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An ALC study of spin exchange of a muoniated cosurfactant in lamellar phase surfactant dispersions

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Abstract

The Avoided Level Crossing muon spin resonance (ALC-μSR) technique has been used to measure the Heisenberg spin exchange rate between the Mu adducts of 2-phenylethanol (PEA) and Ni^{2+} in a concentrated lamellar phase dispersion composed of the dichain cationic surfactant 2,3-diheptadecyl ester ethoxypropyl-1,1,1-trimethylammonium chloride (DHTAC) and water. Ni^{2+} is only dissolved in the aqueous phase, therefore information about the local environment of the PEA can be extracted from the spin exchange rate. In the high-temperature (L_α) phase the spin exchange is very slow, revealing that PEA preferentially resides in the headgroup regime of the surfactant. In the low-temperature (L_β) phase the spin exchange is diffusion controlled, because the PEA is expelled into the water region between the bilayers.

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1. Introduction

Surfactants are molecules consisting of a hydrophobic hydrocarbon chain and a hydrophilic headgroup. Due to their amphiphilic character, surfactants allow mixing of immiscible substances (e.g., oil and water) to an emulsion.

If head and tail of a surfactant are of similar diameter the spontaneous curvature at the water–surfactant interface is low. Such a surfactant will form planar double layers separated by water. The rheological properties of such lamellar structures depend on the type and concentration of the surfactant and are influenced by the presence of additional cosurfactants. Partitioning of these cosurfactants at the water/bilayer interface is hard to predict and difficult to measure. Only recently has this topic been addressed [1–3].

Scheuermann et al. investigated the partitioning of the muoniated 2-phenylethanol (PEA-Mu) radical at the interface of DHTAC and water by means of ALC-μSR [2]. This method was then applied to study other surfactant systems [3]. DHTAC forms a lamellar phase with an L_α/L_β phase transition between 55 and 57 °C. Above this temperature the alkyl chains can be considered "liquid crystalline" like (L_α phase), while below this temperature the system is in the L_β state, with more ordered packing of the hydrocarbon chains.

ALC-μSR is a sensitive magnetic resonance type technique for studying the local environment of muon substituted radicals [4]. The coupling of the electron, muon, and proton spins leads to characteristic sharp peaks (resonances) when the muon polarization is plotted as a function of the external magnetic field. The peaks are due to avoided crossings of quantized magnetic energy levels. Their positions are related to the muon (A_μ) and proton (A_p) isotropic hyperfine interactions in the radical. The positions of the ALC-μSR resonance lines of PEA-Mu

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depend on the polarity of the environment of the radical. By constructing a polarity diagram it could be shown that in the L_β phase PEA resides to >90% in the water region and mainly within the bilayer in the L_α phase [2,3].

The presence of the paramagnetic Ni^{2+} ions in the aqueous region of a DHTAC/water emulsion leads to a broadening of the ALC resonances if the muoniated radical also resides in the aqueous phase and therefore undergoes Heisenberg spin exchange [3].

2. Theory

A quantitative numerical analysis of the effect of spin exchange (in combination with chemical reaction) was developed by Heming et al. [5]. Kreitzman developed an analytical model based on the Liouville formalism for the isotropic case, where only Δ_0 (muon–proton spin flip–flop transitions, conserving the total magnetic quantum number M) resonances appear [6].

An ALC transition is described as follows [6]

$$
\begin{aligned}
p(\lambda_e, \lambda_\mu, \Omega, \Delta\omega) &= \sin^4 \vartheta_\mu \frac{\lambda_\mu}{\lambda_\mu + \lambda_e(1+\cos^2\vartheta_\mu)} \\
&\quad + \frac{1}{2}\cos^4\vartheta_\mu \frac{\lambda_\mu}{\lambda_\mu + \lambda_e \sin^2\vartheta_\mu} + \frac{1}{4}\cos^4\vartheta_\mu \frac{\lambda_\mu}{\lambda_\mu + \lambda_e} \\
&\quad \times \left\{ 1 + \frac{(\lambda_\mu + \lambda_e + \lambda_e\cos^2\vartheta_\mu)^2 \Lambda}{\Omega^2(\lambda_\mu+\lambda_e)^2 + (\lambda_\mu^2 + 2\lambda_\mu\lambda_e + 2\lambda_e^2 \sin^2\vartheta_\mu)\Lambda} \right\},
\end{aligned} \tag{1}
$$

with

$$
\tan 2\vartheta_\mu = \frac{A_\mu}{(\gamma_e - \gamma_\mu)B}, \quad \Lambda = (\lambda_\mu + \lambda_e)^2 + \Delta\omega^2,
$$

$$
\Omega = \frac{A_\mu A_p}{2\gamma_e B}, \quad \Delta\omega = -\gamma_\mu B + \frac{A_\mu}{2} + \gamma_p B - \frac{A_p}{2}, \tag{2}
$$

p is the muon spin polarization, ϑ_μ the mixing angle between Zeeman states, Ω the frequency of the on-resonant oscillation and $\Delta\omega$ the frequency offset. λ_e is the spin flip probability per time unit and λ_μ is defined as the reciprocal muon lifetime.

3. Results and discussion

3.1. Experiment

PEA was dissolved in water in a concentration of 40 mM. $NiCl_2$ concentrations in the range 0–8 mM were added to parts of this stock solution. After adding 15 wt% DHTAC and shear-mixing of the emulsion, the samples were loaded into a brass cell suitable for ALC measurements. The sample preparation was carried out under oxygen-free conditions in a glove box and all substances were degassed prior to use. The experiments were carried out at the Swiss Muon Source at the Paul Scherrer Institute, Villigen, Switzerland.

3.2. Results

Three isomeric cyclohexadienyl-type radicals are formed by Mu addition to PEA, the ortho-, meta- and the para-Mu-PEA (Fig. 1). Three Δ_0 resonances due to the coupling to the ipso-proton are observed in the range 1.8–2.2 T (Fig. 1). In the absence of $NiCl_2$, all three ALC resonances are narrow and well separated. With increasing Ni^{2+} concentration the lines become broader due to faster spin exchange.

3.3. Data analysis

Eq. (1) was modified to obtain an expression for the muon polarization p depending only on the measurable parameters (external magnetic field B, coupling constants A_μ and A_p and relaxation rates λ_e and λ_μ). The electron spin flip rate is given by $k[Ni^{2+}]$, where k is the spin exchange rate constant and $[Ni^{2+}]$ is the concentration of Ni^{2+} ions. Taking into account an additional intrinsic relaxation, the muon spin flip rate is taken as $\lambda_\mu = 1/\tau_\mu + \lambda_0$, where τ_μ is the muon lifetime and λ_0 is the intrinsic relaxation rate. The resulting function is

$$
p \rightarrow p(B, k, [\mathrm{Ni}], A_\mu, A_p, \lambda_0). \tag{3}
$$

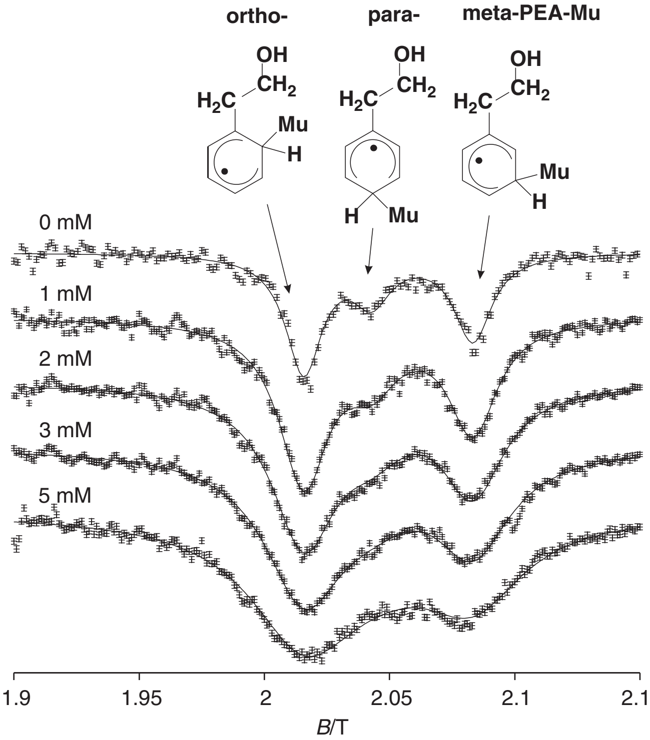

Fig. 1. ALC spectra of PEA-μ in a DHTAC/water solution with different Ni^{2+} concentrations at 25 °C.