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NMR characterization of dispersant-particle interactions in the colloidal dispersions

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1. Introduction

The understanding of stabilization mechanisms in colloidal dispersions is of great importance in many application fields. Analytical tools to provide direct insight into stabilization mechanisms in *in-situ* conditions are in high demand. Approaches and techniques based on solution state NMR are – in principle – well suited to study such systems. We are examining the potential of such approach to probe *in-situ* the interactions between sodium dodecylsulphate (SDS) and quinacridone pigment particles of 70 nm diameter. This model system was chosen as a prelude to the exploration of pigment dispersions that will involve more complex surfactant molecules and formulations. In this contribution we present preliminary results of this investigation.

2. NMR approach to study dispersant-particle interactions

^{1}H NMR techniques were used to study the adsorption/desorption of SDS on the pigment as a function of SDS concentration. At higher SDS concentration (above CMC), both sharp and broad set of resonances are visible that can be attributed to the monomeric SDS (broad signal, molecules in fast exchange with the surface) and to the micellized SDS (sharp signal, micelles in slow exchange with the surface adsorbed or monomeric SDS pool). At lower SDS concentration (below CMC), sharp resonances are not detectable. Given the size of the pigment, we assume that the molecules attached to the pigment surface are not directly visible on ^{1}H NMR spectrum.

A variety of PFG NMR **diffusion techniques** was applied to monitor the diffusion behavior of SDS molecules as a function of its concentration. Unfortunately, the fast transverse relaxation (R_2) rates, confirmed by the CPMG technique, cause severe attenuation of broad resonances during the gradient encoding and decoding periods, precluding the study of corresponding SDS species by PFG diffusion techniques on standard gradient systems. Diffusion induced decay profiles obtained for residual SDS resonances can be fitted to a single exponential. However, the apparent diffusion coefficients are shown to depend on the diffusion time (Δ), indicating that the fast exchange limit is not reached. As the diffusion time (Δ) lengthens, the effect of the bound species on the apparent diffusion coefficient values is enhanced.

From the diffusion and relaxation experiments, the exchange behavior of free and bound SDS may be analyzed using a two-site model developed by Kaerger [1]. In this way, the equilibrium exchange dynamics can be studied and information about SDS bound at the pigment/liquid interface may be obtained.

Adsorption isotherms could be also extracted by recording ^{1}H NMR spectra for increasing SDS concentrations and integrating the SDS proton resonances against an ERETIC signal as internal intensity standard. Assuming that the adsorbed species are not directly visible in ^{1}H NMR spectrum, the amount of free surfactant may be calculated directly from the integrals. These values may then be compared with the values obtained from the two-site model thereby allowing the preliminary verification of the model.

3. Conclusion

The work presented shows that information on the interaction between surfactant and pigment can be accessed using NMR spectroscopy. Since it allows to follow the species individually, a more molecular view of the interaction is afforded, which should complement information on the adsorption properties and the dispersion quality obtained via macroscopic characterization techniques.

References

[1] Kaerger, J., *NMR Self-Diffusion studies in Heterogeneous Systems*, Advances in Colloid and Interface Science, **1985**, 23,129-148