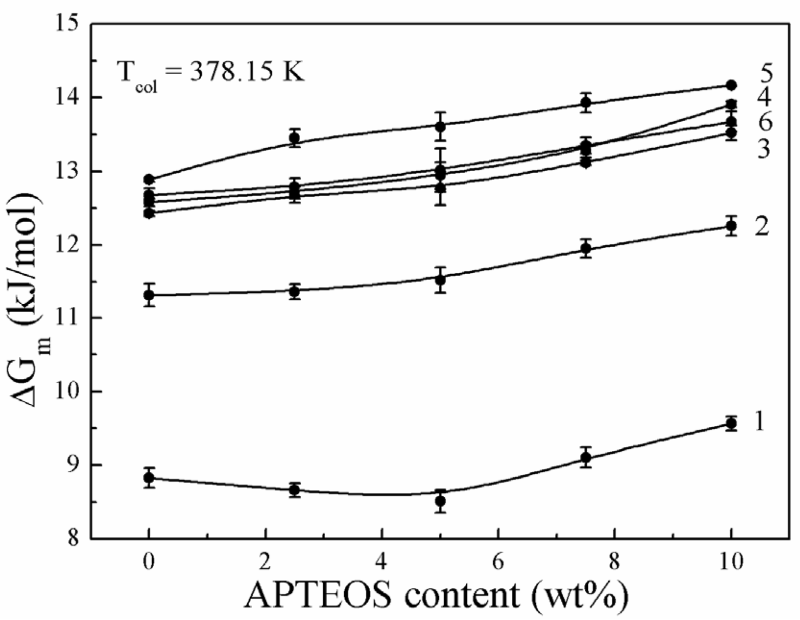
Tables

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

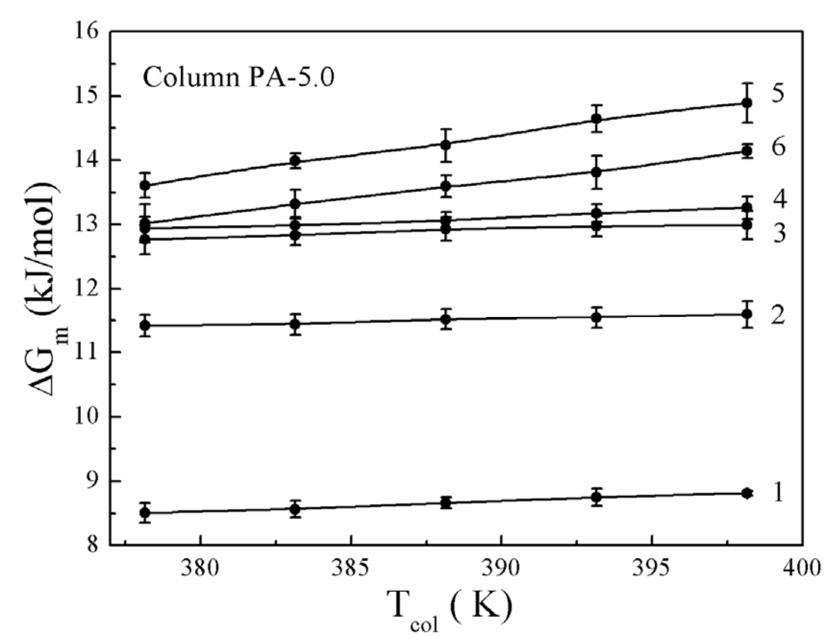
	PVA	PA-2.5	PA-5.0	PA-7.5	PA-10.0
W_p (g)	0.472	0.397	0.401	0.431	0.422
d_p (m)	4.36×10^{-6}	4.29×10^{-6}	4.24×10^{-6}	4.19×10^{-6}	4.16×10^{-6}
ρ_p (g/cm^3)	1.325	1.347	1.361	1.378	1.391

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, ρ_p is the density of the PVA hybrid materials (g/cm^3).

Figures



a



b

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

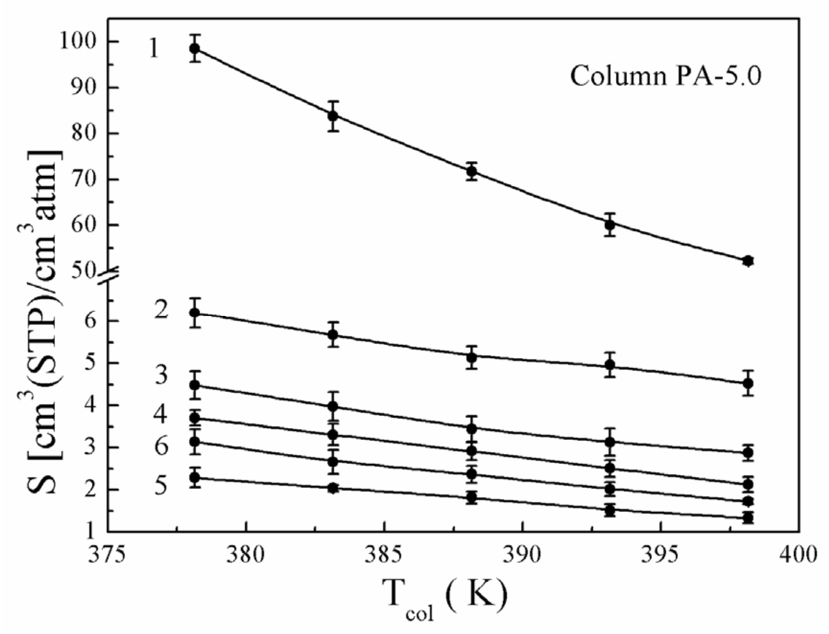


Fig. S2 Temperature dependences of the solubility coefficients of solvents S in PA-5.0 (1 water; 2 methanol; 3 ethanol; 4 isopropanol; 5 cyclohexane; 6 benzene)

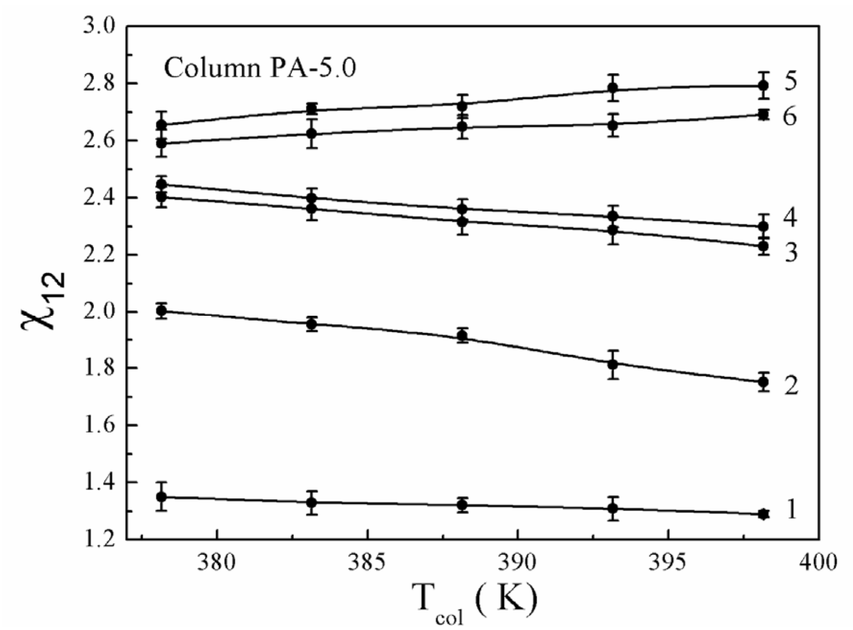


Fig. S3 Temperature dependences of the interaction parameters of PA-5.0-solvent pairs χ_{12}^{∞} (1 water; 2 methanol; 3 ethanol; 4 isopropanol; 5 cyclohexane; 6 benzene)

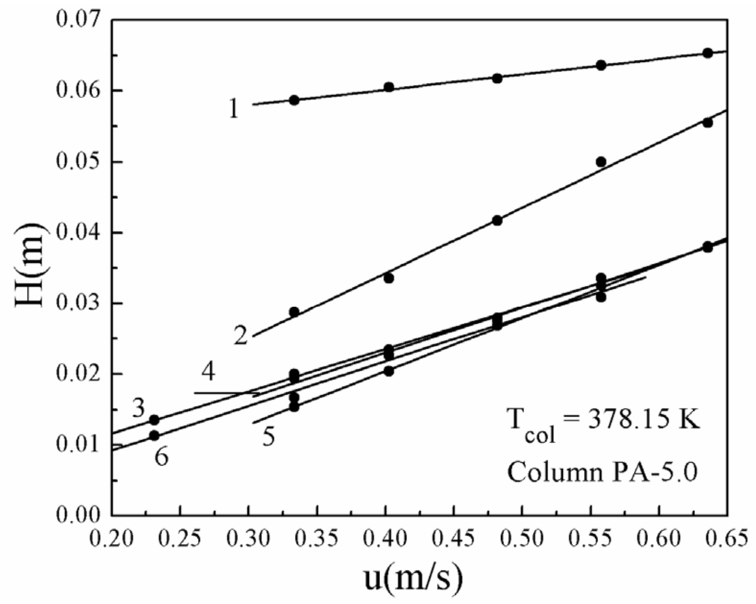


Fig.S4 Relationship of the height equivalent to a theoretical plate H with the linear velocity of carrier gas u in column PA-5.0 at 378.15 K (1 water; 2 methanol; 3 ethanol; 4 isopropanol; 5 cyclohexane; 6 benzene)

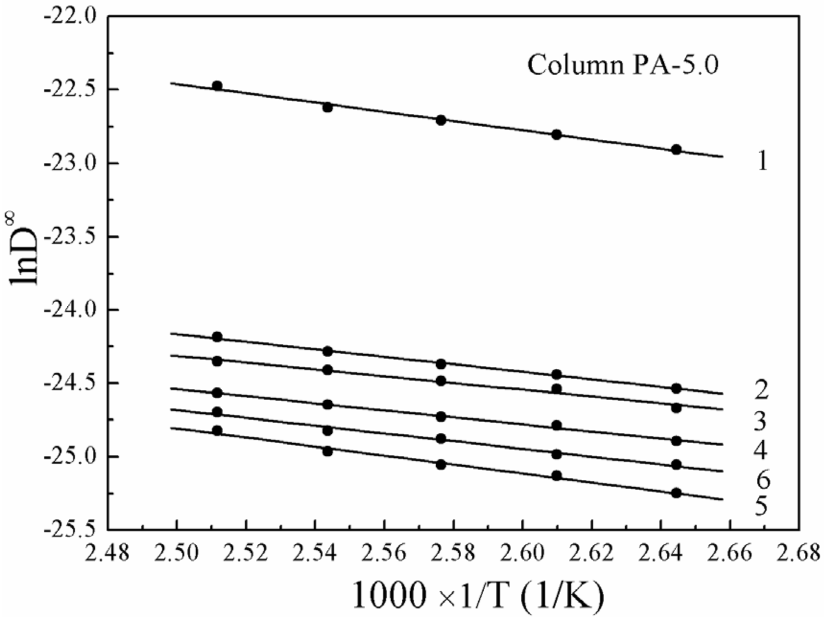


Fig.S5 Arrhenius plots for the infinite dilution diffusion coefficients of solvents in the hybrid materials PA-5.0 (1 water; 2 methanol; 3 ethanol; 4 isopropanol; 5 cyclohexane; 6 benzene)