

$[\text{FeCl}_4]^-$ Ionic Liquid Based Ferrofluids

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Magnetic ionic liquids derived from hydrochloride methyl ester alanine amino acids (AA) and FeCl_3 were synthesized in ethanol and their magnetic properties were investigated. Iron (III) chloride forms ionic liquid in ethanol at saturated concentrations by the transfer of Cl^- anion from one molecule of FeCl_3 to the other molecule with the creation of tetrachloro ferrate anion $[\text{FeCl}_4]^-$ as well as dimer $[\text{Fe}_2\text{Cl}_7]^-$. Raman scattering indicates that after addition of hydrochloride methyl ester alanine to ethanol solutions of FeCl_3 increase the intensities of signal at the frequencies at 318 cm^{-1} and 380 cm^{-1} as markers for the presence of $[\text{FeCl}_4]^-$ and $[\text{Fe}_2\text{Cl}_7]^-$ complexes. The magnetization at room temperature showed in both samples a linear dependence on the applied magnetic field. On the other hand, in the Raman scattering experiments the magnetization is smaller for FeCl_3 sample in the presence of methyl ester alanine.

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1. Introduction

Ionic liquids containing a transition metal (such as Fe, Ni, Co) ions exhibit a magnetic response. Thus, for instance, by using a permanent magnet one can both easily deform their free surface. These magnetic ionic liquids (MILs) with anions containing metal complexes are the earliest developed room temperature ionic liquids [1]. The discovery of the magnetic behavior of the first reported ionic liquid, showing a magnetic response of 1-butyl-3-methylimidazolium tetrachloroferrate, $(\text{BMIM})[\text{FeCl}_4]$, opened a completely new field for ionic liquids and their application [1–4]. Dual functionalities, namely the paramagnetism and useful ability, were recently realized by the combination with the protonated L-amino acid methyl esters in FeCl_3 methanol solutions [5].

In this work, we focused on the magnetic and spectral properties of simple FeCl_3 and FeCl_3 /methyl ester alanine hydrochloride mixture in ethanol solutions.

2. Experimental

Stock solution of 2.96 M $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (Sigma, USA) was prepared similarly as describe Li et al. in their work [5], but instead of methanol was used ethanol by weighing commercial compound and adding 96% ethanol (Sigma, USA) in the desired proportion. By mixing at room temperature commercially available crystalline L-Alanine methyl ester hydrochloride $[\text{L-AlaOCH}_3\text{H}]\text{Cl}$ (Sigma, USA) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ with equimolar amount, dark brown liquid was obtained under air atmosphere at room temperature.

Micro Raman spectrum was obtained by means of optical tweezer consisting of Spatial Light Modulator (Hamamatsu X10468–03) and trapping fiber laser (IPG YLM–10–LP–SC) with maximal output power 10 W at wavelength 1070 nm, combined with micro-Raman spectrometer (Shamrock SR 303i) and low noise camera (Andor newton DU970P), using 532 nm laser (torus532 and mpc 3000, Laser Quantum, England). The integration time was 10 s and the laser power at the sample was approximately 500 mW.

The magnetization of a small amount of FeCl_3 (37.93 mg) and $[\text{L-AlaOCH}_3\text{H}][\text{FeCl}_4]$ (34.89 mg) in ethanol was measured by SQUID magnetometer (superconducting quantum interface device, Quantum Design MPMS5) at 280 K and applied magnetic field up to 50 kOe.

3. Results and discussion

Our obtained Raman spectrum in Fig. 1 shows a vibrational band characteristic for the $[\text{FeCl}_4]^-$ ion at 318 cm^{-1} for the ethanol solution of the 2.9 M FeCl_3 , at room temperature. Second strong signal at 380 cm^{-1} belongs to dimer $[\text{Fe}_2\text{Cl}_7]^-$. This pair of strong bands corresponds well with literature values of Bimin $[\text{FeCl}_4]^-$ [6], indicating that monomer $[\text{FeCl}_4]^-$ and dimer $[\text{Fe}_2\text{Cl}_7]^-$ are the predominant iron-containing species for saturable concentration of FeCl_3 in ethanol. For the existence of $[\text{FeCl}_4]^-$ and $[\text{Fe}_2\text{Cl}_7]^-$ species in FeCl_3 ethanol solution, Cl^- ions have to be transferred from the second molecule of ferric chloride with the creation of some species with four or six ligands, coordinated around iron (III), as was discussed for hydrated melts of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ [7]. While tetrahedral species monomer $[\text{FeCl}_4]^-$ and dimer $[\text{Fe}_2\text{Cl}_7]^-$ have four equivalent ligands, thus the change in polarizability is large. On the other hand for tetrahedral or octahedral iron complexes with different ligands $[\text{FeCl}_2(\text{CH}_3\text{CH}_2\text{OH})_{2-n}(\text{H}_2\text{O})_n]^+$

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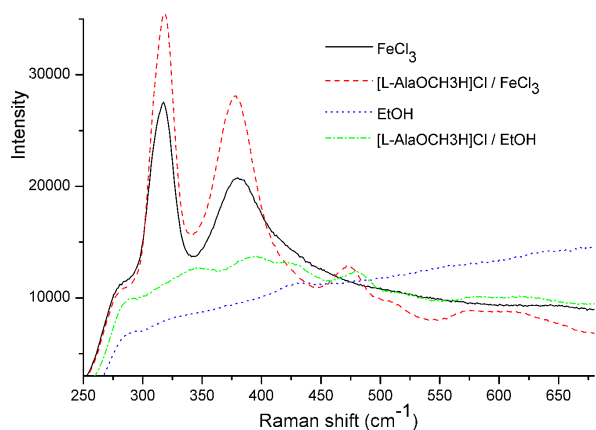


Fig. 1. Raman spectrum of 2.96 M FeCl₃ soluble in ethanol, ionic liquid prepared from [L-AlaOCH₃H]Cl/ FeCl₃·6H₂O in ethanol solution and with [L-AlaOCH₃H]Cl dissolved in ethanol, as well as free ethanol.

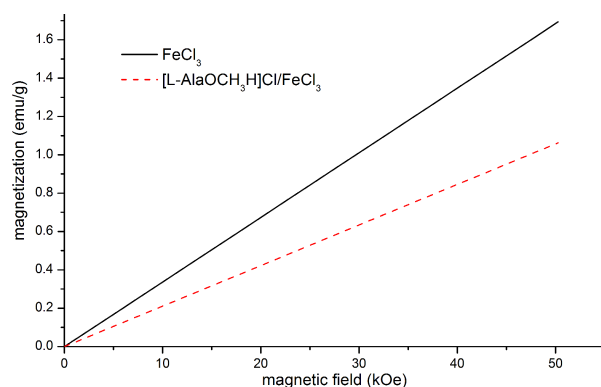


Fig. 2. Magnetic susceptibility for FeCl₃ and [L-AlaOCH₃H]Cl / FeCl₃·6H₂O in ethanol solution measured in range 0-50 kOe of magnetic field at 280 K.

or [FeCl₂(CH₃CH₂OH)_{4-n}(H₂O)_n]⁺ the Raman scattering coefficient is very small, and therefore these are simply not observed in Raman spectrum of our samples. Similarly we cannot rule out the presence of FeCl₃ in ethanol solution, because predicted vibration frequency for FeCl₃ is in the region of vibration frequencies of monomer [FeCl₄]⁻ and dimer [Fe₂Cl₇]⁻ [6].

After the addition of the equimolar amount of crystalline L-Alanine methyl ester hydrochloride to the ethanolic solutions of FeCl₃, the vibrational signals for both species [FeCl₄]⁻ and [Fe₂Cl₇]⁻ at 318 and 380 cm⁻¹ has increased, and new small band at 478 cm⁻¹ is observed. From this behavior we propose that L-Alanine methyl ester hydrochloride shifts the equilibrium of reaction towards creation of more [FeCl₄]⁻ and [Fe₂Cl₇]⁻ species in ethanol solution of FeCl₃.

Most of the magnetic ionic liquids containing the tetrachloroferrate anion, [FeCl₄]⁻ and dimer [Fe₂Cl₇]⁻, have evidenced a paramagnetic dependence of the magnetic susceptibility. We observed the response to the external

magnetic field of L-Alanine methyl ester hydrochloride in the presence of FeCl₃ ethanol solution with increasing magnetic field as soon as in the case of only FeCl₃ in ethanol.

The results are shown in Fig. 2. It can be seen that magnetization intensities show the same linear response to the magnetic field and both samples behave as paramagnetic materials. The slope for sample [L-AlaOCH₃H][FeCl₄] is lower in comparison to FeCl₃, which means that total magnetic moment has decreased in [L-AlaOCH₃H][FeCl₄].

FeCl₃ or [FeCl₂(CH₃CH₂OH)_{2-n}(H₂O)_n]⁺ with ligands have a stronger magnetic effect than the monomer [FeCl₄]⁻ and dimer [Fe₂Cl₇]⁻. A more detailed investigation of this problem is the subject of future research.

4. Conclusions

We have reported about dark brown magnetic ionic liquids [L-AlaOCH₃H][FeCl₄] and [L-AlaOCH₃H][Fe₂Cl₇] formed by mixing equimolar crystalline [L-AlaOCH₃H]Cl and FeCl₃·6H₂O in ethanol at room temperature. This solution forms magnetic [FeCl₄]⁻ a [Fe₂Cl₇]⁻ species similarly as for the simple solution of FeCl₃ in ethanol. The magnetic characterization of the two components shows, that both compounds are paramagnetic with magnetic moment associated with the presence of Fe³⁺ ion. The results show that the magnetic susceptibility in the presence of [L-AlaOCH₃H]⁺ in ethanol solution of FeCl₃ is lower than magnetic susceptibility for FeCl₃ alone in ethanol solution.

Acknowledgments

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