Dissolved or immobile polymer in disperse systems – a simple T2 approach

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Introduction: In disperse polymer-containing formulations, microscopic and macroscopic dynamics of the material can be grossly different from each other, especially if solid mineral components are also present. Due to a combination of turbidity and possibly high viscosity, classical approaches (such as OECD guidelines 105 or 120) for assessing whether a substance is dissolved or not, are often hard to apply in case of such formulations. Additionally, separating the polymer from the formulation is often challenging to do and will of course change its dissolution state anyway. Thus, it is advantageous to utilize a non-invasive technique, such as TD-NMR, which is unaffected by sample turbidity and high viscosity, to probe the dynamics of these systems. Additionally, the presence of mineral components would only have a limited influence, except in the case of paramagnetic or ferromagnetic substances. By means of a combination of a solid echo and a CPMG train, a T2-decay can be recorded over about 6 orders of magnitude in time to provide an assessment of the solution state of various polymer formulations

Methods and discussion: While the measurement of this T2-decay is quite straightforward, classical evaluation strategies such as multicomponent fitting or (1D) inverse Laplace transforms often require user interference and/or come with numerical instabilities, such that a fast automatic assessment of the dissolution state of the polymer is often not easily achievable. Results can also be subject to evaluator biases. To overcome these problems , we propose a simple integral method based on the ratio between the average signal amplitude over the first 15 µs of signal and the first 100 µs of signal in the solid echo, calculating a polymer restricted mobility index according to Eq. 1. This index will be close to zero for a dissolved polymer and increases for samples containing undissolved polymer populations. Samples with different polymer concentrations can then be compared, quantitatively, by normalizing this index by the polymer concentration.

$$x = \frac{\langle s(t) \rangle_{15}}{\langle s(t) \rangle_{100}} - 1 \qquad \text{Eq. 1}$$

The CPMG part of the data is not required in this simple analysis. However, it often provides relevant supplementary insights, such as, for example, the surface relaxivity of non-dissolved disperse polymer, which is lost upon dissolution. The viability of the simple integration approach was checked over a range of data from different instruments by different vendors, indicating consistent results.

In TD-NMR experiments at typical field strengths in the range of 20 MHz, signal/noise ratio and dynamic range can be challenging in samples with low polymer concentrations. In such samples, dynamic range limitations can be overcome by partially or fully deuterating the water phase.