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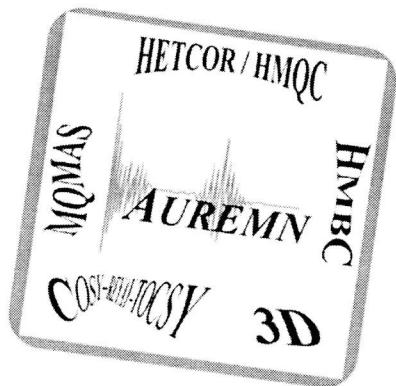
PROGRAM AND ABSTRACTS BOOK

NMR SPECTROSCOPY IN THE FOLLOW UP OF LIGANDS DISPLACEMENT IN REACTIONS OF LANTHANIDE COMPLEXES

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Keywords: NMR SPECTROSCOPY , LANTHANIDE COMPLEXES, REACTIONS

Luminescent lanthanide complexes have a wide range of applications. Syntheses of lanthanide complexes are usually performed by displacement of ionic ligands or non-ionic ligands. The first step of the usual synthesis of $Ln(\beta\text{-diketonate})3(L)$ complex involves the exchange of the ionic ligands of the salt $[Ln(X)2(H2O)6]X$ by β-diketonate ionic ligands. In this step the intermediate is $Ln(\beta\text{-diketonate})3(H2O)2$. In the second step, water ligands are displaced by one bidentate ligand, L, 1,10 phenantroline or 2,2 bipyridine. We developed faster route for the syntheses of these $Ln(\beta\text{-diketonate})3(L)$ complexes. In this work, we employ 1H NMR and 31P NMR to identify the species displaced in every step, either in the usual route or in the new one of $La(DBM)3(BIPI)$ and $La(DBM)3(FEN)$. From the usual route, the 1H NMR spectrum of intermediate $La(DBM)3(H2O)2$ complex showed the displacement of ionic nitrate by the three ionic DBM ligands from $[Ln(NO3)2(H2O)6]NO3$, appearing the following chemical shifts: CH ($\delta16.86$ ppm); phenyl (δ 7.99 - δ 6.86 ppm). In the novel route, the 1H NMR spectrum of intermediate $[Ln(TPPO)4(NO3)2(EtOH)(H2O)3]NO3$ showed the signals for TPPO: phenyl ($\delta7.52 - \delta7.27$ ppm); EtOH: CH2 ($\delta3.64$ppm); OH ($\delta2.39$ppm); CH3 ($\delta1.17$ppm). This indicates that water ligands were exchanged by TPPO and EtOH ligands. In the 31P NMR spectrum, the chemical shift of phosphorous in TPPO is $\delta34.95$ ppm.The final complexes are $[Ln(TPPO)4(NO3)2(FEN)(H2O)]NO3$ and $[Ln(TPPO)4(NO3)2(BIPI)(H2O)]NO3$. The 1H NMR spectra of both complexes has not the signals of EtOH but of BIPI (δ 8.71 - δ 7.42 ppm) and FEN (δ 9,18 - δ 7.31 ppm), indicating that BIPI or FEN are now part of the complex. From 31P NMR spectra for TPPO ($\delta29.55$ ppm). Finally, we showed that NMR spectroscopy is a very useful tool in the follow up of ligand displacement reaction of lanthanium complexes. **FACEPE, CNPq, PRONEX**

NMR STUDY OF BRAZILIAN SILICICLASTIC RESERVOIR ANALOGUES ROCKS

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Keywords: porous media NMR, brazilian reservoir rocks, NMR relaxometry

Porous media NMR relaxometry is largely applied to the study of reservoir rocks, which allows the estimation of some petrophysical properties, e.g. porosity, pore size, permeability, pore connectivity, diffusion coefficients of fluids, wettability and quality and quantity of fluids within the rocks. These properties are estimated from the analysis of T1, T2 relaxation times and diffusion coefficient (D) distributions using 1D or 2D experiments. NMR studies were developed using sandstone samples collected from brazilian outcrops, similar to sandstone reservoir rocks, and the NMR characterization is important for building the knowledge base of these formations in comparison with the usual petrophysical characterizations. Besides NMR, other methods were applied in this study, such as Energy Dispersive X-Ray Fluorescence Spectroscopy, mercury injection, petrographic thin sections analysis and magnetic susceptibility measurements. A LapNMR - Tecmag console with one channel gradient was used to perform this study. NMR probes for both 0.062 and 2 Tesla and magnets were developed in this project and used in all measurements. Results showed the dependence of NMR results on the magnetic susceptibility, relative to the high amounts of iron oxides in the samples. Pore size distributions and porosity obtained from NMR are compatible with other techniques. Permeability were corrected by magnetic susceptibility for the SDR permeability model. Geological properties were consistent with NMR results. Nevertheless, the bias induced by the relatively high amount of paramagnetic and ferrimagnetic minerals in the samples indicated the strong need for improving the current NMR techniques and developing new ones in order to study samples with high magnetic susceptibility. *References: 1) Dunn, K; Bergman, D; LaTorraca, G, 1st ed., Pergamon: London, 2002 2) Oliveira-Silva, R Utilização da RMN no estudo de rochas reservatório siliciclásticas, Tese, USP, 2014* **FAPESP #2013/01825-3, CNPq, CAPES**