



## The physicochemistry and percolation behavior of microemulsions as a function of chain length of cosurfactant and surfactant.

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### ABSTRACT

This study involved investigating phase behavior and physicochemical characterization of microemulsions (MEs) stabilized by mixtures containing polysorbates (C<sub>12</sub>-C<sub>18</sub>) as surfactants and n-alkanols (C<sub>2</sub>-C<sub>6</sub>) as cosurfactants. Distribution coefficients and Gibbs free energy were also determined for the systems containing polyoxyethylene sorbitan monolaurate (Tween® 20) as surfactant. ME with Tween® 20 as the surfactant and ethanol as the co-surfactant exhibited maximum ME area, as well as, water solubilization capacity (WSC). In the presence of all the co-surfactants, values of both of these parameters decreased as the chain length of the surfactant increased with the exception of Tween® 80. This could be attributed to the unsaturated structure of Tween® 80 which possibly allowed for greater spatial configurations of the chain and thus allowing less oil penetration. Furthermore, the transition of w/o MEs to o/w MEs via a bi-continuous structure along the dilution line was confirmed by conductivity, viscosity and droplet size analysis.

**KEY WORDS:** Microemulsions, phase behavior, water solubilization capacity, water dilution line, chain length, thermodynamic stability, Gibbs free energy

### INTRODUCTION

Microemulsions (MEs) are thermodynamically stable, isotropic transparent, low viscosity dispersions of oil, water and surfactants and/or co-surfactants. Ever since their inception, MEs have been studied extensively, theoretically, as well as, experimentally, by many researchers (1, 2). In industrial applications, a mixture of surfactants is used for the formation of MEs.

MEs formed from a mixture of non-ionic surfactants are reported to be more effective than those formed from ionic surfactants. This is because their particle size distribution is smaller (10-100 nm), they are less toxic and they do not require co-surfactants in the formulation. The use of a mixture of surfactants for ME formulations allows flexibility to design and adjust phase behavior (3, 4).

MEs provide a large interface between water and the non-polar solvent and enable the

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coexistence of both water-soluble and oil-soluble materials. The changes in the internal structure of an ME can be analyzed using different methods, e.g., conductivity, viscosity, density and differential scanning calorimetry. It has been reported that the formation, physicochemical and electrochemical properties of the MEs are influenced by the alkyl chain length of the fatty acid component of the oil, as well as, that of the alcohol. This is attributed to the fact that the interfacial composition and distribution of the alcohol are influenced by both the alkyl chain length of the alcohol and that of the oil (5). The nature of the surfactant, alcohol and oil strongly influence the properties of MEs. The influence of the chain length of the surfactant and its combination with alcohols with different chain length is not very well documented in literature.

Therefore, in the present study, phase behavior and the water solubilization capacity (WSC) of MEs was studied as a function of the alkyl chain length of a surfactant ( $C_{12}$ - $C_{18}$ ) in combination with alcohol ( $C_2$ - $C_6$ ) as a co-surfactant. The distribution coefficient of alcohol in oil was also investigated. Additionally, the structure of MEs was investigated using conductivity and viscosity. Isopropyl myristate (IPM) was used as the oil phase because this is one of a commonly used components of industrial MEs.

## MATERIALS AND METHODS

### Materials

Polyoxyethylene sorbitan monolaureate (Tween<sup>®</sup> 20) and Polyoxyethylene sorbitan monooleate (Tween<sup>®</sup> 80) were of commercial grade and purchased from S.D. Fine Chemicals Ltd., Mumbai, India. Polyoxyethylene sorbitan monopalmitate (Tween<sup>®</sup> 40) and Polyoxyethylene sorbitan monostearate (Tween<sup>®</sup> 60) were procured from Sigma Chemical Co. (St. Louis, MO, USA). Isopropyl myristate was obtained from Thomas Baker Pvt. Ltd., Mumbai, India. Ethanol, n-propanol, n-butanol, n-pentanol and n-hexanol were

purchased from Loba Chemie Pvt. Ltd., Mumbai, India. Double-distilled water was used throughout this study.

### Methods

#### *The formulation of ME*

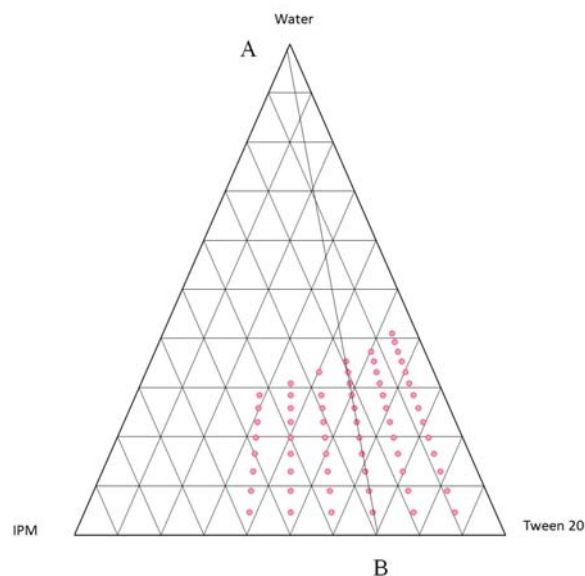
MEs consisting of oil (IPM), surfactant (Tween<sup>®</sup> 20/Tween<sup>®</sup> 40/Tween<sup>®</sup> 60/Tween<sup>®</sup> 80), co-surfactant (ethanol/n-propanol n-butanol/n-pentanol/n-hexanol), and aqueous phase (double-distilled water) were formulated. The weight ratio of oil to surfactant varied from 9:1 to 1:9. Water was added drop-wise to these mixtures and mixed using a magnetic stirrer (REMI, Mumbai, India) at  $25^{\circ}\text{C} \pm 0.05^{\circ}\text{C}$ . Following the addition of each drop of water, the mixture was visually examined for transparency. The changes in the appearance from transparent to turbid and *vice versa* were observed. Transparent, single-phase, and low viscosity mixtures were designated as MEs. Similarly, systems containing alkanols as co-surfactants with surfactant to cosurfactant ratios of 1:1, 1:2 and 2:1 were formulated as described previously. The phase behavior of all the systems was mapped using a ternary phase diagram. The samples were marked as points in the phase diagram and the area covered by these values was considered to be the ME region of existence.

#### *The characterization of the microemulsions*

MEs were prepared after drawing a “water dilution line” in the phase diagrams (Figure 1) representing increasing water content and changing oil to surfactant-cosurfactant ratio along the change in water content (6). These samples were further characterized.

#### *Visual inspection*

All the formulations were mixed with 10 ml of water in a glass tube at ambient temperature and were then gently shaken. These equilibrated samples were assessed for clarity and transparency by visual inspection.



**Figure 1** Phase diagram of an ME system showing the water dilution line.

### Transmittance

The formulated MEs were evaluated for transmittance after dilution (100X) with water at 650 nm with a UV spectrophotometer (Beckman DU 640B UV/VIS Spectrophotometer, USA).

### Water solubilization capacity

The water solubilization capacity of the different formulations, both in the presence and in the absence of, different alcohols was determined. In the present study straight chain alcohols (ethanol to hexanol) and surfactants with different hydrophobic chain lengths (Tweens<sup>®</sup> 20, 40, 60 and 80) were used to study the effect of the chain length of the surfactant, as well as, that of the co-surfactant on the WSC of the MEs. The single phase MEs were prepared by gradual addition of water into the mixture of oil, surfactant and co-surfactant until a clear solution was reached. The maximum WSC was determined using a conventional titration method with further addition of water in the above formulated MEs until the solutions became turbid (7, 8). The WSC was determined according to Equation 1.

$$WSC = \frac{W_m}{S_m} \quad \text{Eq. 1}$$

Where,  $W_m$  = the maximum amount of solubilized water and  $S_m$  = the amount of surfactants required to obtain maximum solubilization

### Dilution experiments

The distribution coefficient of alcohol in the oil and water phase was determined by dilution experiments. Predetermined amounts of the different components i.e., 0.2 g of oil and 0.1 g of water were mixed with 1.8 g of surfactant. Tween<sup>®</sup> 20 was selected as surfactant for this study because it exhibited the maximum ME region. The mixture was stirred using a magnetic stirrer at  $25^\circ\text{C} \pm 0.5^\circ\text{C}$ . The co-surfactant was added slowly with a micro-pipette to the initially turbid mixture until the solution became clear. The volume of co-surfactant added at this point was recorded. An additional amount of oil (1.0 g) was added to the same system to destabilize it i.e., until the solution turned turbid again. The turbid solution was then again made clear by adding the co-surfactant and the volume was recorded (7). This procedure was repeated several times to obtain the quantity of the oil and the co-surfactant added at each step. This procedure ( $n=3$ ) was performed for different alcohols (butanol/pentanol/hexanol) at a constant temperature of  $25^\circ\text{C} \pm 0.5^\circ\text{C}$ .

### Conductivity measurements

The electrical conductivity ( $\sigma$ ) was measured using a microprocessor based pH-EC (ESICO, India) operating at 50 Hz. The conductivity of the selected MEs (along the dilution line) was measured as a function of  $\varphi$  [moles of water/(moles of surfactant + moles of co-surfactant)]. The standard error of conductance measurements was  $\pm 5\%$  ( $n=3$ ). The cell constant of the conductivity meter was

1.099 $\mu$ S/cm. Conductivity measurements were carried out at  $25 \pm 0.5^\circ\text{C}$ .

### **Viscosity measurements**

Viscosities of selected formulations in the ME region were determined using a Brookfield viscometer (Spindle No. 18, LVDV-I-Prime, Brookfield Engineering Laboratories, USA). Samples along the dilution line were prepared specifically for viscosity measurements. Viscosity measurements were performed at  $25 \pm 0.5^\circ\text{C}$  in triplicate ( $n=3$ ).

### **Particle size measurements**

Particle size measurements of the ME formulations (100 times dilution with water) containing Tween<sup>®</sup> 20 with, and without, different alcohols were performed using a Malvern Zetasizer Nano S 90 (Malvern Instruments Ltd, Worcestershire, United Kingdom). A fixed scattering angle of 90 degrees was used and the software generated an auto-correlation function, from which the particle size and distribution were calculated. Particle size of MEs containing Tween<sup>®</sup> 20 and ethanol was analyzed along the dilution line.

### **Stability tests**

#### **Centrifugation**

The stability of the MEs was determined by centrifuging them at  $1609.92 \times g$  for 15 minutes immediately after their formation.

#### **Freeze-Thaw cycles**

The MEs were subjected to a total of 3 freeze-thaw cycles. Each cycle consisted of 24 hours at  $25^\circ\text{C}$  followed by 24 hours at  $-4^\circ\text{C}$  immediately after their formation. The ME formulations containing Tween<sup>®</sup> 20 and ethanol along the dilution line (the selected MEs) were stored at  $25^\circ\text{C} \pm 2^\circ\text{C}$  and  $65\% \pm 5\%$  RH in a stability chamber and then characterized for conductivity and viscosity after a period of 30 days, 60 days and 90 days.

### **Statistical analysis**

ANOVA was performed using the Student-Newman-Keuls method for comparing the data of the different ME formulations containing different surfactants with, and without, co-surfactants. Statistical analysis was carried out at  $P < 0.05$ .

## **RESULTS AND DISCUSSION**

### **The preparation of phase diagrams**

The MEs in the present study formed spontaneously at  $25^\circ\text{C} \pm 0.5^\circ\text{C}$ . Phase diagrams of MEs with, and without, co-surfactants were prepared to identify the ME existence zone and to calculate  $A_t$  (the ME area) (Table 1). The ME area is defined as the area in the ternary phase diagram in which an isotropic, transparent, low viscosity phase forms. Surfactant mixture with different weight ratios (1:1/1:2/2:1) were prepared by mixing different Tweens<sup>®</sup> with different alcohols for constructing phase diagrams. However, the MEs formulated using surfactant/co-surfactant at 1:1 ratios were selected for all the cases as this composition exhibited maximum isotropic ME region (Table 1).

The phase studies revealed that the maximum area of the ME systems occurred with Tween<sup>®</sup> 20 both, in the presence ( $A_t = 36.94\%$ ) and the absence, of a co-surfactant ( $A_t = 32.51\%$ ). It is evident from the results that  $A_t$  of MEs containing Tweens with ethanol, propanol and butanol as co-surfactant was significantly greater than the systems without co-surfactant ( $P < 0.05$ ). However,  $A_t$  was significantly less when pentanol ( $A_t = 27.46\%$ ) and hexanol ( $A_t = 26.93\%$ ) were used as co-surfactants (Table 1).

It is noteworthy that, without exception, the total monophasic area decreased as the chain length of surfactant increased (Table 1). This conforms with the results obtained by Fanun

**Table 1** The composition and ME area ( $A_t$ ) of the different ME Systems

SURFACTANT	COSURFACTANT	FORMULATION CODE OF ME	$A_t$ (%)	WSC	$\phi_p$	$\phi_b$
Tween 20	-	T20W	32.51	0.77	-	-
Tween 40	-	T40W	30.24	0.66	-	-
Tween 60	-	T60W	28.13	0.61	-	-
Tween 80	-	T80W	30.61	0.66	-	-
Tween 20	Ethanol	T20E	36.94	1.11	0.8	1.7
Tween 40	Ethanol	T40E	34.31	0.88	1.0	2.2
Tween 60	Ethanol	T60E	31.67	0.83	1.2	2.8
Tween 80	Ethanol	T80E	33.27	0.94	2.2	3.3
Tween 20	Propanol	T20P	33.88	1.0	2.6	3.8
Tween 40	Propanol	T40P	32.67	0.88	0.4	2.4
Tween 60	Propanol	T60P	28.32	0.72	1.3	3.0
Tween 80	Propanol	T80 P	31.74	0.94	2.0	3.7
Tween 20	Butanol	T20B	32.36	0.83	2.3	4.4
Tween 40	Butanol	T40B	29.34	0.77	2.7	6.1
Tween 60	Butanol	T60B	27.15	0.72	0.8	2.3
Tween 80	Butanol	T80B	31.51	0.77	1.0	3.1
Tween 20	Pentanol	T20PN	27.46	0.61	1.3	3.8
Tween 40	Pentanol	T40PN	26.81	0.55	1.5	4.4
Tween 60	Pentanol	T60PN	20.02	0.50	1.7	5.0
Tween 80	Pentanol	T80PN	26.48	0.55	0.7	2.3
Tween 20	Hexanol	T20H	26.93	0.55	1.1	3.1
Tween 40	Hexanol	T40H	22.06	0.44	1.3	3.8
Tween 60	Hexanol	T60H	18.15	0.38	1.5	4.4
Tween 80	Hexanol	T80H	24.48	0.50	1.7	5.1

which showed that when, sucrose esters with different chain lengths were used as surfactants, the total ME area reduced with increasing surfactant chain length (9).

The order followed by different alcohols as co-surfactants for  $A_t$  was ethanol>propanol>butanol>pentanol>hexanol regardless of the surfactant used. The effect of the different alcohols on the monophasic area could be attributed to the partitioning of the alcohol between the oil and the aqueous phase.

There is always a bending stress associated with droplet formation. Short chain co-surfactant molecules can more easily accommodate

themselves among the surfactant molecules at the droplet interface thereby releasing this bending stress (9). A similar mechanism could be assumed in the present investigation i.e., the contribution of short chain alcohols was greater in releasing the bending stress, thus decreasing the interfacial tension, in turn, resulting in an increase in the interfacial area. However, as the alkyl chain length of alcohol increased, from butanol to hexanol, their oil solubility increased due to favorable hydrophobic interactions between chains, with a consequent propensity to migrate completely in the oil phase (5). Therefore, alcohols higher in the homologous series participate less in the construction of the interface. Thus, the total isotropic ME area in

the phase diagrams decreased as the chain length of alkanol increased.

### Visual inspection

All the formulations along the dilution line were clear and almost transparent when diluted with water. The formulations which remained turbid or opaque were not included in further studies as they were considered to be outside the phase diagram of the ME region.

### Transmittance

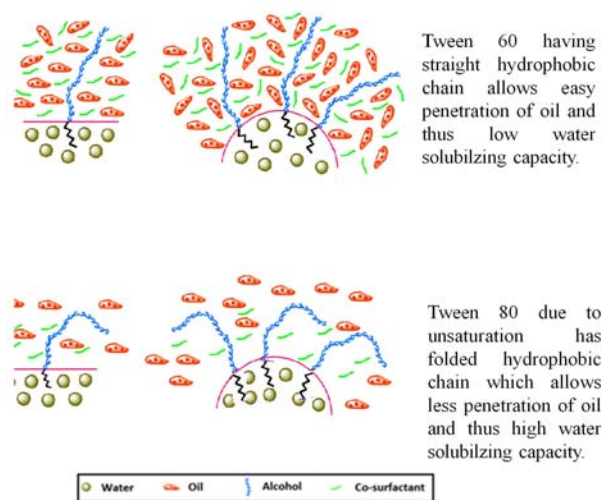
The percentage transmittance of all of the 100X diluted formulations varied from 78% to 86%.

### Water solubilization capacity

The WSC is defined as the maximum amount of water solubilized (wt.) per amount (wt.) of surfactant for a fixed composition of co-surfactant and oil in the isotropic, transparent region of the ME. For different Tweens<sup>®</sup>, WSC depends upon the oxyethylene group (polar portion), the configuration of the polar head group and hydrocarbon moiety of nonionic surfactants and on the type of oil (10). The WSC of the different compositions is summarized in Table 1. For a fixed amount of oil (0.2 g) and surfactant-co-surfactant mixture (1.8 g) the WSC was greatest with Tween<sup>®</sup> 20 and least with Tween<sup>®</sup> 60 for all alcohols studied i.e., the WSC decreased with increasing chain length of the surfactant. It is interesting to note that the WSC of Tween<sup>®</sup> 80 was significantly greater than that of Tween<sup>®</sup> 60 (Table 1). This could be attributed to the unsaturated fatty acid structure of Tween<sup>®</sup> 80 which presumably caused folding of the chain and allowed for less oil penetration (Figure 2). These results are conform with the results of the ME area, where  $A_t$  of Tween<sup>®</sup> 60 was less than that of Tween<sup>®</sup> 80. The values of  $A_t$  without co-surfactant were 28.13% and 30.61% for Tween<sup>®</sup> 60 and Tween<sup>®</sup> 80, respectively (Table 1).

Similarly, results of WSC of Tweens with different alkanols (co-surfactants) increased in the order of ethanol>propanol>butanol>pentanol>hexanol (Table 1). The greatest WSC was observed for ethanol and the least was observed for hexanol regardless of the surfactant used (Table 1). The WSC of the ME containing lower chain length alcohol was greater. As the chain length of alcohol was increased from C<sub>2</sub> (ethanol) to C<sub>6</sub> (hexanol), the WSC decreased. As an example, using Tween<sup>®</sup> 20 as surfactant, WSC with ethanol, propanol, butanol, pentanol, and hexanol were 1.11, 1.0, 0.83, 0.61 and 0.55, respectively. A similar trend was found for the other Tweens<sup>®</sup> (40, 60 and 80). This phenomenon could be explained in terms of the partitioning efficiency of the alcohols i.e., short chain alcohols solubilize both in the oil and water phases but the long chain alcohols solubilize predominantly in the oil phase (7). Alcohols of higher chain length i.e., butanol (solubility 73 g/l in water at 25°C), pentanol (22 g/l in water at 25°C) and hexanol (5.9 g/l in water at 25°C) are partitioned less at the interface due to their increased solubility in the oil phase. On the other hand, short chain alcohols such as ethanol and propanol are soluble in water, as well as, in oil and therefore the ratio of their interfacial amount to the total amount present in the formulation is larger than that of long chain alkanols.

Moreover, this may also be due to the fact that short chain alcohols increase interfacial fluidity due to void formation in aliphatic layer of interfacial film and hence, cause an increase the solubilization capacity while long chain alcohols such as pentanol and hexanol stiffen the interfacial film resulting in decreasing WSC (Figure 3). In the studies carried out by Garti *et al.* (2001) using limonene and medium chain triglycerides as the oily phase, different non ionic surfactants combined with ethanol and polyols as co-surfactants demonstrated a significant increase (from 5% to 20%) in water solubilization in the presence of ethanol compared to the MEs without added co-surfactants (6).

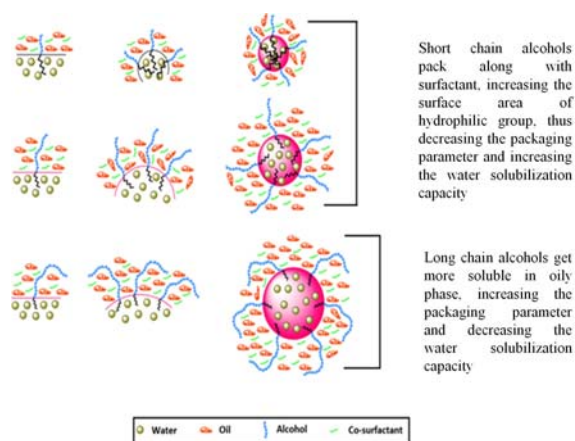


**Figure 2** The effect of the structure of the surfactant on the water solubilization capacity.

Solubilization and phase equilibria of MEs are dependent on two phenomenological parameters, namely the spontaneous curvature and elasticity of the interfacial film when the interfacial tension is very low (as in the case of MEs) (11). Short chain alcohols, such as, ethanol and propanol penetrate into the palisade layers and cause the interface to become curved, thereby favoring a decrease of the critical radius of the droplet leading to formation of smaller w/o ME droplets thus increasing the solubilization capacity. When the chain length of alcohols increases as is the case for butanol to hexanol, there is an increase in the hydrophobic interactions between the oil and the co-surfactant. This causes less participation in interface formation resulting in flat interfaces that have less curvature and reduced solubilization capacity (12).

### The theory of the dilution experiment

The stability of an ME is determined, in part, by the distribution of the co-surfactant molecules (medium chain alcohols) between the oil and the interface at a constant temperature. As the amount of oil is increased, there is a reduction in the interfacial concentration of the co-surfactant leading to an instability of the system. This process can be reversed by adding



**Figure 3** The effect of the chain length of different alcohols on the water solubilization capacity.

a co-surfactant in an amount sufficient to re-establish the interfacial concentration necessary for a stable ME. This sequence of steps is followed in the dilution experiment (7).  $A_t$  the point of clarity, the total number of moles ( $n$ ) of the co-surfactant in the system is given by Equation 2:

$$n_a = n_a^i + n_a^w + n_a^o \quad \text{Eq. 2}$$

Where, the superscript  $i$ ,  $w$ ,  $o$  represent the interface, water and oil phases, respectively, and  $n_a^i$ ,  $n_a^w$ ,  $n_a^o$  represent the number of moles of alcohol present in the interface of water and oil, respectively. The solubility of the co-surfactant in the oil is constant at a given temperature, with respect to the total number of moles of oil which can be written as in Equation 3 and 4.

$$k = \frac{n_a^o}{n_o} \quad \text{Eq. 3}$$

or

$$n_a^o = kn_o \quad \text{Eq. 4}$$

Where,  $n_a^o$ ,  $n_o$  and  $k$  are the number of moles of alkanol in oil, the total number of moles of oil and a constant, respectively. Replacing the value of  $n_a^o$  in equation 3 from equation 4:

$$n_a = n_a^i + n_a^w + kn_o \quad \text{Eq. 5}$$

Dividing the above equation by  $n_s$  (normalization) where,  $n_s$  is the number of moles of surfactant in the system you get:

$$\frac{n_a}{n_s} = \frac{(n_a^i + n_a^w)}{n_s} + k \left( \frac{n_o}{n_s} \right) \quad \text{Eq. 6}$$

Higher alcohols are practically insoluble in water, thus neglecting the water solubility of alcohol ( $n_a^w=0$  for higher alcohols) then Equation 6 can be written as:

$$\frac{n_a}{n_s} = \frac{n_a^i}{n_s} + \frac{n_o}{n_s} k \quad \text{Eq. 7}$$

In the dilution experiment, at fixed  $n_s$ ,  $n_a$  and  $n_o$  are varied to have a series of  $\frac{n_a}{n_s}$  and  $\frac{n_o}{n_s}$

which according to Equation (8) gives  $\frac{n_a^i}{n_s}$  and  $k$  from the linear plot of  $\frac{n_a}{n_s}$  against  $\frac{n_o}{n_s}$  as intercept (I) and slope (S), respectively (Table 2).

The partitioning of alcohol between the continuous oil phase and the interface can be expressed in terms of the distribution constant ( $k_d$ ).  $k_d$  can be calculated from the ratio of mole fraction of alcohol in interfacial composition

( $x_a^i$ ) to mole fraction of alcohol in bulk oil phase ( $x_a^o$ ) (Equation 8).

$$k_d = \frac{x_a^i}{x_a^o} = \frac{I(S+1)}{S(I+1)} \quad \text{Eq. 8}$$

Therefore,  $k_d$  can be calculated knowing the values of  $S$  and  $I$ . Thus, by using Equations 7 and 8, the values of  $n_a^i$ ,  $n_a^o$  and  $k_d$  can be calculated which could provide useful information for the formation of the ME. Evaluation of the  $k_d$  value is needed for understanding the thermodynamics of the process involved.

The  $k_d$  of ethanol and propanol could not be determined accurately as they are miscible with water. However, as the chain lengths of butanol, pentanol and hexanol increased, the solubility of alcohol in the oil also increased and the value of  $k_d$  followed the order of butanol>pentanol>hexanol (Table 2). Thus, for these three alkanols, the maximum mole fraction of butanol is present at the interface followed by pentanol and hexanol. The change in standard Gibbs free energy of transfer ( $\Delta G_t$ ) of alcohols from the oil and the interface is obtained from the relation shown in Equation 9:

$$\Delta G_t = -RT \ln k_d \quad \text{Eq. 9}$$

Table 2 shows that the value of  $\Delta G_t$  was more negative for butanol ( $-1.99 \text{ kJmol}^{-1}$ ) than for pentanol ( $-0.85 \text{ kJmol}^{-1}$ ) followed by hexanol ( $-0.21 \text{ kJmol}^{-1}$ ).  $\Delta G_t$  explains that, regardless of whether the formation of MEs is spontaneous, the more negative the value, the more thermodynamically favorable is the process of migration of alkanol from the bulk phase to the interphase and vice versa (7). The above free energy values indicate that the formation of MEs using butanol was more favorable than that using pentanol or hexanol.



**Table 2** The distribution coefficient and Gibbs free energy of the ME formulations containing different alcohols

ALCOHOL	SLOPE (S)	INTERCEPT (I)	$K_d$	$\Delta G_i$ (kJmol <sup>-1</sup> )
Butanol	0.55	13.3	2.61	-1.99
Pentanol	1.77	31.39	1.51	-0.85
Hexanol	5.75	17.9	1.11	-0.22

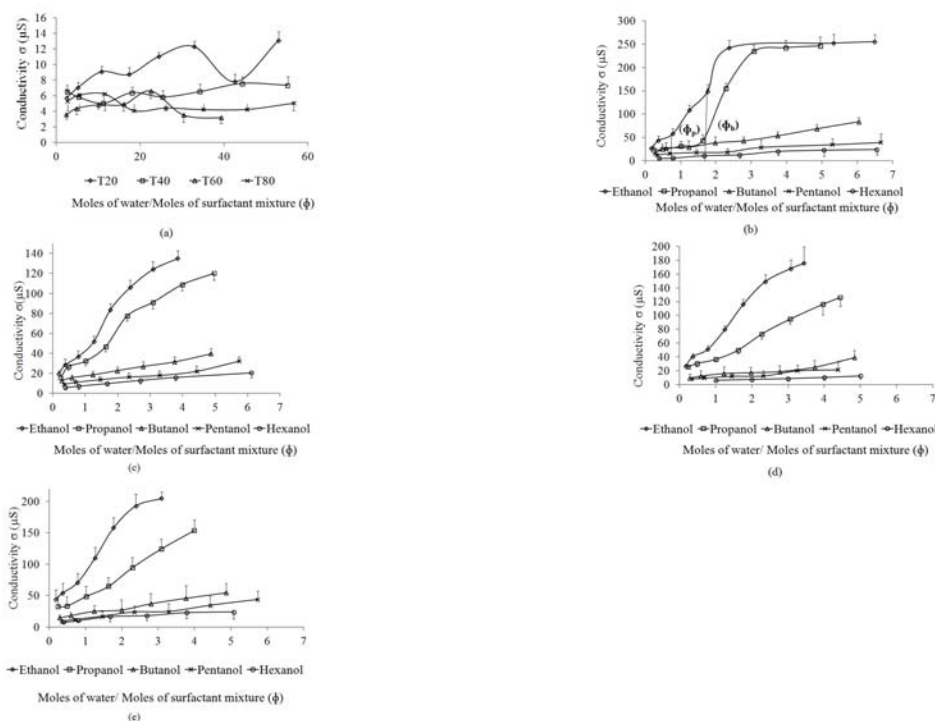
As the chain lengths of the co-surfactant increased, Gibbs free energy of the migration of alkanol from the bulk phase to the interphase increased. Likewise, Bera *et. al.* determined  $k_d$  and Gibbs free energy of 3-methyl-1-butanol at different temperatures using sodium dodecyl sulfate and cetyl trimethylammonium bromide as surfactants, and different hydrocarbons (hexane, heptane, decane and dodecane) as the oil phase. They found that Gibbs free energy for all the oils studied, decreased with an increase in temperature, which indicated that, the transfer of the co-surfactant from the oil to the interface become more favorable by increasing the temperature (7).

## Conductivity

Conductivity is an important tool to investigate the structure of an ME. The compositions of ME for this parameter were selected from the water dilution line on the phase diagram. The plot of electrical conductivity ( $\sigma$ ) as a function of  $\Phi$  [(moles of water (moles of surfactant + moles of co-surfactant)] along the dilution line AB for each system was drawn. Alcohol based MEs were more conductive compared to MEs without alcohols (Figure 4). The variation of conductivity with respect to  $\Phi$  is shown in Figure 4. The behavior shows the profile characteristic of percolative conductivity. The systems containing Tweens<sup>®</sup> together with a co-surfactant not only, showed greater values of conductivity compared to the ME systems without co-surfactant, but also possessed percolative behavior. The conductivity was initially low in the oil/surfactant mixtures and increased with an increase in the mole fraction of water ( $\Phi$ ) (Figure 4b-e). As the value of  $\Phi$

increased, the conductivity ( $\sigma$ ) of the system also increased but to a lesser extent until a specific  $\Phi$ , after this point a drastic change i.e. increase in conductivity to a greater extent was observed (Table 1). This phenomenon is known as percolation and the critical  $\Phi$  at which this change occurs is known as percolation threshold ( $\Phi_p$ ). The values of conductivity below  $\Phi_p$  suggested that probably w/o droplets were discrete and had little interaction, hence leading to the formation of w/o ME. Above  $\Phi_p$ , the value of  $\sigma$  increased steeply. This was probably due to the interaction between the aqueous phase resulting in the formation of conductive channel network i.e., the formation of a bi-continuous ME. An increase in  $\Phi$  beyond  $\Phi_p$ , i.e., close to  $\Phi_b$ ,  $\sigma$  showed again a sudden increase which could be due to the formation of an o/w ME (13).

Other researchers have described a similar behavior with a slightly different interpretation. According to these theories w/o droplets below a critical percolation threshold ( $\Phi_p$ ) are isolated from each other embedded in non conducting continuum oil phase and hence contribute very little to electrical conductance (14). However, as  $\Phi_p$  is reached, some of the conductive droplets come closer to each other and form clusters. The number of such clusters increases rapidly above  $\Phi_p$ , giving rise to observed changes of electrical conductivity. Electrical conductivity above  $\Phi_p$  has been attributed to either the hopping of ions from droplet to within cluster or transfer of counter ions from one droplet to another through water channels operating between droplets during collisions (15). None of the MEs containing Tweens<sup>®</sup> without a co-surfactant (alcohols) exhibited percolation behavior (Figure 4a). This could be due to the rigidity of the interfacial film, large molecular volume and high viscosity of IPM. Similar results have been reported by Zhang *et. al.* using IPM as the oil phase, bis (2-ethylhexyl) sulfosuccinate sodium salt (AOT) as the surfactant and ethanol, propanol, butanol and pentanol as co-surfactants (16). The order of conductivity changed with different alcohols,



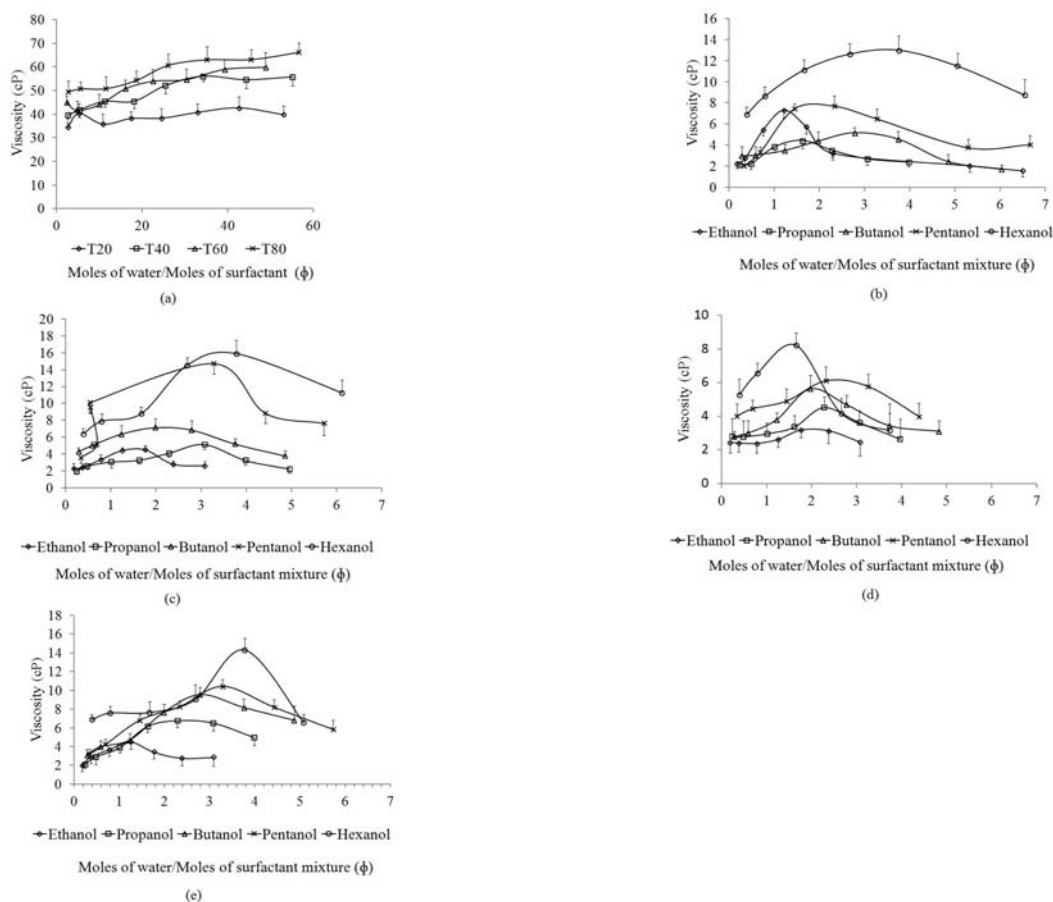
**Figure 4** Plots of conductivity ( $\sigma$ ) versus  $\Phi$  (moles of water/moles of surfactant+ moles of co-surfactant) for MEs containing (a) different Tweens without a co-surfactant, (b) Tween<sup>®</sup> 20 with different alcohols, (c) Tween<sup>®</sup> 40 with different alcohols, (d) Tween<sup>®</sup> 60 with different alcohols and (e) Tween<sup>®</sup> 80 with different alcohols.

and were maximum for ethanol and minimum for hexanol (Figure 4). This behavior could be attributed to the effect of alcohols on the elasticity of the interface. The rigidity/flexibility of the oil/water interface is a guiding factor for connectivity of droplets and the transport or exchange of materials among them. Short chain alcohols such as ethanol and propanol have the ability to reduce the interfacial free energy and tension by incorporation into interfacial layer and thus promote interfacial fluidity resulting in a decrease in the percolation threshold (8). On the other hand, butanol and other higher alcohols stiffen the interfacial membrane and making clustering, aggregation and consequently percolation difficult thus increasing the percolation threshold. The existence and position of these thresholds depend on interaction between droplets which control the duration of collision and degree of interface overlapping (17).

### Viscosity

Viscosity is a characteristic property of any fluid that largely depends on the presence of aggregates, their interaction and concentration. Therefore, it can be used as a parameter to obtain insight into the internal structure of ME. The variation of viscosity at  $25 \pm 0.5^\circ\text{C}$  as a function of  $\Phi$  along the dilution line is shown in Figure 5.

In MEs containing different Tweens<sup>®</sup> (without a co-surfactant) it was observed that as the carbon numbers in the alkyl chain length of the surfactant increased, the viscosity of the systems also increased (Figure 5a). Partly this could be due to inherent viscosity of surfactant systems. However, this did not hold true for Tween<sup>®</sup> 80 as its viscosity (425mPa) was lesser than that of Tween<sup>®</sup> 60 (600mPa). The viscosity curve of all systems containing a co-surfactant was more or less bell shaped. The increase in



**Figure 5** Plots of viscosity as a function of  $\Phi$  (moles of water/moles of surfactant+ moles of co-surfactant) along the dilution line of MEs containing (a) different tweens without a co-surfactant (b) Tween<sup>®</sup> 20 with different alcohols, (c) Tween<sup>®</sup> 40 with different alcohols (d) Tween<sup>®</sup> 60 with different alcohols and (e) Tween<sup>®</sup> 80 with different alcohols.

the viscosity in the mixed oil rich ME could be due to an increase in dispersed droplet size and enhanced attractive interaction between the droplets. The increase in the viscosity of the ME below  $\Phi_p$  indicates an attractive interaction and aggregation of droplets of the water phase including molecular reorganization at the interface where w/o MEs are present. The drastic increase in viscosity between  $\Phi_p$  and  $\Phi_b$  indicates a structural transition from w/o droplets to a bi-continuous structure and a further sharp decrease in the viscosity beyond  $\Phi_b$  could be indicative of water as the outer phase with o/w MEs in existence (Figure 5b-e). In corollary, to present results few researchers have reported that shape of the micelles change from spherical or very short rod to long worm

like micelles due to the reduction in the average sectional area of each surfactant molecule at interface. This change in the micelle shape may result in an increase in viscosity. When mixed oils are solubilized in micellar aggregates, a change in micellar shape is induced depending on the type and structure of the oil which is expected to be reflected in a change of viscosity.

### **Droplet size analysis**

The mean droplet size and polydispersity index (PDI) of formulations containing Tween<sup>®</sup> 20 (surfactant) and different alcohols (co-surfactant) with a composition of 20% (w/w)

of water, 8% (w/w) oil and 72% (w/w) surfactant mixture is summarized in Table 3.

**Table 3** Droplet size and PDI of ME containing Tween 20 with and without alcohol (The ME in the table were diluted 100X with water prior to size measurement)

COMPOSITION OF FORMULATION	DROPLET SIZE (nm)	POLYDISPERSITY INDEX
Tween 20	336.80	0.285
Tween 20 + Ethanol	143.00	0.177
Tween 20 + Propanol	315.90	0.367
Tween 20 + Butanol	491.90	0.398
Tween 20 + Pentanol	498.30	0.387
Tween 20 + Hexanol	501.62	0.423

It can be seen that the droplet size was smallest when ethanol (143 nm) was used as a co-surfactant (Table 3). This conforms with the results stating that lower chain alcohols result in smaller droplet sizes (Figure 3). Thereafter, the droplet sizes were determined for all of the ME formulations of Tween<sup>®</sup> 20 with ethanol along the water dilution line as ethanol was considered to yield the smallest particle size among all the co-surfactants (Table 4).

**Table 4** Droplet size and polydispersity index of MEs containing Tween 20 and ethanol along the water dilution line (The ME in the table were diluted 100X with water prior to size measurement)

OIL (% w/w)	SURFACTANT (% w/w)	CO-SURFACTANT (% w/w)	WATER (% w/w)	SIZE (nm)	POLY-DISPERSITY INDEX (PDI)
30	33.7	33.7	2.5	123.3	0.411
29	33	33	5.0	161.9	0.413
27	31.5	31.5	10	192.9	0.411
26	29.4	29.4	15	198.3	0.561
24	27.9	27.9	20	202.3	0.575
23	25.9	25.9	25	154.4	0.365
22	24	24	30	141.4	0.391
20	22.5	22.5	35	139.0	0.506

The particle size increased from 123.3 nm to 202.3 nm when the amount of water was increased from 2.5% w/w to 20% w/w. This may be because of the fusion or merging of droplets taking place with the increase of water. However, further increasing the water fraction

from 20% w/w to 35% w/w the droplet sizes decreased significantly from 202.3 nm to 139.0 nm.

### Stability

All the MEs formulated with different surfactant mixtures on the water dilution line were subjected to kinetic stability tests i.e., centrifugation and freeze/thaw cycles using freshly prepared formulations. All the formulations on the water dilution line were stable within the parameters of this study and no phase separation was observed. The formulations containing IPM/Tween<sup>®</sup> 20/ethanol had the greatest kinetic stability based on their physicochemical and electrochemical behavior and were subjected to stability studies at  $25 \pm 2^\circ\text{C}$  and  $65 \pm 5\%$  RH for 3 months. After the specific time period the formulations were again characterized for conductivity and viscosity to determine any changes. Conductivity and viscosity did not change over the studied time (Table 5).

### CONCLUSION

Phase diagrams of different surfactant mixtures with different weight ratios were constructed. The total monophasic area,  $A_t$ , as well as, the water solubilization capacity, was maximum when the ME was composed of Tween<sup>®</sup> 20 as a surfactant using ethanol as a co-surfactant. The values of both of these parameters decreased as the chain length of the surfactant increased regardless of the type of co-surfactant, with the exception of Tween<sup>®</sup> 80. This could be attributed to an unsaturated hydrophobic chain structure of the Tween<sup>®</sup> 80 which possibly caused folding of the chain allowing less oil penetration (8). The order followed by different alkanols for both  $A_t$  and the WSC was similar decreasing as the chain length of the alcohol was increased. For longer chain alcohols (i.e., butanol, pentanol and hexanol)  $k_d$  followed the order butanol>pentanol>hexanol and was reversed for  $\Delta G$  depicting the favorable migration of alkanols from the bulk phase to

**Table 5** Conductivity and viscosity of MEs containing IPM / Tween 20 / Ethanol at T = 0, T = 30, T = 60 and T = 90 (T = time in days)

FORMULATIONS ALONG DILUTION LINE HAVING % OF WATER (wt / wt)	$\phi$	CONDUCTIVITY ( $\mu\text{S} / \text{cm}$ )				VISCOSITY (cP)			
		T = 0	T = 30	T = 60	T = 90	T = 0	T = 30	T = 60	T = 90
		2.5	0.182	26.66 $\pm$ 3.05	28.72 $\pm$ 4.73	30.08 $\pm$ 3.82	26.35 $\pm$ 2.56	2.25 $\pm$ 0.45	2.67 $\pm$ 0.34
5.0	0.373	43.7 $\pm$ 9.01	45.62 $\pm$ 8.64	46.83 $\pm$ 8.53	44.82 $\pm$ 6.39	2.76 $\pm$ 0.18	2.11 $\pm$ 0.23	2.45 $\pm$ 0.36	3.82 $\pm$ 0.29
10	0.782	57.86 $\pm$ 10.72	55.43 $\pm$ 12.84	57.63 $\pm$ 13.62	58.83 $\pm$ 16.37	5.43 $\pm$ 0.54	5.93 $\pm$ 0.66	5.83 $\pm$ 0.56	5.92 $\pm$ 0.46
15	1.258	108.33 $\pm$ 10.53	105.63 $\pm$ 9.63	106.83 $\pm$ 10.72	109.73 $\pm$ 12.73	7.32 $\pm$ 0.74	7.72 $\pm$ 0.82	7.63 $\pm$ 0.73	7.92 $\pm$ 0.83
20	1.767	148.33 $\pm$ 14.90	154.63 $\pm$ 15.73	155.83 $\pm$ 13.36	156.83 $\pm$ 15.83	5.76 $\pm$ 0.71	5.62 $\pm$ 0.73	5.63 $\pm$ 0.83	5.83 $\pm$ 0.85
25	2.380	241.73 $\pm$ 16.05	235.73 $\pm$ 18.63	236.84 $\pm$ 17.73	238.83 $\pm$ 19.73	3.22 $\pm$ 0.63	3.89 $\pm$ 0.73	3.74 $\pm$ 0.48	3.83 $\pm$ 0.58
30	5.329	252.1 $\pm$ 19.26	258.64 $\pm$ 22.63	259.73 $\pm$ 24.83	263.62 $\pm$ 18.83	2.04 $\pm$ 0.61	2.73 $\pm$ 0.55	2.74 $\pm$ 0.49	2.83 $\pm$ 0.49
35	6.499	255.43 $\pm$ 15.08	261.74 $\pm$ 17.36	258.33 $\pm$ 19.34	267.73 $\pm$ 34.65	1.56 $\pm$ 0.55	1.84 $\pm$ 0.63	1.93 $\pm$ 0.34	1.73 $\pm$ 0.24

the interface as the chain length of the alkanol decreased among the three alkanols studied.

Furthermore, all the systems containing alcohol as co-surfactant showed percolation behavior and viscosity curves that were bell shaped. These observations could be explained by the transition of w/o ME to o/w ME through a transitional bi-continuous structure. Droplet size distribution of the diluted ME followed a similar trend. Among all the systems, MEs containing ethanol as a co-surfactant had the smallest droplet size.

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