

## Laser Light-Scattering Study of Solution Dynamics of Water/Cycloether Mixtures

Cheng Yang,<sup>†</sup> Wei Li,<sup>‡</sup> and Chi Wu<sup>\*,‡,§</sup>

Department of Chemical and Material Engineering, Southern Yangtze University, Wuxi, Jiangsu 214036, China, Department of Chemistry, The Chinese University of Hong Kong, Shatin, N.T., Hong Kong, and The Open Laboratory of Bond Selective Chemistry, Department of Chemical Physics, University of Science and Technology of China, Hefei, Anhui 230036, China

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The complexation of tetrahydrofuran as well as 1,4-dioxane with water has been investigated by laser light scattering (LLS). The complexation of cycloethers with water molecules makes the diffusion of water clusters visible in LLS. The intensity–intensity time correlation function of a simple mixture of water and tetrahydrofuran (THF) or 1,4-dioxane has two diffusive relaxation modes. The fast mode with a diffusion coefficient in the range  $2\text{--}8 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  is related to mutual diffusion of the complexes formed between small water clusters and THF or 1,4-dioxane. The slow mode with a dynamic correlation length of 200–600 nm can be removed by filtration, indicating that the mixing of water and cycloethers is microscopically incomplete. Further, using a trace amount of spherical poly(*N*-isopropyl acryamide) microgels as probes, we indirectly investigated the water/THF interaction. Our results showed that PNIPAM swell in ether pure water or pure THF but fully collapse when  $[\text{THF}]:[\text{water}] = 0.05\text{--}0.15$ , in which the water/THF complexes are nonsolvent for PNIPAM. When  $[\text{cycloether}]:[\text{water}] > \sim 0.16$ , water is not able to further complex with cycloethers added so that extra cycloethers exist as individual molecules to reswell the microgels, indicating that it is small water clusters, such as the pentamer and hexamer, that solvate PNIPAM.

## Introduction

It has been generally recognized that water has anomalous properties that can be attributed to the hydrogen-bonding-induced structures (clusters). In principle, each water molecule can participate to form four possible hydrogen bonds. Two of them involve the two hydrogen atoms while the other two are related to two lone pairs of electrons of the oxygen atom. It would be naive to think that all the molecules in the liquid state are the same as those in ice and interconnected to be part of a network. Various structural hypotheses have been proposed for different water clusters. Despite its molecular simplicity, these hydrogen bonds in liquid water are too weak to be measured even by modern instrumentation. Computer simulation becomes a powerful tool in this respect. At the present time, the structure of liquid water still remains a big puzzle and a scientific challenge.<sup>1</sup>

Cycloethers, such as dioxane and THF, are macroscopically miscible with water at any ratio. Their structures tell us that no hydrogen bond can be formed among them, but they can form hydrogen bonds with water, disturbing its structure. Therefore, the investigation of the cycloether/water interaction provides an indirect approach to study the structure of water. Many investigations have already been conducted, especially on the study of the dioxane/water mixtures, by various methods, such as thermodynamic techniques,<sup>2</sup> infrared and Raman spectroscopies,<sup>3–5</sup> dielectric relaxation spectroscopy,<sup>6–9</sup> NMR,<sup>10,11</sup> dynamic light scattering,<sup>12</sup> and computer simulation.<sup>13,14</sup> It has

generally been recognized that, when the content of alcohol or THF is very low, guest molecules can enter the water cages to form a clathrate structure.<sup>16,17</sup> The hydrates of cubic structure II with a hydrate number (water/guest molar ratio) of  $\sim 17$  was found at atmospheric pressure in a guest–water binary system if the van der Waals' diameter of guest molecule is about 0.6–0.7 nm.<sup>15</sup> For smaller guest molecules with a diameter smaller than 0.58 nm, the hydrate of cubic structure II with a hydrate number of  $\sim 7$  was observed.<sup>15</sup> Methanol is the smallest alcohol capable of forming a stronger hydrogen bond with water than any other alcohol. It prefers to cluster with water in a one-to-one ratio, not in a hydrate clathrate-like structure. The chance of forming the hydrate clathrate-like structures increases with an increasing hydrophobicity and size of guest molecules.<sup>17</sup>

Stillinger<sup>18</sup> presented a picture of water structure on the basis of the “molecular dynamics” and “Monte Carlo” simulation. In his picture, water emerges as a random and three-dimensional network made of hydrogen bonds in which a large portion of the bonds are strained and broken, but with local preference for a tetrahedral geometry. Only few free or one-bond water molecules exist in the liquid state. Many of them are short-lived polygons and even polyhedra. For dioxane and some other alcohols such as ethanol, propanol, or *tert*-butyl alcohol the hydrate clathrate-like structure partially remains when the molar content of alcohol  $x_{\text{alcohol}}$  is less than  $\sim 0.17$ .<sup>19</sup> The concentration of relatively unstrained and bulky polyhedra increases with an decreasing temperature.<sup>18</sup> The theoretical calculation indicates that in supercooled water, each water cluster on average is made of 15–16 water molecules<sup>20,21</sup> and is probably polyhedra-like ice. Stillinger<sup>18</sup> predicted that in the supercooled state, low-density well-bonded clusters near  $T_s$  (the “Speedy-Angell temperature”) should also produce anomalous light scattering

\* To whom correspondence should be addressed. The Chinese University of Hong Kong, Shatin, N.T., Hong Kong. Telephone: 852-2609-6106. Fax: 852-2603-5057. E-mail: chiwu@cuhk.edu.hk.

<sup>†</sup> Southern Yangtze University.

<sup>‡</sup> The Chinese University of Hong Kong.

<sup>§</sup> University of Science and Technology of China.

because of the divergence of the aggregation of water clusters, which has unfortunately not been confirmed yet.

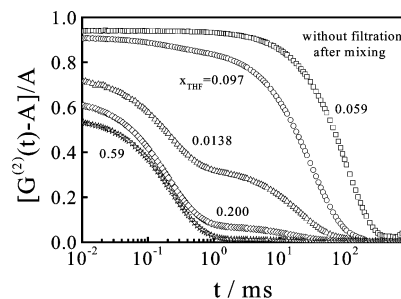
More recently, Takamuku et al.<sup>22</sup> investigated the mixtures of water with different cycloethers, such as 1,4-dioxane, 1,3-dioxane, and tetrahydrofuran, by using X-ray scattering, small-angle neutron scattering, and NMR relaxation. They found that, when the molar fraction of cycloethers ( $x_c$ ) is lower than 10%, some of cycloethers are embedded inside the water network. While in the region of  $x \geq 30\%$ , the disruption of the water network leads to more monomeric water molecules that can interact with oxygen atoms in cycloether molecules through intermolecular hydrogen bonding. They also showed that in the intermediate range  $0.1 < x_c < 0.3$  small clusters made of water and cycloether molecules were formed. These investigations indicate that cycloethers can break the hydrogen bonding of the water network and replace it with a new hydrogen bonding between cycloether and water. It is these new water/cycloether clusters that cause some abnormal properties of the mixtures.

In this contribution, we not only used a modern state-of-the-art laser light scattering to directly reexamine the solution dynamics of different mixtures of water with THF or 1,4-dioxane but also used a trace amount of spherical poly(*N*-isopropylacrylamide) (PNIPAM) microgels to indirectly probe the interaction between cycloether and water. This is because PNIPAM microgels can undergo a reentrant swelling–shrink–swelling transition with an increasing methanol or THF content.<sup>23–29</sup> It has been shown that such a re-entrant phase behavior is related to the cluster formation between water and methanol or THF.<sup>30</sup> A combination of the solution dynamics of the water/cycloether mixture with and without a trace amount of spherical PNIPAM microgels led us one step forward in a long journey of understanding the structure of liquid water.

## Experimental Section

**Sample Preparation.** Tetrahydrofuran (THF, analytical reagent, Labsan Asia Co., Ltd., Thailand) and 1,4-dioxane (Fluka AG, Buchs SG, Switzerland) were used as received. Deionized water with a resistivity of 18 M $\Omega$  cm was used. To prepare the dust-free mixture of water and cycloethers for laser-light scattering, we clarified each mixture in two steps. First, dust-free deionized water and THF or 1,4-dioxane with a desired molar ratio are separately added in a LLS cell and then thoroughly mixed by ultrasonic wave for 1 h. Macroscopically, the solution mixture was clear. Such a dust-free mixture was studied by LLS without further filtration after the mixing. In the second step, the mixture was filtered once more through a 0.2- $\mu$ m filter and measured again by LLS.

The synthesis of spherical poly(*N*-isopropylacrylamide) (PNIPAM) microgels was detailed before.<sup>31</sup> *N*-isopropylacrylamide was recrystallized three times in a benzene/*n*-hexane mixture. *N,N'*-Methylenebis(acrylamide) (BIS, from Aldrich) as cross-linking agent was recrystallized from methanol. Potassium persulfate (KPS, from Aldrich) as initiator and anionic surfactant sodium dodecyl sulfate (SDS) as dispersing agent were used without further purification. Into 250 mL of deionized water in a 500-mL reactor fitted with a nitrogen bubbling inlet and outlet, a stirring magnet, and a reflux condenser were dissolved 4.0 g of NIPAM, 0.076 g of BIS, and 0.076 g of SDS. After the solution was stirred for 40 min at 70 °C under a nitrogen purge, 0.155 g of KPS dissolved into 20 mL of deionized water was introduced to start the polymerization. The reaction mixture was kept at 70 °C for 8 h. Unreacted monomer and most of SDS were removed by adding the reaction mixture dropwise into 250 mL of methanol.



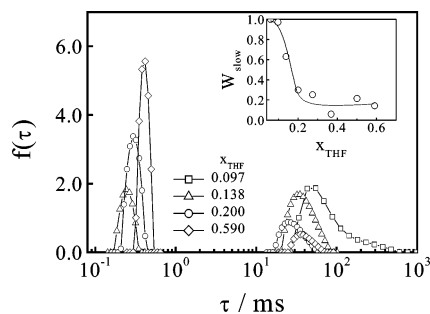
**Figure 1.** Measured intensity–intensity time correlation functions of mixtures of water and THF, prepared by separate filtration before mixing.

The resultant precipitate was redissolved in 80 mL of deionized water and then reprecipitated in an equal volume of methanol. To remove the remaining trace amount of SDS and other impurities, the microgels were further purified by three cycles of successive centrifugation and decantation until the  $\xi$ -potential of dispersion is close to zero. The solvent was removed by freezing drying. To prepare a solution mixture of water and THF with only a trace amount of the microgels, we kept the microgel concentration as low as  $2.0 \times 10^{-6}$  g/mL. On average, each microgel (each monomer unit of microgel chain) is surrounding by  $\sim 10^7$  water molecules. Therefore, we can assume that the existence of such a trace amount of the microgels will not disturb the water structure. The dispersion was clarified by using a 0.45- $\mu$ m filter to remove dust before the LLS study. Viscosities of the mixtures of water and THF or 1,4-dioxane with different molar ratios were measured by an Ubbelohde viscometer with a flow time of longer than 500 s for pure water at  $25 \pm 0.1$  °C. Therefore, the kinetic energy correction was negligible.

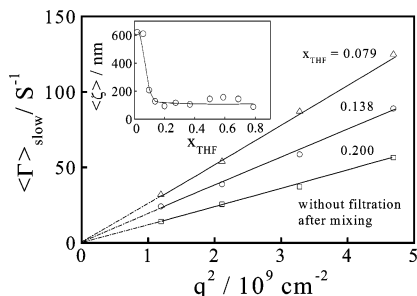
**Laser Light Scattering.** A modified commercial LLS spectrometer (ALV/SP-125) equipped with an ALV-5000 multi- $\tau$  digital time correlator and a He–Ne laser (Uniphase, output power  $\approx 20$  mW at  $\lambda = 632.8$  nm) was used. In dynamic LLS, we measured the density fluctuation-induced-intensity fluctuation via a time correlation function. The Laplace inversion of each precisely measured intensity–intensity time correlation function  $G^{(2)}(t, q)$  in the self-beating mode resulted in a characteristic line-width distribution  $G(\Gamma)$ . The CONTIN Laplace inversion algorithm in the correlator was used. For a pure diffusive relaxation,  $G(\Gamma)$  can be converted to a translation diffusion coefficient distribution  $G(D)$  by  $\Gamma = Dq^2$  or a dynamic correlation length distribution  $f(\zeta)$  or a hydrodynamic radius distribution  $f(R_h)$  using the Stoke–Einstein equation  $\zeta$  or  $R_h = k_B T / 6\pi\eta D$ . Using a modern LLS instrument, we can measure  $R_h$  or  $\zeta$  down to a size of  $\sim 1$  nm because of a fast correlator and a powerful laser. All the LLS measurements were done at  $25.0 \pm 0.1$  °C. The details of the LLS instrumentation and theory can be found elsewhere.<sup>32,33</sup>

## Results and Discussion

Figure 1 shows intensity–intensity time correlation functions of the water/THF mixtures with different molar contents of THF ( $x_{\text{THF}}$ ) prepared by separately filtering water and THF before the mixing. It is helpful to note that the time correlation function of either pure water or pure THF within the same delay time window is flat and structure-less, the same as the baseline parallel to the  $x$ -axis. However, it is very different for the mixture. In the range  $x_{\text{THF}} < 0.13$ , there is one dominant slow relaxation in the mixture. In the range  $x_{\text{THF}} > 0.13$ , another fast relaxation mode becomes more obvious. The characteristic



**Figure 2.** THF-content dependence of characteristic decay time distributions  $f(\tau)$  of mixtures of water and THF, prepared by separate filtration before mixing. The inset shows THF content dependence of relative intensity weighting ( $W_{\text{slow}}$ ) of slow relaxation.

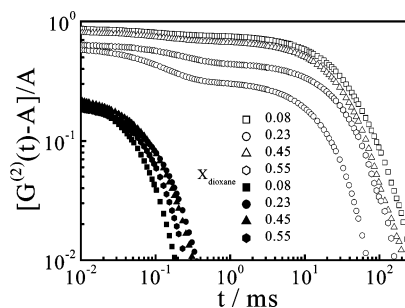


**Figure 3.** Scattering vector ( $q$ ) dependence of average characteristic line-width ( $\langle\Gamma\rangle_{\text{slow}} = 1/\langle\tau\rangle_{\text{slow}}$ ) of slow relaxation in mixtures of water and THF, prepared by separate filtration before mixing. The inset shows corresponding average dynamic correlation lengths ( $\langle\zeta\rangle_{\text{D}}$ ) of slow relaxation.

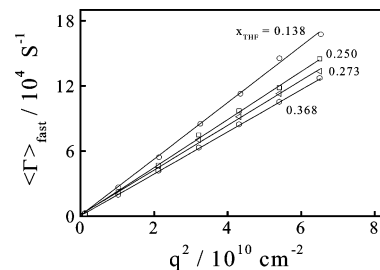
decay time of the slow relaxation and its related intensity contribution decrease with an increasing THF content, as shown in Figure 2. It is well-known that THF or dioxane is macroscopically 100% miscible with water in any molar ratio. However, Figure 1 clearly shows that microscopically, the mixture of water and THF or dioxane is not as homogeneous as we thought. Recently, Guo et al.<sup>34</sup> showed that the mixing of methanol and water is incomplete at the microscopic level on the basis of their X-ray absorption and emission results. We also tried to study the mixture of methanol and water but failed because the refractive indexes of methanol and water do not have a sufficient difference to make them visible in laser-light scattering. The appearance of the slow relaxation forces us to question the miscibility of water and cycloethers and examine the nature of two such relaxation modes.

Figure 3 shows that for the slow relaxation, its average characteristic line width ( $\langle\Gamma\rangle_{\text{slow}}$ ) obtained from each measured time correlation function is a linear function of the square of the scattering vector ( $q$ ) and the extrapolation of  $q \rightarrow 0$  passes through the origin, a characteristic of diffusive relaxation. The apparent average dynamic correlation length ( $\langle\zeta\rangle_{\text{slow}}$ ) estimated from  $\langle\Gamma\rangle_{\text{slow}}$  on the basis of the Stokes–Einstein equation is in the range 200–600 nm, as show in the inset of Figure 3. Enliss and Sorensen<sup>35</sup> also found that the mixture of water with a small amount of *tert*-butyl alcohol was also inhomogeneous, visible in a laser beam as a soft glow with a dynamic correlation length of  $\sim 100$  nm but invisible in normal room light.

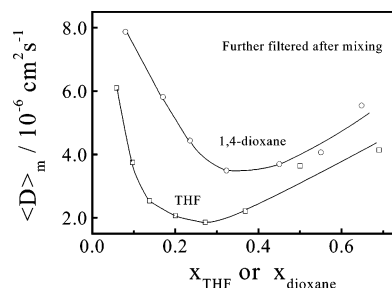
Very similarly, Figure 4 shows that the mixture of water and dioxane also contains a slow relaxation mode. In the range  $x_{\text{dioxane}} < 0.1$ , the slow relaxation mode is dominant with a dynamic correlation length ( $\langle\zeta\rangle_{\text{D}}$ ) of  $\sim 200$  nm, but the fast mode becomes more obvious with an increasing dioxane content, reflecting in the relative amplitude of the two relaxation modes. The contribution of fast relaxation reaches its peak value at



**Figure 4.** Measured intensity–intensity time correlation functions of mixtures of water and 1,4-dioxane without (open symbols) and with (filled symbols) further filtration after mixing.



**Figure 5.** Scattering vector ( $q$ ) dependence of average characteristic line width ( $\langle\Gamma\rangle_{\text{fast}} = 1/\langle\tau\rangle_{\text{fast}}$ ) of fast relaxation in mixtures of water and THF prepared with further filtration after mixing.



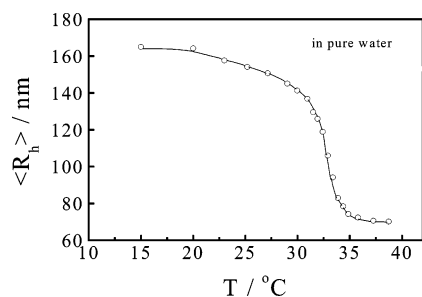
**Figure 6.** Cycloether-content dependence of average mutual translational diffusion coefficient ( $\langle D\rangle_{\text{m}}$ ) of mixtures of water and cycloether prepared with further filtration after mixing.

$x_{\text{dioxane}} \approx 0.55$ . However, the filtration of such mixtures of water and THF or 1,4-dioxane with a  $0.2\text{-}\mu\text{m}$  filter can completely remove the slow mode so that only the fast one remains after the filtration, as shown in Figure 4 by the filled symbols. Note that the slow relaxation was not due to dust because no speckle in the scattering intensity was detected even at small scattering angles.

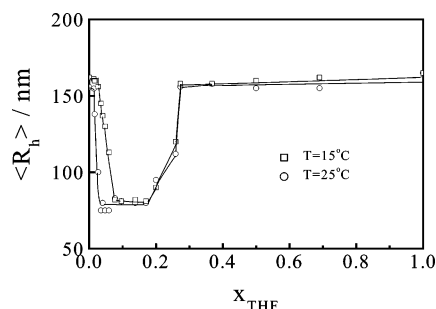
Figure 5 shows that the plots of  $\langle\Gamma\rangle_{\text{fast}}$  versus  $q^2$  are also straight lines passing through the origin; that is, the fast relaxation is also diffusive, presumably related to the mutual diffusion of small water/cycloether clusters because the average dynamic correlation length ( $\langle\zeta\rangle_{\text{fast}}$ ) is in the range 0.3–1.0 nm. For each mixture, an average mutual diffusion coefficient  $\langle D\rangle_{\text{m}}$  can be derived from the slope of a corresponding line in Figure 5. The results are summarized in Figure 6. The mixture generally has a mutual diffusion coefficient smaller than that of either pure water or pure THF or dioxane as well as the diffusion of monomer tracers in water.<sup>36</sup> It is clear that in the range  $0.2 < x_{\text{THF}} < 0.4$ ,  $\langle D\rangle_{\text{m}}$  reaches its minimum value, agreeing well with the maximum static correlation length measured in neutron scattering and diffraction.<sup>22</sup>

Our results convincingly reveal the existence of some water clusters that are invisible in light. The complexation between these water clusters and cycloethers makes them visible because





**Figure 7.** Dispersion-temperature dependence of average hydrodynamic radius ( $\langle R_h \rangle$ ) of spherical PNIPAM microgels in pure water.



**Figure 8.** THF-content dependence of average hydrodynamic radius ( $\langle R_h \rangle$ ) of a trace amount of spherical PNIPAM microgels in mixtures of water and THF at two different temperatures (15 and 25 °C).

cycloethers have different refractive indexes. To have a better picture of such water clusters and complexation, we used a trace amount of thermally sensitive spherical PNIPAM microgels to probe the interaction between water and cycloethers. The swelling and shrinking of PNIPAM depends not only on the temperature but also on the cycloether content.<sup>29</sup> Note that the microgels concentration used here was so low that each monomer unit of PNIPAM was surrounded by  $\sim 10^7$  water molecules. The microgels have no influence on the interaction between water and cycloether as well as on the water structure, reflecting in no alternation of the fast relaxation mode (not shown). It is also helpful to note that spherical PNIPAM microgels swell in either pure THF or pure water. THF is a slightly better solvent for PNIPAM than water.

Figure 7 shows the shrinking of spherical PNIPAM microgels in pure water with an increasing temperature. At higher temperatures, the average hydrodynamic radius of the collapsed microgels decreases to  $\sim 70$  nm. The low critical solution temperature (LCST) of PNIPAM in pure water is  $\sim 32$  °C. Figure 8 shows that for a given temperature, the microgels undergo a shrinking-and-reswelling process with an increasing THF content ( $x_{\text{THF}}$ ). The addition of a small amount of THF results in dramatic shrinking of the swollen microgels. In the range  $0.05 < x_{\text{THF}} < 0.15$ , the microgels remain in the collapsed state. Further addition of THF leads to reswelling of the microgels in the range  $0.15 < x_{\text{THF}} < 0.3$ . Previously, Winnik et al.<sup>29</sup> found that, in the range  $x_{\text{THF}} < 0.13$ , the LCST of PNIPAM decreases sharply from  $\sim 32$  °C in pure water to  $-1$  °C with an increasing THF content. Mukae et al.<sup>26</sup> studied the swelling and shrinking of PNIPAM microgels in the mixture of water and alcohol and also found a swelling minimum ( $x_{\text{min}}$ ). Their results showed that in the mixture of methanol and water,  $x_{\text{min}} \approx 0.17$ , while in the mixture of ethanol and water,  $x_{\text{min}}$  decreases to  $\sim 0.07$ .  $x_{\text{min}}$  further decreases in the mixture of water and 1-propanol or *tert*-butyl alcohol.

On the basis of this study and previous results,  $x_{\text{min}}$  is found to decrease with an increasing size and hydrophobicity of molecules added into water, consistent with the hydrate clathrate

probability of alcohol and cycloether. Thermodynamically, it is understandable that a mixture of two poor solvents can lead to a good solvent, but not a mixture of two good solvents to a poor solvent. The existence of a certain range of  $x_{\text{THF}}$  or  $x_{\text{dioxane}}$ , in which PNIPAM is insoluble, tells us that the mixing is not as simple as we thought. It indicates the formation of some water/cycloether clusters that are nonsolvents for PANIPAM. In other words, the fast relaxation in the mixture of water and THF or 1,4-dioxane is related to the formation of small water/cycloether clusters.

After the addition of THF or dioxane, some cycloether molecules enter the hydrate clathrate cavities, and some are complexed with small water clusters, such as pentamer and hexamer. With an increasing THF or dioxane content, the hydrate clathrate-like structures break into small fragments to accommodate more guest molecules so that more water/cycloether clusters are formed. It has been shown that the pentamer structure is dominated in liquid water.<sup>37</sup> Our previous results also showed that in the range  $0.17 < x_{\text{methanol}} < 0.5$ , methanol and water molecules can form clusters with a structure gradually changing from  $(\text{H}_2\text{O})_{5m}(\text{CH}_3\text{OH})_m$  to  $(\text{H}_2\text{O})_{5m}(\text{CH}_3\text{OH})_{5m}$  via different intermediates  $(\text{H}_2\text{O})_m(\text{CH}_3\text{OH})_n$  with  $m/n = 5/2, 5/3$ , and  $5/4$  as the methanol content increases.<sup>38</sup>

In the present study, as shown in Figure 8, the addition of a small amount ( $\sim 4$ – $8$  mol %, depending on the temperature) of THF leads to the full collapsing of the microgels. This indicates that, on average, each THF molecule complexes with 24–12 water molecules. In the range  $0.15 < x_{\text{THF}} < 0.25$ , the microgels reswell with an increasing THF content. When  $x_{\text{THF}} > 0.25$ , the swelling stops and reaches its maximum, just as in pure THF. Similar results were also reported by Winnik et al.,<sup>29</sup> but their interest was focused on the LCST of PNIPAM, not the water structure. The present study and previous results reveal that when  $x_{\text{THF}} > 0.25$ , PNIPAM are essentially solubilized by free individual THF molecules. In other words, water cannot complex with all the THF molecules when  $x_{\text{THF}} > 0.25$ . From the fully reswelling point, we estimate that one THF molecule, on average, complexes with  $\sim 3$  water molecules, similar to the low-density clusters in supercooled water,<sup>20,21</sup> indicating that water contains short-lived polygons and even polyhedra. The addition of guest molecules in water could strengthen and rearrange these structures. It should be stated that PNIPAM in the mixture of methanol and water reaches its full reswelling at a higher  $x_{\text{methanol}}$  of  $\sim 0.5$ .<sup>22,38</sup> This is because each water pentamer can complex with five methanol molecules.

Next, let us examine the complexation between water and dioxane. As shown in Figure 6, in the range  $0.33 < x_{\text{dioxane}} < 0.6$ , i.e.,  $[\text{dioxane}]:[\text{water}] = 1:2$  to  $3:2$ ,  $\langle D \rangle_m$  reaches a minimum. One dioxane molecule has two oxygen atoms that can form up to four hydrogen bonds with water molecules. If the interaction of dioxane molecules with the water pentamer is similar to that between water and methanol or THF,  $\langle D \rangle_m$  should reach its minimum at a much lower value of  $x_{\text{dioxane}}$ . The actual minimum located in the higher range  $0.33 < x_{\text{dioxane}} < 0.6$  indicates that dioxane might affect the pentamer structure of water. Note that at 25 °C, the microgels do not shrink in the mixture of water/dioxane. Similar results were also reported by Schild et al.<sup>39</sup> They showed that the LCST of PNIPAM was nearly independent of the amount of dioxane added up to  $x_{\text{dioxane}} < 0.35$  and then increases sharply when  $x_{\text{dioxane}} > 0.35$ .

Satoru et al.<sup>8</sup> indeed showed that, while  $x_{\text{dioxane}} > 0.17$ , the pentamer structure of pure water was broken so that water molecules could form micelle-like clusters with dioxane molecules. A possible composition would be that each dioxane

molecule forms two hydrogen bonds with two water molecules. Figure 6 shows that the clusters formed in the mixture of water and THF have a smaller  $\langle D \rangle_m$ , or a larger size, in comparison with those formed in the mixture of water and dioxane, which further supports that the pentamer structure of water was broken in the presence of dioxane. This explains why  $\langle D \rangle_m$  in the mixture of water and dioxane is always larger (smaller size and moving fast) than that in the mixture of water and THF for a given concentration, even though dioxane is larger than THF.

## Conclusions

A simple mixture of water and cycloethers is not microscopically homogeneous. There exists some large-scale concentration fluctuation with a dynamic correlation length of  $\sim 200$ – $600$  nm. Such concentration fluctuation (microscopically imperfect mixing) can be removed by a simple filtration of the mixture with a  $0.2\text{-}\mu\text{m}$  filter. It indicates that the filtration can homogenize the mixture and break microscopic cycloether droplets remaining after mechanic stirring or ultrasonic vibration. The present study together with previous results reveals that in liquid water water molecules exist as a mixture of small clusters, such as pentamer and hexamer. The cycloether molecules added can complex with these water clusters via hydrogen bonding as well as enter the cavities of the water structure. The complexation makes the water clusters visible in laser light scattering. The water/cycloether complexes are nonsolvents for poly(*N*-isopropylacrylamide) (PNIPAM) microgels even though both pure water and pure cycloether are good solvents at lower temperatures. The average mutual diffusion coefficient  $\langle D \rangle_m$  of these water clusters reaches a minimum at  $x_{\text{cycloether}} \approx 20\%$  and  $\approx 33\%$ , for the water/THF and water/dioxane mixtures, respectively. The fact that PNIPAM microgels can reswell to a fully swollen state as in pure THF with an increasing THF content at  $x_{\text{THF}} \approx 25\%$  indicates that each THF molecular can, on average, complex only with three water molecules. When  $x_{\text{THF}} > 30\%$ , some of THF molecules added exist as individual molecules. It is these free THF molecules that resolvate PNIPAM. The minimum value of  $\langle D \rangle_m$  in the mixture of water and dioxane appears in the higher range  $0.33 < x_{\text{dioxane}} < 0.6$ , suggesting a possible breakage of the pentamer structure of water so that liquid water complexes with more dioxane molecules.

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