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ORIGINAL CONTRIBUTION

Viscosity of dilute colloidal dispersions involving polysaccharide-based stabilizers

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Abstract The viscosity of oil-in-water emulsions stabilized by amphiphilic derivatives of dextran (a neutral bacterial polysaccharide) was studied. The oil volume fraction was kept lower than 20% and the mean droplet diameter remained between 200 and 300 nm. The effects of temperature and oil volume fraction on emulsion viscosity were examined using a capillary viscometer. Andrade equation was shown to conveniently account for the variation of viscosity with temperature. Semiempirical equations were derived for the variation of activation energy with oil volume fraction. The established equations were extended to other emulsions using literature data.

Keywords Miniemulsion · Dextran · Polymeric surfactant · Viscosity · Temperature

Introduction

Polymeric surfactants derived from polysaccharides are receiving increasing attention [1–6]. The attachment of hydrocarbon tails onto various polysaccharide backbones has been well-documented since the pioneering work of Landoll [7].

Initially, polymeric surfactants were studied mainly as rheology modifiers. Their ability to significantly increase the viscosity of aqueous phases, as well as the viscoelastic properties they brought to aqueous formulations, appeared valuable in several applications. More recently, their interfacial properties were considered with more interest, especially for the preparation of colloidal suspensions containing particles with well-defined surface characteristics [8–10]. Many aspects of their adsorption at liquid–liquid interfaces are key points in practical situations. The presence of multiple hydrophobic groups along polymer chains lead to a quasi-irreversible adsorption [11, 12]. A direct consequence is the stability of emulsions upon dilution. Additionally, the presence of hydrophilic coils covering oil droplet surfaces brings about steric repulsions. These repulsions prevent droplet coalescence, as well as the adsorption of other macromolecules (like proteins, for instance). In the case of polyelectrolytes, electrostatic repulsions also contribute to droplet stability.

Polysaccharide-stabilized oil-in-water emulsions can serve as intermediates in the preparation of polysaccharide-covered nanoparticles, which find application as potential drug delivery systems. Several processes are concerned, like emulsion–solvent evaporation or miniemulsion polymerization [8, 13]. The control of the properties of the final nanoparticles (size, surface coverage) is achieved by a precise knowledge of several parameters like the viscosity of the continuous phase (an aqueous solution of amphiphilic polymer) and the physical properties of the initial emulsions (size variation with time, stability with temperature, ageing processes, viscosity…). These parameters are essential to design the elaboration process.

In that work, we want to analyze the viscosity behavior of polysaccharide-stabilized oil-in-water emulsions with oil volume fractions lower than 20%. Polysaccharide surfactants

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are derivatives of dextran, a neutral bacterial polysaccharide [14]. In addition, the effect of temperature on viscosity will be particularly considered since it is relevant in many processes of particle preparation (like miniemulsion polymerization). We will try to derive semiempirical equations, which account for the observed results. The obtained relations will be generalized to other colloidal systems on the basis of literature data.

Experimental

Materials

The native dextran sample, T40®, was obtained from Pharmacia (Uppsala, Sweden). It has been characterized by size exclusion chromatography: $\overline{M}_{\mathrm{n}} = 26,000\mathrm{g/mol}$, $\overline{M}_{\mathrm{w}} = 40,000\mathrm{g/mol}$, and $I_{\mathrm{p}} = \overline{M}_{\mathrm{w}}/\overline{M}_{\mathrm{n}} = 1.6$. The other chemicals were from Aldrich (St Quentin Fallavier, France) and were used as received. MilliQ water was used for all the experiments.

Emulsion preparation

Oil-in-water emulsions were prepared by sonication (50% pulsed mode) using a Vibracell model 600W (Sonics & Materials, Danbury, CT, USA). Hexadecane was used without further purification. The volume of aqueous phase was kept equal to 10 mL for all the emulsions prepared. The polymer was previously dissolved under stirring in the aqueous phase for 20 h.

Measurement of average droplet diameters

Average droplet diameters were measured by dynamic light scattering at low concentration using a HPPS-ET from Malvern (Malvern, UK). Although this apparatus is able to measure relatively concentrated samples, emulsions were diluted. Dilution with oil-saturated water or with the initial polymer solution gave the same results as dilution with pure water. This shows that neither polymer desorption nor droplet dissolution occurs while diluting the emulsions. Consequently, pure water was used for preparing diluted samples of emulsions. The diameter obtained is an average value based on the light intensity after three consecutive measurements.

Viscometry

Viscometric measurements with oil-in-water emulsions were carried out using an Ostwald-type capillary viscometer (0.46 mm diameter). The temperature was regulated by a circulating bath. Before emulsion preparation, the aqueous solutions were filtered through 0.2-mm filters. We verified that no kinetic corrections were required (the flow time was proportional to the cinematic viscosity). The densities of emulsions were estimated by weighting known volumes. The relative viscosity of emulsions was calculated using the following relation:

$$\eta_{\mathrm{r}} = \frac{\eta}{\eta_0} = \frac{t\,\rho}{t_0\,\rho_0} \tag{1}$$

In Eq. 1, η and η_0, t and t_0, and ρ and ρ_0 are the viscosity, the flow time, and the density of emulsion and water (respectively). The same apparatus was used for measurements with aqueous solutions of polymers. The experimental procedure was similar.

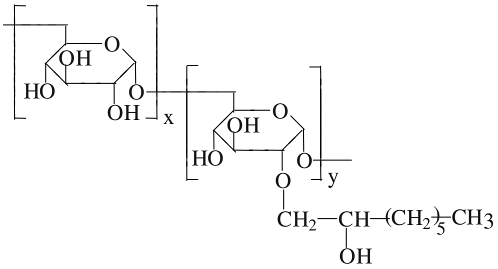
Results and discussion

Chemical structure of polymers

Amphiphilic dextran derivatives were prepared from a commercial dextran sample T40® by a chemical modification procedure, which can be found elsewhere [15]. The percentage of glucose units modified with one hydrocarbon group is called the degree of hydrophobic modification: $\tau = 100 \times y/(x+y)$ (see Scheme 1). The polymers will be named DexC6$_{\tau}$.

Oil-in-water miniemulsions stabilized by amphiphilic polysaccharides

Amphiphilic dextrans can stabilize submicronic oil-in-water emulsions (called miniemulsions) provided that the available amount of polymer in the aqueous phase and the energy input are enough. The relevant parameter for the initial average droplet size is the weight ratio of amphiphilic dextran to oil, a result similar to what is observed with molecular surfactants [16, 17]. In what follows, oil-in-water emulsions have been prepared using a polymer-to-oil weight ratio always equal to 0.05. Previous studies about the adsorption isotherms of amphiphilic dextrans onto



Scheme 1 The detailed study of the position modified by the aliphatic epoxide (among the three possible ones) has not been performed yet

dodecane droplets showed that, in these conditions, the amount of polymer remaining in the aqueous solution is less than 10% of the initial material [17].

For miniemulsions stabilized by amphiphilic dextrans, it has been demonstrated that the aging process follows Ostwald ripening mechanism. The driving force of that process is the variation of chemical potential of the oil with the size of droplets. Consequently, a spontaneous diffusion of oil from small droplets into the biggest ones takes place. Ostwald ripening can be significantly slowed down by the use of oil with extremely low water solubility like hexadecane (kinetic limitation). Hexadecane-in-water emulsions will be considered in what follows, so that aging processes can be ignored within the time necessary for emulsion preparation and viscometric measurements [8].

For all the emulsions considered in that work, the average droplet size was between 230 and 300 nm. The oil volume fraction was varied by diluting an initial emulsion with pure water. The invariance of average droplet size upon dilution was checked. This result can be justified by the well-known kinetic irreversibility of the adsorption of random amphiphilic copolymers [12]. Consistently, it has been demonstrated previously that emulsion aging is not significantly modified upon dilution by pure water [16]. For each amphiphilic dextran, two series of experiments were performed, starting with different amounts of oil and polymer (but with a weight ratio kept equal to 0.05) so as to cover a range of oil volume fractions between 0% and 20%.

The density of hexadecane-in-water emulsions was determined by weighting known volumes. A linear decrease was evidenced as a function of hexadecane volume fraction, between water and hexadecane density, with a slope equal to 226.3 kg/m^3. Assuming a perfect mixture of the two immiscible liquids leads to a theoretical value of 224.9 kg/m^3. Taking into account the experimental errors, these two values are considered to be identical.

Viscosity—oil volume fraction relationship

The variation of the viscosity of miniemulsions with oil volume fraction differs according to the structure of the amphiphilic dextran, for oil volume fractions higher than 0.15 (Fig. 1). The viscosities of the solutions containing polymers alone in water could be calculated on the basis of semiempirical equations reported previously. The comparison demonstrates that the contribution of nonadsorbed macromolecules is negligible (Fig. 1). The formation of a physical network involving both polymer-covered droplets and nonadsorbed macromolecules has been proposed in some systems [18].

For the three polymeric stabilizers, two series of experiments covering different ranges of oil volume fraction gave consistent results. The equation derived by Quemada (Eq. 2) depicts conveniently the experimental variation of relative viscosity with oil volume fraction.

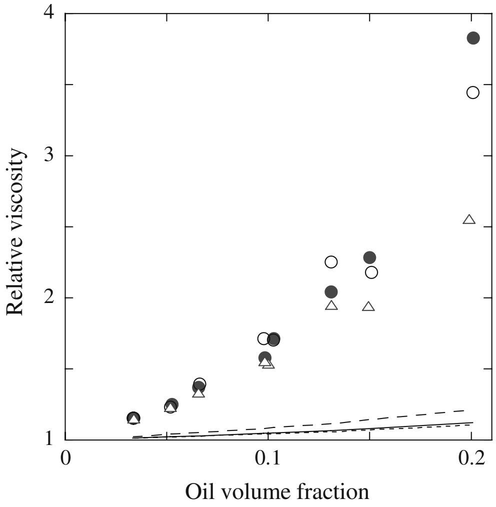


Fig. 1 Relative viscosity at 25°C of hexadecane-in-water emulsions as a function of oil volume fraction. Various amphiphilic dextran derivatives were used. *Closed circles* DexC6$_{12}$, *open circles* DexC6$_{21}$, *triangles* DexC6$_{38}$. The *lines* are the calculated values for aqueous polymer solutions

$$\eta_r = \left(1 - \frac{\phi}{\phi_{mQ}}\right)^{-2} \quad (2)$$

In Eq. 2, $\eta_r = \eta/\eta_0$ is the relative viscosity of the emulsion and φ_{mQ} is the volume fraction corresponding to maximum packing. The found values of φ_{mQ} are generally lower than 0.63 (Table 1), which is the value expected for random close packing of uniform hard spheres [19]. Nevertheless, the oil droplets of the emulsions cannot be considered as hard spheres since the presence of polysaccharide surfactants on the surface induce the existence of steric repulsions.

Table 1 Viscometric parameters for hexadecane-in-water emulsions stabilized with amphiphilic dextran derivatives

Polymeric surfactant	T (°C)	Quemada	Bedeaux		Fedors
		φ_{mQ}	S	φ_{mB}	φ_{mF}
DexC6$_{12}$	25	0.42	2.33	0.43	0.48
DexC6$_{21}$	25	0.44	2.27	0.44	0.50
DexC6$_{38}$	25	0.53	1.81	0.55	0.62
	65	0.55	1.77	0.57	0.65

Three semiempirical equations were considered (for symbols, see text).

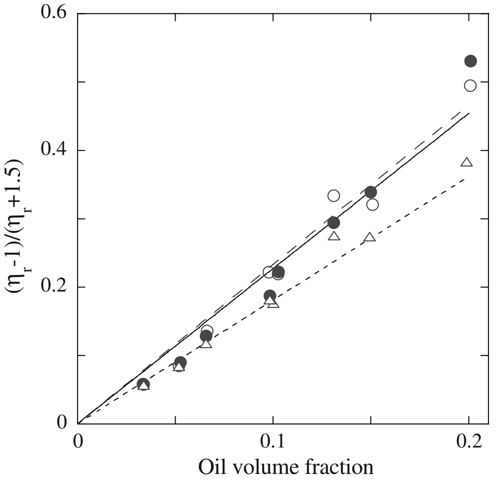


Fig. 2 Application of Bedeaux equation to the viscosity results of polysaccharide-stabilized emulsions. Symbols are identical to those of Fig. 1

Bedeaux proposed to expand an expression originally given by Saitô so as to describe the viscosity of suspensions [20, 21]. Our data are well-fitted by a simplified version of the Bedeaux equation (Eq. 3 and Fig. 2).

$$\frac{\eta_{\mathrm{r}}-1}{\eta_{\mathrm{r}}+\frac{3}{2}}=S\phi \tag{3}$$

In Eq. 3, S is a constant correcting for interactions and correlations between particles. The initial derivation of Saitô corresponds to S=1, and in the work of Bedeaux, S is a function of φ. The values found for S with our results are between 1.5 and 2.5 (Table 1). Similar values are deduced from data about inverse emulsions or microemulsions (Table 2).

Table 2 Viscometric parameters determined for water–isooctane–AOT inverse microemulsions and water-in-oil emulsions

Samples	W_0	T (°C)	Quemada	Bedeaux		Fedors
			φ_{mQ}	S	φ_{mB}	φ_{mF}
Inverse microemulsions	25	12.5	0.60	1.78	0.56	0.67
		30	0.52	2.14	0.47	0.56
	35	12	0.61	1.80	0.56	0.66
		30	0.51	2.30	0.43	0.54
Inverse emulsions		20	0.64	1.77	0.57	0.71
		50	0.67	1.64	0.61	0.74

Data were taken from [24] (inverse microemulsions) and [30] (inverse emulsions). For inverse microemulsions, W_0 is the molar ratio of water to surfactant (AOT). Three equations were considered (for symbols, see text).

It is easy to show that, according to Eq. 3, the relative viscosity is expected to tend to infinity for volume fractions approaching a critical value given by:

$$\phi_{\mathrm{mB}}=\frac{1}{S} \tag{4}$$

The found values of φ_{mB} are close to those given by Eq. 2 (Table 1).

In order to account for the relatively low values of critical volume fraction resulting from viscosity measurements, it must be recorded that the oil volume fractions are based on the amount of oil only, without any contribution of the surface layer. In the real colloidal system, the polymeric layer covering the particles contributes to their hydrodynamic volume [22]. The effective volume fraction for a sphere of radius R covered by a polymeric layer with a thickness δ is $\phi_{\text{effective}}=\phi\left(1+\frac{\delta}{R}\right)^3$ [22]. For the mini-emulsions considered in that work, the average droplet radius is around 130 nm, while the thickness of the layer of adsorbed polymer should be close to 6 nm according to previous studies [13, 23]. These values lead to effective volume fractions around 1.15 times the volume fraction based on the amount of oil.

Nevertheless, the significant influence of the chemical structure of the polymeric stabilizer indicates that other interactions between oil droplets should be considered. Other interactions between oil droplets should be taken into account in addition to hydrodynamic ones. More experiments are required to clarify that point. Smeets et al. showed that attractive interactions take place between water droplets in inverse microemulsions upon heating [24]. The corresponding values of φ_{mQ} exhibit a significant decrease in the same conditions (Table 2).

Fedors proposed an empirical equation for the viscosity of latex suspensions (Eq. 5) [25, 26].

$$\eta_{\mathrm{r}}=\left(1+\frac{1.25\phi}{\phi_{\mathrm{mF}}-\phi}\right)^2 \tag{5}$$

In Eq. 5, φ_{mF} has the same meaning as in Eq. 2. Equation 5 fits the experimental results in a fairly convenient way. The obtained values of φ_{mF} are generally higher than those deduced from Eq. 2 (Tables 1 and 2).

Finally, we can notice that, generally, φ_{m} decreases when the degree of substitution of the amphiphilic dextran is increased. Previous results showed that, for a given ratio of polymer to oil, the droplet surface coverage (in milligrams of polymer per square meter) is approximately the same for all these polymers. Nevertheless, the thickness of the adsorbed polymer layer is significantly lower for the polymer having the higher degree of substitution. This results from a flatter conformation because of the higher number of sticking points and from the aggregation of nonadsorbed hydrocarbon groups within the polymer layer [27]. This could explain why interactions between oil droplets are less important in the case of DexC6$_{38}$ than for the other two amphiphilic dextrans.

Effect of temperature on emulsion viscosity

For a given amphiphilic dextran, the relative viscosity of miniemulsions has a limited dependence on temperature in the range 25–65°C. Since it is expected that the surface of oil droplets is covered by loops of polysaccharide chains, this limited effect of temperature can be compared to that observed for native dextran solutions [28, 29].

At a given oil volume fraction, the viscosity varied with temperature (Fig. 3) in a way consistent with the Andrade equation (Eq. 6).

$$\eta = A\ e^{\frac{E_a}{RT}} \tag{6}$$

In Eq. 6, η is the viscosity (Pa s), A is a pre-exponential factor (Pa s), R is the gas constant (8.314 J/K mol), T is the thermodynamic temperature (K), and E_a is the activation energy (J/mol). Following an approach similar to that proposed previously for polymer solutions, we can derive an expression of the activation energy as a function of oil volume fraction (Eq. 7).

$$E_a = E_{a\ \mathrm{solvent}} + R\,\frac{T_1\,T_2}{T_1 - T_2}\,\ln\left(\frac{\eta_r(\phi, T_2)}{\eta_r(\phi, T_1)}\right) \tag{7}$$

For hexadecane-in-water miniemulsions, the activation energy remains close to that of pure water within the explored range of oil volume fraction. The estimated activation energies are in relatively good agreement with the experimental ones (Fig. 4).

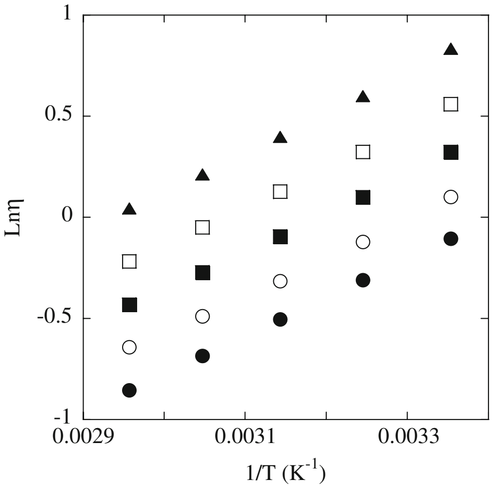


Fig. 3 Arrhenius plot of the viscosity of hexadecane-in-water emulsions stabilized by DexC6$_{38}$ as a function of temperature, for oil volume fractions up to 0.2. *Closed circles* water, *open circles* φ= 0.052, *closed squares* φ=0.100, *open squares* φ=0.149, *triangles* φ= 0.199

On the same graph, values reported for water–isooctane–AOT inverse microemulsions are given and compared to the estimated ones [24]. For that system, interactions between particles are increased upon heating, which gives rise to thermothickening behavior for volume fractions higher that 0.1 above a certain temperature. Nevertheless, below 0.1, the estimated values are consistent with the experimental data (Fig. 4). The same conclusion holds for inverse emulsions using the data given by Farah et al. [30]. As a conclusion, it is possible to estimate the activation energy of flow of emulsions using Eq. 7.

Conclusion

The viscosity of oil-in-water emulsions stabilized by polysaccharide-based surfactants was investigated. Several equations were applied to the viscosity results and compared. The effect of temperature on the viscosity of miniemulsions was determined and interpreted on the basis of the structural characteristics of the adsorbed polymers. The activation energy of the viscous flow was conveniently estimated using a similar approach as that introduced previously for polymer aqueous solutions. The semiempirical equations were generalized using results from the literature.

The results obtained in that work about physicochemical properties of oil-in-water miniemulsions involving amphi-

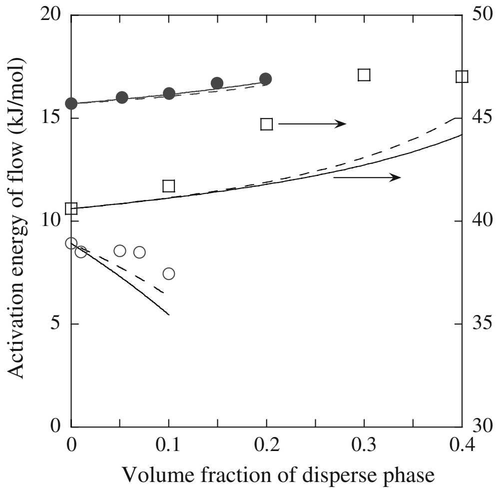


Fig. 4 Activation energy of flow of emulsions (Eq. 7) as a function of the volume fraction of the disperse phase, for details see text. *Closed circles* Hexadecane-in-water emulsion stabilized by DexC6$_{38}$, *open circles* inverse microemulsions (data from [24]), *squares* inverse emulsions (data from [30]). The *lines* are curve fittings by Eq. 7 using Fedors equation (*dotted line*) or Quemada equation (*continuous line*)

philic polysaccharides find direct applications in the design of processes for preparation of polysaccharide-covered nanoparticles. Such results will be the subject of forthcoming papers.

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