

RHEOLOGICAL PROPERTIES OF THE REVERSE MESOPHASES OF THE PLURONIC L64/P-XYLENE/WATER SYSTEM

LUIGI COPPOLA*, DOMENICO GABRIELE¹,
ISABELLA NICOTERA, CESARE OLIVIERO

Department of Chemistry, University of Calabria, Via P. Bucci,
87036 Arcavacata di Rende – Cosenza, Italy

¹Department of Chemical Engineering and Materials, University of Calabria,
Via P. Bucci, 87036 Arcavacata di Rende – Cosenza, Italy

*Email: lg.coppola@unical.it

Fax: x39.0984.492044

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ABSTRACT:

The behaviour of reverse micellar solution and reverse hexagonal and lamellar liquid crystal phases in pluronic L64/water/p-xylene ternary system was investigated by rheological techniques. Samples with an increasing water content along the amphiphilic copolymer-lean side of the ternary phase diagram were analysed at different temperatures and a different behaviour was evidenced by both dynamic and steady tests for each considered phase, depending on the morphology of structure (micellar, lamellar, hexagonal phases). It was observed that the reverse micelles size increases with increasing water concentration and decreases with increasing temperature, without any phase transition. On the contrary the normal micelles become anisometric on temperature, showing a transition to a liquid crystalline phase. The observed mechanical spectra of the liquid crystalline phases are typical of hexagonal and lamellar phases according to the literature [1, 2]. A phase transition with temperature was found for both liquid crystalline phase (lamellar and hexagonal) by rheological tests and was confirmed by ocular inspection.

ZUSAMMENFASSUNG:

Das Verhalten von reverser Mizellaren, reverser hexagonaler Lösungen und lamellarer flüssigkristalliner Phasen in ternären pluronic-L64/Wasser/p-Xylene System wurde mittels rheologischer Methoden untersucht. Proben mit ansteigendem Wassergehalt entlang der amphiphilen kopolymerfreien Seite des ternären Phasendiagrammes wurde bei verschiedenen Temperaturen untersucht und ein unterschiedliches Verhalten wurde durch dynamische und stationäre Tests für jede untersuchte Phase aufgezeigt, abhängig von der Strukturmorphologie (mizellar, lamellar, hexagonale Phasen). Es wurde beobachtet, dass die Grösse der reversen Mizellen mit steigender Wasserkonzentration anstieg, und mit steigender Temperatur abfällt, ohne Phasenübergänge zu zeigen. Andererseits werden die normalen Mizellen mit der Temperatur anisometrisch und zeigen einen Übergang zu einer flüssigkristallinen Phase. Die beobachteten mechanischen Spektren der flüssigkristallinen Phase sind typisch für hexagonale und lamellare Phasen [1, 2]. Ein Phasenübergang mit der Temperatur wurde für beide flüssigkristallinen Phasen (lamellar und hexagonal) mittels rheologischer Tests gefunden und durch optische Beobachtung bestätigt.

RÉSUMÉ:

Le comportement de la solution micellaire inverse et des phases cristal liquides hexagonale et lamellaire inverses du système pluronique ternaire L64/eau/p-xylène est étudié à l'aide de techniques rhéologiques. Des échantillons, à teneur croissante en eau dans la région du diagramme de phase pauvre en copolymère amphiphile, ont été étudiés à différentes températures. Pour chaque phase considérée, des comportements différents sont observés en fonction de la morphologie (phase micellaire, lamellaire, ou hexagonale) lors de tests à la fois en mode dynamique et en mode continu. On observe que la taille des micelles inverses augmente avec la teneur en eau, et diminue avec la température, sans aucune transition de phase. Au contraire, les micelles directes deviennent anisométriques avec la température et présentent une transition vers une phase cristal liquide. D'après la littérature [1,2], les spectres mécaniques des phases cristal liquide observés sont caractéristiques de ceux de phases hexagonales et lamellaires. Pour les deux phases cristal liquide (lamellaire et hexagonale), une transition de phase avec la température est observée à l'aide de tests rhéologiques et confirmée, d'autre part, par inspection visuelle.

KEY WORDS: Rheology, pluronic, reverse phases, L64

(Fig. 12) shows a slight decrease of both moduli until about 50°C, a marked increase is observed probably due to the phase transition observed by ocular inspection, and a peak at about 70°C. At higher temperatures a sharp decrease is observed for both G' and G'' , but these data are affected by the simultaneous presence of two phases (observed by ocular inspection) and they are useful only as a qualitative index of the transition.

For the H_2 and L_α liquid crystalline phases it was not possible to perform flow curves in fact transient viscosity experiments showed a continuous decrease of shear stress with time evidencing that a steady state was not obtainable in the considered time range (240 min). This can be probably due to the structures of the hexagonal and lamellar phases that are continuously destroyed under shear as found for other strongly structured materials [23]. This trend shows that in the considered system a shear induced transition characterised by a shear stress increasing with time in a step shear rate test [16], does not occur.

4 CONCLUSIONS

In this paper it was shown how rheometry is a useful method to investigate the phase diagram of the L64/p-xylene/ H_2O system. The L_2 (reverse micellar) phase is characterised by a viscoelastic behaviour with G'' always greater than G' . In the considered shear rate and temperature range the steady state tests evidenced a constant viscosity value showing as the size of the micelles increase with increasing water concentration while with increasing temperature the micelles size reduce becoming more comparable. Time cure performed on this phase reveals the stability of the structure with the temperature and the absence of any phase transition.

The L_1 phase (normal micellar, 61.1 H_2O wt% sample) shows in steady shear test a thinning behaviour increasing with temperature. A phase transition to a lamellar organization at 45°C was observed by dynamic and steady shear tests. In this case the micelles become presumably anysometric with the temperature. In fact, close to the transition the mixture shows a marked shear thinning behaviour probably due to the orientations of the non spherical micelles.

The H_2 phase (hexagonal), i.e. the 14.2 and 16.1 H_2O wt% samples were characterized by dynamic tests at different temperatures and a phase transition to a lamellar structure was observed. The L_1 (lamellar, 34.3 H_2O wt%) sample shows a stable structure up to 60°C and then a two-phase region was observed where lamellar and hexagonal phases seem to coexist.

Rheometry has proved to be a good instrument to characterise different phase behaviour and to evidence phase transitions from a qualitative and quantitative point of view. This preliminary work can be the starting point for the preparation of a phase diagram for the considered system at different temperatures based on rheometry.

REFERENCES AND FOOTNOTES

- * The notation for the PEO-PPO-PEO pluronics starts with a letter giving their pristine appearance: L for liquid, P for paste, and F for flakes. The symbol R refer to reverse architected pluronics: PPO-PEO-PPO. The first one or two numbers are indicative of the molecular weight of the PPO block (in unit of 0.01 g mol^{-1}), and the last number indicate the weight fraction of the PEO blocks (in unit of 10%). [7].
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