Abstract

Surfactants, amphiphilic compounds with both hydrophilic and hydrophobic groups aggregate in aqueous medium and in presence of other additives to form different organized assemblies e.g. micelles, reversed micelles, microemulsions, liposomes, vesicles etc. In aqueous medium, the aggregation of the surfactants is due to hydrophobic interaction. Nonionic surfactants, mostly having oxyethylene head groups, characteristically exhibit clouding behaviour in micellar or microemulsion media and this behaviour supposed to be due to dehydration of oxyethylene group of the surfactant. The present thesis deals with:

An up-to-date review on the clouding phenomena of surfactant systems is presented in Chapter-I. Clouding behaviour, also known as lower consolute behaviour or coacervate phase behaviour, is a typical physical change in the homogeneous solutions of amphiphilic substances, due to which the solution separates into a surfactant-rich and a surfactant-poor phase at a definite temperature. The temperature, at which phase separation occurs, i.e. the threshold temperature of clouding, is known as the cloud point (CP). The value of CP depends on the structure and concentration of the surfactant and the presence of additives. Phase separation is generally observed by visual inspection. Anionic surfactants also exhibit clouding phenomena in micellar solution in presence of symmetrical quaternary bromides like tetra-\(n\)-butyl ammonium/phosphonium and tetra-\(n\)-amyl ammonium bromides. At low salt concentration, CP linearly increases with the concentration of surfactant, while at high salt concentration CP was independent of surfactant amount. On the other hand, increase in salt concentration decreases the CP. Cationic surfactants also exhibit clouding mostly in presence of a salt with a hydrophobic counterion, such as sodium tosylate (NaTos), sodium salicylate (NaSal), etc.

Oil in water microemulsions, formed due to the mixture of surfactant, cosurfactant, oil and water, may be considered as swollen micelles i.e. oil incorporated in the micellar core. These systems provide multiple microphases of different polarity to solubilise both polar and nonpolar substrates. Microemulsions also form clouds with variation in temperature as well as by addition of electrolytes. An increase in the oil content causes rapid clouding. For microemulsions, the clouding phenomenon has been attributed to the strong attractive interactions of the microemulsion leading to enhanced droplet aggregation.
The number of oxyethylene unit \( (j) \) present in the head group and the carbon chain length \( (i) \) of the hydrophobic group contributes to the CP values of nonionic surfactant in aqueous medium. Increase in oxyethylene unit \( (j) \), keeping carbon chain length \( (i) \) constant, led to the elevation in CP. However, a depression was observed with the increase in \( i \) keeping \( j \) a constant. Quantitative structure-property relationship (QSPR) to predict the CP of some non-ionic surfactants by using several structural, electronic, spatial, and thermodynamic properties as descriptors has also been reported in the review.

Additives play a key role in tuning the CP values of nonionic or ionic surfactants according to the suitability of requirement. Specifically, nonionic surfactants are widely used in many industrial, cosmetics and pharmaceuticals formulations. Therefore, knowledge of CP in presence of additives is worth enough for determining storage stability, since formulations at temperatures significantly higher than the CP may result in phase separation and instability. Besides, clouding phenomena are widely explored for the extraction of many organic, inorganic, and industrial pollutants and preconcentration and extraction of metal ions. The extraction efficiency greatly depends on temperature of the system, and it also makes the extraction method economic viable. Hence the tuning of CP becomes necessary in such processes. CP of nonionic surfactants in micellar solution or in microemulsion is found to be strongly influenced in presence various additives, such as electrolytes, organic additives, nonelectrolytes and ionic surfactants.

With the advent of sophisticated techniques like atomic force microscopy, small angle neutron scattering etc, the investigations on structural morphology of the clouds have been attempted. The aggregate morphology of the surfactants changes from initial globules to rod with the rise in temperature and finally to a mesh structure near cloud point. Clouding behaviour of micellar solution and microemulsion has been widely exploited as cloud point technology for the extraction and preconcentration of various metal ions, organic and inorganic industrial pollutants, pesticides and proteins. The two phase separation of nonionic surfactant solution on heating above the CP is utilized to entrap the wide variety of analytes due to their higher solubility in surfactant rich phase.

In the subsequent chapters cloud point behaviour of microemulsions prepared from nonionic surfactants, cosurfactants like \( n \)-butanol and \( iso \)-butanol, oil like hexane and kerosene and water has been investigated.
The phase behaviour of pseudoternary mixture of emulsifier, oil and water considering Tween 80 as the surfactant has been described in Chapter-II. Phase diagrams of the pseudoternary mixtures have been constructed and electrical conductivity of these solutions with added brine has been measured to identify different systems in the pseudoternary mixtures. The hierarchy of the structures in the isotropic domain from water rich to oil rich system is found to have a trend of micellar medium, oil in water microemulsion, bicontinuous phase, water in oil microemulsion and reversed micellar phase. The CPs in these domains have been determined and the CPs are found to have a quantitative relationship with the composition of the constituents. A representative phase diagram and the CPs at various compositions are shown in Fig.1.

Fig. 1. Phase diagram of pseudoternary mixture of Tween 80 (S) and \( n \)-butanol(C) as emulsifier (E), hexane (O) and water (W) at 30.0±0.2°C. Indicates turbid zone and rest is transparent zone.

The CP of the Tween 80/\( n \)-butanol/hexane/water quaternary system have been found to decrease linearly when water of the microemulsion is replaced by brine. This behaviour has been explained on the basis of salting-out and salting-in phenomena which have an interfacial origin. Temperature induced three-phase separation has been observed in Tween 80/\( n \)-butanol/hexane/water pseudoternary system in Winsor III domain. The pseudoternary mixtures in the marked domain in Fig. 2(b) are of turbid phases, which undergo phase separation with change in temperature of the system.
Fig. 2. (a) Three phase separation of the turbid pseudoternary mixture, (b) Phase diagram representing distribution of components in upper (U), middle (M) and lower (L) layers during phase separation of pseudo-ternary mixture; E, W and O referring to emulsifier, water and oil respectively at 30.0±0.2°C. Indicates turbid zone and rest is transparent zone. is the experimental zone for investigation of temperature effect.

The three phase separation may be attributed to differential solubility of the emulsifier in oil-rich and water-rich regions with the variation in temperature condition. The initial solubilization of the emulsifier in a mixture of water and oil at a definite proportion changes with temperature. At higher temperature, water with some amount of emulsifier separates as a micellar component and remains at the bottom due to its higher density; excess oil with lower density occupies the upper region and the microemulsion system containing all the four components having density lower than micellar system and higher than oil maintains at the middle region. The middle phase has a bicontinuous structure of microemulsion, wherein the oil-in-water microemulsion constitutes the lower side and the upper side of this phase contains water-in-oil microemulsions. Temperature has a direct impact on the density of solutions. Hence, transference of emulsifier occurs with the change in temperature resulting in the change in density of various phases as well as their turbidity. However, the upper phase always remains clear, indicating the transference of the emulsifier being limited only to the middle and lower phases.

As the ternary mixture contains several microdomains, it can be exploited for the differential partition of various nonpolar and polar organic and inorganic solutes, thereby,
leading to separation and/or preconcentration. Some organic coloured probes were used to investigate their partition into different microdomains of the pseudoternary mixture of Tween 80, \(n\)-butanol, hexane and water. When nitrophenol, a neutral polar species, was solubilized in microemulsion and was then partitioned between oil-rich and water-rich phases through clouding, it was found that the species can be preconcentrated to nine times at the upper oil rich phase. Further, to see the effect of hydrophobicity on the partition of some styryl pyridinium dyes, both \(N\)-butyl and \(N\)-hexadecyl cyanine dyes were subjected to the partition studies. The results showed a preferential preconcentration of \(N\)-hexadecyl derivative over \(N\)-butyl derivative in the upper oil-rich region. Similarly, when metal ions were used, even without ligating groups, after clouding, partitioning of metal ion into water rich phase was observed. The assistance of the surfactant in partitioning of metal ion may be due to the ligating oxyethylene groups, which may provide a crown ether type environment to the metal ions. The partitioning of cobalt ion in the lower surfactant rich phase is far better than that of nickel (II) and copper (II) ions.

Kerosene based microemulsion have found potential applications in the various fields of industry, in the synthesis of nano materials and in the determination of trace elements. In the **Second section of Chapter-II**, an attempt has been made to investigate the phase behaviour of mixture of the Tween 80, \(n\)-butanol, kerosene and water with the variation of surfactant and cosurfactant ratio. The surfactant/cosurfactant ratio plays a significant role in shaping Winsor IV domain in the mixture. The clouding behaviour of the different pseudoternary microemulsion was investigated, focusing on the variation of cloud point with change in composition of different components of the micro emulsion. To optimize the clouding behaviour at low temperature, effect of various additives on the clouding phenomenon was investigated. Further, the partitioning of organic as well as inorganic substrates due to clouding phenomena was also studied. The cloud points of the pseudoternary mixture of emulsifier, water and oil varied between 36 to 78°C with change in composition. However, with a fixed ratio of S/C the CP did not vary significantly. With constant emulsifier, in all the three compositions of emulsifier (S/C = 1, 2 and 3), CP increases with increase in oil content. With decrease in cosurfactant composition in emulsifier, CP increases significantly. With constant water contents and decrease in oil content, CP increases. Similarly with constant oil contents and decrease in water content, CP increases.
A generalized model to correlate the CP with the composition has been proposed to predict the CP for all ratios of surfactant and co-surfactant of the Tween 80/kerosene/ n-butanol/water pseudoternary system (Eq 1).

\[ \text{CP} = (5.99 \pm 3.97) + (23.34 \pm 1.38)\text{S/C} + (0.012 \pm 0.002)\text{O}_2 + (0.0025 \pm 0.001)\text{E}_2 \] (1)

The validity of the equation has been well judged from the linear plot of the observed and predicted CPs.

![Plot of predicted CP vrs. Observed CP values of all the microemulsion systems considering equation 1.](image)

**Fig. 3.** Plot of predicted CP vrs. Observed CP values of all the microemulsion systems considering equation 1.

A depression of CP was observed with the addition of NaCl in the quaternary system. The depression was more pronounced in the pseudoternary system with the increase in surfactant in emulsifier. At a high emulsifier content with S/C = 2, where clouding could not be observed, even at 86 °C, in presence of NaCl, clouding was obtained at 56°C. This depression in CP has been ascribed to the salting-out effect by NaCl. However an increase of CP was manifested with the addition of NH₄SCN. The elevation of CP may be attributed to the salting-in effect of the lyotropic salt, NH₄SCN. The addition of sugars like glucose and sucrose in the quaternary system led to slight depression in CP.

Chapter III comprises the investigation on phase behaviour of the pseudoternary mixture with Triton X-100 (TX100) as the surfactant. In section 1 of this chapter hexane has been considered as the oil component. At constant temperature and pressure the pseudoternary
phase diagrams of emulsifier (E) (surfactant(S): TX100 + cosurfactant (C): iso-butanol (S:C::1:1)), oil (hexane(O)) and water (W) system, a representative phase diagram is depicted in Figure 4. The shape of Winsor IV domains and the various aggregates in the mixture vary with change in S/C. With higher surfactant content in the emulsifier, a liquid crystalline/glassy narrow band surrounded by turbid gel region in the oil rich domain at ~20% weight fraction of emulsifier is obtained.

![Phase Diagrams](image)

Fig. 4. Phase diagram of pseudoternary mixture of TX100 (S) and iso-butanol(C) as emulsifier (E), hexane (O) and water (W): (a) S:C :: 2:1 and (b) 2% brine replacing water.. The number inside the phase diagram refers to the CP at that composition point.  

Sodium chloride has made a significant impact on the phase behaviour of the pseudoternary system. The isotropic domain which was mostly water-rich without sodium chloride, transformed to oil-rich and the area decreases from 46% to 35%. A small Winsor IV domain touching the W apex within the turbid region was attributed to the formation of micelles of TX100 solubilizing small amount of hexane and iso-butanol. The conductivity in the isotropic zone, with constant oil: emulsifier ratio is found to be trilinear with two transition points defining the demarcation zones for the O/W microemulsion, bicontinuous and W/O microemulsion systems (Figure 5).
Fig. 5. A representative plot of specific conductance vs. Volume of brine

A quantitative cloud-point composition relationship (QCPCR) has been obtained by using multiple regression analysis (Equation 2) and the predicted values obtained by using the equation has been plotted against the observed value (Figure 6).

\[ CP = (3.89 \pm 2.13) + (14.71 \pm 0.95)S/Co + (0.005 \pm 0.0005)E^2 + (0.013 \pm 0.001)O^2 \]  \hspace{1cm} (2)

Fig. 6. Plot of observed CP vs Predicted CP

By the addition of sodium chloride, a sharp decrease ranging from 8 °C to 18 °C in CP.

Introduction of sodium chloride, a lyotropic salt, into pseudoternary mixture may enhance the reorganization of water structure, breaking the hydrogen bond between water molecule and oxyethylene units of the surfactant resulting in an increase in interfacial tension and lowering of entropy leading to the dehydration of oxyethylene groups. Partitioning of various organic
substrates and metal ions like Ni$^{+2}$ and Co$^{+2}$ in the post clouding biphasic system has been studied. Inorganic ions are concentrated in lower phase while organic solutes are partitioned into upper phase.

The clouding behaviour of TX100/$n$-butanol/kerosene/water mixture at different composition has been presented in Section two of Chapter III. The pseudoternary phase diagrams have been constructed for these mixtures and the different domains have been identified in the phase diagram through conductometric analysis. Microemulsions are highly sensitive to variation in temperature. With a change in temperature, solubility and, hence, partition of the surfactants in water/oil varies, which propels the transfer of surfactants from one phase to other, leading to phase separation. Further, the clouding phenomenon has been exploited for the preconcentration of both inorganic metal ions and organic substrates. The effect of various additives on the clouding behaviour of these pseudoternary mixtures has been investigated to optimize the clouding at low temperature condition. The QCPCR resulted in a regression model (Equation 3) with good predictability.

$$CP = (122.37\pm28.30) + (17.13\pm1.04)S/Co + (0.013\pm0.0017)E^2 + (0.019\pm0.001)O^2 - (82.14\pm19.45)\log E$$

$$R^2=0.98, F=177.99 \text{ and } n=14.$$  

Chapter IV deals with the study of clouding phenomenon of some microemulsions containing surfactant mixture of Tween 80 and TX100 at different proportions. In these studies, $n$-butanol has been taken as the cosurfactant and kerosene as the oil. The pseudoternary phase diagrams of emulsifier (E) (equivalent weight percent of TX100 and Tween 80 with varied amount of $n$-butanol), oil (kerosene, O) and water (W) system at constant temperature and pressure is presented in Figure 7(a-e).
Addition of salts was found to influence the phase behaviour of Tween 80+TX100/n-butanol/kerosene/water pseudoternary mixture. (Table 1)

<table>
<thead>
<tr>
<th>Tween 80</th>
<th>TX100</th>
<th>n-butanol</th>
<th>Water/ Salt</th>
<th>% Isotropic domain</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>0.00</td>
<td>1.0</td>
<td>water</td>
<td>42.50</td>
</tr>
<tr>
<td>0.75</td>
<td>0.25</td>
<td>1.0</td>
<td>Water</td>
<td>35.00</td>
</tr>
<tr>
<td>0.50</td>
<td>0.50</td>
<td>1.0</td>
<td>Water</td>
<td>40.50</td>
</tr>
<tr>
<td>0.25</td>
<td>0.75</td>
<td>1.0</td>
<td>Water</td>
<td>30.50</td>
</tr>
<tr>
<td>0.00</td>
<td>1.00</td>
<td>1.0</td>
<td>Water</td>
<td>34.00</td>
</tr>
<tr>
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<td>0.50</td>
<td>0.5</td>
<td>Water</td>
<td>31.50</td>
</tr>
<tr>
<td>0.25</td>
<td>0.25</td>
<td>1.0</td>
<td>Water</td>
<td>15.25</td>
</tr>
<tr>
<td>0.50</td>
<td>0.50</td>
<td>1.0</td>
<td>2% NaCl</td>
<td>32.50</td>
</tr>
<tr>
<td>0.50</td>
<td>0.50</td>
<td>1.0</td>
<td>2% NaI</td>
<td>34.00</td>
</tr>
<tr>
<td>0.50</td>
<td>0.50</td>
<td>1.0</td>
<td>2% NH₄SCN</td>
<td>33.50</td>
</tr>
</tbody>
</table>

The clouding behaviour of pseudoternary mixture of Tween 80+TX100/n-butanol/kerosene/water was influenced with the variation of composition of constituting components. The above effect led to tune CP of the pseudoternary mixture with the variation of component composition without the introduction of any additive.

1. Elevation of CP with the increase in oil content in the pseudoternary mixture.

2. An increase in CP with increase in emulsifier in the mixture. The increase may be attributed to the solubilization of kerosene and water with the increase in emulsifier
content, thereby stabilising the ternary system bringing together kerosene and water into
the same phase.

3. Elevation of 22 – 24 °C in CP with the increase in surfactant content in the emulsifier of
the mixture.

4. Decrease in water content with constant oil content resulted slight elevation of CP.

At low emulsifier content and high water content, the CP values do not obey an ideal
relationship of the CPs of individual surfactant systems. In most cases the CPs of the mixtures
are found to be less than those of the individual surfactants systems upto an extent of 9°C. This
phenomenon is akin to the depression of freezing point of liquid due to the presence of additives.
This depression of CPs in the mixture from the individual one reflects a surfactant-surfactant
interaction resulting in formation of mixed microemulsion systems instead of having a mixture
of microemulsions with individual surfactants.

The prediction of CP was attempted with the aid of multiple regression analysis. A
nonlinear regression model was obtained by considering CP as the dependent variable and oil,
emulsifier contents and S/C as the independent variables. A generalized equation was obtained
considering all the volume ratio of surfactant and cosurfactant to predict the CP of the Tween
80+TX100/n-butanol/kerosene/water pseudoternary system (Equation 4).

\[
CP = (197.79\pm25.84) + (22.69\pm0.70)S/C + (0.017\pm0.0016)E^2 + (0.014\pm0.001)O^2 - \\
(139.69\pm17.75)\log E \quad (4)
\]

\[R^2 = 0.99, \quad F = 285.36, \quad N = 13\]

Additives like electrolytes, nonelectrolytes and sugars into the pseudoternary mixture of
Tween 80+TX100/n-butanol/kerosene/water (surfactant/cosurfactant = 1) were found to change
the CP to a significant extent. Addition of sodium chloride in the pseudoternary system led to
depression of CP while an increase in CP was manifested with the addition of NH₄SCN.

Temperature induced three-phase behaviour was observed in Tween 80+TX100/n-
butanol/kerosene/water pseudoternary mixture in Winsor III domain. The pseudoternary mixture
assumes turbid phase, which undergo phase separation depending on the change in temperature
of the system. The transition of different phases has been ascribed to (i) the change in
lipophilicity/hydrophilicity of the surfactant with change in temperature and (ii) mass transfer
from one phase to other with change in temperature. The partitioning of different organic and inorganic substrates have been attempted in the biphasic system generated from temperature induced clouding of microemulsion. The inorganic metal ions are partitioned more into water-rich medium while the organic substrates are concentrated in the organic phase.

Thus the work presented in the thesis has tried to answer the following pertinent questions.

- What are the phase behaviour of the pseudoternary mixture of nonionic surfactant + cosurfactant, water and oil?
- To what extent oil or water can be solubilized in an emulsifier-water or emulsifier-oil system respectively?
- What is the stability of microemulsion with respect to temperature?
- What is the minimum temperature to demulsify the microemulsion leading to two distinct phase to be applied in separation technology?
- Is there any quantitative relationship between cloud point and contents of the constituent so that cloud point can be predicted with high confidence level?
- Can this cloud point phenomenon be used for preconcentration of organic and inorganic analytes?

The following papers have been communicated for publication in various journals.

1. Clouding behavior in surfactant systems. (Accepted) *Adv. Colloid Interface Sci.*
4. Phase behavior of TX100-butanol-kerosene-water systems. (Communicated) *Colloid Surfaces.*
5. Phase behavior of TX100-butanol-hexane-water systems. (Communicated) *J. Disp. Sci. Tech.*
6. Phase behavior of mixed nonionic surfactants in butanol-kerosene-water systems. (Communicated) *J. Colloid Interface Sci.*

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