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Phenoxy-substituted dextrans as emulsifying agent: role of the substitution ratio on O/W emulsion stability and interfacial activity

Pascal Imbert, Véronique M. Sadtler*, Edith Dellacherie

Laboratoire de Chimie Physique Macromoléculaire, UMR CNRS-INPL 7568, Groupe ENSIC, 1 rue Grandville, BP 451, 54001, Nancy Cedex, France

Abstract

Oil-in-water emulsions were prepared using dextran, a natural polysaccharide, hydrophobically modified with phenoxy groups. Emulsions were prepared by two different processes which were sonication and microfluidization. The average diameter of oil droplets and the stability with time of the resulting emulsions were investigated as a function of polymer concentration ($C_p=0.1 - 1\%$ w/w in water phase) and the degree of polymer grafting ($t=4.2 - 15.7\%$). The microfluidization process allowed to realize emulsions with lower initial particle size than the sonication method. For the highest degrees of grafting and for C_p values $\geq 0.2\%$ w/w, submicronic emulsions were obtained, which were stable for more than 4 months at room temperature. Interfacial measurements at the *n*-dodecane/water interface clearly showed a better efficiency of the most substituted polymers to lower the surface tension.

Keywords: Emulsions; Polymeric surfactants; Stability; Emulsification; Interfacial tension

1. Introduction

An emulsion is defined as a two phase system of two mutually non-miscible liquids, in which one phase is dispersed in the other to give microscopic or submicroscopic droplets. As the involved

phases are generally oil and water, the formed emulsions are called oil-in-water (o/w) and water-in-oil (w/o), with the bulk phase being named first [1]. Emulsions are widely used in the domains of foodstuff technology, pharmacy, agrochemistry, paints, cosmetics, coatings and adhesives [2].

Droplets do not form spontaneously. Their formation entails an expenditure of mechanical energy such as sonication or vigorous mixing to compensate for the cost of increasing the total interface area between the two liquids. Emulsions are therefore thermodynamically unstable dispersions. When two droplets approach one another,

they may coalesce in order to reduce the interface area.

Consequently, the preparation of emulsions involves the use of emulsifiers to stabilize the interface. The crucial interfacial phase must be taken into account: without, emulsions would not only be thermodynamically, but also kinetically unstable. It would therefore be right to speak of a three-phase system and not a simple two phase emulsion. The emulsifying products employed in stabilizing can be greatly varied according to the particular requirements [3].

Important factors to maintain the stability of emulsions are: (i) interfacial tension; (ii) electrostatic interaction; (iii) steric repulsion; and (iv) viscosity of the outer phase. Surfactants drastically lower the interfacial tension upon their adsorption to liquid-liquid interface and facilitate formation and stabilization of the emulsion. There are usually surfactant small molecules that prevent a rapid coalescence of the droplets by changing the forces that exert at the new liquid-liquid interface formed during emulsification process. In addition, using ionic surfactants, the emulsion is also stabilized by the electrostatic repulsion mechanism. With polymers, the ability to decrease the interfacial tension is much lower compared with that of surfactants. However, a non-ionic polymer provides a layer of particle surface upon adsorption, and, thereby, the emulsion is stabilized by a steric repulsion mechanism. These macromolecular emulsifiers are in fact stabilizers. The mainly stabilizing action of biopolymers is via viscosity modification or gelation in the aqueous continuous phase [4]. Using water-soluble polymer such as gums is an effective method to protect against coalescence by raising the viscosity of the bulk phase. In such systems, the particles have a reduced kinetic energy, so that collisions become less common and take place with a lower energy [5-9].

Polymers often have hydrophilic and hydrophobic subregions so that these amphiphilic polymers act like low-molecular-mass surfactants. However, polymeric surfactants have received little attention comparatively to small surfactant molecules. If the surface activity of block copolymer is well established and makes them useful as emulsifiers

[10,11], only few systematic studies have been reported which include graft copolymers as emulsifying agents [12-16].

For a biopolymer to be surface active, it clearly must have amphiphilic character. A hydrocolloid must contain hydrophobic groups sufficiently accessible on a short timescale to enable the adsorbing molecules to spread out at the interface. The limited emulsifying capacity of most of biopolymers can be attributed to poor solubility, or insufficient amphiphilic character to produce rapid and substantial lowering of the interfacial tension during droplet break-up.

If most of the compounds that promote stable emulsions are molecular surfactants, however, some biopolymers present surface active properties. One group of surface active polysaccharides are the hydrophobically modified cellulose derivatives, notably methyl- and hydroxypropylmethyl-cellulose [17]. Such amphiphilic biopolymers are used as emulsifiers to prepare oil-in-water emulsion, but the droplets produced are much coarser than those made with low-molecular-mass emulsifiers or proteins [18]. Similar arguments can be applied in relation to the emulsifying performance of hydrophobically modified starches and polypropylene glycol alginate. Furthermore, in most cases, the reported surface activity and emulsifying capability of some carbohydrates polymers is attributed mainly to the role of proteins, present either as contaminants [19].

The surface active properties of hydrophobized polysaccharides such as dextran have been studied mainly with regard to the coating of polystyrene particles to provide chromatographic matrices for biomolecule chromatography [20]. Furthermore, the preparation of biocompatible poly(lactic acid) nanospheres by an o/w emulsion evaporation technique using dextran modified with phenoxy group (DexP) as the emulsion stabilizer, was an indication of the emulsifying properties of these amphiphilic polymers [21]. If dextran native do not present surface active properties, there is no value on the surface activity at a liquid-liquid interface of hydrophobized dextran.

The aim of this work was to realize a systematic study on the preparation and stabilization with time of oil-in-water emulsions using phenoxy-

substituted dextrans (DexP) as unique emulsifying agent, and to determine their tensio-active power by interfacial tension measurements at the oil/water interface. Various hydrophobically-modified dextrans were tested in order to evaluate the influence of the substitution ratio on the emulsifying ability. The polymer concentration effect was also studied as well as some emulsification process parameters.

2. Experimental section

2.1. Materials

The phenoxy derivatives of dextran (DexP, Fig. 1) were prepared from dextran T40 ($M_n=28\,500\text{ g mol}^{-1}$ and $M_w=42\,800\text{ g mol}^{-1}$ as given by the supplier) obtained from Pharmacia (Uppsala, Sweden). The fixation of phenoxy groups on the dextran backbone was performed as previously described [21]. The phenoxy content of the polymers was determined by UV spectroscopy at 269 nm. The degree of substitution t (%) was the number of phenoxy groups per 100 glucose units.

The oil phase was n -dodecane, purchased from Sigma and used as received. The water was double-distilled deionized with a Milli-Q system (Millipore).

2.2. Methods

2.2.1. Preparation of emulsions and droplet size measurements

Polymer solution samples were prepared by dissolving the appropriate amount of polymer in purified water (Cp weight/weight of water %);

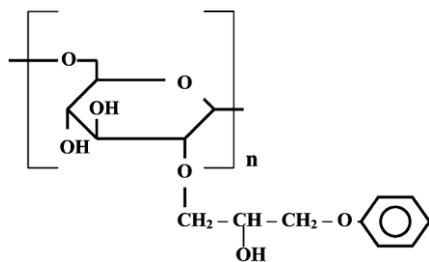


Fig. 1. Schematic structure of phenoxy-dextran.

these solutions were equilibrated for 24 h at room temperature.

Emulsification by sonication was achieved using a sonifier (Sonifier 600 W, Sonic Materials Inc., USA), fitted with a 3 mm titanium probe. 0.1 ml of n -dodecane was added to 4.9 ml of aqueous polymer phase prior to a one-step emulsification process. The two phases were submitted to sonication (1 min, 50% pulse time, 120 W, at ambient temperature). These parameters were optimized in order to obtain emulsions with low particle sizes and narrow size distribution: monodisperse distribution with a span B1.5; span is the measurement of the width of the distribution calculated as $[d(0.9)-d(0.1)]/d(0.5)$, where $d(0.5)$ is the median diameter, $d(0.9)$ and $d(0.1)$ are the sizes of particle below which 90 and 10% of the sample, respectively lies.

In the case of the microfluidization process, a pre-emulsion (2 ml of n -dodecane, 18 ml of aqueous polymer solution) was prepared using an Ultra-Turrax⁺ mixer (model T25, Ika-Labortechnik) for 1 min, 22 000 rpm at room temperature. The resulting pre-emulsion was introduced in the microfluidizer reservoir (Microfluidizer⁺ M110L, Microfluidics Int. Corp., USA), and then driven to the interaction chamber. The number of passes through the interaction chamber and the pressure applied were controlled (1 -20 passes, and 2 -4 bar, respectively).

The average particle size of emulsions was determined by laser granulometric measurement (Mastersizer 2000, Malvern Instr. S.A., USA) just after preparation. Then, the emulsions were stored at ambient temperature and their stability was assessed by measuring the droplet size as a function of time. Error on the size measurement was in the 5% range.

2.2.2. Interfacial tension measurements

Surface tension measurements were carried out by the ring method (Lecomte de Nouÿ) with a K9 tensiometer (Kruÿss, Germany). Water and oil phases were the components used for emulsion preparation. The oil/polymer aqueous solution system was equilibrated for 24 h (time required for getting constant values of the surface tension) at ambient temperature. The Harkins-Jordan

correction was applied [22]. Surface tension of the purified water, at 20 8C, was 71.8 mN m⁻¹. Experimental errors were in the 0.2 mN m⁻¹ range.

2.2.3. Rheological characterization

Flow properties of the polymer in purified water, were investigated, after equilibration (24 h), with a Couette rheometer (RFS II, Rheometric Scientific, USA) at 25 8C. Viscosity was determined in a range of shear rate from 0.1 to 100 s⁻¹.

3. Results

3.1. Effect of polymer concentration C_p and polymer phenoxy ratio t on the initial particle size

The initial particle size of the emulsions was measured as a function of the polymer concentration at various degrees of grafting (t) of the phenoxy dextrans (DexP). Monodisperse distributions were always obtained, with a span range between 0.4 and 0.5. Fig. 2 shows the variation of the average droplet size of the emulsion prepared by the sonication process. For each of the three t values, there was a decrease in the initial particle diameter by increasing the polymer concentration. For instance, the polysaccharide with $t=4.2$ (DexP-4.2) presented an average particle size of 785 nm for a polymer concentration of 0.2% w/w; the initial diameter was 712 nm at $C_p=1\%$ w/w.

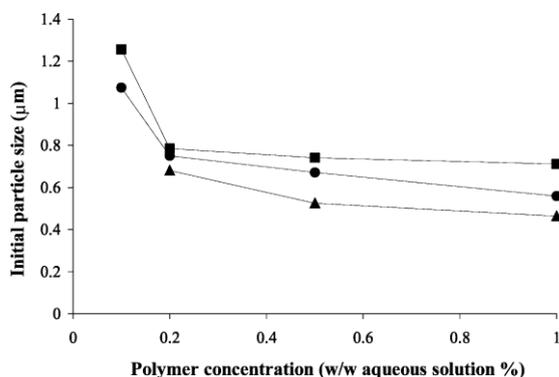


Fig. 2. Initial average particle size of emulsions as a function of polymer concentration at various phenoxy polymer substitution rates: (■) DexP-4.2; (●) DexP-9.8; (▼) DexP-15.7.

In the case of the polymer with $t=15.7\%$ (DexP-15.7), the particle sizes were 845 and 465 nm at $C_p=0.2$ and 1% w/w, respectively.

Regarding the grafting ratio effect, for all the investigated polymer concentrations, the higher was t , the lower was the initial droplet diameter of emulsions. For example, at a concentration of 0.5% w/w, the particle sizes were 742 nm for DexP-4.2 and 525 nm for DexP-15.7. An intermediate behaviour was observed for DexP-9.8, with a droplet diameter at 650 nm.

Furthermore, for polymer concentrations $\leq 0.2\%$, the higher the t value, the stronger the decrease in the particle size when C_p increased. For instance, when the polymer concentration increased from 0.2 to 1%, there was a *ca* 9 and 32% size lowering for DexP-4.2 and DexP-15.7, respectively.

Fig. 3 presents the initial particle size of emulsions obtained by the microfluidization method. Emulsions with lower particle sizes were obtained by using this second process than by using sonication. Furthermore the widths of the size distribution were always lower with microfluidization. An emulsion prepared with DexP-4.2, at $C_p=0.5\%$, presented an initial particle size of 462 nm only after one pass through the interaction chambers at a pressure of 2 bar; using sonication with the same emulsion parameters, the smallest diameter was 762 nm. The droplet size was still lowered after 10

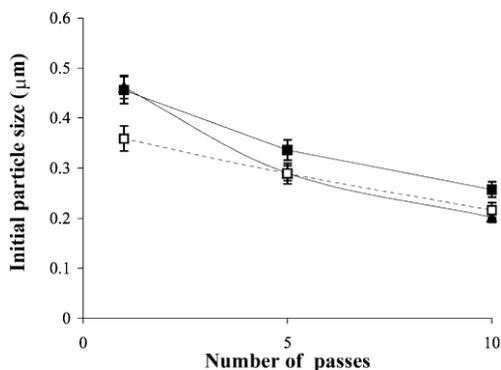


Fig. 3. Initial average particle size of emulsions as a function of number of passes through the interaction chambers of microfluidizer[†] at polymer concentration of 0.5% w/w, and various pressures: (■) DexP-4.2 at 2 bar; (□) DexP-4.2 at 4 bar; (▼) DexP-15.7 at 2 bar.

passes (202 nm, span=1.2). Increasing the number of passes (n) through the interaction chambers (up to 20 passes) did not lead to further reduction of the droplet size.

As in the sonication process, the higher the t value, the lower the initial droplet size. After five passes, the emulsions prepared at polymer concentration of 0.5% w/w, had an average particle size of 360 and 290 nm for $t=4.2$ and 15.7%, respectively. As shown in Fig. 3, it was possible to reduce the particle sizes of emulsions prepared using dextran with low degree of grafting, by increasing the applied pressure. For instance, for $n \geq 5$, similar initial particle sizes were obtained for emulsions prepared with DexP-4.2 and DexP-15.7 by using a pressure of 4 bar instead of 2 bar. For all tested formulations (various C_p and t), it was not possible to obtain emulsion droplets with an initial diameter smaller than *ca* 200 nm.

3.2. Ageing of emulsions

The changes of the emulsion droplet size were investigated at regular time to assess the emulsion stability. We could notice that in spite of the absence of preservers, no bacterial degradation occurred. Fig. 4 shows the variation of the average diameter as a function of time for emulsions prepared by sonication with DexP-4.2 or DexP-15.7, at various polymer concentrations (0.2, 0.5 and 1% w/w). For each formulation, it was

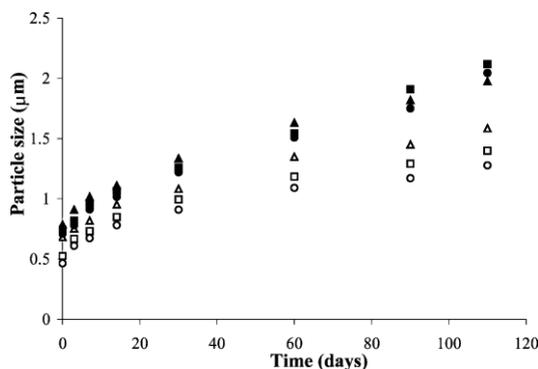


Fig. 4. Average particle size of emulsions prepared with: (■) DexP-4.2 at 0.2% w/w; (▼) DexP-4.2 at 0.5% w/w; (▲) DexP-4.2 at 1% w/w; (●) DexP-15.7 at 0.2% w/w; (◆) DexP-15.7 at 0.5% w/w; (■) DexP-15.7 at 1% w/w, as a function of time.

observed that the particle size grew with time, but the initial size order due to the different t was maintained; furthermore, for all these emulsions, the width of the size distribution decreased with time. For example, at $C_p=0.5\%$ w/w, the emulsion stabilized with the DexP-4.2 presented an average diameter of 1.26 μm (span=1.3) after 30 days, and 1.55 μm (span=1) after 60 days (initial size=742 nm, span=1.5). The emulsion prepared with DexP-15.7 had an average particle size of 0.9 ($\text{span}=1.1$) and 1.19 μm ($\text{span}=0.9$) after 30 and 60 days, respectively (initial size=525 nm, $\text{span}=1.4$).

It can be noted that the influence of the polymer concentration on the particle size growth with time was less important in the case of DexP-4.2 than with DexP-15.7. This result agrees with the remark reported above about the initial droplet size: the higher the t value, the higher the decrease in the particle size with C_p increase. Regarding $C_p=0.2\%$ w/w and 1% w/w, after 110 days, the difference between the droplet sizes for emulsions prepared with DexP-4.2 was *ca* 60 nm, i.e. less than the error range. In the case of DexP-15.7, the gap was *ca* 300 nm. Furthermore, a general slowdown of the size growing after the 2nd month of ageing was observed in the case of DexP-15.7 for all the studied concentrations.

The ageing of some emulsions prepared by the microfluidization process was also studied. As shown in Fig. 5, there was a significant difference of the emulsion behaviour as a function of t . The

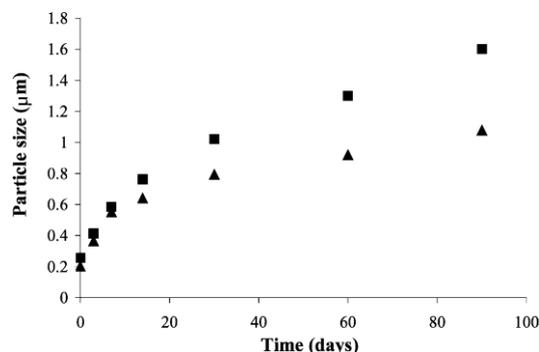


Fig. 5. Average particle size of emulsion prepared by microfluidization with: (■) DexP-4.2; (▼) DexP-15.7, as a function of time. $C_p=0.5\%$ w/w.

size gap between the droplets of emulsions prepared with DexP-4.2 and DexP-15.7 was 60 nm after preparation; 2 months later, this gap was 380 nm.

3.3. Interfacial activity of the hydrophobized polymers

The interfacial tension measurements showed that the highly substituted DexP sample (DexP-15.7) was able to clearly reduce the interface tension between the oil and the water phases (Fig. 6). Thus, while the interface tension between water and *n*-dodecane was 48.8 mN m⁻¹, this parameter was lowered to 17.1 mN m⁻¹ for a Cp of 0.25 g l⁻¹. At polymer concentrations over 0.25 g l⁻¹, the interfacial tension remained constant, which suggested that the interface was saturated.

In the case of DexP-4.2, the interface tension was reduced only to *ca* 32 mN m⁻¹ even for concentrations higher than 1 g l⁻¹. Hence, in the range of our study, the higher the t value, the higher the surfactive efficiency of DexP.

3.4. Rheological behaviour of DexP

The aqueous solutions of DexP at Cp=1% w/w presented a Newtonian viscosity in a wide range of shear rates. The viscosity value was 1.15 × 10⁻³ Pa s (90.05 × 10⁻³ Pa s) for DexP-4.2 and 1.3 × 10⁻³ Pa s (90.14 × 10⁻³ Pa s) for DexP-15.7. If

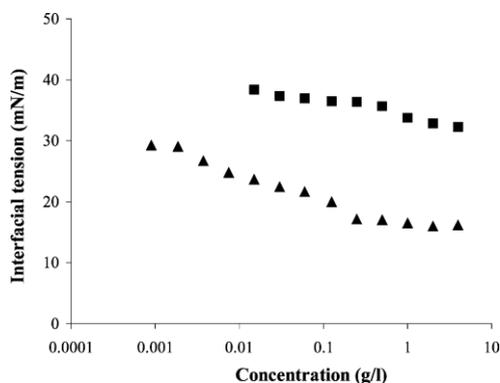


Fig. 6. Variation of the interfacial tension at the *n*-dodecane/water interface as a function of polymer concentration for: (■) DexP-4.2; (▼) DexP-15.7.

the DexP-15.7 solution presented a slightly higher viscosity value than the DexP-4.2 one, however the DexP samples, in the studied t range and at a higher concentration than that used for the emulsion preparation, have very low viscosifying properties.

4. Discussion

The above series of dextrans with moderate hydrophobicity allowed to prepare oil-in-water emulsions, which were quite stable in time as no oil separation occurred. No stable emulsion could be obtained using native dextran as unique emulsifier agent. With the microfluidization process, it was possible to obtain thinner emulsions than with sonication. This can be explained by a higher supplied energy and a better process control.

As in the case of molecular emulsifier, increasing the amphiphilic polymer concentration contributed to reducing the initial particle size of the emulsions. This phenomenon was particularly significant with highly phenoxy-substituted dextran (DexP-15.7 compared to DexP-4.2). Regarding the ageing of emulsions, a more important effect of the polymer concentration in the emulsion stabilization was also observed with highly substituted dextran. A slowdown of the droplet growth seemed to appear from the 3rd month of storage for emulsions prepared with DexP-15.7 for each studied concentration.

A significant decrease in the interfacial tension was observed at the *n*-dodecane/water interface with DexP-15.7 solutions, which strongly suggests that the polymer is located at the interface and acted as a surface active agent. In general, surfactants reduce surface and interfacial tension. Considering the ability of the DexP samples to stabilize emulsions as a function of Cp, and their interfacial activities, they can be regarded as polymeric surfactants and not only as amphiphilic polymers. It is thus possible to examine these polymers from a surfactant point of view, even if steric stabilization could exist due to their macromolecular structure.

At constant Cp, the interfacial tension of the oil/water system was higher with DexP-4.2 than with

DexP-15.7. This can explain the difference of behaviour observed in the emulsion stabilization. In fact it can be supposed that it was possible to create an enhanced Marangoni effect for the systems containing highly hydrophobized polymeric surfactant. An enhanced Marangoni effect could prevent coalescence during emulsification [15].

The higher increase in the particle size with time observed for a given value of t , when C_p decreases, can be explained by the following phenomenon: the polymeric surfactant cannot fully cover the interface at low C_p , thus producing some 'bare' patches responsible for droplet coalescence. This poor stabilization well corresponds to the high interfacial tension measured for the polymer concentration B0.1%.

For each t values, for $C_p > 0.1\%$, the interfacial tension between water and n -dodecane remains constant. So the reasons why the emulsion droplet size decreases when C_p increases is not clear. On the other hand, in spite of its poor tensio-active power, DexP-4.2 allowed the preparation of o/w emulsions even if the globule size was important. At the used concentrations, no viscosifying effect on the dispersed phase could be expected. There was no gelation of the water phase that could have an effect on the macroemulsion stabilization. It clearly appear that DexP can act as molecular surfactant with regard to the surface active property, with polymeric structure that offer steric stabilization, particularly with respect to coalescence prevention. In fact, the mechanisms of emulsion stabilization are various and complex particularly when the used surfactants are amphiphilic polymers. The study of the other parameters of formulation (nature of oil, phase ratio ..) should allow to clarify the ageing mechanisms of these emulsions.

5. Conclusion

In this paper, we have presented the preparation of oil-in-water emulsions using, as unique emulsifier compound, DexP of moderate hydrophobicity. These emulsions were relatively stable with time since no phase separation occurred for a period of

at least 4 months. The emulsification processes had an impact on the initial particle size: microfluidization, for a given formulation, allowed to prepare emulsions with smaller particle size than sonication did. We showed the important effect of the polymer concentration and the effect of the dextran phenoxy content (t) on the emulsion characteristics. The increase in polymer concentration (C_p), especially at high t , induced a notable decrease in the initial droplet diameter. The results obtained in the determination of the DexP surface properties were in agreement with those of emulsion stability, since in both cases it was observed that interfacial tension decreased by increasing C_p , particularly for DexP-15.7. Hence, it can be supposed that the emulsion stabilization is first based on a lowering of interfacial tension.

But, even if no phase separation appeared after more than 120 days, emulsions always presented a significant particle growth. One key to improve the stability of emulsions prepared with DexP will be to determine the main mechanism governing it. Further works have been carried out in this way, and the results will be presented in a forthcoming paper.

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