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ESTERS IN WATER/OIL MICROEMULSION STABILISED BY ANIONIC SURFACTANT AND A MEDIUM CHAIN ALCOHOL

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RINGKASAN: *Empat ester telah dimasukkan ke dalam fasa mikroemulsi minyak dalam air yang mengandungi air/natrium dodesil sulfat (SDS):heksan-1-ol/ hidrokarbon (n-dekana dan ρ-zilena) untuk mengkaji tingkahlaku kelarutannya dalam sistem seumpama itu. Ester-ester yang digunakan ialah etil-n-butirat, etil benzoat, metil oleat dan metil linolenat. Kelarutan ester didapati bergantung pada nisbah SDS:heksan-1-ol dan hidrokarbon. Kelarutan yang tinggi didapati pada nisbah yang besar dengan etil-n-butirat menunjukkan kelarutan tertinggi. Kelarutan ini didapati berkadar songsang dengan kandungan air dalam mikroemulsi. Jenis hidrokarbon didapati tidak memberi banyak kesan terhadap kelarutan ester-ester tersebut.*

ABSTRACT: Four esters were applied in the W/O microemulsion phase of water/ sodium dodecyl sulphate (SDS): hexan-1-ol (35:65)/hydrocarbon (n-decane and *ρ*-xylene) to study their solubility behaviour in such system. The esters used were ethyl-n-butyrate, ethyl benzoate, methyl oleate and methyl linolenate. The solubility of the esters was observed to be dependent of the ratio of the SDS: hexan-1-ol and hydrocarbon. A higher solubility of the esters was observed in a larger ratio with ethyl-n-butyrate showing the highest solubility. The solubility was, however, inversely proportional to the water content of the microemulsion. The type of hydrocarbon was observed to have little or no appreciable effect on the solubility of the esters.

KEYWORDS: Microemulsion, ester, surfactant, refractive index

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INTRODUCTION

Microemulsions are isotropic, thermodynamically stable mixtures of oil and water stabilised by a surfactant, sometimes along with a cosurfactant. The cosurfactant usually consist of a short chain alcohol such as pentanol (Hoar and Schulman, 1943). Based on the content of water, the microemulsions are categorised into water-in-oil (W/O) type having low water content and oil-in-water (O/W) type having high water content. In many studies O/W type microemulsions have received tremendous attention (Fendler and Fendler, 1975). The W/O type microemulsions have not received the corresponding attention it deserved. Only in the last decade have many studies been done in the W/O microemulsion (Fendler, 1982). These previous studies, however have been confined to hydrocarbons, an obvious trend with regard to the importance of microemulsions in the tertiary oil recovery (Shah and Schecther, 1977; Shah, 1981). Recent interest have focussed on microemulsion systems based on triglycerides (Parris *et al.* 1994) and perfumes (Friberg and Gan-Zuo, 1983; Tokuoka *et al.* 1994). The latter such as esters are an important group of compounds in cosmetic and food preparations. Therefore, further evaluation of the interactions from this class of compounds in microemulsions should be an important area of research.

With that in mind, we have presented the phase equilibria of four esters namely ethyl-n-butyrate, ethyl benzoate, methyl oleate and methyl linolenate in systems containing water/sodium dodecyl sulphate (SDS)/hexan-1-ol/hydrocarbon (Hamdan *et al.* 1996). The results are consistent with the pioneering contribution by Friberg and Gan-Zuo (1983). The area of the W/O microemulsion region are dependent on the chain length of the carboxyl group of the esters. This result merits a determination of the solubilisation behaviour of the esters. Hence, in the present comparative study among esters, we extend our previous work (Hamdan *et al.* 1996) to the solubilisation behaviour of esters in W/O microemulsion stabilised by SDS and hexan-1-ol.

EXPERIMENTAL

Materials

Materials used are sodium dodecyl sulphate >99.5% (Mallinckrodt), hexan-1-ol 99% (Merck), n-decane >99% (Sigma) and ρ-xylene 98.5% (BDH). The source, purity and molecular formula of the esters are shown in Table 1 and were used as received. Doubly distilled and deionised water was used.

Table 1. Source, purity and molecular formula of the ester used.

Ester	Source	% Purity	Molecular Formula
Ethyl-n-Butyrate	BDH	> 99	$CH_3(CH_2)_2COOC_2H_5$
Ethyl Benzoate	BDH	> 99	$COOC_2H_5$
Methyl Oleate	BDH	> 99	$CH_3(CH_2)_6CH_2CH{=}CHCH_2(CH_2)_6COOCH_3$
Methyl Linolenate	BDH	> 99	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_4COOCH_3$

Method

The W/O microemulsion as the host were prepared by direct titration with the third component at variable water content. The esters as the guest constituents were then titrated to the resulting transparent and isotropic solutions. The samples were vortexed for mixing purposes and centrifuged at 10,000 rpm to separate the phases. The samples were then left to equilibrate for more than a week in a water bath, at 30 °C. The clear/turbid transition was observed visually and between a crossed polariser. Measurements of the host samples were carried out at 5460 Å and 30 °C on an Abbe (Model Atago 1T) refractometer.

RESULTS AND DISCUSSION

W/O Microemulsion Region

The W/O microemulsion region used in this investigation was formed by the addition of water to the surfactant: cosurfactant (35:65 w/w) and hydrocarbon mixture over a concentration range of 5-45 weight percent. The hydrocarbons used are n-decane and ρ-xylene. The pseudoternary phase diagram built up by using an aliphatic hydrocarbon, n-decane as an apex is shown as solid line in Figure 1. The W/O microemulsion region was found to be protruding from the n-decane free axis, between 13 to 28 percent of water, and curving upwards towards the decane apex with maximum solubility of decane up to 73 percent. A maximum in water solubility was observed at about 3-weight ratio of SDS: hexan-1-ol and n-decane. The region needed a minimum amount of water for it to form.

The broken lines of Figure 1 showed an equivalent pseudoternary phase diagram but for an aromatic hydrocarbon, ρ-xylene. A slightly smaller and narrower region for the W/O microemulsion was observed, but it still maintains the overall shape. The ratio of the SDS: hexan-1-ol and ρ-xylene for the maximum water solubility was found to be 2.33, a difference of about 22 percent as compared to the aliphatic hydrocarbon.

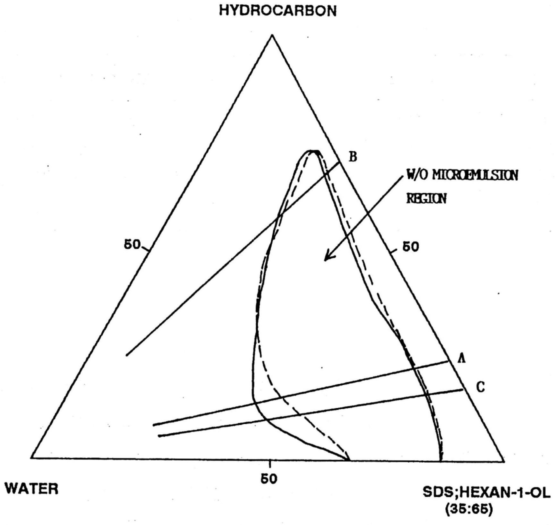

Figure 1. *Pseudoternary phase diagrams for the water/sodium dodecyl sulphate: hexan-1-ol (35:65)/hydrocarbon: (——), n-decane and (-----), ρ-xylene, indicating the W/O microemulsion region.*

Solubility of Esters in W/O Microemulsion

The solubility behaviour of all of the esters in the W/O microemulsion of the n-decane system was investigated in three series (Figure 1), selected with varying water, but with constant SDS: hexan-1-ol/hydrocarbon ratios. Series A was chosen at the maximum water solubility and the other two series with a lower (B) and higher (C) SDS: hexan-1-ol/hydrocarbon ratios. Figure 2 showed the corresponding refractive index of the host components in the W/O microemulsion of the n-decane system plotted against the percentage of water. The refractive index of the host components was observed to be decreasing with the increment of the water content. Figure 3 showed the amount of ethyl-n-butyrate solubilised plotted against percentage of water for the W/O microemulsion system with n-decane. It showed a pronounced dependence on the three ratios. A larger ratio of the SDS: hexan-1-ol to n-decane were able to solubilise higher amount of ethyl-n-butyrate. In addition, the solubility was seen to be decreasing with increasing water content, with also a gradual break between 0.2 and 0.3 water fraction for the A and C series. The break observed is satisfying since the same amount of water was reported by previous workers using conductivity technique (Shah and Hamlin, 1971) and light scattering technique (Sjöblom and Friberg, 1978), suggesting the first formation of inverse micelles or the increase in size of this association structure. The sudden decrease in the solubility of the ester (Figures 2 and 3) after the break point is therefore attributed

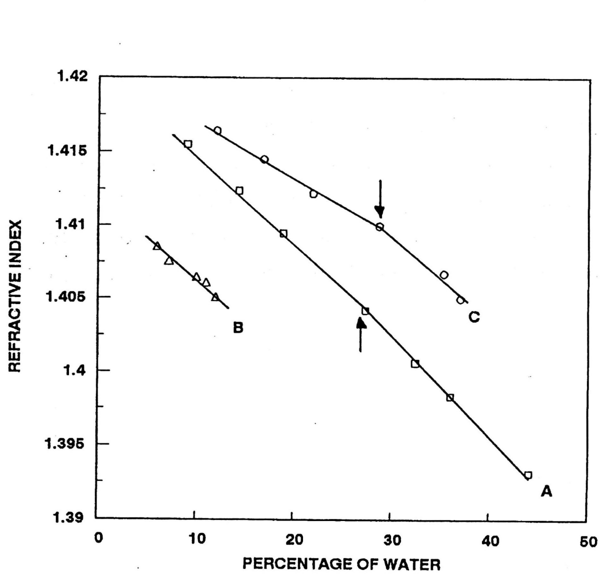

Figure 2. *Variation of the microemulsion region, containing n-decane, refractive index against water percentage.* (□) *Series A;* (Δ) *series B;* (o) *series C.*

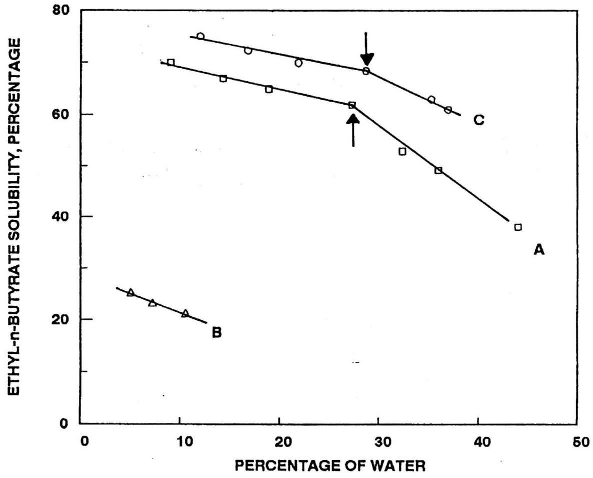

Figure 3. *The solubility of ethyl-n-butyrate in water/sodium dodecyl sulphate: hexan-1-ol (35:65)/n-decane.* (□) *Series A;* (Δ) *series B;* (o) *series C.*

to this association structure. Figures 4-6 showed the equivalent information but for a system with ethyl-benzoate, methyl oleate and methyl linolenate, respectively. More scattered points are observed for these esters but the solubility of the esters still retained its dependence on the three ratios. In order to define whether there is a distinction of solubilisation between the esters, the respective solubility of the esters at A series are chosen and plotted together as shown in Figure 7. The difference in the influence of the esters on the variation of the water content is pronounced for ethyl-n-butyrate, while the other three showed an almost similar behaviour in the microemulsion system. This observation is again in good agreement with our previous work (Hamdan *et al.*, 1996) where ethyl-n-butyrate showed the largest association region.

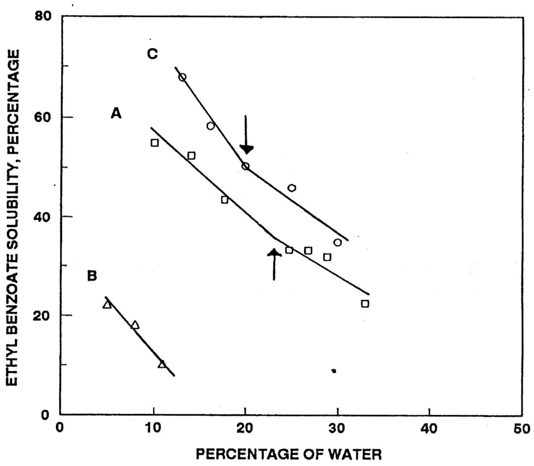

Figure 4. *The solubility of ethyl benzoate in water/sodium dodecyl sulphate: hexan-1-ol (35:65)/n-decane. (□) Series A; (Δ) series B; (o) series C.*

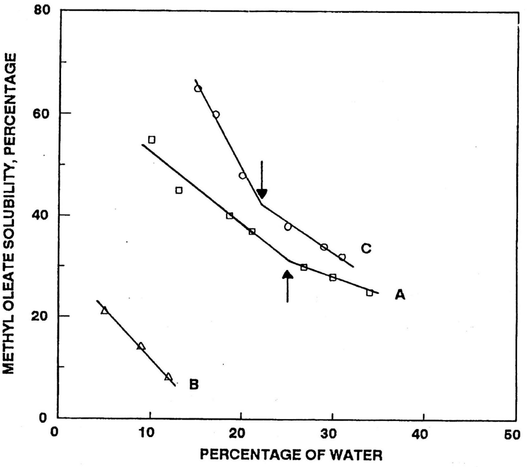

Figure 5. *The solubility of methyl oleate in water/sodium dodecyl sulphate: hexan-1-ol (35:65)/n-decane. (□) Series A; (Δ) series B; (o) series C.*

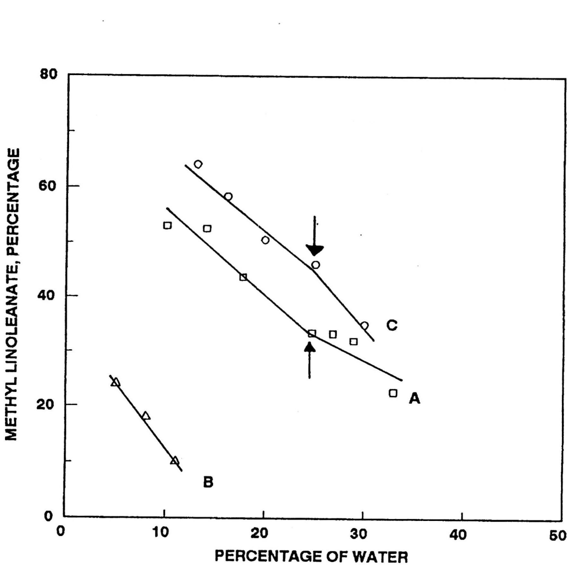

Figure 6. *The solubility of methyl linolenate in water/sodium dodecyl sulphate: hexan-1-ol (35:65)/n-decane.* (□) *Series A;* (Δ) *series B;* (o) *series C.*

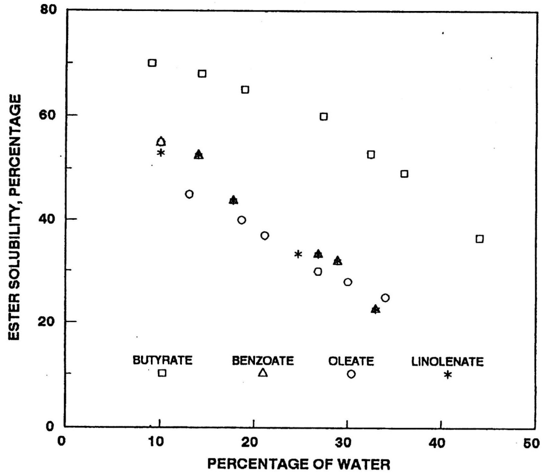

Figure 7. *The solubility of esters in water/sodium dodecyl sulphate: hexan-1-ol (35:65)/n-decane of the A series for:* (□), *ethyl-n-butyrate;* (Δ), *ethyl benzoate;* (o), *methyl oleate and* (*), *methyl linolenate.*

Similar trend was followed for the W/O microemulsion with the aromatic hydrocarbon, p-xylene. The refractive index for the host constituents (Figure 8) also showed a strong dependence on the content of water with a break at the same range of water of 20-30 percent. Figure 9 shows the solubility of all the esters, taken at A series, as a function of percentage of water. Again a break point between 20 to 30 percent of water content is observed for each ester in the series. From these data and from those obtained using n-decane (Figure 7), the differences in the ability of the W/O microemulsion of both systems to solubilise the esters are modest. This observation suggested that the solubility of the esters in such systems are independent of the type of hydrocarbon used.

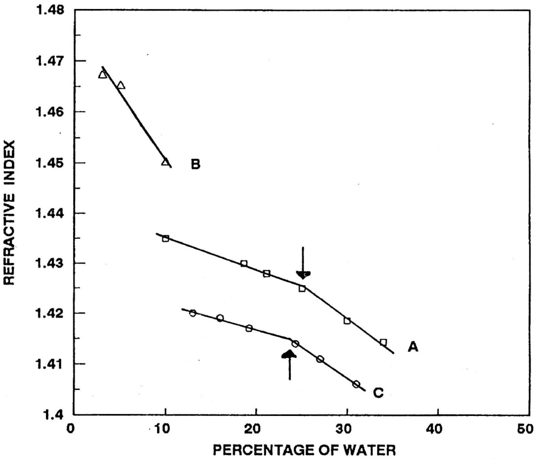

Figure 8. *Variation of the microemulsion region, containing ρ-xylene, refractive index against water percentage.* (□) *Series A;* (Δ) *series B;* (o) *series C.*

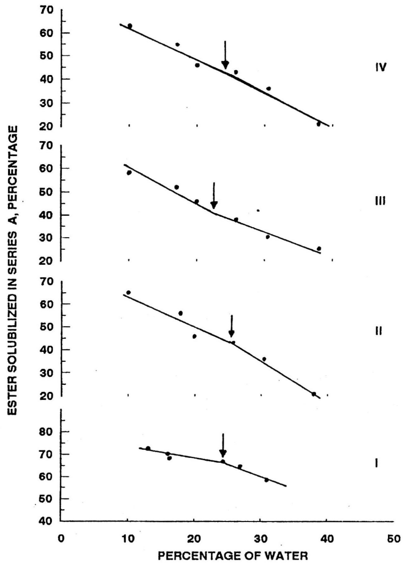

Figure 9. *The solubility of esters in water/sodium dodecyl sulphate: hexan-1-ol (35:65)/ρ-xylene at the A series of; (I) ethyl-n-butyrate; (II) ethyl benzoate; (III) methyl oleate and (IV), methyl linolenate.*

CONCLUSION

This simple study for the solubility of esters in both of the W/O microemulsion with n-decane and *p*-xylene is good evidence that the solubility of esters are dependent on the ratios of surfactant: cosurfactant to hydrocarbon. However, the type of hydrocarbon, aliphatic or aromatic, did not show any effect on the solubility of the esters. Finally, the short chain ester, ethyl-n-butyrate, exhibited the highest solubility in the W/O microemulsion compared to ethyl benzoate, methyl oleate and methyl linolenate.

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