

## MICROEMULSION SYSTEMS OF PALM KERNEL SOAP WITH VEGETABLE OILS AND HYDROCARBONS

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**RINGKASAN:** Sabun isirung sawit (SIS) telah disintesis dari minyak isirung sawit RBD, dan sistem mikroemulsinya dengan minyak sayuran dan hidrokarbon yang distabilkan oleh *n*-butanol telah dikaji. Keputusan menunjukkan bahawa hidrokarbon berantai pendek, *n*-heksana mudah terlarut dalam sistem air-SIS dan membentuk larutan isotropik terbesar berbanding *n*-oktana dan *n*-dekana. Keadaan sebaliknya berlaku bila  $\beta$ -karotena dimasukkan, yang mana *n*-dekana membentuk kawasan mikroemulsi terbesar. Dalam sistem minyak sayuran, olein isirung sawit membentuk kawasan mikroemulsi terbesar berbanding minyak sawit dan minyak kacang soya. Kawasan mikroemulsi menjadi kecil bila minyak sawit dan olein isirung sawit dicampur dengan minyak kacang soya.

**ABSTRACT:** Palm kernel soap (PKS) was synthesised from RBD palm kernel olein and its microemulsions formed with vegetable oils and hydrocarbons, and stabilised by *n*-butanol were investigated. The results showed that the short chain hydrocarbon, *n*-hexane was easily solubilised in water-PKS system (forming the largest isotropic region) compared to *n*-octane and *n*-decane. In the presence of  $\beta$ -carotene, the PKS acted oppositely whereby *n*-decane yielded the largest microemulsion region. Among the vegetable oils studied, palm kernel olein gave the largest microemulsion region compared to palm olein and soybean oil. The regions were significantly reduced when palm kernel oil and palm olein were mixed with soybean oil.

**KEYWORDS:** Palm olein, palm kernel oil, palm kernel soap, microemulsion, phase diagram, isotropic solution.

## INTRODUCTION

Palm kernel oil (PKO) is a co-product of the oil palm industry. Its production reached 1.1 million metric tons in 1996 (Haumann, 1997). PKO, being a saturated oil and solidifies at room temperature has very limited applications and usually sells at a lower price than palm oil. At present, the largest use of PKO is for soap production. High production of PKO necessitates diversification into added value products. Palm kernel oil contains short and medium chain fatty acids (C12 and C14), and their derivatives are more hydrophilic than those of C16 and C18 fatty acids. This property provides a means to control hydrophilic-lipophobic balance (HLB). Therefore, the interfacial properties of PKO derivatives are of importance in numerous detergents, lubricants, cosmetics and emulsions applications. One of the simplest and easy way to prepare PKO derivative is palm kernel salt, which is widely used as toilet soaps. As a surfactant, its properties in microemulsion systems are not fully explored, except for a salt of fatty acid (sodium stearate), which had been used for the formation of microemulsion (Osipow and Rosenblatt, 1966).

Microemulsion is a thermodynamically stable isotropic solution containing hydrocarbon and water, and is stabilised by either a single surfactant or by a combination of surfactant and cosurfactant. Such a system provides oil and water domains where solubilizates are solubilised. Microemulsions are good solvents for molecules that are weakly soluble or insoluble in pure solvents. Among their uses are as solvents for dyes (Wortmuth *et al.*, 1990; Crower, 1987), carriers for flavors in vegetable oils (El-Nokaly *et al.*, 1991), solubility enhancers for example, methanol in triglycerides (Dunn and Bagby, 1994) and water in alkanes (Aveyard *et al.*, 1992), and media for chemical synthesis (Holmberg and Osterberg, 1988; Osterberg *et al.*, 1989; Singh *et al.*, 1994). Recent interest has focused on microemulsion systems based on vegetable oils (Alender and Warnhein, 1989a; Joubran *et al.*, 1993; Parris *et al.*, 1994) with the aim of producing environmentally acceptable formulations. These systems are then used to solubilize additives, for example in cosmetic, food product and lubricant formulations. The presence of water in vegetable oil microemulsions enhance thermal characteristics and provides softness to the product, particularly in cosmetic formulations. In addition, the use of natural fat-based surfactants together with vegetable oils further promote product biodegradability.

In this study, palm kernel soap (PKS) was synthesised and used as a anionic surfactant to investigate the association behaviour with particular emphasis on microemulsion regions. Various vegetable oils were then solubilised in the regions. Results from this study may provide useful information for the formulations of new palm based products.

## **MATERIALS AND METHODS**

### **Materials**

Refined, Bleached and Deodorised (RBD) palm olein, RBD palm kernel oil and RBD palm kernel olein were obtained from Southern Edible Oil Industries, Klang, Selangor. Soybean oil (SBO) was purchased from local market. Other chemicals used were purchased from BDH Limited with purity of more than 99.5%. All alcohols and hydrocarbons used were of normal straight-chain (i.e. n-pentanol, n-butanol, n-hexane, n-decane, n-octane) and referred to as butanol, pentanol, hexane, decane and octane. Water was double distilled.

### **Synthesis of palm kernel soap (PKS)**

Palm kernel soap (PKS) was synthesised in two stages: Firstly, the regeneration of palm kernel fatty acid (FA), followed by neutralisation of FA to form PKS.

### **Regeneration of free fatty acid**

PKO (100.0g) was weighed into a round-bottom flask and 200 ml of KOH solution (1M in 95% ethanol) was added. The mixture was then refluxed over an oil bath until the solution turned clear. The reflux was continued for another 20 min until the saponification was completed after the liquid became homogeneous. Hot distilled water (300 ml) was then added, followed by HCl (100 ml, 35% solution). The mixture was left in the bath with gentle shaking until the separated free fatty acid formed a clear layer above the aqueous solution. The free fatty acid layer was then removed.

### **Preparation of palm kernel soap**

Freshly regenerated free fatty acids (50.0g) was mixed with excess NaOH solution (250 ml, 1M) in a round bottom flask and the mixture was then refluxed for 30 min. Neutralisation was completed when the solution became clear. Water released during neutralisation was removed by freeze-drying using liquid nitrogen. The soap obtained was then washed with water to remove excess NaOH solution and dried in dessiccator under vacuum. The PKS was characterised by IR spectroscopy.

### **Phase diagrams of palm kernel soap**

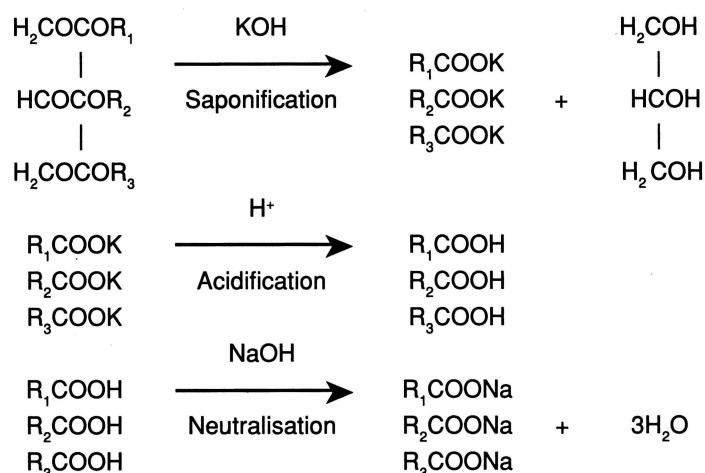
A ternary phase diagram of water/PKS/alcohol system was constructed by titrating a mixture of PKS-alcohol (0.5g) with doubly distilled water. Various ratios of PKS-alcohol mixture were used in the titration. Micelle regions (isotropic solutions) were determined by visual observation for transparency. The mixtures were vortexed (Thermolyne 37600 Mixer) for mixing and centrifuged at 5000 rpm to confirmed solubility. The ratio of PKS-alcohol which gave the largest isotropic region of the water/PKS/alcohol system was chosen for the preparation of

microemulsions. The best ratio was found at 40:60 for PKS:n-butanol mixture. This ratio was used throughout the investigation.

Microemulsion regions containing water/PKS-butanol/hydrocarbon were then determined by titrating a mixture of PKS-butanol/hydrocarbon (0.5g) with water. Similar procedures were used to confirm solubility and transparency of the solution. The samples were allowed to equilibrate in water bath kept at 30°C. An estimated region of the phases was made by noting the transition from turbid to transparent solution. A representative triangular phase diagram was then plotted. The experiments were repeated using various vegetable oils and a mixture of hydrocarbons and  $\beta$ -carotene (0.01%).

## RESULTS AND DISCUSSION

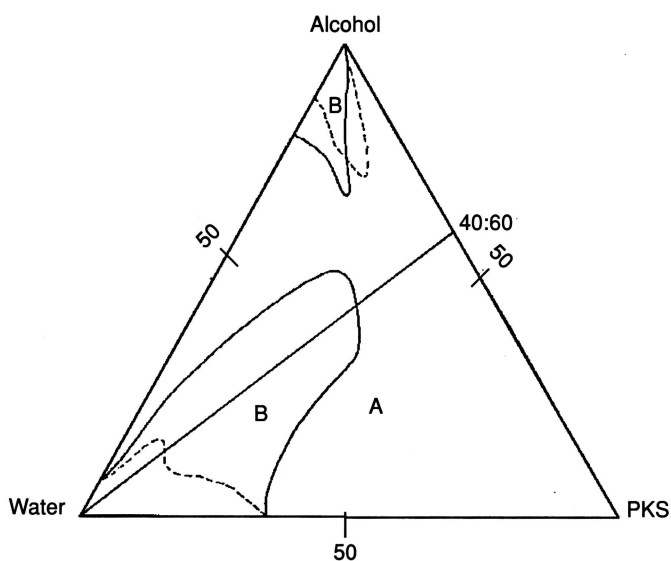
Palm kernel soap used as anionic surfactant in this study was synthesised in two steps. The first step was to eliminate glycerol (coproduct) from the reaction mixture. This step involved a saponification reaction producing potassium salts of palm kernel fatty acids and glycerol, followed by acidification to release free fatty acids which were then separated from glycerol. Second step involved neutralisation of the regenerated fatty acids to form sodium soaps. It was observed that the hardness of the soap varied according to its water content during freeze-drying. Fully dry soap was a white waxy solid which show  $\nu_{\max}$  at 1560  $\text{cm}^{-1}$  (carboxylate ion,  $-\text{COO}^-$ ), 1742  $\text{cm}^{-1}$  (carbonyl group,  $\text{C}=\text{O}$ ), 2922  $\text{cm}^{-1}$  (OH, from trace of fatty acid) and 3419  $\text{cm}^{-1}$  (trace of water). Scheme 1 shows the reaction pathways in the synthesis of PKS.



Scheme 1



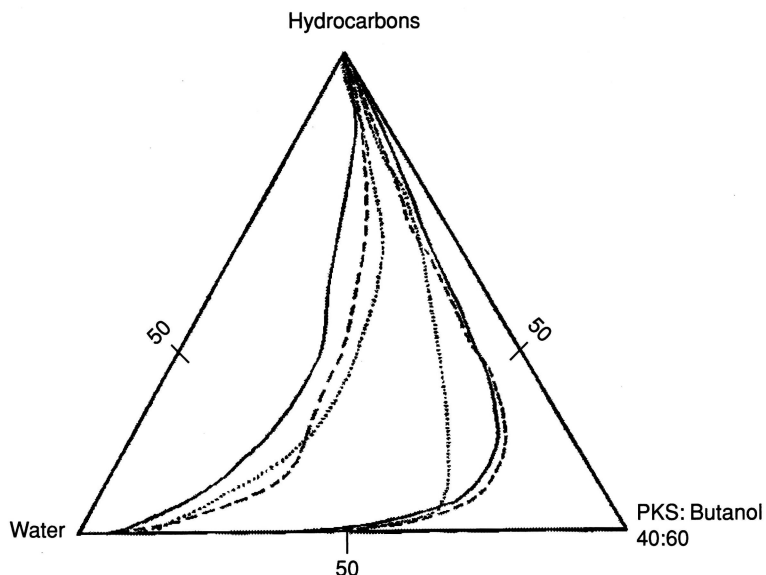
The palm kernel soap was sodium salts of various fatty acids of palm kernel oil, thus it contained mixed surfactants. Microemulsion systems of PKS were studied first by constructing a solubility region of water/PKS/alcohol system to determine the best cosurfactant to be used with PKS. Figure 1 shows the solubility regions for the isotropic solution of the water/PKS/alcohol system. It was observed that n-butanol formed a large isotropic (a homogeneous transparency solution) region compared to n-pentanol. The region extended from the water apex over a wide concentration regime (up to about 35.0 wt% water). From the phase diagram, a ratio 40:60 (w/w) of PKS:n-butanol was selected as the best ratio for further investigation. At this ratio the system maintained isotropic solutions at a wide range of water concentration.



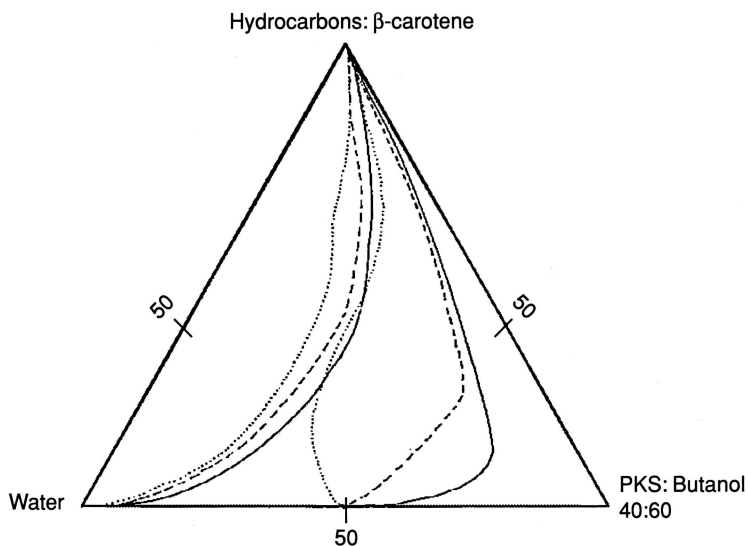
**Figure 1.** Ternary phase diagram of water/PKS/alcohol system: (---) pentanol and (—) butanol; A = two phase region; B = isotropic solution.

The pseudoternary phase diagram for microemulsion region of water/PKS-butanol mixture and three hydrocarbons (hexane, octane and decane) system is shown in Figure 2. The phase diagrams were characterised by the pattern of isotropic solution. With hexane and octane as a lipophilic components, the microemulsion regions were stable at reasonably high surfactant concentrations, up to about 65% PKS-butanol mixture. This was however not the case with the decane where the microemulsion region was slightly narrow. It was particularly difficult for water to interact with decane structure due to the long carbon chain ( $C_{10}H_{22}$ ). The hexane system showed the largest isotropic solution compared to the octane and decane system. The phase behaviour of hydrocarbons/PKS/ water was very dependent on the length of hydrocarbon chain. A smaller hydrocarbon molecule (i.e. hexane) could be easily penetrated into the surfactant layer, thus forming a large microemulsion region (Alender and Warnhein, 1989b). When  $\beta$ -carotene was added into the system, at concentration of about 0.01 wt%, the PKS acted oppositely with decane- $\beta$ -carotene system yielding the biggest isotropic region, up to about 75% PKS-butanol mixture (Figure 3). The isotropic solution of the decane- $\beta$ -

carotene system was found curving towards the surfactant apex, whilst the hexane- $\beta$ -carotene system was projecting downwards, towards the water apex. These observations suggest that the carotene interfere to some extent in the association process of PKS and hydrocarbon solvents.

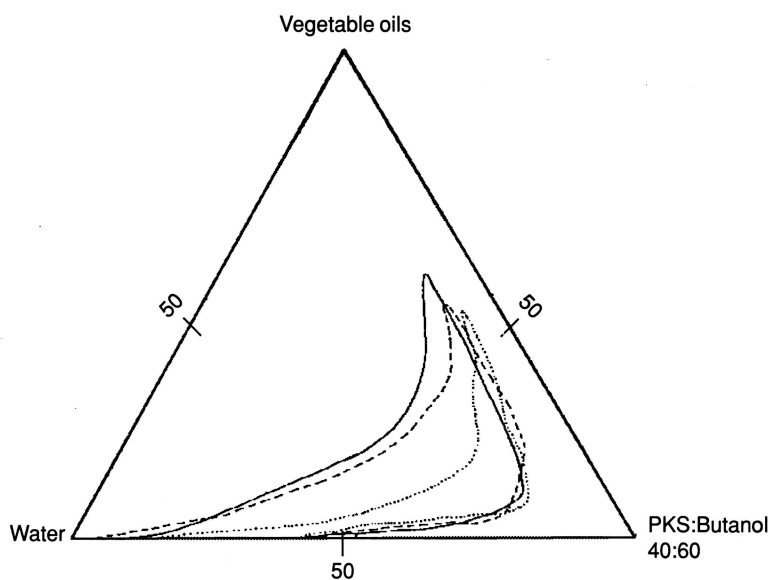


**Figure 2.** Pseudoternary phase diagram of water/PKS-butanol/hydrocarbon system; (.....) decane, (---) octane and (—) hexane

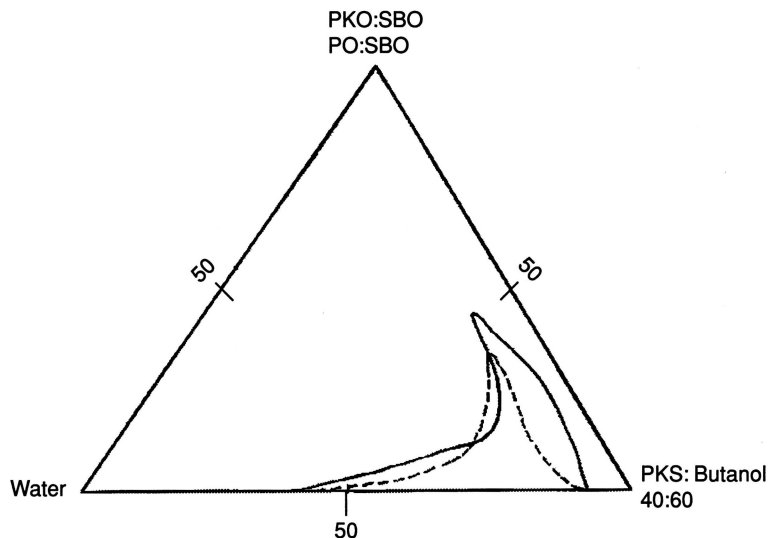


**Figure 3.** Pseudoternary phase diagram of water/PKS-butanol/hydrocarbon- $\beta$ -carotene system; (.....) hexane, (---) octane and (—) decane

Figure 4 shows microemulsion regions of the three different vegetable oils used in the study. A marked reduction in microemulsion regions was observed when hydrocarbons were substituted by vegetable oils. All regions were found projected towards the water apex and extended up to about 79 wt% PKS-butanol mixture. Palm kernel oil produced almost a similar region with soybean oil. However, palm olein (PO) was the most affected, where it showed the smallest isotropic region. This phenomenon was attributed to association behaviour of the components present in the system. A large and relatively bulky structure of vegetable oil triglycerides compared to a linear structure of hydrocarbons were difficult to associate with water, PKS and n-butanol, to form isotropic solution. Therefore, vegetable oils formed a smaller microemulsion region with PKS surfactant compared to hydrocarbon solvents. Similar result was observed by previous workers (Alender and Warnhein, 1989b), and suggesting the same reason for the shrunk of microemulsion regions (i.e. difficulty of large triglyceride molecule to solubilise in microemulsion). At equal amounts of water and vegetable oils more than 45 wt% surfactant mixture was needed to form a microemulsion phase. This was rather high compared to the amount required (27 wt%) to create the same phase at equal amount of water and hydrocarbons. In general, both systems (hydrocarbon and vegetable oil systems) formed a considerably large microemulsion regions. A similar but smaller isotropic regions were observed when PO and PKO were mixed with SBO (50:50, v/v). Again, a relatively large triglyceride structures of PO and SBO compared to PKO accounted for the significant reduction in isotropic regions. A large molecule did not favour formation of micelles due to its difficulty to interact with water and surfactants.



**Figure 4.** Pseudoternary phase diagram of water/PKS-butanol/vegetable oil system; (.....) palm olein, (---) soybean oil and (—) palm kernel olein



**Figure 5.** Pseudoternary phase diagram of water/PKS-butanol/oil mixture system; (—) PKO-SBO (50:50, v/v) and (---) PO-SBO (50:50), v/v)

## CONCLUSION

In summary, the present results showed that a PKS formed a reasonably large microemulsion regions with short linear chain hydrocarbons (octane and hexane) and vegetable oils. Carotene, being a large molecule interfered with the microemulsion of hydrocarbon in the PKS/water systems. All microemulsion region were formed near the surfactant-rich apex.

## ACKNOWLEDGEMENT

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