

Research Communication

## A NMR Method to Probe the Nature of Liquid Clathrates

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**Abstract.** The liquid clathrate formed from  $[\text{N}(\text{CH}_3)_4][\text{Al}_2(\text{CH}_3)_6\text{I}]$  and benzene has been studied using 200 MHz  $^1\text{H}$  FT-NMR. Two resonances, corresponding to the free and guest benzene are observed. The  $^1\text{H}$  spin lattice relaxation times,  $T_1$ , for these molecules were measured and found to be distinctly different. The guest benzene protons relax nearly four times faster than the free molecules which is consistent with a more ordered structure of the benzene molecules within the clathrate.

**Key words:** Liquid clathrate, NMR, aluminium alkyl.

It has been over 15 years since the inclusion compounds formed between salts of the general formula  $\text{M}[\text{Al}_2(\text{CH}_3)_6\text{X}]$  and aromatic molecules were first reported. Despite extensive work in the area, the nature of these liquid clathrates is still not well understood [1–4]. We have begun a series of experiments using FT-NMR which show promise in helping to elucidate the make-up of these very interesting materials. Initial results of our experiments are discussed below.

The liquid clathrate that we chose to study was the one formed by preparing  $[\text{N}(\text{CH}_3)_4][\text{Al}_2(\text{CH}_3)_6\text{I}]$  in the presence of benzene. Its preparation is easily accomplished by adding a 2 : 1 molar ratio of  $\text{Al}(\text{CH}_3)_3$  to  $\text{N}(\text{CH}_3)_4\text{I}$  slurred in benzene. Reaction begins immediately at room temperature, as evidenced by the formation of two liquid layers, and continues until all of the solid salt has dissolved. The resulting inclusion compound has an aromatic/anion ratio of 5.8 [5]. An equal volume of liquid clathrate and benzene were placed in a 10 mm NMR tube. The tube was positioned in the probe so that the center of the coil corresponded to the interface between the two layers. In order to avoid problems that might arise from vortex formation, all measurements were made without spinning the sample. The  $^1\text{H}$  NMR spectrum measured at 200 MHz is shown in Figure 1A [6]. There are two distinct resonances in the aromatic region. The lowfield resonance corresponds to the  $\text{C}_6\text{H}_6$  inside the clathrate as determined by positioning the tube so that only the liquid clathrate layer was in the coil (Figure 1B). It is known that aromatic molecules freely travel across the interface [7]. By replacing the upper free benzene layer with  $\text{C}_6\text{D}_6$ , this process can be studied by monitoring the growth of the free benzene signal and the corresponding decrease of the guest benzene resonance. With no physical mixing of the sample, an equilibrium mixture was obtained after  $\sim 1.25$  h.

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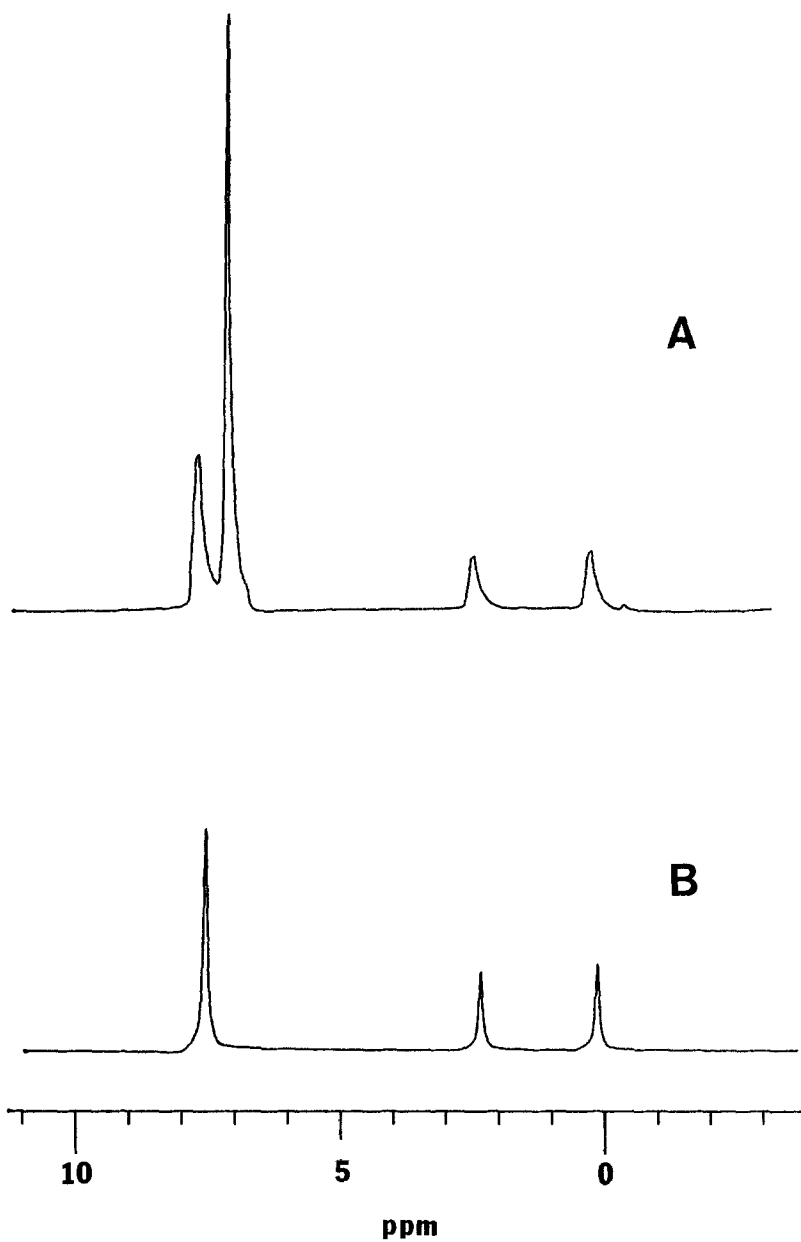


Fig. 1. (A) Coil centered at the interface of benzene/liquid clathrate layer. (B) Only the liquid clathrate layer in the coil.

We next measured the  $^1\text{H}$  spin lattice relaxation times,  $T_1$ , for the free and guest aromatics in this equilibrated mixture. We find that the  $T_1$  for the guest  $\text{C}_6\text{H}_6/\text{C}_6\text{D}_6$  is rather short compared to that of the bulk  $\text{C}_6\text{H}_6/\text{C}_6\text{D}_6$  mixture (9.9 s versus 33 s). The short  $T_1$  is indicative of the guest benzene being held in a somewhat more rigid environment. One possible role for the guest aromatic molecules in these systems is to interact with the cations thus reducing cation–cation repulsion inside the clathrate [8]. The measured  $T_1$  certainly does not refute this hypothesis. Experiments to determine what effect various cations have on the relaxation time of the guest aromatic protons are underway and will help to clarify this point.

The observation of distinct chemical shifts for the free and guest aromatic molecules affords an opportunity to obtain a variety of kinetic data either by replacing the benzene layer with a different aromatic solvent or at steady state using a variety of magnetization transfer techniques [9]. These experiments are currently underway and will be reported separately. By combining the extensive solid state data that presently exist on these systems with the data derived using modern NMR techniques, one should be able to draw a more coherent picture of the nature of this very important class of inclusion compounds.

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### References

1. J. L. Atwood, D. C. Hrnrcir, R. D. Rogers, and J. A. K. Howard: *J. Am. Chem. Soc.* **103**, 6787 (1981).
2. J. L. Atwood, D. C. Hrnrcir, and R. D. Rogers: *J. Incl. Phenom.* **1**, 199 (1983).
3. D. C. Hrnrcir, R. D. Rogers, and J. L. Atwood: *J. Am. Chem. Soc.* **103**, 4277 (1983).
4. J. L. Atwood: *Recent Dev. Sep. Sci.* **3**, 195 (1977).
5. Determined by NMR integration methods.
6. NMR spectra were determined at ambient temperature using a 200 MHz JEOL JNM FX-200 Fourier Transform NMR Spectrometer operating in the FT mode.
7. D. C. Hrnrcir and J. L. Atwood: unpublished studies.
8. J. L. Atwood: *Inclusion Compounds*, Vol. I (eds. J. L. Atwood, J. E. D. Davies, and D. D. MacNicol), pp. 395–426, Academic Press, London (1984).
9. G. A. Morris and R. J. Freeman: *J. Magn. Reson.* **29**, 433 (1978).