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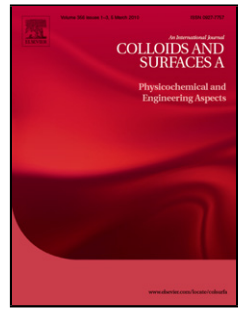


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# Hydrophobically Modified Dextrans as Stabilizers for O/W Highly Concentrated Emulsions. Comparison with Commercial Non-Ionic Polymeric Stabilizers.

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**Abstract**

Two amphiphilic polysaccharides derived from a nonionic bacterial polyssacharide of dextran ($DexP_{10}$ and $DexP_{15}$) have been explored as emulsifiers for preparing highly concentrated oil-in-water emulsions in a semibatch (two-step) process. A fixed amount of stabilizer (10 g/L of emulsion) was employed for preparing emulsions at dispersed-phase volumetric fractions ranging from 0.850 to 0.938. Their performances as stabilizers (interfacial tension, kinetics, droplet size distribution, rheological behavior and stability) were evaluated and compared with a group of four ABA non-ionic commercial stabilizers from Pluronic series (F68, F127, P105 and L64) and a low-molecular-weight surfactant (Tween 80). Our results demonstrate these $AB_n$ graft amphiphilic polysaccharides can be promising stabilizers as efficient as commercial non-ionic polymeric stabilizers for preparing highly concentrated emulsions in spite of lower interfacial tensions, slower kinetics, or showing emulsions a larger droplet size and less monodispersity.

*Keywords:* Non-ionic polymeric stabilizer, Highly concentrated emulsion, Emulsion rheology, Long-term stability

## 1. Introduction

Highly concentrated or High-internal-phase-ratio (H.I.P.R.) emulsions [22], also called gel-emulsions [35] or hydrocarbon gels [41], have many interesting applications within agrochemicals, pharmaceuticals, and personal care products. These emulsions have an extremely high content of dispersed phase volume fraction ($\phi$). When $\phi$ is larger than the maximum packing volume fraction ($\phi$*) of about 0.74 (most compact arrangement of mono-disperse hard spheres [36], reached for a face-centered cubic packing), the drops are no longer present as spheres but are distorted into polyhedral shape. This structure gives rise to a number of peculiar and fascinating properties including high viscosities and viscoelastic rheological behavior [37].

The stability is one of the most important factor to consider in emulsions. An emulsion is stable when there is no change on the droplet size distribution or the spatial arrangement of droplets over the experimental time scale [17]. Currently, there is an increasing tendency to substitute molecular surfactants by macromolecular stabilizers to formulate emulsions because high molecular weight polymeric stabilizers have the advantage that their adsorption onto the droplet surface is much firmer than with low-molecular-weight surfactants. This occurs because polymeric surfactants attach to the droplet surface via several segments. Furthermore, they provide a thick steric barrier against flocculation and coalescence at the droplet surface, and consequently, they can be used in low concentrations and much more efficiently [28]. The most effective stabilization of oil-in-water (o/w) emulsions is generally obtained using ABA block or $AB_n$ graft polymeric stabilizers [50].

Many polysaccharides are amphiphilic polymers that have extended flexible structures [13]. They are particularly attractive because of their good water-solubility, low toxicity and low interaction with living organisms. Some examples of $AB_n$ graft stabilizers can be prepared by chemical modification of dextran [43]. By changing the conditions of the reaction [44], the number of the hydrophobic groups grafted onto the neutral polysaccharide chains can be controlled, giving rise to different amphiphilic dextrans of $AB_n$ graft type, capable for emulsion stabilization. It has already been shown in the literature that amphiphilic polysaccharides can exhibit surface-active properties and to be efficient oil-in-water emulsion stabilizers for oil volume fractions up to 50 %. Nevertheless, to the best of our knowledge, there are no published studies about their use in highly concentrated emulsions ($\phi \geq 0.74$).

This paper has two purposes. On one hand, we want to shine new light on the use of these amphiphilic polysaccharide-based stabilizers for preparing highly concentrated o/w emulsions. On the other hand, we compare their performances as emulsifiers with polymeric stabilizers, and low-molecular-weight surfactants. By using a fixed mass amount of stabilizer (10 g/L of emulsion), and a two step semi-batch process, the effect of $\phi$ on droplet size distributions and storage moduli of the emulsions was examined. The stability of emulsions produced was also evaluated. Stabilizer concentrations were generally higher than critical concentrations determined by tensiometry and critical micelle concentrations reported on literature. This range is still largely unexplored in the literature, however is quite relevant for industrial applications [33].

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