



Electron paramagnetic resonance of nitroxide-doped magnetic fluids

P.C. Morais^{a,*}, A. Alonso^b, O. Silva^b, N. Buske^c

^a Instituto de Física, Núcleo de Física Aplicada, Universidade de Brasília, C.P. 004455, Campus Universitário, 70919-970 Brasília-DF, Brazil

^b Instituto de Física, Universidade Federal de Goiás, 74001-970, Goiânia-GO, Brazil

^c Berlin Heart AG, Wiesenweg 10, D-12247 Berlin, Germany

Abstract

Electron paramagnetic resonance was used to investigate surface-coated magnetite-based magnetic fluids doped with TEMPOL. Two magnetic fluid samples, having magnetite nanoparticles with average diameter of 94 Å and coated with different coating layers (lauric acid plus ethoxylated polyalcohol in one case and oleoylsarcosine in the other case), were doped with TEMPOL (6 mM and pH 7.4) and investigated as a function of the nanoparticle concentration. The resonance field and the resonance linewidth both scale linearly with the nanoparticle concentration.

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Magnetic fluids (MFs) have been traditionally characterized using X-ray diffraction, transmission electron microscopy, magnetization, and birefringence. More recently, magnetic resonance (MR) has been used to characterize as well as to study many of the properties of MFs [1–3]. Most of the MR data published to date, however, are focused on the magnetic nanoparticle as the resonant center [1–3]. Moreover, the resonance measurements have been performed at a fixed microwave frequency and sweeping the external field rather than at zero external fields and varying the microwave frequency. In this case, the effective magnetic field at the nanoparticle site includes the anisotropy field [4]. As a consequence, in such geometry, highly anisotropic MFs require very low excitation frequencies. Therefore, MR at a fixed frequency may not represent a promising characterization technique as it does for moderated and weak anisotropic MFs. This limitation was partially overcome by doping low-pH cobalt-ferrite aqueous-based MFs with Cu^{2+} as a paramagnetic probe [5].

The MR experiment was then focused on the $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ paramagnetic center instead of on the magnetic nanoparticle itself [6]. However, aqueous-complexed ion-transition metals are suitable as paramagnetic probes only for low-pH MFs. In the present study, the nitroxide paramagnetic center is proposed as a highly stable paramagnetic probe for water-based MFs at pH above 7.

The two coating agents used in the production of the first magnetite-based MF sample (sample A) were lauric acid (inner layer) and ethoxylated polyalcohol (outer layer). In the second MF sample (sample B) magnetite nanoparticles were coated with oleoylsarcosine. Original particle concentration in samples A and B were 2.3×10^{17} and 1.1×10^{17} particle/cm³, respectively. Samples A and B were water-diluted (1:10, 1:20, 1:40, 1:80, and 1:160) and doped with TEMPOL (6 mM and pH 7.4) before analyzing in an X-band system (9.774 GHz). Room-temperature measurements were taken as a function of time, between 1 and 100 min after doping, revealing the high stability of nitroxide as a doping agent.

Fig. 1 shows the room-temperature EPR spectrum of TEMPOL (at 6 mM and pH 7.4), revealing the usual

*Corresponding author. Tel.: +55-61-273-6655; fax: +55-61-272-3151.

E-mail address: pcmor@unb.br (P.C. Morais).

three-line hyperfine pattern of the nitroxide [7]. The EPR spectra of the TEMPOL-doped MF samples (A and B), at some representative dilutions, are shown in Fig. 1. We first note that the EPR spectra of the TEMPOL-doped samples are quite similar to the EPR spectrum of TEMPOL. Furthermore, the distance from the extreme high- and low-field peaks does not change as a function of the nanoparticle concentration. However, the EPR linewidth increases with the increasing of the nanoparticle concentration, though indicating a condition more closely related to the isotropic fast-motion limit. In other words, a quick view of the EPR spectra shown in Fig. 1 suggests that the TEMPOL is more likely to be weakly adsorbed at the coating layer of the magnetic nanoparticle rather than strongly bound to it.

Filled symbols (circles and squares) in Fig. 2 show the resonance field (H_R) of the central EPR line versus

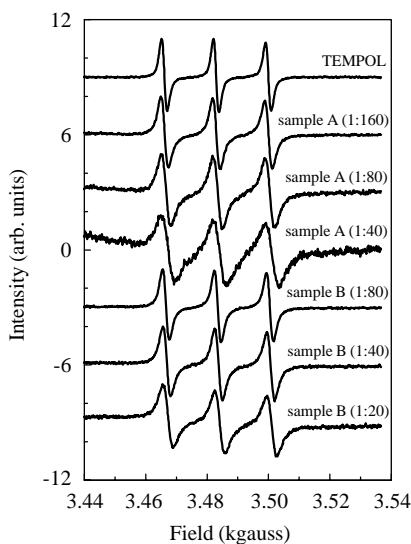


Fig. 1. Comparison of the TEMPOL EPR spectra in solution and as a dopant in two MF samples, at distinct dilutions.

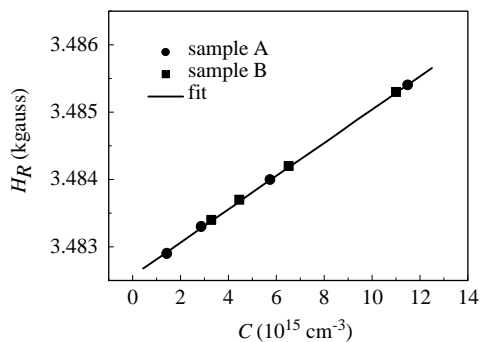


Fig. 2. Resonance field versus nanoparticle concentration. The data refer to the central EPR line.

nanoparticle concentration (C). Despite differences of nanoparticle coatings, the two sets of data shown in Fig. 2 fall along the same straight line. This is a clear indication that only the particle core (same for the two MF samples) matters in determining the resonance field associated to the nitroxide. Fitting the data using a linear function, $H_R = H_0 + aC$, provides $H_0 = 3482.57$ and 3482.60 G for samples A and B, respectively, which is in very good agreement with the value obtained from the EPR spectrum of TEMPOL (3482.92 G). The fitted values for the slope were $a = 0.247 \pm 0.003$ and 0.247 ± 0.001 for samples A and B, respectively.

The simplest description of H_R versus C starts with the basic resonance equation, $H_{\text{EFF}} = \omega_R/\gamma$, where H_{EFF} is the effective field at the resonant site, ω_R is the microwave frequency, and γ is the gyromagnetic ratio. The effective field is essentially a combination of the external field (H_E) plus the dipolar field (H_D). The dipolar contribution scales with $1/d^3$ and so with C , where d is the average separation between nanoparticles. Therefore, a is directly related to the particle saturation magnetization. Interpretation of H_0 and a explain why circles and squares fall on the same straight line in Fig. 2.

Fig. 3 shows the resonance linewidth (ΔH_R) versus C (central EPR line) for samples A and B. Though partially different from the behavior observed in Fig. 2, the data in Fig. 3 still follow a straight line, $\Delta H_R = \Delta H_0 + bC$. The fitted values for the slope were $b = 0.36 \pm 0.02$ and 0.38 ± 0.02 for samples A and B, respectively. The fitting procedure also provides $\Delta H_0 = 2.1 \pm 0.1$ and 0.9 ± 0.1 G for samples A and B, respectively. The corresponding linewidth (central EPR line) of TEMPOL is 1.85 ± 0.01 G. There is a strong indication that the explanation of the ΔH_R versus C data is related to the adsorption of the TEMPOL at the coating layer of the magnetite nanoparticle. While b may account for the dipole-dipole interaction among the resonant centers that scales with $1/d^3$ and so with the

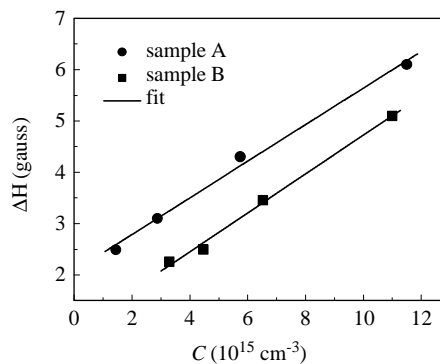


Fig. 3. Resonance linewidth versus nanoparticle concentration. The data refer to the central EPR line.

nanoparticle concentration C [8], ΔH_0 relates to the adsorbed surface density of TEMPOL [9]. Within the model picture presented here the broadening of ΔH_0 from 1.85 G (TEMPOL) to 2.1 G (sample A) is more likely to be due to the dipole–dipole interaction among resonant probes, while the Heisenberg exchange interaction may explain the narrowing of ΔH_0 from 1.85 G (TEMPOL) to 0.9 G (sample B). Therefore, the data suggest that TEMPOL is more effectively adsorbed at the nanoparticle surface in sample B than in sample A. Such difference would be attributed to differences in chemical nature and consequently the chemical interaction of the surface coating species in samples A and B and the doping agent (TEMPOL).

In summary, the electron paramagnetic resonance field and linewidth of TEMPOL introduced as a doping agent in magnetic fluid samples were investigated at room temperature. The samples contain magnetite nanoparticles with average diameter of 94 Å and coated with different coating layers (lauric acid plus ethoxylated polyalcohol in the first case and oleoylsarcosine in the second case). The model picture used in this study is more closely related to the one in which the TEMPOL is weakly adsorbed at the coating layer of the magnetic nanoparticle and thus the spectra are explained in the isotropic fast-motion limit. The resonance field and the resonance linewidth both scale linearly with the nanoparticle concentration. The dipolar field contribution to the effective field at the paramagnetic site accounts for the linear dependence of the resonance field versus nanoparticle concentration, while dipole–dipole interaction among paramagnetic probes adsorbed at the nanoparticle surface responds for the linear behavior

of the resonance linewidth versus nanoparticle concentration. Doping high-pH magnetic fluids with TEMPOL provides an excellent strategy to investigate the structure of the coating layer and the interaction of it with the surrounding medium. In particular it could be useful to probe the nanoparticle concentration in a wide range of values.

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