Inhomogeneous Distribution and Collective Diffusion of Solution Molecules in the Nanochannel of Mesoporous Silica

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^{13}C NMR spectra were observed for the mixed solutions composed of 2-propanol and cyclohexane in contact with a mesoporous silica, MCM-41, to study the distribution and dynamics of these molecules in the nanochannel of MCM-41. From the analysis of the spectral and relaxation data, we deduced that a high concentration gradient exists in the radial distribution of these liquid molecules in the nanochannel: alcohol molecules prefer the region near the surface and cyclohexane molecules the central portion of the nanochannel. Further evidence for this new model have been obtained by the spin-probe ESR observations. In addition, we obtained a model for the movement of solution molecules in the nanochannel: molecules "flow or diffuse collectively" by slipping on the channel surface.

Introduction

Mesoporous silica made by the template method, such as MCM-41,[1] is a promising material for the chemistry of the 21st century, since its nanochannel can be employed as a nano chemical factory,[2−5] a nanodevise,[6] etc. with a novel design of the system. To realize these fascinating functions, we have to clarify the details of molecular interactions, molecular dynamics, and other physicochemical features of the molecules in the nanochannel. In previous studies we observed a large magnetic field effect in the photoreduction of xanthone by xanthene in 2-propanol, which flows in the column packed with MCM-41.[5,7,8] Since a large magnetic field effect occurs only for the systems where the intermediate radical pair keeps pairing for a long period, e.g. more than a few microseconds,[9] we proposed a model wherein the solution molecules in the nanochannel make clusters during the flow and prevent the intermediate free radicals from diffusing away. According to the Hagen−Poiseulle law, a classical theory on the liquid flow in a tube, however, the solution cannot flow in the nanochannel at the rate employed in the experiment. To solve the discrepancy, we made a spin-probe study on the solution flow in the column packed with MCM-41 and succeeded in showing that the spin-probe solution actually gets through in the nanochannel of MCM-41.[10] This result means that the classical fluid dynamics is not applicable to the fluid in the nanochannel. With reference to the previous experiments on the magnetic field effect,[5,7,8] we postulated that the solution molecules slip on the surface of the nanochannel during the "flow".[10]

Several works have been done to study the diffusion phenomena for the molecules in the nanochannel of MCM-41[11−13] by the pulsed field-gradient NMR method.[14] Hansen, Courivaud, and others observed that methylation of the nanochannel surface decreased the diffusion rate of *n*-hexane by 40%, but chlorination increased it by 80%.[11] These results indicate that molecular diffusion in the nanochannel is deeply related to the interaction between the solution molecules and the nanochan-

nel surface. Gjerdaker et al. studied on the physical state of cyclohexane in the nanochannel of MCM-41.[12] They showed that cyclohexane in the nanochannel does not get into the glassy phase at the transition temperature in the bulk. Stallmach et al. observed that the rate of self-diffusion of benzene in the nanochannel of MCM-41 exceeds that in the bulk and presented a model that the molecules diffuse through the gas phase.[13] These studies also suggest that the classical fluid dynamics is not applicable to the fluid in the nanospace.

Though a considerable number of NMR studies have been done on the molecular dynamics in the nanochannel of MCM-41 for pure liquids, as introduced above, there is no study on the mixture solution, which is indispensable to discuss about the chemical reaction in the nanochannel. In the present study we tried to clarify the physical state of mixture solutions in the nanochannel through observing the high-resolution ^{13}C NMR of them in contact with MCM-41 particles. We succeeded in showing that the mixture solution composed of cyclohexane and 2-propanol becomes inhomogeneous in the nanochannel with the liquid character being kept. This new finding has been confirmed by the spin-probe ESR study. In addition, we have presented a model for the collective movement of the solution molecules in the nanochannel which has been suggested in previous works.[5,7,8,10]

Experimental Section

MCM-41 was synthesized by the template method employing hexadecyltrimethylammonium bromide as the micellar component as in the procedure in a literature.[15] The diameter of the nanochannel was calculated to be 3.4 nm from the X-ray diffraction data and the surface area 1100 m[2]/g.[8] The particle size is around 10 μm, as shown in Figure 1, which is a SEM image of the MCM-41 particles. Nuclesil-50, a spherical porous silica developed for chromatography, was purchased from Macherey-Nagel (Germany). The pore diameter is about 5 nm, and the specific surface area is 450 m[2]/g.

DTBN radical (di-*tert*-butylnitroxide) was purchased from Aldrich Chemicals and used as supplied. 2-Propanol and

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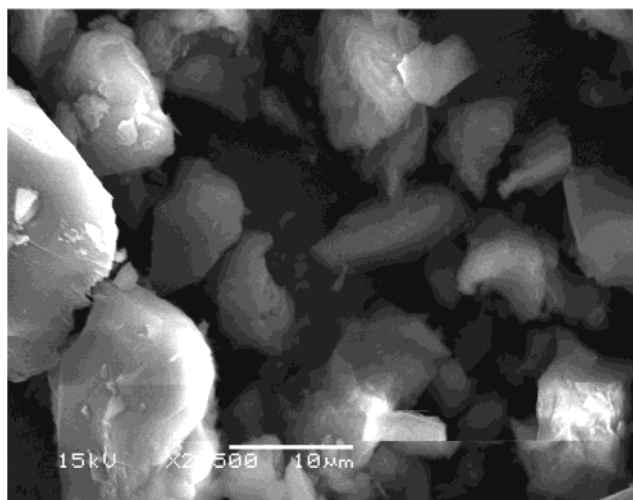
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Figure 1. A SEM image of the MCM-41 particles synthesized and used in the present study.

cyclohexane of guaranteed grade were purchased from Wako pure chemicals and used after dehydration with molecular sieve (3 Å). Measured amounts of 2-propanol and cyclohexane (0.8 mL in total) were transferred in vacuo to a 4.2 mm i.d. (5.0 mm o.d.) NMR tube containing 150 mg of MCM-41, which was dehydrated overnight and additionally for 1 h in vacuo at 400 K. After sealing off, MCM-41 was dispersed completely in the solution and left precipitated to the bottom overnight.

We hereafter call the two parts, the precipitated MCM-41 layer and the upper solution part, the MCM-41 layer and the clear solution part, respectively. The MCM-41 layer is longer when the cyclohexane content is higher. All the NMR observation was made at ambient temperature (air-conditioned at 298 K) with a Bruker MSL-200 spectrometer operated at 50.3 MHz for the ^{13}C nucleus. MCM-41 of the same lot was employed in a series of NMR measurements to reduce the observation error caused by some minor changes in the MCM-41 structure.

For the ESR observation the sample solution in the reservoir was introduced to the quartz cell (3.0 mm o.d.) containing MCM-41 powder. The excess solution was evaporated back to the reservoir by cooling it at 77 K until the powder appears dry, when the cock between the two parts was closed. Thus, all the ESR absorption comes from the spin probes in the nanochannel. The ESR spectrum was observed with a JEOL JES−RE1XM spectrometer at an ambient temperature (298 K).

Results and Discussion

1. ^{13}C NMR Spectrum. Figure 2 shows the broad-band proton-decoupled ^{13}C NMR spectra (a−d) of the solutions in the MCM-41 layer containing 2-propanol and cyclohexane at various ratios. The chemical shift is graduated relative to that of cyclohexane assumed as 27.0 ppm. For comparison, the NMR spectrum for the mixture with Nuclesil-50 (e), a spherical porous silica used instead of MCM-41, and that for the clear solution part (f) are also shown. All the peaks of spectra a−d, those at about 25 ppm for the methyl carbon, 63 ppm for the CHOH carbon of 2-propanol, and 27 ppm for the cyclohexane carbon, are broadened severely even in the presence of broad-band proton decoupling. It is quite interesting to point out that the line widths are reduced to around 1/5, when MCM-41 in the sample is replaced with Nucleosil-50.

Figure 3 shows the line widths of these carbon signals as functions of F_{CHX}, the volume fraction of cyclohexane in the solution. It is noteworthy that the peak for the CHOH carbon
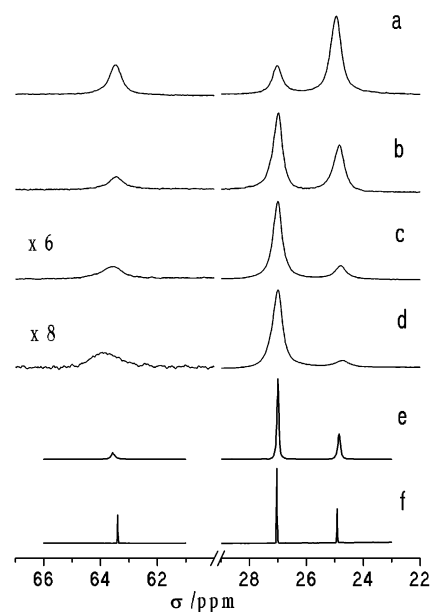

Figure 2. Proton-decoupled ^{13}C NMR spectra of the solutions containing 2-propanol and cyclohexane at various ratios in the layer of MCM-41 (a−d) and spectra for reference (e−f). Spectra a, b, c, and d are those at the volume fraction of cyclohexane, F_{CHX}, 1/8, 3/8, 5/8, and 7/8, respectively. Reference signals: e, Nucleosil-50 employed instead of MCM-41; f, the clear solution part. Spectra a−d were observed within 1−2 days after sample preparation. MCM-41 used in all the observations was produced in the same lot.
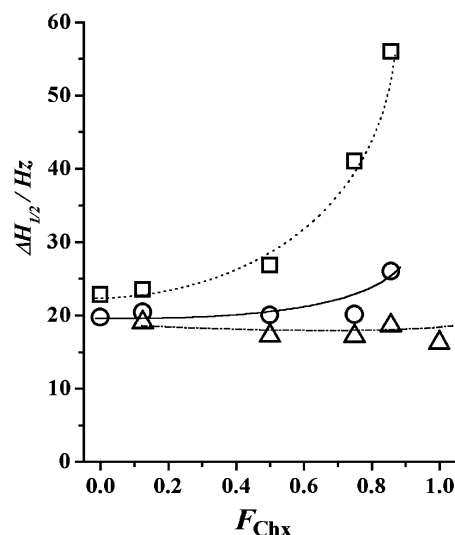

Figure 3. Line widths of the proton-decoupled ^{13}C NMR spectra of the mixed solution of 2-propanol and cyclohexane in the MCM-41 layer as functions of F_{CHX}, the volume fraction of cyclohexane. Circles, squares, and triangles represent the line widths (full width at half-height) for the CH$_3$ and CHOH signals of 2-propanol and the cyclohexane carbon signal, respectively.

of 2-propanol becomes broadened steadily with increasing F_{CHX}; the line width becomes more than double with the increase of F_{CHX} from 0.125 to 0.875. In addition, as Figure 2 shows, the peak shifts by about 0.5 ppm to the lower field at the lowest 2-propanol content ($F_{CHX} = 0.875$). For other NMR signals, however, no appreciable shifts were detected in the peak positions, and changes in the line width were not so large.

First of all we would like to pay attention to the fact that a single broad line was observed for each carbon nucleus (Figure 2, a−d), though considerable molecules in the MCM-41 layer should exist outside the nanochannels.[7] In addition, the line
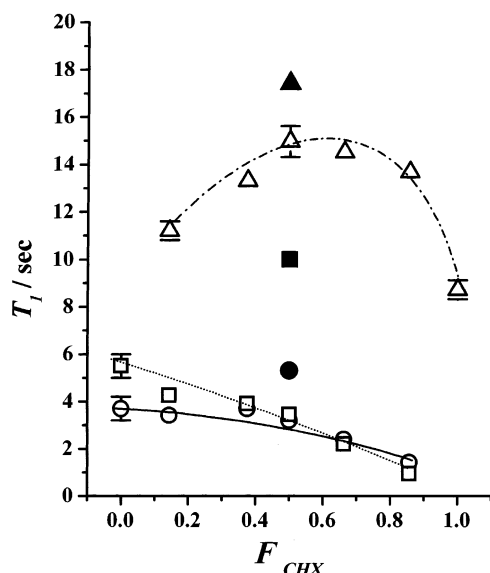
Figure 4. ^{13}C spin lattice relaxation times, T_1's, for the mixed solution of 2-propanol and cyclohexane in the MCM-41 layer as functions of F_{CHX}. Open circles, squares, and triangles represent those for the CH_3 and CHOH carbons of 2-propanol and the CH_2 carbon of cyclohexane, respectively. The closed marks represent T_1's for the clear solution at $F_{CHX} = 0.5$. The proton decoupler is off during the waiting time between the adjacent pulse sequences, which was set as 90 s.
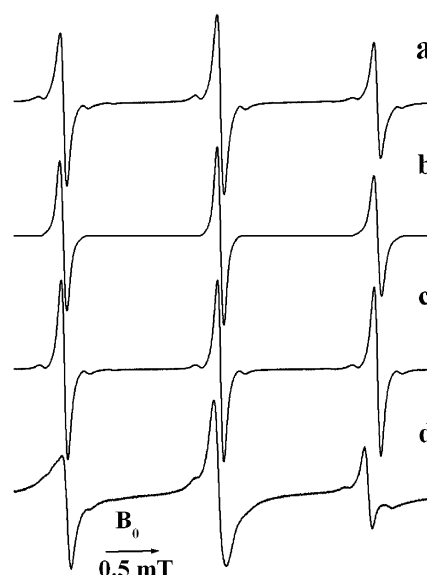

Figure 5. ESR spectra of DTBN under various conditions: (a) 2-propanol solution in the nanochannel of MCM-41, (b) simulation for spectrum a, (c) clear 2-propanol solution, (d) in a mixed solution with cyclohexand and 2-propanol at the ratio of 3:1 in the nanochannel of MCM-41.

shapes of these peaks are Lorentzian in good approximation. These feature of the system did not change largely, even if the observation temperature was lowered to 243 K. On the other hand, the line width of the cyclohexane signal increased by more than 4 times when the solution outside the granules was removed. Therefore, we conclude that the molecules in the above experiment get into and go out of the nanochannels frequently enough to give a single NMR line for each carbon nucleus.[16] A steep increase in the line width and the gradual shift of the CHOH-carbon signal upon decreasing the 2-propanol content indicate that the 2-propanol molecules interact more strongly with the functional groups on the nanochannel surface, e.g. Si−OH,[17] in the system with less 2-propanol content. These phenomena are possible only when 2-propanol molecules are preferably distributed near the surface of the nanochannel with the liquid characteristics being kept.

As for the large line width, we have to consider many factors, including anisotropy in the magnetic susceptibility of MCM-41 and intermolecular magnetic interactions, in addition to the intramolecular C−H dipolar interaction. We will discuss on these factors in a later section.

2. Spin Lattice Relaxation of ^{13}C Nucleus. Figure 4 shows the spin−lattice relaxation times, T_1 values, obtained by the inversion recovery method for the solutions in the MCM-41 layer. T_1's for a clear mixture solution at $F_{CHX} = 0.5$ are also shown for comparison. A single relaxation parameter was obtained from the usual logarithmic plot of the amplitude for each peak of the spectra. When the 2-propanol content decreased from 100% to 12.5% (i.e., from $F_{CHX} = 0.0$ to 0.875), T_1 for the CHOH carbon of 2-propanol decreased monotonically to less than 1/5 of that in the pure system. A considerable decrease in T_1 was also observed for the methyl carbon.

These observations indicate that 2-propanol molecules, which are rather hydrophilic, prefer the positions near the surface of the nanochannel, where the rotational diffusion of the molecule is restricted by the interactions with the surface groups of the nanochannel, e.g. Si−OH.[17] On the other hand, the T_1 value for the CH_2 carbon of cyclohexane, which is hydrophobic, at a

content in the $0.4 < F_{CHX} < 0.8$ range remains longer than 13 s, which is not shortened very much from 17.5 s for the clear solution. It should be noticed that the T_1 value is shortened to about 9 s for neat cyclohexane in the MCM-41 layer. This latter observation indicates that the rotational diffusion of cyclohexane is decelerated considerably without 2-propanol, which may keep out the cyclohexane molecules from the nanochannel surface.[18] Therefore, the relaxation data also supports the model that 2-propanol molecules are preferably located near the surface and cyclohexane molecules are almost at the center of the nanochannel in the mixed system. We may summarize this section as follows: (1) the T_1 value of cyclohexane carbon stays long in the nanochannel of MCM-41, if some 2-propanol coexists in the system. This result clearly indicates that the cyclohexane molecules stays in the central portion of the nanochannel. (2) The drastic decrease in the T_1 value for the CHOH carbon of 2-propanol upon decreasing its content clearly indicates that the 2-propanol molecules exist preferentially near the surface of the nanochannel. (3) From the above statements we get that the molecules are distributed inhomogeneously in the nanochannel, with holding the liquid properties. This was proposed for the first time in a previous study, where the solution flow in the nanochannel was monitored by the spin probe technique.[10]

3. ESR Spin Probe Study. To obtain further information on the mobility of molecules in the nanochannel, we observed the ESR spectrum of a spin-probe, DTBN (di-*tert*-butylnitroxide), introduced in the nanochannel of MCM-41. Figure 5shows the ESR spectrum of a 2-propanol solution of DTBN in the nanochannel (a) and its simulation spectrum (b). In addition to these, spectrum c is that observed for DTBN in 2-propanl in the absence of MCM-41, and spectrum d is for DTBN in a mixed solvent composed of cyclohexane and 2-propanol at the ratio of 3:1 in the nanochannel. ESR spectrum a is a three-line one which is similar to that in the bulk solution (c) except for the relative peak heights among the three lines and their line widths. The averaged correlation time (τ_c) of the anisotropic magnetic interaction for the simulation spectrum (b) was 8.0×10^{-11} s.[19] Since the spectral simulation was successfully made (b) by assuming preferential rapid rotational diffusion of the

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DTBN radical along the longest molecular axis, connecting the two *tert*-butyl carbons, the DTBN molecule must be located in the central portion in the nanochannel. This means that the surface of the nanochannel may be covered with 2-propanol and a relatively narrow region is left for the DTBN molecule, which is basically hydrophobic, in the central portion of the nanochannel. When a hydrophobic solvent, e.g. cyclohexane, is employed, the NO group of DTBN molecule may interact strongly with the surface and the ESR spectrum for an immobilized nitroxide radical (not shown) is observed. When a small part of 2-propanol was added to this system, the ESR spectrum changes to a spectrum similar to d. This means that 2-propanol strips the DTBN molecules off the surface of the nanochannel. These observations also support the inhomogeneous distribution of liquid molecules in the nanochannel.

The ESR spectrum (c) for DTBN in the clear 2-propanol solution appears a little sharper than that in the nanochannel; thus, the mobility of nitroxide radical should be lowered in the nanochannel, though it holds the liquid state as a solute. Since the molecular dimension of cyclohexane is a little smaller than that of DTBN, whose averaged rotational correlation time is 8 $\times$ 10^{-11}s according to the simulation, the τ_c for the intramolecular magnetic interactions, e.g. chemical shift anisotropy and C$-$H magnetic dipolar interaction, of cyclohexane in the solution must be less than the above value.

4. Line Width of ^{13}C NMR Peaks. The large line width of the solution NMR signal for the molecules in the MCM-41 layer may give us important information about the system. As mentioned above, the correlation time for the intramolecular anisotropic interaction for an isolated molecule may be smaller than 10^{-10} s. Therefore, $\omega_0\tau_c \ll 1.0$ and thus $T_1 = T_2$, if the same interactions contribute to both the NMR relaxation parameters. [19] Here, ω_0 is the angular frequency of the ^{13}C NMR transition, $\omega_0 = 3.16 \times 10^8$ s^{-1}. Since the T_1 value for the cyclohexane carbon is longer than 9 s (Figure 4), the large line width ($=2/T_2$) of Figure 2 must not be due to the interactions that contribute to the T_1 process, i.e., intramolecular magnetic interactions, as is usual for the solution NMR experiment. This is also the case for the 2-propanol carbon, though the T_1 values are considerably shorter than that of cyclohexane. Therefore, the large line width must be due to the distribution of the NMR frequency. This type of line width is called "inhomogeneous line width". There must be several mechanisms for the inhomogeneous line width: (1) anisotropy in the magnetic susceptibility of MCM-41, whose structural symmetry is hexagonal and (2) dipole interaction with protons and other magnetic nuclei on the surface of nanochannel. Since the molecules rapidly diffuse in and out of the nanochannel, the resonance frequency changes in correlation with this movement. So, the inhomogeneous line width is averaged by this molecular wandering process and as the result the line shape turns into Lorentzian from Gaussian.[20]

If we employ the usual diffusion theory with a typical diffusion rate of 10^{-9} m^2/s, it takes around 50 ms for the molecules to diffuse in and out of the nanochannel whose length is around 10 μm. This frequency is too small to average out the inhomogeneous broadening to yield a Lolenzian line with the width of around 20 Hz. Therefore, the process for the molecules to go through the nanochannel must be completely different from the usual diffusion process.

5. Collective Diffusion of Molecules in the Nanochannel. As referred to in Introduction, Hansen et al.[11] showed that the diffusion rate in the nanochannel is very much dependent on the chemical structure of the nanochannel surface. They also

showed that *n*-hexane molecules diffuse through the nanochannel of MCM-41 faster, when the diameter of the nanochannel is smaller. In addition, we obtained the results mentioned above that the solution molecules move translationally in the nanochannel at a rate much faster than the rate predicted by the classical diffusion theory. These results indicate that we need a completely new model for the molecular transportation process in the nanospace.

We would like to propose a model here for the rapid movement of solution molecules through the nanochannel, which may be called a "microflow" or "collective diffusion". We consider that this new type of flow or diffusion is induced by a pressure difference between the inlet and outlet of the nanochannel instantaneously arising as a hydrodynamic fluctuation. The concept of this process is between "flow" and "diffusion". It is a flow in a sense, since it is induced by the pressure difference between the inlet and outlet of the tube, i.e., it is a phenomenon in a rather wide area. On the other hand, it may be regarded as a new type of diffusion, since the pressure difference is due to thermal fluctuation. As the most prominent difference from classical diffusion, we consider that the solution molecules in the nanochannel move or diffuse collectively through slipping on the channel surface. This may be because the instantaneous pressure gradient is considerably high, but without the slip on the nanochannel surface the transport process may take a long time as the Poiseulle law predicts. Therefore, we propose that (1) molecules diffuse collectively in the nanochannel. This may be called "collective diffusion" or "microflow", whose feature is far different from those described with the usual diffusion equation or the Poiseulle's law, respectively. (2) Slipping of the molecules on the nanochannel surface is essential for the description of this microflow or collective diffusion.

6. Relation on the Magnetic Field Dependent Reaction in the Nanochannel. In previous studies we observed a large magnetic field dependence in the photoreduction of xanthone in 2-propanol, which was UV-irradiated during the flow in the column packed with MCM-41.[5,7,8] This magnetic field effect was found to be due to an unusually long lifetime of the radical pair intermediate, say 10 μs or more.[7,8] However, it is not commonly accepted that the two free radicals interacting with an energy much smaller than the thermal energy can pair for a long period in a channel opened at both ends. So, we considered that 2-propanol molecules form clusters in the nanochannel and prevent the two free radicals from both recombination and far separation.[7] Here, we had better modify this model a little as described above: due to the collective movement of the solution molecules and radial inhomogenuity of the molecular distribution in the nanochannel, hydrophobic intermediate free radicals flow near the center of the channel without changing their order, i.e., temporally forming a single-file-like flow.[21,22] Since it takes tremendous time for the solution to flow classically through the nanochannel,[23] a new type of flow of the solution molecules in the nanochannel is essential for our experiments.

Although the previous experiments were made with a flow system, MCM-41 was packed in a column and the 2-propanol solution was let flow slowly in it, the essential feature of the molecular transportation through the nanochannel may be similar to the "collective diffusion" of the solution molecules proposed in the present study. The solution flow in the nanochannel in the previous system and the molecular diffusion through the nanochannel in the present system must be essentially the same. The pressure supplied to the column reactor may create the flow of the solution between the MCM-41 particles, and the

transportation through the nanochannel may occur as the "collective diffusion" or "microflow" by the pressure appeared instantaneously as the thermal fluctuation.

Conclusion

As the essential features of the mixture solution in the nanochannel, we list the following: (1) In the nanochannel of MCM-41, an inhomogeneous molecular distribution is created in the radial direction, when a mixed solution is introduced. (2) In the nanochannel, molecules "diffuse collectively " by the pressure difference appearing between the two terminals of the nanochannel as the thermal fluctuation. Thus, solution molecules go through the nanochannels by slipping at the surface of the nanochannel. In addition, hydrophobic solute molecules in a hydrophilic solvent move near the central portion of the nanochannel as approximately a single-file.

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(16) More than 1/4 of the solution exists outside the nanochannel even in the MCM-41 layer (ref 7). So, if the molecules do not exchange their positions between inside and outside of the nanochannel, we should observe an overlapped signal composed of both the sharp and the broad peaks for the molecules in the two regions.

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(18) The T_1 value for the CH_2 carbon of cyclohexane also decreases a little upon decreasing the cyclohexane content. This is simply explained by the increase in the number of alcohol molecules around the cyclohexane molecules.

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(23) Hagen−Poiseuille's law, with which the flow rate is usually calculated for a solution in a tube, predicts that it takes about 3 min to flow a 2-propanol solution through a nanotube (i.d. 3.0 nm, length 3 μm) at a pressure of 200 atm.