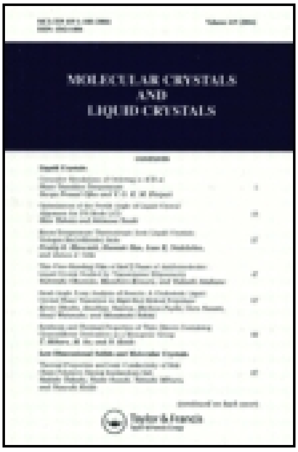

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Shear Induced Phase Transition and Transient Small Angle Neutron Scattering Experiments on Micellar Solutions

J. Kalus [a]
[a] Experimentalphysik I, Universität Bayreuth, D-8580, Bayreuth, F.R.G.

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SHEAR INDUCED PHASE TRANSITION AND TRANSIENT SMALL ANGLE NEUTRON SCATTERING EXPERIMENTS ON MICELLAR SOLUTIONS

JÜRGEN KALUS
Experimentalphysik I, Universität Bayreuth,
D-8580 Bayreuth, F.R.G.

Abstract Time dependent anisotropic small-angle neutron scattering (SANS) patterns of micellar solutions are presented and discussed. Alignements of the anisotropic micelles in a shear gradient, in a magnetic and in an electric field are explored. Typical time constants for relaxation range from 150 ms to hours.

INTRODUCTION

Information on the orientational distribution of anisotropic micellar particles at relatively short time scales can be obtained from SANS measurements when an instrument is used which is capable of two-dimensional data acquisition.[1] The change of anisotropic diffraction patterns by applying or removing external forces enables us to analyze both the structural and the dynamical behaviour of the micelles which are responsible for the scattering patterns. The external forces used in the experiments described in this paper are achieved by applying an electric or a magnetic field, or by a mechanical force induced by a shear. Sometimes a theory can be worked out, at least for non-interacting micelles, which predicts the extent of orientation as a result of the applied force. This can finally lead to the calculated intensity pattern. A comparison of such type of calculated intensity pattern with the measured can lead to an understanding of the structural, dynamical and orientational behaviour of the micelles in question.

THE TRANSIENT ALIGNEMENT IN A SHEARED SOLUTION

SANS-experiments have been performed on a 50 mM/dm^3 aqueous solution of hexadecyloctyldimethylammoniumbromide ($C_{16}H_{33}C_8H_{17}N(CH_3)_2Br$) under a shear Γ, changing its value suddenly from 0 to 600 s^{-1}. This shear is well above a threshold value at which a shear induced phase transition begins.[2] The intensity pattern show a sharp peak P superimposed over an anisotropic pattern as shown in Fig. 1.

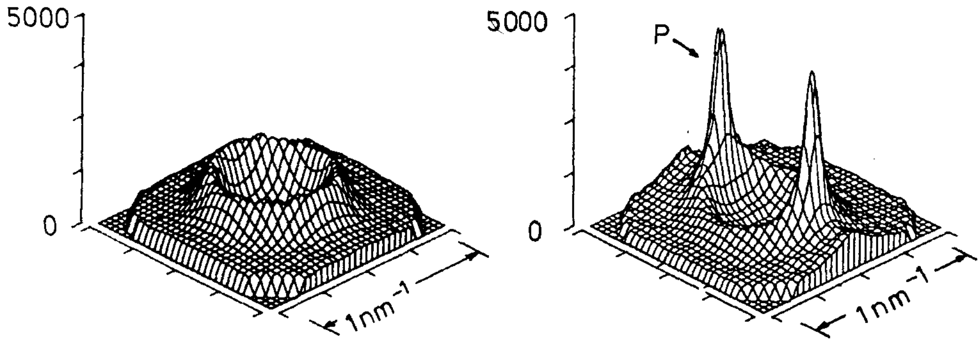

FIGURE 1 Isometric intensity plot as observed on the two-dimensional detector, before (left) and 154 s after (right) the shear rate Γ was increased stepwise from 0 to 600 s^{-1}. T = 30° C.

The analysis showed, that the anisotropic pattern is caused by weakly aligned rod-like micelles (type I micelles), whereas the sharp peak is due to rod-like micelles ordered in a hexagonal liquid crystalline lattice (type II micelles), which starts forming when the shear is applied. The type II micelles are growing in number as time grows, till they reach an equilibrium after about 2 min, as is seen in Fig. 2.

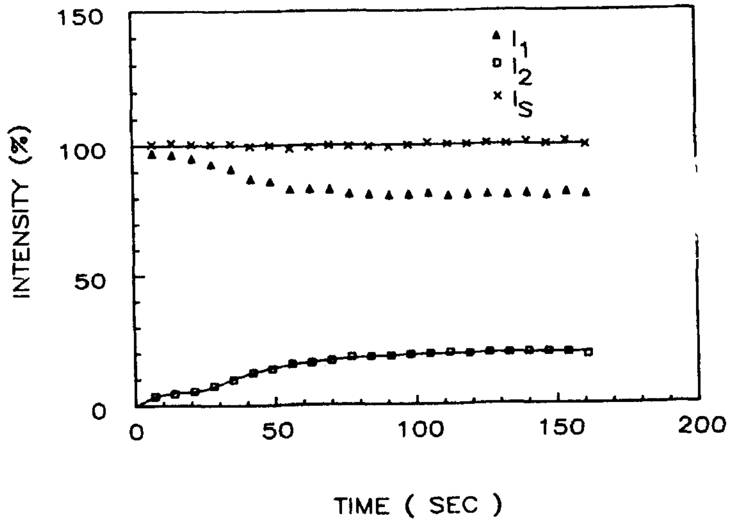

FIGURE 2 Amount of type I (I_1) and type II (I_2) micelles as a function of time. At t = 0 shear Γ was increased stepwise from 0 to 600 s^{-1}. I_s is the sum of I_1 and I_2.

The anisotropic ringlike structure was analysed by the evaluation of the orientational distribution function f of the orientation of the rod axes.[3]

$$\frac{\partial f}{\partial t} = D\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\frac{\partial f}{\partial\theta}\sin\theta\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 f}{\partial\varphi^2}\right] - \Gamma\left\{\frac{\partial[f\omega(\theta)\sin\theta]}{\sin\theta\partial\theta} + \frac{\partial[f\omega(\varphi)]}{\sin\theta\partial\varphi}\right\},$$

$$\omega(\theta) = -\sin^2\varphi\sin\theta \qquad \omega(\varphi) = 0{\cdot}25\sin 2\varphi\sin 2\theta$$

θ is the angle between the rod axis and the z axis of an orthoganol x, y, z system. The velocity vector v is directed parallel to the x axis and has the value v = Γy. φ is the angle between the x axis and the projection of the rod axis into the xy plane. The function f can be evaluated numerically for stationary ($\partial f/\partial t=0$) and transient ($\partial f/\partial t\neq 0$) states. This equation is governed by two parameters, Γ and D. D is a rotational diffusion coefficient. More details about this experiment will be presented elsewhere.[4]

THE TRANSIENT ALIGNEMENT IN A MAGNETIC FIELD

Diamagnetic micelles can be aligned in a magnetic field. In Fig. 3 a sequence of two experiments is shown. The solution was 10.2 % CTAB ($C_{16}H_{33}N(CH_3)_3Br$)+ 9.9 % CTA ($C_{16}H_{33}N(CH_3)_3C_6H_5SO_3$)+ 2.45% n-Dekanol + 77.45 % D_2O. Fig. 3a shows the anisotropic scattering intensity for a prealigned sample. This alignement was achieved in a magnetic field of $\vec{B}_o$ = 5 T, decreasing slowly the temperature from 40°C to 25°C. The lamellar domains are very well aligned, as seen by the huge texture of the Deby-Scherrer like ring. Next, in Fig. 3b $\vec{B}_o$ is zero and a magnetic field $\vec{B}_1$ = 1.2 T, perpendicular to the direction of the neutrons and to $\vec{B}_o$, was applied. As a function of time one can observe, how the peak splits symmetrically and how it turns to the new preferred orientation, related to the direction of $\vec{B}_1$. Finally, a situation like in Fig. 3a is achieved, but turned around an angle of 90°. The time scale in this experiments is long, in the order of one hour (at 28°C). A detailed analysis sheds light on the relaxation phenomena in this lamellar liquid crystal.[5]

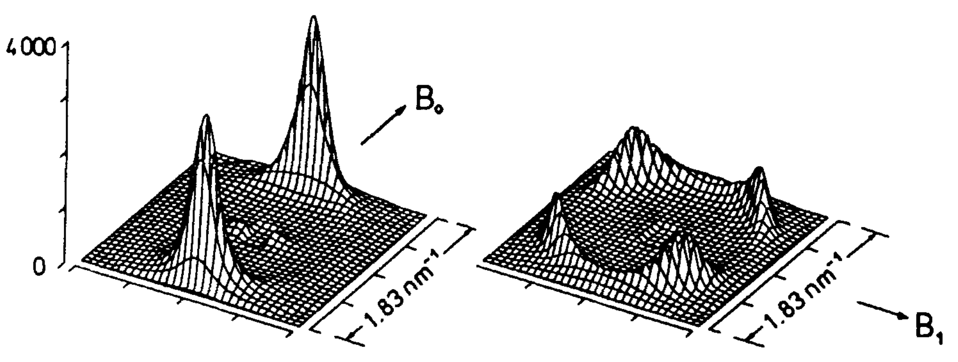

FIGURE 3 The alignment in CTAB. a) in a magnetic field $\vec{B}_o$= 5T, b) in a magnetic field $\vec{B}_1$= 1.2 T. $\vec{B}_1 \perp \vec{B}_o$ and perpendicular to the direction of the neutron beam. T = 28°C.

THE TRANSIENT ALIGNMENT IN AN ELECTRIC FIELD

P-Tetrafluorethylen (p-TFE) fibrilles, coated with the ionic perfluorsurfactant $C_8F_{17}(CH_3)_2CO_2NH_4$ have a diameter around 12 nm and a length of several µm. The sample was a 0.4 % solution by weight of p-TFE dissolved in D_2O and was aligned in an electric field of E_{eff} = 177 V/cm, along which the fibrilles were oriented. We observed the build-up and decay of the anisotropy of the SANS pattern as a function of time when the electric field was turned on and kept at a constant value for 320 ms and then turned off again. The anisotropy of the SANS pattern shows a transient behaviour.[6] A detailed analysis, taking into account the time-dependent distribution of the rod axes[3] showed, that one common relaxation time of 145 ms for both, the increase and decrease of the anisotropy , is describing the transient SANS pattern. From a technical point of view the measurement of such a short relaxation time seems to be remarkable.

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