

A Natural Flavour in an Amphiphilic Association Structure

Hamdan Suhaimi¹, Laili Che Rose and Faujan B.H. Ahmad

*Chemistry Department
Faculty of Science and Environmental Studies
Universiti Pertanian Malaysia
UPM 43400 Serdang, Selangor, Malaysia*

Received 15 February 1994

ABSTRAK

Keterlarutan satu perasa pisang, amil asetat, dalam mikroemulsi air dalam minyak bagi sistem air/natrium dodesil sulfat (SDS): heksan-1-o1 (35:65) dalam n-dekan dan *p*-zilena telah dilakukan pada 30°C. Sistem-sistem telah diuji dengan kaedah kajian fasa dan refraktometri. Keterlarutan bahan perasa didapati bergantung pada nisbah SDS: heksan-1-o1 dan hidrokarbon; keterlarutan yang tinggi didapati pada nisbah yang besar. Keterlarutan ini juga didapati berkadar songsang dengan kandungan air.

ABSTRACT

The miscibility of a banana flavour, amyl acetate, in a water-in-oil microemulsion of water/sodium dodecyl sulphate (SDS): hexan-1-o1 (35:65) in n-decane and *p*-xylene system was carried out at 30°C. The systems were tested by a phase study and refractometry method. The solubility of the flavour was observed to be connected to the ratio of SDS: hexan-1-o1 and hydrocarbon; a higher solubility of the flavour was observed in a larger ratio. The solubility was, however, inversely proportional to the water content.

Keywords: flavour, w/o microemulsion, refractometry

INTRODUCTION

A transparent system obtained by titrating an ordinary emulsion, containing approximately 1 μ m particles to clarity with particles having one to two order of magnitude smaller (100Å) by addition of a medium chain alcohol is known as microemulsion and has been reviewed in several articles (Friberg 1976; Bourrel and Schechter 1988). This transparent, homogeneous, isotropic and thermodynamically stable colloidal solution was brought to the attention of the scientific community in the late 1940s by Schulman and a series of collaborators (Hoar and Schulman 1943; Schulman and Riley 1948; Schulman and Friend 1949). It has a wide industrial application, which is mainly due to its potential ability to solubilize both hydrophilic and lipophilic portions. It has advantages over other vehicles in both better

¹Author to whom correspondence should be send

stability and solubilization characteristics. The latest of its applications is in dye processing, introduced by Barni and coworkers (Barni *et al.* 1991).

With the demand for microemulsion and its advantages, studies on the solubility of flavours often used in food products employing W/O microemulsion as a vehicle seem to be warranted. With environmental concerns in mind, we employed an accepted flavour, amyl acetate, a compound often used as banana flavour or odour in food products as well as a volatile substance in fruit juices (Ashurst 1988). It is our hope that our results will contribute to progress in this field.

MATERIALS AND METHODS

Materials

The sodium dodecyl sulphate >99.5% (Mallinckrodt), hexan-1-ol 99% (Merck), n-decane >99% (Sigma) *p*-xylene 98.5% (BDH) and amyl acetate 99% (Merck) were used as received. The high purity of the surfactant was confirmed by the absence of any detectable minimum in the measured surface tension, γ versus surfactant concentration. Doubly distilled water was used.

Methods

The liquid isotropic phases were determined by titration to turbidity for the solution part of the system. The samples were then vortexed for mixing purposes, and the borders were obtained by continuously vortexing selected composition near phase boundaries and equilibrating for more than a week in a water bath, at 30°C. The appearance of the sample was then observed visually and between cross polarizers. Measurements of the refractive index of selected composition with variable water content were carried out at 5460 Å and 30°C on an Abbe (Model Atago 1T) refractometer.

RESULTS AND DISCUSSION

Fig. 1 shows the base diagram for the inverse micellar region, L_2 for the system water/sodium dodecyl sulphate, SDS/hexan-1-ol at 30°C. The alcohol isotropic region was observed to extend from the alcohol apex to about 43% by weight of alcohol. The maximum water solubility was found at a weight ratio of 3 of SDS to hexan-1-ol, consistent with the value by a previous worker (Clause *et al.* 1988). The W/O microemulsion region was prepared by taking SDS to hexan-1-ol, weight ratio of 1.86 as an apex and combining with water and hydrocarbon. The pseudoternary diagram built up by using n-decane at the hydrocarbon apex is shown in *Fig. 2*. The solubility region of this n-decane and SDS: hexan-1-ol isotropic solution was found to be protruding from the n-decane free axis, between 13 to 28% water, and curving upwards towards the decane apex with maximum solubility of decane of 73%. A maximum in water solubility was also observed at about 3 weight ratios of SDS: hexan-1-ol and n-decane. The region also needed a minimum

amount of water for its formation. This minimum water was found to be a straight line, suggesting the importance of the water/surfactant:alcohol interactions in the formation of small aggregates (Friberg and Buraczewska 1978).

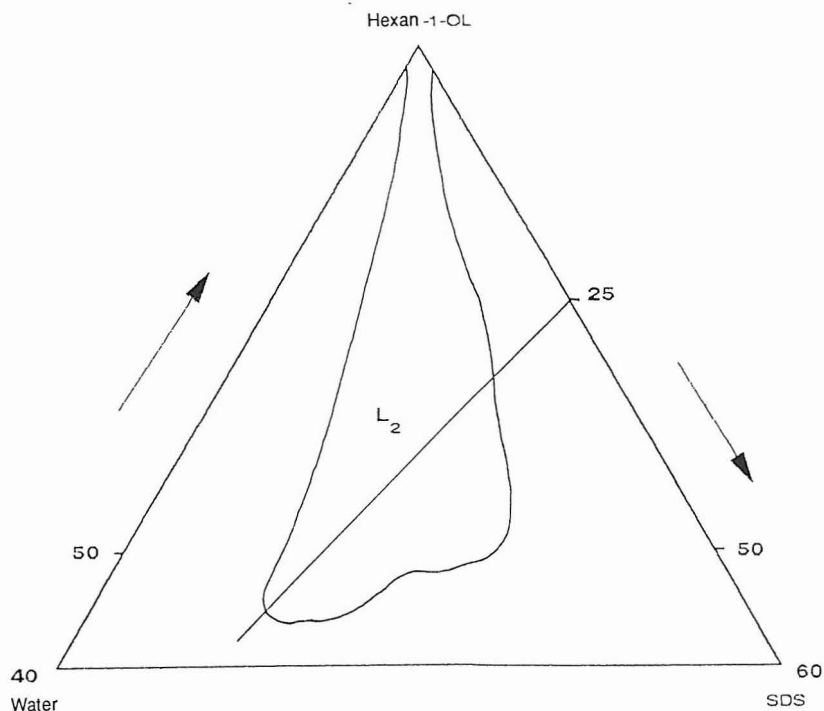


Fig. 1 Solubility region of the inverse micellar region in the system of water/sodium dodecyl sulphate, SDS/hexan-1-ol

The solubility of the flavour in this pseudoternary system was tested at a composition of 1/2, 1/1, 2/1 and 1 amyl acetate/n-decane weight ratios. The solubility region for the above compositions is shown in Fig. 3. No appreciable differences were observed by changing the amyl acetate concentration in n-decane. A slight increase in the water solubility was observed at the intermediate region of the diagram with higher value for lower amyl acetate concentration (Fig. 4). The minimum water solubility was slightly reduced, but the linearity was maintained. The n-decane to SDS: hexan-1-ol ratio for the maximum water solubility was observed to increase only by a smaller extent.

The effect of water content and its corresponding refractive index on the solubility of the flavour was investigated in three series (Fig. 5), selected with varying water, but with constant SDS: hexan-1-ol/n-decane ratios. Series A was chosen at the maximum water solubility and two other series with lower (B) and higher (C) SDS: hexan-1-ol/n-decane ratios. Fig. 5 shows solubilized

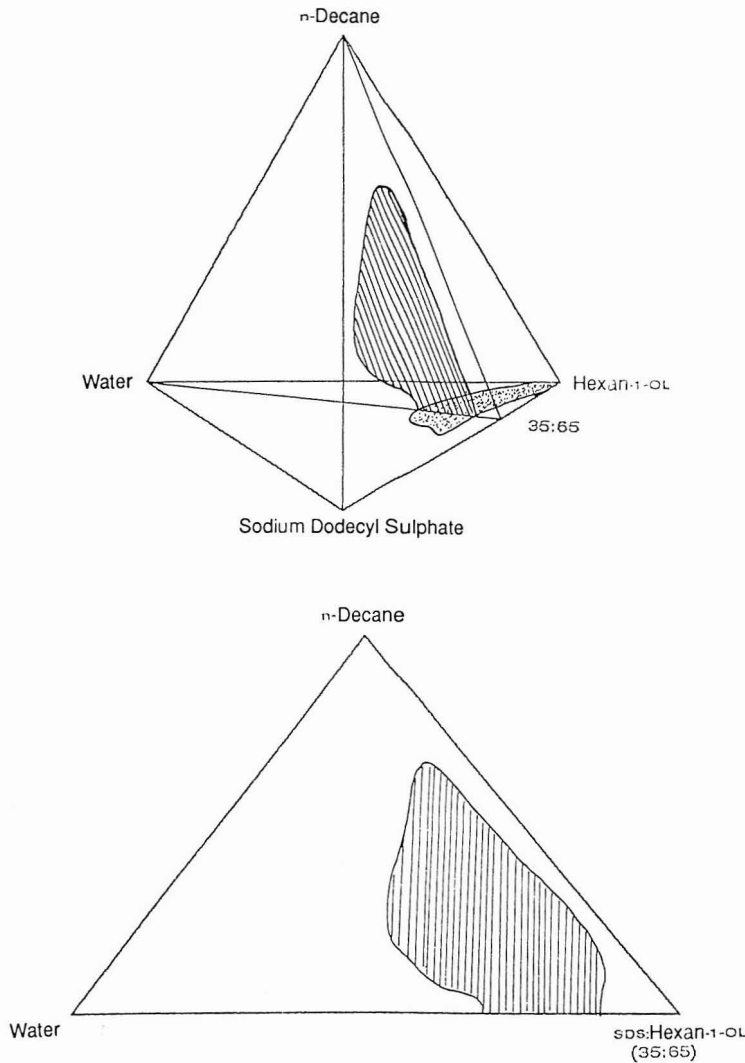


Fig. 2 Pseudoternary phase diagrams for the water/sodium dodecyl sulphate:hexan-1-ol (35:65)/n-decane indicating the W/O microemulsion region

amyl acetate plotted against percentage of water. It shows the solubility of the amyl acetate to be dependent on the SDS: hexan-1-ol/n-decane ratios. A larger ratio gives a higher solubility. The solubility was, however, seen to be decreasing with increasing water content, with a gradual break between 0.2 and 0.3 water fraction for the A and B series. The break observed is satisfying since the same amount of water was found by previous workers using conductivity technique (Shah and Hamlin 1971) and light scattering technique (Friberg and Buraczewska 1978), suggesting the first formation of inverse micelles or the increase in size of this association structure. The sudden

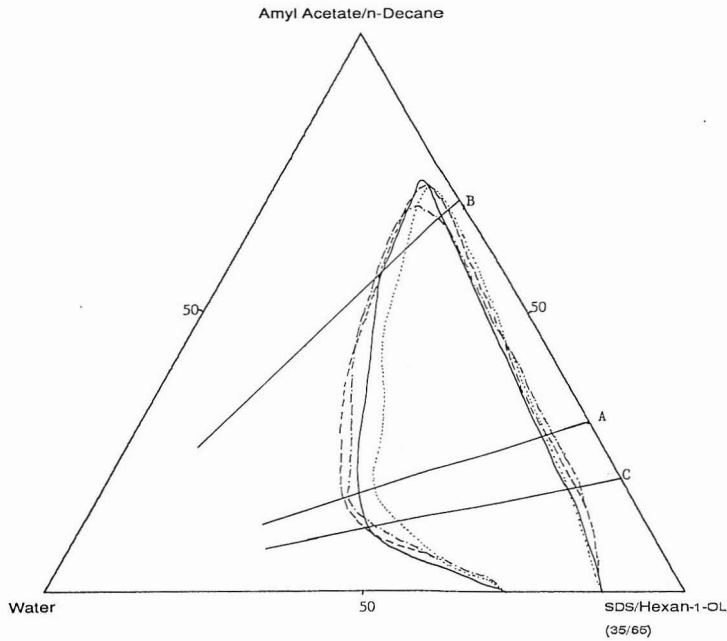


Fig. 3 Pseudoternary phase diagrams for the water/sodium dodecyl sulphate:hexan-1-ol (35:65) with amyl acetate: n-decane weight ratio of (—), 0:1; (-----), 1:2; (-·-·-·-), 2:1 and (········), 1:0

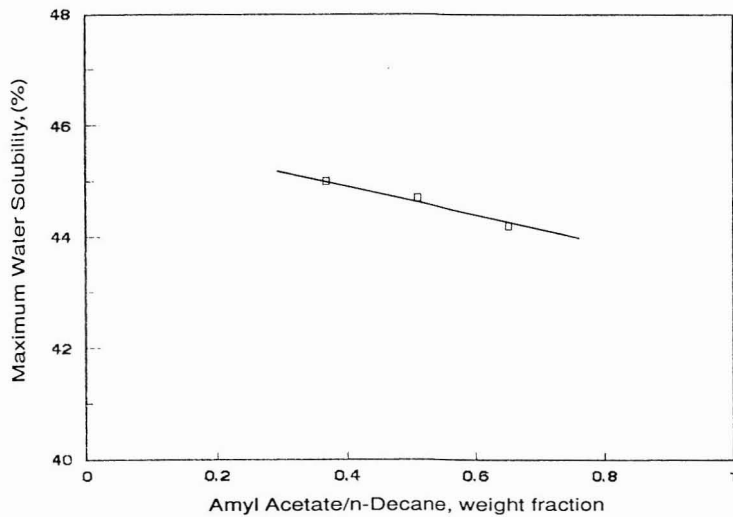


Fig. 4 Variation of maximum water solubility with weight ratio of amyl acetate to n-decane

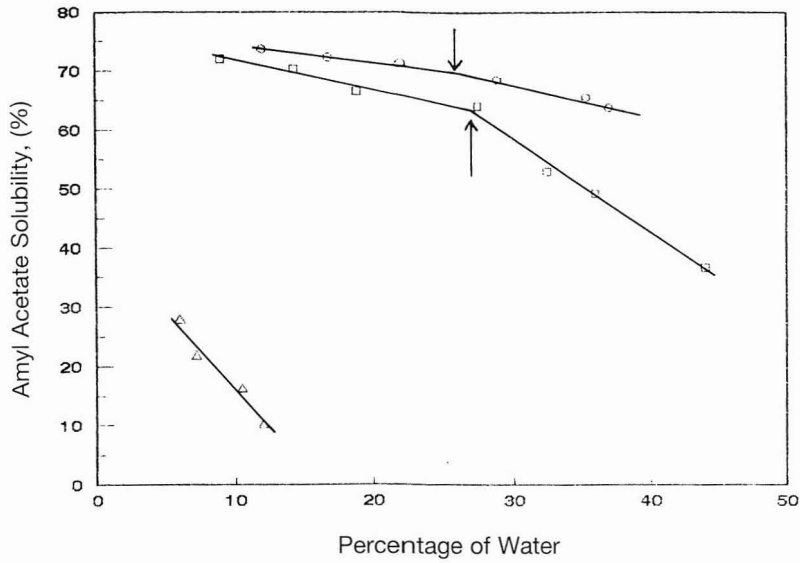


Fig. 5 The solubility of amyl acetate in water/sodium dodecyl sulphate: hexan-1-ol (35:65)/n-decane. (□) Series A; (△) series B; (○) series C

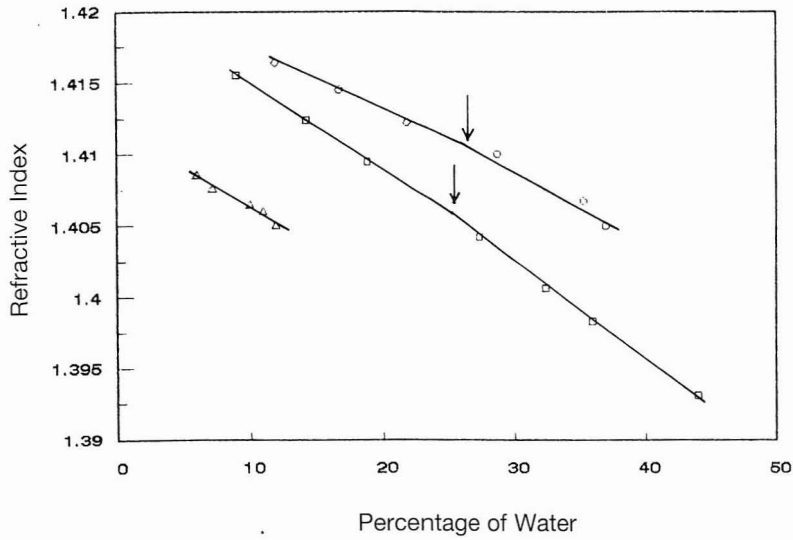


Fig. 6 Variation of the microemulsion region, containing n-decane, refractive index against water percentage. (□) series A; (△) series B; (○) series C

decrease (*Fig. 5*) in the flavour solubility after the break point is therefore attributed to this association structure. A similar result was observed in the plot of refractive index versus percentage of water (*Fig. 6*).

Upon substitution of the n-decane with *p*-xylene at the apex, a pseudoternary diagram as shown in *Fig. 7* was obtained. A slightly smaller solubility region was observed, but it still maintained the overall shape. The SDS:hexan-1-ol/*p*-xylene ratio for the maximum water solubility was found to be 2.33, a difference of about 22% compared to the aliphatic hydrocarbon. The addition of an equal weight of the flavour and *p*-xylene gave an association region as shown in *Fig. 7*. The ratio for the maximum water was still maintained; however, an increase of 2% was observed in the water uptake.

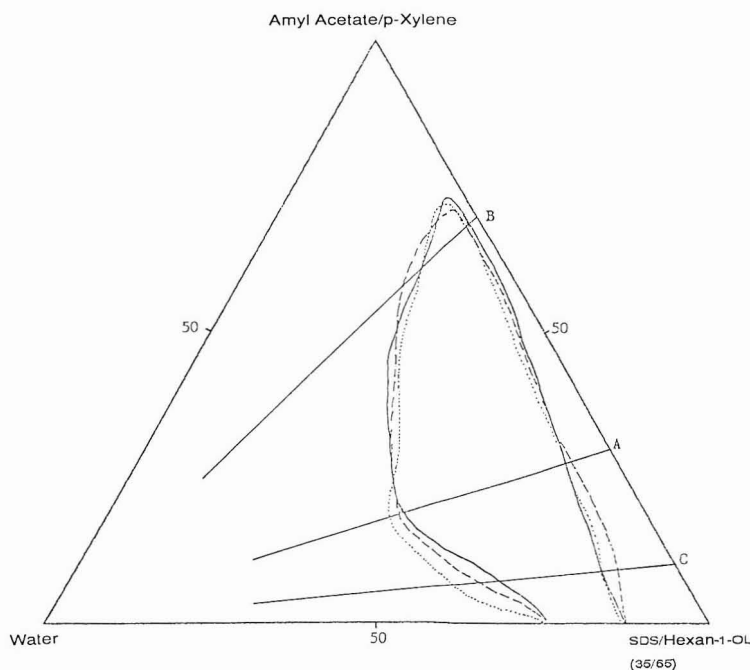


Fig. 7 Pseudoternary phase diagrams for the water/sodium dodecyl sulphate: hexan-1-ol (35:65) with amyl acetate: *p*-xylene weight ratio of: (—), 0:1; (.....) 1:1 and (-----), 1:0

The effect of water content (*Fig. 8*) and the corresponding refractive index (*Fig. 9*) on the solubility of the flavour was also investigated in three series A, B and C. The percentage of amyl acetate solubilized against percentage of water is presented (*Fig. 8*) and shows the same trend as the n-decane system. A similar break is also observed for the series A and B, which resulted in a sudden decrease in the flavour solubility with increasing water content.

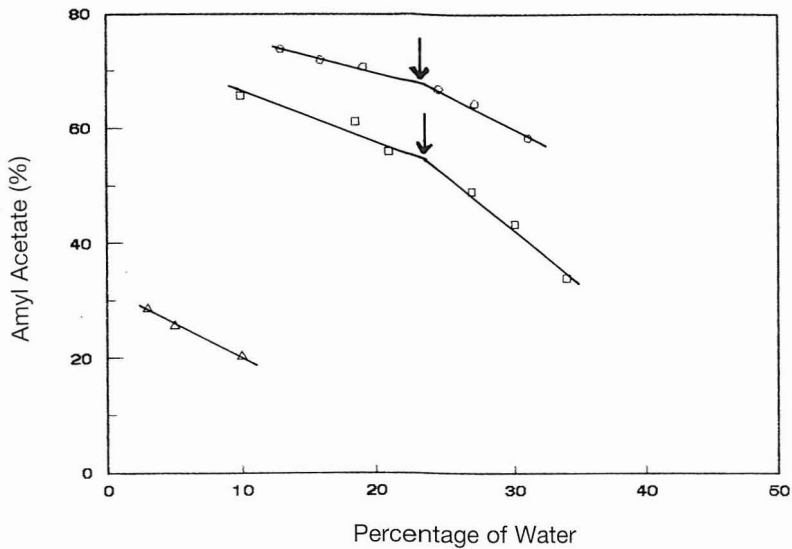


Fig. 8 The solubility of amyl acetate in water/sodium dodecyl sulphate: hexan-1-ol (35:65)/p-xylene. (□) series A; (△) series B; (O) series C

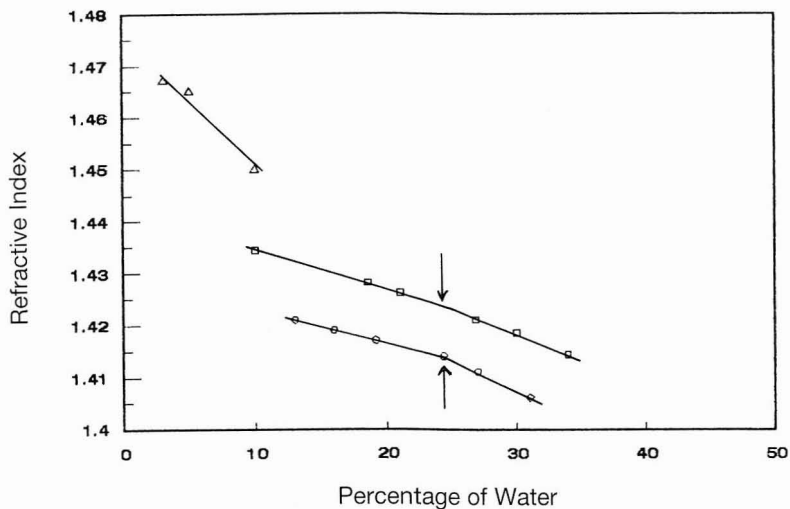


Fig. 9 Variation of the microemulsion region of p-xylene system refractive index against water percentage. (□) series A; (△) series B; (O) series C

The exact amount of water at the break point for both the aliphatic and aromatic hydrocarbon systems is not given, since it is beyond the scope of this work, and the method employed makes such comparison only conjecture. It is, however, important to note that the association structure in the hydrocarbon/SDS:hexan-1-ol is pertinent to the solubility phenomenon observed and merits further investigation.

ACKNOWLEDGEMENT

This research was supported by a grant from Universiti Pertanian Malaysia, UPM (No. 50205) and is gratefully acknowledged.

REFERENCES

- ASHURST, P.R. and I.S.C. HEREFORD. 1988. *Fruit Juices in Food Flavouring*. Glasgow: Blackie.
- BARNI, E., P. SAVARINO, G. VISCARDI, R. CARPIGNANON and G. DI MODICA. 1991. Microemulsions and their potential applications in dyeing processes. *J. Disp. Sci. Technol.* **12**: 257-271.
- BOURREL, M. and R.S. SCHECHTER. 1988. Microemulsion and related system. *Surfactant Science Series* **30**: 1.
- CLAUSSE, M., L.N. MORGANTINI, A. ZRADBA and D. TOURAUD. 1988. Microemulsion systems. *Surfactant Science Series* **24**: 15-81.
- FRIBERG, S.E. 1976. Microemulsions and their potentials. *Chemical Technology* **6**: 124-127.
- FRIBERG, S.E. and I. BURACZEWSKA. 1978. Microemulsions in the water-potassium oleate-benzene system. *Progr. Colloid Polym. Sci.* **63**: 1.
- HOAR, T.P. and J.H. SCHULMAN. 1943. Transparent water-in-oil dispersions-oleopathic hydromicelle. *Nature (London)* **152**: 102.
- SCHULMAN, J.H. and J.A. FRIEND. 1949. Light scattering investigation of the structure of transparent oil-water disperse system. *J. Colloid Interface Sci.* **4**: 497.
- SCHULMAN, J.H. and D.P. RILEY. 1948. Structure of transparent water and oil dispersions. *J. Colloid Interface Sci.* **3**: 383.
- SHAH, D.O. and R.M. HAMLIN. 1971. Structure of water in microemulsions: electrical, birefringence and nuclear magnetic resonance studies. *Science* **171**: 483-485.