Magnetic nanoparticles and superparamagnetic resonance (4)
" Magnetic relaxation of magnetic nanoparticles and fluid "

Product used : Electron Spin Resonance spectrometer (ESR)
ENDOR cavity (ES-14010), Nuclear Magnetic Resonance spectrometer (NMR)

Particle concentration and superparamagnetic resonance

Similar to the dipole-dipole interaction between paramagnetic ions, magnetic nanoparticles (MNPs) show the spectral line-width broadening effect by the interaction between particles, too. Figure 1 shows the superparamagnetic resonance (SPR) spectra of Fe_3O_4 magnetic nanoparticles dispersion in toluene and dependence of line widths on the concentration. Line widths were measured on the narrow components with a diameter of 5 nm and 10 nm, respectively. As shown in Figs.1(c) and (d), although both line widths are proportional to the concentration of the particles, the proportional constant and the line widths of 5 nm particles are larger than that of 10 nm particles. Spectral shapes and g-values remain almost unchanged in both diameter particles, as shown in Figs. 1(a) and (b), but getting broader only a little. It is reported that the magnetic fluid of Fe_3O_4 with a diameter of 9 nm shows a large peak shift and broadening as the concentration increases, in the previous study[1]. This kind of difference could be considered that the shape, the distribution of diameters, and the ligands fixed to particles affects spectral properties. Moreover, the effect of aggregation between particles should be considered, too. The concentration dependence of MNPs lets us know information reflecting the micro environment and structure around particles.

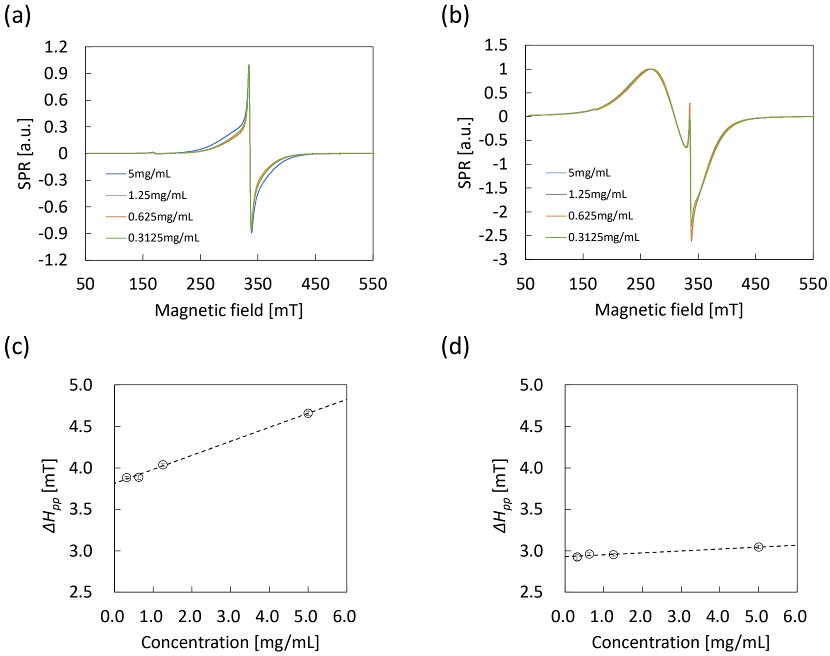

Fig. 1 SPR spectra and line widths dependent on various concentration of Fe_3O_4 magnetic nanoparticles dispersion in toluene. (a) Normalized spectra of particle diameter of 5 nm, (b) 10 nm, (c) relationship between particle (5 nm) concentration and line widths, and (d) relationship between particle (10 nm) concentration and line widths.

Characterization of magnetic fluid using TD-NMR (Time domain nuclear magnetic resonance)

On the evaluation of magnetic particles and fluid, it is important not only to explore the magnetic properties of MNPs itself, but also to evaluate the effects for the environment (solvent or matrixes) around the particles. A contrast agent for MRI (magnetic resonance imaging) or agent for Hyperthermia is used for increasing the image sensitivity or effective elimination of cancer cells. Therefore, the characterization of solvent or matrixes in which MNPs are located is necessary.

The time domain nuclear magnetic resonance (TD-NMR) method is one of the typical material evaluation methods, and is used widely for product administration, research, and development.

The block diagram which Figure 2 shows is an example for the TD-NMR measurement system using ENDOR cavity (^{1}H frequency is 14.55 MHz). Since an RF irradiation coil is usually equipped to ENDOR cavity, basic ^{1}H-NMR relaxometry experiments can be done using a combination of tuning circuit, duplexer, RF-power amplifier, and the NMR spectrometer.

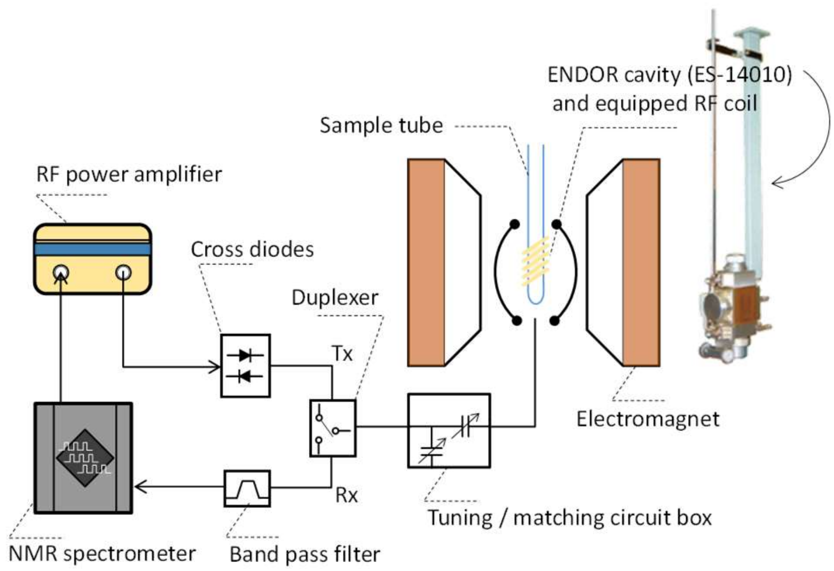

Fig. 2 An example of system block diagram for TD-NMR measurements ($\omega_H/2\pi$ = 14.55 MHz) using ENDOR cavity (ES-14010).

T_1, T_2 measurement methods by TD-NMR

The relaxation time of electron and nuclear spins responds sensitively to viscosity and temperature of solvent, or magnetic variation around them. Therefore, the measurement of relaxation time allows us to characterize the environment around the target's compounds.

As electrons relax very quickly, it is quite difficult to measure its velocity except under special conditions. On the contrary, relaxation time of solvent protons can be easily obtained. There are two types of relaxation times, which are known as spin-lattice relaxation time (T_1) and spin-spin relaxation time (T_2) in spin relaxation times. One of the T_1 typical measurement methods is an inversion recovery method shown in Fig. 3(a). T_1 can be estimated by fitting the spectral intensity I_{IR} using eq.(1), where spectra can be obtained by Fourier transformation of FID (Free Induction Decay) data measured by varying time "tau".

$$I_{IR} = A\{1 - 2\exp(-tau/T_1)\}$$:A is scaling factor. (1)

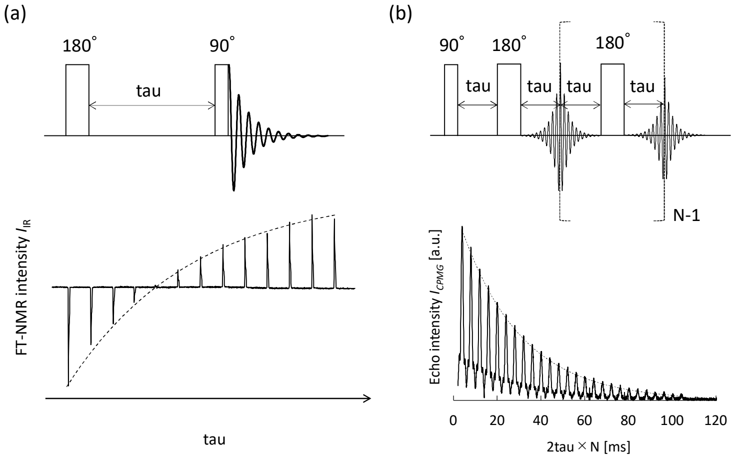

Fig. 3 (a) Pulse sequence of Inversion recovery method and an example of spectral array. (b) Pulse sequence of CPMG method and an example of echo train.

One of the T_2 typical measurement methods is CPMG (Carr-Purcell-Meiboom-Gill) method. In this method, the echo intensity I_{CPMG} is measured by successive N times applying microwave with pulse width of 180 degree every 2 × tau time shown in Fig. 3(b). T_2 can be estimated by fitting the I_{CPMG} using eq.(2).

$$I_{CPMG} = B\exp(-2tauN/T_2)$$: B is scaling factor. (2)

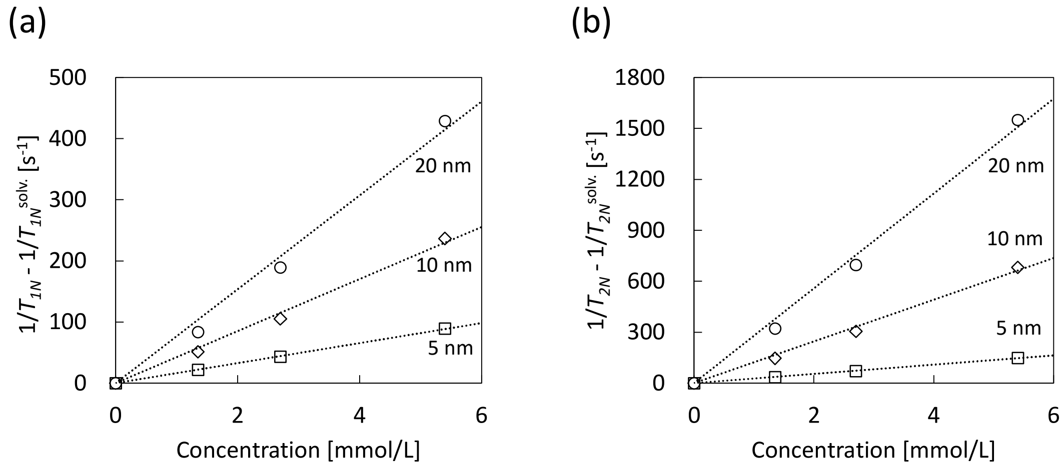

Fig. 4 Various concentration of Fe_3O_4 magnetic nanoparticles dispersion in toluene and relaxation velocity. (a) Molarity of MNPs and spin-lattice relaxation velocity. (b) Molarity of MNPs and spin-spin relaxation velocity. T_{1N} and T_{2N} means T_1 and T_2 of protons of solvent, respectively.

Superparamagnetism of MNPs and relaxivity of magnetic fluid

As an example, the aqueous magnetic fluid MNPs dispersed is widely researched for the development of the contrast agent for MRI. Contrast agents are used for increasing image sensitivity of MRI. One of its evaluation indexes is "relaxivity".

Graphs which Fig. 4 shows are plots of the dependence of relaxation velocity on molarity in Fe_3O_4 magnetic nanoparticles dispersion in toluene. Each relaxation velocity of T_{1N} or T_{2N} is proportional to the concentration of Fe_3O_4 with respective particle diameters, and simultaneously has its intrinsic proportional constant respectively. This constant is called "relaxivity". T_1-weighted contrast agents (positive agents) are designed for generating bright images. Evaluation index for positive agents is a ratio of relaxivty "r_2/r_1", lower value of "r_2/r_1" is regarded more effective[2]. Estimating "r_2/r_1" from magnetic fluid* shown in Fig. 5, MNPs with a diameter of 5 nm shows the lowest r_2/r_1, and would be expected to generate a bright image.

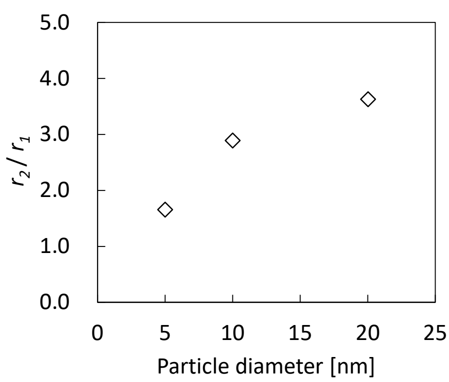

Fig. 5 Particle diameters of MNPs and r_2/r_1.

* Although Fig. 5 shows the results of magnetic fluid of toluene, real contrast agents are evaluated using aqueous magnetic fluid in fact[2].

Reference: [1] M. M. Noginov *et al.*, Journal of Magnetism and Magnetic Materials, **320**, 2228-2232 (2008).
[2] W. Xiao *et al.*, Journal of Magnetism and Magnetic Materials, **324**, 488–494 (2012) .

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