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Magic Angle Spinning NMR Techniques for the Study of Surfactants

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We would like to present our preliminary results of ¹³C magic angle spinning (MAS)¹ NMR spectra of aqueous surfactant solutions which seem superior to solid state cross polarization (CP)/MAS or regular liquid state NMR spectra in terms of spectral resolution. This improved spectral resolution rendered it plausible to clearly identify chemical species newly formed in the solutions due to mechanical treatment. Our results suggest that MAS NMR technique is very useful to identify molecules not only in aqueous surfactant solutions but also in *highly viscous liquid* samples such as polymer solutions. MAS has been used extensively in solid state NMR to remove line broadening caused by chemical shift anisotropy, first order quadrupole interaction, and dipole interactions.^{1,2} Magnetic susceptibility line-broadening of liquid samples as well as of solid state samples was reported to be removed by MAS.³ Proton MAS NMR techniques were proved to be useful to study emulsions by removing the broadening due to magnetic susceptibility mismatch among phases in multiple emulsions.⁴ Recently MAS has been also exploited to remove line-broadening caused by residual dipole interaction from the restricted motions of resin-bound molecules and by magnetic susceptibility mismatch at the boundary of the bead.⁵ But this work is the first report on the promising aspect of the application of MAS to highly viscous liquids such as aqueous surfactant solutions and polymer solutions. In these samples, molecular motions are slow enough to have residual dipole interaction resulting in broad NMR linewidths. Discontinuity of magnetic susceptibility at the boundary of micelle and water could be another line-broadening factor in the NMR spectra of aqueous surfactant solutions. These line-broadenings can be got rid of by MAS.

The samples were taken from the experiment on drag reduction. Drag reduction is a fluid mechanical phenomenon in which the pressure drop in a turbulent pipe flow is substantially lowered when a small amount of polymer or surfactant is added to the flowing solvent. Many researches have been directed toward the proper utilization of this effect to its potential benefit in many systems such as district heating and cooling. However the application of drag reduction has been deterred by the loss of drag reducing ability in prolonged use. In the case of surfactant solution, the drag

reducing ability is completely lost after a certain period of usage. There are several possible mechanisms for the loss of drag reducing ability: micelle sizes and/or shapes are changed; surfactant molecules are chemically altered; the concentration of surfactants is lowered due to the adsorption onto the pipe wall. In this research we check whether the second mechanism is important. The first and third mechanisms can be checked with other analytical methods and will be presented elsewhere.

The surfactant HABON (Hochest Co.) was used without further purification. Surfactant solution of 2000 wppm was prepared by diluting a master solution of 10 wt %. The solvent was distilled water. The master solution was prepared by dissolving desired amount of HABON in 200 mL distilled water. The surfactant solution was subjected to turbulent pipe flow continuously. A peristaltic pump and a plastic tubing were used in the circulation loop. The inner diameter and length of tubing were 4.25 mm and 5.15 m, respectively. The initial Reynolds number based on the solvent viscosity was set at 8,200. Sample I was taken after 26 minutes of circulation. Sample II was taken after 126 hours of circulation at which the drag reducing ability of the surfactant solution is completely lost.

Liquid state ¹³C NMR spectrum of sample I acquired with the Bruker DPX 300 instrument (Bruker Analytische Messtechnik GmbH, Germany) is shown in Figure 1A. The pulse sequence repetition time and the pulse length were 2.5 sec and 2.7 μs (30 degree flip), respectively. Proton decoupling was continuously on⁶ during the NMR experiment. To enhance signal intensity, the sample I was about 10 times concentrated by drying with a vacuum concentrator (Heto Lab. Equipment, Denmark) and dissolving in D₂O. The CP/MAS spectrum of the dried (solid state) sample I in Figure 1B was acquired with the Varian UNITYplus 300 instrument (Varian Associates Inc., U.S.A.) and at the sample spinning speed of 5 kHz. The contact time and the pulse sequence repetition time were 800 μs and 5 sec, respectively. The H₁ field strength was 50 kHz. The MAS spectrum of sample I in Figure 1C was acquired under proton decoupling and at 2.7 kHz spinning speed but without CP. The pulse length and pulse repetition time were 5 μs corresponding to 90 degree flip and 3 sec, respectively. The samples

for MAS were prepared by dissolving each dried sample from 15 mL initial solution to 150 μ L D₂O. All spectra in Figure 1 were processed by multiplication of an exponential function with 15 Hz line-broadening to each FID.

The liquid state NMR spectrum in Figure 1A does not show all the expected peaks since the linewidths were too much broadened to be observed. Even the peaks appeared in the spectrum are relatively broad. The MAS spectrum of the sample I in Figure 1C showed better resolution than the liquid state NMR spectrum in Figure 1A or the CP/MAS spectrum in Figure 1B. The physical state difference of the same sample (solid state *versus* liquid state) resulted in the better resolution of the MAS spectrum even with the same MAS technique used for both spectra in Figure 1B and 1C. The residual dipolar and magnetic susceptibility line-broadening present in the liquid state NMR spectra of the liquid state surfactant samples were removed by MAS. The spinning of the sample along the magnetic field axis at about 20 Hz, which is typically employed in liquid state NMR, can not remove dipolar or magnetic susceptibility line-broadening even with faster spinning.^{1,2} For this work, we used a regular CP/MAS probe in which susceptibility was not optimized in its coil design. Thus, the line-broadening due to the magnetic susceptibility mismatch of probe materials in the probe could not be removed by MAS. The specially designed probe^{5b} to exploit MAS for very small amount of liquid samples would produce better resolved spectra. However, a regular CP/MAS probe can be much more economically utilized, especially for ¹³C NMR spectra in which the chemical shift dispersion^{1,6} is wide.

Another advantage of the MAS technique is that quantitative study is much easier with the MAS spectrum than with CP/MAS spectra. In MAS spectra without CP, the peak intensity is linearly proportional to the number of nuclei as in liquid state NMR spectra acquired under gated decoupling.⁶ On the other hand, in the CP/MAS spectra, the peak intensity is a function of not only the number of nuclei but also the dynamics, thus, quantitative information can not be deduced directly from peak intensities.¹ Also the peak intensity of each site is spreaded to its spinning side bands in MAS spectra of solid state samples when the spinning speed is less than the static linewidth.¹ But the reduced static linewidths due to faster molecular motions in the liquid samples than in the solid state samples result in no spinning side bands even with the slow spinning rate of 1-2 kHz, which simplifies the MAS spectra and the quantitation study with the spectra.

In Figure 1C and 1D, the MAS spectra of the sample I and II are compared. The spectrum of the sample II has new peaks in addition to the ones in the spectrum of the sample I. The results implies that sample II has other chemical species, probably fragmented from the original molecules in the sample I, in addition to the original surfactant molecules and their counter charge molecules. Full peak assignment will be published elsewhere.

In summary, we have demonstrated that the MAS technique can be utilized for the identification of molecules with restricted motions in solutions such as polymers in highly viscous solutions and molecules in aqueous surfactant solutions.

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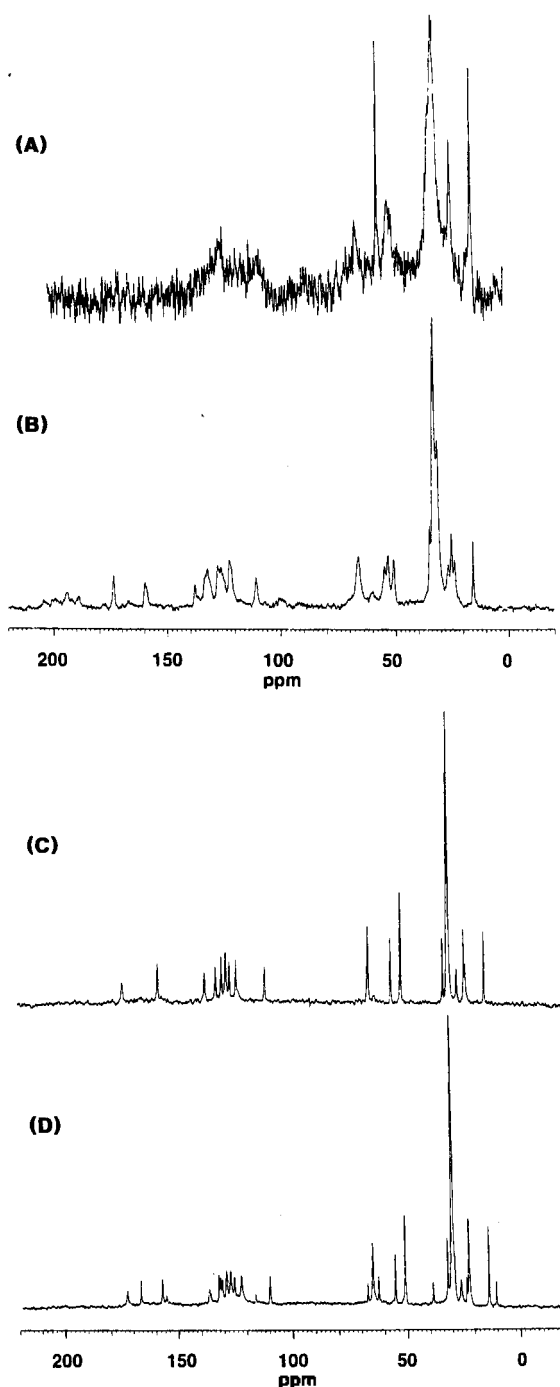


Figure 1. (A) ¹³C liquid state NMR spectrum of sample I 11264 scans. (B) ¹³C CP/MAS spectrum of dried sample I, 722 scans. (C) ¹³C MAS spectrum of dried sample I dissolved in D₂O, 1024 scans. (D) ¹³C MAS spectrum of dried sample II dissolved in D₂O, 1646 scans.

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