

Microstructural Phase Transfer Analysis in Microemulsions and Reverse Micelles of Cetyltrimethylammonium Bromide/1-Butanol/Cyclohexane/Water

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Abstract: Reverse micelles and microemulsions of cetyltrimethylammonium bromide (CTAB) have been prepared over a wide range of compositions and the physicochemical properties have been studied in detail. Conductivity and density increase, while the refractive index decreases with increasing volume fraction of water (ϕ_w) or water to surfactant molar ratio (w_o) in the reverse micelles and microemulsions. Turbidity, viscosity and surface tension plotted against ϕ_w show unusual patterns with increasing ϕ_w indicating different microstructures in microemulsions and reverse micelles. Percolation theory was applied on conductivity results to identify microstructures of microemulsions and reverse micelles. The conductivity values show percolation thresholds (ϕ_c) which correlate well with viscosity, turbidity and surface tension results. The microstructural changes from water-in-oil (w/o) to bicontinuous (BC), ϕ_{c1} and BC to oil-in-water (o/w), ϕ_{c2} give rise to phase transitions in percolation thresholds in the microemulsions. Phase transitions at these percolation thresholds were also observed from volumetric and refraction properties. The structural phase transitions from w/o -BC- o/w microemulsions could be inferred from the profiles of excess volume vs. ϕ_w , excess refraction vs. ϕ_w and excess molar refraction vs. ϕ_w .

Keywords: Microemulsion, Microstructure, Percolation, Phase transition, Physicochemical property, Reverse micelle.

I. INTRODUCTION

Microemulsions are colloidal dispersions of one or more surfactants (or surfactant with cosurfactant) with two mutually immiscible liquids. The microheterogeneous systems are thermodynamically stable, isotropic and transparent fluids [1]. They can solubilize both hydrophobic and hydrophilic compounds as aqueous and nonaqueous environment exist there

simultaneously [2]. Different textures of microemulsions are formed by change in the curvature of interface of surfactant or cosurfactants with the help of parameters such as compositions of different components, temperature, etc. The textures include: water-in-oil (w/o), oil-in-water (o/w), and bicontinuous (BC) structures etc [3]. Interestingly, the structures can be interchanged by change in compositions of aqueous or non-aqueous phase and change in temperature [2].

Physicochemical properties of reverse micelles and microemulsions change with variation in water or hydrocarbon (oil) phase. Since they are disordered media containing different size of droplets with Brownian motion, their properties mostly depend on their internal microstructures. Conductivity depends on the movement of ions in internal microstructures; thus the analysis of conductivity results can give useful information regarding different microstructures, aggregation of droplets and interaction between the droplets [3-20]. Percolation theory which is applicable only for disordered media can be applied for reverse micelles and microemulsions to determine their different internal microstructures. Percolation is a phenomenon where phase transition occurs to form an interconnected random structure in an overall system. The phenomenon is in general governed by percolation scaling law. The *percolation threshold* defines temperature or concentration at which such remarkable change is observed. The percolation is of two types: *static* which occurs in a system with almost zero conductivity below the threshold condition in other words, connectivity and *dynamic* in a system where the droplets move with chances of collisions and a very high value of conductivity is noticeable at the threshold condition [4].

Different microstructures of reverse micelles and microemulsions have so far been recognized by percolation theory using dynamic properties of these media. The structures and dynamics of microemulsions were characterized by using

electrical conductivity [3-20] and viscosity results [12, 15, 17-27]. Lagues and Sauterey [6] described the variation in low-frequency electrical conductivity of microemulsion system of sodium dodecyl sulfate/1-pentanol/cyclohexane/water with increasing water concentration and reported that by applying "stirred percolation" model [6], two transitions were observed at low and high water concentrations: the microemulsion is inverted from *w/o* to *o/w* via *BC* structure. The change in conductivity of sodium bis(2-ethylhexyl) sulfosuccinate (AOT)/water/isooctane system was analyzed by the charge fluctuation model to infer that the theory is applicable to microemulsions of relatively low water content in which a nonconductive oil serves as the continuous phase, and the phenomenon of percolation does not occur [7, 8]. Giustini *et al.* [9] thoroughly investigated the microstructures and dynamics of microemulsion of cetyltrimethylammonium bromide (CTAB)/*n*-pentanol/*n*-hexane/water. The transport properties close to the percolation temperature threshold in microemulsion of AOT/water/decane was studied by measuring conductivity and the self-diffusivity in the range of 10 °C - 40 °C [10] and two different mechanisms of transition of the charge carriers were replied. Fanun [12] observed the structural transition in water/sucrose laurate/ethoxylated mono-di-glyceride/R(+)-limonene microemulsions. The percolation model well described the conductivity results of water/aqueous NaCl/Tween 20/propanol/benzene and these correlated well with viscosity and ultrasonic velocity results [15]. Conductivity measurements at different volume fraction of water (ϕ) were also used for estimating the water percolation threshold (ϕ_c) of microemulsions of alkyl polyglycosides/glyceryl monooleate/*n*-octane/isopropyl alcohol [16]. A progressive transformation of the *w/o* to *BC* could be observed from NMR measurements in sucrose esters/water + propylene glycol/benzaldehyde + ethanol and inversion to *o/w* microemulsions was observed upon dilution with water which is in agreement with conductivity and viscosity results [17]. Percolation theory was used to discuss the microstructures of CaAOT/water/isooctane or CaAOT/water/decane [19]. Borkovec *et al.* [20] studied the structural inversion from *w/o* into *o/w* microemulsion in AOT/decane/aqueous 0.5% NaCl. The viscosity results of water/AOT/oil microemulsions were in agreement with a percolation model and the percolation thresholds were compatible with the conductivity and complex permittivity [23]. The percolation transition in microemulsions was also studied by means of dielectric spectroscopy [13, 25, 28]. The ultrasonic velocity [15], volumetric properties [29, 30] and isentropic compressibility [31] of microemulsions were also used to determine the microstructures.

In spite of numerous studies, the microstructures of reverse micelle and microemulsion systems could not yet be established beyond any reasonable doubt by percolation theory from dynamic properties and correlated with different physicochemical properties simultaneously. In this work, percolation theory was established on conductivity results to study the phase transitions or percolation thresholds for reverse micelles of CTAB/1-butanol/water and microemulsions of CTAB/1-

butanol/cyclohexane/water and different microstructures at above or below percolation thresholds were established by percolation scaling law. Attempts have been made to confirm the percolation thresholds as well as the microstructural transition from *w/o* to *BC* and *BC* to *o/w* from measurements of viscosity, refractive index and surface tension. The ultimate goal has been to predict the type of geometry of micro-environment and unveil the mechanism of microstructural phase transfer in reverse micelles and microemulsions.

II. EXPERIMENTAL

A. Materials

CTAB (E. Merck), absolute ethanol (E. Merck), 1-butanol (Merck), and cyclohexane (Merck) were used as received. The reverse micelles of CTAB/1-butanol/water and microemulsions of CTAB/1-butanol/cyclohexane/water were prepared at a fixed CTAB concentration of 20.0 %wt. The cyclohexane content was 0 and 3.4 %wt. and water and 1-butanol varied over a wide composition from low water to low 1-butanol content [32, 33]. A water purification system (BOECO, Germany) gave de-ionized water with conductivity of 0.055 μScm^{-1} at 25.0 °C and this was used for the preparation of all reverse micelles and microemulsions. The volume fractions of water (ϕ_w) were calculated from the following equation,

$$\phi_w = \frac{V_{\text{Water}} w_o}{V_{\text{Surfactant}} + V_{\text{Water}} w_o} \phi_{\text{Water+Surfactant}}$$

where, w_o = water to surfactant ratio = [water]/[surfactant], V = molar volume, $\phi_{\text{Water+surfactant}}$ = volume fractions of dispersed phase [25].

B. Methods

The homogeneity of reverse micelles and microemulsions was checked by centrifugation at 3000 rpm for 15 min using a centrifuge CENCOM II (230 VAC Spain). The isotropic nature and optical transparency of reverse micelles and microemulsions were studied by measuring transmittance at 650 nm through a double beam Shimadzu UV visible spectrophotometer (UVD - 3500), equipped with a thermo-regulated cell (path length 1 cm) compartment with purified water as blank. Turbidity was also measured with Shimadzu UV visible spectrophotometer (UVD-3500) which reads absorbance and gives turbidity at a particular wavelength [34, 35]. Specific conductivities, viscosities, refractive indices, densities and surface tensions of different reverse micelles and microemulsions were measured at controlled temperatures with a Jenway 4510 conductivity meter, AntonPaar Lovis 2000 M/ME microviscometer, Abbemat 300 refractometer), AntonPaar vibrating-tube density meter (DMA 4500 ME) and a Sigma Force Tensiometer (At tension Sigma-701) with a platinum Wilhelmy plate, respectively. Wilhelmy plate was cleaned with absolute ethanol and heated with a strong flame source comparable to the Bunsen burner (temperature > 1000 °C) prior to measurements of surface tension.

Dynamic light scattering (DLS) method was used to measure Z-average diameters of different reverse micelles and microemulsions droplets using a ZetasizerNano ZS90 (ZEN3690). The measurements were made using a He-Ne laser beam of 633 nm wavelength at a fixed scattering angle of 90° . 50 runs were conducted for each measurement and cumulative mean of the intensity average gave the Z-average diameters. At least 3 measurements were used to check the reproducibility. A built-in Peltier device regulated the temperature of the apparatus to within $\pm 0.01\text{K}$. Zeta potentials of different reverse micelles and microemulsions were also measured by ZetasizerNano ZS90. Samples were placed in clear disposable zeta cells and results were recorded.

III. RESULTS AND DISCUSSION

A. Stability and Homogeneity

The microemulsions of CTAB/1-butanol/cyclohexane/water and reverse micelles of CTAB/1-butanol/water were centrifuged at rpm 3,000 for 30 min at room temperature and homogeneity could be ensured. The reverse micelles and microemulsions were stored at ambient temperature and the visual inspection (phase separation) and % transmittance indicated shelf-life to be more than one year in each case [36].

B. Turbidity

Fig. 1 shows the turbidity of microemulsions of CTAB/1-butanol/cyclohexane/water and reverse micelles of CTAB/1-butanol/water at 25°C with increasing ϕ_W or w_o . The turbidity decreases up to $\phi_W = 0.17$ ($w_o = 19.7$) and $\phi_W = 0.20$ ($w_o = 23.2$) and then increases for $\phi_W = 0.17 \sim 0.46$ ($w_o = 19.7 \sim 50.1$) and $\phi_W = 0.20 \sim 0.50$ ($w_o = 23.2 \sim 53.5$); while after $\phi_W = 0.46$ ($w_o = 50.1$) and $\phi_W = 0.50$ ($w_o = 53.5$), the turbidity again decreases for microemulsions and reverse micelles, respectively. Decrease in turbidity up to $\phi_W = 0.17$ and $\phi_W = 0.20$ is due to electrostatic repulsions between the water droplets and the increase in turbidity for $\phi_W = 0.17 \sim 0.46$ and $\phi_W = 0.20 \sim 0.50$ is caused by coalescence or enhancement of attractive interactions, or a combination of both. After $\phi_W = 0.46$ and $\phi_W = 0.50$, the electrostatic repulsions in o/w microemulsions cause decrease in turbidity [34, 35].

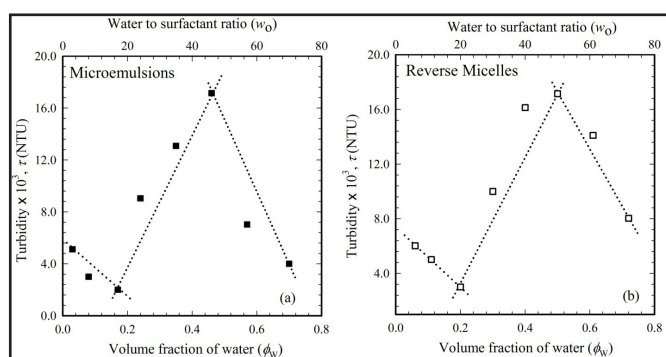


Fig. 1: Turbidity as a Function of ϕ_W or w_o for (a) Microemulsions of CTAB/1-butanol/cyclohexane/water and (b) Reverse Micelles of CTAB/1-butanol/water. Dotted Lines are Used to Understand the Change in Turbidity Clearly

C. Surface Tension

Fig. 2 shows the change in the surface tensions of microemulsions of CTAB/1-butanol/cyclohexane/water and reverse micelles of CTAB/1-butanol/water at 25°C with increasing ϕ_W or w_o . The surface tension decreases up to $\phi_W = 0.17$ ($w_o = 19.7$) and $\phi_W = 0.32$ ($w_o = 33.3$) and increases after $\phi_W = 0.46$ ($w_o = 50.1$) and $\phi_W = 0.50$ ($w_o = 53.5$); while for $\phi_W = 0.17 \sim 0.46$ ($w_o = 19.7 \sim 50.1$) and $\phi_W = 0.32 \sim 0.50$ ($w_o = 33.3 \sim 53.5$), the surface tension slightly increases with increasing ϕ_W or w_o for microemulsions and reverse micelles, respectively. The decrease in surface tension up to $\phi_W = 0.17$ and $\phi_W = 0.32$ may be due to a weakening of hydrophobic-hydrophobic interactions existing in cyclohexane-1-butanol and development of weaker hydrophobic-hydrophilic interactions between cyclohexane, 1-butanol and water. With increasing ϕ_W , development of hydrophilic-hydrophilic interaction between CTAB, 1-butanol and water caused a constant increase in surface tension for $\phi_W = 0.17 \sim 0.46$ and $\phi_W = 0.32 \sim 0.50$. After $\phi_W = 0.46$ and $\phi_W = 0.50$, the surface tension increases sharply due to diminishing stronger hydrophobic-hydrophobic interaction of cyclohexane-1-butanol and developing stronger hydrophilic-hydrophilic interaction of CTAB, water and 1-butanol [37].

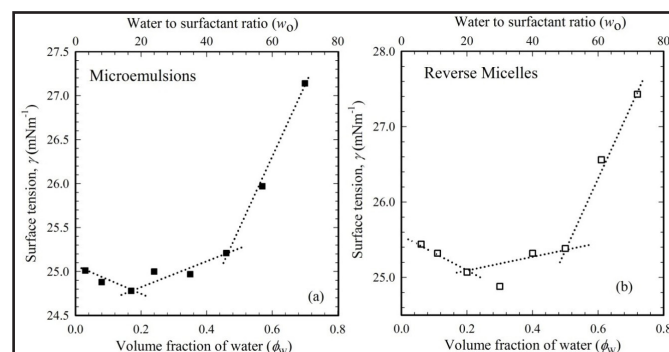


Fig. 2: Surface Tensions as a Function of ϕ_W or w_o for (a) Microemulsions of CTAB/1-butanol/cyclohexane/water and (b) Reverse Micelles of CTAB/1-butanol/water. Dotted Lines are Used to Understand the Change in Surface Tensions Clearly

D. Density

Fig. 3 shows the change in the density of microemulsions of CTAB/1-butanol/cyclohexane/water and reverse micelles of CTAB/1-butanol/water at 25°C with respect to ϕ_W or w_o . The densities of water at 25°C (0.9940 gm^{-3}) is higher than that of 1-butanol (0.8089 gm^{-3}) [33]. The density of reverse micelles and microemulsions increases with ϕ_W or w_o due to changes of the structure of water as well as transfer of 1-butanol from the dispersed phase to the continuous phase. A changeover from reverse micellar (w/o) to micellar (o/w) via BC phase is apparent (vide supra) with increasing ϕ_W or w_o . Water resides in the hydrophilic moiety of the reverse micelle (core) and in outer part of the micellar phases.

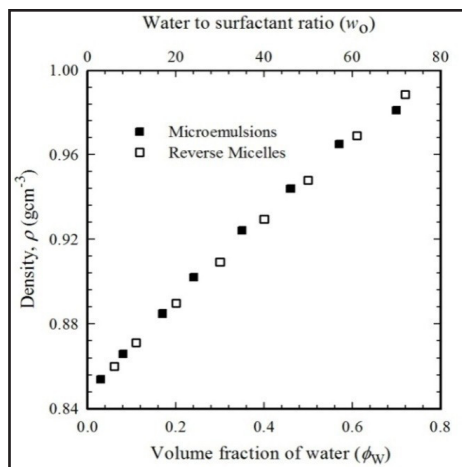


Fig. 3: Density as a Function of ϕ_W or w_o for Microemulsions of CTAB/1-butanol/cyclohexane/water and Reverse Micelles of CTAB/1-butanol/water

E. Conductivity and Viscosity

In reverse micelles and microemulsions, macroscopic transport properties: conductivity and viscosity are controlled by internal microstructures. This is due to the fact that interdroplet interactions dictate the magnitude of viscosity [38] and conductivity relies on the local viscosity the charge carriers experience [39]. In a previous study, it has been shown that both conductivity and viscosity increase with increasing ϕ_W or w_o at 25 °C [32]. The viscosity versus ϕ_W or w_o profiles show special patterns in different structures of reverse micelles and microemulsions while the conductivity increases monotonically with ϕ_W or w_o (Fig. 4). The sharp increase in conductivity with ϕ_W or w_o is indicative of the commencement of a macroscopic chain of droplets. Additionally, the special patterns in viscosity results correspond to the different inter-droplets interaction between the water droplets in oil phase and oil droplets in oil phase with increasing ϕ_W or w_o [32]. Thus, from viscosity results, three different microstructures can be obtained in reverse micelles and microemulsions.

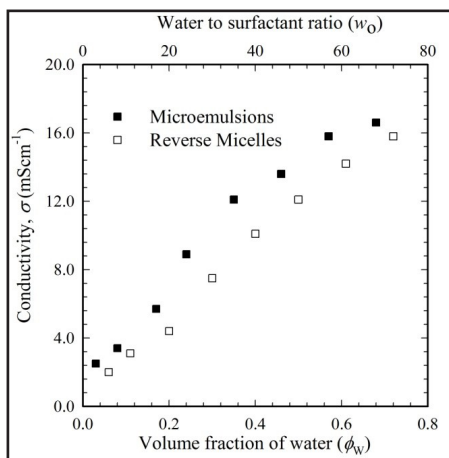


Fig. 4: Conductivity as a Function of ϕ_W or w_o for Microemulsions of CTAB/1-butanol/cyclohexane/water and Reverse Micelles of CTAB/1-butanol/water

i. Percolation Thresholds from Conductivity Results

Based on percolation theory, lower conductivity is found upto a certain value of ϕ_W ; w/o microemulsions exist in the non-conducting continuous oil phase. When value of the ϕ_W reaches or exceeds a critical point, in other words percolation threshold, i.e., ϕ_C , a fraction of water droplets in oil swell and come to close proximity and form clusters. A possible efficient transfer of ions between the droplets by hopping of charge or transient integration of associated droplets with contact between the water moieties results in the sharp increase of conductivity. The presence and position of this threshold are determined by the interactions between droplets that control duration of collision and the degree of interface overlapping, hence the probability of hopping or integration [15]. Interestingly, theoretical percolation models [16] have not been a requisite to predict the percolation threshold from numerical optimization of $d(\log\sigma)/d\phi_W$ vs. ϕ_W , by determining the water content at which $d(\log\sigma)/d\phi_W$ gives the maximum or minimum value and also show unusual patterns in $d(\log\sigma)/d\phi_W$ vs. ϕ_W plots [12, 17].

Water and oil percolation threshold are of two types which can be found in reverse micelles and microemulsions over a wide range of compositions. These are the indicators of microstructural transition from w/o to BC (water percolation) and BC to o/w microemulsions (oil percolation). These can be frequently determined from the $d(\log\sigma)/d\phi_W$ against ϕ_W profiles by using conductivity measurements. Thus, these are the important physical properties to identify different phase transitions as well as different microstructures in reverse micelles and microemulsions [20, 40, 41]. The percolation thresholds of microemulsions of CTAB/1-butanol/cyclohexane/water and reverse micelles of CTAB/1-butanol/water can be determined from conductivity results by $d(\log\sigma)/d\phi_W$ vs. ϕ_W plots (Fig. 5a and Fig. 5b). The phase transitions occur in microemulsions of CTAB/1-butanol/cyclohexane/water (Fig. 5a), at $\phi_W = 0.17$ and 0.45 , while for reverse micelles the phase transition occurs only at $\phi_W = 0.30$ (Fig. 5b). Lang *et al.* [42] reported that the value of these percolation thresholds depend on the value of the interdroplet exchange rate constant.

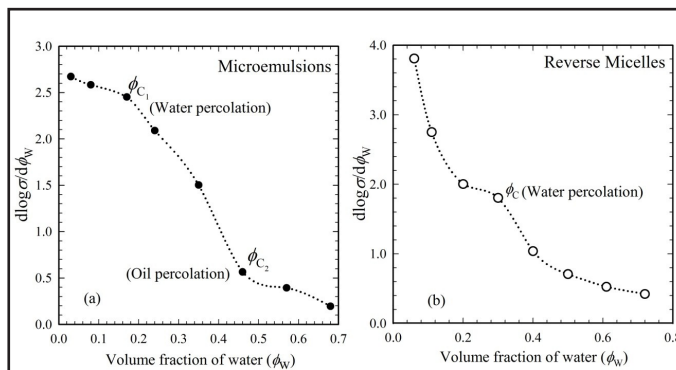


Fig. 5: The $d\log\sigma/d\phi$ vs. ϕ plots for (a) Microemulsions of CTAB/1-butanol/cyclohexane/water and (b) Reverse Micelles of CTAB/1-butanol/water. Dotted Lines are Used to Understand the Phase Transitions Clearly

It has been established from Fig. 5 that both water percolation and oil percolation threshold can be found in microemulsions of CTAB/1-butanol/cyclohexane/water which are known as *double percolation* system. In reverse micelles of CTAB/1-butanol/water, only water percolation is found and such systems are *single percolation* systems.

ii. Analysis of Microstructures by Percolation Scaling Law from Conductivity Results

Three different microstructures may be formed in microemulsion systems depending on their composition of different components: surfactants, co-surfactants, polar (water) and nonpolar (oil) phase. In *w/o* microemulsion water droplets are dispersed in continuous oil phase; while oil droplets are dispersed in continuous water phase in *o/w* microemulsion. A *BC* phase is present at an intermediate ratio of oil and water. By varying temperature at a constant water content or changing water content at a constant temperature, the microstructures of microemulsion can be changed from *w/o* to *BC* and from *BC* to *o/w* phase [34]. According to percolation scaling law, the conductivity can be expressed by two separate laws.

$$\sigma = A(\phi_C - \phi)^{-s} \text{ where, } \phi < \phi_C \quad (1)$$

$$\sigma = B(\phi - \phi_C)^t \text{ where, } \phi > \phi_C \quad (2)$$

Where, s and t are critical exponents and A and B are free parameters.

The s and t parameters can be determined from the slopes of the $\log\sigma$ vs. $\log(\phi_C - \phi)$ plot for $\phi < \phi_C$ and $\log\sigma$ vs. $\log(\phi - \phi_C)$ for $\phi > \phi_C$ plots, respectively [4]. The departure of s and t from the predicted value differentiates *dynamic* from *static* percolation. The t generally ranges between 1.5 and 2. The value of s helps assigning the percolation regime which is dependent on time. Thus, $s < 1$ and $s > 1$ (ca. 1.3) recognize *static* and *dynamic* percolation regime, respectively [4].

In reverse micelles and microemulsions, the *static percolation* occurs due to the appearance of *BC* microemulsions [43] where conductivity shows a sharp increase as counterions and to a small extent ionic surfactant species can move through a integrated water channel in the system. The formation of a continuous connected disperse phase (water) is mainly responsible for the increase in conductivity. In contrast, the *dynamic percolation* [44] refers to the rapid fusion and fission among the droplets of reverse micelles and microemulsions in which transient water channels can be formed by breaking down the interface of surfactants in the event of collisions or through the integration of droplets. Thus, the movement of counter ions along the water channels dictates the conductivity [32]. The $\log\sigma$ vs. $\log(\phi_C - \phi)$ for $\phi < \phi_C$ and $\log\sigma$ vs. $\log(\phi - \phi_C)$ for $\phi > \phi_C$ plots for microemulsions of CTAB/1-butanol/cyclohexane/water and reverse micelles of CTAB/1-butanol/water are shown in Fig. 6 (a) and 6 (b), respectively.

In *static* systems the exponents t and s should be < 1 and in *dynamic* systems t and s should be > 1 , respectively [6]. In this study for microemulsions of CTAB (Fig. 6a), we obtained the value of $t = 0.32$ and $s = 0.78$ at above the $\phi_C = 0.17$ which indicates *static* percolation system i.e. the *BC* microemulsions and above $\phi_C = 0.45$, the values of $t = 1.6$ and $s = 1.02$ signify *dynamic* percolation system arising from droplets of *w/o* or *o/w* microemulsions. Above $\phi_C = 0.30$, $t = 0.31$ and below $\phi_C = 0.30$, $s = 0.92$ for reverse micelles of CTAB (Fig. 6b) to infer *static* percolation system due to the appearance of *BC* microemulsions. Thus, it may be possible that in reverse micelles, phase transition occurs from *w/o* to *o/w* via *BC* phases.

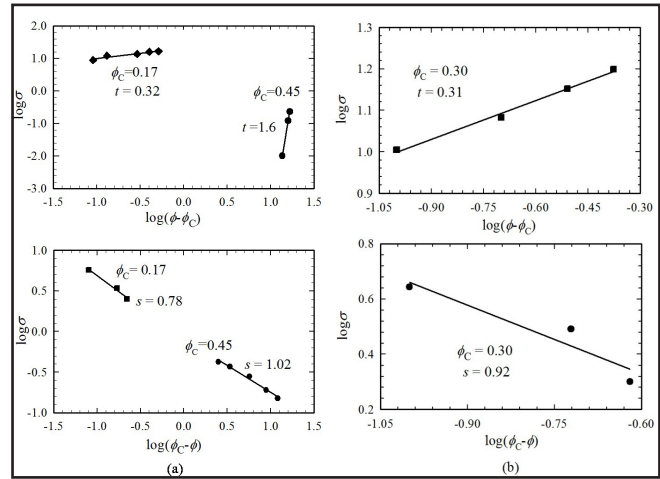


Fig. 6: Plots of $\log\sigma$ vs. $\log(\phi - \phi_C)$ for $\phi > \phi_C$ and $\log\sigma$ vs. $\log(\phi_C - \phi)$ for $\phi < \phi_C$ for (a) Microemulsions of CTAB/1-butanol/cyclohexane/water at $\phi_W = 0.17(\phi_{C1})$ and $0.45(\phi_{C2})$ and (b) Reverse Micelles of CTAB/1-butanol/water at $\phi_W = 0.30(\phi_C)$

F. Excess Volume from Density Results

The excess volume of the reverse micelles and microemulsions formation can clarify the variation of density with ϕ_W [30]. The excess volume (V^E) of formation of reverse micelles and microemulsions can be expressed as

$$V^E = V_{\text{Mic}} - \sum_i \phi_i V_i \quad (3)$$

where, V^E = the excess volume, V_{Mic} = the measured specific volume of microemulsions or reverse micelles, ϕ_i = the volume fraction of component i in microemulsion or reverse micelles and V_i = the specific volume of component i . Fig. 7 represents the V^E of microemulsions of CTAB/1-butanol/cyclohexane/water and reverse micelles of CTAB/1-butanol/water as a function of ϕ_W at 25 °C. In microemulsions of CTAB/1-butanol/cyclohexane/water Fig. 7 (a), the value of V^E decreases for $\phi_W < 0.17$. For $\phi_W = 0.17 \sim 0.45$, the V^E is almost constant. For $\phi_W > 0.45$, the V^E increases. In reverse micelles of CTAB/1-butanol/water (Fig. 7 (b)), the value of the V^E decreases up to $\phi_W = 0.30$, then increases. Negative values of the V^E in reverse micelles and microemulsions indicate contraction of the system

upon mixing. Structural transition in the microemulsion region is apparent at $\phi_W = 0.17$ (ϕ_{C1}) and 0.45 (ϕ_{C2}) whereas in the reverse micelles the transition occurs at $\phi_W = 0.30$ (ϕ_C) [30].

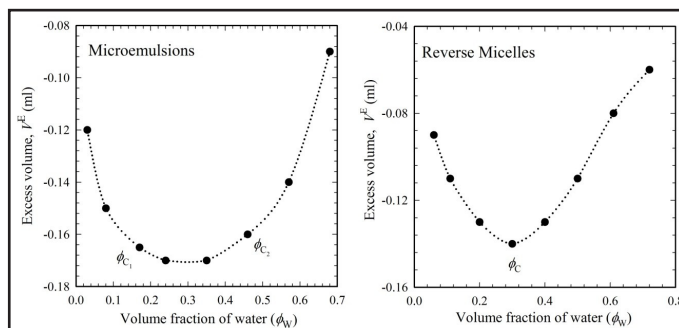


Fig. 7: The V^E of (a) Microemulsions of CTAB/1-butanol/cyclohexane/water and (b) Reverse Micelles of CTAB/1-butanol/water as a Function of ϕ_W . Dotted Lines are Used to Understand the Phase Transitions Clearly

G. Excess Refractive Index from Refractive Index Results

The refractive index of microemulsions of CTAB/1-butanol/cyclohexane/water and reverse micelles of CTAB/1-butanol/water decreases with increasing ϕ_W or w_o [32]. The excess refractive index (n^E) can be calculated from the following relation [45],

$$n^E = n_{Mic} - \sum_i \phi_i n_i \tag{4}$$

where n_{Mic} = the measured refractive index of microemulsions or reverse micelles, ϕ_i = volume fraction of component i in microemulsions or reverse micelles and n_i = refractive index of component i . Fig. 8 represents change in the n^E of microemulsions of CTAB/1-butanol/cyclohexane/water and reverse micelles of CTAB/1-butanol/water with ϕ_W at 25 °C. In microemulsions of CTAB (Fig. 8a), the value of the n^E decreases sharply for $\phi_W < 0.17$. For $\phi_W = 0.17 \sim 0.45$, the n^E decreases slightly. For $\phi_W > 0.45$, the n^E increases. In reverse micelles of CTAB (Fig. 8b), the n^E decreases up to $\phi_W = 0.30$ and then increases. This may correspond to the structural transitions in microemulsions at $\phi_W = 0.17$ (ϕ_{C1}) and 0.45 (ϕ_{C2}); whereas in the reverse micelles the transition occurs at $\phi_W = 0.30$ (ϕ_C).

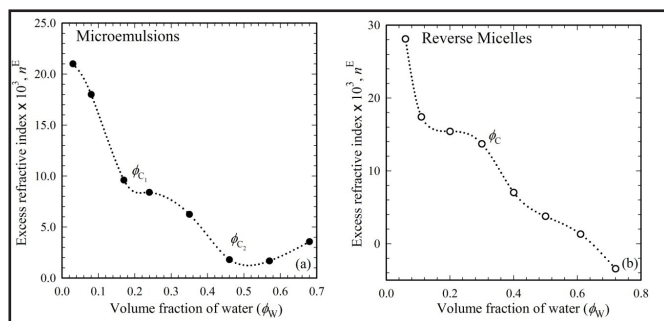


Fig. 8: The n^E of (a) Microemulsions of CTAB/1-butanol/cyclohexane/water and (b) Reverse Micelles of CTAB/1-butanol/water as a Function of ϕ_W . Dotted Lines are Used to Understand the Phase Transitions Clearly

H. Excess Molar Refraction from Refractive Index Results

Excess molar refraction (R^E) values give more information than the n^E about the mixture phenomenon since molar refraction is directly related to the dispersion forces [46]. The R^E values were calculated for all the mixtures using equation (5)

$$R^E = R_{Mic} - \sum_i \phi_i R_i \tag{5}$$

where, R_{Mic} = the molar refraction of microemulsions or reverse micelles calculated from refractive index results, ϕ_i = volume fraction of component i in microemulsions or reverse micelles and R_i = the molar refraction of component i . Fig. 9 represents change in the R^E of microemulsions of CTAB/1-butanol/cyclohexane/water and reverse micelles of CTAB/1-butanol/water with ϕ_W at 25 °C. The phase transitions in microemulsions (Fig. 9 (a)) and reverse micelles (Fig. 9 (b)) of CTAB were further confirmed by the R^E vs. ϕ_W profiles where the R^E decreases with increasing ϕ_W with different patterns in different regions of microemulsions and reverse micelles due to various microstructures. These profiles also give two phase transition points in microemulsions and one phase transition in reverse micelles which are similar to other results.

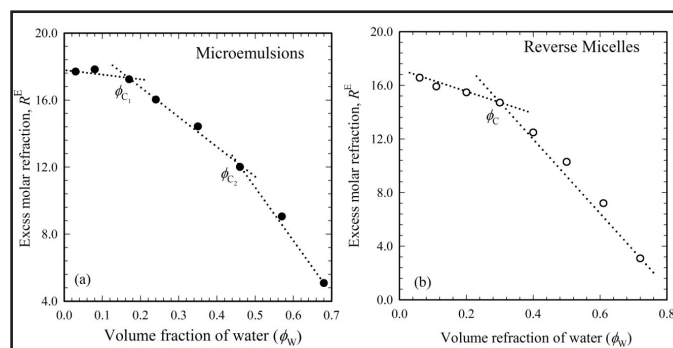


Fig. 9: The R^E of (a) Microemulsions of CTAB/1-butanol/cyclohexane/water and (b) Reverse Micelles of CTAB/1-butanol/water as Function of ϕ_W . Dotted Lines are Used to Understand the Phase Transitions Clearly

I. Droplet Sizes

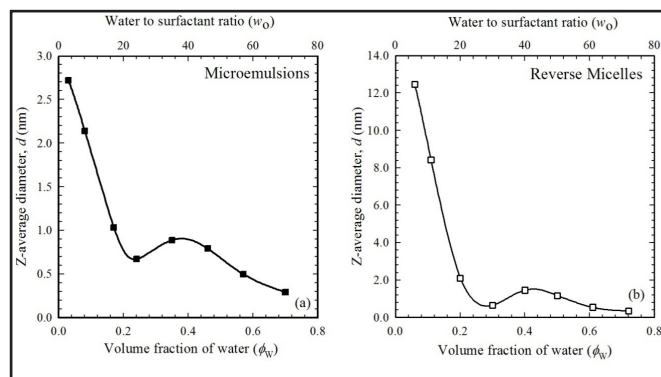


Fig. 10: Shows Z-Average Diameter vs. w_o or ϕ_W for Microemulsions of CTAB/1-butanol/cyclohexane/water and Reverse Micelles of CTAB/1-butanol/water [32]

The droplet sizes of all the microemulsions and reverse micelles were found to be smaller than 100 nm [47]. It may be noted that the Z -average diameters of microemulsions of CTAB/1-butanol/cyclohexane/water are smaller than the corresponding reverse micelles of CTAB/1-butanol/water and the value decreases with increasing w_o [32]. The larger size at $\phi_W = 0.03$ ($w_o = 3.64$) (for microemulsions) and $\phi_W = 0.06$ ($w_o = 7.00$) (for reverse micelles) corresponds to the formation of reverse micelles of CTAB in 1-butanol. The electrostatic repulsion between the cationic polar heads of CTAB is screened by 1-butanol and assists in the formation of larger size of the droplets [48]. As the w_o or ϕ_W increases, the droplet size decreases since the number of reverse micelles decreases. At $\phi_W = 0.70$ ($w_o = 70.9$) (for microemulsions) and $\phi_W = 0.72$ ($w_o = 73.7$) (for reverse micelles), the very small droplet sizes correspond to the micelles of CTAB in water. Furthermore, in the middle region, the constancy of the droplet size indicates the transition from reverse micellar to micellar phase, via BC microemulsions. Thus, it is also clear from Z -average diameter vs. w_o or ϕ_W profile that two phase transitions: w/o to BC and BC to o/w structure occur at $\phi_W \sim 0.20$ and $\phi_W \sim 0.46$, respectively as well as in reverse micelles, a transition from w/o to o/w via BC structure occur at $\phi_W \sim 0.30$.

J. Zeta Potentials

Zeta potentials, related to the surface charge, of different reverse micelles and microemulsions were also measured to further confirm three different microstructures in reverse micelles and microemulsions. Zeta-potential average values of different microemulsions ranged from -0.15 mV to 0.45 mV with increasing w_o from 3.64 to 70.9 ($\phi_W = 0.03$ to 0.70) and for reverse micelles, the zeta potential average values ranged from -0.09 to 0.32 mV with increasing w_o from 7.0 to 73.7 ($\phi_W = 0.06$ to 0.72). The highest zeta potential corresponds to the microemulsions or reverse micelles to suggest o/w or BC structures where charges of CTAB accumulate in the surface; whereas the lowest refer to microemulsions or reverse micelles with reverse hexagonal and micellar structures where charges of CTAB are in the core of the reverse micelles or w/o microemulsions [49].

IV. MICROSTRUCTURES OF REVERSE MICELLES AND MICROEMULSIONS

According to percolation theory and percolation scaling law, the phase transitions in microemulsions of CTAB/1-butanol/cyclohexane/water from conductivity results are noticed at $\phi_W = 0.17$ (ϕ_{C_1}) (19.6 %wt. of water) and 0.46 (ϕ_{C_2}) (49.6 %wt. of water) whereas for reverse micelles of CTAB/1-butanol/water, the transitions occur at $\phi_W = 0.30$ (ϕ_C) (33.0 %wt. of water). Thus, we can identify three different microstructures in w/o , BC , o/w microemulsions which are also in accordance with the calculated V^E and n^E results. As a result, in general,

the phase transitions from w/o - BC and BC - o/w occur at 20.0 %wt. and 50.0 %wt. of water, respectively. Below the percolation thresholds (ϕ_{C_1}), the isolated water droplets in oil (w/o microemulsions) are separated from each other. Above the percolation thresholds (ϕ_{C_1}), the water droplets are weakly bound to form clusters or interconnected channels known as BC phase where the aggregation number of CTAB changes and the counterions can migrate through the channel. With further increase in the ϕ_W (above the ϕ_{C_2}), the organization of the CTAB changes reversely and forms o/w microemulsions. The schematic diagram in Fig. 11 shows three different microstructures in reverse micelles and microemulsions at the percolation thresholds with increasing ϕ_W .

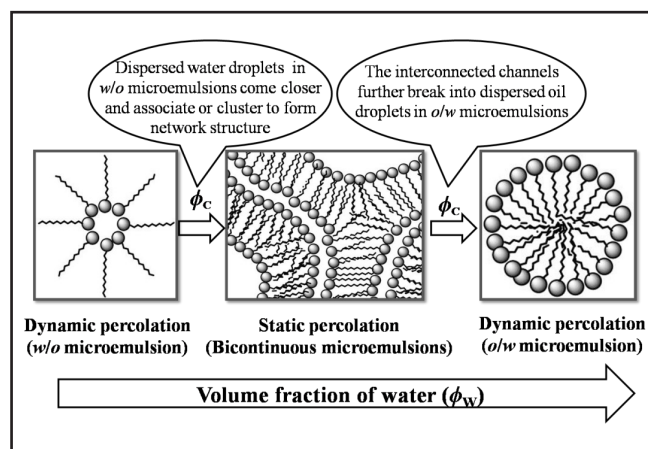


Fig. 11: Microstructures of Microemulsions with Increasing ϕ_W

V. CONCLUSIONS

The dynamic properties: conductivity, viscosity and surface tension results provide definite indication about the microstructures of microemulsions of CTAB/1-butanol/cyclohexane/water and reverse micelles of CTAB/1-butanol/water. For these systems, three different microstructures, water-in-oil, bicontinuous and oil-in-water microemulsions can be observed from percolation thresholds. When the ϕ_W is below the percolation thresholds, the interaction between the isolated water droplets in oil is relatively weak. Above the percolation thresholds, the water droplets may form weakly bound clusters or a bicontinuous phase to bring about changes in the aggregation number of CTAB. With further increase in the ϕ_W , the o/w microemulsions are produced by changing the organization of CTAB in a reverse manner. The profiles of excess volume vs. ϕ_W , excess refraction vs. ϕ_W and excess molar refraction vs. ϕ_W for these systems also indicate that structural phase transitions take place from water-in-oil to oil-in-water microemulsions via BC microemulsions. These would help predicting the geometry of reverse micelles and microemulsions and understanding of the microstructural phase transition in such systems and other microemulsion systems comprising designer solvents, such as ionic liquids [50].

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