Dynamic Rheological Analysis of MLVs and Lamellar Phases in the System $C_{12}E_4$ / D_2O

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Abstract:
The mechanical properties of the lamellar phase, L_α, of the system $C_{12}E_4/D_2O$ were studied along an isoplethal path (30 wt% $C_{12}E_4$) in the temperature range 10 - 60°C. A dynamic analysis was determined by small strain oscillatory rheometry. The multilamellar vesicles ("MLVs") ("onions") were transformed by shearing the lamellar phase. The micellar phase was investigated by steady and dynamic rheological experiments. The micellar aggregate size increases slightly upon heating and the transition from micelles to lamellae appears to be a first order transition. The mechanical spectra of the lamellar phase show a strong dependence of the moduli on the frequency. This is typical of defective lamellar phases. They are different from MLVs mechanical spectra. The MLVs viscous and storage moduli are almost independent from the frequency and they exhibit the characteristics of a strong gel. The temperature of formation of the MLVs phase influences the mechanical properties of the MLVs. Three different packing states of the MLVs phase were observed in the temperature range 25 - 55°C.

Zusammenfassung:
Die mechanischen Eigenschaften der lamellaren Phase (La) des Systems C12E4/D20 wurden entlang eines isoplethischen Pfades (30 Gew.% C12E4) in dem Temperaturbereich 10-60 °C untersucht. Eine dynamische Analyse wurde mittels Oszillationsrheometrie bei kleinen Dehnungen durchgeführt. Die multilamellaren Bläschen ("MLVs") ("Zwiebeln") wurden durch Scherung der lamellaren Phase transformiert. Die mizellare Phase wurde durch stationär- und dynamisch-rheologische Experimente untersucht. Die Größe der mizellaren Aggregate steigt etwas an während des Heizens, und der Übergang von Mizellen zu Lamellen scheint ein Phasenübergang erster Ordnung zu sein. Die mechanischen Spektren der lamellaren Phase zeigen eine starke Abhängigkeit der Moduln von der Frequenz. Die ist für fehlerhafte lamellare Phasen typisch. Ihre Spektren unterscheiden sich von den mechanischen Spektren der MLVs. Der Verlust- und der Speichermodul der MLVs sind nahezu unabhängig von der Frequenz und zeigen die Charakteristika eines starken Gels. Die Temperatur der Bildung der MLVs-Phase beeinflusst die mechanischen Eigenschaften der MLVs. Drei unterschiedliche Packungszustände der MLVs-Phase wurden in dem Temperaturbereich 25-55 °C beobachtet.

Résumé:
Les propriétés mécaniques de la phase lamellaire La du système C12E4/D2O ont été étudiées le long de l'isoplèthe (30% en poids de C12E4) dans la gamme de températures allant de 10 à 60°C. Une analyse dynamique a été réalisée par rhéométrie oscillatoire à petite déformation. Les vésicules multilamellaires (oignons-MLVs) ont été transformées en cisaillant la phase lamellaire. La phase micellaire a été étudiée par des expériences de cisaillement stationnaire et dynamique. La taille de l'agrégat micellaire augmente légèrement en chauffant et la transition de micelles à lamelles semble être du premier ordre. Les spectres mécaniques de la phase lamellaire présentent une grande dépendance fréquentielle des modules. Ceci est typique des phases lamellaires comportant des défauts. Ils sont différents des spectres mécaniques des MLVs. Les modules élastiques et visqueux des MLVs ne dépendent pratiquement pas de la fréquence et présentent les caractéristiques d'un gel fort. La température de formation de la phase de MLVs influence les propriétés mécaniques des MLVs. Trois états différents de package de la phase MLVs sont observés entre 25 et 55°C.

Key words: $C_{12}E_4$, rheology, MLVs, lamellar phase, mechanical spectra.

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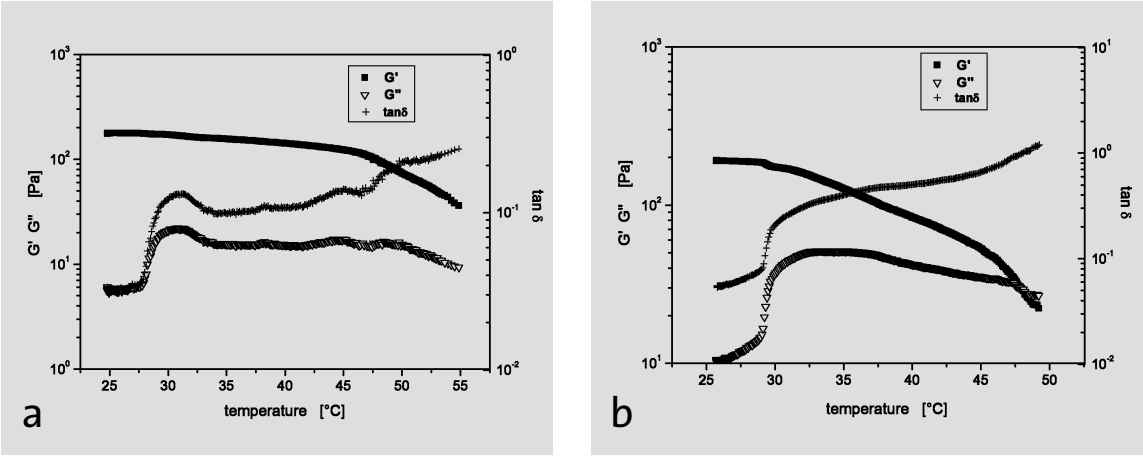

Figure 10:
Time cure test: (a) from 25 to 55°C performed on the MLVs phase within the linear viscoelastic region; (b) from 25 to 50°C performed on the MLV phase out the linear viscoelastic region.

med this experiment just to mark the changes in *G'* and *G''* profiles with the temperature and to evidence the different rheological regions.

Le et al. [19] studied the structure of MLVs phase by SANS spectrometer. They fixed the shear rate at 100 s^{-1} and recorded the 2D SANS spectra while increasing the temperature of the sample at a steady rate. They observed distinct packing states of multilamellar vesicles under shear. By analysing the dynamic experiments, we therefore retain that the three packing states of MLVs are observed. These are marked by the three different rheological behaviour in temperature.

4 CONCLUSIONS

In this article we studied the MLVs phase by dynamic rheological experiments and we showed that rheology is useful in probing the structural transition and analysing the structural changes that occur in the phases. The monitored isoplethal line was 30 wt%. The micellar phase was investigated by steady and dynamic rheological experiments. The micellar size growth increases slightly with the temperature and the L_1 - L_α transition appears to be a first order. The mechanical spectra of the Lamellar phase and the MLVs phase are completely different. The lamellar phase shows *G'* and *G''* profiles versus frequency as usually observed in defective lamellar systems and they are typical of the weak gels systems. This would confirm that the MLVs formation could depend on the defects present on the layers of the lamellae. The MLVs phase shows an elastic nature and the strong gels spectra, additionally the rheological behaviour of the dynamic properties depends on the temperature formation of the MLVs phase. The temperature sweep experiments evidenced three possible different states in the MLVs.

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