PALM-BASED LAURYL ALCOHOL ETHOXYLATE BEHAVIOURAL STUDY AND RECOMMENDATIONS IN PERSONAL CARE APPLICATIONS

Lim Hong Ngee[1], Anuar Kassim[1], Atan Sharif[1], Dzulkefly Kuang[1], Ambar Yarmo[2], Zarina Edris[2], Rosnah Ismail[3], and Huang Nay Ming[4]

[1] *Chemistry Department, Faculty of Science, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor Darul Ehsan, Malaysia.*
[2] *School of Chemical Sciences and Food Technology, Faculty of Science and Tachnology, Universiti Kebangsaan Malaysia, 43000 Bandar Baru Bangi, Selangor Darul Ehsan, Malaysia.*
[3]*AOTD MPOB, Lot 9 & 11, Jalan P10/14, Seksyen 10, 43650 Bandar Baru Bangi, Selangor Darul Ehsan, Malaysia.*
[4] *School of Applied Physics, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43000 Bandar Baru Bangi, Selangor Darul Ehsan, Malaysia.*

Abstract

Palm-based lauryl alcohol ethoxylate was synthesized with 6 moles of ethylene oxide using an ethoxylation reactor. The 6 moles of ethylene oxide chain length was approximately the same length as the palm-based lauryl alcohol. The synthesized lauryl alcohol ethoxylate consisted of an average of 6 moles of ethylene oxide and was labeled as $C_{12}EO_6$. The molecular structure of lauryl alcohol ethoxylate was determined by Fourier Transformed Infrared Spectroscopy (FTIR). The ternary phase diagrams for olive or olein oil/water/$C_{12}E_6$ systems were investigated at 25^oC. The important features of the ternary phase diagrams are the emulsion and the concentrated emulsion phases. Optical microscope, particle size analyser and rheometer were used to characterize the different compositions of emulsions. Different consistencies of emulsions were recommended for the personal care applications.

Keywords: palm-based lauryl alcohol ethoxylate, ethoxylation reactor, ternary phasediagram, emulsion, concentrated emulsion

Introduction

Emulsions are dispersions of at least two immiscible liquids stabilized by emulsifiers, which are often surfactants [1]. The droplets of one liquid is dispersed through a second, which is termed the continuous phase. Surfactants, which possess polar and non-polar regions, are absorbed to the phase interfaces and thus, decrease the interfacial free energy.

Concentrated emulsions are gaining interest amongst the researchers in recent years [2, 3]. The internal phase volume fraction of the concentrated emulsion is in the range of 0.8 to 0.99. These concentrated emulsions are named biliquid foams due to their foam-like structure where the internal phase consists of polyhedral compartments. These emulsions are also termed as high internal phase ratio emulsions (HIP) [4] or gel-emulsions [5]. They can be either W/O or O/W type emulsions. One highlight of the highly concentrated emulsions is their long-term stability despite very low surfactant concentrations, as reported by Kizling et al [6]. The emulsions characteristic resemblance to stiff gels is attributed to its internal structure being similar to that of foams with large air/liquid ratio.

In emulsions, the droplets or particles are rather far away one from another and interact only when the Brownian motion brings them together. In concentrated emulsions, the probability of interactions is significantly enhanced. They have a tendency to be confined in the region of the well of energy; this configuration leads to the formation of structures [2].

In this study, the phase behaviour of emulsions prepared using olive or olein oil/water/$C_{12}E_x$ systems was examined. The emulsions were characterized using optical microscope, particle size analyzer, small angle x-ray scattering (SAXS) and rheometer. Different consistencies of emulsions were recommended in the formulation of personal care products.

Experimental

Materials

Distilled water was used throughout this study. Lauryl alcohol with a purity of 99% was obtained from Cognis (M) Oleochemicals Sdn Bhd. Ethylene oxide 100% was obtained from Fluka. Potassium hydroxide 85% and citric acid were obtained from Sigma-Aldrich. Olive oil with a purity of 100% was obtained from Bronson & Jacobs. Olein oil with a purity of 99% was obtained from Moi Foods Malaysia Sdn. Bhd. Brij 40 (Tetraethylene glycol dodecyl ether - $C_{12}EO_4$) was obtained from Fluka. All the excipients were used as received.

Synthesis of palm based lauryl alcohol ethoxylate ($C_{12}E_6$)

Da Vinci reactor was used for the ethoxylation of lauryl alcohol with 6 moles of ethylene oxide using potassium hydroxide 1 w/w % as the catalyst. The reaction was left to complete for three hours at 140^{o}C, at atmospheric pressure and stirred at 100 rpm. The pH of the synthesized liquid sample was neutralized to the range of 5.0-7.0 using citric acid. The neutralized liquid sample was centrifuged at 10 000 rpm for 20 minutes to remove salt formed during neutralization. Finally, the liquid sample was vacuumed at 40^{o}C for two days to remove water. The as-synthesized sample was labeled as $C_{12}E_6$ with 6 as the average number of moles of ethylene oxide.

Fourier Transformed Infrared Spectroscopy (FTIR)

Perkin Elmer Model GX type FTIR was used to investigate the structural carbonyl group of $C_{12}E_6$. Wave number was in the range of 500 to 4000 cm^{-1} with a resolution of 1 cm^{-1}. Sample preparation was based on KBr disk technique.

Phase Behaviour Determination

Ternary phase diagram of $C_{12}E_6$ surfactant was studied. The three components of the phase diagrams were $C_{12}E_6$ as surfactant, water as aqueous phase and olive or olein oil as oil phase. Two diagrams were assigned namely $C_{12}E_6$/water/olive oil and $C_{12}E_6$/water/olein oil. The regions in the phase diagram were determined by titrating oil phase into water/surfactant (w/w) in the 15mm x 100 mm test tubes. The ratios of water/surfactant were in the range of 0.11 to 9.0. Results of the phase diagrams were plotted. AND analytical balance was used to determine the weight of the materials. Thermolyne vortex was used to homogenize the samples.

Macroscopy Analysis

Organoleptic characteristics and homogeneity of emulsions were observed to identify visible instability such as creaming, flocculation or coalescence. Centrifugation was carried out for visibly stable emulsions using Hettich Retafix 32 to affirm their stability. Each emulsion sample was submitted to a cycle of 2 min at 4000 rpm at room temperature. At the end of the cycle, a macroscopic evaluation was made to observe any possible phase separation.

Particle Size Analysis

Droplet size distributions of the emulsions were measured using Mastersizer 2000s. This system measures droplet size with the help of light scattering technique. Owing to their opaque nature, the parent emulsion samples were to be diluted. The samples were diluted at the ratio of 1:1000 with distilled water in the equipment chamber and sonicated before analysing.

Microscopy Analysis

Size and morphology of the emulsions were analysed microscopically in bright field under optical microscope. Droplet image of the emulsions was observed under light microscopy at room temperature (25^{o}C). A small drop of emulsion was place onto the microscope slide and carefully covered. After equilibrated for 1 min, photomicrographs (x100 magnification) were taken using Nikon microscope (Japan) equipped with a digital camera (XLi, USA). The size of the emulsion droplets were measured using I-Solution Image Analyzer (IMT Inc.).

Rheological Study

A Rheometer (PAAR Physica MCR 300), operated by Rheoplus software, was used to evaluate steady–shear analysis of emulsion and concentrated emulsion. The analysis was carried out using cone and plate geometry. The plate gap was set to 0.125 mm. The steady-state analysis was used for characterization of the emulsion and concentrated emulsion behaviour under shear. Measurements were carried out on emulsion samples to determine the role of shear in the eventual destruction of the emulsion. The controlled shear rate (CSR) procedure was selected for flow curve evaluation. Values of maximal and minimal apparent viscosity were used for characterization of the samples for flow analysis. The speeds were varied to produce the two curves (ascendant and descendant). Flow index data and viscosity were obtained at different times during the test. All samples were tested at 25 ± 2°C.

Results and Discussion

Fourier Transformed Infrared Spectroscopy (FTIR)

In Fig. 1, the spectrum of lauryl alcohol showed a weak absorption of C-O band at 1120 cm^{-1}. The spectra of the standard and the synthesized sample of $C_{12}E_6$ displayed a strong C-O stretch at 1120 cm^{-1} which was attributed to C-O single-bond stretching of the ether (polyoxyethylene) group.

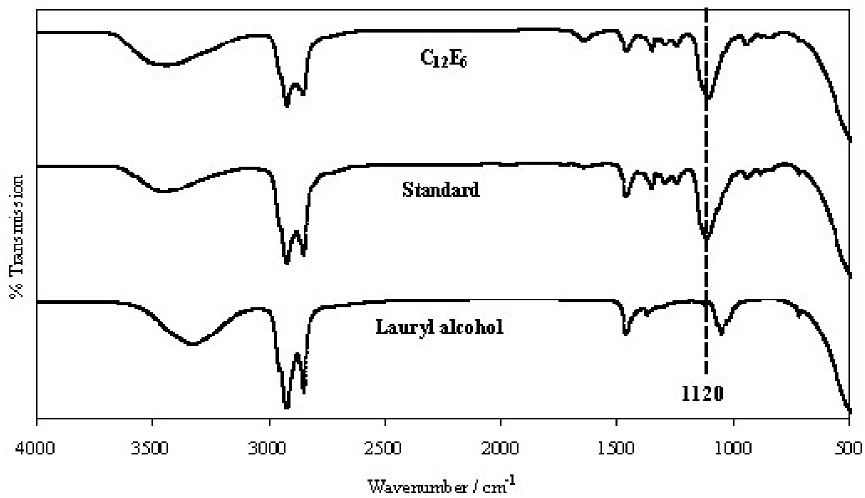


Fig. 1: FTIR spectrum of palm-based lauryl alcohol, Brij 40 ($C_{12}EO_4$) as a standard and the synthesized sample of $C_{12}EO_6$.

Phase Behaviour Determination

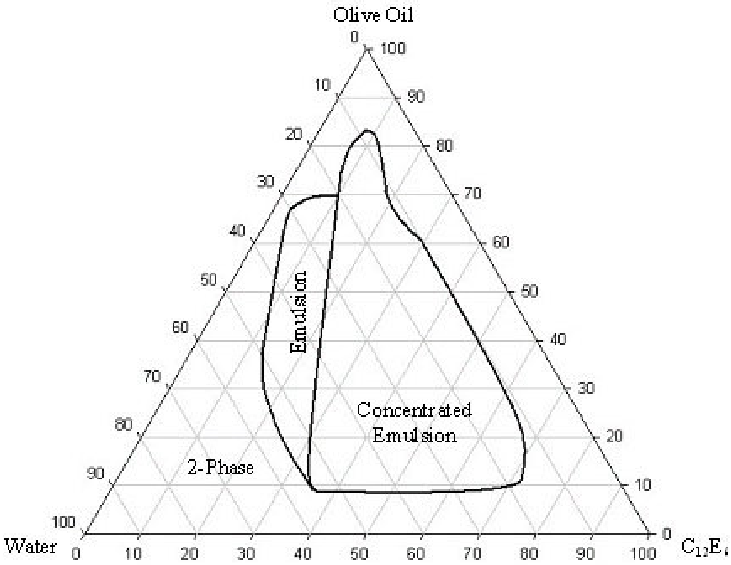
The two distinct features in Fig. 2 (a) are emulsion and concentrated emulsion areas. The emulsion phase comprises of a narrow area with $C_{12}EO_6$ in the range of 3-35%. The concentrated emulsion gave a smooth and stiff texture with $C_{12}E_6$ in the range of 8-70%. Fig. 2 (b) has a narrower emulsion and concentrated emulsion areas compared to Fig. 2 (a). The emulsion contains $C_{12}E_6$ in the range of 5-20% whereas the concentrated emulsion consists 5-35 % of $C_{12}E_6$. The concentrated emulsion area in both the ternary phase diagrams is located close to the oil phase. This shows that a high concentration of oil is used and that the oil droplets are closely arranged in the continuous water phase as observed under the optical microscope. The O/W concentrated emulsions could be prepared using only a small amount of surfactants, approximately 4-10%, depending on the oil-water ratio. Overall, the ternary phase diagram consisting olein oil shares similiar attributes to the ternary phase diagram of olive oil

Macroscopic Evaluation

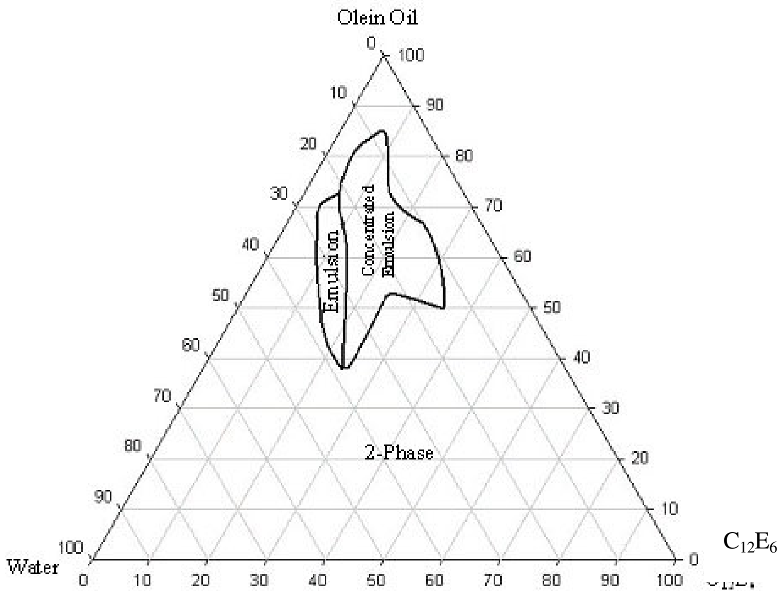
All emulsions were classified as macroscopically stable, without any signs of phase separation or creaming, after centrifugation at 4000 rpm for 2 minutes, at the start of the stability studies. Latreille and Paquin [7] reported that ageing period is stimulated by centrifugation which accelerates destabilization of the emulsions.

Particle Size Analysis

The average droplets size of $C_{12}E_6$/water/olein oil (2.5%/22.5%/75.0%) emulsion and $C_{12}EO_6$/water/olive oil (8.3%/8.3%/83.4%) concentrated emulsion samples were 1.120 µm and 5.987 µm respectively. Therefore, concentrated emulsion displayed smaller droplets size than emulsion which is due to the closely packed arrangement of droplets in the concentrated emulsion.



2 (a)

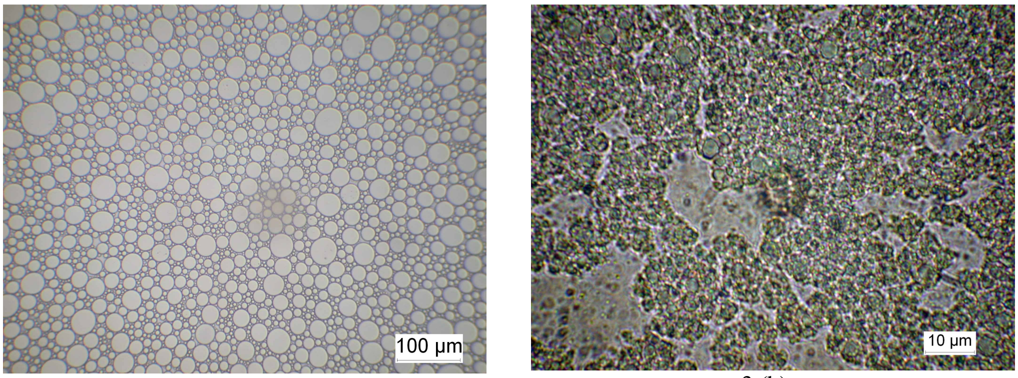


2 (b)

Fig. 2: Ternary phase diagrams of (a) $C_{12}EO_6$/water/olive oil and (b) $C_{12}E_6$/water/olein oil.

Microscopic Evaluation

Fig. 3 (a) depicts the emulsion of the $C_{12}E_6$/water/olein oil (2.5%/22.5%/75.0%) system observed under optical microscope. The average size of the emulsion oil droplets by counting at least 1000 droplets is 6.45 µm, which is similar to the particle size measured by light scattering method. Fig. 3 (b) shows the droplets arrangement of concentrated emulsion of the $C_{12}EO_6$/water/olive oil (8.3%/8.3%/83.4%) system. The droplets are found to be closely arranged with the oil droplets dispersed in the continuous water phase. The average size of the oil droplets for the concentrated emulsion is 1.01 µm, which is close the particle size analysed by light scattering method.



3 (a) 3 (b)

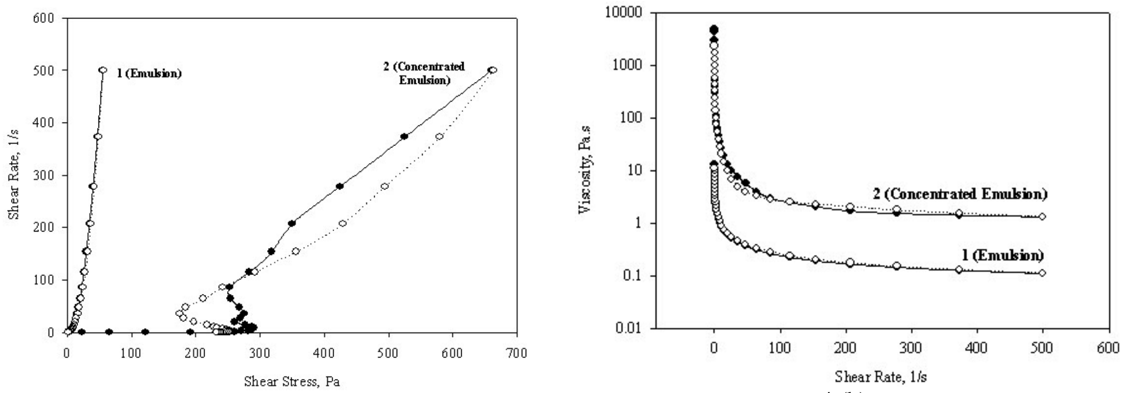
Fig. 3: Morphology of the (a) $C_{12}E_6$/water/olein oil emulsion and (b) $C_{12}E_6$/water/olive oil concentrated emulsion.

Rheological Study

Both the flow curves in Fig. 4 (a) indicated shear thinning. The smooth flow curve (1) indicated a stable emulsion. In contrast, concentrated emulsion indicated by flow curve (2) was complex and different from flow curve (1). The ascendant and descendant curves crossed over imply that the shearing cycle itself might cause structural build-up, rather than destruction [8]. A yield stress of approximately 25 Pa is observed in flow curve (2). The ascendant and descendant curves in flow curves (1) were almost the same. This means the shear does not induce irreversible structural changes [9]. Both the curves in Fig. 4 (b) decreased in viscosity as shear rate increased. This feature also indicated shear thinning behaviour. In curve (2), the high apparent viscosity value indicated that the concentrated emulsion was thicker and more resistant to structure breakdown [8]. The apparent viscosity of concentrated emulsion containing smaller droplets (1.12 µm) was significantly greater than emulsion containing larger droplets (5.98 µm).

Recommendations in Personal Care Applications

In this study, different consistencies of emulsions were obtained to satisfy the requirements of cosmetic products. To develop a lotion or cream, at least three components are needed; oil, water and surfactant. Emulsions are suitable to be turned into lotion as the low to medium viscosity suits the physical sensory of the product. The concentrated emulsions are recommended to be turned into creams as they possess a yield stress and thus, contribute to the physical sensory of the product. As both the emulsions and concentrated emulsions possess shear thinning behaviour, the more force applied, the less the viscosity. This is an important factor in cosmetic so that lotions and creams can be applied onto skin with some rubbing. The higher the shear thinning, the easier it is to apply the materials onto skin. Usually selected polymer like polyacrylates or cellulose is incorporated into emulsions and concentrated emulsions to strengthen the stability of the system.



4 (a) 4 (b)

Fig. 4: (a) Flow curves of the olein oil/water/$C_{12}E_6$ emulsion (1) and olive oil/water/$C_{12}E_6$ concentrated emulsion (2) with ● (closed circle) - ascendant curve and ○ (open circle) – descendant curve, (b) Viscosity for emulsion of the olein oil/water/$C_{12}E_6$ system (1) and concentrated emulsion of the olive oil/water/$C_{12}E_6$ system (2) with ● - descendant curve and ○ – ascendant curve.

Conclusion

Lauryl alcohol ethoxylate with an average number of 6 moles of ethylene oxide was successfully synthesized. The study of the ternary phase behaviour of oil/water/$C_{12}E_6$ systems demonstrates two main features namely emulsion and concentrated emulsion. Emulsions are less viscous compared to the stiff concentrated emulsions. The particle size of concentrated emulsion is smaller than that of emulsion. Optical microscope exhibits a dense arrangement of the oil droplets in the concentrated emulsion. The concentrated emulsion has rather narrow droplets size distribution with average particle size of 1.12 µm. The concentrated emulsion has a yield stress which shows that a minimum amount of stress is required for the system to flow.

Acknowledgement

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