

# Analyzing solubility and diffusion of solvents in novel hybrid materials of poly(vinyl alcohol)/ $\gamma$ -aminopropyltriethoxysilane by inverse gas chromatography†

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Novel hybrid materials were prepared through sol–gel reaction of poly(vinyl alcohol) (PVA) and  $\gamma$ -aminopropyltriethoxysilane (APTEOS). Solubility and diffusion behavior of a series of solvents in the PVA/APTEOS hybrid materials were studied by inverse gas chromatography (IGC) fitted with a packed column. Solubility thermodynamics parameters at infinite dilution, such as the activity coefficient  $\Omega_1^\infty$  and the solubility coefficient  $S$  of solvents in the hybrid materials, the partial molar excess free energy of mixture  $\Delta G_m$ , and the Flory–Huggins interaction parameter  $\chi_{12}^\infty$  were determined. The infinite dilution diffusion coefficients  $D^\infty$  of the solvents in the hybrid materials were also calculated. Effects of APTEOS content in the stationary phase and the column temperature on the solubility and diffusion of solvents in the hybrid materials were investigated. The hybrid material containing 5.0 wt% APTEOS has the strongest interaction with water, the largest  $S$  and  $D^\infty$  for water, and the hybrid material has a promising application in membrane separation, such as pervaporation dehydration of alcohol solution. The solubility parameter  $\delta_2$  of the hybrid materials was estimated, and it decreased with increasing APTEOS content. The dependence of  $D^\infty$  on temperature was in good agreement with the Arrhenius equation.

## 1 Introduction

Organic–inorganic hybrid materials lie at the interface of the organic and inorganic realms. These materials are formed by the combination of nanoscale inorganic and organic domains, and offer exceptional opportunities not only to combine the important properties from both materials but to create entirely new compositions with truly unique properties.<sup>1–3</sup> These hybrid materials are new generation functional materials applied in many fields, such as biology, environment, electronics, energy, ionics, mechanics, medicine, membrane separation and optics.<sup>3–5</sup>

In membrane separation processes, these hybrid materials are viewed as the next generation membrane materials, which offer specific advantages for the preparation of artificial membranes exhibiting high permselectivity and permeation flux, as well as good thermal and chemical resistance.<sup>6,7</sup> These organic–inorganic hybrid membranes have good permeation performances and special microstructures and physico-chemical properties, which have been investigated widely in gas separation and pervaporation, such as polyimide-based,<sup>8–12</sup> chitosan-based<sup>13–16</sup> and PVA-based<sup>2,4,17–19</sup> hybrid membranes.

Furthermore, these organic–inorganic hybrid materials used in gas separation and pervaporation are dense membranes; mass transfer through the membrane is generally described by the solution-diffusion model. The permeation process can be separated into three consecutive steps: (1) adsorption, (2) diffusion and (3) desorption, and the desorption can be usually neglected.<sup>20</sup> Therefore, in order to comprehend well the mass transfer of molecules through the membrane and provide academic guidance in the design of hybrid membrane materials, it is important to investigate the solubility and diffusion characteristics of penetrants in the hybrid membranes.

Inverse gas chromatography (IGC) is a simple, fast, reliable and powerful tool for the investigation of the sorption and diffusion behavior of small molecules in polymers.<sup>21–23</sup> This method can be used to determine the main sorption thermodynamic parameters of polymer–solvent systems, such as, activity coefficient, solubility coefficient, the Flory–Huggins interaction parameter and solubility parameter, partial molar excess free energy of mixture and enthalpy of sorption.<sup>24–28</sup> The infinite dilution diffusion coefficients of solvent and no-solvent in polymer can be measured exactly.<sup>22,23,29,30</sup> Many of these properties, such as the solubility coefficient and diffusion coefficient, are especially important for membrane separation processes.

Poly(vinyl alcohol) (PVA) is one of the most important materials for pervaporation dehydration of organic mixtures and separation of cyclohexane–benzene mixtures.<sup>2,4</sup> In order to enhance the physicochemical structure and separation performance of PVA membranes, PVA/tetraethoxysilane (TEOS) and  $\gamma$ -glycidylxypropyltrimethoxysilane (GPTMS) hybrid membranes have been prepared through sol–gel

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† Electronic supplementary information (ESI) available: Calculation of solubility and diffusion properties; table of parameters of the columns packed with hybrid materials with various APTEOS contents; effects of APTEOS content and column temperature on the partial molar excess free energy of mixture; temperature dependences of the solubility coefficients and interaction parameters; height–linear velocity of carrier gas plot; Arrhenius plots. See DOI: 10.1039/b709592a

reaction,<sup>2,4,31</sup> which have good thermal stability and separation properties. Zhang successfully prepared novel PVA/APTEOS hybrid membranes by sol-gel reaction.<sup>18,19</sup> The incorporation of APTEOS into the PVA matrix effectively adjusted the physicochemical structure of the hybrid membranes. The effects of the cross-linker on the pervaporation performance and morphology of the PVA/APTEOS hybrid materials were also investigated; the hybrid membranes showed significant improvement in separation factor and permeation flux in the pervaporation of water-ethanol (or isopropanol) mixtures.

In this work, the solubility and diffusion characteristics of water, methanol, ethanol, isopropanol, cyclohexane and benzene in the PVA/APTEOS hybrid materials were investigated by using the IGC method, and the effects of cross-linker and column temperature were investigated.

## 2 Experimental

### 2.1 Materials

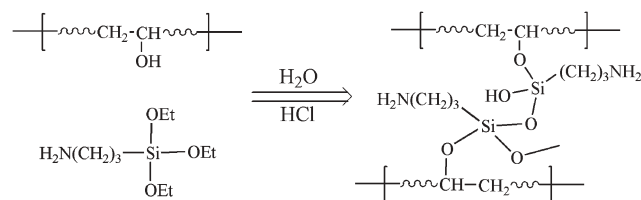
PVA (polymerization degree of  $1750 \pm 50$ , saponification of 98.0%) was supplied by Sinopharm Chemical Reagent Co. Ltd. (China).  $\gamma$ -Aminopropyltriethoxysilane (APTEOS) was purchased from Shanghai Yaohua Chemical Plant (China). Chromosorb-G (60–80 mesh, density of  $0.7474 \text{ g cm}^{-3}$ ) was purchased from Shanghai No.1 reagent manufactory of China. Methanol, ethanol, isopropanol, cyclohexane and benzene were analytical grade and were purchased from Sinopharm Chemical Reagent Co. Ltd.

### 2.2 Preparation of packed column

PVA was dissolved in deionized water at  $90^\circ\text{C}$  for 3 h, then the hot solution was filtered, and the mass fraction of PVA in solution was 2 wt%. A measured amount of APTEOS was added to the PVA solution, HCl was added as a catalyst to accelerate the hydrolysis of APTEOS, and the mixture was stirred at  $30^\circ\text{C}$  for 10 h.

The resulted solution was coated onto the Chromosorb-G support material by agitation and slow evaporation of the water to obtain a uniform polymer coating at  $90^\circ\text{C}$ . The coated support material were dried under vacuum at  $80^\circ\text{C}$  for 10 h, and then filled by vibrating into a 200 cm long, 3 mm diameter stainless steel tube with the aid of a vacuum pump. The ends of the tube were blocked loosely with gas chromatograph quartz wool. The packed tube was treated in the carrier gas (hydrogen, concentration  $\geq 99.999 \text{ wt}\%$ ) with a low flow rate at  $135^\circ\text{C}$  for 12 h before use.

In preparation of the gas chromatograph stationary phase, sol-gel reaction took place between PVA and APTEOS (Fig. 1). APTEOS was hydrolyzed in the presence of HCl, which led to the formation of silanol groups. Siloxane bonds were formed through a dehydration or dealcoholysis reaction between the hydroxyl groups in one silanol dispersed in the PVA solution and those in another silanol or the hydroxyl groups in PVA during the material drying.<sup>18,19</sup> The content of the hybrid materials in the solid carrier is 8 wt%, the mass fraction of APTEOS was 0.0, 2.5, 5.0, 7.5 and 10.0 in the hybrid materials, and the resulting hybrid materials or packed



**Fig. 1** Sol-gel reaction of poly(vinyl alcohol) and  $\gamma$ -aminopropyltriethoxysilane.

columns were designated as hybrid materials or columns PVA, PA-2.5, PA-5.0, PA-7.5, and PA-10.0, respectively. The density of the hybrid materials was measured by the flotation method using a benzene-carbon tetrachloride mixture at  $25^\circ\text{C}$ , and the temperature dependence of the polymer density was neglected. Parameters of the five packed columns used in this work are listed in Table S1 (see Electronic Supplementary Information (ESI)†).

### 2.3 Apparatus and procedure

The gas chromatograph in the experiment was a GC-14C (Shimadzu (Suzhou) Instruments Manufacturing, Co. Ltd) equipped with a thermal conductivity detector (TCD), a column injector, and an air-circulating oven. Hydrogen was used as the carrier gas in all experiments. The carrier gas flowed directly through the injection block to the column, and then to the TCD detector. The temperatures of the injection block and detector were set 50 K above the boiling point of water to avoid condensation in the injector and detector. The flow rate of the carrier gas was measured by means of a soap bubble flowmeter. Experiments were performed over a wide range of flow rates at each temperature from 378.15 K to 398.15 K at intervals of 5 K. The pressure drop through the column was measured by a highly accurate manometer at each flow rate.

Solvent (water, methanol, ethanol, isopropanol, cyclohexane and benzene;  $0.4 \mu\text{L}$ ) was injected into the column through a silicone rubber septum with a  $1 \mu\text{L}$  syringe, and  $10 \mu\text{L}$  of air were injected as a marker gas to determine the average velocity of the carrier gas in the column. From the difference between the retention time of the solvent and that of the marker gas, the equilibrium behavior could be determined. The output signal from the detector was fed to a chromatographic workstation and stored in a computer for further analysis. Each run was repeated at least five times, then five data were used in the subsequent calculation, and their errors were less than 0.5%.

### 2.4 Data analysis

The IGC of polymers is based on the gas chromatography equilibrium theory. In the IGC method, retention times of sorbed  $t_R$  and 'non-sorbed' component (air in this study)  $t_M$  are measured. The specific retention volume  $V_g$ , calculated from  $t_R$  and  $t_M$ , is a key parameter to obtain the thermodynamic properties of polymer-solvent systems. Furthermore, the solubility thermodynamic parameters of the polymer-solvent systems were obtained. In this study, the activity coefficient  $\Omega_1^\infty$  and the solubility coefficient  $S$  of the solvents in

the PVA hybrid materials, the partial molar excess free energy of mixture  $\Delta G_m$ , and the Flory–Huggins interaction parameter  $\chi_{12}^\infty$  of the hybrid material–solvent systems were estimated. The calculation method can be found in ESI Part A.†

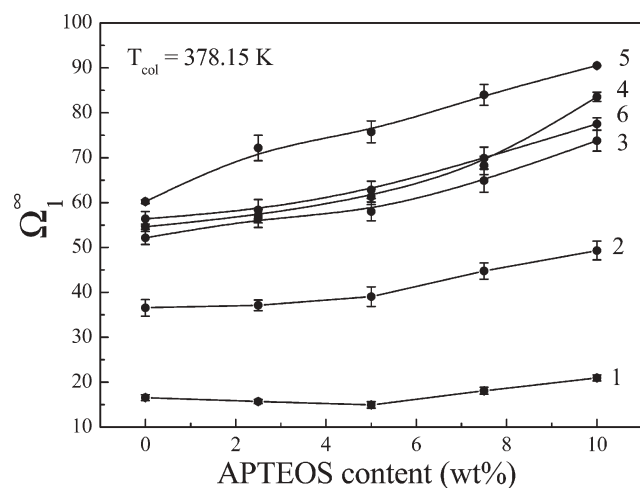
The infinite dilution diffusion coefficients of solvents  $D^\infty$  in the PVA/APTEOS hybrid materials were calculated according to Van Deemter's model. Effects of APTOES content and column temperature on  $D^\infty$  were investigated. The calculation of  $D^\infty$  can be found in ESI Part B.†

### 3 Results and discussion

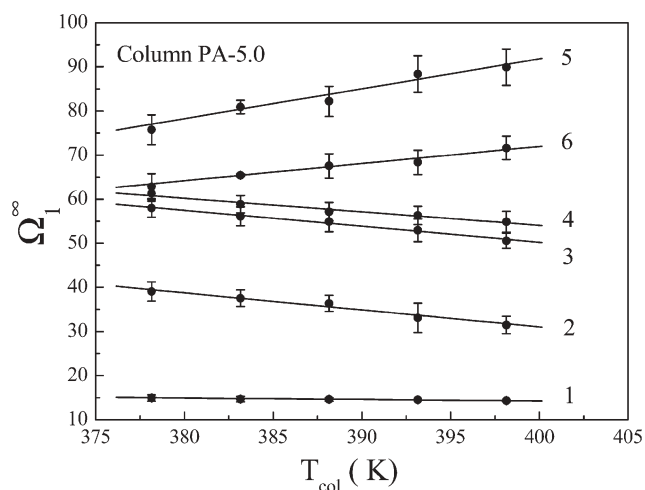
#### 3.1 Activity coefficients

PVA is a semi-crystalline polymer with glass transition temperature about 80 °C,<sup>17</sup> and the thermal decomposition temperature is above 200 °C. Therefore, PVA and its hybrid materials are rubbery polymers in the temperature range studied.<sup>32</sup> The infinite dilution activity coefficients  $\Omega_1^\infty$  of solvents in the polymer phase were studied. Fig. 2 shows  $\Omega_1^\infty$  of the solvents in the hybrid materials at 378.15 K.  $\Omega_1^\infty$  values of water are much lower than those of other solvents due to the PVA-based hybrid material being a hydrophilic polymer, and  $\Omega_1^\infty$  values increase in the order: water < methanol < ethanol < isopropanol < benzene < cyclohexane.  $\Omega_1^\infty$  of the solvents other than water increased with increasing APTEOS content. This is due to the chemical cross-linking of the PVA chain and APTEOS in the PVA matrix leading to a decrease in the mobility of the PVA chains, thus further restricting the mobility of the solvents in the PVA-based matrix. On the other hand, the hybrid materials were more hydrophilic than PVA when APTEOS content was less than 5 wt%,<sup>19</sup> which resulted in a slight decrease in the activity coefficient of water.

The effect of the column temperature on  $\Omega_1^\infty$  of the solvents in column PA-5.0 was investigated (Fig. 3).  $\Omega_1^\infty$  of the solvents which have hydroxyl groups, such as water, methanol, ethanol and isopropanol, decreased with increasing column temperature. The same phenomenon can be found in PVA<sup>23</sup> and other PVA/APTEOS hybrid materials. In contrast,  $\Omega_1^\infty$  of



**Fig. 2** Effects of APTEOS content on the infinite dilution activity coefficients  $\Omega_1^\infty$  of solvents in the hybrid materials (1 water; 2 methanol; 3 ethanol; 4 isopropanol; 5 cyclohexane; 6 benzene).



**Fig. 3** Temperature dependence of the infinite dilution activity coefficients  $\Omega_1^\infty$  of solvents in PA-5.0 (1 water; 2 methanol; 3 ethanol; 4 isopropanol; 5 cyclohexane; 6 benzene).

cyclohexane and benzene increased with increasing column temperature. It may be that both the mobility of the PVA chains and the dissociative hydroxyl group in the PVA chains increased with increasing column temperature.

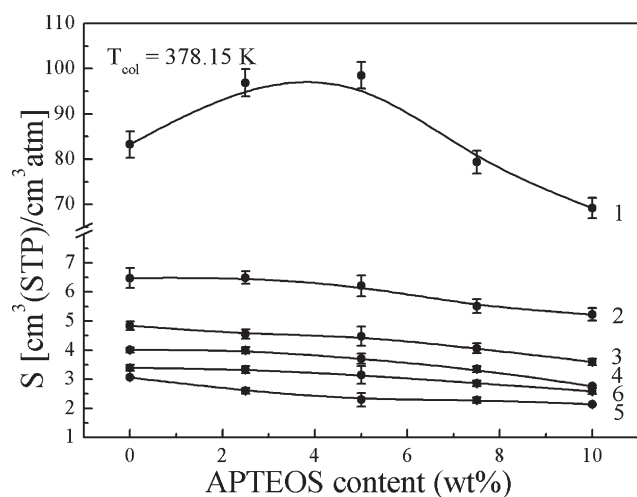
#### 3.2 The partial molar excess free energy of mixture

The partial molar excess free energy of mixture is the criterion for the mixing process: the larger the partial molar excess free energy of the mixture, the more difficulty it is for the mixing process to take place. The partial molar excess free energy of mixture of polymer–solvent at infinite dilution  $\Delta G_m$  can be obtained from the activity coefficient  $\Omega_1^\infty$  (see Part A of ESI†).

In the PVA/APTEOS hybrid material–solvents systems,  $\Delta G_m$  of the mixture of hybrid material–water is smaller than that of other hybrid material–solvents, and  $\Delta G_m$  of all mixtures of hybrid material–solvent are positive and increase in the order: water < methanol < ethanol < isopropanol < benzene < cyclohexane. On the other hand,  $\Delta G_m$  of mixtures of all hybrid material–solvents except for hybrid material–water increased with increasing APTEOS content, owing to the chemical cross-linking taking place between PVA and APTEOS. Simultaneously,  $\Delta G_m$  of the mixture of hybrid material–water decreased due to an increase in the hydrophilicity of the hybrid materials when APTEOS content is less than 5.0 wt%. It is found that  $\Delta G_m$  of all mixtures of hybrid material–solvent increased slightly with increasing column temperature (see Fig. S1 of ESI†).

#### 3.3 Solubility coefficients

The infinite dilution solubility coefficient  $S$  of a solvent in a polymer, which indicates the sorption capability of the solvent in the polymeric material, can be calculated by the specific retention volume  $V_g$ .  $S$  of the solvents in the hybrid materials at 378.15 K are shown in Fig. 4.  $S$  of water in the hybrid materials is much greater than those of the other solvents, which reveals that PVA can be dissolved in water at a higher temperature.  $S$  of other solvents in the hybrid materials were less than 9 cm<sup>3</sup>(STP) cm<sup>-3</sup> atm<sup>-1</sup> and decreased with



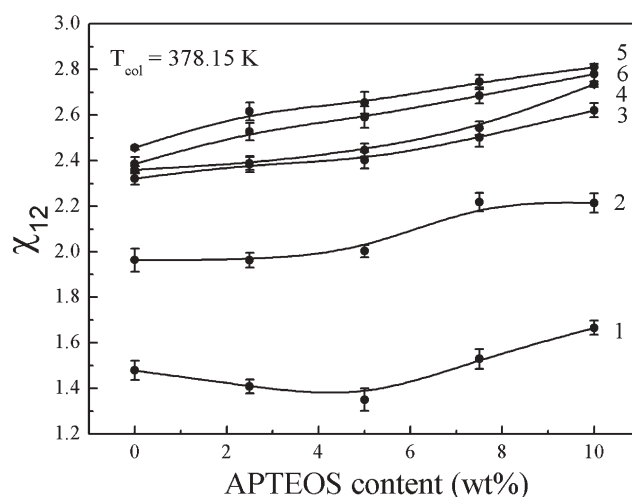
**Fig. 4** Effects of APTEOS content on solubility coefficients  $S$  of solvents in the hybrid materials (1 water; 2 methanol; 3 ethanol; 4 isopropanol; 5 cyclohexane; 6 benzene).

increasing APTEOS content. The reason is that the hybrid materials become more compact owing to the formation of chemical cross-linking with increasing APTEOS content. However,  $S$  of water in the hybrid materials increased almost linearly for the hybrid materials containing up to 5.0 wt% APTEOS, and then decreased at higher APTEOS content. Of the hybrid materials, water has the highest  $S$  value in PA-5.0.

Furthermore, the effects of the column temperature on  $S$  of the solvents in the hybrid materials were investigated.  $S$  of the solvents in hybrid materials decreased almost linearly with column temperature increasing (see Fig. S2 of ESI†). This is because of an increase in the mobility of the solvents in the polymer matrix and the kinetic energy of the solvent molecules with increasing temperature.

### 3.4 Flory–Huggins parameter and solubility parameter

The dissolution of vapors in a rubbery polymer is usually described using Flory–Huggins theory. The Flory–Huggins parameter characterizes the interactions between the solvent and the polymeric stationary phase. The infinite dilution Flory–Huggins parameter  $\chi_{12}^{\infty}$  of polymer–solvent can be calculated by the IGC method assuming a sufficiently large molecular mass of polymer.<sup>24</sup> Fig. 5 shows  $\chi_{12}^{\infty}$  of hybrid material–solvent pairs at 378.15 K. It is found that  $\chi_{12}^{\infty}$  increased in the order: water < methanol < ethanol < isopropanol < benzene < cyclohexane.  $\chi_{12}^{\infty}$  between water and the hybrid materials decreased when APTEOS content was less than 5.0 wt%, and increased when APTEOS content was over 5.0 wt%. This suggests PA-5.0 has the largest interaction with water.  $\chi_{12}^{\infty}$  between other solvents and the hybrid materials also increased with increasing APTEOS content. The effect of temperature on  $\chi_{12}^{\infty}$  was also studied. It was found that  $\chi_{12}^{\infty}$  of water, methanol, ethanol and isopropanol decreased with increasing column temperature, however,  $\chi_{12}^{\infty}$  of cyclohexane and benzene increased (see Fig. S3 of ESI†). This is a reflection of the positive and negative values of the partial molar enthalpy of mixture.<sup>24</sup>



**Fig. 5** Effects of APTEOS content on interaction parameters  $\chi_{12}^{\infty}$  of hybrid material–solvent pairs (1 water; 2 methanol; 3 ethanol; 4 isopropanol; 5 cyclohexane; 6 benzene).

On the basis of the Flory–Huggins model and the Hildebrand–Scatchard solution theory, the solubility parameter of polymer phase at infinite dilution,  $\delta_2$  ( $\text{J cm}^{-3}$ )<sup>1/2</sup>, can be estimated using<sup>33</sup>

$$\frac{\delta_1^2}{RT} - \frac{\chi_{12}^{\infty}}{V_1} = \frac{2\delta_2}{RT} \delta_1 - \frac{\delta_2^2}{RT} \quad (1)$$

where  $V_1$  ( $\text{cm}^3 \text{mol}^{-1}$ ) is the solute molar volume, and  $\delta_1$  ( $\text{J cm}^{-3}$ )<sup>1/2</sup> is the solubility parameter of the solvent which can be obtained by using

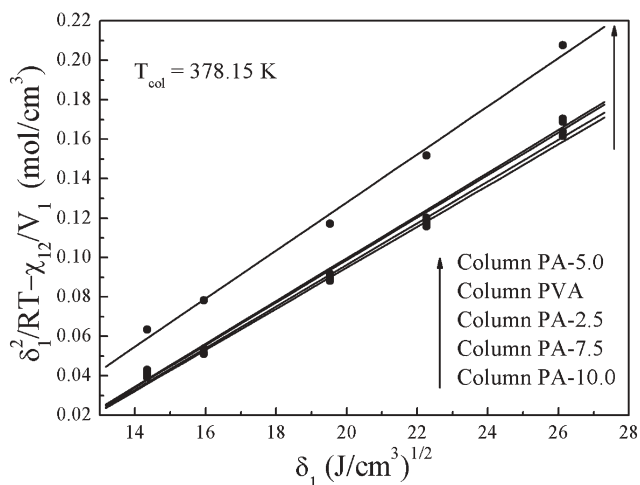
$$\delta_1 = \left[ \frac{\Delta H_V - RT}{V_1} \right]^{1/2} \quad (2)$$

where  $\Delta H_V$  ( $\text{J mol}^{-1}$ ) is the heat of vaporization of the solvent. A straight line with a slope of  $2\delta_2/RT$  and an intercept of  $\delta_2^2/RT$  can be obtained by plotting  $\delta_1^2/RT - \chi_{12}^{\infty}/V_1$  vs.  $\delta_1$ . Then  $\delta_2$  is determined from both the slope and the intercept of the straight line.<sup>22,24,25</sup>

The solubility parameters  $\delta_2$  of the hybrid materials at 378.15 K were calculated. It is clear that  $(\delta_1^2/RT - \chi_{12}^{\infty}/V_1)$  and  $\delta_1$  have a good linear relationship (Fig. 6),  $\delta_2$  was obtained by either the slope or the intercept of the resulting straight line, as listed in Table 1. It is found that  $\delta_2$  obtained from the slope differs slightly to that from the intercept. In general,  $\delta_2$  of the hybrid materials is lower than that of PVA and decreased slightly with increasing APTEOS content. This indicates that the cohesive energy of the hybrid materials decreased. The reason may be that APTEOS dispersed randomly in the PVA matrix leading to a decrease in the order degree of the PVA chains.

### 3.5 Diffusion coefficients

IGC was used to measure the infinite diffusion coefficients  $D^{\infty}$  of water, methanol, ethanol, isopropanol, cyclohexane and benzene in the hybrid materials at different temperature. Measurements for each hybrid material–solvent pair were



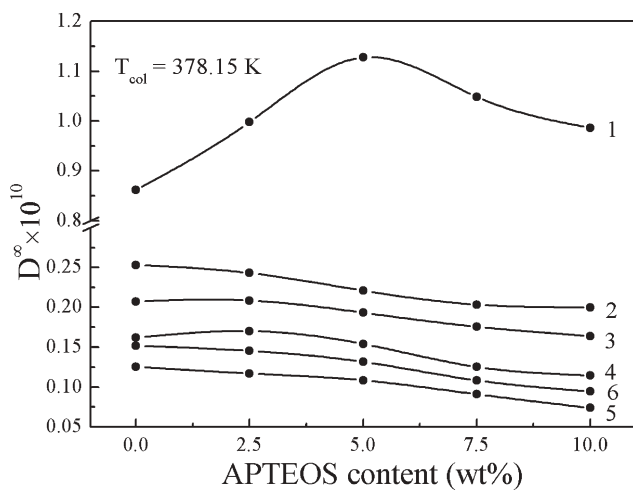
**Fig. 6** Estimation of solubility parameter  $\delta_2$  of the hybrid materials at 378.15 K (1 water; 2 methanol; 3 ethanol; 4 isopropanol; 5 cyclohexane; 6 benzene).

**Table 1** Solubility parameters  $\delta_2$  ( $\text{J cm}^{-3}$ )<sup>1/2</sup> of the hybrid materials with various APTEOS contents at 378.15 K

| $\delta_2$                | PVA   | PA-2.5 | PA-5.0 | PA-7.5 | PA-10.0 |
|---------------------------|-------|--------|--------|--------|---------|
| $\delta_2$ from slope     | 19.45 | 19.42  | 19.34  | 19.26  | 19.13   |
| $\delta_2$ from intercept | 19.49 | 19.39  | 19.38  | 19.06  | 18.83   |

obtained at various carrier flow rates in order to obtain parameter  $C$ , which is the key parameter to calculate  $D^\infty$ . The plot of height equivalent to a theoretical plate  $H$  vs. the linear velocity of carrier gas  $\mu$  yields a straight line with slope  $C$ . All  $R$  values were greater than 0.98 in this study (see Fig. S4 of ESI†).

Fig. 7 shows  $D^\infty$  of the solvents in the hybrid materials at 378.15 K. It is found that of the solvents decrease in the order: water > methanol > ethanol > isopropanol > benzene > cyclohexane. This is owing to the differences in the sizes of the solvent molecules and the interaction between the solvents and



**Fig. 7** Effects of APTEOS content on the infinite dilution diffusion coefficient  $D^\infty$  of solvents in the hybrid materials (1 water; 2 methanol; 3 ethanol; 4 isopropanol; 5 cyclohexane; 6 benzene).

the hybrid material. The smaller the size of the molecule, the larger is  $D^\infty$ ; the larger the interaction between the solvents and the hybrid materials, the is larger  $D^\infty$ . This proves that the PVA-based hybrid materials can be used as membrane materials applied in pervaporation dehydration of alcohol solution and separation of benzene–cyclohexane mixtures.<sup>2,32,34,35</sup>

With increasing APTEOS content in the hybrid materials,  $D^\infty$  of all the solvents except for water decreased gradually (see Fig. 7). This is due to the fact that the formation of chemical cross-linking in the PVA matrix leads to decreasing in the size of meshwork between PVA chains, resulting in a reduction in the permeation of a solvent molecule through the hybrid material. On the other hand,  $D^\infty$  of water in the hybrid materials increased with increasing APTEOS content, and decreased when APTEOS content was over 5.0 wt%. This is owing to the increase of the hydrophilicity and the free volume of the hybrid materials resulting in an increase in the permeation of water when APTEOS content was less than 5.0 wt%; however, the decrease of its hydrophilicity led to a decrease in the sorption and diffusion in the hybrid materials when APTEOS content was more than 5.0 wt%.<sup>18</sup> In the above work, it can be found that PA-5.0 has good water permselectivity through the study on  $D^\infty$  of the solvents; this was confirmed by the permeation experiments.<sup>18,19</sup>

In general, the temperature dependence of diffusion coefficient is given by the Arrhenius equation

$$D = D_0 e^{-\Delta E_D / RT} \quad (3)$$

where  $D_0$  is the diffusion constant of the diffusion process independent of temperature,  $\Delta E_D$  is the activation energy for a diffusing compound in a given polymer matrix to escape from its present surroundings and move into an adjacent different surrounding. In dilute solutions, where the diffusing species does not often encounter polymer molecules, the diffusion rate is limited by the energy required for the diffusing species to escape from its present surroundings and move into an adjacent environment.<sup>23</sup>

The temperature dependence of  $D^\infty$  of the solvents in the hybrid materials was investigated; it was found that the plot of  $\ln D^\infty$  vs.  $1/T$  was linear, which confirmed that  $\Delta E_D$  was independent of temperature in the range of temperature investigated (see Fig. S5 of ESI†).  $\Delta E_D$  and  $D_0$  for the solvents were calculated from the fitted straight lines and are shown in Tables 2 and 3.  $\Delta E_D$  of water and alcohols in PVA decreased in the order: water > methanol > ethanol > isopropanol. This is due to PVA being a hydrophilic polymer; the larger the hydrophilicity of the solvent, the larger the activation energy through the polymer.  $\Delta E_D$  of cyclohexane and benzene are

**Table 2** Activation energies  $\Delta E_D$  ( $\text{kJ mol}^{-1}$ ) for diffusion of solvents in the hybrid materials with various APTEOS contents

| Solvent     | PVA   | PA-2.5 | PA-5.0 | PA-7.5 | PA-10 |
|-------------|-------|--------|--------|--------|-------|
| Water       | 28.28 | 26.61  | 26.14  | 25.37  | 22.88 |
| Methanol    | 24.63 | 21.94  | 21.33  | 19.53  | 18.24 |
| Ethanol     | 23.06 | 19.31  | 19.13  | 19.19  | 20.01 |
| Isopropanol | 22.55 | 20.27  | 20.02  | 19.60  | 20.25 |
| Cyclohexane | 26.22 | 24.60  | 25.36  | 26.31  | 27.47 |
| Benzene     | 25.76 | 22.22  | 21.93  | 24.83  | 24.49 |

**Table 3** Diffusion constants  $D_0$  ( $\times 10^{-8}$  m<sup>2</sup> s<sup>-1</sup>) of solvents in the hybrid materials with various APTEOS contents

| Solvent     | PVA   | PA-2.5 | PA-5.0 | PA-7.5 | PA-10 |
|-------------|-------|--------|--------|--------|-------|
| Water       | 69.94 | 47.36  | 45.64  | 33.27  | 15.19 |
| Methanol    | 6.22  | 3.46   | 1.95   | 1.02   | 0.67  |
| Ethanol     | 3.21  | 0.96   | 0.87   | 0.78   | 0.97  |
| Isopropanol | 2.14  | 1.07   | 0.90   | 0.65   | 0.71  |
| Cyclohexane | 5.44  | 2.95   | 3.45   | 4.01   | 4.66  |
| Benzene     | 5.42  | 1.71   | 1.40   | 2.90   | 2.28  |

larger since their molecules are bigger than the other solvents. On the other hand, there are the similar trends for  $D_0$  of solvents and they decrease in the order: water > methanol > cyclohexane > benzene > ethanol > isopropanol.

With increasing APTEOS content in the hybrid materials,  $\Delta E_D$  of water and methanol decreased in the APTEOS content range investigated, which agrees with the results obtained by Zeng *et al.*<sup>23</sup> For other solvents,  $\Delta E_D$  decreased first, and then increased when APTEOS content was more than a certain value. The reason for this is because the chemical cross-linking in the PVA matrix restrains the diffusion of solvents through hybrid materials when the APTEOS content is above a threshold. The change trend of  $D_0$  of solvents is the same as that of  $\Delta E_D$ .

## 4 Conclusions

Solubility and diffusion of a series of solvents in the hybrid materials at infinite dilution were studied by IGC. Effects of APTEOS content in the hybrid materials and the column temperature were investigated. Conclusions are as follows.

1. With APTEOS content increasing,  $\Omega_1^\infty$ ,  $\Delta G_m$  and  $\chi_{12}^\infty$  of water in the hybrid materials decreased, and then increased when APTEOS content was more than 5.0 wt%; however,  $S$  changed in the opposite manner, increasing first and then decreasing when APTEOS content was over 5.0 wt%. For other solvents,  $\Omega_1^\infty$ ,  $\Delta G_m$  and  $\chi_{12}^\infty$  in the hybrid materials were larger than those in the PVA and increased with increasing APTEOS content; while  $S$  decreased with increasing APTEOS content.

2. With column temperature increasing,  $\Omega_1^\infty$  of the solvents except for cyclohexane and benzene in the hybrid materials decreased;  $\Delta G_m$  of all mixtures of hybrid material–solvent increased, while  $S$  decreased. On the other hand,  $\chi_{12}^\infty$  of hybrid material–solvent pairs have a good linear relationship to the column temperature.

3.  $D^\infty$  of water in the hybrid material increased with increasing APTEOS content, and then decreased when APTEOS content was over 5.0 wt%. However,  $D^\infty$  of the other solvents decreased gradually with increasing APTEOS content. Temperature dependence of the diffusion of solvents in the hybrid materials can be elucidated by using the Arrhenius equation, and the diffusion activation energy  $\Delta E_D$  and the diffusion constant  $D_0$  were obtained.

4. Solubility parameter  $\delta_2$  of the hybrid materials is lower than that of PVA, and decreased with increasing APTEOS content. Incorporation of APTEOS into PVA resulted in a decrease in the cohesive energy of the PVA matrix.

5. The hybrid material containing 5.0 wt% APTEOS has the strongest interaction with water, the largest  $S$  and  $D^\infty$  for water. This indicates that PA-5.0 can be used as a good membrane material for application in pervaporation dehydration of organic solutions with high water permselectivity and permeation flux, which was proved by pervaporation separation of water–ethanol and water–isopropanol mixtures.<sup>18,19</sup>

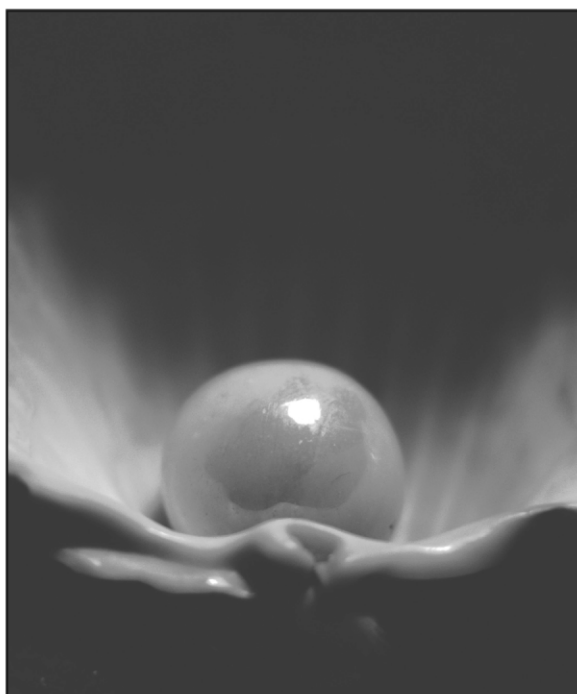
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