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SHORT COMMUNICATION

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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 X100 (TX100), $CH_3C(CH_3)_2$ $CH_2C(CH_3)_2$–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

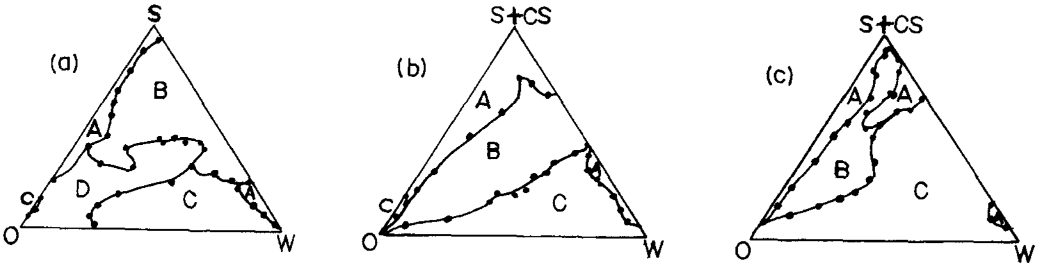

Fig. 1 Pseudoternary phase diagram of cyclohexane (O)/TX 100(S) + ethylpropionate (CS)/ water system at 30 °C: (a) S:CS = 1 · 0 (w/w); (b) S:CS = 1:1; (c) S:CS = 1 · 2 (w/w), A = 1ϕ region; B = viscous; C = L/L; D = L/Visc

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 (MX3, 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	–	–

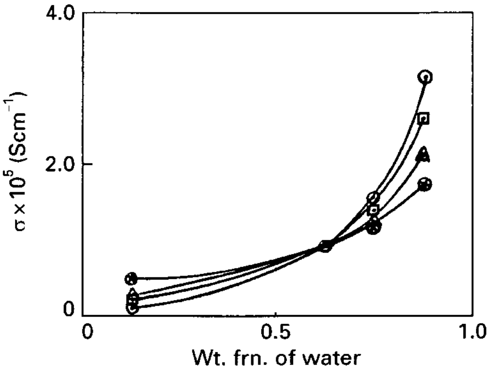

Fig. 2 Plot of specific conductance (σ) vs. weight fraction of water with S:CS = 1:1 (w/w) at various temperatures ʘ 30; □ 35; △ 40; ⊗ 45 °C

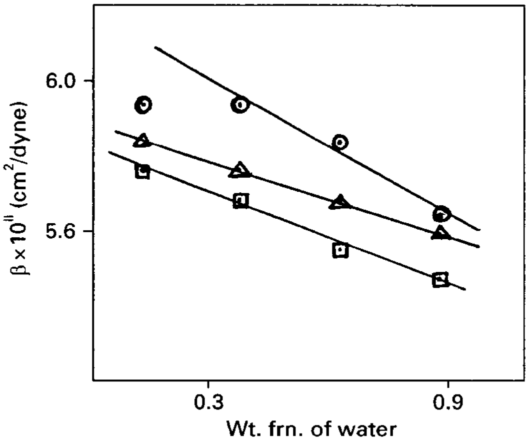

Fig. 3 Plot of adiabatic compressibility (β) vs. weight fraction of water at various temperatures (S:CS = 1:1). □ 35; △ 40; ⊙ 45 °C

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. Specific 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 the 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.

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

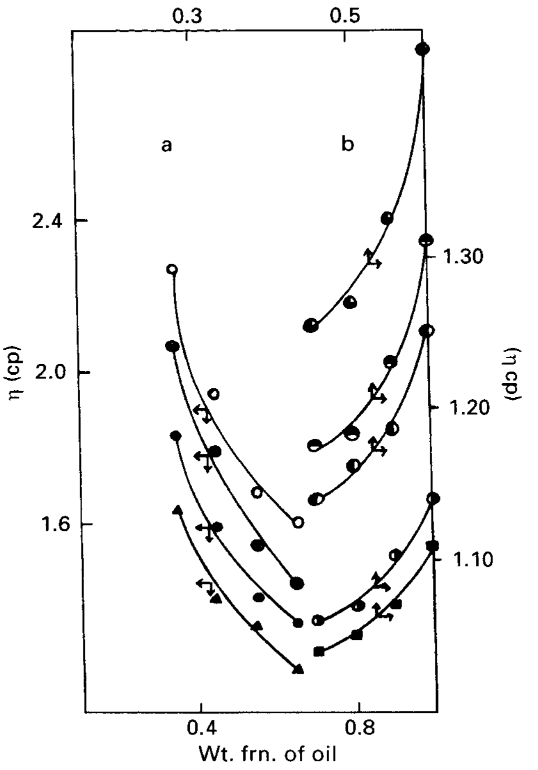

Fig. 4 (a) Plot of viscosity (η) vs. weight fraction of oil (S:CS = 1:1) ○ 30; ⊛ 35; ● 40, △ 45 °C. (b) Plot of viscosity (η) vs. weight fraction of oil (S:CS = 1:2). ◒ 30; ◓ 32.5; ◐ 35; ◑ 37.5; ■ 40 C

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

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/TX100 + ethylpropionate/water were drawn with TX100 + 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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