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Towards detergency in liquid CO_2 – A surfactant formulation for particle release in an apolar medium

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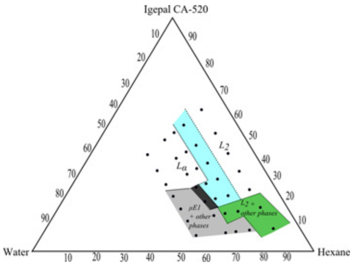
HIGHLIGHTS

- ► A new hydrocarbon surfactant and formulation for liquid CO_2 dry-cleaning introduced.
- ► In the formulation lamellar mesophases coexist with reverse micellar phase.
- ► Surfactant mesophases reduce adhesion force between a silica particle and cellulose.
- ► Formulation has five times better soil removal ability than control in liquid CO_2.

GRAPHICAL ABSTRACT



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ABSTRACT

In this paper we propose, characterize and test a surfactant formulation, consisting of a branched polyoxyethylene type commercial non-ionic surfactant (Igepal CA520), n-hexane and water, for use in CO_2 dry-cleaning to enhance the removal of particulate soil. In the formulation lamellar mesophases L_α coexist in an L_2 microemulsion (reverse micellar) phase. We hypothesize that enhanced soil removal would be possible due to the adsorption of lamellar liquid crystalline phases at the fabric–soil interface, the presence of water pools, the improvement of the solvent quality of liquid CO_2 by the presence of n-hexane, and the enhanced viscosity due to the presence of the lamellar mesophases. We have characterized the formulation by optical microscopy with crossed polarizers, confocal microscopy, dynamic light scattering and shear viscometry to determine the phase behaviour, the size of the reverse micelles and the flow behaviour. AFM force measurements in n-hexane show that large adhesion forces between a model soil particle (silica) and fabric surface (cellulose) in water-saturated hexane can be reduced by the action of the surfactant mesophases. In the presence of the surfactant formulation the interaction forces were found to be decreased from ∼15 nN to 0.5 nN. The formulation, applied as a pre-treatment on standard soil test monitors and followed by washing in liquid CO_2, showed a five times better soil removal ability than the control.

1. Introduction

Traditional dry cleaning is carried out with perchloroethylene (PERC) which is toxic, harmful, carcinogenic and a depletant of the ozone layer. Therefore a more sustainable alternative is needed. Liquid CO_2 has been identified as a promising replacement for PERC in dry cleaning, as it is environmentally benign, non-toxic and cheap [1]. Tests with liquid CO_2 as a medium for textile cleaning have shown that it indeed is capable of removing fatty and greasy substances, which are sufficiently soluble. Moreover, polar compounds are also fairly well removed, in particular when a little water (1–2%) is added [1]. However, particulate dirt (soil) is poorly removed by liquid CO_2. This is to some extent expected, as the physical properties of liquid CO_2 make it a rather unfavourable

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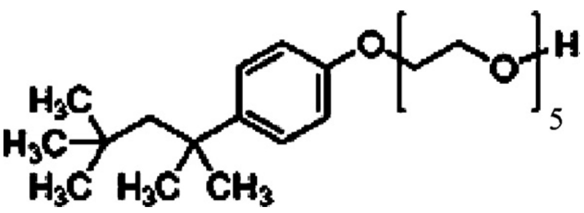

Fig. 1. Chemical structure of Igepal CA520, branched polyoxyethylene (5) isooctylphenyl ether.

medium for particle detachment and dispersion [1,2]. At industrially relevant pressures and temperatures (45–60 bar, 5–10 °C) liquid CO_2 has a very low dielectric constant [1]. This implies that particle–textile interactions (van der Waals forces) are likely to be much stronger than that in PERC. Moreover, the viscosity of liquid CO_2 is low, so that hydrodynamic forces exerted on attached particles are also expected to be weak [1]. Finally, the search for additives that might take the role of detergent in the cleaning process has so far had little success, mainly because the low cohesive energy density of liquid CO_2 prohibits dissolution of many candidate surfactants [1]. As a consequence, particle detachment, if successful at all, is prone to be followed by redeposition because there is no stabilizing dispersant.

The shift from the traditionally employed toxic, harmful chemical PERC to the environmentally friendly liquid CO_2 is urgent, but unless a suitable surfactant or surfactant formulation is developed, the numbers of dry-cleaners using liquid CO_2 as the cleaning medium will remain limited. Previous research shows that there are possibilities to improve the cleaning results for particulate soil in CO_2 [2]. However, far too many parameters play a role to allow for a trial-and-error method to optimize the process. Instead a combination of fundamental and practical research is needed.

In this paper we propose a new surfactant formulation to solve the problem of insufficient particle detachment and stabilization in liquid CO_2, based on the above presented analysis of that problem and on the existing knowledge on surfactants used in liquid and supercritical CO_2. Therefore, we start with a short overview of what is known about surfactants for CO_2, and then rationalize our choices for the new surfactant formulation in terms of the desired properties. The proposed formulation consists of a commercial surfactant (Igepal CA520, see Fig. 1), n-hexane and water. We hypothesize that the most important aspect for its detergency action would be the formation of mesophases such as reverse micelles and lamellar phases. Thus, we explore the three-component phase diagram of the IgepalCA520/hexane/water system and assess the nature, size and composition of the mesophases. Furthermore, we present the viscosity as a function of total water and surfactant concentration to investigate the potential use of the formulation as a viscosity modifier for liquid CO_2. Finally, we test the detergency action of the new surfactant formulation in two different ways: firstly, by directly measuring the effect on the adhesion force between a model soil (silica) particle and a cellulose surface, and, secondly, by a practical test using the IgepalCA520/hexane/water system as a pre-treatment formulation in pilot-scale CO_2 dry-cleaning experiments. With respect to the first method, atomic force microscopy seems very appropriate to study the adhesive force profile between silica and cellulose. Unfortunately, it is still not possible to perform AFM force measurements under high pressure such as needed for liquid CO_2. Hence, we decided to first explore the forces in hexane. Although there are differences, this might give some hints as to the strength and range of the forces operating in CO_2. We compare the adhesion forces between silica and cellulose in (wet) hexane in the absence and presence of the Igepal C520, and discuss these data in the context of the phase behaviour.

2. Surfactants for liquid CO_2 – state of the art

Research on surfactants for liquid CO_2 was started by trying out various commercially available surfactants. Consani and Smith [3] tried 130 commercially available surfactants and found that none of them was promising to be employed as a cleaning aid in liquid CO_2. In general, overcoming the surfactant tail–tail attraction in liquid CO_2 was one of the main challenges. To achieve solubility of surfactants in liquid or supercritical CO_2 design of novel molecules gained momentum. In synthesizing novel surfactants two approaches were taken: introduction of fluorine in the apolar tail of the surfactant replacing hydrogen [4–6] and introduction of hydrocarbon branching in the apolar tail [7]. The incorporation of fluorine in the tail was motivated by fluorine and CO_2 having similar cohesive energy densities [4]. However, fluorination did not solve the problem for CO_2 dry-cleaning, firstly because one has to increase the pressure above 150 bar to solubilize these surfactants [4–6] and secondly because the fluorinated surfactants themselves are not environmentally friendly. The second route, i.e., methyl branching of the tail tip was motivated by the prediction (using "fractional free volume" (FFV) theory [7]) that such branching leads to low density structures which should dissolve more easily in liquid CO_2. Ryoo et al. used a surfactant called polyoxyethylene 2,6,8-trimethyl-4-nonyl ether (Tergitol TMN) having methyl branching at 2, 6 and 8 positions of the apolar tail, and compared its solubility with a surfactant having a linear alkane chain as the tail [7]. The surfactant showed a cloud point at ∼100 bar, which is quite good but still higher than the pressure employed by the dry-cleaning industry [7].

Thus, the search for suitable surfactants to enhance particle release in CO_2 dry-cleaning is still going on. In Section 3 we will describe a novel surfactant formulation based on a commercially available surfactant, and explain step by step the rationale of the design.

3. Rationale of the design of the surfactant formulation

Our target properties in designing a surfactant formulation for liquid CO_2 were (i) a strong adsorption or wetting by the surfactant at the fabric–soil interface, (ii) enhancement of liquid CO_2 viscosity, (iii) deployment of a water pool to improve the removal of polar soils and (iv) improvement of solvency power of liquid CO_2 by n-alkanes. We hypothesized that a lyotropic lamellar liquid crystalline phase of a surfactant should have a good adsorption/wetting capability at the fabric–soil interface: due to its flat structure (packing parameter ≈ 1) it has a strong tendency to adsorb in multilayers [8]. Based on the idea of branching to enhance solubility in liquid CO_2, supported by FFV theory, we looked for a surfactant with branched tail, with a molecular weight restricted to ∼400–500 g mol^{-1}. A higher molecular weight would result in low or no solubility in liquid CO_2. Thus, a non-ionic surfactant, polyoxyethylene (5) iso-octylphenyl ether ($M_w = 427$ g mol^{-1}, Fig. 1), which is commercially available under the name Igepal CA520, was selected.

The second idea was to use n-hexane as a solvent in the surfactant formulation. The use of short chain alkanes such as heptane as a co-solvent (30%, v/v) in CO_2 to improve the "solvent quality" had already been reported by Hollamby et al. [9,10]. They showed by SANS measurements that it is possible to use a CO_2-heptane blend to drive the self-assembly of AOT in the solvent mixture when CO_2 is in the supercritical state. The dependence of the aggregation behaviour on solvent quality for surfactants such as AOT and $C_{12}EO_5$ has been rationalized by the Snyder polarity parameter, dielectric constant and Hildebrand solubility parameter [9,10]. In our formulation, n-hexane was chosen since its dielectric constant is close to that of liquid CO_2 (1.5 at 60 bar and 10 °C) [11], so that it is likely to be miscible with that liquid.