

12<sup>th</sup> NUCLEAR MAGNETIC  
RESONANCE USERS MEETING  
3<sup>rd</sup> IBEROAMERICAN NMR MEETING

MAY 4<sup>th</sup> - 08<sup>th</sup>, 2009 - HOTEL DO FRADE, ANGRA DOS REIS,  
RJ, BRAZIL



EXTENDED  
ABSTRACTS  
BOOK

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## RELAXOMETRIC TITRATION: A NEW ANALYTIC APPROACH TO MEASURE SOLUBILITY CONSTANT

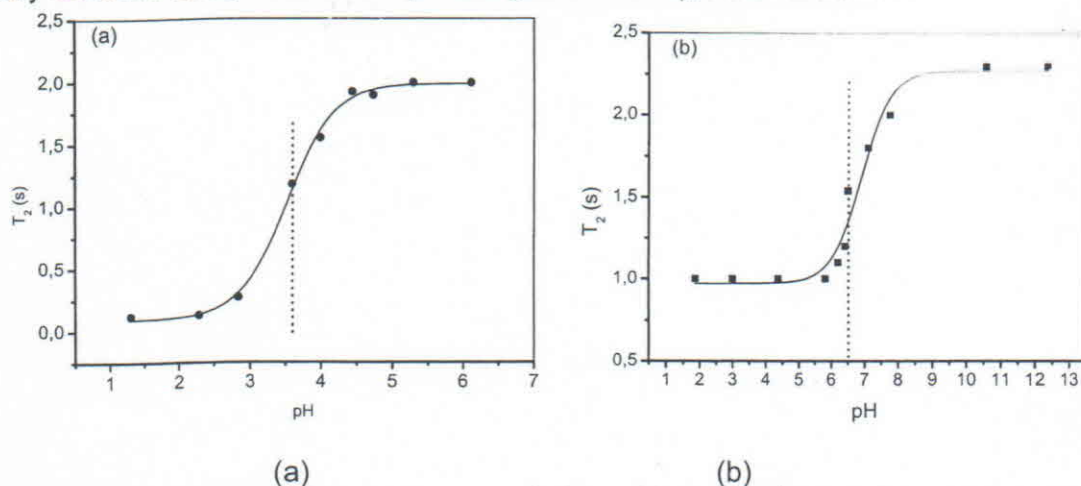
Lucio Leonel Barbosa\*, Lucinéia Vizzotto Marconcini and Luiz Alberto Colnago  
 Embrapa Instrumentação Agropecuária, São Carlos-SP, Brasil  
 \*luciolb@cnpdia.embrapa.br

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Solubility constant ( $K_{ps}$ ) is an equilibrium constant, which describes the balance between dissolved ions from the salt and undissolved salt. It is important information used in the precipitation of ions, such as  $Ca^{2+}$  and  $Mg^{2+}$  in the sea water,  $Pb^{2+}$  and  $Hg_2^{2+}$  in the samples soil [1] and in other applications. Therefore, the  $K_{ps}$  determination is very important to analytical and environmental studies. The methods used for  $K_{ps}$  determination are based on potentiometry, coulometry and amperometry [1]. In this paper we are proposing a new tool for  $K_{ps}$  determination based on  $^1H$  transverse relaxation time ( $T_2$ ) of water molecules, which is strongly affected by the presence of paramagnetic ions.

The  $T_2$  measurements were carried out on a SLK-SG-100 (Spin Lock Magnetic Resonance Solutions, ARG), 0.23 Tesla (10 MHz for  $^1H$ ) bench-top spectrometer, using a 32 mm probe and the CONDOR IDE software. The measurements were performed at 25°C. The pulse sequence used was the CPMG Qdamper pulse sequence, employing a  $\pi/2$  pulse width of 4.2  $\mu s$ , echo time ( $\tau$ ) of 1.8 ms, acquisition time of 10.6  $\mu s$  at each even number of echo ( $n$ ) of 2,400, recycle delay of 15 s and 4 scans.

Figure 1 shows the relaxatiometric titration curves of  $FeCl_3 \cdot 6H_2O$  (a) e  $CuSO_4 \cdot 5H_2O$  (b). It can be observed that  $T_2$  increase with pH from 0.2 to 2.0 s for iron (a) and from 1.0 to 2.3 s for copper (b). The first derivative of the curves exhibits only one end-point when the pH reached 3.6 at an a  $[OH^-]/[Fe^{3+}]$  molar ratio of 1:3 and 6.5 at an a  $[OH^-]/[Cu^{2+}]$  molar ratio of 1:2, corresponding to the formation of the  $Fe(OH)_3$  and  $Cu(OH)_2$ , respectively. The  $K_{ps}$  calculus from the figure 1 reveals accurately the  $K_{ps}$  values of  $3.6 \times 10^{-39}$  for  $Fe^{3+}$  and  $1 \times 10^{-20}$  for  $Cu^{2+}$ , both values is coherent with literature ( $2.67 \times 10^{-39}$  [4] and  $5 \times 10^{-20}$  [5], respectively). This technique is sensibility to  $Cu^{2+}$  ion in  $2.3 \times 10^{-5}$  M. This concentration is much lower than the one measured by spectrophotometry ( $1.3 \times 10^{-3}$  M [6]), since the bulk water signals serves as an "amplifier" of paramagnetic ions in solutions [3]. Therefore the method proposed is a very sensitive analytical tool for paramagnetic ions  $K_{ps}$  determination.



**Figure 1-** Variation of  $T_2$  of aqueous solution of  $3.6 \times 10^{-4}$  M of  $FeCl_3 \cdot 6H_2O$  (a) and  $CuSO_4 \cdot 5H_2O$  (b) in function of pH

The "relaxometric titration" has several advantage over electroanalytical methods: (a) unlike the potentiometric method, the technique can be used in high viscosity solvents and present great tolerance in relation the activity of the ion in solution; (b) differently from potentiometry and condutimetry, the "relaxometric titration" does not need chemical indicators and ion-selective electrodes and (c) in contrast to amperometry it does not need to use electrolyte supports to eliminate currents migrations that interfere in the analysis.

In conclusion we believe that the "relaxometric titration" can be a useful technique in analytical and environmental chemistry of various systems, include ions single and complex, protein, sugars, chemicals and others.

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