Viscosity and Volume Effects on Convective Flows in PGSE-NMR Self-Diffusion Measurements at High Temperature

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Abstract : The effects of the sample viscosity and volume on the convective flows induced by temperature gradient in PGSE-NMR self-diffusion measurements at high temperature have been investigated. The experimental results showed that the viscosity of the liquid sample strongly affects the magnitude of the convective flows as well as the diffusion coefficient itself. It was also found that the convective flows increase as the sample volume increase.

Keywords : diffusion, convection, volume effects, viscosity, NMR

INTRODUCTION

The diffusion experiments using pulsed-gradient-spin-echo (PGSE) NMR have been adopted in many fields and for various purposes due to their simplicity and usefulness.[1,2] However, it was found out that the liquid convection (e.g. buoyancy-driven convection) which can interrupt the accurate measurement of diffusion coefficients occurs in a sample tube at high temperatures. There has been many efforts to suppress it in various ways, such as applying convection compensating pulse sequences,[3] decreasing sample size,[4] and using modified NMR tubes.[5,6] To reduce these convectional

flows effectively, it is necessary to understand the physical characteristics associated with the convection. There should be several factors to induce convective flows and to determine its degree in a sample tube.

In this study, by using we investigated the effects of the sample viscosity and volume on the convective flows induced by temperature gradient along the sample tube using PGSE-NMR self-diffusion measurements at high temperature. From these experimental results, we could know that the viscosity of the liquid sample strongly affects the strength of the convective flows as well as the diffusion coefficient itself. Additionally, the convective flows increase as the sample volume increases.

EXPERIMENTAL METHODS

Acetone-d_6 (99.9%), methanol-d_4 (99.8%), pyridine-d_5 (100%) and NMR tubes which were used in this research were purchased from Sigma-Aldrich Co. The deuterated solvents were used without further purification. All the NMR experiments were performed at various temperatures on a Bruker Avance 600 and a Varian VNS 600 spectrometers, and all diffusion experiments detecting residual proton signals of deuterated solvents were performed using the bipolar pulse longitudinal eddy current delay pulse sequence (BPPLED).[7] The spoil gradients were also applied at the diffusion period and the eddy current delay. Typically, a value of 1~2 ms was used for the gradient duration (δ), 70~100 ms for the diffusion time (Δ), and the gradient strength (g) was varied from ca. 1.5 G/cm to 70 G/cm in 16 steps. Each parameter was chosen to obtain ~90% signal attenuation at the last step

experiment. The pulse repetition delay (including acquisition time) between each scan was 10~12 sec. The time for temperature stabilization after changing the target temperature was more than 20 min. Data acquisition and self-diffusion coefficients calculation were performed using the Bruker topspin software.

To evaluate the effects of the sample volume, each deuterated solvent was placed in conventional 5 mm o.d. NMR tubes with 3 different sample heights (4, 8, 12 cm) in addition to a 2mm o.d. capillary tube for control experiments.
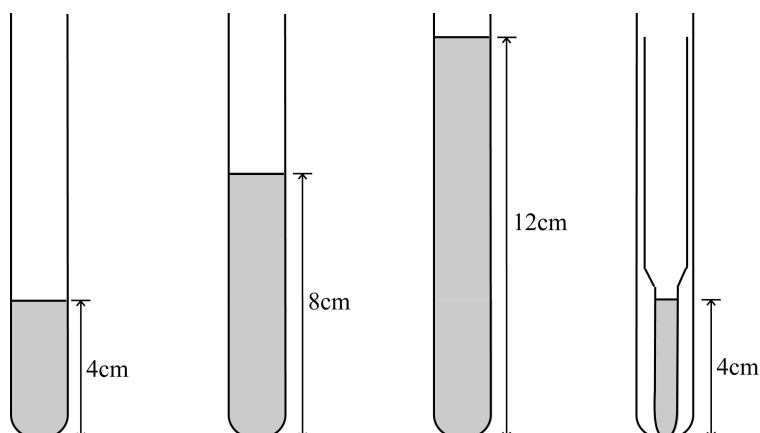
RESULTS AND DISCUSSION

The diffusive motions of molecules are related with the solvent viscosity by the well-known Stokes-Einstein equation:[7]

$$D = \frac{kT}{c\pi\eta r_H} \qquad (1)$$

where c is the Stokes-Einstein number, k is the Boltzmann constant, T is temperature, r_H is the hydrodynamic radius, and η is the viscosity of the solvent. The number c is generally expressed as 4 for slip boundary condition and 6 for non-slip boundary condition. Viscosity varies in inverse proportion to diffusion coefficient value according to this equation. To investigate the overall influence of liquid viscosities on diffusion experiments, three deuterated solvents (acetone-d_6, methanol-d_4, and pyridine-d_5) having different viscosities respectively have been used in PGSE-NMR experiments at 298, 308 and 318K.

It is a well-known fact that the viscosity of liquid is a function of temperature, and we succeeded to find out whole set of viscosity for three deuterated solvents by literature search[10] except that of methanol-d_4 at 318K. To obtain the value, we have introduced the Vogel–Fulcher–Tammann (VFT) equation which is widely used for determining viscosity values.[8,9] It represents the absolute viscosity as follow,

$$\ln \eta = A + \frac{B}{C + T} \qquad (2)$$

where η is viscosity and T is absolute temperature. The viscosity value of methanol-d_4 at 318K could be calculated by the three parameters (A, B, C) obtained from the known viscosity values at three different temperatures.[10] As listed in Table 1, the viscosity of each deuterated solvent increases in the order of acetone-d_6, methanol-d_4, and pyridine-d_5 at the range of 298~318K.

To compare the effect of solvent viscosity on self-diffusion coefficient itself without convection, a capillary tube was used because it is known that the self-diffusion coefficient values obtained from

liquids in a capillary tube are free from convection.[11,12] The self-diffusion coefficients of three solvents increase almost linearly as temperature increases, and they are in inverse proportion to the absolute viscosities of the solvents (see Figure 1).

Table 1. Absolute viscosities, densities, and calculated kinematic viscosities of acetone-d_6, methanol-d_4, and pyridine-d_5.

Temp	acetone-d_6			methanol-d_4			pyridine-d_5		
	absolute viscosity (cP)	density (g/ml)	kinematic viscosity (cSt)	absolute viscosity (cP)	density (g/ml)	kinematic viscosity (cSt)	absolute viscosity (cP)	density (g/ml)	kinematic viscosity (cSt)
298K	0.326	0.782[a]	0.417	0.602	0.786[c]	0.765	0.945	0.978[e]	0.898
308K	0.297	0.771[a]	0.385	0.528	0.777[d]	0.680	0.821	0.968[e]	0.789
318K	0.271	0.759[b]	0.357	0.471	0.768[c]	0.614	0.721	0.958[e]	0.704

All the absolute viscosities are obtained from Ref. 10 except that of methanol-d_4 at 318K.

[a] Ref. 16; [b] Extrapolated value from the data of Ref. 16; [c] Extrapolated values from the data of Ref. 17; [d] Ref. 17; [e] Ref. 18.
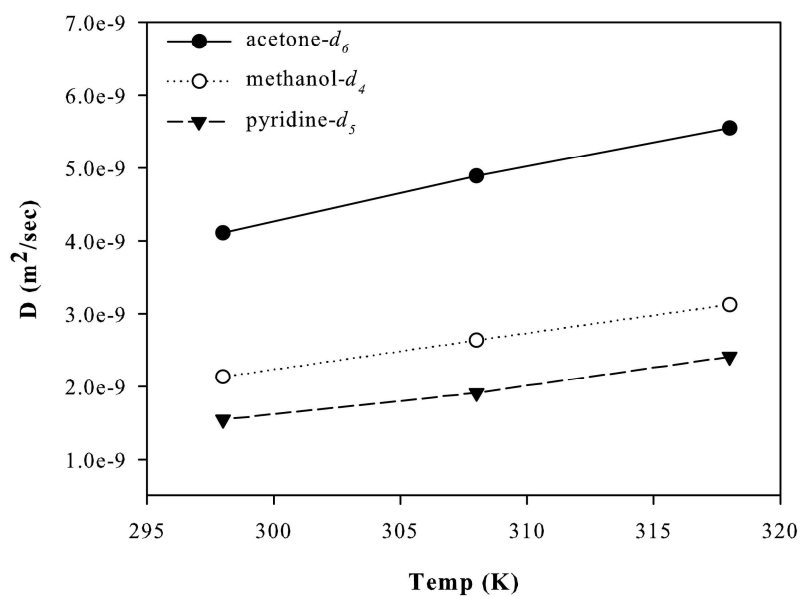
Figure 1. The temperature dependency of the observed self-diffusion coefficients of acetone-d_6, methanol-d_4, and pyridine-d_5 in capillary tubes.

Figure 2 showed the temperature dependency of the obtained diffusion coefficients of three deuterated solvents in the 5mm o.d. NMR tubes with varying the sample volumes up to 3 times. As it is a well-known fact that there exists convective flows in the 5mm tubes above room temperature due to natural convection induced by temperature gradient along the sample axis.[4,6] The diffusion coefficient values obtained above 298K increased significantly compared with those values obtained from the capillary tubes due to the convective flows in the 5mm sample tubes. It was also found that the observed diffusion coefficients increased as sample volumes increased in this temperature range.
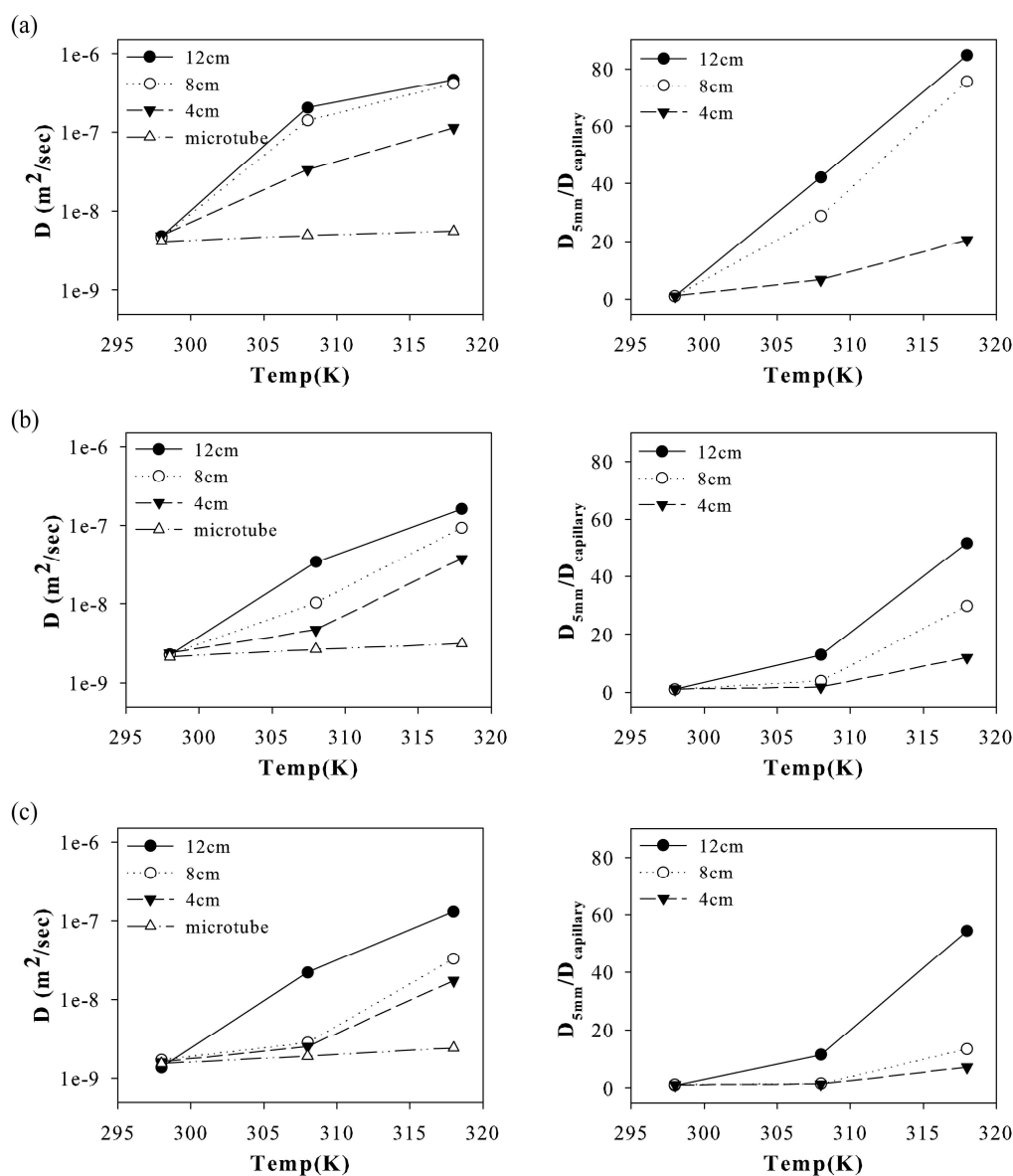
Figure 2. The temperature dependency of the observed self-diffusion coefficients of (a) acedone-d_6, (b) methanol-d_4, and (c) pyridine-d_5 with the sample height of 4cm, 8cm, 12cm each in a 5mm o.d. tube and 4cm in a capillary tube. The ratios of the diffusion coefficient values from the 5mm o.d. tubes to that from the capillary tube (right) are also presented to allow the magnitudes of the convective flows to be easily compared. Note that the diffusion coefficient values are expressed in common logarithm scale.

NMR signals are generally obtained from the central part of ~1cm in a sample tube. In this study, we have set the same signal acquiring part for all samples in normal 5mm tubes. Thus the liquid volume above the signal acquiring part increases as much as the increment in the sample height. Typically, if there were something above, the molecular diffusion could be obstructed. However, according to the experimental results, as shown in Figure 2, the convective flows seem to be enhanced as the sample volume increases to 2~3 times.

Goux et al. had introduced Rayleigh-Bénard number for explaining the stength of convective flows in a 5mm NMR tube above room temperature,[11] which is defined as;

$$R_a = \frac{g\beta\Delta TL^3}{\nu\alpha} \qquad (3)$$

where g is the acceleration of gravity, ΔT is the temperature gradient along the sample, L is the sample height, α is the thermal diffusivity of the sample, ν is the kinematic viscosity, and β is the coefficient of thermal expansion. Kinematic viscosity is defined as the ratio of a fluid's absolute viscosity to its density. Rayleigh-Bénard number characterizes the convective flows which are generated from the differences in liquid's temperature gradient along the sample tube axis, because the temperature gradient creates differences in liquid's density. As the temperature gradient increases, solvent's viscosity and thermal conductivity cannot stabilize the liquid anymore and buoyancy driven convection begins.[11,13]

According to Eq. (3), Rayleigh-Bénard number is proportionate to the cube of sample height. This means that convective flows will arise more vigorously as sample height is lengthened, which is consistent with the experimental results. The kinematic viscosity is another factor to be considered

since its temperature dependency is much larger than those of the other parameters. In liquid samples, the variations according to temperature changes of thermal diffusivity (α) and coefficient of thermal expansion (β) are generally ca. 1~3% while that of the kinematic viscosity is ca. 10~30%[14,15] (see the listed values in Table 1). To calculate the kinematic viscosities of 3 deuterated solvents, the reported values were used and some of them were extrapolated using the reported data at the other temperatures.[16~18]

As shown in Figure 2, the increment of the observed diffusion coefficient values on raising temperature is in the order of acetone-d_6 > methanol-d_4 > pyridine-d_5, which is the opposite order in the kinematic viscosity. On the change of the sample height, acetone-d_6 is most sensitive and pyridine-d_5 is least sensitive. As it is seen in the Rayleigh-Bénard number, the relatively large value of the kinematic viscosity of pyridine-d_5 or methanol-d_4 in the denominator will stabilize the effect of increase in temperature gradient and/or sample height in the numerator, which can explain the overall tendency in our experimental results.

CONCLUSION

It was ascertained that the viscosity of the liquid sample strongly affects the strength of the convective flows as well as the diffusion coefficient itself in PGSE-NMR diffusion measurements at high temperature. Additionally, the convective flows have tendency to be invigorated as the sample volume increases. This means that the convection effects might be somewhat suppressed just by

decreasing sample volume in a normal 5mm tube, especially it should be effective in low viscosity solvents.

Acknowledgement

REFERENCES

1. S. W. Jeong, D. F. O'Brein, *Langmuir* **18**, 1073 (2002).

2. 2. L. Avram, Y. Cohen, *J. Am. Chem. Soc*. **124**, 15148 (2002).

3.   G. H. Sorland, J. G. Seland, J. Krane, H. W. Anthonsen, *J. Magn. Reson.* **142**, 323 (2000).

4. W. J. Goux, L. A. Verkruyse, S. J. Saltert, *J. Magn. Reson.* **88**, 609 (1990).

5. K. Hayamizu, W. S. Price, *J. Magn. Reson.* **167**, 328 (2004).

6. K.-C. Chung, H.-Y. Yu, S. Ahn, *Bull. Korean Chem. Soc*. **32**, 1970 (2011).

7. C. S. Johnson, *Prog. Nucl. Magn. Reson. Spectrosc*. **34**, 203 (1999).

8. G.W. Scherer, *J. Am. Ceramic Soc*., **75**, 1060 (1992).

9. C. J. Seeton, *Tribology Letters* **22**, 67 (2006).

10. M. Holz, X.-A. Mao, D. Seiferling, *J. Chem. Phys.* **104**, 672 (1996).

11. W. J. Goux, L. A. Verkruyse, S. J. Salter, *J. Magn. Res*. **88**, 609 (1990).

12. E. Martinez-Viviente, S. Pregosin, *Helvetica Chimica Acta* **86**, 2364 (2003).

13. T. Yanagisawa, Y. Yamagishi, *J. Earth Sim*. **4**, 11 (2005).

14. M. F. Gelder, Ph.D. Thesis, Virginia Polytechnic Institute and State University **(1998)**.

15. P. Navia, J. Troncoso, L. Romani, *J. Chem. Eng. Data* **55**, 595 (2010).

16. S. F. Babak, V. V. Udovenko, *J. Gen. Chem. USSR* **20**, 2203 (1950).

17. S. A. Levichev, *Fiziko-chimiceskie Svojstva Rastvorov (J.80)*, Leningrad, (1964).

18. R. Anantharaj, T. Banerjee, *J. Ind. Eng. Chem.* **18**, 331 (2012).