MRI Experiments as a Tool to Study Asymptotic-Shear Flow Behaviour of a Worm-Like Reverse Micellar Phase

Luigi Coppola[1], Domenico Gabriele[2], Isabella Nicotera[1], Cesare Oliviero[1]*

[1] Department of Chemistry, University of Calabria, Via P. Bucci, Cubo 14/D, 87036 Arcavacata di Rende – Cosenza, Italy
[2] Department of Chemical Engineering and Materials, University of Calabria, Via P. Bucci, Cubo 45/A 87036 Arcavacata di Rende – Cosenza, Italy

* Email: cesare.oliviero@unical.it
Fax: x39.0984.492044

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Abstract:
This paper deals with a Magnetic Resonance micro-Imaging (MRI) analysis of asymptotic kinematics which is a condition adopted in some rheological characterisations. Asymptotic kinematics (for example the slow shearing) aim is to evaluate material properties at "equilibrium", avoiding structural changes induced by external stimuli. Measured material functions in these mechanical conditions deal with the structure/morphology of materials and can be used to investigate the structure as a function of the state variables only, as temperature, pressure and composition. In this paper MRI experiments were performed to study some shear flow behaviours of surfactant wormy micelles made by lecithin/water and diluted in cyclohexane (reverse micellar phase L_2). MRI was used as a non-invasive tool in order to follow the structural responses both during slow shearing and when the sample is stirred outside the linear behaviour range. Relations can be found between the typical NMR parameters, strictly related to the microstructure, and the rheological macroscopic parameters as zero-shear viscosity.

Zusammenfassung:
Dieser Artikel befasst sich mit einer Magnetresonanzmikroabbildungsanalyse (MRI) einer asymptotischen Kinematik, die eine Voraussetzung ist, die bei einigen rheologischen Charakterisierungsmethoden angewandt wird. Eine asymptotische Kinematik (z.B. die langsame Scherung) zielt darauf, Materialeigenschaften im Gleichgewicht auszuwerten und dabei die strukturellen Änderungen, die durch externe Stimuli erzeugt werden, zu vermeiden. Die bei diesen mechanischen Bedingungen gemessenen Materialfunktionen sind mit der Struktur bzw. der Morphologie der Materialien verknüpft und können dazu verwendet werden, um die Struktur ausschliesslich als Funktion der Zustandsvariablen, z.B. der Temperatur, des Druckes und der Zusammensetzung, zu untersuchen. In dieser Arbeit werden MRI-Experimente durchgeführt, um das Verhalten von „Surfactant Wormy"-Mizellen aus Lecithin/Wasser und verdünnt in Cyclohexan (umgekehrte mizellare Phase L_2) in Scherung zu untersuchen. MRI wurde als eine nicht-invasive Methode angewandt, um die strukturelle Antwort sowohl während der langsamen Scherung als auch ausserhalb des linearen Bereichs zu erhalten. Beziehungen zwischen den typischen NMR-Parametern, die sich ausschliesslich auf die Mikrostruktur beziehen, und den rheologischen makroskopischen Parametern wie die Schernullviskosität können erhalten werden.

Résumé:
Cet article traite de l'analyse de la cinématique asymptotique, qui est une condition adoptée dans certaines caractérisations rhéologiques, au moyen de la micro-imagerie par résonance magnétique (MRI). Le but de la cinématique asymptotique (par exemple le cisaillement lent) est d'évaluer les propriétés des matériaux à l'équilibre, en évitant les changements structurels provoqués par des stimuli externes. Les propriétés du matériau qui sont mesurées dans ces conditions mécaniques sont reliées à la structure/morphologie du matériau, et peuvent être utilisées pour étudier la structure en fonction uniquement de variables d'états telles que la température, la pression et la composition. Dans cet article des expériences de MRI ont été effectuées afin d'étudier des comportements en écoulement de cisaillement de micelles vermiformes de surfactants composées de lécithine et d'eau et diluées dans du cyclohéxane (phase micellaire inversée L_2). La MRI a été utilisée en tant que technique non invasive afin de suivre les réponses structurelles aussi bien pendant le cisaillement lent que lors du régime correspondant au comportement non linéaire de l'échantillon. Des relations peuvent être trouvées entre les paramètres classiques de RMN qui sont strictement reliés à la microstructure, et les paramètres macroscopiques rhéologiques tels que la viscosité à cisaillement nul.

Key words: asymptotic kinematics, slow flow, MRI, micellar phase

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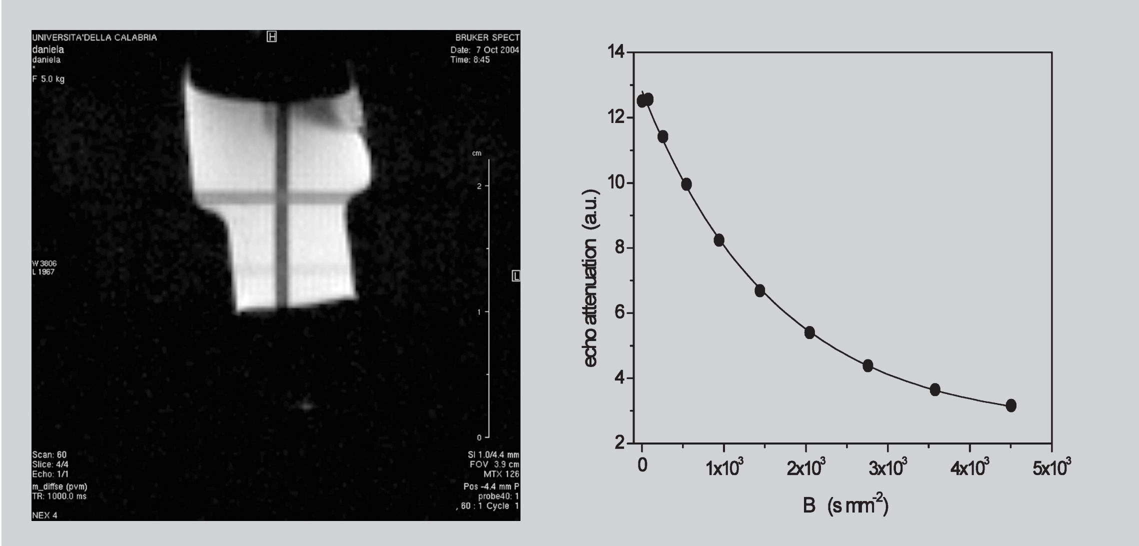

Figure 6 (above): Self diffusion image for the sample during slow flow at 15°C, representing a map of mobility of protons inside the sample (a). The echo attenuation as a function of the experimental B parameter. The solid lines is the best fit to data using Eq. 2 (b).

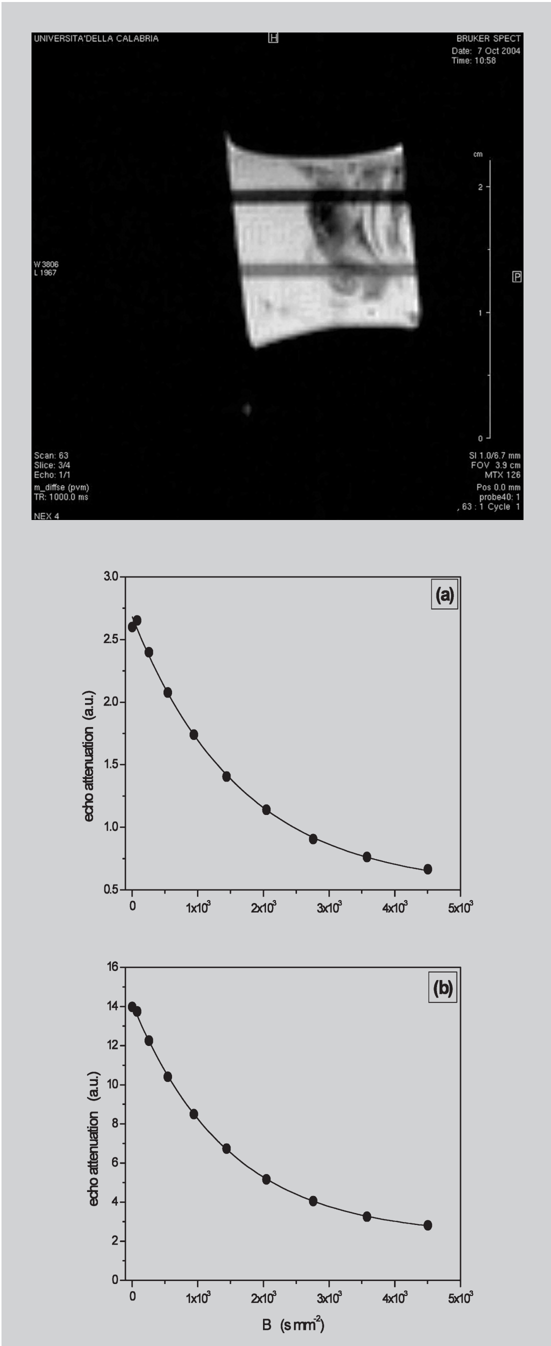

Figure 7: Self diffusion image for the sample after strong shearing at 15°C and the echo attenuation plot for the lateral zone (a) and for central zone (b) of the sample. The solid lines are the best fit to data using Eq. 2.

the black zones evidence shorter values of T_2, and they cover the sample in asymmetric way due to the particular imposed kind of stirring.

It is worth to note that the strong change in the structure occurs especially in the central zone while the external structure is quite similar to "no perturbed" structure. In fact the T_2 values from the lateral zones are similar to those calculated for the sample at rest or during a slow shearing. This is probably due to the fact that the centrifuging of the sample damage mainly the central part of the sample modifying the structural organisation, even if it is important to mark once again that it is improper to discuss about lateral and central zones for the asymmetry of the structural changes.

Self diffusion weighed images were recorded to elucidate better relationship between an asymptotic behaviour and the structure. The results from these experiments confirm what said above about structural changes; in fact the self diffusion coefficients are always similar for both cases (sample at rest and under slow flow), with 3.24 and 3.25 $\times$ 10^{-4} mm²/s respectively. On the contrary the values of the self diffusion obtained after strong shearing are similar in lateral zone to those obtained from the "no perturbed" sample (3.25 $\times$ 10^{-4} mm²/s) while they are different within the central zone where it is 4 $\times$ 10^{-4} mm²/s. Figures 6 and 7 show self diffusion weighted images for the sample under slow flow (Fig. 6) and after strong shearing (Fig. 7) and the corresponding echo attenuation plot.

4 CONCLUSIONS

Asymptotic kinematics are one of the most powerful tools adopted for material structure characterization, due to their non destructive nature. In this paper the effect of a particular asymptotic kinematic, a slow flow, on micellar inverse phase L_2 structure, was shown by using a I-NMR

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technique. Two typical NMR parameters were identified as structure "markers": the spin-spin relaxation time T_2, and the self diffusion coefficient, *D*, and they were evaluated in two different flow conditions.

No structural variation, described by the NMR parameters, was observed during slow flow, confirming that this kinematic is able to describe the real equilibrium structure of materials. Although this could be considered a well consolidated statement, it has to be reminded that an experimental study of "what really happens" during this flow is not so common due to the difficulty to "give a glance" inside the structure avoiding any kind of disturbance to the flow conditions. A relation between the NMR parameters and zero shear viscosity could be investigated to better understand as the microstructure affect macroscopic parameters.

On the other hand a significant change was observed after a strong stirring of the sample, due to the breakage of the structure; it is important to remind that the NMR parameters are able to quantify the intensity of the structure damage, caused by the applied shear rate, giving more information than a classic rheological test, like a flow curve does. In fact, although structural changes are evidenced by steady shear tests where viscosity usually decreases with increasing shear rate, it is difficult to quantify them and make assessments concerning microstructural features. Many different microrheological models can be adopted but no direct evidence of microstructure is commonly available. The MRI can be a powerful tool to confirm the theoretical relationships between macroscopic parameters, such as steady shear viscosity, and microscopic features, giving experimental and quantitative evidence.

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