Journal of Oil Palm Research Vol. 23 August 2011 p. 1051-1054

PALM OIL-BASED METHYL ESTER SULPHONATE PREMIXES FOR USE IN DISH-WASHING LIQUIDS

ZAHARIAH ISMAIL*; MOHD SURIA AFFANDI YUSOFF* and KHAIRUDIN HASHIM*

ABSTRACT

We describe palm-based methyl ester sulphonate premixes, which are mixtures of methyl ester sulphonates (MES) and fatty alcohol ethoxylate sulphonates (FAES), and their application in liquid detergent formulations. The best ratios of these compounds were obtained from ternary phase diagrams of MES, FAES and deionised water at 70°C. The phase changes – from isotropic to liquid crystalline regions – were observed visually using polarised film, and the liquid crystalline birefringent optical patterns were subsequently confirmed using a polarising microscope. Based on the phase diagrams obtained, the optimal liquid crystalline region was selected for the preparation of a palm oil-based premix. Stable premixes can be used to produce liquid detergent products such as dish-washing liquids, laundry detergents, hand washes, kitchen cleaners and floor cleaners. The active levels of the palm-based MES premixes were measured using an autotitrator for dish-washing liquid formulation. The physical stability of the model dish-washing liquids (DWL) was assessed by conducting stability tests at room temperature (24°C) and also at 45°C, over a three-month period. Other properties such as detergency, foaming power, pH and viscosity were measured, and comparisons were made with current typical commercial products. A dermal irritation assay confirmed that the product is non-irritant to the skin.

Keywords: methyl ester sulphonate premix, fatty alcohol ethoxylates, liquid crystalline structure, stability test, detergency.

Date received: 20 April 2010; **Sent for revision:** 22 September 2010; **Received in final form:** 12 November 2010; **Accepted:** 19 April 2011.

INTRODUCTION

Surface-active agents or surfactants are used in many commercial products such as cosmetics, as well as personal care and household products. Methyl ester sulphonates (MES) are a new class of anionic surfactants which are derived from palm oil. With the banning in Malaysia of non-biodegradeable branched alkyl benzene sulphonate (BAS) detergents, producers of detergent-based products have now switched to linear alkyl benzene sulphonates (LABSA). One of these, MES, has received a lot of attention as an active ingredient in washing and cleaning products for a variety of reasons. They include:

- good lime-soap dispersing characteristics (Yoneyama, 1996);
- good detergency, especially in hard water, even in the absence of phosphates (Yamane *et al.*, 1989; Ismail *et al.*, 1998);
- C14, C16 and C18 of methyl esters have the best detergency (Okumura *et al.*, 1976; Ahmad *et al.*, 1997; 1998; 2004); and
- biodegradability (Ghazali, 2002).

Similarly, fatty alcohol ether sulphates (FAES) are anionic surfactants which can also be derived from palm oil. These derivatives are extensively used in the production of washing and cleaning products. The objective of this study was to develop a suitable MES/FAES premix for the production of liquid detergents. The premix was selected based on the ternary phase diagram for these products. Possible synergistic detergency effects might be

* Sime Darby Research Sdn Bhd,
42960 Carey Island, Selangor, Malaysia.
E-mail: zahariah.ismail@simedarby.com

expected for the correct phase behaviour of such mixtures.

MATERIAL AND METHODS

Materials

MES of chain length C16-C18 (active ingredient 85%, disalt 4%) were purchased from the Malaysian Palm Oil Board (MPOB). FAES, glycerine and fatty acid alkanolamide were purchased from Orion Sdn Bhd, Malaysia. Suitable preservatives and perfumes were purchased from DCM Sdn Bhd, Malaysia.

Methods

Constructing the MES/FAES ternary phase diagram. Various ratios of MES and FAES and water, from 0% to 100%, with a total weight of 0.5 g for each, were mixed in 10 ml test tubes. The tubes were placed in a water bath (Haake) maintained at 70°C in order to melt the mixtures. Approximately 0.01% water was added to each sample, and then the mixtures were homogenised by vortexing (Velp Scientifica). The samples were remelted and centrifuged (Universal centrifuges) at 5000 rpm for 15 min. Each sample was heated and centrifuged at least three times, and then allowed to equilibrate in a water bath for at least 1 hr. The samples were checked visually through a cross polariser for separation after centrifugation. The phase behaviour of the mixtures for the isotropic and anistropic regions was identified visually through a cross polariser and then by polarised microscopy (Olympus AX70) in combination with a heating stage, according to Ismail (2002).

Selection of the region in the ternary phase for MES premix formulation. Selection of the MES premix formulations was based on the liquid crystal region in the ternary system plotted.

Active ingredient in MES /MES premix/MES premix in dish-washing liquid. The percentages of active ingredient in MES, MES premix and MES premix in a dish-washing liquid (DWL) were determined using an autotitrator with Hyamine 1622 as a titrant (Metrohm Method).

Physical properties of MES premix and MES premix in DWL.

a. Stability storage studies

The MES premix in the DWL samples was evaluated at 45°C, and also at room temperature (24°C), over three months. The samples were monitored through visual observations for any appearance of separation. Samples that showed separation were noted as *NS* (not stable), while those that were stable were noted as *S* (stable).

b. Viscosity

The apparent viscosity of the MES premix and MES premix in DWL samples was measured using a Brookfield viscometer with spindle No. 3 or No. 4 at 30 rpm.

c. Foaming properties

A 2-litre beaker was filled with 200 ml distilled water and 0.2 g DWL was added. Using a fabricated perforated stainless steel propeller, the solution was stirred for 1 min at 1300 rpm. The top and bottom levels of the foam were recorded immediately. The difference between the two levels gave the volume of foam formed or the foaming power (foam height). The solution was left standing for 5 min, after which the top and bottom levels of the foam were again recorded. The difference between the top and bottom levels indicated the foam stability.

d. pH

A 1% w/v solution was prepared using each test sample, and its pH measured with an MP 220 pH meter at 24°C.

e. Cloud point

Thirty grams of a sample were poured into a test tube. The test tube was stoppered with a rubber bung which had a thermometer inserted. The test tube was placed in an ice bath at -21°C. The temperature reading was noted when the sample turned cloudy as the temperature of the sample decreased.

f. Detergency power

The detergency performances of the DWL samples were evaluated using a soiled glass plate. The detergency performances were compared to the performances of two commercial DWL samples available in Malaysia. The percentage of dye removal was calculated based on Leenert's improved detergency test (Japanese method) as shown below:

$$\text{Detergency} = \frac{\text{wash with } CHCl_3 \text{ without sample} - \text{wash with } CHCl_3 \text{ with sample}}{(CHCl_3 - \text{sudan}) - (CHCl_3 + \text{sudan} + \text{oils})}$$

Formulations

i) A typical formula for DWL consists of:

Deionised water	up to 100 g
MES premix	8-10 g
Glycerol/propylene glycol	5-20 g
Lemon (fragrance)	0.5-1.0 g
Water-soluble preservatives	0.01-0.05 g

ii) Preparation of MES premixes and MES premixes in DWL

The MES premixes were prepared by mixing the three ingredients (MES, FAES and deionised water) at varying percentages at 70°C. They were coded as MES premix (MESPM) MES PM1, MES PM2 and MES PM3. The pourable viscosity sample of MESPM was selected for DWL preparation. The final product was measured for storage stability, viscosity, foaming power, pH, cloud point, and detergency.

RESULTS AND DISCUSSION

Ternary Phase Diagram of MES, FAES and Deionised Water

The behaviour of the MES, FAES and deionised water mixtures was plotted in a phase diagram (*Figure 1*). The ternary mixture of MES and co-surfactant (FAES) with deionised water revealed the formation of lamellar liquid crystals at various concentrations and ratios between MES and the co-surfactant (FAES). This was noted as the appearance of birefringence in the sample. At the centre of the phase diagram, the phases showed a transition from the liquid crystalline phase (LC) to a two-phase region and then to an isotropic region (L1). The liquid crystalline phase was further confirmed with a polarising microscope as shown in *Figure 2*.

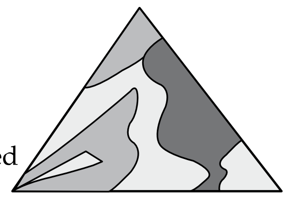
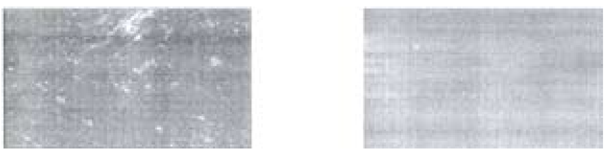


Figure 1. Ternary phase diagram of methyl ester sulphonates (MES) with fatty alcohol ethoxylate sulphonates (FAES) as co-surfactant and deionised water at 70°C.



Liquid crystal region Isotropic region

Figure 2. Typical appearance of the liquid crystal and isotropic regions as seen in the polarizing microscope.

Selection of Composition for MES Premix

The criteria for selecting the composition points were a higher percentage of surfactant and a low percentage of co-surfactant in the liquid crystalline region as shown in *Figure 1*.

MES Premixes

Four MES premixes were prepared and coded as MES PM1, MES PM2 and MES PM3. *Table 1* shows the viscosities and active ingredients of the MES PM series. Based on viscosity, MES PM2 was selected for the DWL preparation, because it was neither too liquid nor too viscous.

MES Premix in DWL

MES PM2 was selected for the preparation of a dish-washing liquid (DWL PM 001). *Table 2* shows the performance of DWL PM 001, DWL 002 (which was without the premix) and two typical commercial samples.

The results in *Table 2* indicate a higher cloud point for DWL PM 001 than for DWL 002 and the commercial samples. This was due to the physical characteristics of MES itself. However, a previous study (to be published later) has shown that synergistic effects in lowering the cloud point can be achieved by combining the two different actives (MES and linear alkyl benzene sulphates) at specific percentages. Higher detergency performance was found in DWL PM 001 than in DWL 002 and the commercial samples. DWL PM 001 had liquid crystals that can stabilise the system. Another advantage is that MESPM can be an intermediate stock of raw material for preparing any other type of liquid detergent. All the products were found to be non-irritant as shown in *Table 3* and stable for three months at pH 7.

TABLE 1. METHYL ESTER SULPHONATES (MES) PREMIX PROPERTIES

MES premix	Viscosity (cps) (Brookfield) spindle/rpm		Active ingredient (%)	Remarks
	4/30	4/60		
MES PM1	*	*	35.4	Too viscous
MES PM2	9 490	8 750	25.4	Pourable
MES PM3	92	98	15.2	Too liquid

Note: *cannot measured – too viscous.

TABLE 2. PERFORMANCE OF DISH-WASHING LIQUIDS

Parameter	DWL PM 001 at 8% active ingredient	DWL 002 without PM at 8% active ingredient	Commercial sample 1	Commercial sample 2
Detergency (%)	92	87	89	89
Cloud point (°C)	13	8	-10	8
Foam height/stability	1 125/950	1 150/970	1 175/990	1 200/1 000
pH at 24°C	7.0	7.0	7.8	7.3
Storage stability (45°C and 24°C)	S	S	S	S
Dermal irritation* assay	Non-irritant	Non-irritant	Non-irritant	Non-irritant

TABLE 3. DERMAL IRRITATION ASSAY OF DISH-WASHING LIQUIDS

Samples	Dose (mg)	HIE score	Predicted dermal irritancy classification
DWL PM 001	125	0.00	Non-irritant
DWL 002	125	0.00	Non-irritant
Commercial 1	125	1.07	Non-irritant
Commercial 2	125	0.92	Non-irritant

CONCLUSION AND RECOMMENDATION

MES premixes were successfully developed as new intermediate raw materials for the preparation of liquid detergents. Further improvement on the properties could possibly be achieved by substituting MES with LABSA at a specific percentage to obtain the correct cloud point.

ACKNOWLEDGEMENT

The authors wish to thank Sime Darby Plantation Sdn Bhd for permission to publish this article.

REFERENCES

AHMAD S; ISMAIL, Z and SAMSANI, J (1998). Washing behaviour of palm-based sulphonated methyl ester. *J. Amer. Oil Chem. Soc.*

AHMAD, S; ISMAIL, Z and SAMSANI, J (1997). Palm-based sulphonated methyl esters and soap. *J. Oil Palm Research Vol. 10*: 15-34.

AHMAD, S; SIWAYANAN, P; ABD MAURAD, Z; ABDUL AZIZ, H; KASSIM SHAARI, N Z and ISMAIL, Z (2004). Methyl ester sulphonates palm stearin. Paper presented at the 4th China Surfactant, Personal Care and Homecare Markets Conference.

GHAZALI, R (2002). The effect of disalt on biodegradability of methyl ester sulphonates (MES). *J. Oil Palm Research Vol. 14*: 45-50.

ISMAIL, Z (2002). *Association Behaviour and Rheology of Palm-based Emulsion Using Sugar-based Emulsifiers*. Ph.D thesis, Universiti Putra Malaysia.

ISMAI, Z; AHMAD, S and SAMSURI, J (1998). Palm-based sulphonated methyl esters and soap. *J. Oil Palm Research Vol. 10 No. 1*: 15.

OKUMURA, O T; SAKATANI, and YAMANE (1976). Mechanism of sulfonation of fatty acid esters with sulfur trioxide and properties of alpha-sulpfo fatty acid esters. *Comite International des denves Tensio-actives*: 225-237.

YAMANE, I and MIYAWAKI (1989). Manufacturing process of α-sulphomethyl esters and their application to detergents. *Proc. of the 1989 PORIM International Palm Oil Development Congress.* p. 132-141.

YONEYAMA, Y (1996). Palm oleochemicals for used in detergent-lion's prespective on the application of methyl ester sulfonate. *Proc. of the 1996 PORIM International Palm Oil Development Congress.* p. 515-524.