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# Use of Ionic liquid + nanoparticles as media for fuel desulfurization

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In recent years, considerable attention has been given to deep desulfurization of gasoline due to the higher restrictions concerning sulfur-compounds content level in fuels. Sulfur oxides formed in gasoil combustion process contribute to acid rains, global warming and air pollution. Those affect urban as well as industrial areas and are harmful for human health due to secondary inorganic aerosol gases formation. The European Union gradually reduced the maximum sulfur concentration in fuels to avoid high emission of gases resulting from combustion of heavy fuels. Since 2010, the total sulfur content cannot be higher than 10 ppm. Deep desulfurization of gasoline and diesel is very complex problem for petroleum industry and has to be solved to minimize the pollution from fuel oils exhaust gas.

Results of extraction of sulfur containing compounds from gasoline oil using ILs indicate that such a process could be an attractive alternative to common desulfurization by hydrotreating. Indeed, the values of thiophene selectivity (about 1000) obtained with 1-ethyl-3-methylimidazolium thiocyanate [EMIM][SCN] or 1,3-dimethylimidazolium methylphosphonate [DMIM][MP] are large but the distribution factor values still remain to be improved (0.6 – 0.8 and 0.2 – 1.1 respectively). The aim of this study is to investigate the possible use of these ILs in presence of nanoparticles of TiO<sub>2</sub> or Fe<sub>2</sub>O<sub>3</sub> as solvents for the separation problems frequently encountered in petroleum industry {aromatic sulfur compound + aliphatic hydrocarbon}.

## Experimental Procedure

The liquid-liquid equilibria measurements of ternary mixtures have been performed in jacketed glass cells. The experimental set up consists of a cell with an internal volume of about 30 cm<sup>3</sup> kept at constant temperature of 298.15 K using a thermostated bath. The ternary mixtures, with compositions inside the immiscible region of the system, are weighted using a METTLER analytical balance. All the mixtures were vigorously mixed using a teflon coated magnetic stirrer for 2h to reach a good contact between both phases and kept overnight in order to settle down.

Samples of both layers were taken from the cell using a syringe. The compositions of organic compounds such as n-heptane, thiophene were determined by gas chromatography. For determination of the ionic liquid composition, density measurements of both phases were performed at 298.15 K or 302.15 K with a vibrating tube densimeter (Anton Paar, model DMA601).



## Thermodynamic study of the ternary systems {Thiophene or Pyridine / n-Heptane / IL} in the presence of nanoparticles

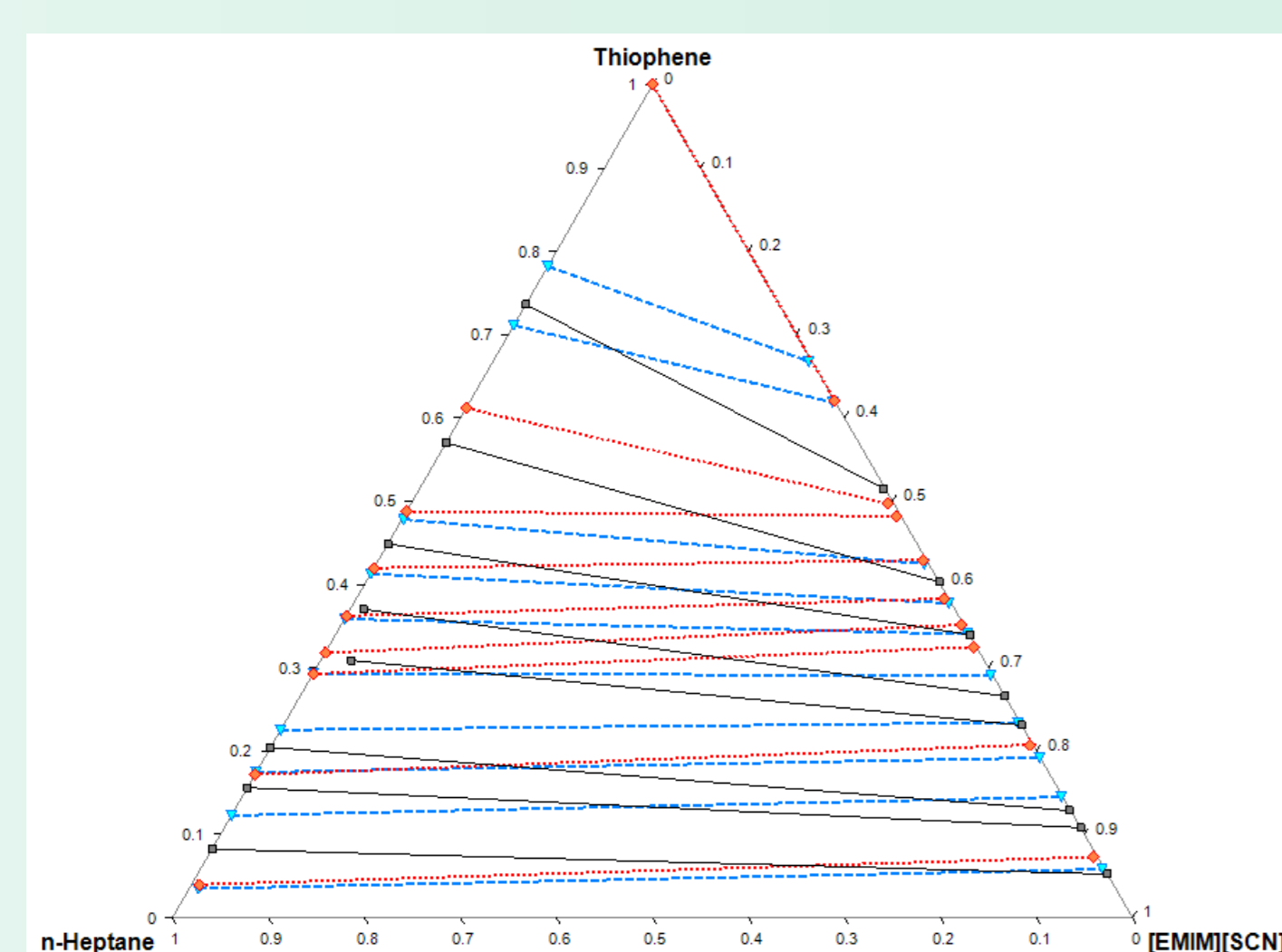


Figure 1. Effect of TiO<sub>2</sub> nanoparticles addition on the tie lines of ternary system {Thiophene + Heptane + [EMIM][SCN]} at 298.15 K. Nanopowder concentration in IL: 0.05 wt %: ♦ and .....; 0.1 wt %: ▼ and -----. Mixture without nanoparticles: ■.

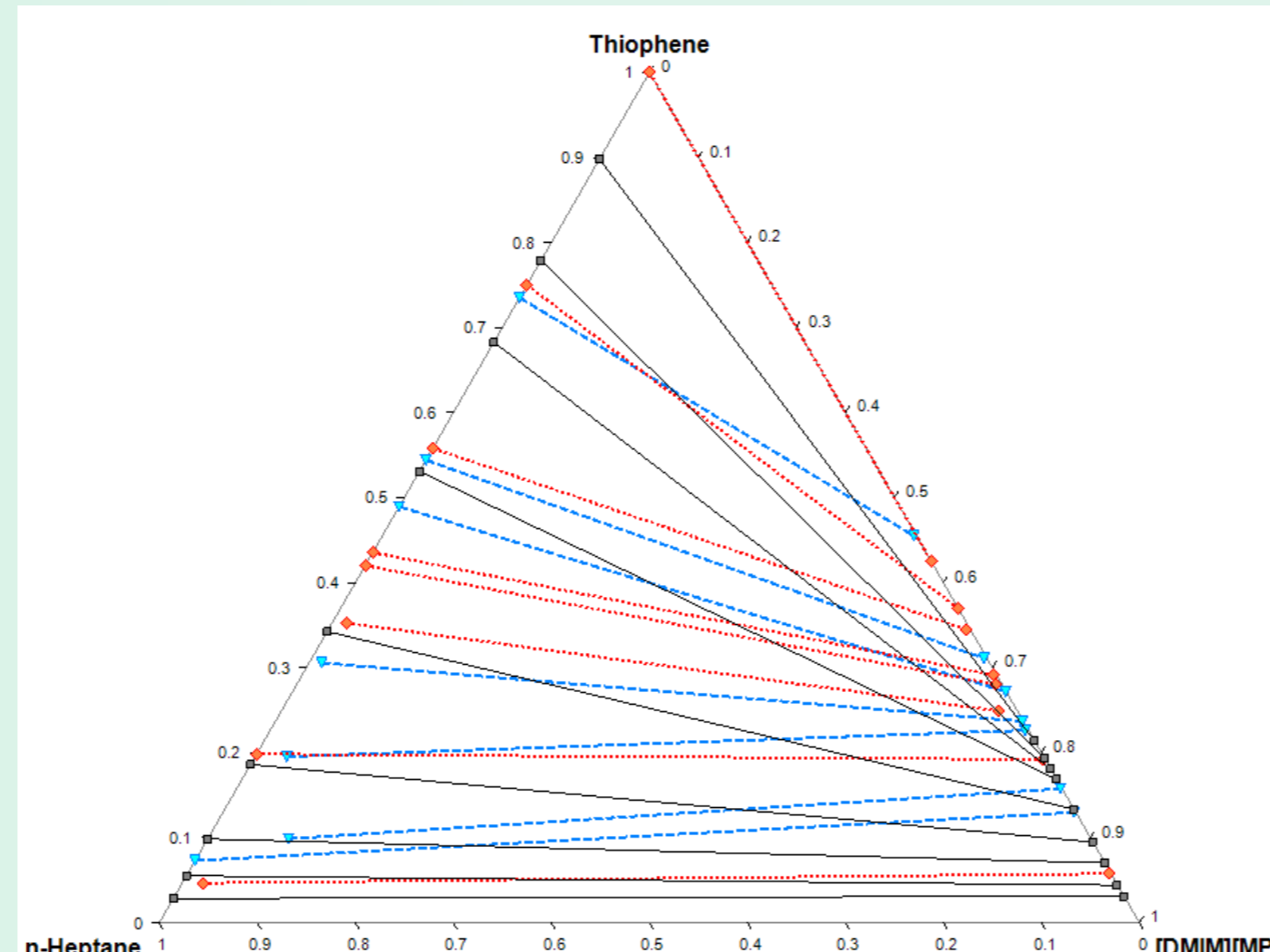


Figure 2. Effect of TiO<sub>2</sub> nanoparticles addition on the tie lines of ternary system {Thiophene + Heptane + [DMIM][MP]} at 298.15 K. Nanopowder concentration in IL: 0.05 wt %: ♦ and .....; 0.1 wt %: ▼ and -----. Mixture without nanoparticles: ■.

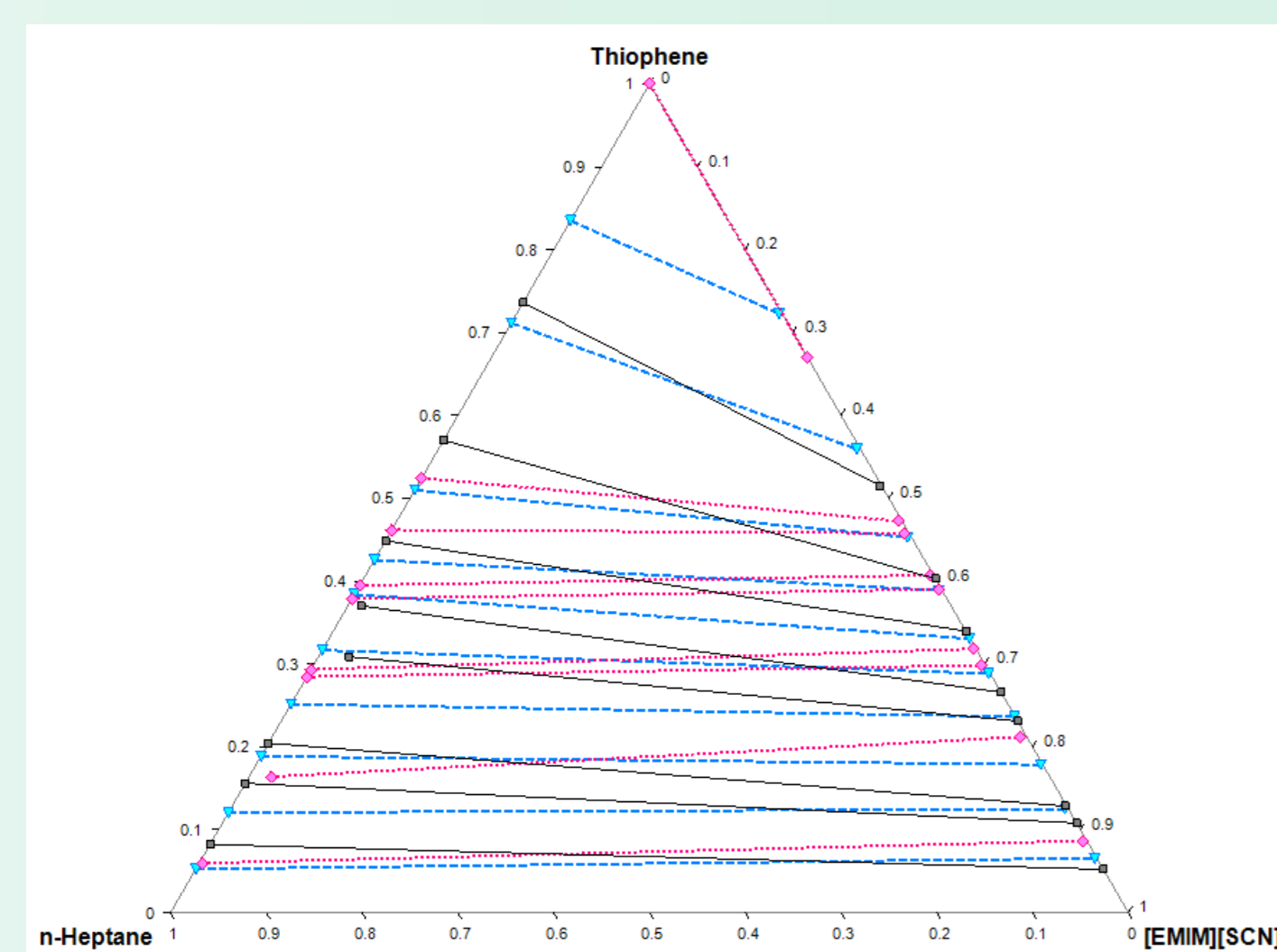


Figure 3. Effect of Fe<sub>2</sub>O<sub>3</sub> nanoparticles addition on the tie lines of ternary system {Thiophene + Heptane + [EMIM][SCN]} at 298.15 K. Nanopowder concentration in IL: 0.05 wt %: ♦ and .....; 0.1 wt %: ▼ and -----. Mixture without nanoparticles: ■.

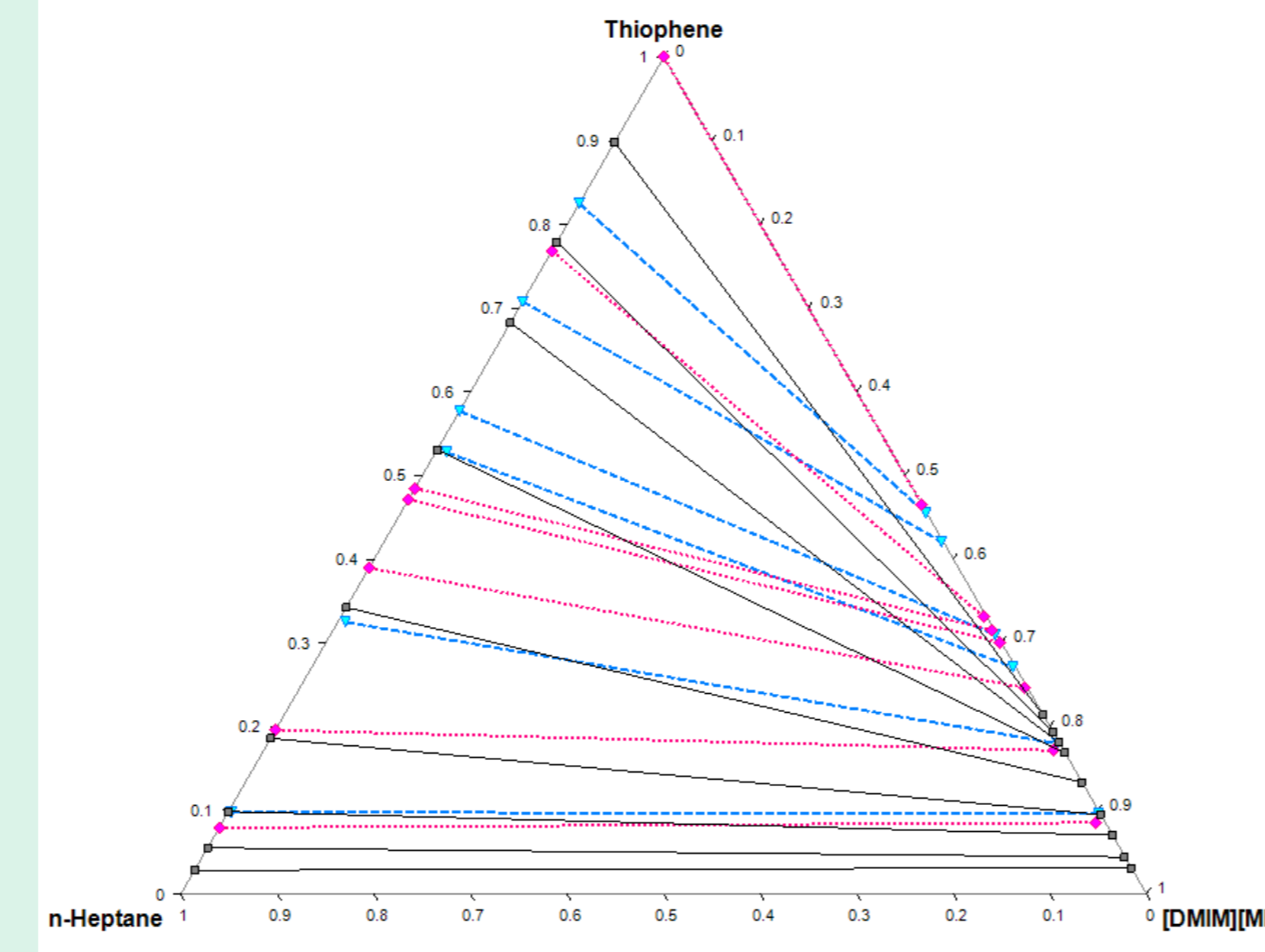


Figure 4. Effect of Fe<sub>2</sub>O<sub>3</sub> nanoparticles addition on the tie lines of ternary system {Thiophene + Heptane + [DMIM][MP]} at 298.15 K. Nanopowder concentration in IL: 0.05 wt %: ♦ and .....; 0.1 wt %: ▼ and -----. Mixture without nanoparticles: ■.

In these ternary phase diagrams, the low thiophene concentration part should be considered in order to investigate deep desulfurization of fuels using ionic liquids.

[DMIM][MP] is also highly selective for thiophene but the solute distribution ratio is twice smaller than with [EMIM][SCN].

The capacity and the selectivity of {[EMIM][SCN] + nanoparticles} for thiophene extraction from hydrocarbon solvent increases when the mass of nanoparticles increases from 0.05 wt % to 0.1 wt %.

The presence of nanoparticles in the ionic liquid phase increases the solute distribution ratio  $\beta$  of about 25 %.

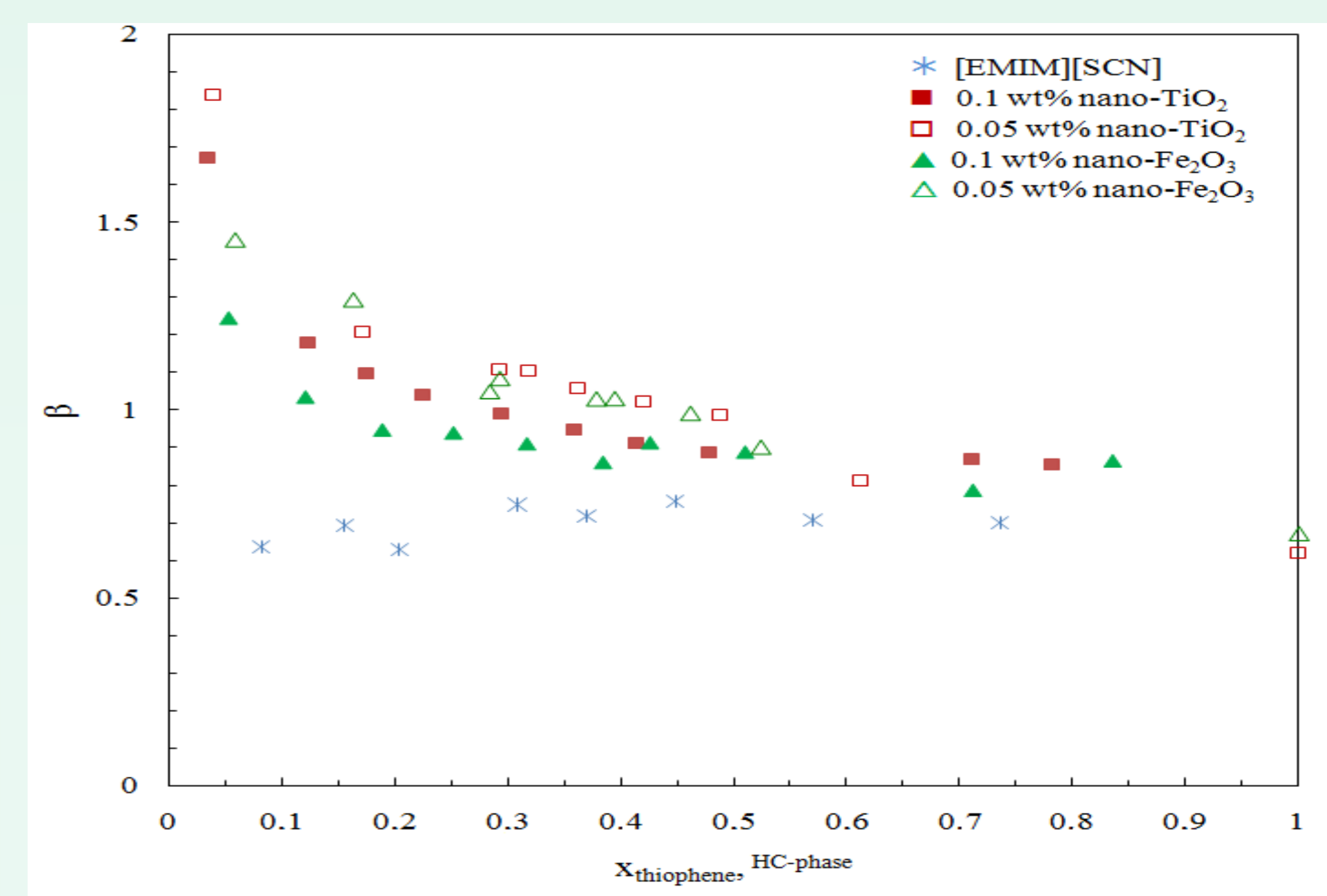


Figure 5. Solute distribution ratio  $\beta$  as function of solute mole fraction (thiophene) in hydrocarbon-rich phase, at 298.15 K for pure [EMIM][SCN] and its suspensions with TiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> nanopowders.

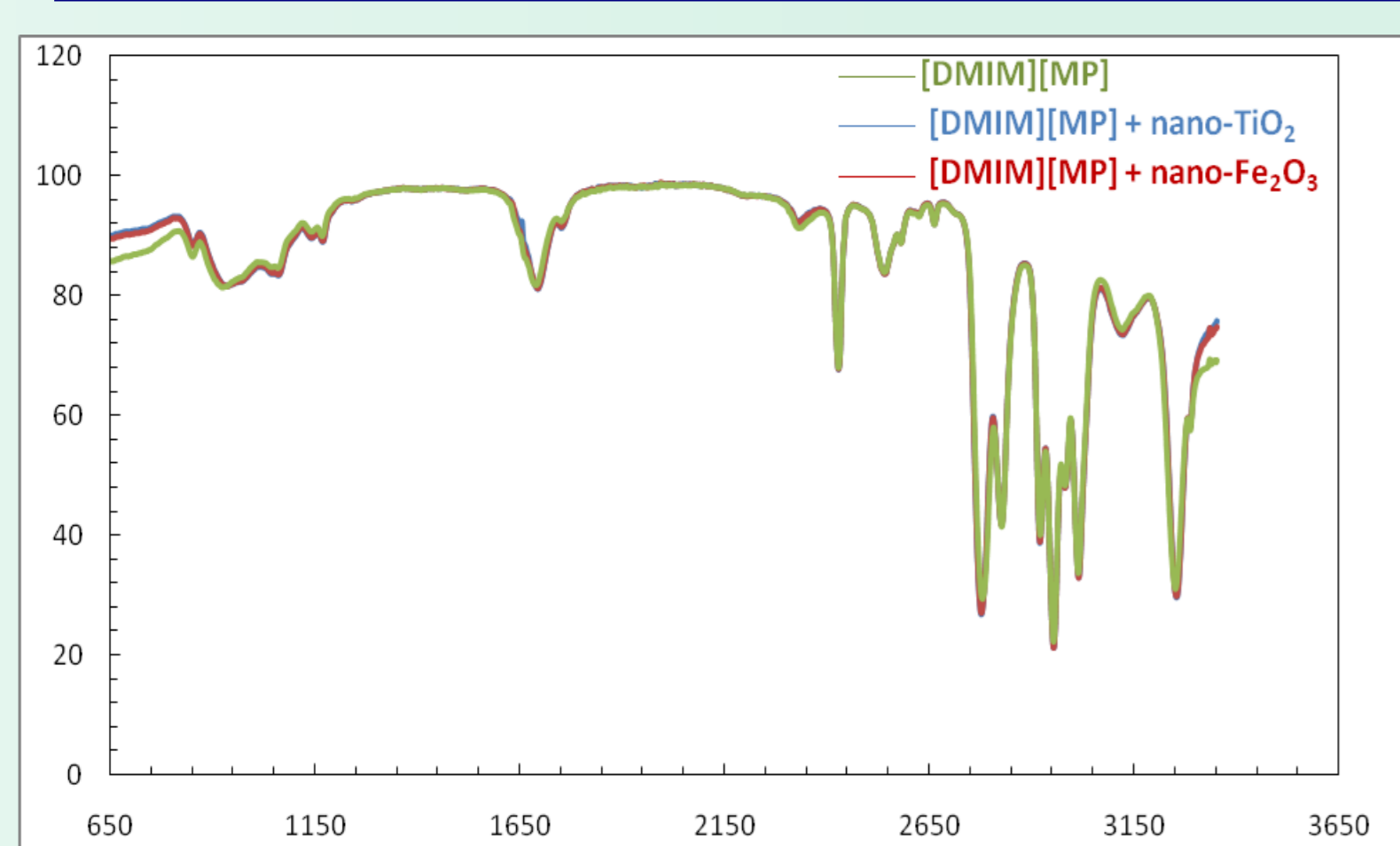


Figure 6. IR spectra of ILs and their suspensions with nanopowders.

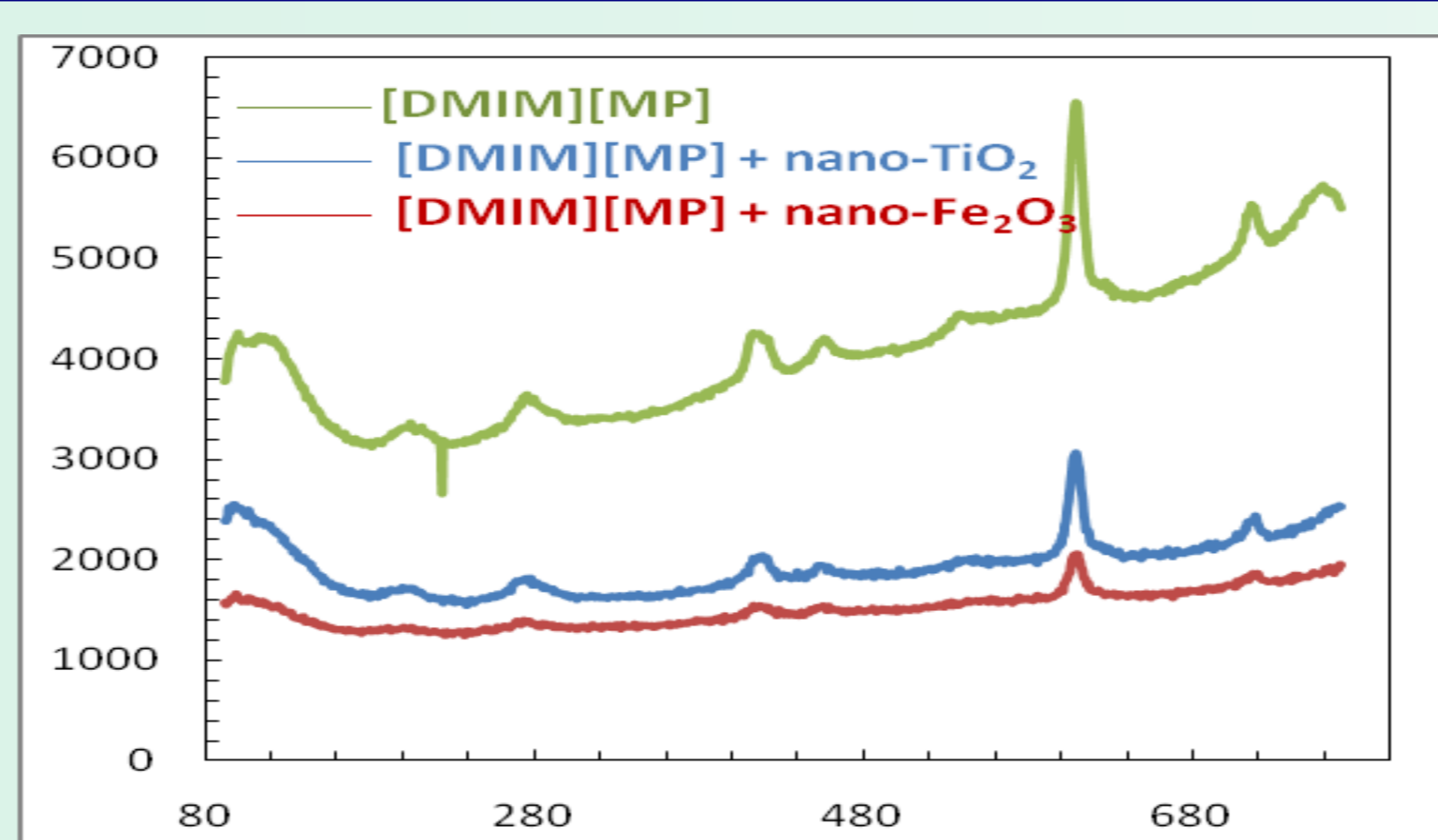


Figure 7. Raman spectra of [DMIM][MP] and suspensions with nanoparticles.

➡ No structural changes in the ILs are observed

The size of aggregates of nanoparticles strongly depends on the anion grafted on the cation (figure 8). The interactions between nanoparticles and ILs seem to be less favorable in [EMIM][SCN] than in [DMIM][MP]. Nanoparticles also aggregate to form a bigger gathering. For example, with TiO<sub>2</sub>, the particles size distribution strongly decreases from  $d = 579$  nm in [EMIM][SCN] to  $d = 243$  nm in [DMIM][MP].

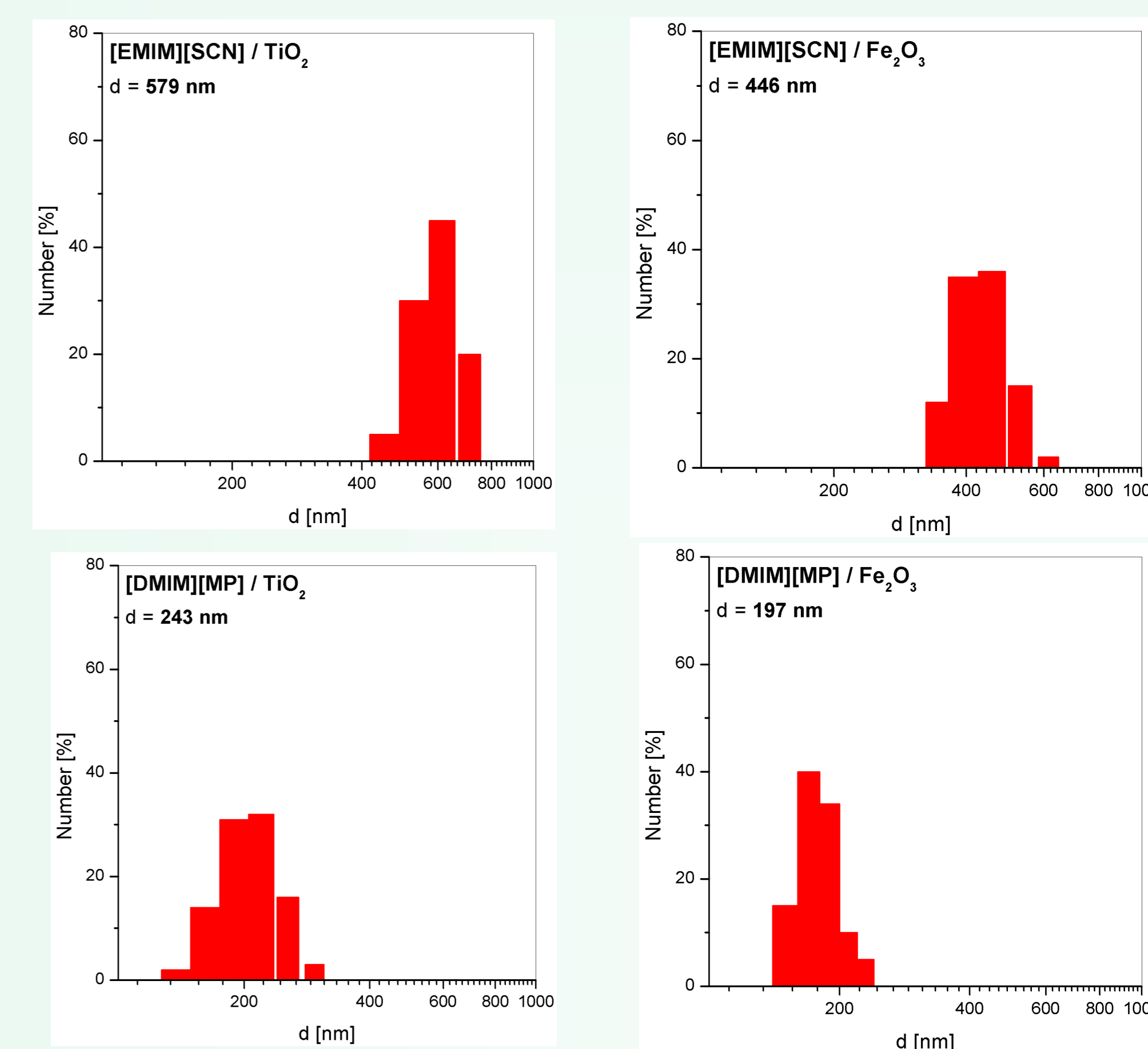


Figure 8. Particles size distribution for nanoparticles suspension in [DMIM][MP] and [EMIM][SCN].

## Conclusion

(Liquid + liquid) equilibrium data for the two ternary systems {thiophene + n-heptane + [EMIM][SCN]} and {thiophene + n-heptane + [DMIM][MP]} in the presence of nanoparticles at  $T = 298.15$  K were determined. All ternary systems correspond to the Type 2 category, with partial or total immiscibility of the IL with the thiophene and the hydrocarbons. The presence of nanoparticles in the ionic liquid phase increases the solute distribution ratio  $\beta$ . In [DMIM][MP], the interactions with the nanoparticles are more favorable than in [EMIM][SCN].