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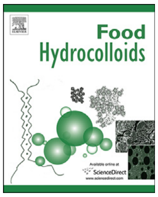

Hydrocolloids acting as emulsifying agents – How do they do it?

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ABSTRACT

We consider the essential compositional and molecular structural features controlling the formation and stabilization of oil-in-water emulsions by hydrocolloid ingredients. The theoretical principles underlying adsorption of polymers and steric stabilization by polymer layers are outlined with particular reference to copolymer morphology and chain branching. These basic concepts are used to interpret at the molecular level the experimental interfacial functionality of three classes of biopolymer emulsifying agents: gum arabic, pectin, and hydrophobically modified starch (OSA starch). Some inferences are made concerning the mechanistic significance of certain generic features in relation to the surface activity and emulsification characteristics of hydrocolloids — the presence of covalently bound protein, the diversity of carbohydrate polymer structure, and the heterogeneity of natural ingredients.

Foreword

This author's personal journey to try to understand hydrocolloid functionality in food emulsions was to a great extent inspired by the influential research on gum arabic (*Acacia senegal*) carried out by Professor Glyn Phillips and his collaborators. The intellectual challenges offered to me by this subject area were further sustained through the stimulating discussions that took place every couple of years at the Gums and Stabilisers Conferences in Wrexham. Surely one of Glyn's great strengths is his ability to bring together active scientists and industrialists in a congenial atmosphere of collaboration and discovery. Especially memorable for me in the context of the present article are two noteworthy scientific events: a workshop session on Emulsion Stabilization during the 4th Gums and Stabilisers Conference (Phillips, Wedlock & Williams, 1988), and, some 20 years later, an International Forum on Natural Hydrocolloid Emulsifiers, also in Wales, organized by Phillips Hydrocolloids Research in conjunction with the Japanese ingredient company San-Ei Gen F.F.I. Inc. (Phillips, 2008b). For observers of his boundless enthusiasm and commitment to this field over the past 40 years, both before and after his formal retirement from NEWI, it is difficult to overstate Glyn's contribution to the promotion and development of our global hydrocolloid research community. Under his compelling spell of Welsh charm and a warm generosity of spirit, this researcher — like many others — has been enticed and welcomed into the extended hydrocolloid research family. So it is a personal privilege and pleasure for me to dedicate this article to Professor Phillips on the occasion of his 90th birthday.

1. Introduction

Hydrocolloids are widely employed in the food industry as functional ingredients for preparing and stabilizing oil-in-water emulsions. In fact, as judged by the technical literature that commonly accompanies the supply of commercial food ingredients, it would appear that almost any available hydrocolloid can provide protection against emulsion breakdown; but clearly some are more effective than others. Over the 30-year lifetime of the journal *Food Hydrocolloids* there have been numerous published reports on the functionality of natural gums and individual biopolymers in emulsified systems. And various authors of these studies have typically offered some kind of intuitive interpretation of this functionality in mechanistic terms. Over this same timescale, there have been regular reports of studies aiming to compare the performance of different hydrocolloid ingredients, and the ongoing value of these comparative studies has been steadily enhanced by the development of reliable experimental methodologies for the quantitative characterization of emulsion stability (McClements, 2005, 2007). On the assumption that useful progress has been made over this period, one may reasonably ask a couple of related questions. Firstly, what is the current scientific consensus regarding

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the underlying mechanistic basis of this type of hydrocolloid functionality? And, secondly, how can one explain the evident differences in emulsification performance between hydrocolloids of different chemical structure and biological origin?

A clue to the intrinsic functional identity of the hydrocolloid is, of course, to be found in the name itself — a hydrophilic (polymeric) material with colloid-like character. That is, the hydrocolloid is a highly water-soluble (or water-dispersible) material that readily dissolves (or disperses) to form highly hydrated entities of colloidal (nanoscale) dimensions. Each dissolved polymer molecule of a hydrocolloid ingredient is deemed to interact strongly via hydrogen bonding with its surrounding water molecules (and also with any neighbouring hydrocolloid molecules). Due to the tendency of these large hydrophilic macromolecules to overlap and join together into entangled networks and macroscopic gels, most food hydrocolloids have the capability to function as viscosity modifiers and thickeners in aqueous media at relatively low concentrations. This universal behaviour allows these hydrocolloid ingredients to make a significant contribution to the provision of long-term stability to aqueous suspensions of solid particles or oil-in-water emulsions. In particular, the generation of a hydrocolloid-containing medium with a very high viscosity at a limiting low applied shear stress facilitates effective immobilization of dispersed oil droplets, thereby inhibiting gravity-induced creaming and any accompanying serum separation during extended emulsion storage. Xanthan gum, for instance, is especially effective in providing stabilization by means of such rheological control (Dickinson, 2004, 2009b). Furthermore, this same non-adsorbing hydrocolloid polymer is also a common participant in the closely related phenomena of phase separation and depletion flocculation, with further important implications for emulsion serum separation and gravity induced creaming instability (Dickinson, Ma, & Povey, 1994; Moschakis, Murray, & Dickinson, 2006).

To be effective as an emulsifying agent, the hydrocolloid ingredient should possess some surface activity. That is, it should have the capacity to lower the interfacial tension at the oil–water interface; and this tension lowering should occur over a timescale that is relevant to the process of emulsion preparation. In other words, the rate of polymer adsorption at the freshly formed oil–-water interface, and the associated rate of development of the transient adsorbed layer during emulsification, should exceed the rate of droplet–droplet collisions caused by the hydrodynamic forces of laminar and turbulent flow (Walstra & Smulders, 1998; Walstra, 2003). In molecular terms, this means that the predominantly hydrophilic macromolecules of the hydrocolloid ingredient should contain a sufficient proportion of accessible hydrophobic groups to enable them to stick to and spread out at the interface, thereby stabilizing the freshly formed emulsion droplets against immediate recoalescence. A further practical consideration is that the emulsifying agent should not be prone to strong aggregation or gelation; otherwise the resulting high viscosity of the aqueous phase will inhibit the disruption of the dispersed oil phase into sufficiently small droplets. In practice, these criteria are fully satisfied by only a small number of hydrocolloid ingredients. Consequently, even though essentially all polysaccharide thickeners and gelling agents can contribute usefully to the long-term stability of emulsions after preparation, only a limited number of hydrocolloids are suitable as primary emulsifying agents.

The origin of the surface activity of certain hydrocolloids has previously been attributed to specific molecular features (Dickinson, 1988, 2003, 2009a). The only food protein that can properly be described as a hydrocolloid — namely, gelatin — has been found to demonstrate significant surface activity and useful emulsifying properties under favourable conditions (Dickinson & Lopez, 2001). For this uniquely hydrophilic food protein, the surface activity is nevertheless attributable to the intrinsic hydrophobicity of a small proportion of its amino-acid residues. Some food polysaccharides appear inherently surface-active due to the presence of short hydrophobic side-chains such as methyl and acetyl groups. Other carbohydrate polymers contain a small amount of proteinaceous material that is firmly linked to the polysaccharide by covalent bonding or physical complexation. It is supposed that these specific molecular structural features enable natural ingredients such as gum arabic (*Acacia senegal*) and certain kinds of pectin to function as highly effective emulsifying agents. In addition, ingredient suppliers have introduced various kinds of hydrophobic chemical modifications into starch and cellulose polymers in order to prepare ‘green’ biopolymer-based surface-active polymers having favourable emulsification properties. For the cases of both the natural and the chemically modified biopolymers, this article will assess how the work of some researchers has recently contributed to our improved understanding of their interfacial hydrocolloid structure–function relationships.

Once an oil-in-water emulsion has been prepared, the main function of the hydrocolloid emulsifier is to act as a steric stabilizing agent to protect the dispersed droplets against aggregation and coalescence during subsequent processing and storage (Dickinson, 1992; McClements, 2005, 2009). There are three main requirements for effective steric stabilization by interfacial polymers: complete surface coverage, strong adsorption, and the existence of a thick adsorbed layer. In the first place, there should be sufficient hydrocolloid present during emulsification to fully cover the newly formed oil–water interface. Secondly, the stabilizing polymer molecules should remain effectively attached to the interface over the life-time of the emulsion system. And, thirdly, the adsorbed layer should contain some bulky hydrated polymer chains that can extend well into the aqueous medium. In combination with steric stabilization, the coexistence of a fraction of non-adsorbed polymeric material can make an additional contribution to colloid stability through the depletion stabilization mechanism (Semenov & Shvets, 2015). Furthermore, the presence of charged groups on some hydrocolloid molecules provides the source of a supplementary electrostatic contribution to the stabilization mechanism, especially under conditions of low ionic strength (Dickinson, 1992; McClements, 2005; Semenova & Dickinson, 2010).

To understand why one particular hydrocolloid ingredient might possess superior emulsifying properties to another we must first have reliable knowledge of the chemical identity and distribution of the hydrophobic groups along the carbohydrate polymer chain. In addition, we need to have an appreciation of how the molecular architecture of the hydrocolloid affects the interfacial structure of the adsorbed polymer layer. Finally, we need to establish how the adsorbed layer structure influences the interaction forces between individual hydrocolloid-coated droplets and hence the overall colloidal stability of the emulsion system. This article represents an attempt to assess how close we are to reaching such a state of fundamental understanding for some of the main classes of hydrocolloid emulsifying agents. Attention is directed here towards the behaviour of soluble hydrocolloid ingredients that exist as individual molecular species in aqueous media. The interested reader is invited to look elsewhere for information on the emulsion-stabilizing properties of two important varieties of particulate biopolymer ingredients — polysaccharide-based solid particles and hydrocolloid microgels (Dickinson, 2013, 2015a, 2016a,b; Berton-Carabin & Schroën, 2015; Lam, Velikov, & Velev, 2014; Rayner et al., 2014; Tavernier, Wijaya, van der Meeren, Dewettinck, & Patel, 2016).

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