Surface chains and balls

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Abstract

Carbopol® (acrylate) molecules added added to oil-in-water emulsions (carrying a hydrophobic drug), along with a primary emulsifier (Tween 80) served as emulsion stabilisers by acting as a bulk viscosifier and a surface structuriser. In some cases based on higher bulk and thus higher interfacial loading the hydrophilic polymers was found to modify the nano-scale architecture and cause destabilisation.

Interfacial effects and the nano-scale disruption in adsorbed-layer of acrylate polymer-Tween 80 fabricated steroid-bearing emulsions: a rheological study of supramolecular materials.

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***Modified and extracted text*.**

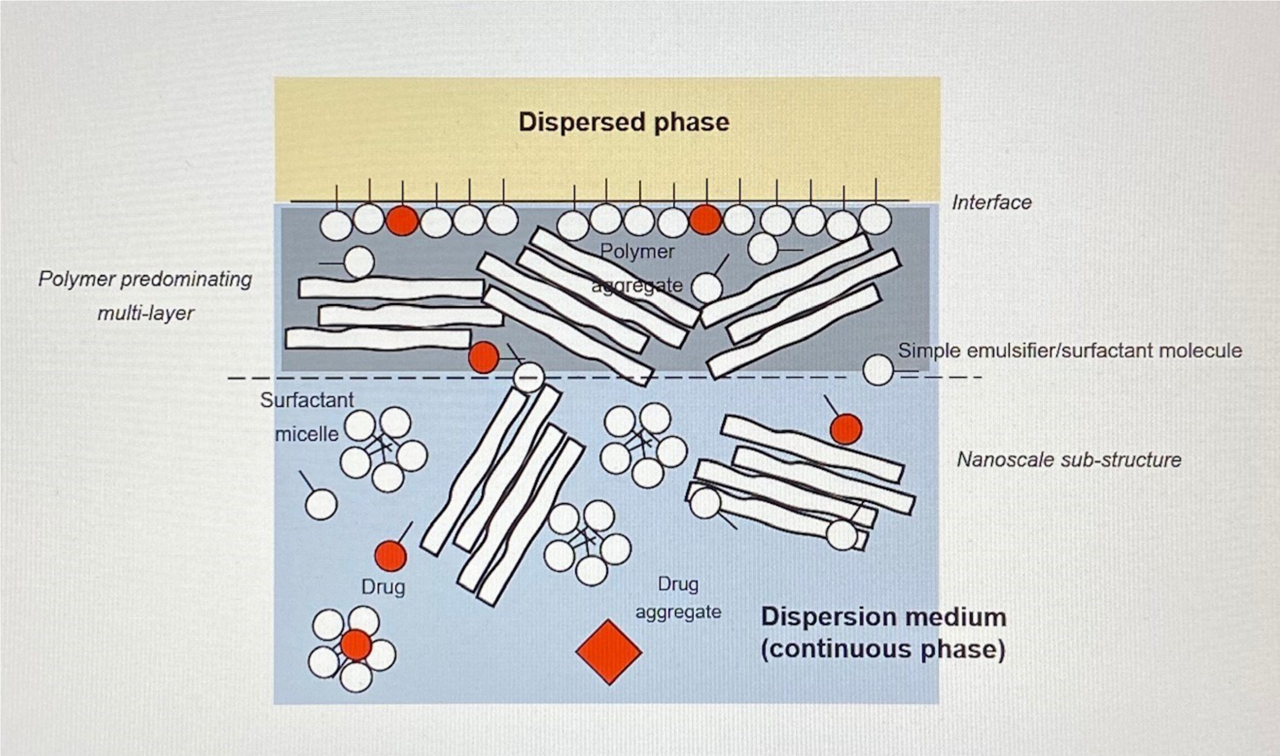
Emulsions, which are coarse or crude dispersions of spherical oil droplets in a dispersion medium of solvent, usually water are maintained in a metastable form by the employment of surface-active agents (aka surfactants or amphiphilic polymers) that accumulate at the interface between oil and water. Emulsions are used for a large range of complex products such as pharmaceuticals (e.g. anaesthetics, creams, skin patches), personal care product (e.g. emollients), vaccine adjuvants (excipients for immunopotentiation), cosmetics (e.g. lip salve, hair conditioners), printing inks, foods (e.g. mayonnaise) and petrochemicals (e.g. crude oil), including lubricants (e.g. engineering cutting fluids). Traditionally, hydrophilic polymers, where acrylate-based forms feature routinely, which bind water though polar functional group or ionised chemical groups on the molecule find applications as thickeners and product texturisers. Acrylate polymers (Carbopols) are favoured in many commercial products because of their limited toxicity minimal allergenicity and favourable biocompatibility. Geometric molecular forms are also highly variable and depend on molecular substitution of the backbone with sugars and other molecules, spacing between intramolecular cross-links and overall molecular weight. Examples include, Carbopol 971 (pH 4-6, 238 kDa spacing, size 1.3 MDa) a loose planar "net-like" structure and Carbopol 974 (pH 4-6, 104 kDa spacing, size 3.0 MDa) a denser hairy "fluffball-like" structure. Polyoxythylene sorbitan esterified lipids surfactants, such as Tween 80, are used rather ubiquitously in hygiene products, medicines and foods as emulsification agents.

A recent piece of physical chemistry research (published in *Nanomaterials*) in the are of nanomaterials looked into the structure of the interfacially-adsorbed later composed on hydrophobic steroid drug, simple non-ionic emulsifier molecule, and carbopols in terms of the influence architectures on the nano-scale (made from polymeric chain, aggregates of polymer, aggregates of dug, aggregates of surfactant, as ball-like structures, made on the relative stability of larger micro-sized oil droplets made from paraffin oil. A range of techniques were used to evaluate the sub-structure of adsorbates including light scattering (photon-correlation spectroscopy and zeta-potential), interfacial tensiometry, light microscopy, scanning electron microscopy (SEM) and rheology (apparent viscosity, creep measurements and mechanical spectra). Several of the techniques work in harmony since rheology in the sense of viscosity and parameters derived from mechanical spectra (complex viscosity, storage modulus (G') and loss modulus (G'')) reveal the composition of the polymer involved, which complement SEM that shows 3D-like images down to the several nanometre scale. G' and G'' values indicated the bulk sample and surface of oil droplets were covered by a mix of chains and balls of the polymer and the emulsifier (along with other combinations such as drug-surfactant, drug polymer, polymer surfactant) and these were also shown clearly on SEM imaging at the nanoscale.

The effect of the presence of carbopol polymers is shown in experiments on Tween 80-stabilised oil-in-water (O/W) emulsions. Here, the droplet size is increased as the concentration of carbopol is increased. Two possibilities exist — displacement of the Tween, which is unlikely given the higher surface tensions or domination of the surface by a Tween-polymer complex and aggregate. Bulk viscosity values recorded are indeed likely to retard creaming over the control formed from only Tween 80 with an aqueous phase bulk viscosity of that of tap water. In line with the aggregate hypothesis it seems that the polymer aggregates (carbopols) are always present and may increase emulsion droplet size (based on the control experiment samples). Thus, one particular type of carbopol (loose structure) seems to cause more rapid coalescence and transition from 50 or so microns to visible oil droplets (500 microns) in the emulsion portion appears to cause a degree of aggregation of oil droplets. This aggregation could be driven by the formation of a Tween-carbopol complex and even explain

the failure of emulsions over Tween only emulsions as the complex precipitates or is poorly soluble. This association-linked disproportionation can be evidenced as a precipitated "sludge or residue" that sits at the oil-water interface, which points to the poorer solubility of the loose-structured polymer. Charge-screening and its influence on solubility are also likely to drive the process of adsorption, flocculation of the surfactant and polymer and thereby create a poor surface coverage of oil droplets promoting droplet fusion.

Based on the peer-reviewed finding we propose a model of interfacial structure that is rather complex despite using a sample for testing that was far more simplistic than that found in commercial preparations. the test sample only involved buffered water (pH 7.00) as the dispersion medium, liquid paraffin (emulsified oil fraction), Tween 80, trace quantities of sodium azide as an antimicrobial (used in shelf life work), a cortico-steroidal drug betamethasone and carbopol.



In summary

Carbopol polymers are surface-active and interfere with the mechanism where simple surfactants stabilize the interfaces of oil droplets dispersed in water within oil-in-water emulsions. The increase in consistency of the bigger carbopol (carbomer) over the smaller carbopol (carbomer) is also responsible for an increased breakage seen in the various heights of the emulsion although light scattering data indicate a smaller average droplet size for emulsions fabricated with the former. It is likely that bridging various mechanisms of polymer-induced flocculation, formation of a tightly bunched cream layer of particles and interfacial inconsistencies due to mal-adsorption are responsible for the increased volume of oil and emulsion breakage. The work throws up interesting insights into the role "inert" formulation ingredients can have on the complex pharmaceutical and cosmeceutical products and their shelf stability and provides yet further insights into the nanostructuring of surface adsorbed materials.

Useful reading:

Sarker D.K., Wilde P.J. and Clark D.C. (1995) Competitive adsorption of L-a- lysophosphatidylcholine/b-lactoglobulin mixtures at the interfaces of foams and foam lamellae. Colloids Surfaces B: Biointerfaces, 3: 349-356.

Sarker, D.K. (2005) Engineering of nanoemulsions for drug delivery. Current Drug Delivery, 2: 297-310.

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Keywords

nanostructure;particles;hydrophilic polymers;architecture