

# THERMOGELATION ANALYSIS OF F127-WATER MIXTURES BY PHYSICAL CHEMISTRY TECHNIQUES

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## ABSTRACT:

Aqueous solutions of F127 pluronic systems exhibit an interesting thermal gelation above a certain concentration. This phenomenon concerns the transition from a liquid-like behavior at low temperatures to a solid-like behavior at high temperatures, and it is due to different temperature responses from the different polymer segments, polypropylene oxide (PPO) and polyethylene oxide (PEO). Such property leads to a structural change in the self assembled macromolecule upon heating, from an isotropic micellar structure to an ordered cubic structure. These two types of assembly are clearly distinct with respect to their rheological behavior. This contribution emphasizes the rheological properties of the pluronic system in micellar and cubic phase, in combination with NMR, Dynamic Light Scattering and DSC information. The results emphasize the gelation process upon heating and a cubic phase characterized by higher storage modulus and higher A and z Weak Gel Model exponents than the micellar phase. Micellar growth upon heating was found within micellar phase. The presented data support the hypothesis that each polymer segment actively participates in the formation of the different phases: while PPO is responsible for micelle formation, PEO plays a dominating role in cubic phase formation. Finally, different stiffness between the core and the corona of the aggregates in the two phases is observed.

## ZUSAMMENFASSUNG:

Wässrige Lösungen von F127 Pluronic-Systemen weisen oberhalb einer gewissen Konzentration ein interessantes thermisches Gelbildungsverhalten auf. Dieses Phänomen betrifft den Übergang vom flüssigen Verhalten bei niedrigen Temperaturen zum festkörperartigen Verhalten bei hohen Temperaturen und wird durch die Antwort der verschiedenen Polymersegmente (Polypropylenoxid, PPO, und Polyethylenoxid, PEO) bei unterschiedlichen Temperaturen verursacht. Diese Eigenschaft führt zu strukturellen Änderungen (von einer isotropen mizellaren Struktur zu einer geordneten kubischen Struktur) in dem selbstorganisierten Makromolekül während des Heizens. Diese zwei unterschiedlichen Organisationstypen können bezüglich ihres rheologischen Verhaltens eindeutig unterschieden werden. Dieser Beitrag befasst sich mit den rheologischen Eigenschaften des F127 Pluronic-Systems in Kombination mit NMR, dynamischer Lichtstreuung und DSC-Messungen. Die Resultate verdeutlichen den Gelbildungsprozess während des Heizens und führen zu einer kubischen Phase, die durch einen höheren Speichermodul und höhere A- und z-Exponenten des sogenannten schwachen Gel-Modells als in der mizellaren Phase charakterisiert wird. Ein Wachstum der Mizellen während des Heizens wurde in der mizellaren Phase beobachtet. Die gemessenen Daten unterstützen die Hypothese, dass jedes Polymersegment aktiv bei der Bildung der unterschiedlichen Phasen teilnimmt: Während PPO für die Bildung der Mizellen verantwortlich ist, spielt PEO eine dominierende Rolle bei der Bildung der kubischen Phase. Darüber hinaus wurde eine unterschiedliche Steifigkeit im Kern und in der Korona der Aggregate in beiden Phasen festgestellt.

## RÉSUMÉ:

Les solutions aqueuses de Pluronic F127 présentent une gélation thermique intéressante au-dessus d'une certaine concentration. Ce phénomène est associé à une transition entre un comportement de type liquide à basse température et un comportement de type solide à haute température, et il est dû à des réponses thermales différentes des segments de polymères différents, l'oxyde de propylène (PPO) et l'oxyde de polyéthylène (PEO). Cette propriété conduit à un changement de structure dans l'auto assemblage macromoléculaire lors du chauffage, partant d'une structure isotrope micellaire pour arriver à une structure cubique ordonnée. Ces deux types d'assemblage sont clairement distincts du point de vue rhéologique. Cette contribution met l'accent sur les propriétés rhéologiques du Pluronic dans les phases micellaire et cubique, et relie ces propriétés avec les informations obtenues au moyen de la RMN, la diffusion dynamique de la lumière, et la DSC. Les résultats décrivent le

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posed of the strongly hydrated PEO [8, 32, 33].  $\Delta v_{hw}$  increases upon heating for both peaks and for both mixtures, up to a certain temperature. The increase is more pronounced for the PPO groups than the PEO groups. In both cases the strong increase of  $\Delta v_{hw}$  is due to a decrease of correlation times for aggregate tumbling and the diffusion associated to micelles formation.

At 30°C,  $\Delta v_{hw}$  reaches a constant value of approximately 35 and 40 Hz for 15 and 18 wt% mixtures respectively (values corresponding to PPO methylene groups). The organization into large micellar network is complete and  $\Delta v_{hw}$  remains nearly constant. It is important to underline the different slopes of  $\Delta v_{hw}$  of PPO and PEO during heating; in the micellar region, the slope of PPO is higher than the one related to PEO. In the gel phase,  $\Delta v_{hw}$  values of PPO slightly decrease whilst  $\Delta v_{hw}$  of PEO slightly increase. This clearly indicates different fluidity between corona and core part of aggregate in both regions. During the micellar formation, the core becomes stiffer and more rigid compared to the corona. In the gel phase an opposite trend can be observed. When the gel network is formed, the coronas interact to each other reducing the mobility of the molecules whilst the core is influenced only by temperature. The higher rigidity of the core is in agreement with data found in the literature [32].

#### 4 CONCLUSION

Different physical-chemical techniques were used to investigate the sol-gel transition in F127-water systems. Structural changes that occur during heating can be pictured out by using rheology and DLS: spherical micelles grow as the temperature increases, ultimately packing in a cubic phase (FCC). This cubic phase is characterized by higher storage moduli and higher A and z weak gel model exponents respect to the micellar phase. The structure block copolymer micelles is well described by the core-corona model, in which a spherical core composed of PPO is surrounded by a corona composed of the strongly hydrated PEO. The effective interaction potential among the micelles can be varied by changing the temperature and thus the micellar size and the relative size of the micellar core and corona can also be changed. NMR studies shows different fluidity between corona and core part of aggregate: in micellar region, the core becomes

stiffer and more rigid than the corona, while the opposite trend occurs in the gel phase

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