

WATER/PERFUME MICROEMULSION REGION STABILIZED BY HYDROPHOBIC SURFACTANTS AND THEIR MIXTURES

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RINGKASAN: Kawasan mikroemulsi air/bahan wangian yang distabilkan oleh Aerosol-OT dan Tween 20, serta campurannya telah ditentukan. Kawasan tersebut adalah lebih besar berbanding dengan komponen-komponen yang sama tetapi dengan dekana. Kawasan ini juga didapati bergantung kepada nisbah berat campuran Aerosol-OT dan Tween 20; kawasan yang lebih besar dengan peningkatan kandungan Aerosol-OT. Secara keseluruhannya, sifat hidrofilik bahan wangian hanya menunjukkan kesan yang kecil terhadap variasi kawasan mikroemulsi, samada dalam sistem surfaktan tulen atau campuran.

ABSTRACT: The water/perfume micro-emulsion region stabilized by Aerosol-OT and Tween 20, and their mixtures were determined. The regions were more extended than those of equivalent components with hydrocarbon. The regions were also found to be dependent on the weight ratio of the mixed Aerosol-OT and Tween 20; a larger region resulted with increased amount of Aerosol-OT. Overall, the hydrophilicity of the perfumes showed little effect on the variation of the micro-emulsion region, either on the pure or mixed surfactant systems.

KEYWORDS: Microemulsion, limolene, estragole, aerosol-OT (sodium bis-2-ethylhexyl sulfosuccinate), Tween 20 (polyoxyethylene sorbitan monolaurate)

INTRODUCTION

The introduction of micellar solution and solubilization concept by McBain (1919) had since attracted researchers to further understand the mechanism of enhanced solubility of a compound. The compound to be solubilized or the solubilize may simply be associated with the amphiphile between the nonpolar (hydrocarbon) layers or be located in the polar region of the amphiphatic structures. In the last two decades, mixture of surfactants had been employed as solubilizers in many industrial applications since solubilization by mixed surfactants is often superior to the solubilization by the singular surfactants (Clint, 1975; Clint *et al.*, 1975; Chaiko *et al.*, 1984; Holland & Rubingh, 1992; Norihiro *et al.*, 1992; Hamdan & Harun, 1994). The solubilization of compound in micellar surfactant or mixed surfactant systems has been widely exploited. However, the solubilization in microemulsion systems has not received similar attention. The latest report was by Barni and coworkers (1991) on the solubilization of dyes in microemulsion for dyeing processes.

The application of surfactants in cosmetic and perfumery preparations has added one more dimension to this already interesting branch of colloid science. So far, the literature has been confined to the use of hydrocarbon and alcohol as the essential ingredients for the formation of both the micellar and microemulsion systems. Recently, Tukuoka and coworkers (1994) have replaced the conventional hydrocarbon with some synthetic perfumes. They reported that the solubilization of the perfumes in the micellar solutions of anionic and/or nonionic surfactants system are affected by the hydrophilicity of the perfumes and the length of the hydrocarbon chain of the nonionic surfactant. Our contribution (Hamdan *et al.*, 1995) in this area has been directed towards the formation of micro-emulsions with perfumes employing ionic surfactant and medium chain alcohol as a cosurfactant. With the growing awareness on the possible hazards associated with alcohols, we found the opportunity to investigate the solubilization of perfume in an alcohol-free system to be appealing.

In this paper, we adopted similar work from a previous publication (Hamdan *et al.*, 1995) but used hydrophobic surfactants and their mixtures instead. The resulting water/perfume microemulsion region was compared to the equivalent system with hydrocarbon.

MATERIALS AND METHOD

Materials

The basic materials source and purity for the pseudoternary systems are listed as follows. The surfactants, Aerosol-OT (sodium bis-2-ethylhexyl sulfosuccinate) Tween 20 (polyoxyethylene sorbitan monolaurate) were obtained from Fluka. The perfumes, limonene and estragole were supplied by Universiti Kebangsaan Malaysia (UKM), Bangi and Sigma, respectively. These materials were all used as received and no further purification was performed. Double distilled, deionised water was used.

Determination of phase behaviour

The phase equilibria were determined by mixing two of the components and titrating with a small amount of the third component to turbidity. The samples were thoroughly mixed to homogeneity with a vortex meter (Thermolyne Maxi Mix II), centrifuged (Rexmed Model DSC-1512SDT) at 5000 rpm and then allowed to equilibrate in a water bath maintained at 30°C. The phases were examined by visual inspection between cross polarizers and under a polarizing microscope.

RESULTS AND DISCUSSION

Water/Hydrocarbon Microemulsion

The ternary phase diagrams of the previously constructed water/surfactant/hydrocarbon systems (Hamdan *et al.*, 1996) and their isotropic solution region are shown in Figure 1. The surfactants were Aerosol-OT and Tween 20, while the hydrocarbon component was decane. All the components were dispersed in an isotropic solution at compositions shown by the shaded region of Figure 1. The isotropic region with Tween 20 and Aerosol-OT, separately at the surfactant apex emanated from two different limits of the phase diagram. The former extended from the hydrocarbon-free axis and the latter from the water-free axis (part a and b of Figure 1, respectively). The influence of the perfumes namely, limonene and estragole on the variation of the isotropic region can be obtained by replacing decane with the perfume as an apex.

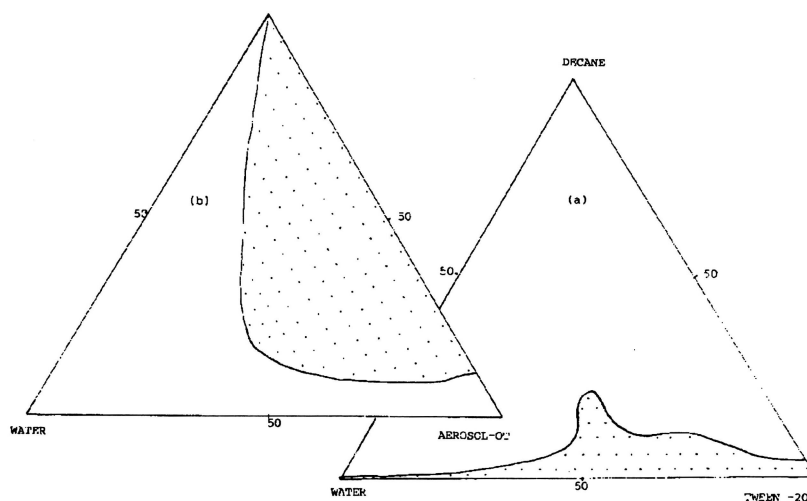


Figure 1. Partial phase diagrams of water, decane and a third component consisting of (a) Tween 20 and (b) Aerosol-OT (Hamdan *et al.*, 1996). The microemulsion solubility area are shown by the shaded region.

Water/Limonene Microemulsion

Figure 2 shows equivalent phase diagrams but with limonene as replacement of decane. The isotropic solution region in the water/Tween 20/limonene system (part a of Figure 2) emanates from both the water-free and the limonene-free axes. The solubility region can be divided into three sub-regions in its ability to solubilize limonene. The largest sub-region at a low content of limonene (< 25 wt %), followed by a medium sub-region ranging from 25 and 57 % of limonene, and the smallest sub-region with a limonene content ranging from 57 % onwards. The solubility region of the water/Aerosol-OT/limonene system (part b of Figure 2) is found to be protruding from the water-free axis between 15 to 100 % limonene, and curving towards the water apex with maximum water solubility of 50 %. The weight ratio of the Aerosol-OT/limonene that exhibits the maximum uptake of water is at 75/25. A higher ratio than that previously reported (Hamdan *et al.*, 1996) resulted using equivalent systems but with decane instead of limonene.

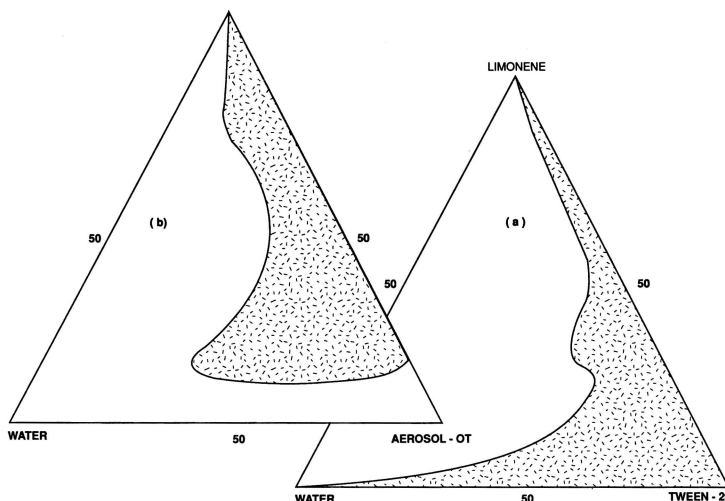


Figure 2. Partial phase diagrams of water, limonene and a third component consisting of (a) Tween 20 and (b) Aerosol-OT. The microemulsion solubility area are shown by the shaded region.

Parts a and b of Figure 3 show the pseudoternary phase diagrams formed from water, limonene and a third component consisting of a fixed amount of Aerosol-OT and Tween 20 of 20/80 and 65/35 (w/w), respectively. As can be seen from these diagrams, the isotropic region where the limonene is solubilized increases with the content of Aerosol-OT. The comparison between the decane (part c and d of Figure 3) pseudoternary systems and the limonene (part a and b of Figure 3) shows that the isotropic region covers a larger area by exchanging decane for limonene. This suggests that limonene is superior to decane with regard to the formation of the isotropic solution or micro-emulsion.

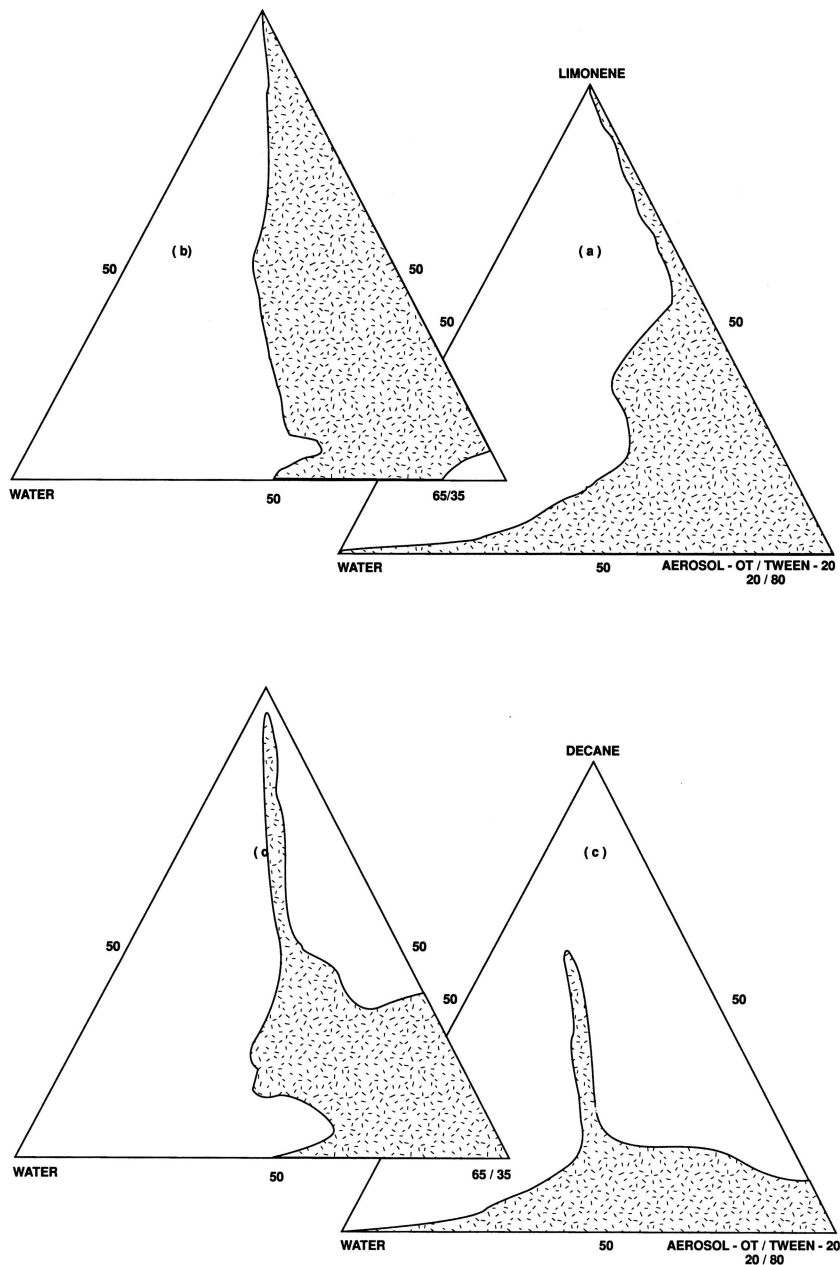


Figure 3. Partial pseudoternary phase diagrams of water, limonene and a third component consisting of mixture of Aerosol-OT/Tween 20 at weight ratios of (a) 20/80 and (b) 65/35. Part (c) and (d) are equivalent system with decane replacing limonene (Hamdan et al., 1996).

Water/Estragole Micro-emulsion

The phase diagrams with a more hydrophilic perfume, estragole, as replacement of decane in pure Tween 20 and Aerosol-OT systems are shown as part a and b of Figure 4, respectively. The isotropic solution region in the Tween 20 system (part a of Figure 4) shows a limited solubility of estragole in Tween 20 ($\cong 85\%$ by weight of estragole), while the surfactant and water are mutually completely soluble. The solubility region is curving towards the Tween 20 apex. On the other hand, the solubility region for the equivalent data with Aerosol-OT (part b of Figure 4) shows a solubilization of about 75% by weight of Aerosol-OT in estragole. Initially, the water is insoluble in estragole, but with the presence of Aerosol-OT, it becomes solubilized into inverse micelles at higher amount of surfactant; reaching a maximum value of 50% water by weight at a estragole/Aerosol-OT weight ratio of 70/30; a difference of 5% by weight to that of decane system.

The effect of the mixed surfactants, at a fixed weight ratio of Aerosol-OT and Tween 20 of 20/80 and 65/35, on the variation of the solubility region are shown in part a and b of Figure 5, respectively. Once again, the system with higher ratio of Aerosol-OT shows a higher ability to solubilize the perfume.

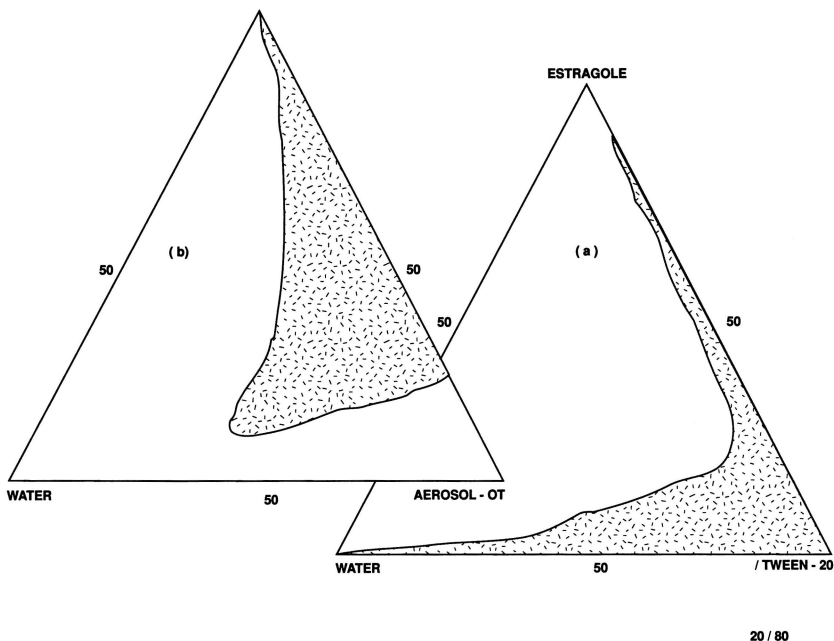


Figure 4. Partial phase diagrams of water, estragole and a third component consisting of (a) Tween 20 and (b) Aerosol-OT.

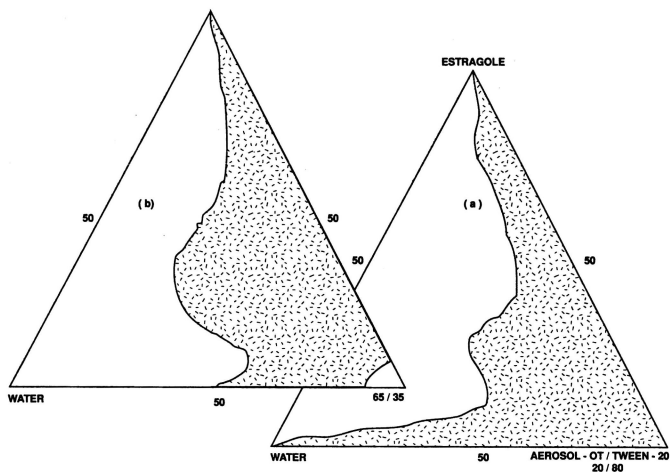


Figure 5. Partial pseudoternary phase diagrams of water, estragole and a third component consisting of mixture of Aerosol-OT/Tween 20 at weight ratios of (a) 20/80 and (b) 65/35.

Comparison between the Phase Diagrams of Decane, Limonene and Estragole

Tokuoka and coworkers (1994) suggested that the isotropic solution region is dependent on the hydrophilicity of the perfume i.e. an increase in hydrophilicity led to an extended region. As an illustration, in order to see whether there is a distinction of solubility regions on the hydrophilicity of the perfume, the corresponding phase diagrams are superimposed as shown in Figure 6. Obviously, the region with a more hydrophilic perfume i.e. estragole, failed to show any marked differences when compared to the corresponding less hydrophilic limonene. However, it is important to note that both of the water/perfume micro-emulsion regions are larger than the water/decane microemulsion.

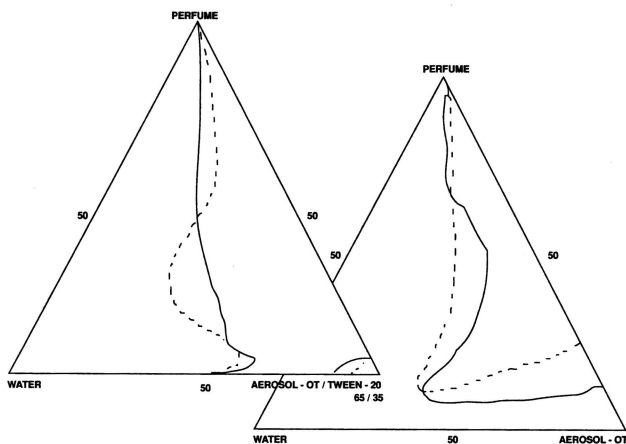


Figure 6. The solubility region for water and Aerosol-OT (and mixture) with perfumes: —, limonene and - - - -, estragole.

CONCLUSION

From the above results, it can be concluded that the perfumes are superior to decane with regard to the formation of micro-emulsion. The solubility region of the individual perfume is dependent on the weight ratio of mixed surfactant. However, no appreciable influence of the hydrophilicity of the perfume is observed within the solubility region.

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