OPTIMISATION OF HYBRID SURFACTANT CHEMICAL STRUCTURE FOR WATER-IN-CO_2 MICROEMULSIONS STABILISATION

THESIS SUBMITTED IN FULFILLMENT OF THE REQUIREMENT FOR THE
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ABSTRACT

This research aimed to investigate the optimisation of hybrid CO_2-philic surfactant chemical structure in stabilising water-in-CO_2 (w/c) microemulsions. The optimisation was carried out by synthesise anionic surfactants analogue of Aerosol-OT (sodium bis (2-ethylhexyl) sulfosuccinate) template with the modification on hydrocarbon CO_2-philic chain type and surfactant headgroup. Proton Nuclear Magnetic Resonance (^{1}H NMR) spectroscopy and CHNS-O elemental analysis were used to characterize the chemical structure and purity of the surfactants. The performances of surfactant were investigated through high-pressure phase behaviour, surface tension measurement, and UV-Visible spectroscopy. Research finding showed that fluorination on hybrid AOT analogue surfactant structure is the key factor affecting the CO_2-philicity of the surfactant. The CO_2-philicity of hybrid AOT analogue surfactants enhanced by utilising highly methylated branched hydrocarbon tail hence reduces the interfacial tension between CO_2 and water interface. In conclusion, changing sulfosuccinate into sulfoglutaconate headgroup has found to gives influence in surfactant ability to stabilise w/c microemulsions. This study generates new insight of surfactant molecular structure requirement in designing hybrid CO_2-philic AOT analogue surfactant. It is also beneficial for developing economic and non-bioaccumulative surfactants for CO_2-based technology.

PENGOPTIMUMAN STRUKTUR KIMIA SURFAKTAN HIBRID BAGI PENSTABILAN MIKROEMULSI AIR-DALAM-CO_2

ABSTRAK

Kajian ini bertujuan menyiasat pengoptimuman struktur kimia surfaktan hibrid CO_2-filik dalam menstabilkan mikroemulsi air-dalam-CO_2 (w/c). Pengoptimuman dilakukan dengan mensintesis templat analog surfaktan anionik Aerosol-OT (natrium bis (2-etil-heksil) sulfosuksinik) dengan pengubahsuaian pada jenis rantaian hidrokarbon CO_2-filik dan kumpulan kepala surfaktan. Spektroskopi Resonans Magnet Nukleus proton (^{1}H RMN) dan analisis unsur CHNS-O telah digunakan untuk mencirikan struktur kimia dan ketulenan surfaktan. Prestasi-prestasi surfaktan telah dikaji melalui kelakuan fasa tekanan tinggi, pengukuran tegangan permukaan, dan spektroskopi UV-nampak. Dapatan kajian menunjukkan bahawa penfluorinan pada struktur analog surfaktan hibrid AOT menjadi faktor utama yang mempengaruhi kefilikan-CO_2 suatu surfaktan. Kefilikan-CO_2 analog surfaktan hibrid AOT dipertingkatkan dengan menggunakan ekor hidrokarbon kumpulan metil bercabang yang mengurangkan tegangan permukaan dalam kalangan antara muka CO_2 dan air. Kesimpulannya, penukaran kumpulan kepala sulfosuksinik kepada sulfoglutakonik didapati mampu mempengaruhi keupayaan surfaktan untuk menstabilkan mikroemulsi w/c. Kajian ini memberi pemahaman baharu terhadap struktur molekul surfaktan yang diperlukan dalam mereka bentuk analog surfaktan hibrid AOT yang CO_2-filik. Ia juga bermanfaat kepada pembangunan surfaktan yang ekonomik dan tidak bioakumulatif bagi teknologi berasaskan CO_2.

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^1H NMR	Proton Nuclear Magnetic Resonance
a/w	Air-water
AOK	Aerosol-octyl-ketone
AOT	Aerosol-OT
AO-Vac	Aerosol- vinyl acetate
c/w	CO_2-in-water
cmc	Critical micelle concentration
CPP	Critical packing parameter
CTAB	Cetyltrimethylammonium bromide
FFV	Fractional free volume
HCB	Hydrophilic–CO_2-philic balance
HLB	Hydrophilic–lipophilic balance
HP-SANS	High-pressure small-angle neutron scattering
ILs	Ionic liquids
K_p	Krafft point
LAS	Linear alkyl benzene sulfonate
MO	Methyl orange
MW	Molecular weight
o/w	Oil-in-water
P_c	Critical pressure
P_{trans}	Cloud pressure

sc-CO_2	Supercritical carbon dioxide
SCFs	Supercritical fluids
SDS	Sodium dodecyl sulfate
T_c	Critical temperature
TLC	Thin layer chromatography
USEPA	United States Environmental Protection Agency
VOCs	Volatile organic solvents and compounds
w	Water-to-surfactant molar ratio
w/c	Water-in-CO_2

CHAPTER 1

INTRODUCTION

1.1 What is Green Solvent?

Solvents are used in large amounts and play a major part in industrial activities. One of the most common solvent used in this field are volatile organic solvents and compounds (VOCs). Waste VOCs solvents from industrial activities are ending up inevitably contaminate the ecosystems and are considered as a huge threat for environmental damage (Bloemen, Burn, & Wallace, 1993; Moran, Zogorski, & Squillace, 2006; Ott & Roberts, 1998; Sarigiannis, Karakitsios, Gotti, Liakos, & Katsoyiannis, 2011; ScienceDaily, 2012). Figure 1.1 shows the common used organic solvent in industries and its environmental effect.

In recent years, academic researchers have been conducted extensively in designing environmentally benign chemical products to replace volatile organic solvents and compounds (Anastas & Eghbali, 2010). The concept of "green solvent" was then accepted as the viable VOCs replacement for the greener future. On that point, there are four ways for developing green solvents (Capello, Fischer, & Hungerbu¨hler, 2007): (1) substitution of hazardous solvent with ones that show better environmental, health, and safety properties; (2) bio-solvents; (3) supercritical fluids (SCFs); and (4) ionic liquids (ILs).

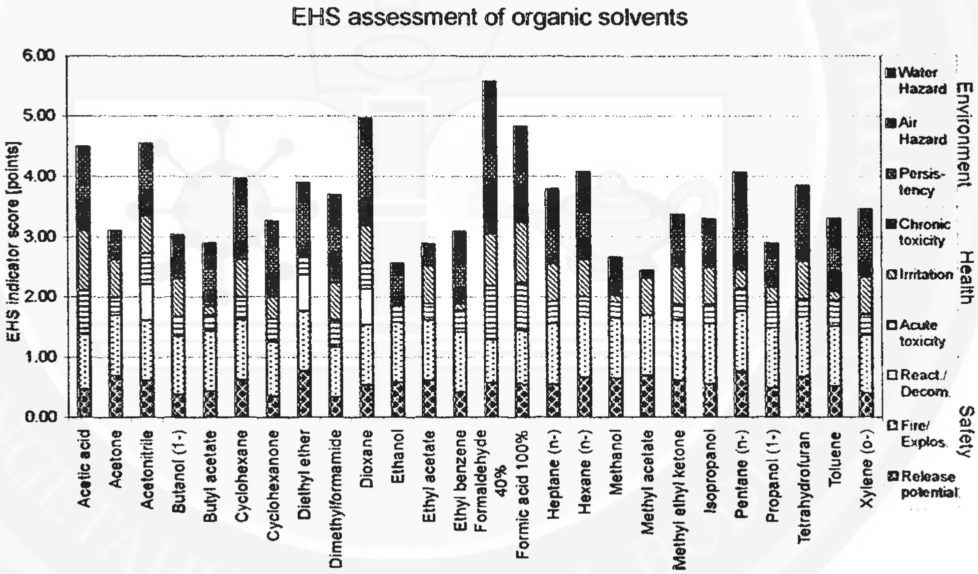

Figure 1.1. Environmental, health, and safety assessment of common organic solvents (Capello et al., 2007).

Of the four options, supercritical fluids (SCFs) have proven to be one promising alternative to traditional solvents and have been extensively studied in the past decades (Anastas & Eghbali, 2010; Brunner, 2004; Cansell & Aymonier, 2009; Eckert, 1996; McMillan & Stanley, 2010; Young & Raynie, 2011). Supercritical fluid states of a compound achieved when the temperature and pressure are beyond its critical point; critical pressure (P_c) and critical temperature (T_c) as can be seen in Figure 1.2. Any distinctions between liquid and gas phases are no longer exist, giving intermediate properties of liquid and gas phases. The SCFs properties such as density, viscosity, and solubility parameter can be easily tuned by varying temperature or pressure (Brunner, 2004; Deiters & Kraska, 2012; Eckert, 1996; Johnston & Penninger, 1989).

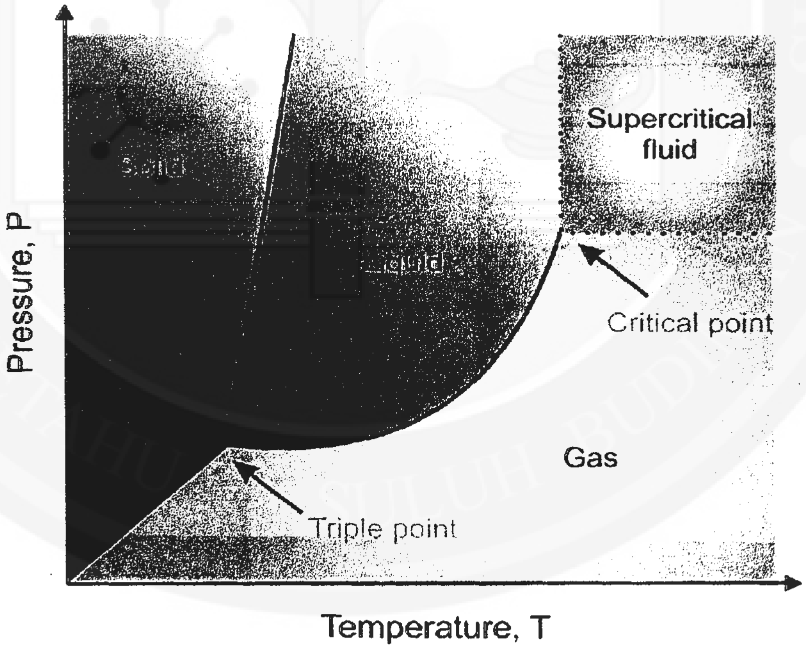

Figure 1.2. Phase diagram for supercritical fluid showing the critical point region (T_c, P_c) (Mohamed & Eastoe, 2011).

What makes SCFs quite interesting is the ease of solvent removal, by simultaneously heated and compressed above their critical point. The common used SCFs for example are water, carbon dioxide, methane, methanol, ethanol, or acetone. Up until now carbon dioxide is one of the most frequently used SCFs (Anastas & Eghbali, 2010). Being not regulated by US Environmental Protection Agency (USEPA) as a volatile organic compound does make CO_2-based processes is environmentally favourable (Gopalan, Wai, & Jacobs, 2003).

1.2 Supercritical Carbon Dioxide (sc-CO_2)

Recently, Jessop (2011) has pointed out the potential candidates for the future green solvents. The green solvents are forecasted dominated by sc-CO_2 for about 30.2%, followed by water (22.9%), selected organic solvents (18.8%), ionic liquids (ILs) (12.5%), switchable solvents (6.3%), glycerol (4.2%), solventless (3.1%), and bio-derived solvents (2.3%) (Jessop, 2011; Young & Raynie, 2011). sc-CO_2 has relatively accessible critical point compare to other common organic solvents (Table 1.1) and is widely used for materials and chemicals processing. Moreover, it is abundant, non-toxic, non-flammable and also inexpensive (Eastoe & Gold, 2005).

Being well established for natural products extraction for the past decades (Saldana, Mohamed, Baer, & Mazzafera, 1999), the utilisation of sc-CO_2 in larger areas have been extensively investigated. Nowadays, the use of sc-CO_2 ($T_c = 31.1\ ^{\circ}C$; $P_c = 72.8$ bar) as a solvent is being realised in several areas, such as dry cleaning (Banerjee et al., 2012; DeSimone, 2002), microelectronics (Weibel & Ober, 2003), nanomaterial processing (Bell, Anand, Fan, Enick, & Roberts, 2005; Eastoe, Hollamby, & Hudson, 2006c), beans and coffee decaffeination (Icen & Guru, 2009; Perva-Uzunalic´ et al., 2006; Tello, Viguera, & Calvo, 2011) and so on.

Table 1.1

Critical points of common organic solvents.

Fluid	**T_c/°C**	**P_c/bar**
Carbon dioxide	31.0	72.8
Ethane	32.2	48.8
Ethylene	9.2	50.4
Propane	96.7	42.5
Propylene	91.8	46.0
Ammonia	132.4	113.5
Water	374.2	221.2
Cyclohexane	280.4	40.7
n-pentane	196.6	33.7
Toluene	318.7	41.0

Source: Eastoe & Gold, 2005

However, sc-CO_2 is a poor solvent owing to its nonpolar nature. Compare to other common organic solvents, sc-CO_2 has a lower dielectric constant, dipole moment, and polarity, thus limiting its solubilisation power (Eastoe, Yan, & Mohamed, 2012; Mohamed & Eastoe, 2011). On the other hand, solubility is one important factor of a compound to be implemented in wider applications. In general, as shown in Table 1.2 most of non-polar compounds are quite soluble in sc-CO_2. Meanwhile moderately polar, polar, and high molecular weight (MW) materials are practically insoluble in sc-CO_2. The limited number of materials soluble in sc-CO_2 does impede future development of sc-CO_2-based technology for material and chemical processing.

Table 1.2

Solubility of organic compounds in sc-CO_2.

Very soluble	**Sparingly soluble**	**Almost insoluble**
Nonpolar and slightly polar, low molecular weight (MW) materials (<250) e.g., acetic acid, glycerols, acetates, benzaldehyde, thiazoles	Higher MW materials (<400) e.g., oleic acid, decanol, saturated lipids up to C_{12}	Polar, ionic, high MW materials e.g., sugars, proteins, amino acids, glycine, carotenoids

Source: Mukhopadhyay, 2000

1.3 Water-in-CO_2 (w/c) Microemulsions

The limitations in using sc-CO_2 as a solvent could be vastly improved by encapsulating nanodomain of polar compound in the sc-CO_2 phase (Eastoe, Gold, Steytler, 2006b; Mohamed & Eastoe, 2011). Water is readily abundant and the cheapest solvent used in the material and chemical processing. The dispersion of water in sc-CO_2 combines the interesting properties of each solvent to be implemented as a universal solvent for CO_2-based processes. Water dispersion in sc-CO_2 induces the formation of reverse micelle, hence aids the solubilisation materials which would be otherwise insoluble due to the non-polar nature of sc-CO_2 (Eastoe et al., 2006b; Johnston et al., 1996; Mohamed & Eastoe, 2011). Reverse micelle, as shown in Figure 1.3 refers to domain (2-5 nm) form in the sc-CO_2 bulk phase (Eastoe et al., 2006b; Johnston et al., 1996; Mohamed & Eastoe, 2011). The formation of reverse micelle in sc-CO_2 has triggered the use of w/c microemulsion for nanomaterial processes (Fernandez and Wai, 2006; Ji, Chen, Wai, & Fulton, 1999; Liu, Ikushima, & Shervani, 2003a), biological processes (Holmes, Steytler, Rees, & Robinson, 1998; Ihara, Suzuki, Maeda, Sagara, & Hobo, 1995), organic and inorganic synthesis (Hong et al., 2003; Jacobson, Lee, & Johnston, 1999; Moisan et al., 2007; Pandey, Baker, Kane, Bonzagni, & Bright, 2000).

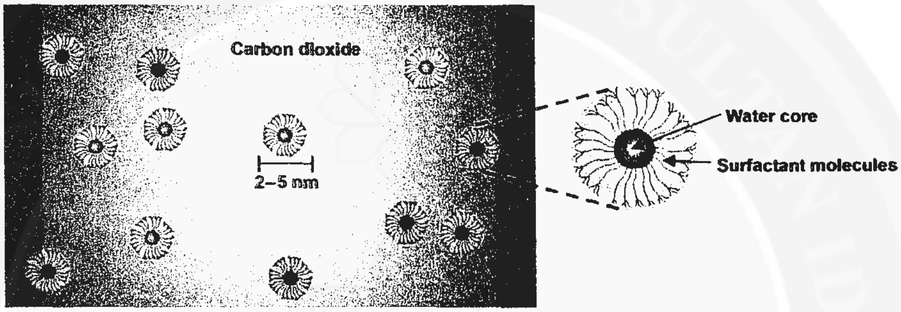

Figure 1.3. Schematic representation of w/c microemulsions and reverse micelle structure (Mohamed & Eastoe, 2011).

However, the solubility of water in sc-CO_2 is relatively low (0.1 – 0.2 wt. %) at 15°C and 450 bar (Eastoe, Downer, et al., 2000a; Eastoe & Gold, 2005). The solubility of water in sc-CO_2 though significantly higher compare to those on oil, ethane, and propane (Eastoe et al., 2000a; Harrison, Goveas, Johnston, & O'Rear, 1994). In fact, the stable formation of w/c microemulsions is challenging and needs the use of efficient CO_2-philic surfactants which is active at CO_2-water interface (Johnston et al., 1996; Stone, da Rocha, Rossky, & Johnston, 2003). Over 130 commercially available surfactants have been investigated by Consani and Smith (1990), even so there are relatively few surfactants that soluble in sc-CO_2. Thus made the search for excellent CO_2-philic surfactant is quite interesting.

The efficiency of a CO_2-philic surfactant in stabilising w/c microemulsions could be scaled by cloud pressure (P_{trans}) and water-to-surfactant molar ratio (w). P_{trans} is pressure at a given composition and temperature which remains a clear one phase (1Φ) microemulsions. Below the P_{trans}, phase separation occurred in which the mixture is visibly turbid, indicating the transition of microemulsions to macroemulsions (2Φ). The lower the P_{trans} value, the more efficient a CO_2-philic surfactant is. Water-to-surfactant molar ratio; w (Eq 1.1) or w_c (Eq 1.2) is properties which characterise the water content in microemulsion and are define as follows:

$$w = \frac{[\text{water}]_{\text{dispersed}}}{[\text{surfactant}]} \tag{1.1}$$

$$w_c = \frac{[\text{water}]_{\text{dispersed}} - [\text{water}]_s}{[\text{surfactant}]} = w - \frac{[\text{water}]_s}{[\text{surfactant}]} \tag{1.2}$$

Where w is raw water-to-surfactant molar ratio in the w/c system, w_c is corrected water-to-surfactant molar ratio, $[\text{water}]_{\text{dispersed}}$ is moles of water dispersed in the w/c system, $[\text{water}]_s$ is moles of water soluble in pure sc-CO_2 and [surfactant] is moles of surfactant in the system (Mohamed et al., 2012; Sagisaka et al., 2008; Sagisaka, Kudo, Nagoya, & Yoshizawa, 2013b; Sagisaka et al., 2003a,b). The higher w value indicating the more water dispersed in sc-CO_2 and therefore the more efficient a surfactant for sc-CO_2. The formation of reverse micelle in sc-CO_2 could be experimentally determined by visual observation of aqueous dye solubilisation in water-CO_2-surfactant system (Sagisaka et al., 2009).

1.4 Design of CO_2-philic Surfactant

Great deal efforts have been devoted since relatively few commercial surfactants soluble in CO_2 (Eastoe et al., 2003b,c; Liu et al., 2002). Over 130 commercially available surfactants have been investigated and many of them are insoluble in CO_2 (Consani & Smith, 1990). The research was then directed to the development of CO_2-philic surfactants (Cummings, Trickett, Enick, & Eastoe, 2010; da Rocha, Johnston, & Rossky, 2002; Eastoe et al., 2003b; Eastoe et al., 2006b; Eastoe & Gold, 2005; Hoefling, Beitle, Enick, & Beckman, 1993; McClain et al., 1996; Sarbu, Styranec, & Beckman, 2000). The ability of surfactants in stabilising w/c microemulsions in reasonable conditions (pressure and temperature) therefore is important for CO_2-philic surfactant design.

1.4.1 Fluorinated CO_2–philic Surfactants

The ability of fluorocarbon chain to interact with CO_2 was first suggested by Iezzi et al. (1999). The study has revealed that fluorination on alkane chain enhances the miscibility in CO_2 as well as promoting the formation of reverse micelle in CO_2 bulk phase (Iezzi, Bendale, Enick, Turberg, & Brady, 1989). A study by Consani and Smith (1990) again confirmed the solubility of fluorinated surfactant in carbon dioxide. Over 130 commercial surfactants studied, those contained fluorine – carbon bonds are soluble in CO_2. Later, the result triggered Beckman group to investigate the use of fluorinated and fluorinated analogues of Aerosol-OT (AOT) surfactant for stabilising w/c system. AOT (sodium bis(2-ethyl-1-hexyl) sulfosuccinate) itself is a