

PHASE BEHAVIOR AND RHEOLOGY OF FATTY ALCOHOL SULPHATE, FATTY ALCOHOL ETHER SULPHATE FROM PALM BASED AND MIXTURES WITH OTHER SURFACTANTS

(Kelakuan Fasa dan Reologi Lelemak Alkohol Sulfat, Lelemak Alkohol Eter Sulfat Berasaskan Sawit dan Campuran dengan Surfaktan Lain)

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Abstract

The phase diagrams of fatty alcohol sulphate (FAS)/ fatty alcohol ether sulphate (FAES)/soap (4.5:4.5:1.0)/propylene glycol/water mixtures were established at 60°C. The birefringence was observed under cross polarisers and their phases changes examined under a polarized microscope. The results showed that the liquid crystalline region for FAS and FAES occurred only in a small region. The optical patterns of lamellar liquid crystal were identified as oily streaks structure. The rheological tests of lamellar liquid crystal were carried out in the region of 4.5/4.5/1 FAES/FAS/soap with 0% PG and 10% of water. The rheological tests used were flow curve, 3 interval thixotropy test (3ITT), oscillation (dynamic test) stress sweep test and frequency sweep test measurement done using a cone-plate sensor (25mm, 1°). The flow curve was fitted to a Casson model to obtain values for the consistency coefficient and the flow behavior index. The lamellar liquid crystal show typical flow behavior and stress influenced the recovery of the structure. Linear visco-elastic (LVE) range analysis show the critical stress value at 0.475%, and elastic modulus was dominant over an angular frequency range studied.

Keywords: Lamellar liquid crystal, FAS, FAES, ternary phase diagram, rheology

Abstrak

Gambarajah fasa campuran lelemak alkohol sulfat (FAS)/lelemak alkohol eter sulfat (FAES)/sabun (4.5:4.5:1.0)/propelina glikol/air telah dibina pada suhu 60°C. Dwibiasan telah diperhatikan melalui pengutub bersilang manakala perubahan fasa telah dikaji dengan menggunakan mikroskop berkutub. Keputusan menunjukkan hablur cecair bagi FAS dan FAES terbentuk pada kawasan yang kecil. Ciri optikal bagi hablur cecair lamella didapati mempunyai struktur carikan berminyak. Kajian reologi yang dijalankan seperti lengkuk aliran, tiksotropi 3 tahap (3ITT), tegasan perubahan dan frekuensi perubahan di ukur dengan menggunakan gelendung (25mm, 1°). Lengku aliran dibina berdasarkan model Casson untuk memperolehi nilai koefisien dan indek lengku aliran. Struktur hablur cecair lamella menunjukkan kelakuan aliran dan tegasan mempengaruhi pembentukan semula strukturnya. Julat visko-elastik linear (LVE) menunjukkan nilai nilai tegasan kritikal pada 0.475%, dan modulus elastik dominan terhadap frekuensi yang dikaji.

Kata kunci: Hablur cecair lamella, FAS, FAES, gambarajah fasa tenari, reologi

Introduction

Soap and anionic surfactants have traditionally been the major constituents in many cleaning agents [1]. Fatty alcohol sulphates and fatty alcohol ether sulphates derived from palm oil were produced from Chemiton technology in Malaysian Palm Oil Board (MPOB). Preliminary pilot plant trials for these surfactants showed low activity and therefore the two surfactants were mixed to obtain a synergistic effect in their properties. Many other works on other mixtures have shown the advantages of using mixed surfactants in terms of enhancing the performance of

single surfactants [2-6]. To further understand the physico-chemical behaviour of surfactants systems, a study of ternary phase system was carried out to identify the contribution of the different components to a formulator for developing new products [7]. The phase behaviour and other properties of mixed surfactants have been carried out by Hofman et al. [8-10]. The mesophase change can be described from phase diagrams. The type of liquid crystal has a major influence on product properties. About seven different classes of liquid crystals have now been recognised, the major ones being lamellar, hexagonal, cubic, nematic and gel phase [11]. Surfactant liquid crystal is commonly used in products such as detergents, shampoos, and household cleaners [7].

Mixtures of anionic and nonionic surfactants are used in products such as laundry detergents, dishwashing detergents and cleaners. The phase behavior and rheological properties of these mixtures play an important role in the formulation and use of product. The phase behavior of surfactant systems is also a crucial factor in the production of product and in the choice of emulsifiers [12]. Investigation has already been conducted on the phase behavior of many commercially interesting individual surfactants [13] and mixtures [14].

Rheology is the study of the deformation and flow of matter. Solids and fluids exhibit different flow behaviors under shear. Solid store mechanical energy and are elastic, whereas fluids dissipate energy and are viscous. Knowledge of the complete flow and viscosity curve over a broad shear rate range is crucial for practical application whereas knowledge of the viscoelastic properties which can be determined by dynamic oscillating experiments is useful for elucidating structure effect principles in surfactants-containing formulation [13,15]. The characteristics and concentrations of surfactants are important factors affecting the structure and the rheological properties [16]. There has been no known systematic investigation into the rheological properties of lamellar liquid crystals. However, investigations into shear viscosity and its dependence on temperature have been published [17]. The rheological properties, in addition to characteristics and concentration of the surfactants, are affected by the interfacial rheology of the surfactants film, volume fraction of the disperse phase, viscosity of disperse droplets, droplets size distribution as well as viscosity and chemical composition of the medium [18]. The viscoelastic properties provide a deep insight into structural and dynamic aspect of structure systems. Besides characterizing the optically anisotropic liquid crystalline range, dynamic oscillating experiments are also able to describe the optically isotropic regions, which cannot be detected by polarization microscopy, such as viscoelastic networks of rod micelles or cubic gel phases [19]. The aim of this work is to identify the phase behaviour in ternary system using FAES/FAS /soap (4.5:4.5:1.0)/PG/ water mixtures and rheological properties of lamellar liquid crystal.

Materials and Methods

Materials

FAS and FAES were obtained from Advanced Oleochemical Technology Centre (AOTC), Malaysian Palm Oil Board (MPOB). The specification of these compounds is shown in Table 1. Soap was obtained from Unichema Sdn. Bhd. and its specification as shown in Table 2. Propylene glycol (PG) was 99% purity. These materials were used without further purification.

Table 1. Specification of FAS and FAES

Properties	FAES	FAS
Active	27.37 %	27.65
Unsulphonated matter	0.32%	0.74%
Moisture	68.62%	71.77%
Color	0.4 R,	2.0 R,
Petroleum ether extraction	3.7 Y	10.0 Y
PH (10%)	-	1.13%
	-	9.61

Table 2. Specification of soap

Properties	
Total fatty matter %	9-81
Moisture %	10.5-12.5
Free fatty acids %	1.3 max
Sodium chloride %	0.4-0.6
Glycerol %	0.1-0.2
Sequestrants	Present
Typical titer (Fatty acids) deg. C	44-47

Phase diagram

Phase diagram of FAES/FAS/soap (4.5:4.5:1.0)/PG/water mixtures were prepared at 60°C (to dissolve the soap component). 0.5g mixtures was placed in a test tube. Approximately 0.5% (total mixtures) deionised water was added into the mixture and homogenized at 4000 rpm for 15 minutes (Jouan CR3I) to homogenate and eliminate the air bubbles. Each sample was centrifuged for at least 3 times. The sample was then allowed to equilibrate in water bath at 60°C for at least 15 minutes. Then the phases were identified by visual observation between polarized film and crossed polarizing microscope in combination with a heating stage (Olympus AX70). More water was added to the test tube and the procedure repeated.

Rheology

Rheological properties were determined using a MCR 300 rheometer equipped with US 200 software. The cone-plate module with 25 mm in diameter and cone angle of 1° was used. Measuring temperature was maintained at 60.00±0.01°C by a Peltier Plate temperature controller (Model Viscotherm VT2). The tests performed were flow curve, 3-interval thixotropy test (standard test rotational), oscillation stress sweep test and frequency sweep test. The flow curve was fitted to a Casson model because it gives the lower standard deviation (±2.66) compared with Bingham, instead the result cannot be calculated by Herschel-Bulkley model. 3ITT test was used to determine how far the structure of a material can be re-built after shear or how long time the recovery takes. To be able to do this, the sample is measured with a three-interval test: rest-shear-rest. The first and the third interval usually have identical measurement parameters. The first interval is necessary to obtain a reference value for sample properties at rest (1Pa), during the second interval the material is sheared (50Pa, 75Pa and 100Pa) and the third interval (1Pa) the recovery of the structure can be observed. The calculate structure recovery after is a method that used for calculation of recovery interval. This method calculates the degree of recovery by comparing the viscosity after a selected period with the value at the end of the rest interval. The structure recovery is given in percent.

Dynamic test

In the oscillation stress sweep the stress was increased from 0.1 to 100 Pa and the frequency was kept constant (1 Hz). The linear viscoelastic region of each sample was determined with oscillation stress sweep test. In the linear viscoelastic region the ratio of stress and strain is a function of time alone [20]. Small-amplitude, oscillatory frequency sweep were conducted using a constant applied strain of 0.1% over an angular frequency range 0.1-100 rads^{-1} . The strain amplitude was found to be within the LVE range for the samples tested.

Results and Discussion

Phase diagram

The ternary system of FAES/FAS/ water is plotted at 60°C. Using the same ratio at equal amount of FAES and FAS, soap was added. The ratio of this study was 4.5:4.5:1.0 of mixed FAS, FAES and soap respectively as shown in Figure 1. Result showed that the LC region formed at 100% FAS/FAES with soap in 4% to 14% water. The phase transition results are summarized in Table 3. The optical patterns of LC are observed as shown in Figure 2. The texture of lamellar liquid crystal obtain was comparable with literature [7, 8].

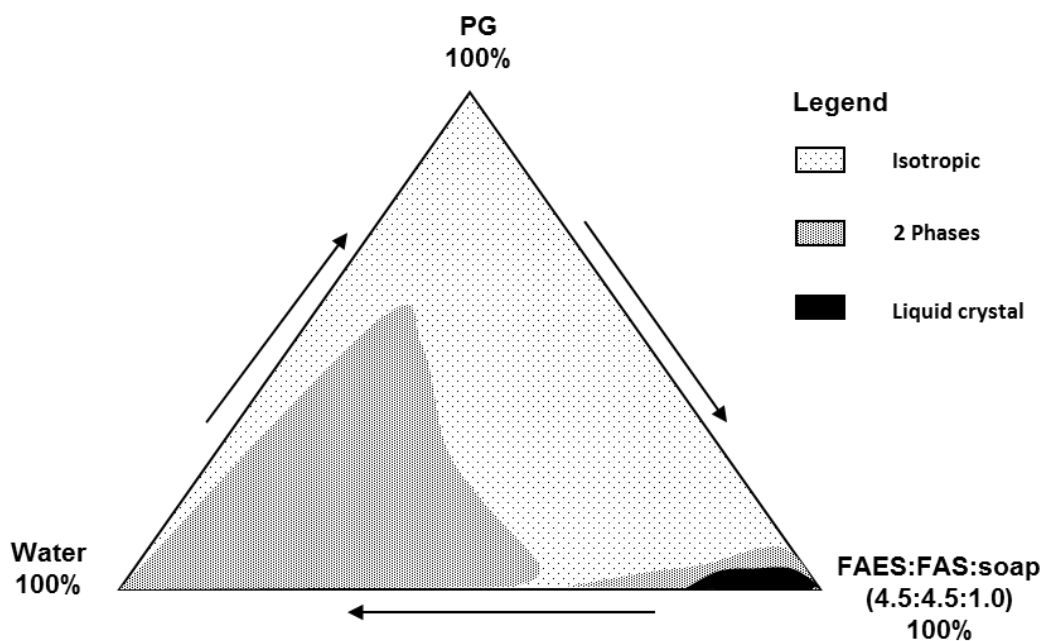


Figure 1. Phase diagram of (FAES:FAS:soap)/PG/water at 60°C

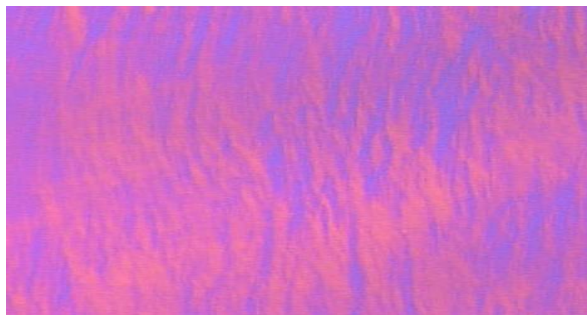


Figure 2. Optical pattern of oily streaks texture of 4.5/4.5/1 FAES/FAS/soap with 0% PG and 10% of water, 100x magnification.

Flow curve

The flow behavior of liquid crystal can be described by flow or viscosity curve. In flow curves, the shear stress of a sample is plotted against the shear rate which produces shearing. The Casson equation describes the flow curve of a material with yield stress and a non-newtonian behavior at stress above the yield stress. It often provides a good fit for blood and for food product. The yield stress is given as the analysis result. As seen in Figure 3, shear stress as a function of the shear rate and the consistency curve for a pseudoplastic material with low yield stress (1.5376×10^{-6} Pa). Yield stress is a minimum stress to make substance flow. At stress below the yield stress, the substances act as an elastic material. The shear stress of a pseudoplastic substance increase with increasing shear rate. The curved rheogram for pseudoplastic materials results from a shearing action on the long-chain molecules of materials such as linear polymers. As the shearing stress is increased the normally disarranged molecules begin to align their long axes in the direction of flow. This orientation reduces the internal resistance of the material and allows a greater shear rate at each successive shear stress [21].

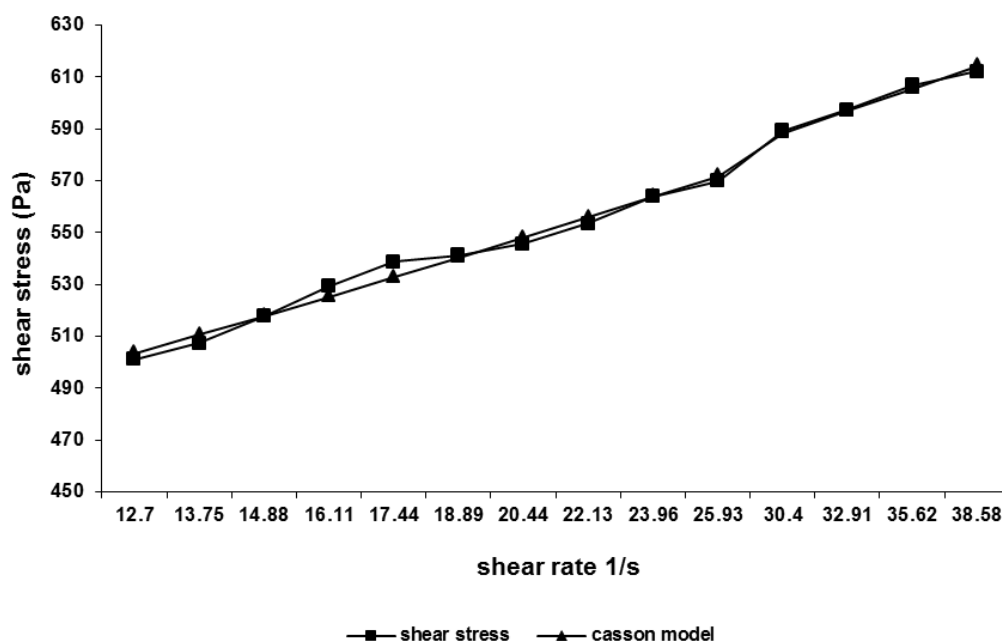


Figure 3. Flow curve of liquid crystal of 4.5/4.5/1 FAES/FAS/soap with 0% PG and 10% of water.

Thixotropic

Figure 4 shows the results of 3ITT for the sample, which is, differ by load interval 50 Pa, 75 Pa, 100 Pa respectively. The calculation for recovery was compared with the value at the end of the rest interval and the value at the end of recovery interval (100 seconds after stress). The recovery after stress is 51.57%, 48.10% and 46.16% of 50 Pa, 75 Pa, and 100 Pa respectively. At load interval, there was a significant difference between 3 stress-applied show the viscosity was decreased with stress. The consequences by load influenced the structure recovery, which indicates low recovery after high stress.

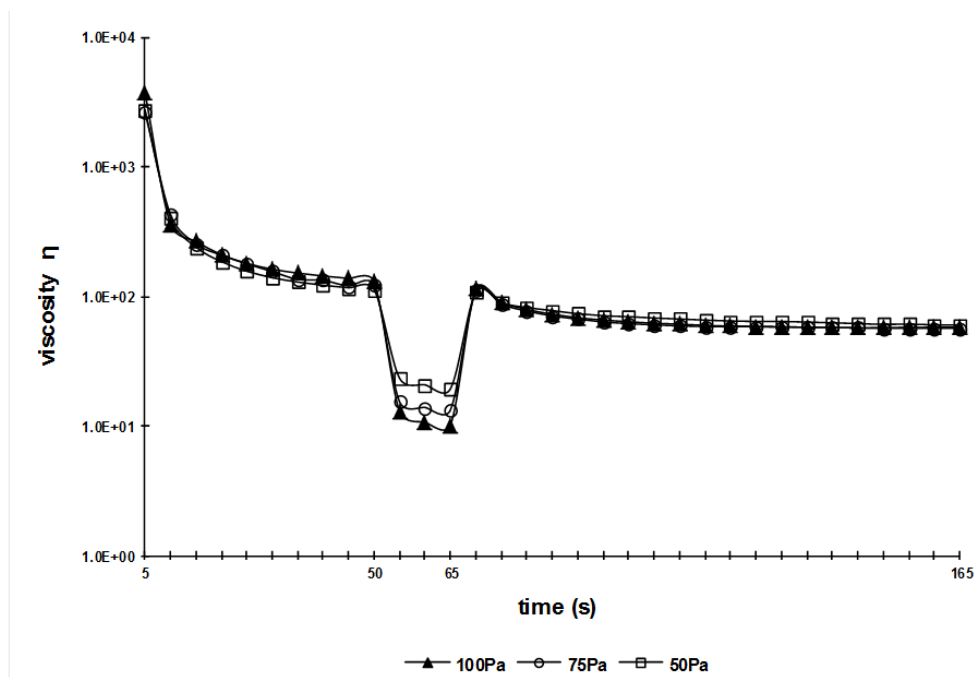


Figure 4. 3 Interval Thixotropy Test of liquid crystal of 4.5/4.5/1 FAES/FAS/soap with 0% PG and 10% of water at stress of 50Pa, 75Pa and 100Pa.

Stress sweep

In order to determine the strain amplitude range over which linear visco-elastic (LVE) prevails, stress sweep experiments were carried out at a frequency of 1 Hz in the overall strain amplitude of 0.1%-100%. Figure 5 shows a linear of the storage modulus G' and loss modulus G'' at low strain, followed by a sharp decrease when the system passes from linear to nonlinear viscoelastic regime. The G' and G'' started to decrease continuously at slightly higher strain amplitudes. That point is called critical strain. The critical strain characterizing the limit of the LVE regime. The critical strain at 0.475%, and 0.1% strain were used in the frequency sweep as suggested by the LVE range analysis. The lamellar liquid crystal had the low critical stress and the optical microphotographs show a clearly weak structure (Figure 2). In the theory of LVE, the relevant equations are linear differential equations and the coefficients of the time differential are constants, i.e. are material constant. Leaving this LVE range by selecting higher amplitudes and consequently higher stress means no accountable deviation for the measured data of the materials tested linked to the chosen test parameter and the instrument used. Under these conditions the sample is deformed to the point that the internal temporary bonds of molecules or of aggregates are destroyed.

Frequency sweep

Having determined the amplitude that keeps test of a particular sample safety within the LVE region, one can then proceed with further test using the frequency sweep to measure the sample's visco-elastic behavior and predict the storage stability of suspensions. This necessitates using low-deformation oscillatory measurements. The data obtained hold valuable information about the particle-particle interaction. Figure 6 show the frequency dependence (rad/sec) of the viscoelastic parameters, G' and G'' . The results show the elastic or storage modulus, G' , is the dominant response over the frequency range investigated. At low frequencies the sample are elastic, i.e., the storage modulus G' is higher than the loss modulus G'' , the phase angle is below 45° . At high frequencies, the samples are also elastic but showed greater deviation. The G' and G'' values show a small frequency dependant over the frequency range. These are characteristics of a strongly associated, but stable viscoelastic liquid crystal.

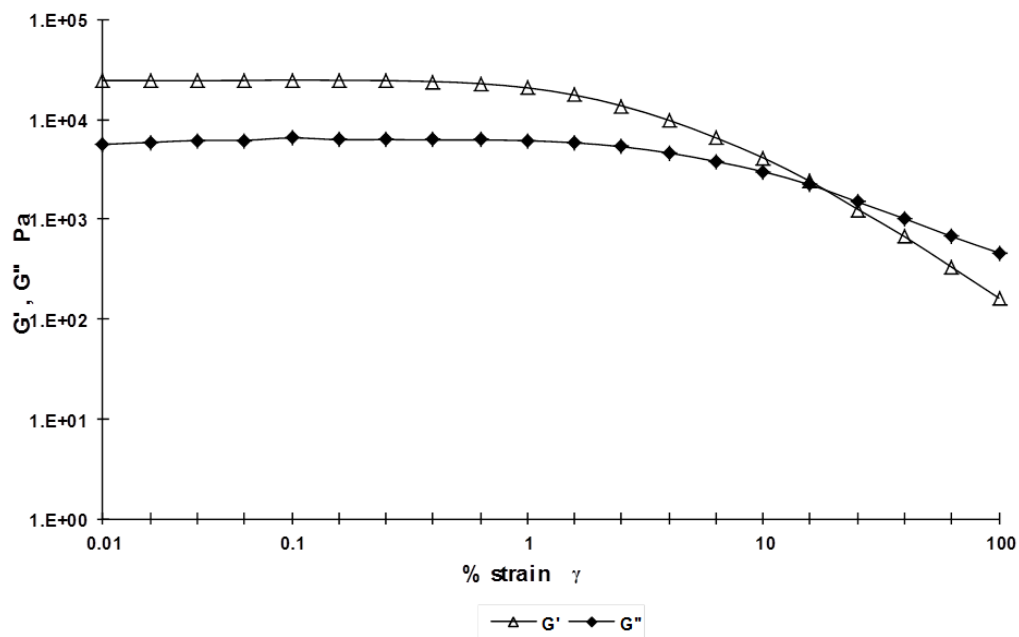


Figure 5. Dynamic stress sweep of liquid crystal of 4.5/4.5/1 FAES/FAS/soap with 0% PG and 10% of water at 1Hz

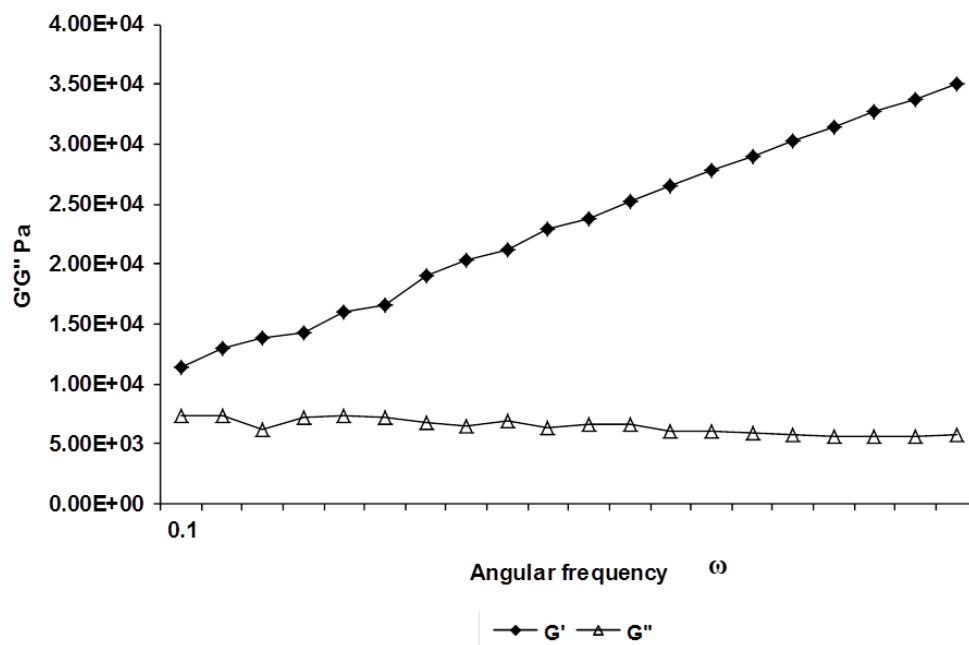


Figure 6. Dynamic frequency sweeps of liquid crystal of 4.5/4.5/1 FAES/FAS/soap with 0% PG and 10% of water at 0.1% strain.

Conclusion

In conclusion, the phase diagrams of fatty alcohol sulphate /fatty alcohol ether sulphate/soap /propylene glycol/water mixtures were established at 60°C. The results showed that the liquid crystalline region for FAS and FAES occurred only in a small region and the optical patterns of lamellar liquid crystal were identified as oily streaks structure. The rheological tests show typical behavior of liquid crystal and it is very useful to be used in development of household products.

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