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Separation behaviour of particles in biopolymer solutions in dependence on centrifugal acceleration: Investigation of slow structuring processes in formulations

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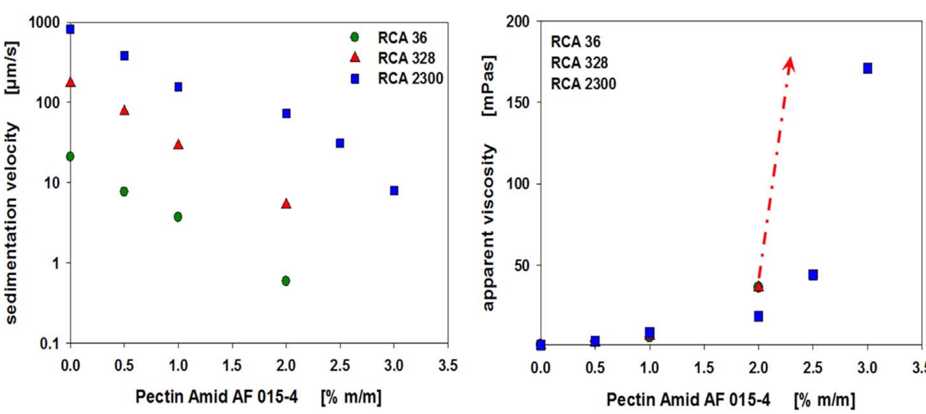
GRAPHICAL ABSTRACT

Determination of sedimentation velocity of tracer particles with known properties as function of biopolymer concentration and relative centrifugal acceleration allows to determine apparent viscosity, characteristic for centrifugal separation process.



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ABSTRACT

Dispersion based formulations have a broad and diverse range of uses, e.g. for construction materials, paints, cosmetics, food and pharmaceuticals. Gravity driven processes potentially may affect their spatial and temporal composition and this way their appearance and functionality. Therefore physical stability has to be evaluated and predicted in process of development and quality control. For products with shelf life of several month or even years accelerated testing using analytical centrifugation is one option. For this purpose dependence of separation velocity on acceleration applied has to be characterized, which is also important for solid-liquid and liquid–liquid separation processes in centrifugal field. However, situation in case of non-Newtonian liquids is complex and not yet completely understood. Another, but related problem is structuring of dispersion based formulations after production and filling processes over time of storage until final use. From an experimental point of view it is very difficult to investigate this process without breaking these soft structures during sampling for measurement.

In this paper we describe investigations into both, separation behaviour of particles dispersed in non-Newtonian continuous phase in dependence on gravity and aging of dispersions during storage. To this end we chose suspensions of nearly monosized silica particles in pectin solutions as model system. Separation behaviour of freshly prepared model dispersions was investigated as function of pectin concentration and centrifugal

Abbreviations: DE, degree of esterification; DA, degree of amidation; RCA, relative centrifugal acceleration

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acceleration. To visualize and quantify aging of dispersions they were filled into cells after preparation and stored for aging different times before measuring separation behaviour in centrifugal field. This way the process of structure build up can be investigated quasi in-situ.

Results are presented regarding particle separation of suspensions formulated of non-Newtonian continuous phases in dependence on centrifugal acceleration. The model system allows to investigate the separation in non-Newtonian fluids in centrifugal field, determine actual apparent viscosity of pectin solutions and study interaction between biopolymer and particles (flocculation).

1. Introduction

Dispersion based formulations have a broad and diverse range of uses, e.g. for construction materials, paints, cosmetics, food and pharmaceuticals. Gravity driven processes potentially may affect their spatial and temporal composition and this way their appearance and functionality. Therefore physical stability has to be evaluated and predicted in process of development and quality control. For products with shelf life of several month or even years accelerated tests are necessary. In this regard analytical centrifugation is one option [1]. For this purpose dependence of separation velocity on acceleration applied is of basic interest. This is also important for solid-liquid and liquid–liquid separation processes in centrifugal field [2–4]. The underlying question is whether it is feasible to extrapolate from separation quantified at given centrifugal acceleration(s), to the behaviour at other accelerations or at earth gravity.

Separation processes basically can be described by extended Stokes law taking into account hindrance for concentrated dispersions [1,5–7]. To deduce behaviour under high gravity in centrifuges one can assume that separation velocity scales linearly with acceleration in Newtonian liquids. For several Newtonian liquids this was experimentally shown [1], even in case of concentrated dispersions [8]. Situation in non-Newtonian liquids is more complicated [9–14] and not yet completely understood. E.g., the problem of non-Newtonian behaviour in downstream processing of biotech industry is more the rule than an exception. Even more, separation is complicated by interactions of multiple components and shear sensitivity of agglomerates or flocs.

A somewhat related, often not recognized phenomenon consists in structuring of polymer solutions and dispersions. Dispersion based formulations usually exhibit structuring processes after production and filling processes over time of storage until final consumption or use. This leads to change in dispersion state and product quality over time. Examples are biopolymer (e.g. pectin) stabilized food products. From an experimental point of view it is very difficult to investigate process of aging without changing or breaking the structure due to sampling for measurement. To overcome these problems specialized laboratories use sophisticated methods like optical microrheology, diffusive wave spectroscopy [15–17]. Amin et al. [18] used a combination of dynamic light scattering and Raman spectroscopy. This paper suggests an alternative simpler approach to track structuring processes as well as to determine apparent viscosity characteristic for separation in non-Newtonian liquids in centrifugal field. Separation behaviour of well characterized, nearly monodisperse silica particles was in-situ visualized by fingerprints and quantified by STEP-Technology [1,4,10,11,19–22]. (STEP-Technology is an acronym for Space and Time resolved Extinction Profiles). Silica particles served the role of tracer particles to characterize solutions of pectin, as a model for biopolymer solutions, regarding behaviour as continuous phase during separation in centrifugal field as well as regarding structuring behaviour during aging.

Pectins are complex biopolymers – pectinic acids (linear polygalacturonic acids), partially neutralized, which contain methyl ester groups [23]. Degree of esterification (DE) is the proportion of carboxyl groups in esterified form. For modification of properties pectins are sometimes used in amidated form, where part of ester groups are removed by reaction with ammonia (DA stands for degree of amidation). Due to their structure pectins have high water binding capacity and may interact through hydrogen bonding, electrostatic interactions and hydrophobic bonding. Obviously structure of pectins and media composition (e.g. pH, sugar, multivalent ions) has a marked impact on rheological behaviour [23].

Freshly prepared model dispersions were investigated as function of pectin concentration and centrifugal acceleration at moderate and low particle concentration. To visualize and quantify aging of dispersions they were filled into measurement cells after preparation and stored for aging different times before measuring separation behaviour. This way the process of structure build up was investigated quasi in-situ.

2. Materials and methods

2.1. Instrumental methods used for characterization

STEP-Technology (time and space resolved detection of extinction profiles over the entire sample height) is a baseline technology developed by LUM for comprehensive characterization of dispersion state. According to ISO 13097 [24] position resolving techniques in particular

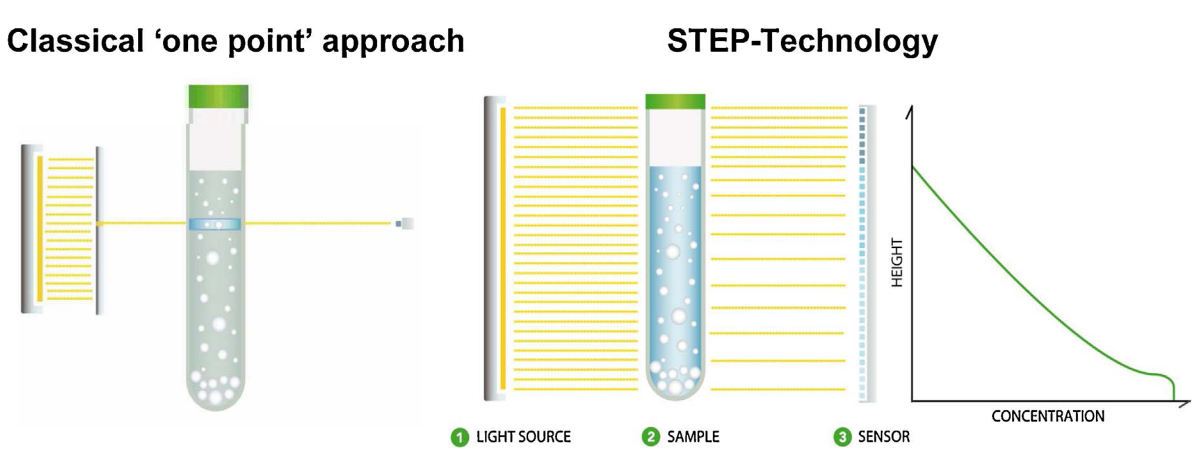

Fig. 1. Principle scheme of STEP-Technology in comparison to classical 'one point' approach.