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Solubilization of TX-100^{TM} and PEG-PPG-PEG in Liquid Carbon Dioxide

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Carbon dioxide (CO_2) at the subcritical, near-critical, and supercritical states has been found to be a powerful solvent with tunable characteristics. It is currently considered an alternative solvent to the conventional organic solvents and has attracted numerous industrial activities (processes). However, CO_2 has been limited in its application due to challenges with dissolving polar macromolecules, which limits its applications. This article presents the solubilization of surfactant; octylphenol ethylene oxide (TX-100^{TM}) and poly(ethylene glycol)-block-poly (propylene glycol)-block-poly (ethylene glycol) (PEG-PPG-PEG) in liquid carbon dioxide. The TX-100^{TM} is solubilized in the liquid CO_2 in a programmable phase equilibrium analyzer at varying temperatures and pressures. The emulsion characteristics as well as the water capacity of TX-100^{TM} and PEG-PPGPEG each in liquid CO_2 is predicted by using ethyl acetate as substituted solvent. For PEG-PPG-PEG and TX-100^{TM} emulsion systems, microemulsion form at water-to-surfactant volume ratios of less than 1.0 and 1.2 with their corresponding liquid CO_2 volume of greater or equal to 94% and 94.6%, respectively.

Keywords liquid and supercritical co$_2$; microemulsion; miniemulsion; near critical fluids; reverse micelles; surfactants

INTRODUCTION

In recent years, there has been growing interest in capitalizing the solvating capabilities of supercritical fluids (SCFs) in a number of applications of commercial importance. These SCFs are alternate solvents to the environmentally damaging conventional volatile organic solvents that are used in large quantities and often are very difficult to contain. Each year, over 30 billion pounds of organic and halogenated solvents are used worldwide, resulting in the emission of large amounts of these solvents into the environment (1). Several other supercritical fluids are in use, but the final choice depends on the specific application, availability, and factors such as safety, flammability, phase behavior, solubility at the operating conditions, and the cost of the fluid (2).

Some advantages of SCFs include:

1. the achievements of separations usually not achieved by the conventional methods,
2. the extraction of thermally labile products with minimal damage (3), and
3. their inertness to most products.

Industrial application of SCFs may include:

1. the extraction of nutriceuticals, dyes and flavors (4),
2. the distillation of crude oil residues (2),
3. the production of pharmaceutical active ingredients from herbal plants avoiding decomposition (2),
4. the denicotinization of tobacco and decaffeination of coffee (4),
5. the elimination of residual solvents from wastes, and
6. the decontamination of soils (2).

Water and carbon dioxide, among other supercritical fluids, are the most available and have been found to be compatible with the earth's environment. Supercritical water is also recognized for its capacity for destroying toxic and hazardous materials, and also as a medium for chemical synthesis (5). However, applications involving water led to a huge amount of water contamination, which is discouraging its use (5). The properties of CO_2 at the subcritical, near-critical and supercritical states have been found to be environmentally benign and are employed in numerous processes. Liquid CO_2 and supercritical CO_2 ($SCCO_2$) have found applications in the fields of separation, extraction, cleaning, fractionation, and synthesis with extensive applications in polymer science and engineering (5). Despite the advantages of liquid CO_2 and $SCCO_2$, they have limited applications involving polar or ionic or water-philic substances and macromolecules (6). Some applications of CO_2 to these polar or ionic or water-philic substances and macromolecules have been achieved through the use of surfactant to form of micelles. This led to extensive research for surfactants with the ability to solubilize such substances in $SCCO_2$.

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Technological breakthroughs over the last decade found CO_2 both in the liquid and supercritical states as greener alternatives than most of the SCFs (with the exception of water). Certain properties of CO_2 that have made it more attractive than the rest of the SCFs are the relatively low critical temperature and pressure, unique solvation power, higher diffusivity, tunable characteristics over a wide range of solvent quality, coupled with its availability, recyclability, low-cost, non-explosiveness, non-oxidization, nonflammability, and non-toxicity (2).

Conventionally, CO_2 was applied as a solvent for the solubilization of small organic molecules including fluorinated compounds. Recently, the emerging technology of microemulsion and reverse micelle formations has expanded CO_2 applications to solubilizing polar and higher molecular weight compounds including biomolecules.

In a number of ways, surfactants can improve the solubility of polar and hydrophilic substances and biomolecules in $SCCO_2$. The role of surfactants is to reduce the interfacial tensions between these two immiscible compounds by forming microemulsions. Reverse micelle can be created by adding water to these amphiphilic molecules in SCF systems (7). Progressive addition of water to the systems swells the polar core forming unstable micelles and results in phase separation after addition of excessive water.

It has been shown that microemulsions can be created in SCFs below and above their critical points ($T/T_c < 0.75$ and $T/T_c > 1.1$) using sodium bis(2-ethylhexyl) sulfosuccinate (AOT) (8). Some surfactants form varieties of geometrical microstructures in some SCFs, and it appears that these fascinating geometries may be present in all supercritical fluids. Several different water (*w*) in-oil (*o*) spherical droplets have been formed in these fluids containing cationic, anionic, and non-ionic surfactants (8). It is known that microemulsions exist in an array of phase structures. In addition to the normal globular *o*/*w* or *w*/*o* systems for swollen micelles, various cubic and lamellar mesophases have been identified particularly at high surfactant concentration and have led to various polymerization reactions and also fabrications involving polymers of high specific surfaces (9).

The properties of these microemulsions include:

1. structural dimensions in the range of 5–100 μm,
2. optical clarity (poor scatter of visible light),
3. good thermal stability,
4. non-static emulsion that is continuously breaking and reforming, and
5. size that is tunable by the volume of water added to the microemulsion system (2).

At low water concentrations, the microemulsions are spherical and in the dispersed phase. Typically, water volume (v) of less or equal to 26% ($v \leq 26\%$) of an emulsion system results in the formation of inverted structure, termed as "reverse micelle". Water volume in the range, normally greater than 26% but less than 74% ($26\% \leq v \leq 74\%$) forms a bicontinuous structure (also lamellar structure) while above 74% ($v \geq 74\%$) forms a normal micelle structure. The dissolution capacity of the polar or ionic substances in the micelles is thus dependent on the volume of water in the emulsion (2).

These fluids possess a high value for the dielectric constant at high frequencies that govern the intermicellar forces and also accounts for the short-range attractive forces between the surfactant tails. Reverse micelle formation in supercritical fluids possesses unique and useful properties. These include:

1. variation of the density with changes in pressure or temperature to effect changes of phase behavior of the reverse micelle system,
2. the ability to effect a change in micelle size or micelle cluster size by variation of the density,
3. high diffusivities of solutes and micelles in near-critical and supercritical fluids, and
4. the ability to control selectivity for a specific solute by variation of density (7).

The surfactant molecules used in the near-critical and $SCCO_2$ possess two mutually incompatible components, CO_2-philic and CO_2-phobic tails. The CO_2-philic tails attract CO_2 molecules whereas CO_2-phobic tails repels the CO_2 molecules and form a head in the core. This type of micelle is normally referred to as reverse or inverted micelle as shown in Fig. 1.

It is this core where the polar or hydrophilic species reside in the reverse micelle. By this process, most CO_2 insoluble or sparingly soluble compounds are solubilized

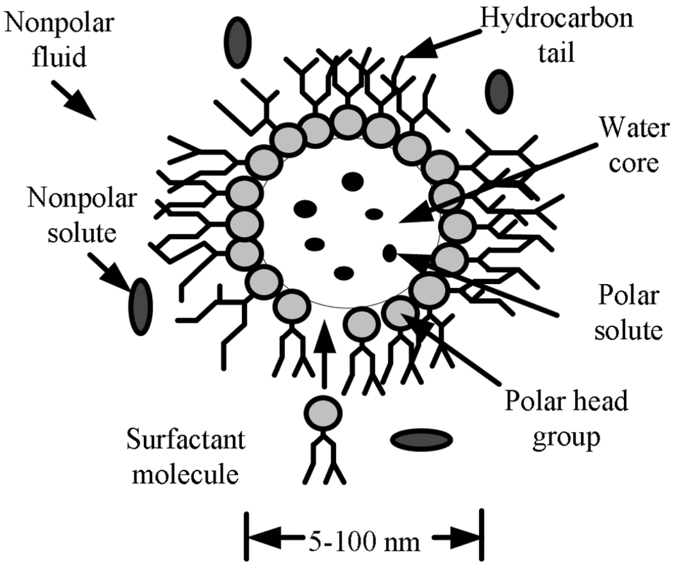


FIG. 1. Basic structure of a microemulsion and reverse micelle in CO_2.

(10). The advantages of microemulsion and reverse micelle over the conventional micelle systems generally include the conduction of a variety of chemical reactions, extraction and separation processes. Specifically, the advantages of microemulsions include:

1. faster separation, extraction, and reaction rates because of the enhanced mass transport properties of supercritical and near-critical fluids (2),
2. diffusivities of solutes and micelles can be 5–100 times higher in near-critical liquids and supercritical fluids than they are in liquids (2),
3. the ability to manipulate reaction pathways (i.e., selectivity) or rates by varying system pressure and temperature,
4. the ability to recover products or catalysts after separation or reaction by changing system density by adjusting temperature or pressure (2),
5. the ability to separate mixtures, and controlling selectivity of separation, by varying system density, and
6. the ability to extract solutes from the liquid or solid phases at high rates, with greatly augmented recovery of the two phases after separation (2,11) All of these properties play a big role in chemical synthesis inside the reverse micelles of microemulsions.

This research investigates the dissolution of TX-100^{TM} (octylphenol ethylene oxide) and PEG-PPG-PEG (poly (ethylene glycol)-block-poly (propylene glycol)-block-poly (ethylene glycol)) surfactants in liquid CO_2. The TX-100^{TM} dissolution is investigated under varying pressure and temperature in a phase equilibrium analyzer as well as formation of emulsions. The solubilization and phase behavior of PEG-PPG-PEG and TX-100^{TM} each in liquid CO_2 is predicted using ethyl acetate at room temperature as candidate solvent (12). TX-100^{TM} is used because of its excellent detergency and oil removal characteristics as well as its solubility in both water and organic solvents. Moreover, TX-100^{TM} is effective on textiles and semiconductor wafers, and has made it very attractive for both domestic and industrial applications, particularly the dry cleaning of semiconductor wafers and integrated circuits (5). The PEG-PPG-PEG is known for its anti-releasing characteristics in addition to its solubility in both water and organics (13). It is ideal for dry cleanings involving semiconductor wafers, integrated circuits, biofilms, and biofoulants. The cleaning of biofoulants and biofilms could be aided by salts incorporated into the emulsion (14). This makes the water and organic solubility characteristics of both TX-100^{TM} and PEG-PPG-PEG attractive for these applications.

MATERIALS AND METHODS

Materials

In this investigation, octylphenol ethylene oxide with trade name Triton X-100 (TX-100^{TM}) and PEG-PPG-PEG were obtained from Aldrich-Sigma. TX-100^{TM} (MW ~ 625 g/mol) is slightly hydrophilic, nonionic, and biodegradable. It is used as a wetting agent and emulsifier (15). The PEG-PPG-PEG (MW~1100 g/mol) is very hydrophilic, nonionic, non-biodegradable and used as solubilizers, emulsifiers, and wetting agents (13). The PEG is larger in size than the PPG. Also, the PEG is hydrophilic while the PPG is hydrophobic, and this interesting characteristic makes PEG-PPG-PEG suitable for aqueous-organic systems. The industrial grade compressed or liquid CO_2 was obtained from the National Welder Supply Company Inc., while ethyl acetate (used as candidate solvent for the liquid CO_2) and HPLC water were obtained from Tedia Company.

The solubility measurements were carried out in a phase equilibrium analyzer (PEA-30ML) manufactured by Thar Design Technologies. The analyzer is programmable and capable of varying the density or volume of the liquid CO_2, the temperature, and the pressure of the solution system until dissolution (cloud point) is reached. The dissolution process can be studied through video visualization.

Experimental Procedure

The solubilization of TX-100^{TM} in liquid CO_2 and $SCCO_2$ was carried out by placing a known amount of TX-100^{TM} and liquid CO_2 in the solubility chamber of the phase equilibrium analyzer and varying the density or volume of the liquid CO_2, the temperature, and the pressure of the solution system until the cloud point when TX-100^{TM} starts to dissolve.

Ethyl acetate is known to behave as liquid CO_2 (12) and it was used as a substituted solvent for CO_2 to predict the emulsion system of either TX-100^{TM} or PEG-PPG-PEG with water in liquid CO_2. The procedure involves adding a known volume of distilled water to a known volume of surfactants and agitating until mixing. In the case of TX-100^{TM}, distilled water at about 40°C was used to promote the dissolution while distilled water at room temperature was used for the PEG-PPG-PEG. Known volumes of ethyl acetate were added to each of the solutions of TX-100^{TM} or PEG-PPG-PEG and agitated for uniform mixing.

The appearance of optically clear solutions after addition of ethyl acetate to the PEG-PPGPEG or TX-100^{TM} and distilled water solution suggested the formation of reverse micellar microemulsion. Otherwise, very small visible suspended miniemulsions, which were either stable or unstable, or larger emulsions flocculating to form separate phases were realized. Various ratios between the volumes of PEG-PPG-PEG/water/ethyl acetate or TX-100^{TM}/water/ethyl acetate were collected and standardized for general application to systems consisting of PEG-PPGPEG/water/liquid CO_2 or TX-100^{TM}/water/liquid CO_2. The established ratios for PEG-PPG-PEG or TX-100^{TM}, water, and ethyl acetate at which the different emulsion systems formed, were used to represent the emulsion systems of PEG-PPG-PEG or TX-100^{TM}, water, and liquid CO_2.

RESULTS AND DISCUSSION

Solubilization of TX-100^{TM} in Liquid and $SCCO_2$

The TX-100^{TM} has limited solubility in liquid CO_2 near the critical point. It was found that the solubility of TX-100^{TM} depended on both the temperature and the pressure. The solubilization of TX-100^{TM} in liquid CO_2 was studied in the pressure range of 67.0 and 98.8 bars at temperatures of 22.9, 24.6, and 27.4°C.

At 22.9°C and 98.8 bars, only 0.31 wt% of the TX-100^{TM} was solubilized in CO_2. The solubilization of TX-100^{TM} in liquid CO_2 as a function of pressure is shown in Fig. 2 at 24.6°C and 27.4°C, respectively. The solubility increased non-linearly with pressure. A small increase in temperature increases TX-100^{TM} solubility in liquid CO_2 by several fold. At a relatively higher temperature (27.4°C), a small change in pressure results in a sharp change in solubility. From Fig. 2, an average pressure rise of about 1.8% (67.2 to 68.4 bars) resulted in about 53.0% (1.7 to 2.6 wt%) increase in TX-100^{TM} solubility at 27.4°C. On the other hand, at 24.6°C, an average pressure rise of about 14.3% (71.1 to 81.3 bars) resulted in 71.4% (i.e., 0.7 to 1.2wt%) increase in the TX-100^{TM} solubility (Fig. 2).

From the CO_2 phase diagram (Fig. 3), the temperature and pressure coordinates of 22.9°C and 98.8 bars falls in the region of liquid CO_2 which has lower diffusivity and is expected to have a lower solubility compared to the supercritical region. The temperatures of 24.6°C and 27.4°C with their respective pressure ranges of 71.1 to 81.3 bars and 67.2 to 68.4 bars lie in the region of the liquid CO_2. Within the liquid region, the higher temperature resulted in increased solubility as the liquid CO_2 approached that of the $SCCO_2$, which has higher solvation power and diffusivity. This explains why the increased temperature from 24.6 to 27.4°C resulted in considerable increase in the TX-100^{TM} solubility, offsetting the increased pressure effects in the range of 67.2 to 68.4 bars compared to that of 71.1 to 81.3 bars. From the above observation, it can be inferred that changes in temperature have a more pronounced effect than the pressure on TX-100^{TM} solubilization.

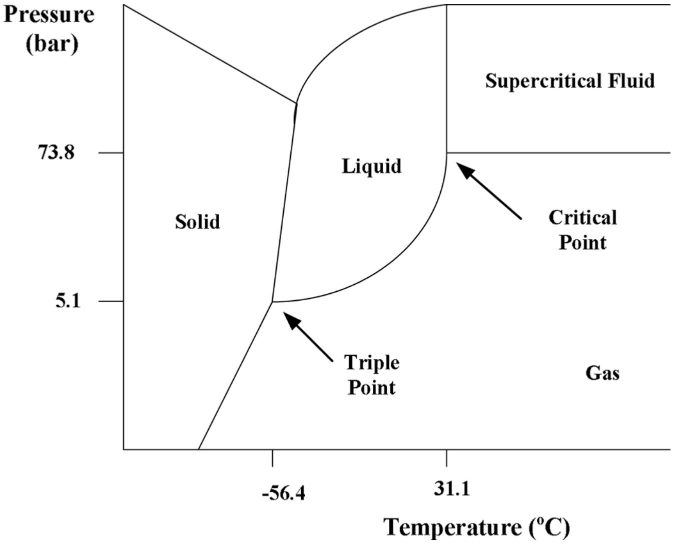


FIG. 3. Carbon dioxide phase diagram.

The temperature effects on TX-100^{TM} solubility in liquid CO_2 are shown by a bar graph in Figure 4 where the solubilities at the temperatures of 24.8 and 27.1°C were compared at an average pressure of 69 bars. As shown in Fig. 4, for a temperature rise of 9.3% (i.e., 24.8 to

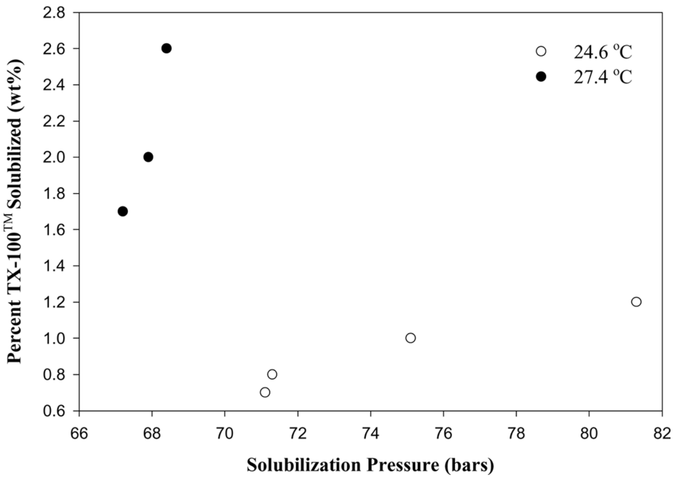


FIG. 2. Weight percent TX-100^{TM} solubilized in liquid CO_2 with pressure at 24.6°C and 27.4°C, respectively.

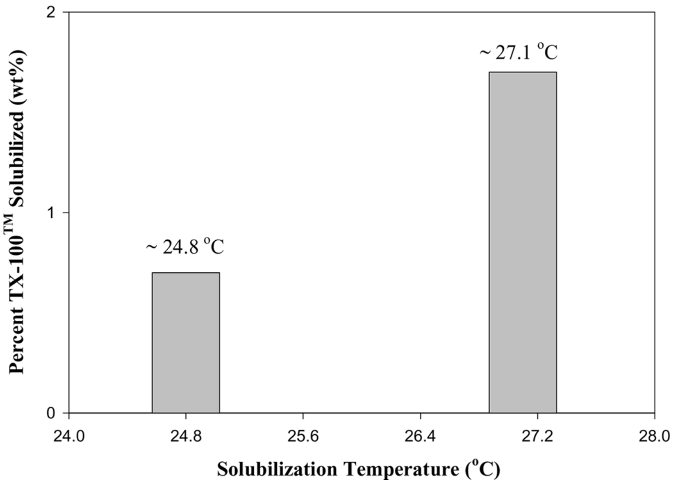


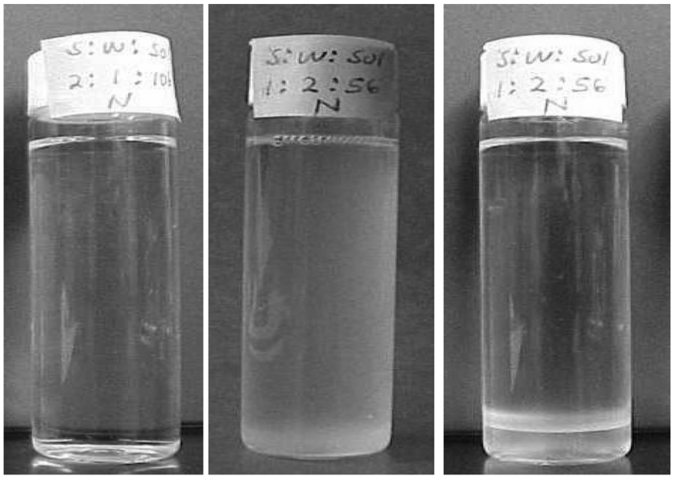
FIG. 4. Bar graph of TX-100^{TM} solubilized (in wt%) at 69 bars in liquid CO_2 at two temperatures.

27.1°C), the solubility of TX-100^{TM} increased by 142% (i.e., 0.7 to 1.7 wt%) at 69 bars. It is observed that the solubility increased as the temperature increased because of the increasing diffusivity of the liquid CO_2 with temperature.

Prediction of Emulsion Systems of TX-100^{TM} in Liquid CO_2

Like other fluids, CO_2 (c) forms emulsion in the near-critical and supercritical state with water (7). Formation of stable water-to-CO_2 (w/c) or CO_2-to-water (c/w) emulsions depend on the properties of the surfactants occupying the interface of the water and the liquid CO_2. Ethyl acetate was used as a substituted solvent for liquid CO_2 because it behaves as CO_2 in the liquid state (12). The various water-to-surfactant (w) volume ratios from 0 to 2.0 at constant volume of ethyl acetate were found to form three emulsion systems of TX-100^{TM} in liquid CO_2.

The three emulsion systems of TX-100^{TM} in liquid ethyl acetate formed by varying the amount of water to TX-100^{TM} at constant volume of ethyl acetate is shown in Fig. 5(a–c). Figure 5a is a picture of an optically clear stable emulsion system associated with microemulsions (typical size <100 nm). Figure 5b shows a colloidal system which is stable or unstable because of the swollen water core which could flocculate depending on the amount of water associated with miniemulsions (typical size 50–500 nm) (9). A phase separated emulsion system is shown in Fig. 5c. These phenomena can be explained by the fact that the nature of the emulsion systems depends on the interactions between the surfactant tails and the cores of the reverse micelle, which is water. In microemulsions, the repulsive forces between the tails of the surfactant are so pronounced that they overcome the attractive force between the cores of the reverse micelle, keeping the cores as far apart as possible. As the water-to-surfactant volume ratio (w) increases, water is introduced into the system. Above some critical point, water swells these micellar cores resulting in minimal repulsive forces. These visible emulsions are termed as miniemulsions, which could be stable or unstable depending on the extent of attraction and repulsion. Phase separation occurs as a result of the attractive forces between the cores overcoming that of the repulsive forces; and as a result, by nucleation and growth, the cores flocculate to form layers.



(a) (b) (c)

FIG. 5. Photograph of the emulsion systems of TX-100^{TM} with water in ethyl acetate: (a) Optically clear microemulsion, (b) Miniemulsion, and (c) Phase separated emulsion system.

Based on the above criterion, it was found that microemulsions form at water-to surfactant volume ratios of less than or equal to 1.2 ($w \leq 1.2$) with corresponding ethyl acetate volumes (v) of less than or equal to 94.6% ($v \geq 94.6\%$) of the system. The miniemulsions form within "w" of 1.2 and 1.4 inclusive ($1.2 \leq w \leq 1.4$) with ethyl acetate volumes of 94 to 95% ($94.6\% \leq v \leq 95\%$). Phase separation occurs at "w" greater than or equal to 1.4 ($w \geq 1.4$) with ethyl acetate volumes of less or equal 93.0% ($v \leq 93.0\%$). A pictorial representation of these observations is given in Fig. 6a and 6b for water-to-TX-100^{TM} (w) and ethyl acetate volumes (v) in TX-100^{TM} emulsions, respectively.

The experimental results for the three emulsion systems are presented in Fig. 7 in dimensionless form for general application to the emulsion systems consisting of TX-100^{TM}, distilled water and ethyl acetate. Figure 7 is a plot of TX-100^{TM} volume/water volume against water volume/ethyl acetate volume. From Fig. 7, the various proportions of the water, TX-100^{TM}, and liquid CO_2 in a particular emulsion system could be predicted.

Prediction of Emulsion System of PEG-PPG-PEG in Liquid CO_2

To study the emulsion systems of PEG-PPG-PEG in liquid CO_2, ethyl acetate was used as substituted solvent for CO_2. The microemulsion of PEG-PPG-PEG in ethyl acetate formed by varying the water content is shown in Fig. 8a; while the phase separated emulsion system is

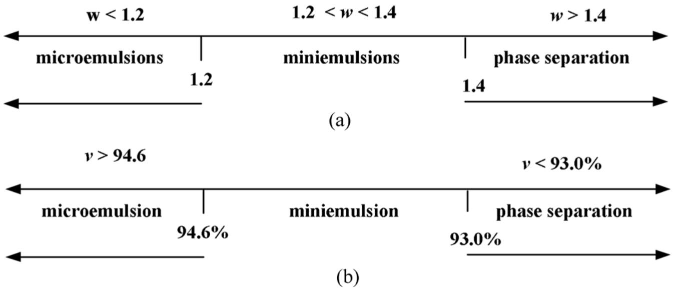


FIG. 6. (a) Water-to-TX-100^{TM} ratios (w) in the various emulsion systems, and (b) Volumes (v) of ethyl acetate corresponding to the various TX-100^{TM} emulsion system.

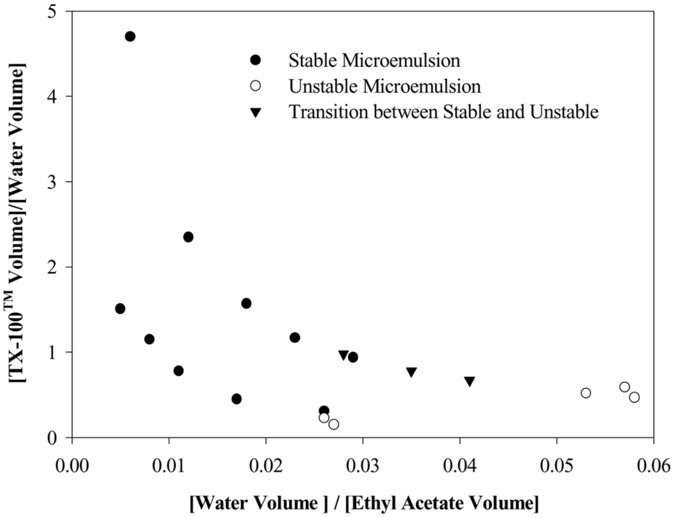
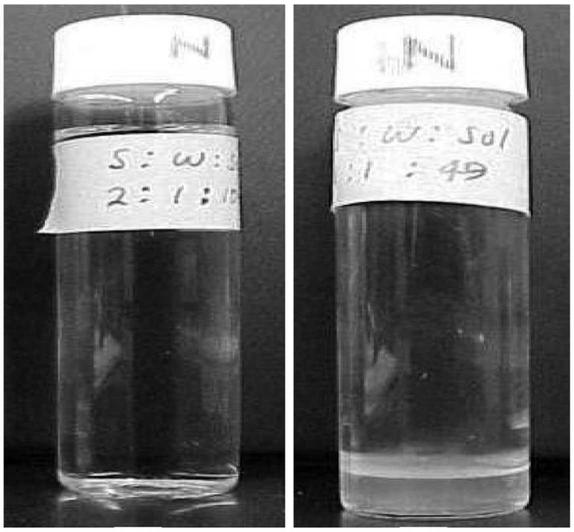


FIG. 7. Variation of ratio of [TX-100^{TM} volume]/[water volume] with [water volume]/[Ethyl acetate volume] for stable and unstable microemulsion system at room temperature.

pictured in Fig. 8b. The microemulsion pictured in Fig. 8a was optically clear and stable. This emulsion was formed at water-to-surfactant volume ratios (w) of less than or equal to 1.0 ($w \leq 1$) with the corresponding ethyl acetate volume of greater than or equal to 94% ($v \geq 94.6\%$) of the total emulsion systems (Fig. 8a). Miniemulsions were formed with associated visible emulsion cloudiness at $1.0 \leq w \leq 1.2$ corresponding to ethyl acetate volumes of 94% ($v \approx 94\%$). The phase separation was observed at $w \geq 1.2$ corresponding to $v \leq 94.0\%$ (Fig. 8b). These observations are shown pictorially in Figs. 9a and 9b for water-to-PEG-PPG-PEG (w) and ethyl acetate volumes (v) in PEG-PPG-PEG emulsions, respectively.



(a) (b)

FIG. 8. Photograph of emulsion systems for PEG-PPGPEG at room temperature: (a) Stable microemulsion system, and (b) Phase separated emulsion system.

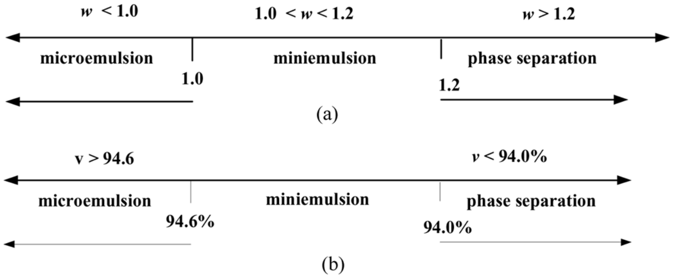


FIG. 9. (a) Water-to-PEG-PPG-PEG ratios (w) for the various emulsion systems, and (b) Volumes (v) of ethyl acetate corresponding to the various PEG-PPG-PEG emulsion systems.

Figure 10 is a dimensionless plot for general application of the various PEG-PPG-PEG emulsion systems in ethyl acetate. This dimensionless plot can be used to predict the various proportions of the water, PEG-PPG-PEG, and liquid CO_2 in a particular emulsion system.

The PEG-PPG-PEG is more soluble in water than the TX-100^{TM} (14,16) and hence the PEG-PPG-PEG emulsion systems are expected to have a higher capacity for water. However, this was not the case; the TX-100^{TM} emulsion systems rather had a higher capacity for water. Liquid CO_2, having a smaller size, is known to solubilize very small molecules. The TX-100^{TM} being smaller compared to PEG-PPG-PEG, one would expect the TX-100^{TM} to have higher capacity for water. The low water capacity of the PEG-PPG-PEG emulsion is impacted by its larger size. The forces that exist in an emulsion system are mainly the

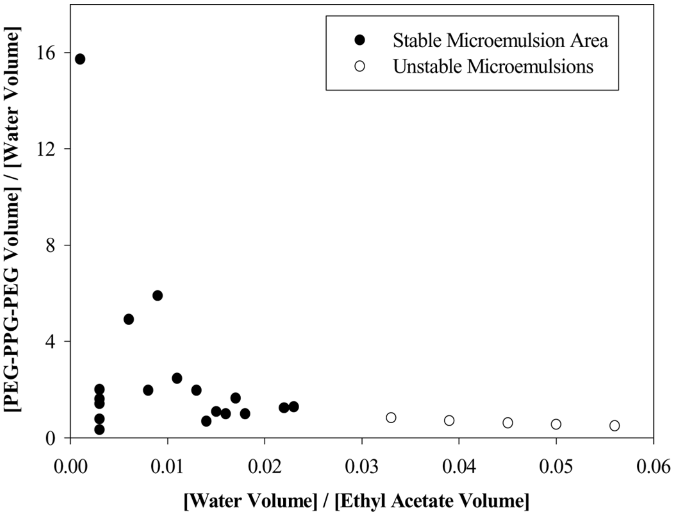


FIG. 10. Variation of ratio of [PEG-PPG-PEG volume]/[water volume] with [water volume]/[ethyl acetate volume] for stable and unstable microemulsion system at room temperature.

weight of the water core, the attraction and repulsion among the cores and tails, respectively, and the density of the solvent. Because of the size differential, the PEG-PPG-PEG will form emulsions with the water core larger than that of the TX-100^{TM} for the same amount of water. The higher micelle core weight is what overcomes the resultant attraction and repulsion forces at the same amount of water resulting in the lowering water capacity in stable emulsions.

CONCLUSIONS

The effect of temperature on the solubility of TX-100^{TM} in liquid CO_2 is stronger than that of pressure. Ethyl acetate known to behave as liquid CO_2 has been used to predict the emulsion systems of TX-100^{TM} and PEG-PPG-PEG. Irrespective of the nature of the surfactant, the stability of the emulsion is impacted by the bulkiness of the surfactant. The bulkiness of the PEG-PPG-PEG lowered the water capacity of the stable emulsion system. The low water capacity of the PEG-PPG-PEG emulsion system compared to that of the TX-100^{TM} is attributed to its low capacity to solubilize hydrophilic substances.

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