Colloid Polym Sci 276:1019–1023 (1998)

ORIGINAL CONTRIBUTION

W.-M. Kulicke
O. Arendt
M. Berger

Characterization of hydroxypropylmethylcellulose-stabilized emulsions

Part I: Particle size determination

Received: 12 May 1998
Accepted: 24 June 1998

W.-M. Kulicke (✉) · O. Arendt
M. Berger
Institute of Technical and Macromolecular Chemistry
University of Hamburg
Bundesstr. 45,
D-20146 Hamburg
Germany

Abstract Emulsions stabilized with hydroxypropylmethylcellulose were characterized with respect to their particle size and their flow behavior. This part of the study focuses on the former.

Active laser scanning revealed that the particle size is independent of the hydroxymethylcellulose content. The critical density of the surface film was determined to be ≤ 0.01 g/m^2. This is the basis for the interpretation of the flow behavior, which is described in detail in part II of this contribution.

Key words Hydroxypropylmethylcellulose – emulsions – particle size – active laser scanning

Introduction

In its simplest form an emulsion is a two-phase system consisting of two mutually miscible liquids, where one phase is dispersed in the other in the form of microscopic or submicroscopic particles [1, 2]. As the two phases involved are normally oil or fat and water, emulsions are classified as oil-in-water (O/W) and water-in-oil (W/O) types, with the disperse phase being named first [3, 4].

Emulsions are put to use in branches of foodstuffs technology [5], pharmacy, the paint industry and cosmetics [6], but are also components of agrochemicals, bitumen, inks, coatings and adhesives. Examples of O/W emulsions are milk, mayonnaise and ice-cream; examples of W/O emulsions are butter, margarine, sandwich spreads, chocolate and lipstick.

The simplest type is the *two-phase emulsion*. However, the nomenclature is misleading since the crucial interfacial phase of the emulsifier is not taken into account, and without this the emulsion would not only be thermodynamically, but also kinetically unstable. It would therefore be correct to speak of a three-phase system. On the other hand, and this is the origin of the nomenclature, only two immiscible fluid phases are used to produce these conventional emulsions.

The emulsifying system employed in stabilizing can be greatly varied according to the particular requirements. Hence, co-emulsifiers (generally long-chained alcohols) are added to the emulsifier: firstly to reduce the interfacial tension and secondly to form an autonomous system with the emulsifier [7].

The flow behavior of emulsions is of great interest from both the technical and practical aspects since many industrial processes, such as mixing, pumping, filling or packaging, call for a good knowledge of the flow properties in order to optimize the design of the equipment required, such as mixers and pumps.

However, flow properties are also of great importance in the application itself. For instance, according to the application, high demands may be placed on the flow from out of the packaging, the drop-forming characteristics and the formation of a film.

After from stability and consumer acceptance aspects, determination of the flow properties of emulsions can also offer more detailed insight into the various forms and forces of interaction that may occur in an emulsion system. For example, the viscosity of the oil employed in O/W emulsions only has a slight influence on the viscosity of the emulsion, whereas the rising particle density due to the increasing phase volume fraction, ϕ, leads to a greater occurrence of interactions between the particles.

Consequently, the viscosity of the entire system increases [8]. The viscoelastic properties of the emulsions are then influenced by the particle size and its distribution, the shape of the particles and their ability to be deformed. However, the influence of the continuous external phase is often many times greater [9]. However, if for reasons of flexibility, e.g. related to the composition of the emulsion or improved quality assurance, further components such as co-emulsifiers or additives are used, then the viscoelastic behavior of the emulsions becomes almost impossible to predict and extremely complex.

A common problem in emulsions is their instability, both thermodynamic and particularly kinetic. One method of effective protection against coalescence of the particles is to raise the viscosity of the outer phase with the aid of a polymer. In such systems the particles have a reduced kinetic energy, so that collisions become less common and take place with a lower energy content [10]. On the other hand, polymers often have hydrophilic and hydrophobic subregions so that these amphiphilic polymers act like low-molar-mass emulsifiers.

The processes that take place during the stabilization of an emulsion particle by macromolecular emulsifiers are divided into three stages [11–13]:

(1) the polymer diffuses to the phase boundary and an interfacial film is formed by adsorption (only a few adsorption sites are formed and the macromolecule largely retains its coiled configuration);
(2) the adsorbed macromolecules spread out and unfold at the phase boundary;
(3) the molecules of the polymeric emulsifiers are reoriented according to their hydrophilic and hydrophobic properties.

In order to achieve effective protection against coalescence, there has to be a dense concentration of suitable polymers and they must be firmly anchored in the oil phase. The polymers at this interface can be visualized as being in the form of loops, tails and trains [11, 14].

To date the flow behavior of emulsions has only been understood qualitatively. There is a lack of good quantitative understanding, because of the dynamic behavior of the emulsion's droplets instead of a static behavior of dispersion particles.

Investigations of hydroxypropylmethylcellulose (HPMC)-stabilized emulsions have hitherto concentrated on the aspects relevant to pharmaceutical technology, such as long-term stability and storage tests as well as their compatibility with added medicinal agents [15, 16]. In our investigations, particular attention was paid to changes in particle size and its distribution over substantial periods of time.

In former investigations, we have determined particle sizes by size exclusion chromatography coupled with multi angle laser light scattering [17] and flow field-flow fractionation coupled with multi angle laser light scattering, respectively [18, 19 and references cited therein]. As these methods are not suitable for the emulsions, in this contribution active laser scanning was employed.

Using (HPMC)-stabilized emulsions, this paper therefore aims to investigate the extent to which rheological experiments and particle size determination can contribute to the characterization of emulsion systems. This part focuses on the latter.

Experimental

Preparation of emulsions

Emulsifier

The emulsions investigated in this study were stabilized with an aqueous 2.5% w/w solution of a short-chained hydroxypropylmethylcellulose (HPMC) ($\eta_{2\%} = 100$ mPa s, $DS_{Me} = 1.4$, $MS_{HP} = 0.2$). This was produced by Shin Etsu Chemical, Tokyo, Japan, and kindly supplied by Syntapharm GmbH, Muelheim/Ruhr, Germany. The stabilization was carried out firstly to ensure that the interfacial films obtained were as dense as possible and secondly to avoid having to take into account any of the previously described viscosity and stabilization effects caused by high polymers. In addition, if polymers with an excessively high molar mass were employed, the degradation that might occur during the dispersal process would make interpretation of the results very difficult.

To synthesize the HPMC-stabilized emulsions, the mass of polymer required for the solution was weighed and diluted with the calculated quantity of deionized water. The polymer was dissolved by permanent agitation over a period of ten days.

Oil component

Stability investigations of emulsions with medium-chained triglycerides as the oil phase exhibited particularly high stabilities [15]. Therefore, the emulsions synthesized for this study used medium-chained triglycerides made from palm kernel oil and coconut oil having undergone re-esterification with glycerin (Miglyol^{TM} 812 from Huels AG, Marl, Germany and Myritol^{TM} 318 from Henkel AG, Duesseldorf, Germany).

To prepare 400 ml quantities of emulsion the required quantity of oil phase was combined with the polymer solution in a glass beaker. This preparation was then emulsified using a T-50 Ultra-Turrax^{TM} from IKA (Schopfheim, Germany) fitted with a G 45 M dispersion head at a speed of 10 000 rpm. The heat dissipation due to stirring resulted in the emulsion heating up so quickly that the emulsifying process was terminated after five minutes. The prepared emulsions were transferred to brown-glass bottles. All experiments on the emulsions were carried out after they had been standing for at least one day.

By preparing the emulsions under uniform conditions it was possible – at constant emulsifier concentration – to vary the phase volume fraction, ϕ, systematically and obtain emulsions with a milky-white, homogeneous appearance, which exhibited no coalescence. Coloring the outer, aqueous phase with methylene blue enabled all the emulsions to be classified as being of the O/W type.

Active laser scanning

A type ECA 040 emulsion-characteristics-analyzer from Messtechnik-Schwartz GmbH (Duesseldorf, Germany) was employed. A laser diode with an output of ≤ 3 mW produces a laser beam of wavelength $\lambda = 785$ nm. The laser beam is controlled by a 75 Hz rotating, electrically driven optical system on a paraxial path with a diameter of 8.5 mm, which results in path speed of 2 m/s.

The probe was immersed vertically in a 600 ml beaker with the emulsion to be investigated. A four-blade propeller stirrer with a diameter of 6 cm was driven by a stirrer motor with 400 rpm so that the current generated was forced up against the probe window.

The measurements were evaluated in such a way that in each case the mean of five measuring cycles could be assigned to one of the 39 logarithmically distributed comparison intervals. These channels correspond to the diameter of spherical particles in the range from 0.4 to 125 μm. In total between 50 and 100 measurements were stored for each sample in this way. Statistical evaluation of the measured raw values was performed with the DOS-program "dispas 2.20" from Messtechnik-Schwartz GmbH (Duesseldorf, Germany) on a conventional PC.

Results and discussion

Determination of particle size

Determination of the drop size in an emulsion is of importance for numerous reasons: the changes in this parameter can lead to conclusions about various influential factors such as transport, storage and temperature being quantified. As the absolute determination of particle size is difficult, relative methods are usually employed [20]. Under controlled conditions, determination of the particle size and its distribution enable a detailed understanding to be gained of the emulsion as a multiphase system, as well as allowing molecular processes to be explained and interpreted.

In contrast to particle solutions, one problem almost always occurs when determining the droplet size in emulsions, namely that the emulsion under investigation usually has to be diluted to a great extent in order to be able to detect laser scattering or to count the individual droplets. As emulsions are dynamic systems, dilution may, however, raise the problem that the film of emulsifier around the droplet becomes destabilized and coalescence, for example, may occur, which affects the droplet size distribution.

In the emulsions investigated here a large range of viscosity has been covered so that it was not possible to examine the drop size distribution exactly for all emulsions with the methods of polarization microscopy. The problem arose here that the highly viscous emulsions did not independently form a translucent, thin film, but it was detected that all emulsion droplets showed a spherical shape. Under mechanical force a significant change was observed in the droplet size distribution and in droplet morphology.

For this reason the method of active laser scanning was employed for this investigation. This offers the following advantages [21]:

(1) the emulsions being examined do not have to be diluted,
(2) high phase volume fractions can be included in the investigation,
(3) the investigation can be carried out on-line in the reactor,
(4) there is no need to prepare, dry or otherwise process the sample.

The measuring method of laser scanning is designed for flowing fluids and gases because the particles to be detected have to be fed past a measuring window. The continuous flow against the measuring window means that there is no risk of relatively thick boundary layers forming nor of local separation.

In laser scanning a laser beam is generated in a diode, which is then directed through an optical waveguide to a beam splitter. An adjoining rotating optical system creates a laser focal point in the measuring medium parallel to the axes, which then scans the sample at a constant rate.

If this focal point passes over a particle, then the light that hits the particle is scattered diffusely. Part of this scattered light returns to the optical system and is recorded by a photodetector as the intensity curve of the backscattered light.

As the laser beam rotates on a circular path, the impulse delay can be equated with the arc length of the particle segment that is scanned. If a large number of these arcs are measured they can be classified into size fractions and summed. This results in a relative chord length distribution, which, using chord statistics that also contain the particle shape and the deviations from the chord length and "true" chord lengths, can be converted into a particle size distribution [22].

Table 1 summarizes the results of the measurements.

On the assumption that all droplets were spherical, these data were used to calculate the number of particles in the emulsion in terms of the phase volume fraction, ϕ, employed. The number of particles was then used in turn to calculate the total surface area of the particles. On the assumption that all the emulsifier employed is bound to the particle surface, it is then possible to derive ratios for the surface film density. The results of these calculations are shown in Fig. 1.

A linear relationship was determined between the number of particles and the phase volume fraction, ϕ. This reflects the fact that no altered particle diameters or distributions were determined when the phase volume fraction and emulsifier concentrations were altered. However, a different pattern of behavior is seen for the surface concentration of the emulsifier. The plot obtained against the phase volume fraction was almost exponential and tended towards a limiting value. This means that no constant value was determined for the surface film density, as would be expected for completely bound emulsifiers.

These findings suggest that an optimal surface film density is established between the emulsifier and the oil phase that is independent of the phase volume fraction. This has to be determined according to Fig. 1, with a value that is significantly lower than 10^{-14} g/μm^2 (0.01 g/m^2). The higher emulsifier concentrations at the droplet surface calculated at low oil contents then indicates that a correspondingly high concentration of free, excess unbound emulsifier is present in the aqueous phase.

Table 1 Particle radius, R, for different phase volume fractions, ϕ, from active laser scanning of the emulsions

ϕ	No. distribution R [μm]	Vol. distribution R [μm]
0.1	3.8	23.7
0.2	3.5	18.1
0.3	3.3	16.3
0.4	3.6	17.6
0.5	3.7	21.7
0.6	3.8	21.0

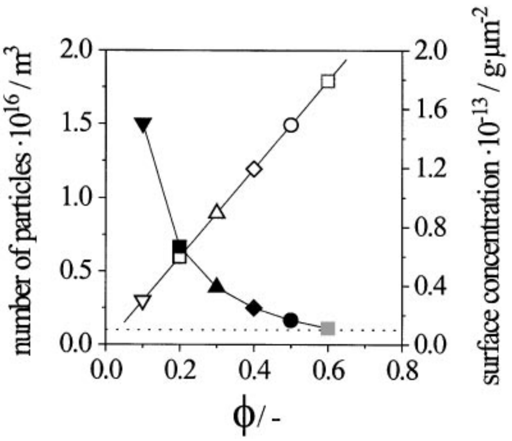

Fig. 1 Number of particles (hollow symbols) and surface concentration of emulsifier (solid symbols) as a function of phase volume fraction, ϕ. Dotted line: extrapolated minimum density of surface film

The establishment of an optimal surface film density was additionally supported by the fact that it was not possible to synthesize emulsions with a phase volume fraction of $\phi > 0.7$ and even lower emulsifier concentrations. Furthermore, the emulsions demulsified, if more oil was added. If it is assumed that the particle radii are independent of the phase volume fraction, the quantity of available emulsifier was no longer sufficient to achieve the required surface film density, so that the oil droplets coalesced and the emulsion separated. The possible alternative process of a phase inversion was not observed. It should also be pointed out at this stage that the limit is dependent upon the emulsification process.

Acknowledgements We thank Prof. R. Daniels, Institute of Pharmaceutical Technology, Technical University of Braunschweig, for the possibility to perform measurements with active laser scanning. Also we gratefully acknowledge the support of "Fonds der Chemischen Industrie" for a doctoral grant. In addition, we wish to express our most sincere gratitude to the Federal Ministry for Education, Science, Research and Technology and the Deutsche Forschungsgemeinschaft for the financial support.

References

1. Sherman P (1983) In: Becher P (ed) Encyclopedia of Emulsion Technology, Vol 1. Marcel Dekker, New York, p 405
2. Block LH (1988) In: Liebermann H, Rieger M, Banker G (eds) Pharmaceutical Dosage Forms: Disperse Systems, Vol. 2. Marcel Dekker, New York, p 335
3. Becher P (1988) Encyclopedia of Emulsion Technologies, Vols 1 & 2. Marcel Dekker, New York

4. Miner PE (1993) In: Laba D (ed) Rheological Properties of Cosmetics and Toiletries. Marcel Dekker, New York, p 313
5. Weipert D, Tscheuschner H-D, Windhab E (1993) Rheologie der Lebensmittel. Behr's Verlag, Hamburg
6. Brummer R, Hamer G (1997) Appl Rheol 7:19
7. Eccleston GM (1990) J Soc Cosmet Chem 41:1
8. Tadros TF (1994) Coll Surf A: Physicochem Eng Asp 91:39
9. Pons R et al (1995) Langmuir 11: 1966
10. Robins MM (1991) In: El-Nokaly M, Cornell D (eds) ACS Symp Ser 448, Washington, p 230
11. Fleer GJ (1989) Colloid Surf 35:151
12. Hunter RS (1989) In: Hunter RJ (ed) Foundations of Colloid Science, Vol 1. Clarendon Press, Oxford, p 450
13. Dickinson E (1992) An Introduction to Food Colloids. Oxford Science Publications, Oxford, p 73
14. Edwards DA et al (eds) (1991) Interfacial Transport Processes and Rheology. Butterworth-Heinemann, Boston
15. Daniels R (1994) Habilitationsschrift. University of Regensburg, Germany
16. Rimpler S (1996) PhD thesis. University of Regensburg, Germany
17. Kulicke W-M, Roessner D, Kull W (1993) Starch/Staerke 45:445
18. Thielking H, Roessner D, Kulicke W-M (1995) Anal Chem 67:3229
19. Thielking H, Kulicke W-M (1998) J Microcol Sep, 10(1):51
20. Friedrich H, Mansour A (1995) Nachr Chem Tech Lab 43 (Supplement S) 53
21. Schwartz F H (1991) Elektronik Journal 10:42
22. Schwartz F H (1996) User's Manual of dispas 2.1. ECA Messtechnik Schwartz GmbH, Duesseldorf