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Biopolymer scleroglucan as an emulsion stabilizer

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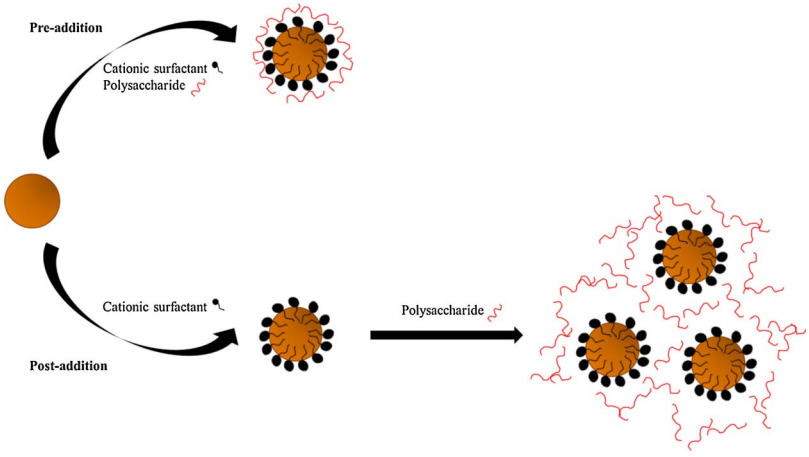
GRAPHICAL ABSTRACT



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ABSTRACT

In this study, we investigated the Stabilization of bitumen emulsions by scleroglucan, a rigid triple-helix forming biopolymer, in combination with a pH-sensitive cationic surfactant. Various aspects of the emulsification process and the final composition influence the Stabilization. We examined two different methods to add scleroglucan to the emulsion: either by adding it to the aqueous surfactant solution before emulsification, denoted 'pre-emulsification addition' (pre-EA), or by addition to the emulsion after emulsification (post-EA). We investigated scleroglucan concentrations in the aqueous phase ranging between 0.017 and 0.07 w/w%. The emulsions were evaluated according to the European EN 13808 standard used for cationic bituminous emulsions, as well as by rheological analysis. We observed an improvement of the storage stability upon pre-EA at a biopolymer concentration as low as 0.017 w/w% in combination with an increased particle size, whereas the breaking index (characterising breaking of the emulsion in presence of 'aggregates' = stones) was not influenced. The rheological data show a minor viscosity increase by scleroglucan in the pre-EA formulation at low scleroglucan concentrations (0.017–0.05 wt.%) where Stabilization already improved dramatically. This indicates that the stabilization mechanism is not only governed by a viscosity increase but also by interfacial stabilisation effects were polymer is adsorbed onto the adsorbed surfactant. In a separate experiment we changed the conformation of scleroglucan by subjecting it to extreme pH values and by dissolution in DMSO, in order to study the role of the triple helix conformation in the stabilization mechanism. Scleroglucan becomes less effective in a denatured and

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hydrolysed state confirming the crucial role of the triple helix conformation in the Stabilization of bitumen emulsions.

1. Introduction

Bitumen is a residue obtained from crude oil through a distillation process and consists of four groups of components, i.e. asphaltene, saturates, aromatics and resins. Thus, forming a complex mixture of hydrocarbons with some traces of sulphur, nitrogen, and oxygen, as well as metals like vanadium and nickel [1]. The composition depends on the crude oil source and distillation process. Therefore, the properties of bitumen can strongly vary such as viscosity at 60 °C which can vary between 50 and 930 Pa s [1]. At this temperature bitumen behave as viscous liquid and viscosity is almost constant with shear rate. According to Rodriguez-Valverde et al. [2] the charge of bitumen depends on the pH of the medium. In an acidic environment, the polar asphaltene fraction becomes positively charged. In a more basic environment it may be charged negatively. Bitumen can be emulsified into O/W (Oil-in-Water) type emulsions and used for pavement constructions. Bitumen emulsions have many environmental benefits such as the elimination of emissions associated with heating and solvents [3]. These emulsions can be cationic, anionic or non-ionic depending on the chosen emulsifier. They are usually designed as cationic emulsions in the pavement industry where the surface of the bitumen droplets is coated with a positively charged emulsifier giving the droplet a positive surface charge. This positively charged surface will provide good adhesion with the negatively charged gravel/aggregates used during pavement [1,3,4]{Cotiuga, 2010 #153}. The storage stability of such emulsions is crucial, since we aim to obtain a long shelf life and good processability. However, it is also required that the emulsion sets instantly on the aggregates during paving. These conflicting requirements represent a challenge for bitumen emulsion formulations. Furthermore, the storage stability of these emulsions depends strongly on the viscosity of the used bitumen. The higher the bitumen viscosity, thus a lower penetration grade and a higher density, the more difficult it becomes to achieve complete emulsification resulting in a less stable emulsion. This makes it difficult to emulsify high viscous types of bitumen into stable emulsions even with a higher emulsifier content [1,3].

When considering the storage stability of emulsions, it is important to distinguish between thermodynamic stability and kinetic stability [5,6]. All cationic bitumen emulsions are thermodynamically unstable and it is the rate by which several destabilization processes occur (sedimentation, coalescence, flocculation, aggregation, etc.) that determine the lifetime of an emulsion [6].

Lack of stability of bitumen emulsions can lead to the formation of solid sediment causing severe problems in storage tanks, spray trucks, pipes, pumps, etc. In particular this is the case with emulsions produced from high-density bitumen. Improved lifetime of cationic bitumen emulsions can be obtained by increasing the emulsifier content, which will induce smaller droplets [7]. Although this improves the storage stability, it is likely to have an adverse effect on the setting[1] properties of such emulsions, because the concentration of free surfactant after emulsification is likely to be higher, unless more intense emulsification is applied. An increase of stability is also achieved by adding solvent to the bitumen phase. The density difference between the bitumen and water phase decreases by adding solvent. However, this is not attractive from an environmental point of view, as the solvent needs to evaporate. According to Firoozifar et al. [8] lowering the pH to 1.5 also gives rise to a more stable emulsion. This way of increasing the stability is not preferred from a practical point of view as it is considered too acidic. Another possibility is to use high-molecular-weight water-soluble polymers as rheology modifier [9,10]. However, the increase of viscosity will negatively affect the processability of the emulsions, e.g. spraying, pumping, etc. Thus, to improve emulsion properties without affecting its setting behaviour and processability, we looked into biopolymers that tend to adsorb onto the cationic surface of the droplet and thus will not affect the viscosity of the emulsion. Lommerts et al. [11] found that the polysaccharide scleroglucan improves the storage stability of cationic bitumen emulsions without affecting its proccesability.

Polysaccharides are frequently used to stabilize O/W emulsion through various mechanisms: 1) Increasing the viscosity and slowing down the movement of the droplets, including sedimentation [9,10] 2) adsorption onto the oil droplets creating steric hindrance, thus preventing aggregation and coalescence [10,12], and 3) The formation of a three-dimensional network (a gel) creating a sufficient yield stress which prevents sedimentation. When the polymer solution comes in contact with a surface, like that of bitumen particles, polymers may or may not adsorb. For a polymer chain to adsorb, it needs a gain in adsorption energy that compensates for the loss in conformational and translational entropy. Rigid polymers possess less conformational entropy, and thus adsorb much more easily than flexible polymers [13].

Previous studies have shown that a certain polysaccharide of the class 1,3-β-glucans work as a bitumen emulsion stabilizer as it is chemically and physically stable at temperatures up to 50 °C and pH values as low as ~2 (the typical conditions used to produce cationic bitumen emulsions). As observed by Lommerts et al. [11], a significant improvement of the storage stability of a cationic bitumen emulsion occurs when this polysaccharide is added at very low concentrations to the soap phase before emulsification. This biopolymer, known as scleroglucan, is a neutral polysaccharide produced by the fungus *Sclerotium rolfsii* by an aerobic fermentation process [14,15]. Scleroglucan is a branched neutral homopolysaccharide consisting of a (1 → 3)-linked β-D-glucan linear main chain with (1 → 6)-linked β-D-glucopyranosyl groups attached to every third residue along the main chain [14,16,17]. Scleroglucan is produced by the fungus, in the form of linear rod-like triple helices held together by intermolecular hydrogen bonds [18,19]. Hydrogen bonding induced by water molecules are formed between main chain/side chain and side chain/side chain as presented by Okobira et al. [19] The driving forces for the high stability of the triple helix are: 1), a dense hydrogen-bonding network at its center. 2), inter-chain hydrogen bonds between main-chain and lateral glucose residues, 3) when dispersed in water, H-bonds between the main chains and the water molecules as well as side/main chains H-bonds or side chain / side chain H-bonding via water molecules [18–20]. The chemical composition of the scleroglucan backbone, the main chain/side chain and the side chain/side chain hydrogen bonding are presented in Fig. 1a) and b). Fig. 1c) is a simplified artistic impression of scleroglucan without side chains.

The triple-helix is very stiff, with a persistence length of approximately 150 nm at room temperature [17,20,21], making it a good candidate to adsorb onto surfaces. Due to the fact that the adsorption on a surface of a stiff polymer chain hardly influences the chain entropy.

In the present study, we investigate the stabilization ability of Scleroglucan in a 40/60 pen-grade bitumen emulsion and the factors that may influence such systems, and we formulate a hypothesis for the underlying stabilization mechanism.

[1] Setting is the breaking process of sprayed cationic bitumen emulsion on the aggregates used during pavement.