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Review Article

Emulsion Properties of Bentonite Clay for Human Use

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Abstract

Many conventional emulsions suffer from physical-chemical instability and accompanying variations in texture and appearance and bioavailability of intrinsic components due to temperature changes, extreme pH values and high salt concentrations. As the emulsifiers used in the food industry, cosmetics and pharmacy have proven to be more and more harmful, the introduction of less harmful emulsifiers and co-emulsifiers is being sought. Clay minerals are gaining more and more importance primarily for safety reasons. In our work, we will review both clay minerals as emulsion emulsifiers and a new type of emulsion with small particles, the so-called Pickering emulsion. They are increasingly using ecological emulsions for protecting fruit, making food products, and making cosmetic products. In particular, clay minerals should be highlighted as drug carriers with the dosed release of the active substance. Liposomal preparations are increasingly being developed for more efficient delivery of the active component of food or medicine with clay minerals. More recent research should develop emulsions based on clay minerals and amino acids for soaking in the bathtub as part of a lifestyle philosophy.

Keywords: *Emulsion; Swelling Clay; Montmorillonite; Pickering; Cationic Surfactants*

Introduction

Montmorillonite clay minerals are used in some pharmaceutical and cosmetic products because of their many beneficial properties. These minerals are increasingly used as carriers of active substances. The advantages that make them used in pharmaceutical formulations are high active surface area and ion exchange, rheological properties, chemical inertness and low toxicity for the patient. Clay is most often used in the form of powder, suspension, emulsion or gel. Electromagnetic properties, followed by ion exchange, adsorption and emulsification properties should be highlighted.

The term "clay minerals" refers to aluminosilicate minerals having two or three-layer crystal structures. Clay minerals are used more and more in pharmaceutical formulations, primarily due to their biological activity. The production of emulsions based on mineral particles is an important area of research [1-3]. These minerals typically exhibit high specific surface area, significant surface charge density (cation-exchange capacity), and low hydraulic conductivity.

Stabilization of colloids is achieved with organic polymers. Mineral solids, including clays that are organically modified, can be dispersed in oils [4].

In modern practice, the terms lyophilic and lyophobic (especially hydrophilic and hydrophobic) are often used to characterize surfaces, in addition to colloidal dispersions. This sometimes leads to confusing usage. These properties of clay can seem confusing at first. Because the dispersion of clay in water can be classified as a lyophobic colloid with hydrophilic surfaces. Even though the particles are irregular in shape, their dispersion structure has a unique effect [4]. Water-external microemulsions have been used in some creams and lotions [5].

These have the advantage of being able to accommodate significant volume fractions of the dispersed phase, from 20 - 40%, without significantly increasing the viscosity [6]. When Pharmacopoeia classified drugs during the Renaissance, it also included clays. Clay minerals are mainly used as additives in the pharmaceutical industry. Clays are used as an oral treatment of diarrhoea, as a gastrointestinal protector; or for local dermatological applications. Besides, they have found applications in nutrition, cosmetics and pharmacy [1,7,8]. Clays and modified clays have been used as diluents, lubricants, taste correctors, and active ingredient carriers [2,8,9].

Clay minerals and their characteristic properties

Natural clay minerals have mixed cations present on the surface and in the interlayer space. The surface properties do not allow for wider use of raw clay. That's why clays are modified by saturating the interlayer space of clay minerals with the desired cations so that the physicochemical properties are adjusted for specific applications. Clay minerals are saturated with the desired cations that improve their physicochemical properties, which makes them unique for certain applications. Adsorption capacity, specific surface and permeability affect the utility value of clay [8]. Various methods have been used for ion exchange modifications of clay using cationic or anionic and organic/organic complexes. Also relevant are binding of inorganic/organic anions, mainly at the edges, reaction with acids, colouring with different types of poly(hydroxy metal) cations, interlamellar or intraparticle and interparticle, polymerization and physical treatments such as lyophilization, ultrasound and plasma. Modification of clay by changing its structure improves the physical and chemical properties of clay. These are primarily thermal stability, porosity and active surface [10,11].

A known method of ion exchange is the use of alkylammonium ions to make clay minerals compatible with a hydrophobic material. The new clay-based hybrid materials are made by modification with some organic compounds such as tyramine and spermine. Organic molecules incorporated into the interlayers of clay minerals increase the adsorption capacity [12]. Cationic modifications of clay are also carried out with inorganic molecules such as Al, Cr, Zn, Ti, etc. by introducing clay minerals into the interlayer. Clays modified in this way are widely used in environmental protection [13].

Emulsions stabilised by bentonite clay particles

Emulsions are thermodynamically not stable systems, they are more or less susceptible to coagulation and phase separation during storage and external effects. The relative contribution of the different breaking effects to the instability of the dispersions depends mainly on their composition and physicochemical characteristics. The action of the solid particles therein remains a relatively undisclosed phenomenon [14].

Microemulsions have not, however, been used much for cosmetic skin care products because high concentrations of surfactant are needed, which increases both the cost and the risk of the product, causing skin irritation [15].

The choice of emulsifier for cosmetic skin care products is usually based on HLB. The numerical value of HLB indicates the ratio between the hydrophilic and lipophilic parts within the emulsion. One means of minimizing toxicity concerns is to use large molecules that will not penetrate the outermost layers of skin (stratum corneum) [16].

Some emulsifiers can irritate by interacting with proteins and causing swelling of the outer layer of the skin. Non-ionic surfactants may be used instead of ionic surfactants since the former either does not bind to proteins or bind weakly at most [17].

Cationic surfactants have been suggested for their ability to improve the sensory feel of skin care creams and lotions [18]. The European Pharmacopoeia (EP) and the United States Pharmacopoeia (US P) contain monographs on the mineral properties of clay. The FDA database lists bentonite clay as an inactive ingredient [19].

Double emulsions, due to the two aqueous phases within the system, enable the homogenization of two incompatible hydrophilic materials, one in the internal aqueous phase and the other in the external [6]. In addition, multiple emulsions-based clays tend to provide a more prolonged release of dermatologically-active agents than when single emulsions are used [19].

The surface tension of suspensions of clay particles is several times higher than the surface tension of pure water [20]. Surface tension increases as a result of strong interactions between water and clay particles. Compared with the effect on the surface tension of aqueous solutions of inorganic electrolytes, the effect of the presence of clay particles and their counter-ions can be of much greater magnitude than would be expected based on the addition of the same number of equivalents of the clay-counter-ions with simple anions [20]. High-density montmorillonite particles have a significantly higher surface tension than kaolinite [21].

Pickering emulsions

A primary step in forming an emulsion is the subdivision of the internal phase into the continuous phase, i.e. the creation of a dispersion. The surface tension of the mixture of continuous and dispersed phases enables the separation of the two phases. The increase in the contact area of the two phases increases with the square of the decrease in particle size. From the thermodynamic point of view, the joining of two or more phases is inevitable [22].

The homogenization of the two phases occurs by modifying the interphase voltage. This is achieved by mechanical stirring with the help of a suitable emulsifier [23].

Semi-solid formulations of clay are often obtained using polymers [24].

Since standard emulsifiers are increasingly excluded from the cosmetic and pharmaceutical industry, emulsions based on small particles, so-called Pickering emulsions are gaining more and more importance. Bentonite clay is increasingly represented in Pickering emulsions. Some studies show that Pickering clay-based particles show promise not only for designing emulsions resistant to coalescence but also for controlling and generally reducing the rate and extent of free fatty acid release during intestinal digestion.

Emulsions based on crushed particles, the so-called Pickering, are increasingly used in industry. Pickering emulsions are particularly advantageous because they avoid synthetic surfactants, which is a requirement of the pharmaceutical industry. That is why bentonite particles are used in the formulation of Pickering emulsions [25-29].

Pickering emulsions are created in four steps: (i) droplet formation by shearing the phase to be dispersed, (ii) approach and collision of the solid particles with the droplets, (iii) adsorption of the particles, and potentially (iv) network formation and stabilization of the droplets [30].

To reduce the volume of organic solvents, the use of Pickering emulsions is increasingly being used to avoid coalescence, bentonite clay is activated with double-layered hydroxide. To obtain a stable O/W emulsion, the mass fraction of clay is 0.1%, while the mass fraction of hydroxide/bentonite varies in the range of 0.25 - 4. With a higher proportion of hydroxide, the surface of the oil particles is covered with hydroxide [31].

Preparation of emulsions

Emulsions are increasingly present in many branches of industry. Stable emulsions are subjected to testing in all branches of industry where they are used. The wide spectrum of application of clay minerals in pharmacy is precisely due to their biological activity and good excipient [1,3,8]. Contemporary research is increasingly dealing with the physical stability of emulsions with ecological emulsifiers [32,33].

Pickering emulsions are made in four stages: (1) shearing, (II) particle collision, (III) adsorption and network stabilization of droplets [30]. Once formed, Pickering emulsions are graded based on stability, character and droplet size. As shown in the next sections, each of these characteristics is driven by physicochemical phenomena that are specific to Pickering emulsions.

A large number of emulsions that will be encountered in practice do not form spontaneously when the phases come into contact because they are thermodynamically unstable, which is why separation occurs over time. An emulsion can be formed if two immiscible liquids are simply mixed in a container and then shaken well, but without some sort of stabilization (emulsifier) an emulsion is not likely to be very stable. Several surfactants can be used to stabilize emulsions [31].

Emulsifiers can be used that reduce surface tension while preventing separation or clumping. In the classic way of preparing an emulsion, the emulsifier is dissolved in the phase in which it is most soluble, after which it is transferred to the second phase. Intensive mixing is then carried out, which achieves intensive shearing. Non-contact ultrasonic mixing is becoming increasingly popular, which is very effective [34,35].

The latter mixing can be provided using paddles, propellers, turbine mixers and ultrasound. A wide range of emulsions can now be designed using ultrasound [6].

The layers of clay minerals look like razor blades, so montmorillonite clay, for example, is 0.3 mm in size with a thickness of 2 nm. By dispersing the particles in water, the particles carry a negative charge in a wide range of pH. This is due to the negative charge of the particles created by the replacement of cations of lower charge with cations of higher charge within the clay lattice. These properties are most present in montmorillonite clay [36].

Among other benefits, clay minerals improve the functionality of products, whether they are emulsions or suspensions [37,38]. The physical sorption characteristics of clay, which are reflected in the improvement of the contact surface, rheology and adsorption, are gaining more and more importance [39]. Based on their positive chemical and physical properties, clay minerals have photoprotective protection for many organic molecules [40,41]. They are often used as ultra-antioxidants.

That is why clay minerals are used as carriers or as active substances in veterinary medicine and pharmacy [42,43].

Organic drug molecules are incorporated into the lamellar-modified clay spaces, making them stabilized and bioavailable for use [44,45].

Many conventional emulsions suffer from physicochemical instability and accompanying variations in texture, appearance and bioavailability of intrinsic components due to changes in temperature, extreme pH values and high salt concentrations. Consequently, there is increasing interest in designing emulsions with improved and/or more controlled stability. Most important among the distributions e developments was the expansion of the spectrum of particle-stabilized emulsions (Pickering emulsions), due to their greater resistance to coalescence and Ostwald ripening [46,47].

The bioavailability of active components using new emulsions is increasingly relevant. Dispersed liquid-in-liquid systems (emulsions) are thermodynamically unstable and phases tend to separate over time, which requires precise rheological control and stability control. Clay minerals are often used in liquid and semi-solid healthcare formulations. Increasingly, they have more than one role in the formulation. Clay minerals have an ion exchange and adsorption function [48]. Particularly interesting is the swelling properties of clay, which can hold a large amount of water. Large contact surface, ion exchange and adsorption capacity enable clay to be widely used in the food, cosmetic and pharmaceutical industries.

The good adsorption and ion-exchange properties of clay allow it to be used in the field of environmental protection, as a geomembrane in the agro-industry and the storage of nuclear waste and the protection of nuclear facilities. Due to its exceptional physical and chemical properties, clay is increasingly being used to improve people's health. We should emphasize oral application, creams, and clay-based emulsion for soaking in the bath. The advantages of clay enabled it to actively participate in pharmacy, spas and aesthetic cosmetics. Being good adsorbents and mucus stabilizers, clay minerals are also useful as drugs in the treatment of intestinal disorders [49-51].

The use of clay minerals throughout history was both for making dishes and as a geomaterial. The very structure of phyllosilicates based on tetrahedral or octahedral lattices enabled anisotropy in the technology of application [14]. Thanks to forces at a short distance (van der Waals) or a weak dipole moment, it enabled modification in the interlayer space [52].

Clay minerals as natural resources for drug carrier applications

Several formulations based on clay minerals for dermatological applications have been developed, since clay minerals, such as kaolinite, talc, and smectite, show nonfibrous morphology and high adsorption capacity. Besides the pharmaceutical application, clay minerals have been extensively used as excipients in some formulations; as lubricants in manufacturing pills; disintegrants; anticaking and thickening agents; binders and diluents; emulsifiers; and carriers of biologically active molecules for improving drugs bioavailability [53].

There are also limitations in the application of clay due to the uncontrolled release of the active substance. A controlled release can be achieved by impregnating the drug and clay with cationic polymers [54].

Drug–clay mineral hybrids can improve drug solubility, increase bioavailability [55,56] modify/control release [57,58] and increase stability. Clay minerals and drugs were the main topics, and next the refinement keywords were delimited: clays and pharmaceutics, clays and cosmetics, clays and dermo-cosmetics, drug stability, clays and drug stability, drug photostability, clays and drug photostability, clays and biological applications, and clays and biotechnological applications [59].

Bentonite is a mineral of the smectite group with colloidal and plastic properties [60]. Due to its high capacity for change and adsorption, montmorillonite clay has long been used to bind organic substances, bacteria, heavy metal ions, viruses and other toxins [61,62]. In particular, the energy of the water bond, which stops the development of many pathogens, should be emphasized. In addition, the positive effects of montmorillonite in preventing hyperlipidemia suggest that it may be an excellent nutraceutical to bind excess fat from the digestive tract [63]. Clay binds toxins in the stomach and intestines and accelerates wound healing [64,65]. Bentonite is a natural material consisting mainly of smectite minerals. Bentonite is formed by the alteration of volcanic ash in a marine environment and occurs as layers sandwiched between other rock types. The smectite in most bentonites is the mineral montmorillonite, which is dioctahedral smectite, but occasionally other types of smectite may be present [66]. It is increasingly being used to develop health-enhancing products such as functional foods, cosmetics and pharmaceuticals [67,68]. Clay-based products are used in soft tissue sarcoma [69] and wound healing [70] as a therapeutic agent and for the acclimatization of recovery rooms [71]. Bentonite is useful for stomach pain, and then for irritable bowel syndrome [72].

Skin protection from particles in the air

The antibacterial properties of clay are reflected in the exchange of cations in the antibacterial process. Aqueous leachates of antibacterial clay effectively kill bacteria. By heating gina to 200°C, dehydration occurs, then by further heating up to 550°C or more, dehydroxylation occurs, and finally, around ~900°C, destruction of the mineral structure of the clay occurs. By identifying degraded components after each heating step and testing the bactericidal effect of the heated product, toxins (eg microbes, organic compounds, volatile elements) are removed [73].

In the mixture of solid particles as air pollutants we find smog, tobacco smoke and soot, various types of dust, pollen, mites and gaseous components from industry or traffic. Furthermore, nanoparticle PM has been shown to enhance the production of proinflammatory cytokines and chemokines, such as IL-1α and IL-8, by human keratinocytes [74,75].

Since these PM-induced reactions lead to skin ageing, it is important to develop formulations for the protection of skin from exposure to PM. To avoid toxic components, the mixtures are made from natural components including biological surfactants because they have low toxicity, biodegradability and greater stability [76].

In an experiment, a reconstructed human epidermis (RHE) with inflammation caused by PM (aerosol and cedar pollen) was used to evaluate the protective quality of a new water-in-oil emulsion with natural surfactant lecithin and modified bentonite. A water-in-oil emulsion with lecithin as an emulsifier and modified bentonite reduce skin damage from city dust and cedar pollen. Simulated experimental results based on modified clay and lecithin confirm the protection of the skin from aerosols from the air as well as from pollen [77].

Conclusion

Since ancient times, the human species has used clay, externally or internally, to maintain the health of the body or treat some diseases. The clay is mixed with water, animal fat, bile salts and acids, and plant extracts, which significantly increased its effectiveness. A large part of the preparations used by the old cultures was in the form of gels, suspensions or emulsions. Soaking in a bath with clay particles in the form of an emulsion with oil extracts of herbs was especially important. Bentonite clay is a natural heterogeneous mineral that has been used in many cultures as a food, medicine or protective agent. Pickering emulsion based on clay and herbal extracts is a new subject of study in spas by bathing in a bathtub. Diffusion, ion exchange and adsorption characteristics of the emulsion are adapted to the skin for communication. It removes toxins from the body and drains the lymphatic system. Clay is a source of negative ions, which is especially important for oral, cosmetic or aerosol use. Its physical and chemical properties, primarily ion exchange, adsorption and catalytic, give it an advantage in the production of cosmetic, pharmaceutical and nutritional preparations. In particular, the mechanisms of action in the intestinal flora towards favouring the formation of short-chain fatty acids in the large intestine should be studied. Bentonite clay occupies a special place in nanotechnologies.

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