



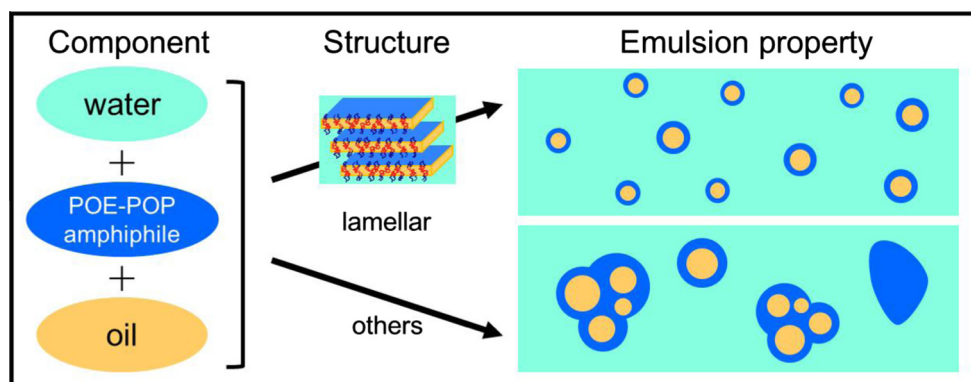
Effect of surfactant phase behavior on emulsification



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GRAPHICAL ABSTRACT



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ABSTRACT

In order to improve our understanding of the effects that the equilibrium phase behavior and structure of amphiphiles have on the emulsification process and the properties of emulsions stabilized by these amphiphiles, we have exploited the known phase behavior of polyoxyethylene–polyoxypropylene–polyoxyethylene (POE–POP–POE) amphiphilic block copolymers (Pluronic) in the presence of two immiscible solvents. Specifically, we considered ternary systems consisting of Pluronic F38, L64, P84, P104, or L121 with water and *p*-xylene which exhibit a very rich phase behavior, including a variety of water-continuous and oil-continuous lyotropic liquid crystalline (LLC) phases. We prepared emulsions having the same (final) compositions but through different emulsification paths, and evaluated the emulsions on the basis of homogeneity and droplet size. We found finer and more homogenous emulsions to result when O/lamellar gel structures (as revealed by small-angle X-ray scattering) were formed during the emulsification process, or when the emulsification path traversed the lamellar LLC phase. This can be attributed to the favorable properties of the lamellar structure: high oil solubilization capacity with concurrent facile dispersibility in water, relatively low interfacial tension, and relatively low viscosity. The findings reported here are relevant to the preparation of emulsions for diverse applications such as skin-care products, pharmaceuticals, food products, coatings, inks, agrochemicals, oil dispersants, and nanomaterials synthesis.

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1. Introduction

Emulsions are liquid–liquid dispersions, typically stabilized by amphiphiles (surfactants, synthetic polymers, polysaccharides, proteins, nanoparticles), that are widely used in various products

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such as pharmaceuticals, skin-care, foods, coatings, dispersants, and agrochemicals [1].

A variety of emulsions can be formed, having different droplet diameters, viscosities, and types of dispersed phase and continuous phase: macro-emulsions and nano- or submicron-emulsions (also called mini-emulsions) [2]; gel emulsions (concentrated emulsions) [3]; oil-in-water, water-in-oil, water-in-oil-in-water, oil-in-water-in-oil, oil-in-[lyotropic liquid crystal] [3], oil-in-[lyotropic liquid crystal]-in-water [4,5], water-in-[lyotropic liquid crystal], [6] and oil-in-[surfactant polymer complex]-in-water emulsions [7,8].

Emulsions are non-equilibrium, kinetically stabilized systems, and as such, their properties including structure, stability, appearance, or texture, depend not only on their constituent components (chemical structures and physicochemical properties of amphiphiles, oil, and water) and their compositions, but also on the emulsion preparation process under different thermodynamic conditions (temperature and pressure) and different mechanical conditions (input energy, mixing time, equipment type, preparation scale) [9,10]. The choices of ingredients, thermodynamic conditions, and mechanical conditions are often limited because of practical considerations, so the preparation process becomes of great importance to emulsions.

Emulsions are typically prepared by a combination of interfacial chemistry and mechanical methods. Representative interfacial chemistry preparation methods encompass the condensation method, low-energy emulsification methods [2] (where the system goes through low interfacial tensions during the emulsification process) such as phase inversion temperature emulsification [11], D-phase emulsification method where the system goes through self-assembled structures of amphiphiles such as D-phase (surfactant-rich phase having nanoscale order but weaker than that of the lamellar phase) during the emulsification process, [12,13] liquid crystal emulsification method which involves lamellar lyotropic liquid crystals [4,5], and the aqueous polymer gel emulsification method [14]. Representative mechanical preparation methods include high-pressure homogenizer emulsification [15,16], sonication emulsification [17,18], and membrane emulsification [19]. Interfacial chemistry-based emulsion preparation methods tend to be most versatile, but they require knowledge of phase behavior effects on the emulsification process in order to prepare emulsions with desirable ingredients and properties.

In systems stabilized by typical, low molecular weight surfactants, it has been established that homogeneous O/W emulsions can be prepared by going through the D-phase (surfactant phase) [11–13] and/or the lamellar lyotropic liquid crystalline (LLC) phase [4,5] during the emulsification process, because of the low interfacial tension of these phases. O/W or W/O gel emulsions can be prepared by going through “normal” (i.e., water-continuous) micellar cubic LLC phase [3] or “reverse” (i.e., oil-continuous) hexagonal LLC phase [6] along the emulsification path. The involvement of self-assembled surfactant structures leads to relatively stable emulsions because these ordered structures remain at the droplet surface [20–22] or as the (very viscous) continuous phase and thus prevent coalescence of the dispersed phase [3,6].

Our research group has an on-going interest on polymeric surfactants, especially on polyoxyethylene–polyoxypropylene–polyoxyethylene (POE–POP–POE) block copolymers (commercially available as Pluronics or Poloxamers) [23]. We have investigated extensively the equilibrium phase behavior of Pluronic–water–or ganic solvent ternary systems and have established that the structural polymorphism of these polymeric surfactants is much richer than that of low molecular weight surfactants due to the conformational flexibility conferred by their high molecular weight and monomer types in POE–POP–POE block copolymers [24–27]. Such rich and well-characterized structural polymorphism offers

an opportunity to probe the connection between equilibrium amphiphile phase behavior and structure, and emulsification process and emulsion properties.

In order to improve the fundamental understanding of the relationship between (a) emulsion preparation process and properties and (b) equilibrium phase behavior and structure, we utilize here several well characterized POE–POP–POE block copolymer – water–*p*-xylene ternary systems [25,28–30]. In particular, we present information on the relationships between equilibrium phase behavior and properties of O/W emulsions prepared (1) through various O/W, lamellar, and W/O self-assembled structures in the Pluronic P84 (EO₁₉PO₄₄EO₁₉) system, (2) through the same emulsification paths for a set of Pluronics of different molecular weights but similar HLB (hydrophile–lipophile balance) value (Pluronic L64: EO₁₃PO₃₀EO₁₃, P84: EO₁₉PO₄₄EO₁₉, P104: EO₂₇PO₆₁EO₂₇), and (3) through the same emulsification paths for a set of Pluronics having different HLB values but similar molecular weights (Pluronic L121: EO₅PO₆₈EO₅, P84: EO₁₉PO₄₄EO₁₉, F38: EO₄₃PO₁₆EO₄₃) [11,31]. Finally, (4) we discuss the influence of the lamellar structure on the properties of emulsions prepared in a path that traversed through this structure.

2. Materials and methods

2.1. Materials

The Pluronic F38, L64, P84, P104, and L121, polyoxyethylene–polyoxypropylene–polyoxyethylene (POE–POP–POE) block copolymers were obtained from BASF Corp. and used as received. Their chemical formulas, molecular weights, and calculated HLB values [31] are reported in Table 1. *p*-Xylene (1,4-dimethylbenzene) (p.a. 99%) was purchased from Acros (Geel, Belgium). Millipore-filtered water was used for all sample preparations. The dipole moments of *p*-xylene and water are 0.1 and 3.11, and their octanol/water partition coefficients (log P) –3.15 and –1.38, respectively [32–34].

2.2. Emulsion preparation

Emulsions with compositions α (Pluronic, water, *p*-xylene = 1.1, 97.6, 1.3 wt%), β (Pluronic, water, *p*-xylene = 1.1, 96.0, 2.9 wt%), or γ (9.9, 86.8, 3.3 wt%) were prepared through various emulsification paths following preparation methods (A) or (B) as discussed below.

2.2.1. Preparation method (A)

(i) Appropriate amounts of Pluronic and water were weighed into 8 mm (i.d.) glass tubes which were flame-sealed immediately. The samples were centrifuged repeatedly in alternating directions to mix these components [25,28–30]. Appropriate time was allowed for thermodynamic equilibration of the samples prior to proceeding to the next step [35,36]. The equilibrated samples were observed under polarized light to check for possible anisotropic LLC structure. (ii) Appropriate amount of *p*-xylene was weighed and added gradually (immediately after breaking the seal) to the binary samples prepared by procedure (i), while mixing thoroughly with a pencil mixer DX (Iuchi Corp.). (iii) Appropriate amount of distilled water or binary Pluronic–water solutions were weighed and added gradually to the ternary mixtures prepared by procedure (ii), while mixing vigorously with a pencil mixer. (iv) The emulsions prepared by procedure (iii) were finally mixed with a magnetic stirrer for an hour in Teflon-sealed sample tubes at 25 °C (for breaking up possible “flocs”). We note that the procedure involving steps (i), (ii), and (iii) constitutes one of the basic emulsification processes utilized in the cosmetics industry to prepare O/W products such as lotions and creams [4,5,12,13]. We have

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