Variable temperature electron paramagnetic resonance investigations of an ionic ferrofluid†

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An aqueous based ionic ferrofluid has been studied by EPR spectroscopy technique from room temperature to liquid nitrogen temperature to detect the magnetic phase transitions and their variation at low temperatures. The line-width of EPR signal has been found to increase with decreasing temperature and this has been assigned to magnetic phase transition from ferromagnetic to a spin glass or cluster glass state mainly due to freezing of the carrier fluid. Line-width variation with temperature also suggests that bulk rotation mechanism is the dominant mode of relaxation. Any evidence of the presence of super-paramagnetism has not been observed.

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Magnetic fluid systems have been receiving considerable interest in the last few years because of their wide applications in the domain of nanostructured material technologies1. In such fluids, in the absence of external magnetic field each particle may be considered independent and its magnetization direction is randomly oriented, hence such a system resembles a paramagnetic gas. In the presence of magnetic field, these particles orient themselves along the applied magnetic field direction by two distinct mechanisms: (i) the bulk rotation of the particles with the magnetic moments locked in the easy direction of the magnetization (Brownian rotation) and (ii) the rotation of magnetic vector out of the easy direction (Neel rotation). However, when the number density of magnetic particles is large, dipole-dipole interaction between the particles play an important role to manifest the dynamic properties of these magnetic fluids2-4. Recently, electron paramagnetic resonance (EPR) technique5,6 has emerged as one of the very sensitive tools to probe the type of processes that may influence the magnetic properties of such ultra-fine colloidal dispersion of different magnetic fluids7-10. In this paper, we have reported the results of EPR measurements of a water dispersed ionic ferrofluid made at different temperatures to understand the relaxation behaviour and phase transitions present in the ferrofluid.

Experimental Procedure

The ultra-fine nanoparticles of Fe3O4 ionic ferrofluid can be prepared by different methods like glass crystallization, ball milling, chemical co-precipitation or citrate precursor technology. In the present case, ionic ferrofluid was prepared by the chemical co-precipitation method as described earlier11 using analytical grade FeCl3, FeCl2 and NH4Cl. Particle size distribution and crystallinity were determined by using transmission electron microscope JEM-200CX. This aqueous based ferrofluid was having particle size ranging from 2 to 15 nm and 80G saturation magnetization11.

EPR spectra were recorded on an X-band reflection type, model E-112 (M/s Varian, USA) spectrometer. The ionic ferrofluid taken in quartz capillary tube was aligned in TE₁₀₂ cavity centre to avoid deterioration of the RF field configuration and power loss. Magnetic field was modulated at 100 kHz frequency and low microwave power was used to avoid saturation effects. Low temperature spectra were taken by gas flow method using Varian variable temperature accessory V-4502 using liquid nitrogen as coolant from 80 to 300 K temperature. As usual, the first derivative of the power absorption was recorded as a function of applied magnetic field. Reference sample

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DPPH was used as a standard field marker for \( g \)-value determination.

**Results and Discussion**

A single asymmetric broad line EPR signal was obtained at all temperatures for present ferrofluid sample as shown in Fig. 1. Variation of the peak-to-peak line width (\( \Delta H_{pp} \)) with temperature is shown in Fig. 2 and it has been found to increase monotonically with decreasing temperature. Line-width data yield information on spin relaxation processes. At low temperatures line-widths observed are very broad therefore one has to take into account the relaxation phenomenon in the analysis of the EPR signals. Assuming that observed pattern is due to superposition of microwave absorption of identical ellipsoid particles, i.e., with the same form factor, magnetization and relaxation factor, following simple expression between the resonance field \( H_{\text{res}} \) (without relaxation effect) and \( H_{\text{obs}} \) (with relaxation effect) can be derived using Landau-Lifshitz formulation\(^{12} \).

\[
H_{\text{res}} = H_{\text{obs}} + \gamma_4 (\Delta H_{pp}^2/H_{\text{ref}}) \quad \ldots(1)
\]

where \( \Delta H_{pp} \) is observed line-width, \( H_{\text{obs}} \) is observed resonance field, \( H_{\text{ref}} \) is DPPH signal resonance field value and \( H_{\text{res}} \) is corrected resonance field at temperature \( T \). The dimensionless parameter \( g \), defined as proportionality constant between the frequency and the resonance field, has been evaluated by using the corrected resonance field data. Fig. 3 shows the variation of calculated \( g \)-value of this ionic ferrofluid verses temperature.

The broad line signal observed herewith has been assigned due to ferromagnetic resonance of single crystal magnetite particles (\( \text{Fe}_3\text{O}_4 \)) well dispersed in the carrier fluid\(^{13} \). The signal observed is less broad and less asymmetric compared to \( \text{Fe}_3\text{O}_4 \) powder EPR spectra\(^{13,14} \) because the deviation of the easy axes direction of magnetization from the direction of applied field \( H \) has been reduced due to the bulk rotation of the magnetic particles in the matrix liquid of the ferrofluid\(^{13,15} \).

Fig. 2—Variation of peak-to-peak line-width (\( \Delta H_{pp} \)) with temperature for the water based ionic ferrofluid

Fig. 3—Variation of \( g \)-value as a function of temperature for the water based ionic ferrofluid
The peak-to-peak line-width continuously decreases with increase in temperature as observed earlier in other magnetic fluids. This variation of line-width can be explained using two-level system for which EPR line-width is given by

\[ \Delta H = L \tanh \left( \frac{\Delta E}{2kT} \right) \]  
\[ L = 5 g\beta n S/R^3 \]

where \( n \) is total number of magnetic centres, \( R \) is the distance between adjacent particles, \( S \) is the effective spin of magnetic particles and all other symbols have their usual meanings. For a given system, \( L \) is constant and therefore line-width variation is mainly determined by energy gap \( \Delta E \) between the two levels. In general, this barrier arises due to terms like dipole-dipole energy (\( E_{dd} \)), anisotropy energy (\( E_a \)) and dipole field energy (\( E_d \)). For the present very dilute system, contribution of \( E_{dd} \) and \( E_a \) are negligible and may be neglected. The dipole energy \( E_d \) is given by \( J M_s VH \) where \( J \) is the coupling constant, \( M_s \) is the saturation magnetization and \( V \) is the volume of magnetic particle. This suggests that weakening of the magnetic coupling with rise in temperature is responsible for observed decrease in line-width.

Further, at room temperature all the spins in water based ferrofluid can be imagined to adopt a unidirectional orientation under the influence of external magnetic field. At this stage the carrier liquid does not exert any force that may disturb the unidirectional alignments of the spins. The higher \( g \)-value and lower line-width may be due to this alignment of spins. At lower temperature, the viscosity of the carrier liquid begins to increase which hinders the bulk rotation mechanism of the ferrofluid particles. Once the sample is frozen, it leads simultaneous freezing of the spins in whatever random direction they existed at that moment. Moreover, the initiation of the process of freezing of the water medium at any localized site in the body of the ferrofluid may cause local expansion, which in turn causes the de-alignment of the spins, i.e., the randomness in the spin orientation. This new state is known as spin glass or cluster glass state. The anisotropic magnetic fields arising from the randomly organized spins smear out and lead to lower \( g \)-value and a broader line-width. In substance, when a dynamic phenomenon is considered, the freezing process leads to a slowing down of the spin fluctuations, which in turn causes slower relaxation process. The observed behaviour of \( g \) and \( \Delta H_{pp} \) are obviously due to the freezing of the carrier liquid.

Single domain ferro- or ferrimagnetic particles of a ferrofluid relax by two distinct processes namely Brownian and Neel relaxation. If the relaxation time constant due to the Neel process (\( \tau_N \)) is less than due to the Brownian process (\( \tau_B \)), the system is called intrinsically superparamagnetic. Alternatively, if \( \tau_B < \tau_N \), it is called extrinsically super-paramagnetic. However, when the relaxation time constant is much greater than the time of EPR measurement, i.e., the Larmor precession time (\( \tau_L \approx 10^{-9} \) s), the system may be regarded as ferromagnetic. Usually, magnetic fluid is a poly-dispersed system and there will be a fraction of particles which may be super-paramagnetic. Since relaxation time depends upon particle size and the temperature of the system, it may be possible to observe the variation of the spectra from ferromagnetic to super-paramagnetic state either by varying the size of the particles or by varying the temperature of the ferrofluid.

During the temperature variation study, we have not observed any superimposed narrow line signal having \( g \approx 2.0 \) which is indicative of super-paramagnetic state of the ferrofluid. Similar observations were also reported by Sharma and Waldner who could not observe super-paramagnetic phase in water based commercial \( \text{Fe}_3\text{O}_4 \) ferrofluid. This suggests that in the present ionic ferrofluid, magnetic particles having size smaller than the critical size required to obey Neel relaxation phenomenon in this temperature range are not present.

### Conclusions
The temperature variation EPR spectroscopic studies of the ionic ferrofluid dispersed in aqueous medium showed that system follows bulk rotation relaxation process. The complete randomisation of spins and collapse of ferromagnetic phase take place at low temperatures. This causes increase in line-width and decrease in \( g \)-value at low temperatures due to the formation of spin glass or cluster glass state. Since narrow EPR signal due to super-paramagnetic phase at any temperature was not obtained, this suggests that sufficient number of ferrite particles of appropriate size required for super-paramagnetic behaviour, were not present in this ionic ferrofluid.

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