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# Ionic strength effect on magnetic fluids: a resonance study

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## Abstract

Magnetic resonance data showing the ionic strength effect in ionic water-based magnetic fluids is reported for the first time. Changes in the effective radii of the suspended particles is considered as the main source for magnetic resonance changes. The effective radius is analyzed as a function of the ionic strength taking into account the electrostatic screening effect. A simple particle charge–discharge mechanism due to changes in ionic strength of the solution is proposed.

Magnetic resonance emerges as a powerful technique to study both particle–particle [1] and particle–solvent interaction [2] in magnetic fluids. Particle–solvent interaction studies can be performed by changing the ionic strength of ionic magnetic fluids by addition of acid or base. Strong non-linear changes in the surface charge density can be achieved by changing the ionic strength of the solvent within a small range. In addition to that and as a consequence of the variation in the surface charge density one may change the effective radius associated with the orientational motion of the magnetic particle as well. Interesting details related to the surface charge density and effective radius are now being revealed through magnetic resonance data. In this paper we briefly review the approximation we use to treat the evolution of the magnetic resonance linewidth [3] and how it is related to the effective radius of a magnetic particle suspended in ionic magnetic fluids. We use the Debye–Hückel theory for electrostatic screening [4] to discuss the ionic strength dependence of the effective radius. A very simple charge–discharge mechanism that connects surface charge density and ionic strength will be presented.

To describe magnetic resonance linewidth data we start with a Hamiltonian  $\mathcal{H}$  that takes into account Zeeman, exchange and dipolar interactions between first-neighbor identical and regularly spaced magnetic centers suspended in a non-magnetic matrix:

$$\mathcal{H} = g \beta H \sum_j S_{zj} + \sum_{k>j} A_{jk} S_j S_k + \sum_{k>j} B_{jk} S_{zj} S_{zk}, \quad (1)$$

where  $A_{jk} = -2J_{jk} + (g^2 \beta^2 / 2r_{jk}^3)(3\gamma_{jk}^2 - 1)$  and  $B_{jk} = (3g^2 \beta^2 / 2r_{jk}^3)(3\gamma_{jk}^2 - 1)$ . The magnetic dipolar interaction appears in the second and third terms of Eq. (1). The  $z$ -component of the spin operator and the usual exchange integral are described by  $S_{zj}$  and  $J_{jk}$ , respectively.  $H$  is the external magnetic field,  $g$  is the  $g$ -factor,  $\beta$  is the

Bohr magneton,  $r_{jk}$  is the vector from the  $j$ th to the  $k$ th magnetic center and  $\gamma_{jk}$  is the direction cosine of  $r_{jk}$  relative to the  $z$ -axis. The effect of the dipolar interaction on the magnetic resonance linewidth is calculated using the Van Vleck method of moments [5]. The broadening of the resonance line is calculated as the mean square deviation of the resonance frequency from the Larmor value  $\langle \Delta \nu^2 \rangle = \langle (\nu - g \beta H / h)^2 \rangle = \langle \nu^2 \rangle - g^2 \beta^2 H^2 / h^2$ . In order to estimate mean values we consider our system as being composed of magnetic centers arranged in a bcc-like structure. Here the magnetic centers are  $\text{MnFe}_2\text{O}_4$  superparamagnetic particles bearing a net spin  $S' \gg 1$ . We estimate the net spin as  $S' = \Delta n S$ , where  $S$  is the effective spin of the magnetic center inside the particle and  $\Delta n$  is the net population of spins aligned along the easy axis of magnetization. Assuming a two-level potential well thermal fluctuation will induce spin orientational motion between the two states against an energy barrier  $\Delta E$ . According to the calculation described in Ref. [3], the broadening ( $\Delta \Gamma$ ) of the magnetic resonance line is:

$$\Delta \Gamma = (5g \beta S n / D^3) \times \tanh(\Delta E / 2kT), \quad (2)$$

where  $n$  is the total number of magnetic centers inside each particle and  $D$  is the mean distance between adjacent particles. The energy barrier in Eq. (2) should include all contributions to the orientational motion of the magnetic moment of the particle. In ionic magnetic fluids one can identify contributions to  $\Delta E$  which are independent of  $D$  as, for instance, the interaction between the magnetic moment of the particle and the external field, the magnetocrystalline anisotropy term and the Brownian orientational term. The Brownian term ( $3\alpha \eta V$ ) includes  $\alpha$ ,  $\eta$  and  $V$  which are respectively a coupling constant given in units of frequency, the viscosity of the carrier fluid and the hydrodynamic volume of the particle. There are contributions that depend upon the particle–particle distance  $D$  as,

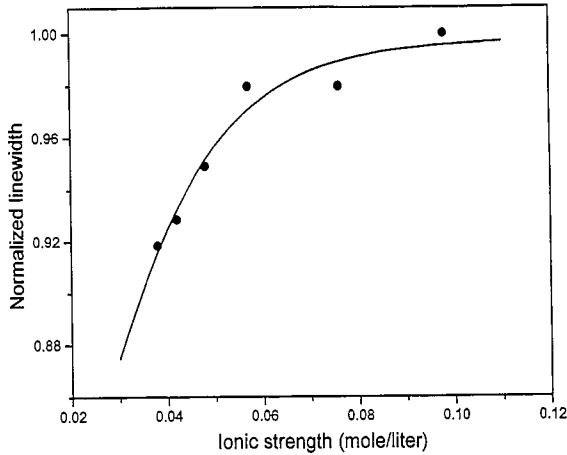


Fig. 1. Magnetic resonance linewidth (vertical scale) normalized to 596 G as a function of ionic strength (mol/liter). The data were taken at room temperature.

for instance, the magnetic dipole–dipole interaction, the electrostatic interaction and the electrostatic dipole interaction. In a highly concentrated ionic magnetic fluid having non-spherical magnetic particles we might expect at least six contribution to the energy barrier. Our experiment, however, was performed in order to keep all the energy contribution terms constant except the Brownian orientational term. Though the Brownian contribution ( $6\eta V$ ) does not itself represent energy, it is important to recall that it comes about as a constant connecting the torque due to the inner frictional force and the angular velocity of the spherical magnetic particle in suspension [6]. In other words, to rotate a particle in a fluid of viscosity  $\eta$  one has to do work which is proportional to what we call the Brownian contribution ( $6\eta V$ ). In the Brownian orientational term we identify the hydrodynamic radius of the particle as its effective radius  $R_e$ . A set of six samples were prepared by diluting a concentrated 4.0% volume fraction ( $6.3 \times 10^{16}$  grains/cm<sup>3</sup>) iron–manganese ionic magnetic fluid sample down to 1.5% volume fraction ( $2.4 \times 10^{16}$  grains/cm<sup>3</sup>). The starting sample was diluted by adding acid solution at different pH values. The ionic strength  $\xi$  of the diluted samples runs from 0.038 mol/liter up to 0.098 mol/liter. As far as phase separation is concerned this is a safe range for ionic strength variation [7]. The magnetic resonance spectra of the samples were taken at room temperature in a X-band spectrometer. Points in Fig. 1 show the normalized resonance linewidth as a function of the ionic strength. With the above comments in mind Eq. (2) can be rewrite in a normalized way as:

$$\Delta \Gamma_n = \tanh\left(\frac{\Delta E_r}{2kT} + \frac{2\pi\alpha\eta R_e^3}{kT}\right). \quad (3)$$

The first term ( $\Delta E_r$ ) in Eq. (3) includes all contributions to the energy barrier that are independent of the ionic strength. The second term ( $2\pi\alpha\eta R_e^3/kT$ ) in Eq. (3) includes the

effective radius of the particle that we assume to be dependent of the ionic strength.

To explain how the effective radius depends on the ionic strength we consider a system composed of a charged particle with a surface charge density  $\sigma$  inside an electrolyte solution and the counterions surrounding the charged particle. A counterion can be bounded at the particle surface provided that its thermal energy  $kT$  is equal to or less than the attractive electrostatic energy  $U$ . Within the Debye–Hückel model the interaction between a charged particle and a monovalent counterion is given by  $U = (R_0^2 e \sigma / \epsilon d) \exp(-\delta \sqrt{\xi} d)$ , where  $R_0$  is the particle radius,  $e$  is the elementary charge,  $\epsilon$  is the dielectric constant of the solvent and  $d$  is the distance between the counterion and the center of the charged particle. The thermal and electrostatic energies match one another at a given distance that we call the effective radius:

$$R_e = (R_0^2 e \sigma / \epsilon kT) \exp(-\delta \sqrt{\xi} R_e), \quad (4)$$

where  $\delta = (2 \times 10^3 N e^2 / \epsilon kT)^{1/2}$ ,  $N$  being the Avogadro number.

The final step to be performed in order to connect resonance linewidth and ionic strength is to find a way to write the surface charge density as a function of the ionic strength. This can be done by considering a simple charge–discharge mechanism for particles in ionic solution at a given ionic strength. Potentials  $\phi_{pr}$  and  $\phi_{rs}$  respectively are associated with the surface particle and electrolyte solution with respect to a reference potential  $\phi_r$ . We assume that a charge–discharge mechanism is driven by the potential difference  $\phi_{ps} = (\phi_{pr} + \phi_{rs})$  between the particle surface and solution. The capacitance  $C$  of the particle surface is related to the surface charge  $Q$  by  $\phi_{pr} = Q/C$ . The gradient  $\nabla_\xi(Q)$  close to the particle surface by unit potential we consider as a constant  $\Lambda$  related to the solvent  $\Lambda = \nabla_\xi(Q)/\phi_{rs}$ . Therefore a charge–discharge mechanism is set up which can be described by:

$$\sigma(\xi) = \sigma_s [1 - \exp(-\xi/\xi_0)], \quad (5)$$

where  $\sigma_s$  is the saturation surface charge density and  $\xi_0$  is a constant related to the system.

Taking Eqs. (4) and (5) into Eq. (3) we have a description for the magnetic resonance linewidth behavior as a function of the ionic strength:

$$\Delta \Gamma_n = \tanh(A + B \times R_e^3), \quad (6)$$

where  $A = \Delta E_r / 2kT$  and  $B = (2\pi\alpha\eta/kT) / (R_0^2 e \sigma_s / \epsilon kT)^3$ . The full line in Fig. 1 represents the fit of the experimental data using Eqs. (6), (5) and (4). The fitted values are  $A = 1.01$ ,  $B = 4.068$  and  $\xi_0 = 0.05$  mol/liter. The saturation charge density  $\sigma_s = 0.18$  C/m<sup>2</sup> is obtained considering  $\alpha = 10$  s<sup>-1</sup>,  $\eta = 10^{-2}$  N s/m<sup>2</sup> and  $B = 4.068$ . The fitted value for the saturation charge density is in excellent agreement with the experimental value obtained by chemical methods [8]. From  $\sigma_s$  and  $\xi_0$  we have a description of the particle charge–discharge mechanism

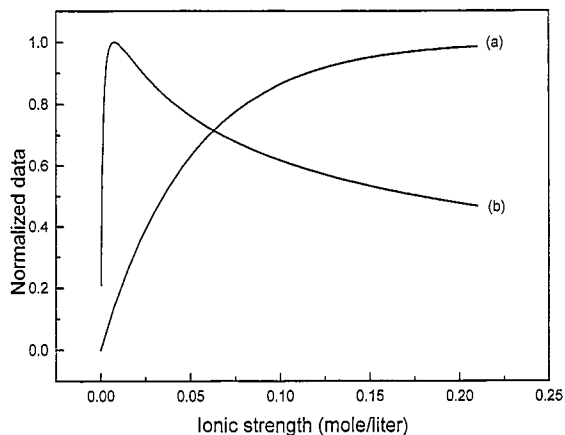


Fig. 2. Normalized values (vertical scale) for surface charge density (a) and effective radius (b) of a magnetic particle as a function of the ionic strength (mol/liter). The maximum values for the surface charge density and effective radius are respectively  $\sigma_s = 0.18 \text{ C/m}^2$  and  $R_{em} = 6.6 \text{ nm}$ . The mean value of the particle radius as determined by electron microscopy is  $R_0 = 5.5 \text{ nm}$ .

through Eq. (5) as shown in Fig. 2(a). It is well known that by increasing the ionic strength the surface charge very quickly reaches its saturation point. A second important point is the description of the effective radius as a function of the ionic strength. This is done by considering  $R_0 = 5.5 \text{ nm}$ ,  $\sigma_s = 0.18 \text{ C/m}^2$ ,  $\epsilon = 80\epsilon_0$ ,  $T = 300 \text{ K}$ ,  $\xi_0 = 0.05 \text{ mol/liter}$  and  $\delta = 3.244 \times 10^9 \text{ m}^{1/2}$ . A plot of the effective radius as a function of ionic strength is shown in Fig. 2(b). The effective radius reaches a maximum value  $R_{em}$

$= 6.6 \text{ nm}$  at an ionic strength of the order of  $\xi_m = 0.01 \text{ mol/liter}$  coming down slowly and reaching the value for the particle radius  $R_0 = 5.5 \text{ nm}$  at an ionic strength of  $0.034 \text{ mol/liter}$ . The maximum value  $R_{em} = 6.6 \text{ nm}$  is a very interesting result since it means that a solvent layer of  $1.1 \text{ nm}$  thick is electrostatically bonded to the particle surface. Though we have not included here aspects like polydispersity, van der Waals interaction and finite-size corrections for counterions bounded to the particle surface, both effective radius description and charge-discharge mechanism provide very consistent results.

*Acknowledgement:* This work was partially supported by the Brazilian agencies CAPES and CNPq.

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