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Physicochemical Behaviour of Ternary System Based on Coconut Oil/ $C_{12}E_8$ /*n*-pentanol/Water

SARISH S. JOSHI and SUNIL S. BHAGWAT*

Department of Chemical Engineering, Institute of Chemical Technology, Nathalal Parekh Marg, Matunga, Mumbai-400 019, India

Abstract — Physicochemical properties of a system based on Coconut Oil, nonionic surfactant $C_{12}E_8$, cosurfactant *n*-pentanol and water has been studied. The phase behavior, effect of temperature and electrical conductivity of the system was studied at different surfactant (S) to cosurfactant (C) ratios, the ratios being 1 : 1, 1 : 1.5, 1 : 2 (w/w). Pseudoternary phase behavior of these ratios was studied, the phase diagrams generated distinguishes between monophasic/isotropic and biphasic/anisotropic regions. The monophasic region was found to be a strong function of the S : C ratio. The largest monophasic region was obtained when the S : C ratio was 1 : 1, the monophasic region gradually depleted with decrease in amount of S in the order 1 : 1 > 1 : 1.5 > 1 : 2 . The effect of temperature was examined on the phase behavior of the system, and for all S : C ratios it was observed that the monophasic region decreased with increase in temperature. The electrical conductivity of the system increases with aqueous phase content indicating a transition from water-in-oil to oil-in-water microemulsions.

Keywords : *Phase behavior, coconut oil, nonionic surfactant, temperature, conductivity, microemulsion.*

INTRODUCTION

Microemulsions are thermodynamically stable, transparent, isotropic dispersions of oil and water having droplet size between 1–100 nm. These dispersions are stabilized by a appropriate surfactant, generally in combination with a short or medium chain length alcohol which acts as a co-surfactant. The cosurfactant interacts with surfactant monolayer group, where it distributes itself at the interfacial film among the surfactant

*Corresponding author. E-mail : ss.bhagwat@ictmumbai.edu.in, Phone : +91-22-3361-2001, Fax : +91-22-3361-1020

monomers, which further reduces the interfacial tension to very low levels [1, 3]. This affects the packing of surfactant monolayer at the interface and the curve of the interfacial film. Cosurfactant plays an essential role in not allowing formation of gel and liquid crystals, thus lowering the viscosity of the system.

Microemulsification of oils from vegetable and plant is a very difficult task as compared to microemulsification of mineral oil. Microemulsion of these oils with compatible emulsifiers may have wide applications from cosmetics to medicines. Coconut oil is widely used in household and cosmetic purposes. The interaction of a nonionic surfactant with coconut oil resulting into stable microemulsion can have a large scope for study. The formation, stability and various properties of microemulsions have been widely studied [4–8]. In many investigations, the emphasis was laid on the phase behaviour of microemulsions [9–11] and various other factors influencing the phase behaviour were studied. The type of surfactant and cosurfactant and the ratio in which these are taken considerably alters the phase behaviour [12–14]. Variation in temperature results in structural changes especially in nonionic type of surfactant, affecting its solubilization capacity [15–18]. Electrical conductivity of microemulsions varies with water content, surfactant type and is greatly affected by presence of additives [19, 20]. Electrical conductivity helps distinguish between water-in-oil, oil-in-water type microemulsion thus illustrating the structure of microemulsion [21, 22]. The phase behavior, effect of temperature and electrical conductivity of system consisting a triglyceride such as coconut oil, ethoxylated surfactant of the type C_iE_j (i refers to the carbon chain length and j refers to the number of ethylene oxide molecules) and a middle chain length alcohol *n*-pentanol with water is not reported in literature. The aim of the current study was to investigate the effect of surfactant C12E8 and co-surfactant *n*-pentanol at various ratios on phase behavior of pseudoternary system consisting Coconut Oil/ $C_{12}E_8$ /*n*-pentanol/Water. Nonionic surfactants are temperature sensitive, thus their phase behavior would be vastly influenced by temperature. Also, the electrical conductivity will be substantially influenced with increasing aqueous phase content [20, 23]. Hence, the effect of temperature and conductivity on the ternary system of Coconut Oil/ $C_{12}E_8$ /*n*-pentanol/Water was studied.

EXPERIMENTAL

Materials :

Refined Coconut Oil was procured from by M/S Marico Industries, India. The Acid Value for the coconut oil used is in the range of 0.0 to 0.1 mg KOH/g of oil, Saponification Value approximately 250 mg KOH/g of oil and Iodine Value between

8 to 10 mg I₂/g of oil.

Nonionic surfactant C₁₂E₈ was provided by M/S Galaxy Surfactants, India. The oil and surfactant were used as received. Cosurfactant n-pentanol of A. R. grade was obtained from S. D. fine chemicals Ltd, India. Deionized water was used for all experiments.

Methods :

Determination of Phase Behavior —

The pseudoternary phase diagrams were generated by weighing calculated amount of surfactant and cosurfactant and mixing them in specific ratios and further titrating them with water. The Surfactant (S) and Cosurfactant (C) were mixed till a clear homogeneous mixture was obtained. Oil was added to the S+C mixture and this mixture was vigorously shaken using a vortex mixer. Water was carefully added to the above mixture and the mixture was again mixed vigorously. Water was added till turbidity or phase separation started to appear in the clear mixture, which confirmed the transition from monophasic to bi/multi-phase. The main focus was on studying the phase behavior of the isotropic systems, the compositions deviating from this were termed as multiphase systems. Further detailed characterization of multiphase systems were not carried out. So, these diagrams can also be termed as partial pseudoternary phase diagrams.

Monophasic mixtures were observed under cross polarizing sheets to confirm their isotropic nature and detect any anisotropy. The resulting clear, monophasic, homogeneous, isotropic solutions were kept at constant temperature in sealed test tubes for one week and till their clear appearance was confirmed after one week.

Effect of Temperature —

The effect of temperature on monophasic samples was studied on a Thermo/HAAKE DC10-K10 constant temperature bath, by placing the sealed glass capped test tubes in the bath for 12 hours. The change in their physical appearance was noted by visual observation.

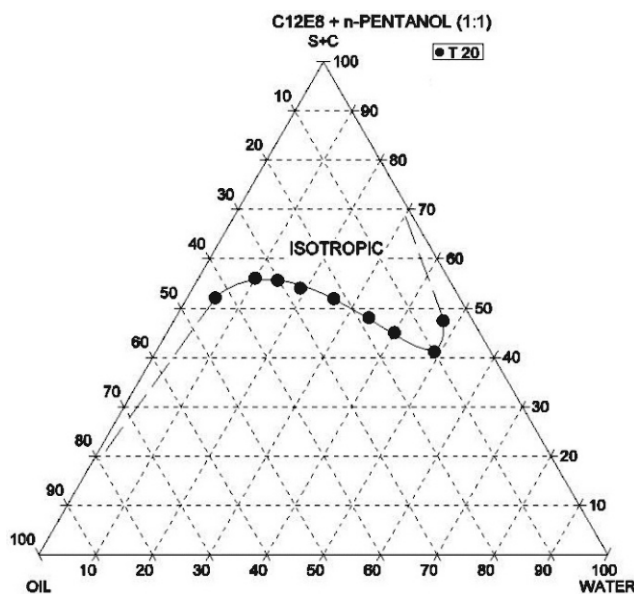
Electrical Conductivity —

The electrical conductivity was measured using a LT-23 digital conductivity meter from Labtronics, India. The application range of the conductivity meter extended between 1 μ S/cm to 2 S/cm. The conductance of microemulsion samples was measured by dipping the electrode in sample till equilibrium was attained and reading became stable. Cell constant was calibrated using standard KCl solutions and was checked at frequent intervals during conductivity measurements.

RESULTS

Phase Behavior :

The phase behavior of Coconut oil, $C_{12}E_8$, n-pentanol and water was studied at different S : C ratios (w/w) 1 : 1, 1 : 1.5 and 1 : 2, Fig. 1, shows pseudoternary phase diagrams of these systems. The quaternary system was converted into pseudoternary system by considering $C_{12}E_8$ and n-pentanol as single amphiphile (S+C) component. In each triangle, the apex represents the amphiphile (S+C) with varying ratios, the bottom left hand corner of the triangle represents Coconut oil and the bottom right corner represents water. Surfactant $C_{12}E_8$ showed complete miscibility with water and n-pentanol, whereas n-pentanol was found to be slightly soluble in water. In the phase diagrams, distinction between monophasic and bi-multiphase is made by a boundary separating them. The region above the boundary, towards the S+C apex is monophasic. Whereas, the region extending below the boundary towards the base of the triangle is biphasic. The observations made are indicated with points with a continuous line and the behavior expected towards the axis is demarcated by dotted line. The compositions in the monophasic region were examined under cross polarizing sheets which confirmed their isotropic nature. The phase diagrams show that the largest monophasic region was found for the ratio 1 : 1. The microemulsion region here was found to be more towards higher amphiphilic region which tapered



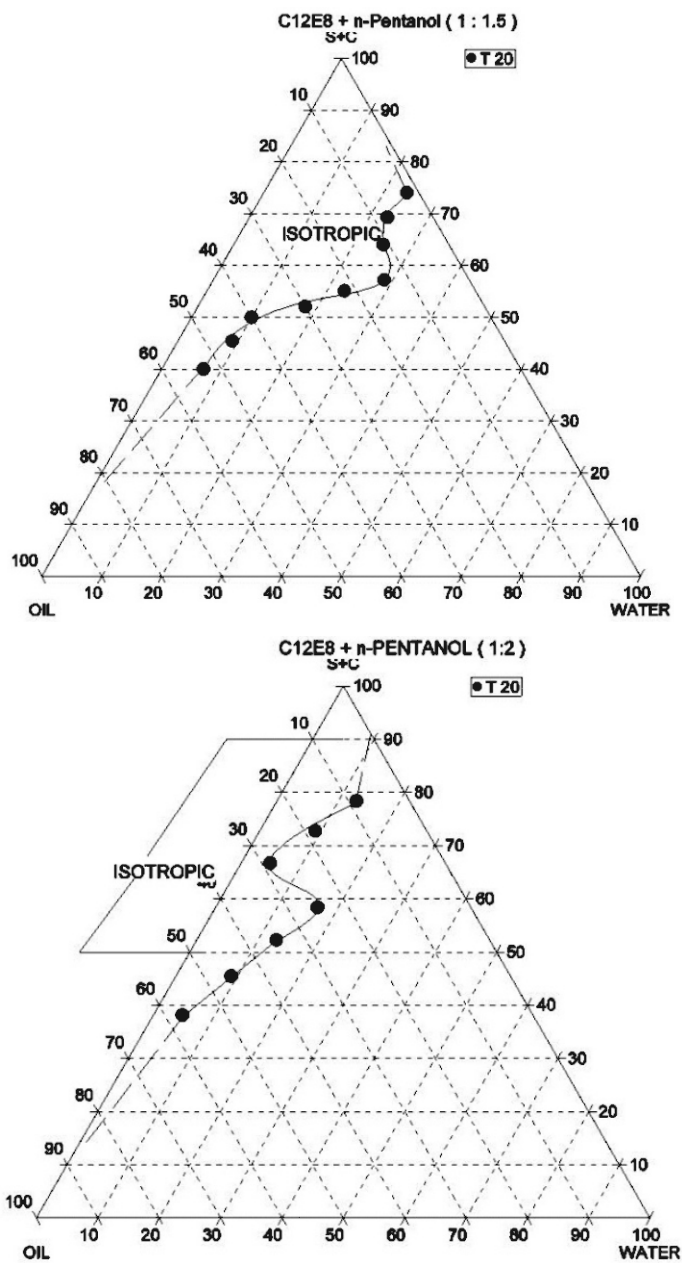


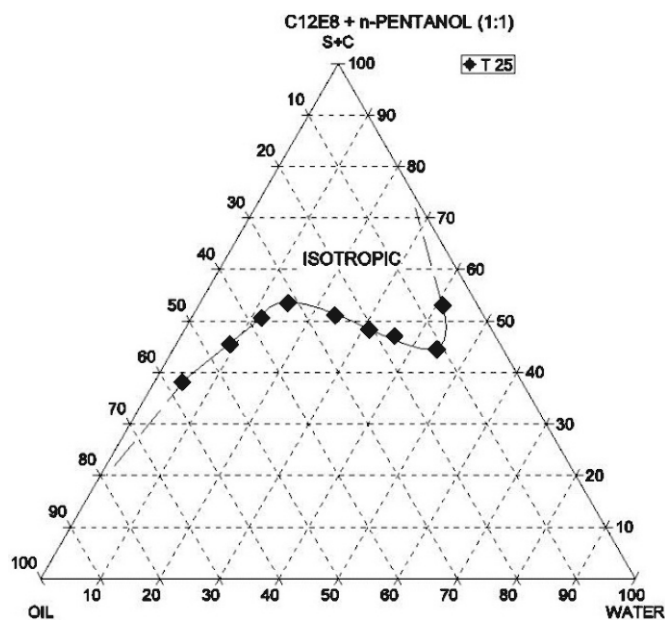
Fig. 1. Ternary phase diagrams of C12E8/n-pentanol/Coconut Oil/Water at 293 K.
 (a) S+C ratio is 1 : 1 (b) S+C ratio is 1 : 1.5 and (c) S+C ratio is 1 : 2.

towards oil region.

Furthermore, with decreasing amount of surfactant the monophasic region drastically decreases, this results into a clear distinct lobe leaning towards S+C and oil region. The monophasic regions in the phase diagrams were computed, it was observed that at 293 K, the monophasic region is 26 % (S+C ratio 1 : 1) which decreases to 20% (S+C ratio 1 : 1.5) and reaches to 11% (S+C ratio 1 : 2). Similarly, at 298 and 303 K the monophasic region decreases with decrease in surfactant amount. At 298 K the monophasic region decreases from 24 % (S : C ratio 1 : 1) to 13% (S : C ratio 1 : 1.5) till 9% (S : C ratio 1 : 2). And at 303 K the monophasic region decreases from 21% (S : C ratio 1 : 1) to 11% (S : C ratio 1 : 1.5) till 8% (S : C ratio 1 : 2).

Effect of Temperature :

The phase behavior of ternary system Coconut oil/ $C_{12}E_8$ /n-pentanol/water for all S : C ratios was studied at three different temperatures, 293, 298, 303 K. The monophasic samples sealed glass capped test tubes were placed in a constant temperature bath for 12 hours and the change in their physical appearance was noted by visual observation. Fig. 2, shows the pseudoternary phase diagrams for the systems. It is observed that the monophasic region decreases with increase in temperature, and this trend is also observed at all S : C ratios.



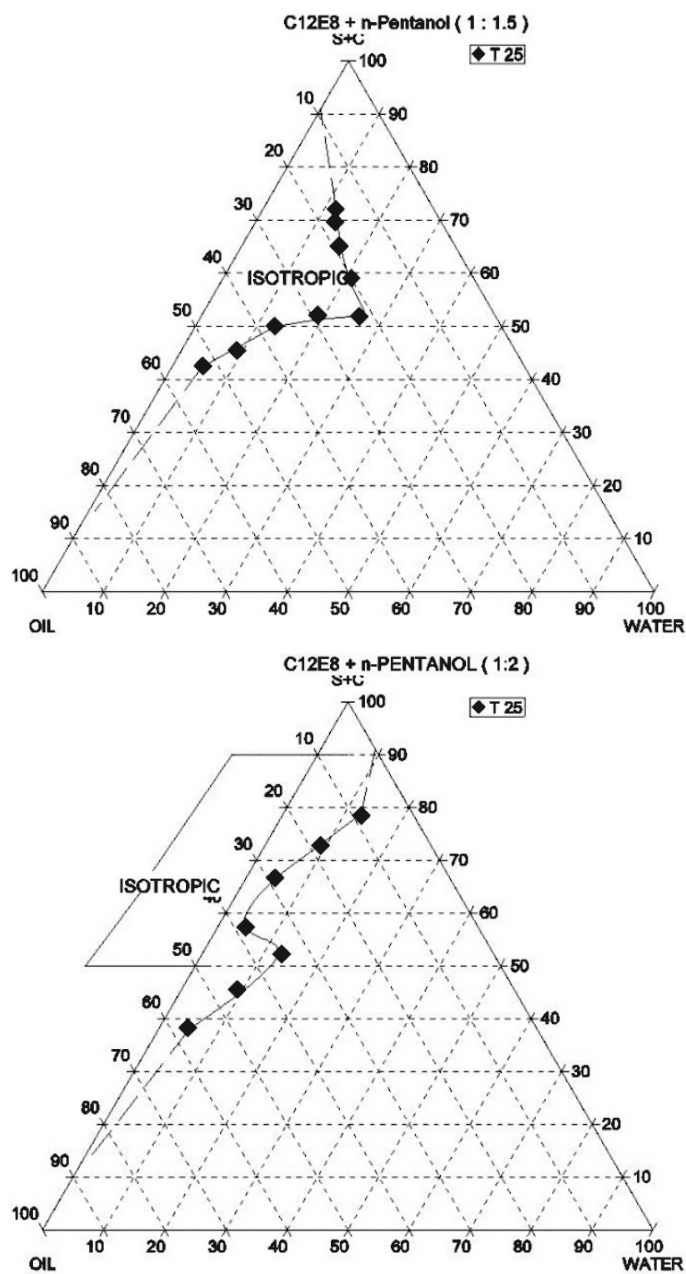


Fig. 2. Ternary phase diagrams of Cl_2E_8 /n-pentanol/Coconut Oil/ Water at 298 K.
 (a) S+C ratio is 1 : 1 (b) S+C ratio is 1 : 1.5 and (c) S+C ratio is 1 : 2.

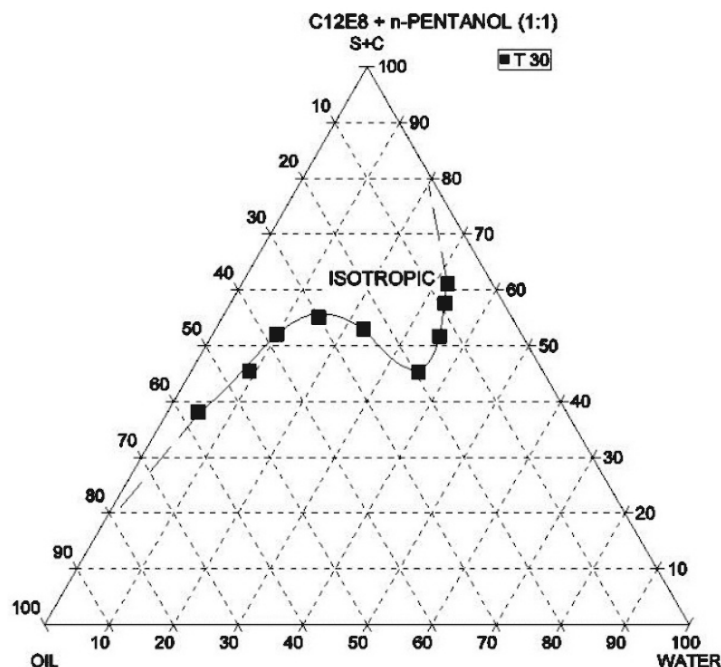
Electrical Conductivity :

The electrical conductivity of ternary system Coconut oil/ $C_{12}E_8$ /n-pentanol/water was studied at 298 K for S : C ratio 1 : 1. Conductance was measured for microemulsion samples with constant S+C amount of 55 % with varying oil and water content. The conductivity of the studied microemulsion samples was initially very low when the amount of oil was higher than that of water. With increasing amount of water the conductance rose smoothly and steadily without any abrupt sharp rise, indicating possible transition through bicontinuous microemulsions. Thus, conductivity increased with increasing aqueous content which is clearly evident from Fig. 4.

DISCUSSION

Phase Behavior :

The pseudoternary phase diagrams plotted for the system Coconut oil/ $C_{12}E_8$ /n-pentanol/water, shows two distinct regions categorized into monophasic and biphasic. It is observed that at any particular temperature, the monophasic region is higher with S : C ratio is 1 : 1 as compared to 1 : 1.5/1 : 2. The monophasic region decreases with decrease in surfactant fraction [12–14] as shown in Fig. 1, Fig. 2, Fig. 3. Thus, at any temperature the largest isotropic/microemulsion region is formed when equal



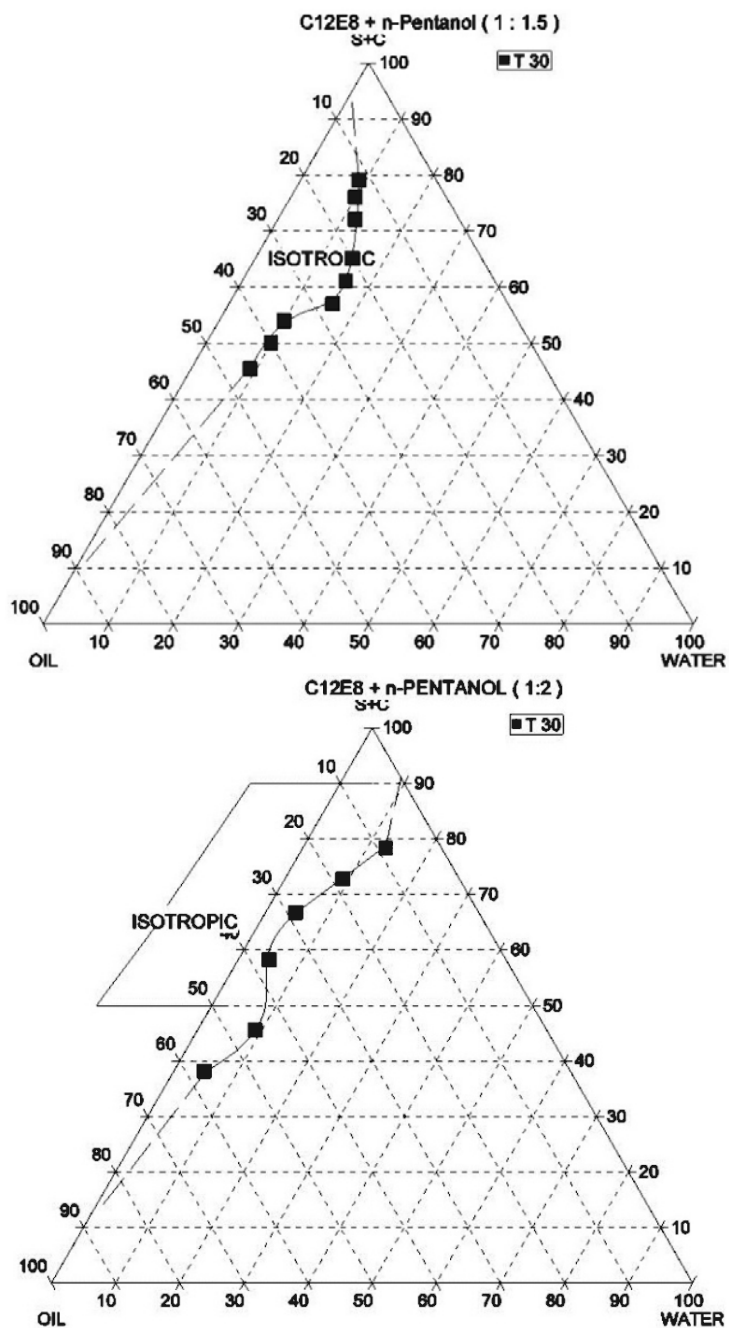


Fig. 3. Ternary phase diagrams of C₁₂E₈/n-pentanol/Coconut Oil/Water at 303 K.
 (a) S+C ratio is 1 : 1 (b) S+C ratio is 1 : 1.5 and (c) S+C ratio is 1 : 2.

amounts of surfactant $C_{12}E_8$ and cosurfactant n-pentanol are present. When the S : C ratio is altered from 1 : 1 to 1 : 1.5, it can be observed that the isotropic region extending towards o/w region at lower S : C concentration diminishes and shifts towards higher S : C concentration region. Similarly, when the S : C ratio is 1 : 2, the isotropic region limits itself to high S : C region and the overall region under isotropic phase drastically decreases. Behavior of similar kind was observed for all studied temperatures.

Also, with increase in temperature the tendency of surfactant to form w/o microemulsion increases. At all the temperatures studied, the region in pseudoternary phase diagram towards w/o region is not affected by increasing temperature as compared to o/w region. This behavior can be attributed to the fact that, more the amount of surfactant larger would be the interaction of polyoxyethylene chain and water leading to larger solubilization of water in micelles and oil in reverse micelles. Thus, from the phase diagrams it is clear that with S : C ratio 1 : 1, large monophasic region was obtained and the monophasic region diminished with decrease in surfactant amount irrespective of temperature in the order 1 : 1 > 1 : 1.5 > 1 : 2.

Effect of Temperature :

It is well known that nonionic surfactants are highly temperature sensitive [15]. Change in temperature brings about structural changes in nonionic surfactant, which greatly affects its solubilization capacity [24, 25]. Increase in temperature leads to dehydration of oxyethylene group which makes the nonionic surfactants more lipophilic [14, 26, 27]. The solubility of surfactant in oil increases with increasing temperature because the polar end group-water interaction becomes less favourable and as the thermal energy is imparted to the system, many of the existing hydrogen bonds are ruptured leading to higher lipophilicity [28, 29]. As shown in Fig. 1 the largest monophasic region with all S : C ratios was observed at 293 K. As shown in Table 1, the amount of the maximum amount of water solubilized at 293 K when S : C ratio is 1 : 1 was 50% (with S+C 40% + Oil 10%) and Oil 24%(with S+C 56%

TABLE 1.

The effect of temperature of Oil and H_2O with S+C ratio 1 : 1

Temperature K	Oil	H_2O
293	24	50
298	57	44
303	57	35

+ Water 20%).

The monophasic region decreases with increase in temperature. At 303 K the maximum amount of solubilized water was observed to be 35.5% (S+C 45.1% + Oil 19.4%) and maximum amount of oil solubilized was found to be 57.1% (S+C 38.1% + Water 4.8%). Similar trend was observed with S : C ratios 1 : 1.5 and 1 : 2 as shown in Fig. 2 Fig. 3. Thus, the decrease in monophasic region shows increase in lipophilic tendency of nonionic surfactant with increasing temperature. The cloud point for the surfactant was measured and was found to be 62 °C.

Electrical Conductivity :

The conductivity of microemulsions is greatly dependent on its aqueous phase content [20, 23]. In the present system the conductivity measurements were carried out without any addition of electrolyte. The microemulsion system has very less conductivity when reverse micelles are present within a continuous oil phase [21–23]. With increase in water content the conductivity slowly increases with sharp increase at higher aqueous phase content, where micelles are dispersed in continuous aqueous phase as shown in Fig. 4.

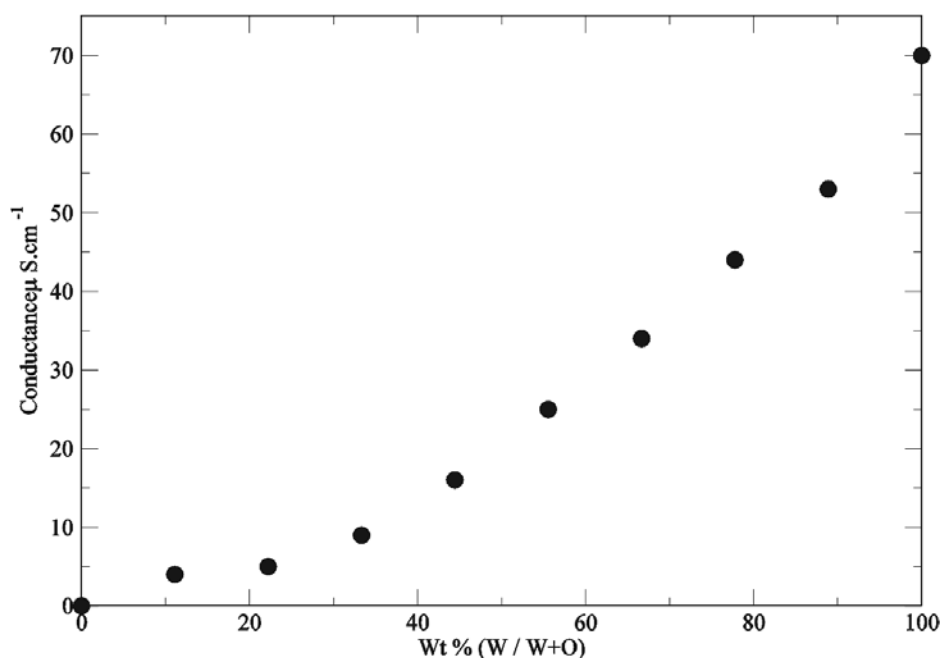


Fig. 4. Conductance of microemulsion as a function of water concentration.

The conductivity of the system was negligible when the aqueous phase content was less than 20 wt%, suggesting presence of reverse micelles where water droplets in continuous oil phase had little interaction with each other. The conductivity increased substantially with increasing aqueous phase content beyond 30 wt%. The rise in conductivity confirmed the increasing interaction between aqueous phase domains. And the higher conductivity beyond 30% water content indicated the presence of discreet oil phase within continuous water phase.

CONCLUSIONS

The physicochemical properties namely phase behavior, effect of temperature and electrical conductivity of a coconut oil based pseudoternary system consisting nonionic surfactant $C_{12}E_8$, cosurfactant n-pentanol and water were studied. The pseudoternary phase behavior study at different S : C ratios distinguished between monophasic and biphasic regions. The monophasic region was found to be a strong function by S : C ratio. The monophasic region depleted with decreasing amount of $C_{12}E_8$ in the order $1 : 1 > 1 : 1.5 > 1 : 2$. The microemulsion system was sensitive to temperature changes at all S : C ratios. The monophasic region decreased with increasing temperature, same trend was observed for all S : C ratios. The electrical conductivity of the microemulsion system exhibited rise in conductance with increasing amounts of water. The change in electrical conductance assisted to characterize the change in microemulsion type from W/O to O/W.

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