LETTER

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Very high solubilities of hydrogenated *n*-alkyl CO_2-philes in supercritical carbon dioxide at moderately low temperature and pressures†

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Unusually high solubilities, up to 80 wt %, of long-chain *n*-alkyl surfactants such as a polyethylene glycol mono-*n*-alkyl ethers, *n*-alkyl esters, and acids have been observed in CO_2 at the moderately low temperature and pressure of 308 K and 7.9 MPa, respectively. A very strong structure-solubility relationship for hydrogenated *n*-alkyl surfactants in supercritical carbon dioxide is explained in terms of the CO_2-philicity of the surfactants.

Since the discovery[1] of microemulsions in supercritical ethane and near-critical propane, much attention has been focused on the preparation of these aggregates in supercritical carbon dioxide (SC CO_2) because of its low critical temperature ($T_c = 304.1$ K) and environmentally benign characteristics. Several authors have reported the preparation[2,3] of microemulsions in SC CO_2 using fluorinated surfactants, which are expensive and difficult to synthesize. To prepare low-cost microemulsions in SC CO_2, the commercial hydrogenated surfactants should be explored. However, hydrogenated surfactants have limited miscibility with CO_2 because of its poor solvent strength. Therefore, in this work we have carried out solubility measurements on a variety of hydrogenated surfactants to provide directionality to develop low-cost surfactants that can stabilize microemulsions in SC CO_2. Applications of nontoxic, non-flammable and inexpensive SC CO_2 microemulsions in the extraction and synthesis of biochemical, cosmetic, pharmaceutical compounds and inorganic nanomaterials can be hoped for.

Consani and Smith[4] observed the solubilities of over 130 surfactants in SC CO_2. They obtained only general qualitative information regarding the solubility of the surfactant molecules in SC CO_2, such as (1) the solubility of compounds increased with increasing CO_2 density at higher pressures as a result of increased intermolecular forces and (2) molecules with a greater intermolecular hydrogen bonding ability in CO_2 were found to be more soluble than those with weaker hydrogen bonding ability. However, their experiments did not yield any quantitative information to guide the design of sustainable surfactant-in-CO_2 systems. Fluorocarbon surfactants such as perfluorinated alkylpolyethers[5] and block copolymer surfactants[6] showed promising miscibility with CO_2 at moderately low temperature and pressure. But because of their higher production cost these compounds are not suitable for commercial CO_2-based processes. Solubilities of various amorphous polyethers, polyacrylate and polysiloxane homopolymers, and a variety of commercially available block copolymers in CO_2 have also been measured.[7] Beckman and co-workers[8,9] synthesized low-cost, sustainable CO_2-philes. They showed that functionalization of polyethers with carbonyl groups or carbonates in the side chain or backbone significantly lowers the cloud point pressures of polyethers in CO_2. Lewis acid-Lewis base interactions between these functionalized polyethers and CO_2 were invoked to explain the increased solubilities of these polyethers in CO_2. The structure-solubility relationship of hydrogenated solutes in CO_2 has been investigated by several authors.[7,10] But to date, no study leading to a relationship between the structures of hydrogenated surfactants and their solubilities in CO_2 has been conducted.

To study the structure-solubility relationship of hydrogenated surfactants in terms of CO_2-philicity in SC CO_2, we carried out solubility measurements of polyethylene glycol mono-*n*-alkyl ethers, *n*-alkyl esters, acids, and alcohols. Solubilities (wt %) of solutes were obtained using a high pressure viewing cell and recording the cloud point pressures as described in the Experimental. We have selected compounds of approximately similar molar mass and *n*-alkyl chain length but different CO_2-philic polar groups. The compounds investigated are acetic acid *n*-decyl ester ($C_{10}H_{21}OOCCH_3$, denoted C_{10}–$OOCCH_3$), ethylene glycol mono-*n*-dodecyl ether [$C_{12}H_{25}(OCH_2CH_2)OH$, denoted C_{12}–$(EO)_1$], *n*-dodecanoic acid ($C_{11}H_{23}COOH = C_{11}$–$COOH$) and *n*-dodecanol ($C_{12}H_{25}OH$ or C_{12}–OH). Solubilities of two different polyethylene glycol mono-*n*-alkyl ethers, namely triethylene glycol mono-*n*-dodecyl ether [C_{12}–$(EO)_3$] and pentaethylene glycol mono-*n*-hexyl ether [C_6–$(EO)_5$], of approximately similar molar mass (the latter is only 4 mass units heavier than the former) but very different CO_2-philicities, were also measured.

Figs. 1 shows photographs taken through the windows of the high pressure viewing cell loaded with a C_{12}–$(EO)_1$(2.82 g)–CO_2 mixture under different operating conditions. Fig. 1(A) shows the mixture at CO_2 pressures of 1 MPa to less than 17.4 MPa when the stirrer is off. Two clear phases can be seen: at the bottom of the cell is the viscous C_{12}–$(EO)_1$ surfactant and the upper phase is liquid CO_2. When the stirrer is turned on, mixing of C_{12}–$(EO)_1$ and liquid CO_2 occurs and a heterogeneous turbid solution is obtained, as seen in Fig. 1(B). When the pressure of CO_2 is raised to or above 17.4 MPa, C_{12}–$(EO)_1$ is dissolved completely in CO_2 to form a transparent homogeneous solution shown in Fig. 1(C); the cloud point pressure can be considered to be 17.4 MPa.

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† Electronic supplementary information (ESI) available: colour version of Fig. 1. See http://www.rsc.org/suppdata/nj/b3/b317037c/

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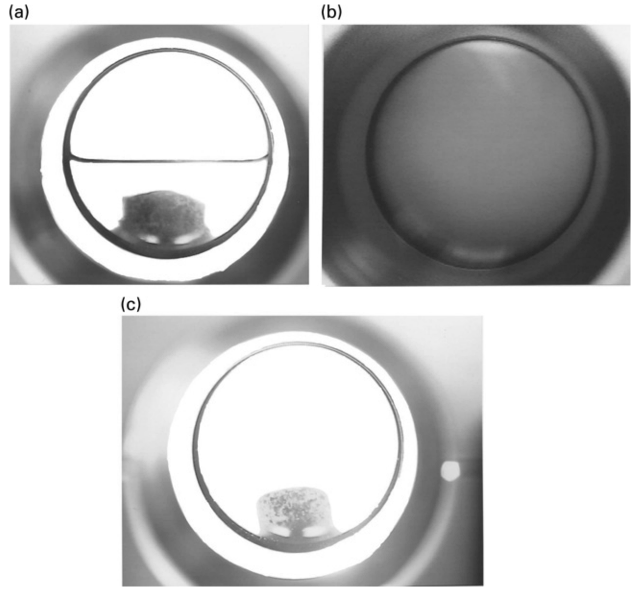

Fig. 1 Photographs illustrating the cloud point determination in the high-pressure viewing cell containing ethylene glycol mono-*n*-dodecyl ether (2.82 g) in SC CO$_2$ at 308 K and various pressures: (A) 1 to $<$17.4 MPa, stirrer is off; (B) 1 to $<$17.4 MPa, stirrer is on; (C) $\geq$17.4 MPa, stirrer is on.

Similarly, the cloud point pressures of other systems were recorded and the phase diagrams of different surfactant–CO$_2$ systems were constructed.

To establish the structure-solubility relationship of surfactants in SC CO$_2$ we have compared the miscibility or cloud point pressure plots (Fig. 2) of *n*-dodecanol, *n*-dodecanoic acid, ethylene glycol mono-*n*-dodecyl ether and acetic acid *n*-decyl ester in SC CO$_2$ at 308 K. As shown in the plot, the solubilities of the surfactants can be arranged in the order of ester $>$ ethylene glycol $>$ carboxylic acid $>$ alcohol. The solubility order observed above in wt % was found to be the same as that calculated in terms of moles of the surfactants. The above solubility pattern of the surfactants in CO$_2$ can be explained on the basis of the extent of specific molecular Lewis acid–base interactions between CO$_2$ and the polar head groups of the surfactants. An IR spectroscopic study[11] has shown that introduction of electron-donating functional groups, such as carbonyl, into a hydrophobic molecule causes Lewis acid (CO$_2$)-base (*e.g.*, carbonyl) type specific interactions that dramatically enhances the miscibility of solutes in CO$_2$. Sarbu *et al.*[8,9] reported dramatic increases in the solubilities of propylene oxide, ethylene oxide and cyclohexene oxide ethers by introducing an acetate or carbonate group in the chains of these polyethers. These authors have also attributed the higher miscibility of functionalized (acetate or carbonate) polyethers to the Lewis acid–base interactions. Furthermore, attachment of a methyl group to a carbonyl carbon such as in acetate enhances the solubility as a result of hydrogen bonding between the oxygen atom of CO$_2$ and the hydrogen atom of the acetate methyl group. The solubility order of the surfactants, as shown in Fig. 2, can be explained on the basis of the strength of the interactions, as described above, between CO$_2$ and the functional group of the surfactants. Acetic acid *n*-decyl ester has the strongest interaction with CO$_2$, followed by ethylene glycol mono-*n*-dodecyl ether, *n*-dodecanoic acid and *n*-dodecanol.

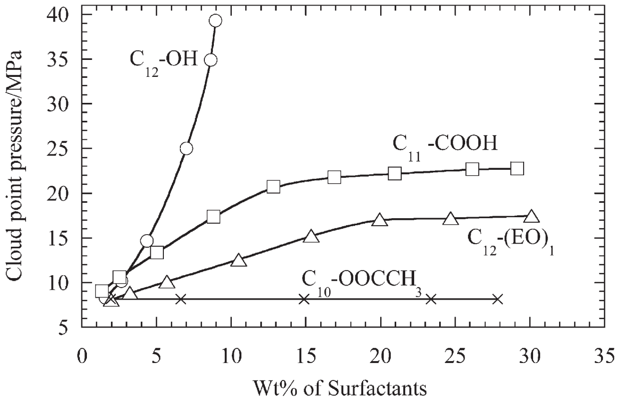

Fig. 2 Limit of the solubility of various amphiphiles in SC CO$_2$ at 308 K as determined by cloud point measurements. Pressure *vs.* amphiphile concentration curves shown delimit the phase diagram boundaries corresponding to the solubility limit of each amphiphile.

Apart from solute-solvent interactions, solute-solute interactions also play an important role in determining the solubility of solutes in solvents. Therefore, in this work we also have justified the extent of the solubility of surfactants in CO$_2$ in the context of surfactant-surfactant interactions. The solubility data of homopolymers and block copolymers of poly(ethylene oxides) (PEO), poly(ethylene oxide)dimethoxy ethers (PEO-DME) and poly(propylene oxides) (PPO) in CO$_2$ were interpreted[7] considering polymer-polymer interactions. There exists strong polymer-polymer interactions in PEO due to hydrogen bonding of the terminal hydroxy group. Polymer-polymer interactions decrease in PEO-DME, followed by PPO, because of decreased hydrogen bonding due to replacement of the hydroxyl group in PEO-DME by dimethoxy groups. Compared to PEO, PPO has fewer intermolecular interactions because of the methyl substitution on each monomer unit in the chain. In the case of PPO the molecular interactions decrease because of the steric hindrance of the substituted methyl group. Considering the polymer-polymer interactions the order of solubilities of the polymers in CO$_2$ becomes PPO $>$ PEO-DME $>$ PEO. Based on the above solute-solute interactions, the solubility order we have observed in hydrogenated surfactants can be justified. As *n*-dodecanol has the highest hydrogen bonding ability and acetic acid *n*-decyl ester has the least, therefore the latter has the highest CO$_2$ miscibility and the former has least.

The solubility results of these amphiphiles have suggested that acetylation or pegylation of long-chain hydroxyl compounds or other functional groups is a viable approach to dissolve compounds in the low dielectric but Lewis acid CO$_2$. Fig. 3 compares the solubilities of two different polyethylene glycol mono-*n*-alkyl ethers, triethylene glycol mono-*n*-dodecyl ether [C$_{12}$–(EO)$_3$] and pentaethylene glycol mono-*n*-hexyl ether [C$_6$–(EO)$_5$] of approximately similar molar mass but different CO$_2$-philicity. The miscibility pressure decreased from 25.2 to 18.9 MPa in SC CO$_2$ when the alkyl chain was shortened from C$_{12}$ to C$_6$ and the number of ethylene glycol moieties

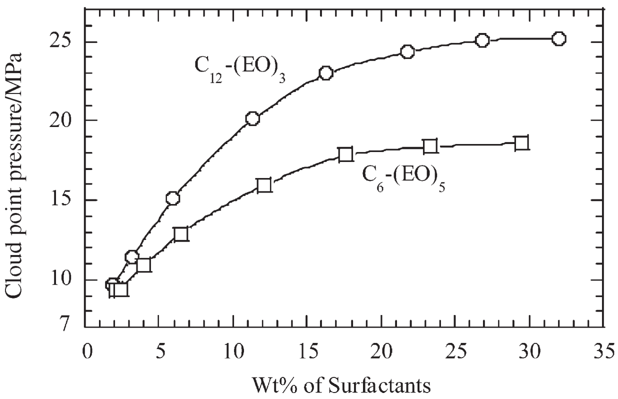

Fig. 3 Comparison of the miscibility of triethylene glycol mono-*n*-dodecyl ether and pentaethylene glycol mono-*n*-hexyl ether in CO$_2$ at 308 K.

was increased from 3 to 5. This significant lowering of the miscibility pressure is attributed to the increased CO_2-philicity of C_6–$(EO)_5$ compared to C_{12}–$(EO)_3$.

In separate experiments, the pressure dependence of the miscibility of four different polyethylene glycol mono-*n*-alkyl ethers, namely, tri- and tetraethylene glycol mono-*n*-dodecyl ethers [C_{12}–$(EO)_3$ and C_{12}–$(EO)_4$, respectively] and tri- and tetraethylene glycol mono-*n*-decyl ethers [C_{10}–$(EO)_3$ and C_{10}–$(EO)_4$, respectively] were measured in CO_2 at 308 K. At a pressure of 7.9 MPa, the solubilities of these polyethylene glycol mono-*n*-alkyl ethers were found to be 80 wt % in CO_2. The high solubilities of these *n*-alkyl C_i–$(EO)_j$ solutes in CO_2 are due to strong intermolecular interactions between CO_2 and the oxygen and hydrogen atoms of the ethylene glycol moiety, which substantially lower the cloud point pressures of alkyl ethylene glycols. Solubility measurements of two long-chain *n*-alkyl esters in SC CO_2 at 308 K were also conducted. Acetic acid *n*-decyl and *n*-dodecyl esters also showed a miscibility of 80 wt % at a moderately low pressure of 8 MPa. The high miscibility of these esters in CO_2 has been attributed to the interaction between CO_2 and the acetyl group of esters and is also supported by the weak intermolecular hydrogen bond due to the steric effect of the ester methyl group.

Based on the results obtained from the structure-solubility relationship study of hydrogenated surfactants in SC CO_2, easily soluble and low-cost surfactants can be designed to prepare surfactant–CO_2 systems. The results of the present study show, for the first time, that similarly to non-surfactant hydrogenated solutes, the Lewis acid–base interactions between CO_2 and functional groups of the hydrogenated surfactants and solute-solute interactions play an important role in determining the miscibility of hydrogenated surfactants in CO_2. The CO_2-phobic long-chain alkyl compounds can be turned into CO_2-philes by capping their terminal hydroxyl or other functional groups with electron-donor species (Lewis bases) such as carbonyl, ethylene glycol, carboxylic acid or ester groups, which can dramatically lower cloud point pressures of hydrogenated surfactant–CO_2 systems. The miscibility of the long *n*-alkyl chain surfactants observed at rather low pressure in SC CO_2 can allow the application of these compounds in various processes using the environmentally benign, cheap and recyclable CO_2 medium. We have used the data obtained in this work to prepare reverse micelles in CO_2 using low cost commercial surfactants and the results have been described in an article published recently.[12]

Experimental

Polyethylene glycol mono-*n*-alkyl ethers, $C_{12}(EO)_1$, $C_{12}(EO)_3$, $C_{12}(EO)_4$, $C_{10}(EO)_3$ and $C_{10}(EO)_4$, were purchased from Nikko Chemicals. Pentaethylene glycol mono-*n*-hexyl ether, $C_6(EO)_5$, was obtained from Bachem. A 10 ml high pressure viewing cell, fitted with a pair of sapphire windows, a stirrer, and a jacket surrounding the cell for water circulation to maintain the temperature, was employed for monitoring the cloud point pressure of the surfactants by looking visually across the windows of the cell. A weighed amount of surfactant was loaded through the injection port of the cell and then the cell was closed. After removing air by flowing CO_2 at 0.5 MPa from the apparatus circuit, pre-cooled CO_2 was introduced at 5 MPa until a transparent homogeneous solution was obtained. Thus, cloud point pressures for increasing amounts (wt %) of surfactants were determined at a fixed temperature of 308 K. The wt % (w/w) of surfactants dissolved in SC CO_2 was determined very accurately by using a direct method to determine the amount (g) of CO_2 introduced at the cloud point pressure. The high pressure cell was removed from the line after closing the inlet and outlet of the cell using valves and plugging unions, attached to and near the valves by stoppers to make sure that no leakage of the CO_2–surfactants mixture occurred. Thus, the cloud point pressure *vs.* wt % phase diagrams for various surfactants were constructed. To take photographs of the high pressure viewing cell containing the CO_2–surfactants mixture in various phases, a Sony XC-003 camera connected to a video monitor and a printer was used.

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