^{13}C-^{1}H Dipolar Couplings vs Temperature Studies on Water Mixtures Using the R-PDLF Method

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Self assembly of surfactants and other amphiphilic molecules has been the subject of numerous studies since the beginning of colloidal science. One way to investigate the relationship between the conformational distribution of molecules and macroscopic structure of aggregates, is to measure the orientation/distance dependent deuterium quadrupolar couplings. This approach has been used to study lamellar or hexagonal phases of various nonionic surfactants [1-3]. The drawbacks of this practice come from the required isotopic labeling of the samples, since ^{2}H natural abundance is very low (0.01%).

The same information can be obtained by measuring ^{13}C-^{1}H dipolar couplings, rather than quadrupolar, using more recently developed 2D NMR experiments. We applied the R-PDLF method proposed by Dvinskikh [4], in order to obtain the ^{13}C-^{1}H dipolar couplings present in a number of nonionic surfactant/water mixtures ($C_{10}E_3$, $C_{12}E_5$, $C_{16}E_6$) and compared them with results from previous quadrupolar coupling experiments [1-3]. The R-PDLF method incorporates a $R18^{1}_{7}$ recoupling pulse sequence designed by Levitt [5] into a proton-detected local field (PDLF) protocol. This allows one to obtain a 2D NMR spectrum that combines the chemical-site high resolution provided by MAS and ^{1}H decoupling with the information about conformational and dynamical constrains given by the dipolar couplings. Combining time and frequency domain analysis in the indirect dimension, higher accuracy and smaller couplings than the previous ^{2}H NMR results were obtained. The ^{13}C-^{1}H dipolar couplings of the tail and head parts of the various surfactants were measured in wide temperature ranges. The results can be explained on a conformational basis supported by results from previous theoretical calculations.

References

[1] W. Schnepp and C. Schmidt, Ber. Bunsenges. Phys. Chem. 98, 248 (1994).
[2] M. Baciu, U. Olsson, M. S. Leaver, and M. C. Holmes, J. Phys. Chem. B 110, 8184 (2006).
[3] A. Tonegawa, K. Ohno, H. Matsuura, K. Yamada, and T. Okuda, J. Phys. Chem. B 106, 13211 (2002).
[4] S. V. Dvinskikh, H. Zimmermann, A. Maliniak, and D. Sandstr • om, J. Mag. Res. 168, 194 (2004).
[5] M. H. Levitt, J. Chem. Phys.(2008), DOI: 10.1063/1.2831927.