

## Micellar Diffusion Study of TTAB/Water and TTAB/NaBr/Water Systems by PFG-NMR

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**Abstract:** *Translational diffusion of tetradecyltrimethylammonium bromide (TTAB) micelles in water was investigated by pulsed field gradient  $^1\text{H}$  NMR (PFG-NMR). A series of TTAB/water samples with different concentrations of TTAB was studied, and a similar ternary series was prepared having fixed NaBr/TTAB concentration ratios. The  $[\text{NaBr}]/[\text{TTAB}]$  ratio ranged from zero to 1.5 in six different series. All samples were isotropic and above the cmc, with TTAB mass fraction ranging from about 0.01 to 0.33. At higher concentrations this system forms a nematic liquid crystalline phase. Different pulse sequences were tested, and the parameters were optimized to measure the range of diffusion coefficients observed for micellar diffusion. The diffusion coefficients ( $D$ ) decreased in all series with increasing  $[\text{TTAB}]$  value and reached a limiting value. The addition of the electrolyte initially increased the micelle size, probably due to change in micelles critical packing parameter (CPP), and stabilized the micelle size at lower TTAB concentrations.*

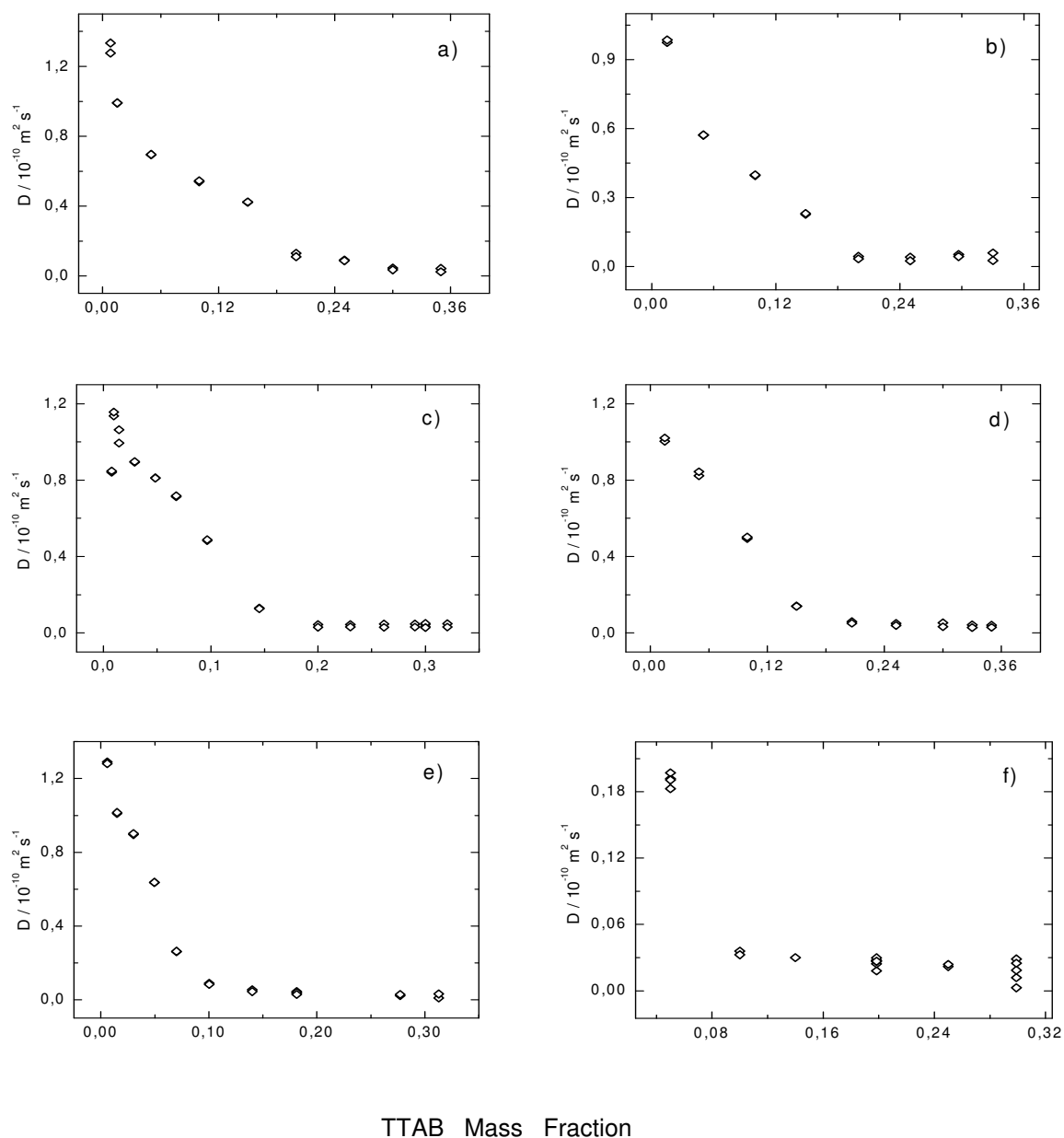
Magnetic field gradients can be used to monitor molecular displacement by relative dephasing between spins starting from the same point and diffusing to different places. This dephasing occurs because, under magnetic field gradient, nuclei in different positions in the gradient direction experience different resulting fields and precess with different velocities. Freely diffusing particles tend to spread from an original position to adopt a gaussian population distribution around this point. This causes nuclear spins to dephase, which reduces the overall intensity of the macroscopic magnetization.

Modern pulse sequences combine pulsed field gradients (PFG) with spin echoes.<sup>1</sup> We use here GCSTESL, whose sequence is  $90^\circ, g, 90^\circ, -g, \Delta, -g, 90^\circ, g, \lambda$  acquisition, where  $g$  is an axial gradient pulse,  $\Delta$  is a delay for particles diffusion and  $\lambda$  is a spin lock. The two

$-g$  pulses while magnetization is axially oriented are intended to cancel eddy currents produced by the alternately applied  $g$  pulses;  $\Delta$  and  $g$  were adjusted for each sample. Typically,  $\Delta = 0.3$  s and  $g$  ranged from 30 to 95 gauss/cm, with duration of 2 to 5 ms.

Using  $^1\text{H}$  PFG-NMR, we measured translational diffusion in water solutions of TTAB (tetradecyltrimethylammonium bromide). The results are shown in Figure 1.

A series of binary samples with different TTAB concentrations was studied, and a similar series was prepared by adding NaBr at fixed NaBr/TTAB concentration ratios. The  $[\text{NaBr}]/[\text{TTAB}]$  ratio ranged from zero to 1.5 in six different series. All samples were isotropic and above the cmc, with TTAB mass fraction ranging from about 0.01 to 0.33. The gradients were calibrated using a standard sample of water at  $25^\circ\text{C}$ , the same temperature of all other experiments.



**Figure 1.** Diffusion coefficients of TTAB by  $^1\text{H}$  PFG-NMR as function of TTAB mass fraction for sample series with the following  $[\text{NaBr}]/[\text{TTAB}]$  ratios: a) zero (binary); b) 0.05; c) 0.33; d) 0.65; e) 1.14 and f) 1.50.

From the frequency domain spectra we used the integral intensities of the TTAB signals to fit the data to the general equation<sup>1</sup> for the spin echo amplitude, in order to calculate the translational diffusion coefficient ( $D$ ). The data plotted in Figure 1 show that  $D$  decreases with increasing  $[\text{TTAB}]$  and reaches

a limiting value of approximately  $3 \cdot 10^{-12}$ , which remains constant up to the phase transition. Before reaching this limit, the addition of NaBr also increases micelle size due to change<sup>2</sup> in micelles critical packing parameter (CPP). No quantitative approach to particle size through Stokes-Einstein relation could be made

because viscosity information would be necessary for that.

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#### **References**

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