# Effect of Clathrate Hydrate Formation and Decomposition on NMR Parameters in THF−D$_2$O Solution

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**ABSTRACT:** The NMR spin−lattice relaxation time ($T_1$), spin−spin relaxation time ($T_2$) and the diffusion coefficient D were measured for $^1$H in a 1:17 mol % solution of tetrahydrofuran (THF) in D$_2$O. The aim of the work was to clarify some earlier points raised regarding the utility of these measurements to convey structural information on hydrate formation and reformation. A number of irregularities in $T_1$ and $T_2$ measurements during hydrate processes reported earlier are explained in terms of the presence of interfaces and possible temperature gradients. We observe that $T_1$ and $T_2$ in solution are exactly the same before and after hydrate formation, thus confirming that the solution is isotropic. This is inconsistent with the presence of memory effects, at least those that may affect the dynamics to which $T_1$ and $T_2$ are sensitive. The measurement of the diffusion coefficient for a number of hours in the subcooled solution before nucleation proved invariant with time, again suggesting that the solution remains isotropic without affecting the guest dynamics and diffusion.

NMR Spectra of Decomposing THF Hydrates
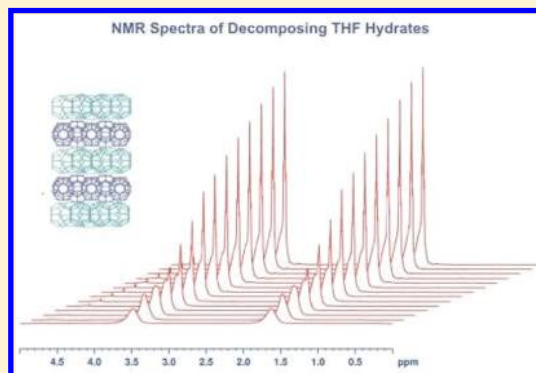
## INTRODUCTION

Tetrahydrofuran (THF) hydrate[1] has attracted a lot of attention as a "model clathrate" for a variety of studies.[2] It is far easier to prepare and handle than the natural gas hydrates for which it has been used as a proxy.[2] It can be formed simply by freezing a solution of the correct stoichiometry, THF·17H$_2$O, with the congruent melting point being 4.4 °C.[1] It is a sII hydrate with a unit cell M$_L$·2M$_S$·136H$_2$O where the M$_{L,S}$ stand for the large and small cavities.[3] When THF is the only guest, all of the large cavities are occupied by THF molecules within experimental error. However, if other small atoms or molecules are present, even at low pressures, these will be incorporated into the small cavities, eg species such as O$_2$, N$_2$, CH$_4$, Xe.[4] As well, hydrates containing THF and small-cage guests can be prepared that cover nearly a full range of compositions by adjusting the concentration of THF in solution and the pressure of the gaseous guest, a phenomenon known as composition tuning.[5] In such cases the small-cage guest may occupy a large fraction of the large cages as well. This approach offers a trade-off between the amount of gas that can be stored and the pressure required to make the hydrate.[6]

The dynamics of both the THF guest and host lattice were first studied many years ago, first by dielectric measurements[7] and then by $^1$H and $^2$H NMR.[8] In summary, it was shown that the THF guest becomes orientationally mobile in the 5$^{12}$6$^4$ cage at quite low temperatures (<50 K). This cage has tetrahedral symmetry on average, although for each individual cage the symmetry is lower at low temperatures ($T < \sim$200 K) as the motion of the water molecules freezes in and the water protons take up one of two disordered positions between water oxygens. Both reorientation and diffusion of water molecules in the solid have been observed.[7,8] More recently, various

additional NMR studies ($^1$H, $^2$H, and $^{17}$O) have appeared which have added to and elucidated the guest and host dynamics further.[9]

An important aspect of technology involving clathrate hydrates is the need for control of hydrate processes. Hydrates of natural gas form plugs in oil and gas pipelines, sometimes with disastrous consequences, and their control has been a much studied subject since their initial identification.[10] On the other hand, hydrates have been identified as materials for both storage of gases[5,6] and separation of gas mixtures.[11] In these cases the efficient production of gas hydrates becomes a priority. It is generally accepted that in order to address the various technical properties associated with hydrates it is necessary to elucidate the mechanism of hydrate formation, or in the context of memory effects, hydrate reformation. This includes measurements such as the macroscopic viscosity,[12] induction times for nucleation,[13] as well as the use of NMR parameters.[14] However, definitive results have proved elusive. As we will show, there are a number of factors which require close attention, both in experimental detail and in the interpretation of experimental results. It is still a moot point whether THF hydrate is a good proxy for natural gas hydrates in all aspects.

In this work, NMR measurements (diffusion coefficients, $T_1$, $T_2$) were made on a stoichiometric solution of THF in water, carefully degassed so as to avoid contributions of small molecules to hydrate formation or decomposition, or to relaxation processes. Emphasis was placed on comparing the

behavior during subcooling before hydrate formation and after subsequent hydrate decomposition. The three parameters measured all can be expected to be sensitive to aggregate formation in solution as this would be expected to affect the diffusion constant and the dynamic processes that govern the relaxation times.

## ■ EXPERIMENTAL SECTION

**NMR.** A 17:1 molar ratio $D_2O$/THF solution was prepared by weighing, transferred to an NMR tube, degassed using the freeze−pump−thaw technique and then the tube was sealed. NMR experiments were performed using a Bruker AV-III 400 NMR spectrometer equipped with a 5 mm broad band direct observe probe capable of producing field gradients of up to 5.35G/mm. The temperature controller was calibrated using the chemical shift difference between the $^1H$ signals of neat methanol. Diffusion constants were measured using the standard Bruker pulse sequence for the double stimulated echo experiment which compensates for convection caused by temperature gradients.

Diffusion measurements were controlled using the DOSY (diffusion ordered spectroscopy) automation program and analyzed using the Bruker Topspin software.

For the diffusion versus temperature experiment, diffusion constants were measured from 20 °C down to −19 °C. The diffusion time in the pulse sequence was increased in regular increments from 50 to 98 ms as the diffusion constant decreased. A $^1H$ spectrum was also recorded at each step. Hydrate formed suddenly after decreasing the temperature from −19° to −20° as indicated by the broadening of the lines in the $^1H$ spectrum.

For the diffusion versus time experiment, the sample was cooled slowly to −19 °C and then $^1H$ spectra and diffusion measurements were recorded continuously under the control of a Python script. The diffusion time in the pulse sequence was 110 ms. Hydrate formation occurred suddenly after 10.5 h.

$^1H$ spin−lattice relaxation times ($T_1$) of the THF $^1H$ signals were measured using the standard Bruker inversion recovery pulse sequence, before and after hydrate formation. The sample was cooled to 9 °C where 6 $T_1$'s were measured followed by another 6 at 8 °C. The sample was then cooled to −20 °C to cause hydrate formation. Integration of the $^1H$ spectrum showed that 92% of the THF was in the hydrate form with the remainder as liquid. The sample was then warmed to 8 °C and $T_1$'s were measured continuously for 1 h and 35 min, followed by further measurements for another 1 h and 18 min at 9 °C. At this point, the $^1H$ spectrum indicated that all of the THF had returned to the liquid form.

## ■ RESULTS AND DISCUSSION

Figure 1 shows diffusion constants of THF in 17:1 solution of $D_2O$/THF as measured from $^1H$ DOSY NMR. The semilog plot vs inverse temperature can be reasonably well approximated by a straight line with some deviation at higher temperatures. We note that the diffusion coefficients in organic solvents appears to follow Arrhenius behavior, however, for water this is not the case and a Speedy−Angell power law was used to fit the data.[15] Below ~8 °C, the equilibrium phase should be the solid sII clathrate, so that in fact the material under study over most of the temperature range is the subcooled liquid. At temperatures below the melting point, the time before the solid nucleates is commonly known as the
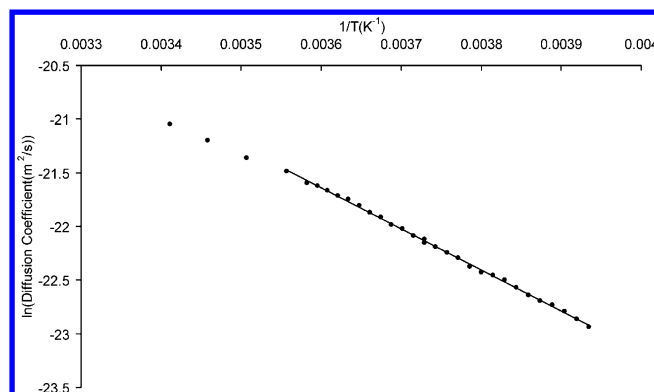


**Figure 1.** Logarithm of the diffusion constant of 1:17 tetrahydrofuran in D2O as measured from $^1H$ DOSY NMR experiments plotted against inverse temperature. The solid line is a least-squares fit to the data.

induction time and the liquid phase is metastable. An Arrhenius fit to the linear portion of the data gives a value of 31.9 kJ/mol for the diffusion coefficient. This compares with values of ~14 kJ/mol for a number of nonassociating liquids, 24 kJ/mol for an associating liquid like *n*-pentanol. Previously, measurements of viscosity of THF−water solutions have been reported,[12] and it was noted that the viscosity increased during the induction period until the solid phase nucleated. Since the viscosity can be related directly to the diffusion coefficient, measurement of the latter as a function of time in the induction region should illustrate any anomalous viscosity behavior. Figure 2 shows a
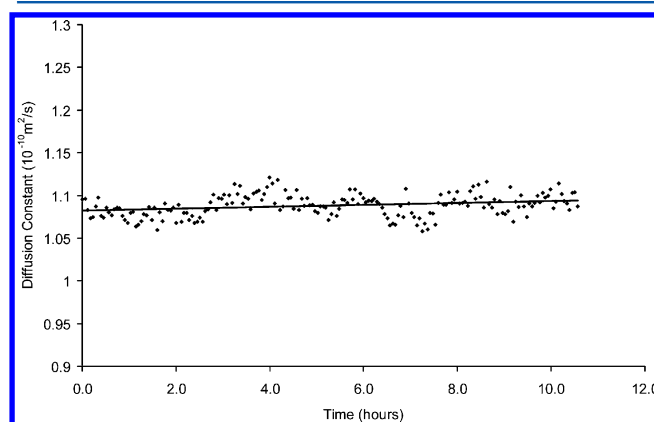


**Figure 2.** Measurement of the diffusion constant as measured 1:17 THF in $D_2O$ by $^1H$ DOSY NMR as a function of time at −19 °C, the lowest temperature achievable without crystallization of the subcooled solution.

measurement of the diffusion constant over period of more than 10 h at −19 °C, just below the temperature where the subcooled solution nucleated quite consistently. There is only a very weak time dependence, most likely arising from long-term drifts in ambient conditions.

Next we measured $T_1$, first just above the melting point at 8 and 9 °C, then again at the same temperatures after hydrate formation at −20 °C and the results are shown in Figure 3.

At 9 °C, if we take into account only the $T_1$'s where they have leveled out after the sample has melted completely the $T_1$'s before and after hydrate formation are identical within experimental error. It is clear that after hydrate formation, at 8 °C the sample is still melting even after waiting ~1.5 h so that
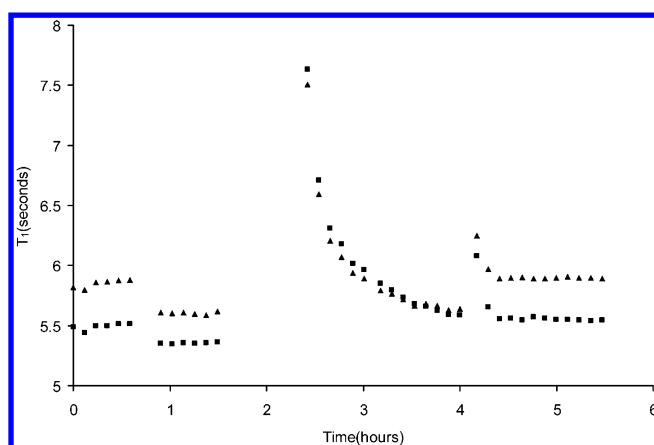
**Figure 3.** $^1H$ spin–lattice relaxation times ($T_1$) were measured over time for THF in 17:1 $D_2O$/THF. $T_1$'s for low field (triangles) and high field (squares) THF signals were measured continuously at 9 °C and then 8 °C. The sample was then cooled to −20 °C where hydrate formation occurred. The sample was then warmed to 8 °C, where relaxation time measurements were measured as a function of time, and then 9 °C where again $T_1$'s were measured as a function of time.

the $T_1$ values have not returned to their original prehydrate formation values. This is also clear from the actual spectra (Figure 4) where the resonances are seen to be composites of
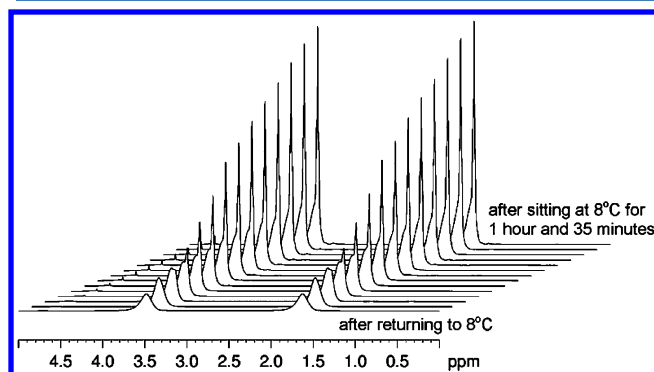


**Figure 4.** Appearance of $^1H$ NMR spectra of THF·17$D_2O$ during the melting process at 8 °C. A sharper line from the isotropic liquid is superimposed on a broader base, assignable to liquid influenced by interfaces.

two contributions: there is a sharp structured resonance, characteristic of THF in the isotropic liquid, plus a broader underlying contribution. We can attribute the broader contribution to the resonance lines to THF molecules near hydrate interfaces, perhaps also liquid inclusions in the hydrate as it is known that the presence of solid–liquid interfaces affects both $T_1$[16] and $T_2$.[17] We did not attempt to analyze $T_1$ contributions from each component separately. As hydrate processes are exothermic during formation and endothermic during decomposition, the temperature of the sample will not actually be the same as that of the temperature set on the NMR sample temperature controller during either hydrate formation or decomposition. This was especially evident during hydrate formation, where the probe temperature was seen to increase significantly as the solution froze.

Spin–spin relaxation measurements ($T_2$) were made in the same manner as described above for $T_1$, that is at 9 °C before and

after hydrate formation. The values found are again the same within experimental error (see Table 1).

**Table 1. $^1H$ Spin−Lattice and Spin−Spin Relaxation Times of THF·17$D_2O$ at 9 °C before Freezing and after Freezing and Melting**

| $T_1$, $T_2$ (s) measurements at 9 °C | before freezing | after freezing and melting |
|---|---|---|
| $T_1$ (high field signal) | 5.51 | 5.55 |
| $T_1$ (low field signal | 5.87 | 5.90 |
| $T_2$ (high field signal) | 5.01 | 5.01 |
| $T_2$ (low field signal) | 4.35 | 4.38 |

The results obtained for the diffusion coefficient measurements indicate that there is no evidence for aggregate formation during the induction time. This agrees with one set of macroscopic viscosity measurements,[12b] but not the other.[12a] In the latter case, the quality and reliability of the data is questionable, however.

In the case of $T_1$ measurements, previously published data show that $T_1$ was different before and after freezing, and this was interpreted in terms of a better dispersion of THF molecules in solution when the clathrate hydrate melts. It is difficult to see how a solute that is fully miscible with water can change its degree of dispersion. There is some published work from light scattering in various ether solutions,[18] including those of THF, that suggests the presence of slow-relaxing supramolecular aggregates,. However, this feature has since been ascribed to the presence of air nanobubbles.[19] We note that the authors of the NMR study did degas their sample with a flow of nitrogen,[14] so that the presence of gas, either dissolved or as bubbles, certainly is possible. As described earlier, small gas molecules can easily be trapped in the small cages of sII hydrate, and thus will be released again during hydrate melting. This may cause somewhat different states of the solution before and after freezing.

The same authors report that $T_1$ and $T_2$ values change markedly during hydrate formation and decomposition and attribute this to changes in solution structure. However, they did not take into account that the presence of a solid phase, which by itself will affect both the diffusion of molecules, and therefore $T_1$, and also the presence of interfaces with associated magnetic susceptibility discontinuities, will affect $T_2$. Thus, $T_1$ and $T_2$ values in solution in the presence of an increasing or decreasing solid phase do not say anything about changes in solution structure per se.

It is also valid to comment on the observation of the $T_1$ values obtained in previous work. A single value $T_1$ value was reported for the THF protons, indicating that the signals from the inequivalent protons in THF were not resolved. The reported values therefore are an average $T_1$ for the two inequivalent sets of protons which have $T_1$'s that differ by some 10%. Similarly, the distributed $T_2$ values for the liquid phase may arise because the two sets of inequivalent protons have $T_2$ values that differ by some 10%. In a homogeneous solution $T_2$ is expected to be single valued, as observed in our experiments. However, the presence of magnetic field inhomogeneities over the large sample may contribute to the observation of a distribution. As well, the presence of solid interfaces will affect $T_2$, as also observed in the high field experiments where the resonance line was seen to be composed of at least two components. The distribution in $T_2$'s observed for the solid

phase is likely a limitation of the fitting routine used during data reduction as the line shape in the solid state approximates that of a Gaussian because of residual dipolar couplings.

## CONCLUSIONS

A number of points can be stated about the procedure for NMR experiments in the context of previous related work:

1. NMR parameters obtained in solution in the presence of a solid phase will be affected by the solid phase because of limitations on diffusion and the presence of magnetic susceptibility interfaces. As well, when a hydrate process is active, either hydrate formation or decomposition, the actual temperature of the sample will not necessarily reflect that indicated on the temperature controller because of latent heat effects.

2. $T_2$ parameters obtained in solution will be affected by the presence of a gas phase (bubbles), again because of magnetic susceptibility interfaces.

3. For hydrate-forming solutions to be studied by NMR, besides removal of paramagnetic oxygen from the sample, it is important to remove all gases that may enter some of the cavities in the hydrate. Upon decomposition, gas released from the hydrate may well form bubbles (see point 2 above).

As well, some specific results related to hydrate formation and reformation can be made.

1. Relaxation times ($T_1$ and $T_2$) are identical within experimental error at the same temperature before and after a hydrate formation–decomposition cycle.

2. Diffusion coefficients do not depend on time in a subcooled solution during the induction period.

These results are consistent with the absence of structure or cluster formation before hydrate formation, that persist on time scales to which $T_1$ and $T_2$ are sensitive as well as memory effects after hydrate decomposition. It should be noted that the scope of the work reported here is limited to gas-free solutions of water-miscible hydrate formers. Cases where hydrates form in the presence of gaseous guests of limited solubility in water clearly will behave in a very different way during a hydrate formation–decomposition–reformation cycle.

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### Author Contributions
The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

### Notes
The authors declare no competing financial interest.

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