LIST OF PUBLICATIONS

1. The Physicochemical Properties of a Nonaqueous Microemulsion : Cyclohexane/Triton X 100/Dimethylformamide at 40°C.

   E.I. Tessy, A.K. Rakshit; Bull. Chem. Soc. Jpn., 68, 2137, 1995.

2. Studies of Cyclohexane/TX100+ethyl propionate/water system : effect of ethylpropionate as consurfactant.

   E.I. Tessy, A.K. Rakshit; Colloid Polym. Sci. (in Press).

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The Physicochemical Properties of a Nonaqueous Microemulsion: Cyclohexane/Triton® X-100/Dimethylformamide at 40 °C

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The phase diagram of a nonaqueous microemulsion system containing cyclohexane/Triton® X-100/DMF was determined at 40 °C. The one-phase microemulsion area increased in the presence of a cosurfactant. Physical properties like viscosity, adiabatic compressibility, specific conductance, and contact angle are discussed at a surfactant concentration of 15% to explain the microstructure. A cyclohexane/TX 100+ 1-propanol/DMF system shows percolation, though not high, with ca. 0.15 mole fraction of DMF. Contact angle measurements of cyclohexane/TX 100/DMF at various cyclohexane/DMF ratios show a DMF continuous system. In the presence of a cosurfactant, the contact angle values show a continuous change indicating an 0/DMF to bicontinuous to DMF/0 structure. NaI does not introduce a three-phase liquid system.

As a continuation of our interest in the properties of microemulsions,[1—4] it was decided to study the properties of a system where water is replaced by a polar organic liquid. It is well-known that microemulsions are generally obtained by mixing water (w), oil (o), and an amphiphile (s), either ionic or nonionic. These are spontaneously forming, transparent, isotropic, homogeneous, and thermodynamically stable colloidal systems. They can be classified as w/o, o/w, and bicontinuous systems.[5] Aqueous microemulsions have gained considerable importance due to their potential applications in tertiary oil recovery. It should be noted, though, that not as many studies have been done on nonaqueous microemulsions. Rico and co-workers[6,7] have studied chemical reactions in nonaqueous microemulsion systems where water was replaced by formamide. Friberg and Liang[8] used glycerol with anionic surfactants and Holmberg et al.[9] studied chemical reactions using a mixture of water and glycerol as the polar solvent. Recently, Schubert and co-workers[10—12] studied nonaqueous microemulsions of formamide with ionic and nonionic surfactants. The present study involves Triton® X-100 (TX 100) as the amphiphile and dimethylformamide (DMF) as the polar liquid. Cyclohexane is the nonpolar liquid. By studying the physicochemical properties one can understand the microstructure in a microemulsion system. Hence we decided to study phase diagram, conductance, viscosity, adiabatic compressibility, and contact angles to get valuable information on the microstructure of the cyclohexane/TX 100/DMF nonaqueous microemulsion system. We have also studied the effect of the presence of 1-propanol on the properties of the above system.

Experimental

Dimethylformamide was obtained from Qualigens, India. It was distilled just before use. Triton® X-100 was obtained from Kochlight Laboratories U.K., and was used as received. Cyclohexane and 1-propanol (E. Merck, India) were distilled before use.

i) Phase Diagrams. Ternary phase diagrams of the microemulsion stabilized by TX 100 were constructed at 40±0.05 °C. The microemulsion was prepared in a stoppered glass test tube. A known amount by weight of surfactant and cyclohexane were added to the test tube and this was then placed in a thermostated bath. After the sample attained the temperature of the bath, it was titrated with DMF kept in a burette in a dry atmosphere. Such titrations were also done when the effect of 1-propanol was determined. In this case, TX 100, 1-propanol (two times by weight of TX 100), and cyclohexane were placed in the test tube, which was stoppered and placed in the thermostat. The stopper was always taped with Teflon® tape to minimize the escape of the liquid vapor. This was then titrated with DMF. The process was repeated with different weight ratios of surfactant and oil (the surfactant–propanol ratio always being two) to cover the entire phase diagram and to determine the phase boundaries. The end point of the titration was the disappearance of turbidity and was visually obtained.

ii) Physical Properties. The viscosities of these systems were measured at 40±0.05 °C with an Ubbelohde viscometer placed in a thermostated bath assuming Newtonian behavior. The flow time was determined visually with the help of a hand-held stopwatch. The viscosity of water (at 40 °C) was taken to be 0.06529×10^{-2} Pas[13] and this was used for the calculation of the viscosity of the microemulsions. The error in the flow time was less than ±0.1 s.

Conductance was measured with a Mullard conductivity bridge at 40 °C. NaI was used as the added electrolyte for the conductivity studies of the system. The concentration of NaI was kept at 0.01 M under all conditions (1 M=1 mol dm^{-3}) The phase diagram of the system did not change markedly with such a small amount of NaI.

The adiabatic compressibilities of the microemulsions with various weight fractions of DMF were obtained by measuring the ultrasonic velocities, u, with a multifrequency interferometer (MX 3. Mittal Enterprises, New Delhi, India). The densities. ρ, of the solutions at 40 °C were determined with the help of a pycnometer. The compressibility, β, was computed from the relation $\beta=1/\rho u^2$. The average of 5 different independent readings were taken as β. The error in β was computed to be less than 1%.

The contact angles of the microemulsions with a poly(tetrafluroethylene) (Teflon®, obtained from samson India) surface were determined by using a contact θ meter obtained as a gift from the Department of Color Chemistry, Leeds University, Leeds, U.K. The surface was treated with chromic acid and then with copious quantities of water, and acetone and dried before use. At least 10 different drops on various parts of the Teflon® surface were made for a particular microemulsion and the contact angles were determined. The average of these readings are reported. The error in these values was ±2°. The contact angles were studied at room temperature (ca. 25 °C).

Results and Discussion

The phase diagram of the DMF/TX 100/cyclohexane system is shown in Fig. 1a Above the boundary line, the system exists as a one-phase microemulsion and below it, there is a biphasic region. The surfactant apex shows a single phase region and this gradually extends to the DMF corner. At higher concentrations of cyclohexane, the solubility decreases and a liquid–liquid biphasic region exists where the microemulsion is in equilibrium with excess oil. Formation of a one-phase micellar system in a cyclohexane–DMF mixed solvent is possible. However. the concentration is low and cannot be shown in the phase diagram at this scale.

Figure 1b shows the effect of 1-propanol on the phase diagram. The one-phase microemulsion area covers almost 90% of the phase diagram. Below 10% surfactant concentration, there exists a liquid–liquid biphasic region around the 50% cyclohexane concentration range. As the cyclohexane concentration increases and that of DMF decreases, more monophasic microemulsion area becomes available. Addition of a short chain alcohol increases the efficiency of the amphiphile. It enters the amphiphilic monolayer and reduces the interfacial tension between cyclohexane–DMF further[14] which results in a larger one-phase area.

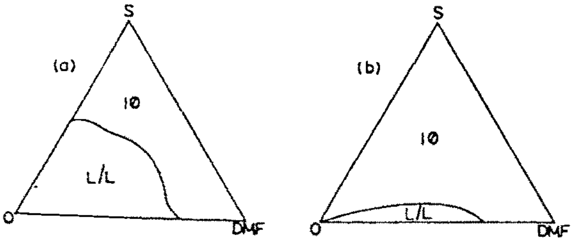

Fig. 1. a) Pseudoternary phase diagram of cyclohexane (O)/Triton® X 100 (S)/DMF system at 40 °C. b) Pseudoternary phase diagram of cyclohexane (O)/Triton® X 100+1-propanol (S)/DMF system at 40 °C.

In Fig. 2, the viscosity variation with varying DMF composition (and hence cyclohexane) is shown. The surfactant[15] concentration was kept constant at 15%. It is clear that the viscosity remains almost constant indicating that the change in DMF content does not have any observable effect on the microstructure of the microemulsion. This suggests that the microemulsion is bicontinuous in nature. In the presence of 1-propanol, the viscosity is somewhat lower. This may be due to the use of less Triton® X-100 (ca. 5%) whereas 1-propanol was ca. 10%. In this case, there is a continuous decrease in the viscosity with the addition of cyclohexane. It was mentioned earlier that in the case of an aqueous microemulsion,[16,17] a decrease in viscosity was generally due to a decrease in the size of the water conduit. However, in this case the decrease in viscosity may be due to structural changes of the microemulsion as the O/D ratio increases. It is not prudent to make more specific comments as the changes in viscosity are not large. The dilution effect brings the viscosity down in the case of an aqueous system,[16] though this was not observed here within the concentration range studied.

In Fig. 3, the adiabatic compressibilities of various microemulsion systems with different DMF–cyclohexane ratios at a constant surfactant concentration (15% w/w) are shown. It is obvious that the adiabatic compressibility decreases with an increase in the DMF concentration. DMF is a relatively more structured sol-

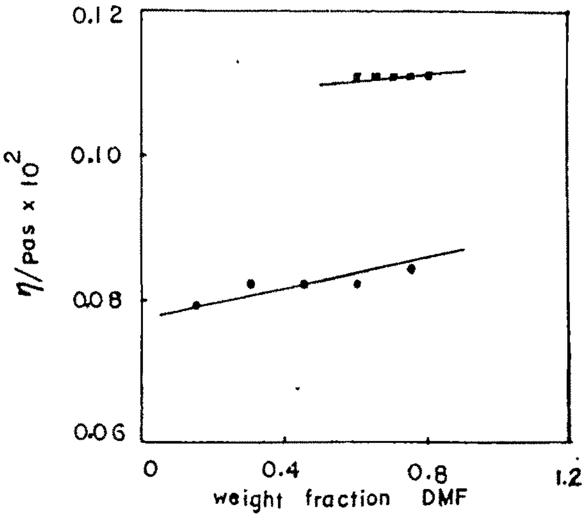

Fig. 2. Plot of viscosity (η) versus weight fraction of DMF. ● Cyclohexane/TX 100+1-propanol/DMF. ■ Cyclohexane/TX 100/DMF.

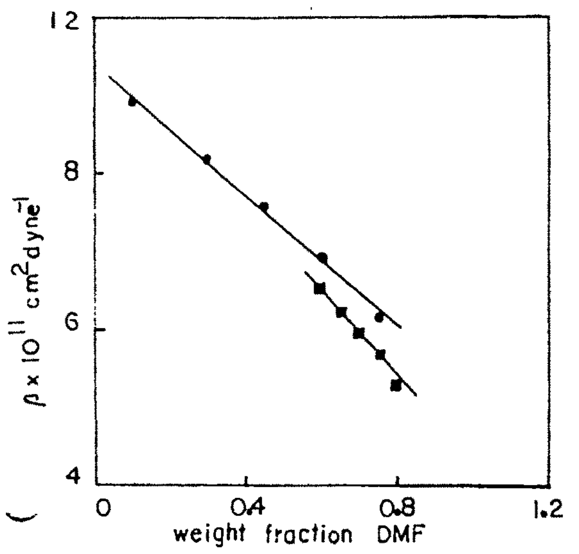

Fig. 3. Plot of adiabatic compressibility (β) versus weight fraction of DMF. ● cyclohexane/TX 100+ 1-propanol/DMF. ■ cyclohexane/TX 100/DMF.

vent than cyclohexane and hence the compressibility decreases. This is basically a gross property[2,16] and it does not give much indication of the microstructural nature of the medium.

Figure 4 shows the specific conductances increase from a low DMF content to a high DMF content with 15% S. NaI (0.01 M) was used as the electrolyte. The systems do not show any percolation behavior which suggests a single structured form at the different compositions studied. The specific conductance increases gradually as the DMF concentration is raised. This suggests the absence of percolation. The increase is much sharper in the systems where a cosurfactant, 1-propanol, was present. This indicates that percolation cannot be totally neglected when 1-propanol was also present. However, we did not observe any percolation in an Alkane/Brij 35+1-propanol/water nonionic aqueous microemulsion.[3] The steady increase in conductance with the addition of DMF suggests a similar type of structure over the entire cyclohexane/DMF range studied. In the aqueous microemulsion[3] mentioned above, percolation was observed at high w/s ratios. We have not studied a system with a higher DMF/surfactant wt. ratio. However in the presence of 1-propanol, the DMF/TX 100 ratio becomes much higher. When NaI is the electrolyte, it resides in the DMF pool of the microemulsion. The structure is bicontinuous [and a DMF continuum]. At a high cyclohexane concentration, a change [to a cyclohexane continuum] also seems to occur as the O/D ratio becomes very high.

It was suggested by Ninham et al.[18,19] that the specific conductance of a microemulsion, k, is proportional to the volume fraction of the polar solvent DMF, ϕ_{D}, i.e. $k \propto (\phi_{\mathrm{D}} - \phi_{\mathrm{D}}^{\mathrm{P}})^t$ where $\phi_{\mathrm{D}}^{\mathrm{P}}$ is the percolation threshold, i.e. the concentration above which percolation can be seen. It was also suggested that for a bicontinuous system $t=8/5$, i.e. $k \propto (\phi_{\mathrm{D}} - \phi_{\mathrm{D}}^{\mathrm{P}})^{8/5}$ or $k^{5/8} = A(\phi_{\mathrm{D}} - \phi_{\mathrm{D}}^{\mathrm{P}})$ where A is the proportionality constant. Thus a plot of $k^{5/8}$ versus ϕ_{D} should meet the X-axis at $\phi_{\mathrm{D}}^{\mathrm{P}}$. Figure 5 presents such a plot. For a system without 1-propanol, a negative $\phi_{\mathrm{D}}^{\mathrm{P}}$ is obtained indicating no percolation at all. However, for a DMF/TX 100+1-propanol/cyclohexane system, a low $\phi_{\mathrm{D}}^{\mathrm{P}}$ is observed at 0.15 mole fraction DMF. This indicates that the percolation threshold does exist in this case though percolation is not very high. This indicates some type of change in the structure from a

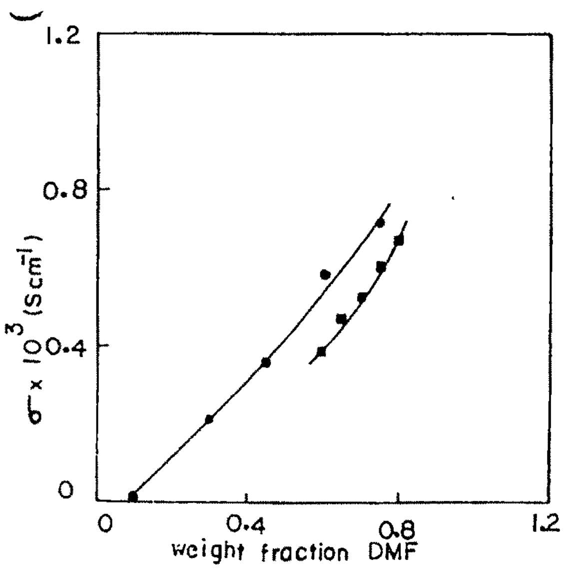

Fig. 4. Plot of specific conductance (k) versus weight fraction of DMF. ● cyclohexane/TX 100+ 1-propanol/DMF. ■ cyclohexane/TX 100/DMF.

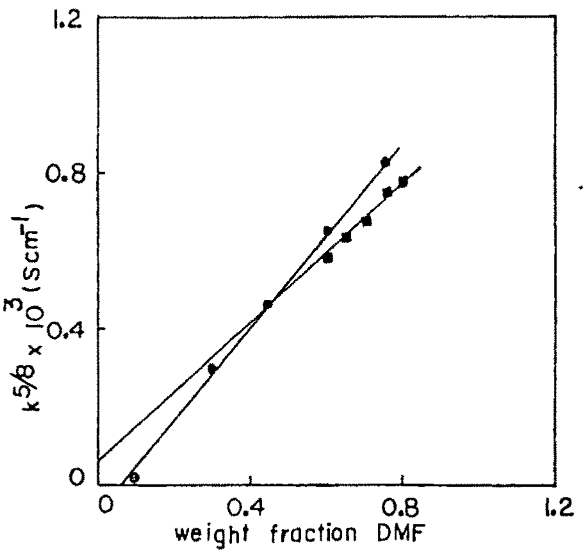

Fig. 5. Plot of (specific conductance, $k^{5/8}$) versus weight fraction of DMF. ● cyclohexane/TX 100+ 1-propanol/DMF. ■ cyclohexane/TX 100/DMF.

Table 1. Contact Angle (θ) of Microemulsions with Teflon® at Room Temperature

System a Cyclohexane/TX 100/DMF (O) (S)				System b Cyclohexane/TX 100+1-propanol/DMF (O) (S)			
O	S	DMF	θ/°	O	S	DMF	θ/°
0	0	100	132	0	0	100	132
5	15	80	131	10	15	75	121
10	15	75	118	25	15	60	103
15	15	70	117	40	15	45	89
20	15	65	114	55	15	30	86
25	15	60	99	70	15	15	65
100	0	0	56	100	0	0	56

DMF continuum to a cyclohexane continuum through a bicontinuous form. Peyrelesse[20] et al. also observed percolation in a nonaqueous microemulsion.

Table 1 shows the contact angles, θ, of various microemulsions with a Teflon® surface. The microemulsions without 1-propanol (Table 1a) have values almost as high as that of pure DMF with Teflon®. This suggests to us that the DMF of the microemulsion is in contact with the teflon. In presence of 1-propanol (Table 1b), the θ values are similar to those in Table 1a up to 25% cyclohexane. This indicates that both microemulsions have a similar structure up to this composition range. Further addition of cyclohexane changes the contact angle in a gradual fashion (Table 1b). Hence we assume that an O/D to D/O structural change occurs and in the middle composition range a bicontinuous system may be present where the surfactant (i.e. TX 100 with 1-propanol) is 15% by weight.

The addition of an electrolyte generally has a drastic effect on an aqueous microemulsion involving phase inversion and formation of three-phase systems. However, earlier authors have failed to get a three-phase system by addition of electrolytes to nonaqueous microemulsions.[21] We have confirmed this. The addition of NaI to a one-phase microemulsion, both in the presence and absence of 1-propanol, did not lead to a three-phase system. We also used urea to see whether any effect was observed on the phase. Again, no phase seperation was observed at all. To our knowledge, no nonaqueous microemulsion has shown phase separation by the addition of an electrolyte as is observed in aqueous microemulsions.

Conclusion

Microemulsions can be formed with a polar organic liquid like DMF and show physical properties somewhat similar to those of aqueous systems. The presence of 1-propanol as a cosurfactant changed the area of a one-phase microemulsion drastically, increasing it by almost 2 times. The physical properties changed, but the similarity of the changes in the properties remained the same as a function of the DMF concentration. However, the effect of an electrolyte which shows phase changes in an aqueous microemulsion was not observed in this nonaqueous microemulsion. The presence of 1-propanol as cosurfactant induces the presence of O/D, bicontinuous, and D/O structural patterns.

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ORIGINAL CONTRIBUTION

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Studies of cyclohexane/TX 100 + ethylpropionate/water system: effect of ethylpropionate as cosurfactant

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Abstract Pseudoternary phase diagram of cyclohexane/TX 100-ethylpropionate/water system was determined at 30 °C. One phase microemulsion was obtained over a small area. The surfactant/cosurfactant ratio was both kept at 1:1 and 1:2 w/w. Viscosity, conductance, adiabatic compressibility values at various temperatures show the expected trend. The addition of NaCl changes one phase microemulsion to Winsor II system and no Winsor III system was obtained. Contact angle data, conductance, etc., show oil continuous system at a constant surfactant weight fraction. The microstructure of Winsor IV microemulsion seems to be W/O.

Key words Microemulsion – cosurfactant – ester – TritonX 100 – cyclohexane

Introduction

As a part of our general interest [1–5] in microemulsion, we studied cyclohexane/TX 100 + ethylpropionate/water system, both in the absence and the presence of ethylpropionate, to determine the effect of ester as a cosurfactant. Microemulsions are isotropic thermodynamically stable dispersion of oil, water, surfactant (S) and cosurfactant (CS). These are generally spontaneously forming low viscous solutions. Short-chain alcohols and amines are generally used as cosurfactants [6, 7]. Significant amount of research publications are available with short-chain alcohols as cosurfactant [1–5, 8–12]. Ester as cosurfactant in microemulsion formation is not well explored though there is high technological importance [13]. The cosurfactant helps in the decrease of interfacial tension between oil and water and thereby increase the efficiency of surfactant in dissolving one into the other. It also helps in the destruction of the order of liquid crystals. In this paper, we present the properties of a microemulsion system with ethylpropionate as cosurfactant. As esters are commonly used in cosmetics and in pharmaceutical field [14–16], the present study helps in understanding and relating the properties with their use. Structure of these colloidal systems are determined by studying the physicochemical properties like viscosity, specific conductance, adiabatic compressibility, phase volume measurements and contact angle.

Experimental section

Triton X 100 (TX 100), $CH_3C(CH_3)_2$ $CH_2C(CH_3)_2$–ϕ–$O(CH_2CH_2O)_{9.5}H$, were obtained from Sigma. It was used as received Ethylpropionate (National Chemicals, Baroda b.p. 99 °C (Lit. 99.1 °C) [17]) and cyclohexane (Merck, India b.p. 81 °C (Lit. 80.74 °C [17])) were distilled before use. Water used was triply distilled from alkaline $KMnO_4$.

Phase diagram

A simple titration technique was used for the preparation of microemulsion [4, 18, 19]. A known amount of oil or

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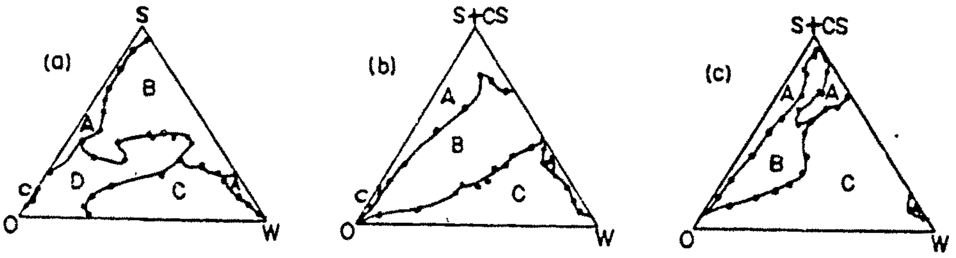
Fig. 1 Pseudoternary phase diagram of cyclohexane (O), TX100 (S) + ethylpropionate (CS) water system at 30 °C. (a) S/CS = 1:0 (w/w), (b) S/CS = 1:1, (c) S/CS = 1:2 (w/w), A = 1φ region; B = viscous, C = L/L, D = L/Visc



water was taken with surfactant (i.e., S or S + CS) in stoppered test tubes kept in a temperature-controlled water bath (30 ± 0.05 °C). The mixtures were then titrated with water or oil, respectively, from a microburette. After each addition, the mixtures were allowed to attain the temperature. Teflon tape was used to seal the test tubes to stop evaporation. The appearance or disappearance of turbidity marks the boundary of microemulsion region and the amount of water or oil consumed at this juncture was noted. The weight percentage of each component was then calculated and plotted in a triangular graph. A pseudoternary phase diagram of cyclohexane–water system in the presence of TX 100 and ethylpropionate was constructed at 30 ± 0.05 °C. The TX 100 to ethylpropionate ratio was kept at 1:0, 1:1 or 1:2 (w/w) (Fig. 1).

Physical properties

Physical properties of the system with 1:1 and 1:2 (w/w) surfactant to cosurfactant ratios were studied. The viscosities of these systems were measured at various temperatures with an Ubbelohde viscometer placed in a thermostated bath (30 ± 0.05 °C) assuming Newtonian behaviour. A pyknometer was used for determining the density.

Conductance measurements of microemulsion samples along the entire monophasic region were performed with a Mullard, England, conductivity bridge and a conductivity cell of cell constant 0.1417 cm^{-1}.

An ultrasonic interferometer (Mx 3, Mittal Enterprises, India) was used for the ultrasound velocity measurements and the adiabatic compressibilities were calculated by the relation $\beta = 1/\rho u^2$ where ρ and u are the density and ultrasound velocity, respectively.

The contact angles of one phase microemulsion with a polytetrafluoroethylene (teflon) surface were determined by using a contact θ meter [2] obtained as a gift from the Department of Colour Chemistry, Leeds University, UK. The surface of Teflon tape was treated with chromic acid and then with copious quantities of water, with acetone and dried before use. At least 10 different drops on various parts of the Teflon tape surface were made with a given liquid and the contact angles were determined. The average of these readings are reported (± 2°). Calibrated graduated stoppered test tubes were used for the phase separation studies. Compositions were prepared and kept at the required temperature. After attaining the desired temperature, these were shaken and re-equilibrated. The average of two runs was taken as the final volume. The error in volume was always less than 1%.

Results and discussion

Figures 1a–c is a pseudoternary phase diagram of cyclohexane/TX 100 + ethylpropionate/water at 30 °C. No ethylpropionate was present in the phase diagram shown in Fig. 1a but in Fig. 1b and c the surfactant to cosurfactant weight ratio was 1:1 and 1:2, respectively. At the surfactant apex, we get a one phase microemulsion extending towards the oil corner (Fig. 1b) for 1:1 system. The centre of the phase map shows a large viscous region. The base of the phase diagram shows a liquid/liquid biphasic region. A small one phase microemulsion area at the water corner was also observed. The viscous fluid was found to be birefringent with polarizing microscope. Ethylpropionate is highly hydrophobic and seems not to have much effect on oil–water interfacial tension. Hence, it is difficult to get one phase microemulsion with small percent of surfactant. With high surfactant concentration interfacial tension gets reduced to a low value and it solubilizes both oil and water and forms a monophasic region around the surfactant apex. With very small amount (i.e., very low percentage) of cyclohexane, interfacial tension is sufficiently reduced to solubilize both the water and cyclohexane in presence of TX 100 at the interfacial film. However, with 1:2 surfactant–cosurfactant weight ratio, the phase map becomes very complicated. One phase microemulsion region is a very narrow strip along the oil–surfactant axis. However, the overall 1ϕ area remains essentially same in both cases. A large liquid–liquid biphasic area was obtained. This seems to arise at the cost of viscous region of Fig. 1b. This indicates that the addition

Table 1 % area of various regions of pseudoternary phase diagrams of Figs 1a–c

Region	Fig 1a	Fig 1b	Fig 1c
A 1φ	8 8	22 4	22 2
B Visc	35 3	40.3	32 0
C 2φ (L/L)	30 7	37.3	45 8
D 2φ (L, Visc)	25 2	–	–

of ethylpropionate helps in the formation of microemulsion Higher percentage of ethylpropionate decreases the solubility of cyclohexane and water in presence of TX 100 due to its higher hydrophobicity. In Table 1, the percent area of various regions of phase diagrams are presented. We believe that the one phase liquids obtained (area A of the Figs. 1a–c) are microemulsions and are not molecularly dispersed simple solutions. This is because by definition a homogeneous mixture of oil and water in presence of a surfactant is microemulsion [20]. Moreover it was found that TX 100 forms reverse micelles in cyclohexane, ethylpropionate and mixture of the two (1:1 v/v). By iodine solubilization method [21] reverse critical micelle concentration was found to be 1 6, 2.0 & 2.51 mM at 30 °C. This shows that the system is microemulsion with the possibility of droplet formation.

Specific conductance of one phase microemulsion samples for the system where surfactant/cosurfactant ratio was 1:1 is plotted against water volume fraction in Fig. 2 at various temperatures with 80% S + CS composition. Percolation, a sudden increase in electrical conductivity [22–24], as a function of water concentration was absent. The absolute magnitude of conductance was low. However, the electrical conductivity increased with increase of water oil ratio. This indicates the same structure over the entire o/w range studied at this surfactant concentration. Non-percolative conductance variation in these systems and also the very low conductance indicate a water-in-oil structure. An interesting feature of the graph is the higher conductance at low temperature. This also indicates w/o microemulsion.

Specific conductance of one phase microemulsion for 1 2 S to CS ratio was studied with constant water fraction of 2.5% by weight. It was not possible to look at the variation of conductance over the whole oil/water region at a fixed surfactant composition as can be noted from Fig. 1c. At this low weight percent of water no measurable conductance was observed with 0 1 and 1 M NaCl. The NaCl concentrations are with respect to water only. Speci-ic conductance of one phase microemulsion with 1:1 S to CS ratio for constant water fraction of 2.5% by weight does not also show any conductance. This may be due to he nature of the system which is water-in-oil microemulsion. The concentration of water is very low and it is dispersed over the whole oil region. Therefore, the ions of the electrolytes have not much freedom of transport and hence cannot induce any observable conductance.

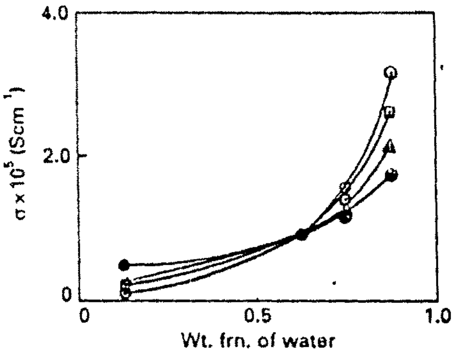


Fig. 2 Plot of specific conductance (σ) vs. weight fraction of water with S CS = 1:1 (w/w) at various temperatures ● 30; □ 35; △ 40; ⊗ 45 °C

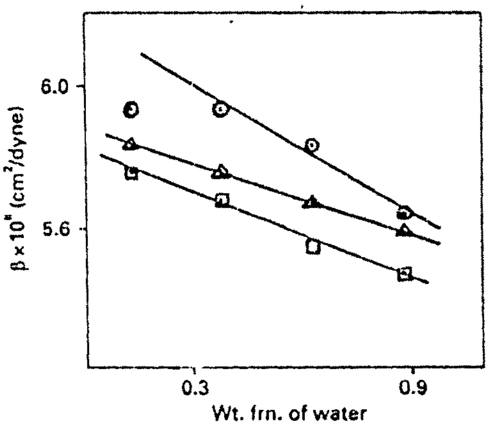


Fig 3 Plot of adiabatic compressibility (β) vs weight fraction of water at various temperatures (S CS = 1.1) □ 35, △ 40, ⊙ 45 °C

In Fig. 3, the linear variations of adiabatic compressibility (β) with water weight fraction at various temperatures at 80% S + CS concentration are shown. This linearity indicates that the increase of water fraction decreases adiabatic compressibility. This is expected as β is a macroproperty. Water is more structured than cyclohexane. Therefore, higher w/o ratio will induce less compressibility. Increase of temperature increases the hydrophobicity of the interfacial surfactant film due to dehydration of the polyethylene oxide chain of TX 100 [25] Moreover, rise in temperature should provide kinetic energy to loosen the interfacial film. Also at higher temperatures, the water is less structured. These effects are expected to enhance the penetration of the cyclohexane

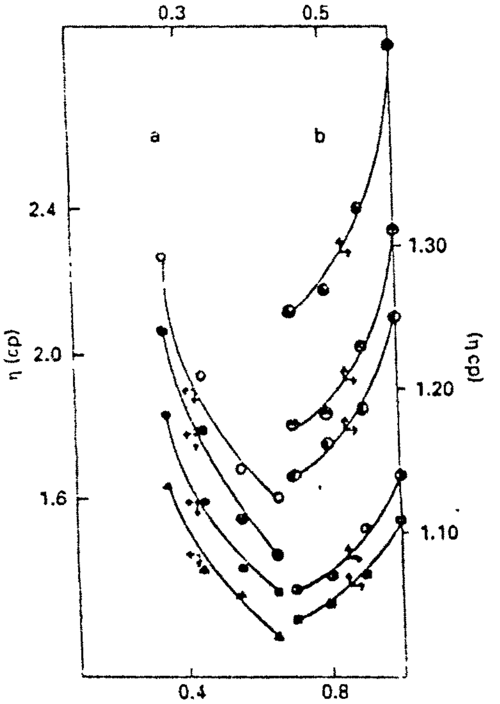


Fig. 4 (a) Plot of viscosity (η) vs weight fraction of oil (S:CS = 1:1) ○ 30, ◉ 35, ● 40, △ 45 °C (b) Plot of viscosity (η) vs. weight fraction of oil (S:CS = 1:2) ◒ 30, ◓ 32.5; ◐ 35, ◑ 37.5, ■ 40 °C

molecules into the interfacial film, swelling the dispersed phase and therefore the compressibility will be higher at higher temperature. From Figs. 2 and 3, it is clear that specific conductance and adiabatic compressibility show an inverse relationship at a fixed temperature. With increase in volume fraction of water, specific conductance increases, the β decreases though the product $\sigma\beta$ was not found to be constant.

Viscosity of one phase microemulsion of cyclohexane/TX100 + ethylpropionate/water with constant weight fraction of water is plotted against varying oil fraction for 1:1 and 1:2 S to CS ratio in Figs. 4a and b. With 1:1 S to CS ratio, viscosity decreases with increasing weight fraction of oil and with 1:2 S to CS, it increases with increase in oil fraction. In case of 1:1 S to CS ratio, the surfactant mixture is viscous and flow time increases with respect to surfactant and decreases with respect to oil. So the surfactant–cosurfactant ratio is a major factor in viscosity of these compositions studied. Viscosity of system with S to CS ratio 1:2 is less than that with S to CS ratio 1:1, which may also be attributed to the dilution of the system. The dependency of viscosity on temperature is systematic. In both cases it decreases with increasing temperature.

The viscosity activation quantities $\Delta H^{\ddagger}$ (activation enthalpy) and $\Delta S^{\ddagger}$ (activation entropy) were calculated by applying the Eyring–Frenkel equation for viscous flow and is written as [26]

$$\ln\frac{\eta V}{Nh} = \frac{\Delta H^{\ddagger}}{RT} - \frac{\Delta S^{\ddagger}}{R}$$

where V, N, h, R and T are molar volume of the solution, the Avogadro's number, Planck's constant, universal gas constant and Kelvin temperature, respectively. From the slope and intercept of the straight line graphs obtained by plotting $\ln \eta V/Nh$ against T^{-1}, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were calculated for 1:1 and 1:2 S to CS weight ratio (Table 2). With 55 wt% of oil, we get a minimum in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for 1:1 S to CS ratio. For 1:2 S to CS ratio, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values show a gradual decrease.

In case of ionic surfactant, an electrolyte like NaCl decreases the hydrophobicity and there is possibility of the formation of a three phase microemulsion [3]. The presence of electrolytes reduces the repulsive interaction between charged surfactant molecules and hence affects the solubility [27]. Addition of electrolyte causes the inversion of an oil continuous upper phase microemulsion. The effect of NaCl on system of composition S + CS (40%), oil (57.5%) and water (2.5%) shows that till 0.9 M NaCl concentration the system is Winsor IV and from 1 to 4 M aq. NaCl (i.e., replacing water) it is a two phase system at 40 °C and at higher temperatures. Below 40 °C, it is 1ϕ microemulsion. For this particular system we were not able to get a Winsor III system probably due to the higher

Table 2 Viscosity activation quantities of viscous flow

(S:CS = 1:1)			(S:CS = 1:2)		
Weight percent oil	$\Delta H^{\ddagger}$ [kJ mol^{-1}]	$\Delta S^{\ddagger}$ [J mol^{-1}K^{-1}]	Weight percent oil	$\Delta H^{\ddagger}$ [kJ mol^{-1}]	$\Delta S^{\ddagger}$ [J mol^{-1}K^{-1}]
65	13.4	− 6.4	60	20.5	17.5
55	10.0	− 18.1	55	16.8	6.0
45	15.9	− 0.6	50	15.3	1.1
35	16.3	− 0.9	45	14.8	− 0.6

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Table 3 Contact angle (θ) obtained by various 1ϕ microemulsions with Teflon surface

(S.CS = 1:1)				(S:CS = 1:2)			
O	S	W	θ'	O	S	W	θ
0.0	0	100	152	0	0	100	152
2.5	80	17.5	72	45	52.5	2.5	50
7.5	80	12.5	69	50	47.5	2.5	50
12.5	80	7.5	67	55	42.5	2.5	49
17.5	80	2.5	65	60	37.5	2.5	50
100.0	0	0	56	100	0	0	56

hydrophobicity of the surfactant–cosurfactant interfacial film.

Table 3 shows the contact angles θ of various compositions with a Teflon surface. From Table 3a it can be concluded that for the system, with surfactant/cosurfactant ratio 1:1, the system is oil continuous with water probably dispersed as droplets. For 1:2 surfactant to cosurfactant system, the contact angle is studied with constant water fraction. Low, somewhat constant, contact angles were obtained indicating that the system was too hydrophobic and there was no structural change. The system here also seems to be oil continuous.

Conclusion

Pseudoternary phase diagrams of cyclohexane/TX 100 + ethylpropionate/water were drawn with TX 100 + ethylpropionate ratio as 1:0, 1:1 & 1:2. This was done to determine the effect of an ester (i.e., ethylpropionate) as a possible cosurfactant. The percent area of single phase Winsor IV region was very low. A large birefringent viscous region was observed for 1:1 system which gives way to a large extent to L/L biphasic region when surfactant/cosurfactant ratio was changed to 1:2. The higher percentage of ethylpropionate makes the system more hydrophobic. The changes in the physical properties follow the expected trend. No concentration percolation was observed. Temperature percolation was also not present. The conductance values were low. The results indicate w/o microemulsion. Viscosity shows a dependence on the surfactant–cosurfactant weight ratio. Two phase systems were obtained by the effect of sodium chloride on one phase Winsor IV system. However, no Winsor III system was obtained within the salinity range studied and hence optimal salinity could not be determined. The conductance, viscosity and contact angle values indicate a w/o microstructure of the Winsor IV region for this present system.

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