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ORIGINAL CONTRIBUTION

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Application of a new separation analyzer for the characterization of dispersions stabilized with clay derivatives

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Abstract The performance of a newly developed separation analyzer is demonstrated by characterization of the sedimentation kinetics and the swelling behavior of organoclays in binary solvent mixtures (toluene/cyclohexane) as well as by investigation of oil-in-water and water-in-oil emulsions stabilized by clay derivatives. The automatic measuring system – LUMiFuge 114 – is based on a special centrifuge with an integrated optoelectronic sensor system which allows the measuring of spatial and temporal changes of light transmission during the rotation in a variable centrifugal field (12–1200*g*). By using the new device a fast and reproducible characterization of settling behavior and dispersion stability was possible. Moreover, the evaluation of the long-term stability of samples with high separation stability as well as of the heterogenity of the separation process, the sample transparency and the elasticity of the sediment as a function of alternating centrifugal force could be carried out.

Key words Separation analyzer · Organoclay dispersions · Elasticity · Emulsion stability · Emulsions stabilized by clay derivatives

Introduction

In many technical fields (pharmacy, foods, cosmetics, paints and varnishes) the thickening effect of colloidal additives is used regularly. Layered silicates with high swelling properties have a broad range of applications. Various clay products with different properties are available on the market to match special demands. Determination of separation and swelling properties is essential for product optimization and control; however, methods available for this purpose are generally simple but time-consuming.

The application of an analytical ultracentrifuge for the study of dispersions of layered silicates has been described by Tombácz and coworkers [1, 2]. Their investigations focused on compression behaviour.

The intent of the present report is to demonstrate the potential of a novel separation analyser – LUMiFuge 114 – for the fast and reproducible characterization of settling behavior and stability. The automatic measuring system is based on a special centrifuge [3] and has been used for different applications [4–8], i.e. characterization of packing and volume elasticity of microcapsules and microbeads [4], optimization of separation processes in waste water and sludge treatment [6, 8].

Experimental

Materials

Clay derivatives

Tixogel VZ and Tixogel MP 250 are technical grade organoclays, commonly used as thixotropic and antisettling agents for medium- to high-polarity systems in mixtures with aliphatic and aromatic hydrocarbons. Both are octadecylbenzyldimethylammonium bentonites. Tixogel MP 250 contains surplus octadecylbenzyldimethylammonium surfactant as an activator to ease optimum dispersion. The average particle size of Tixogels is approximately 25–30 μm. Optigel CK is a hydrophilic, activated bentonite. All clay derivatives are products of Süd-Chemie Münich, and were used as received without additional drying.

Solvents and oil

Toluene and cyclohexane were both A.R. grade. The organic phase in the emulsion studies was castor oil (oleum ricini raffinatum DAB 10).

LUMiFuge 114 measuring system

The automatic measuring system – LUMiFuge 114 – is based on a special centrifuge [3]. Preset centrifugal acceleration of 12–1200*g* is used to speed up the separation process, thereby reducing the time necessary for investigation. Up to eight samples can be investigated simultaneously using rectangular (path length 2 mm) or cylindrical (inner diameter 10 mm) cells.

The measuring scheme is depicted in Fig. 1. An integrated optoelectronic sensor system allows spatial and temporal changes of light transmission during the rotation to be detected. In contrast to other approaches [9] the local transmission is determined over the entire sample length simultaneously. The instrument is controlled by a computer. Throughout the measurement, transmission profiles are recorded and can be displayed on the monitor. The separation process can be depicted as a time course of the relative position of the boundary between supernatant and sediment (resolution better than 100 μm) or of the transmission averaged over the entire or a chosen part of the sample length. On the basis of the data obtained values of the sedimentation constants, the packing density, etc., can be derived. For further details see http://www.lum-gmbh.de.

Characterization of the sedimentation and swelling behavior of organoclays

The sedimentation and swelling behavior was investigated in binary solvent mixtures of toluene/cyclohexane as function of the weight fraction of toluene (x).

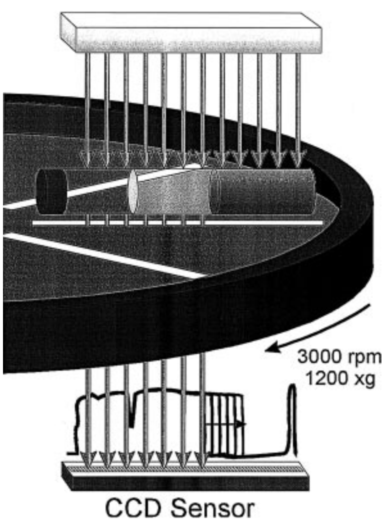


Fig. 1 Measuring scheme of the separation analyzer

First, a 5 wt% stock suspension was prepared by dispersing 0.25 g Tixogel into the corresponding solvent or solvent mixture on a magnetic stirrer for 30 min (250 rpm for Tixogel VZ and 500 rpm in the case of Tixogel MP 250). Then, the dispersions were transferred into graduated 10-cm^3 tubes and diluted by half. After shaking by hand the sedimented volumes were recorded at different times. Alternatively, 2 cm^3 of the resulting 2.5 wt% dispersions was filled into 1-cm glass cells and measured with the LUMiFuge at 750 rpm (73*g*). After approaching a constant sediment volume an alternating centrifugal acceleration was applied as a step function between values of 1200 and 73*g* (rotational speed 3000 and 750 rpm).

Stability evaluation of emulsions stabilized with clay derivatives

Castor oil/water emulsions were prepared by dispersing oil and tap water together with stock suspensions of either Tixogel MP 250/castor oil (weight ratio 1:12, obtained after 3 h stirring at 50 °C) or Optigel CK/water (tap water, weight ratio 1:20, obtained after 30 min stirring at room temperature). The emulsions were intensively homogenized (Ultra Turrax, 30 min at 10 000 rpm). In each case the clay concentration was kept constant (1.5 wt% Optigel CK or 2.5 wt% Tixogel MP 250).

The stability of the emulsions was evaluated in more detail with the LUMiFuge (Tixogel-stabilized emulsions in 1-cm cells, 15 h at 1200*g*; Optigel-stabilized emulsions in 0.2-cm cells, 2 h at 1200*g*).

Results and discussion

Investigation of sedimentation behavior of organoclays in binary solvent mixtures

The sedimentation behavior of the two different organoclays with respect to the solvent composition as evaluated by the naked eye (graduated tubes, 1*g*) is compared in Fig. 2a.

Except for Tixogel VZ in pure cyclohexane, sedimentation is characterized by a gradual shrinking of the network structure formed during dispersion. In the case of Tixogel VZ in pure cyclohexane, in a first fast step a sediment is formed by the settling of the individual clay particles and this is followed by a slow decrease in sediment volume.

The following trends are obvious. On increasing the weight fraction of toluene the settling rate is decreased and the swelling of the organoclays as measured by the final sediment volume is enhanced. Tixogel MP 250 exhibits far more pronounced swelling behavior; therefore, this product is a more suitable antisettling agent, especially for formulations with reduced content of aromatic solvents.

The settling and swelling behavior is determined by various factors. The disperse systems contain loose flat-to-flat ordered aggregates of silicate platelets. The degree of disaggregation, i.e. the content of individual platelets and smaller flat-to-flat ordered aggregates, is enhanced by the additional surfactant contained in Tixogel MP 250 and by increasing the content of toluene in the

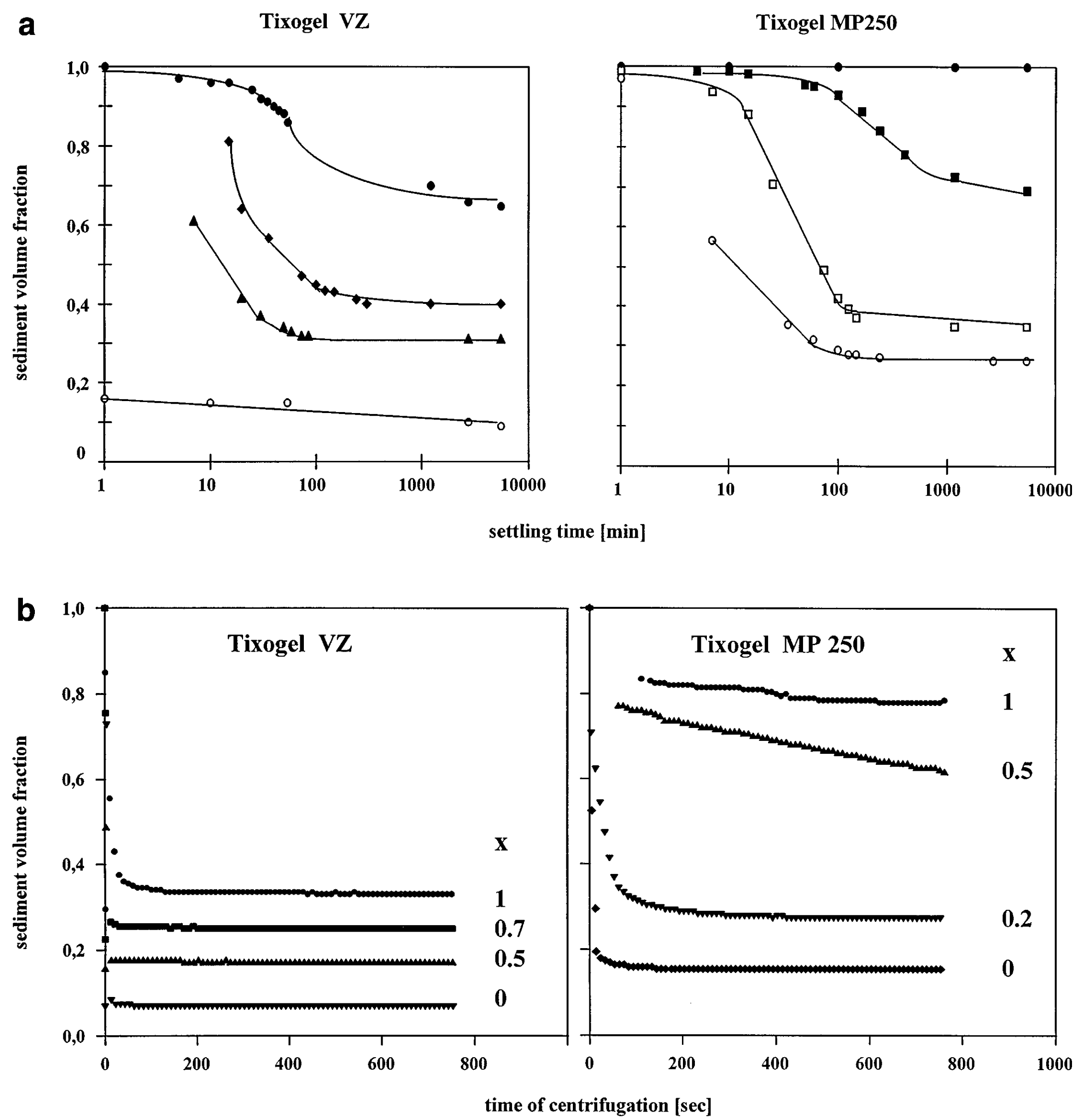


Fig. 2 a Sedimentation of organoclay dispersions at 1*g* – influence of solvent composition. $x = 0$ (○); $x = 0.1$ (□); $x = 0.3$ (■); $x = 0.5$ (▲); $x = 0.7$ (◆); $x = 1$ (●). **b** Sedimentation of organoclay dispersions at 73*g* – influence of solvent composition

solvent mixture. Dispersed platelets partly form edge-to-face aggregate network structures. The extent of the formation of these structures will increase with the degree of disaggregation, i.e. with toluene content and the presence of an activator. As under practical circumstances, water molecules play a substantial role in the stabilization of a network structure by hydrogen-bond formation between silanol groups of different platelets or platelet aggregates. The amount of water in the system increases with toluene content. Finally, interlamellar swelling is enhanced in the presence of additional surfactant and is far more pronounced for aromatic solvents compared to nonpolar hydrocarbons [10, 11].

The settling curves obtained with the LUMiFuge (73*g*, 750 rpm) depicted as the time course of sediment volume fraction gave similar results (Fig. 2b). The higher centrifugal acceleration leeds to a higher compaction of the sediment. It is obvious that these measurements provide a far faster characterization of the settling and swelling behavior. Moreover, additional information can be obtained. Especially, direct evaluation of the transmission profiles (transmission along the sample length) gives further insight.

Temporary profiles of dispersions of Tixogel MP 250 for $x = 1$, 0.7, 0.5 and 0.3 (after 10 s at 73*g*) are compared in Fig. 3. With increasing weight fraction of toluene the brightness of the samples is enhanced by gel formation. The time dependence of the transmission profiles of dispersions ($x = 1$, 0.7, 0.5) are depicted in Fig. 4. In the case of $x = 0.5$, but also for dispersions with $x < 0.5$ (results not shown), sedimentation is

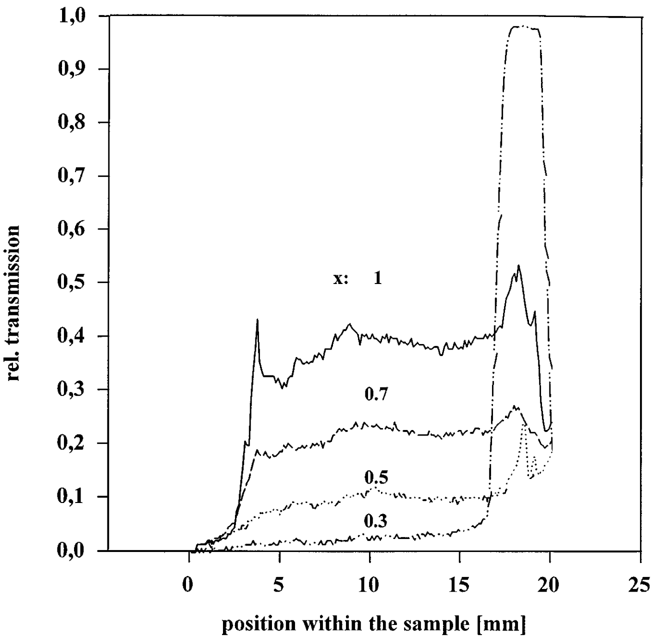
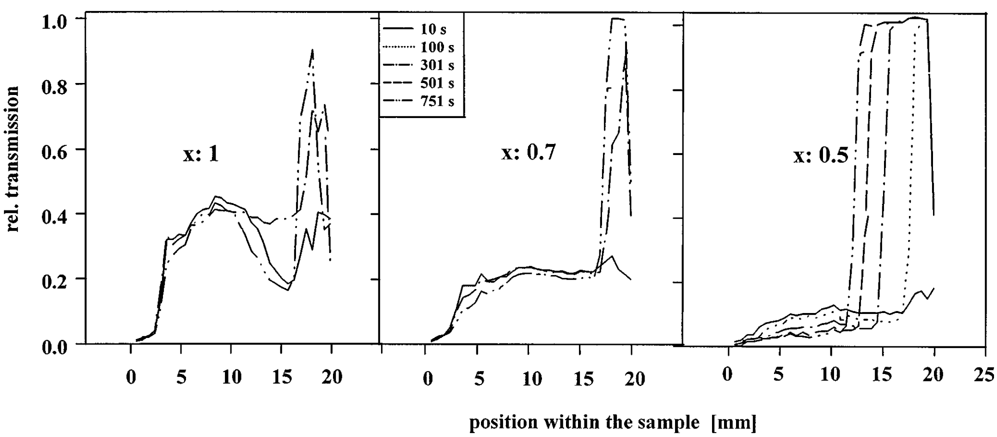


Fig. 3 Influence of solvent composition on transmission profiles of dispersions of Tixogel MP 250 (0 mm corresponds to the bottom, 20 mm to the top)

characterized by steep transmission profiles, indicating the pronounced compaction of a more or less loose network of swollen clay particles. In the case of $x = 1$, and 0.7 only a gradual clearing up of the top layer could be observed.

The LUMiFuge 114 separation analyzer also allows the behavior to be studied at alternating centrifugal acceleration. The time course of the compression and decompression cycles after reaching a final sediment volume at 73*g* is shown in Fig. 5. As expected, the alteration of sediment height is proportional to the final sediment volume of precompression, i.e. no (Tixogel VZ) or only a very small (Tixogel MP250) alteration could be detected at $x = 0$. Interestingly, over a wide range of solvent compositions full reversibility of compression was observed, indicating the elastic behav-

Fig. 4 Time dependence of transmission profiles of dispersions of Tixogel MP 250 at 73*g*



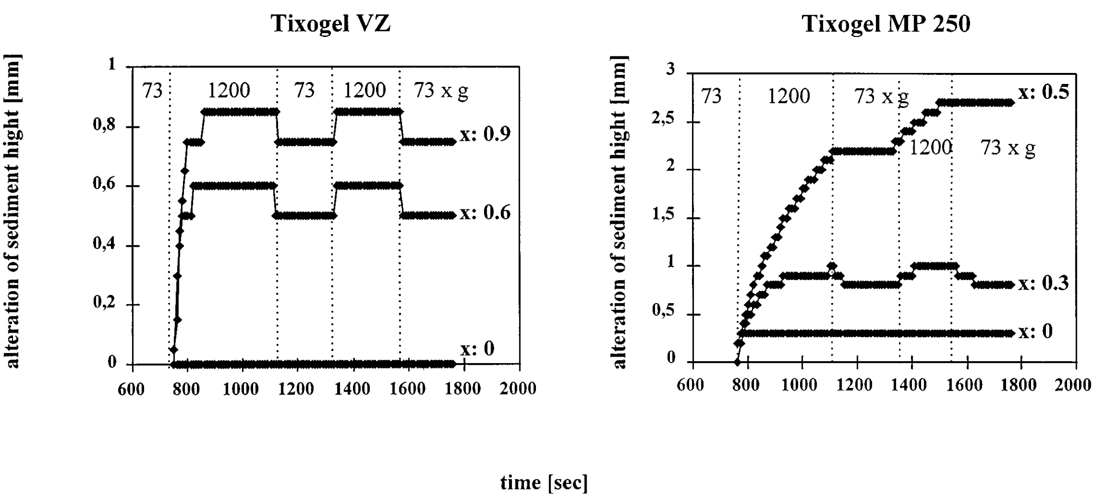


Fig. 5 Time course of compression and decompression cycles after settling at 73*g*

ior of such sediments; however, at high toluene content ($x \geq 0.5$) the compaction process of Tixogel MP 250 gels continues at higher centrifugal acceleration but no decompression could be obtained by lowering the centrifugal force.

The results may be discussed as follows. To change the interlayer swelling state high centrifugal forces have to be applied [1]; therefore, only the space in-between the network of swollen clay particles is compressed further by increasing the centrifugal acceleration to 1200*g*. In response to increasing compression, the free liquid around the dispersed aggregates is squeezed out of the sediment. Except for the Tixogel MP 250 dispersions at a toluene content of $x \geq 0.5$, this compression is reversible, i.e. under a reduced centrifugal field the network expands and solvent is taken up again. In other words, the distance between different aggregates and individual platelets is changed, but the network structure is maintained without alteration. At a toluene content of $x \geq 0.5$ Tixogel MP 250 dispersions form a very loose network which corresponds with the very high degree of swelling. During compaction parts of this network are broken down, whereby closer packing of aggregates is obtained.

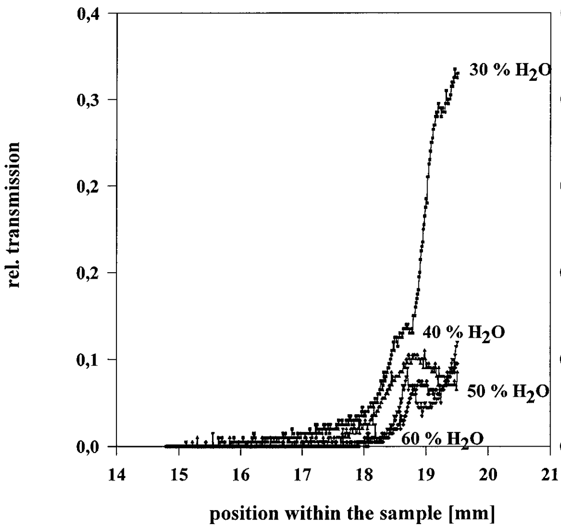


Fig. 6 Transmission profiles of emulsions stabilized with Tixogel MP 250 (top layer, after 15 h at 1200*g*)

Investigation of emulsion stability

The formation of stable emulsions of plant oils is far more problematic than in the case of mineral oils. For the stabilization of such emulsions the application of clay minerals with good swelling properties is promising. It is commonly supposed that hydrophilic clay minerals, which swell in water, will stabilize oil-in-water (o/w) emulsions, whereas organoclays, which swell in organic solvents, will stabilize water-in-oil (w/o) emulsions.

Emulsions stabilized with Tixogel MP 250 formed stable w/o emulsions in the range up to 60 wt% water; however, spontaneous creaming occurred at 70 wt% water. The differences in the stability of the emulsions

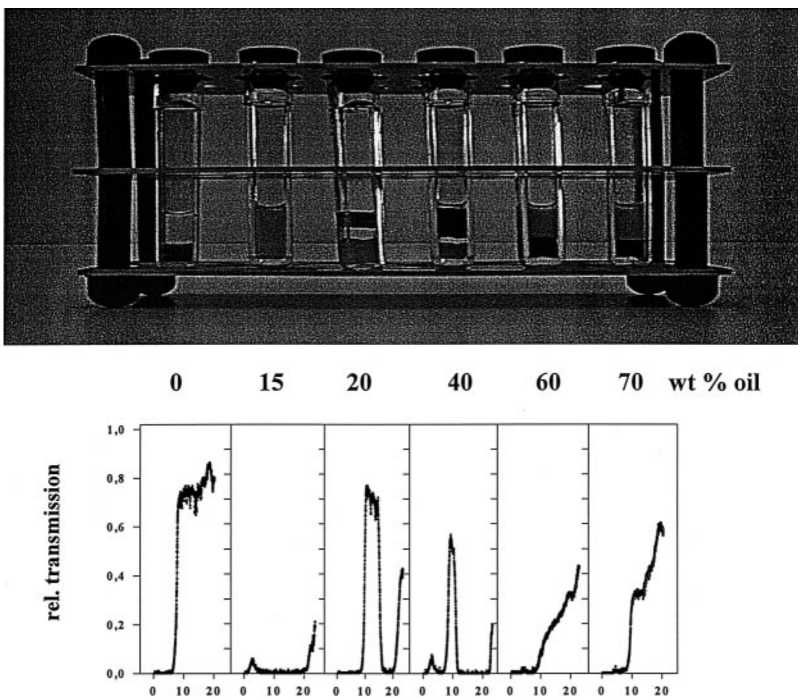


Fig. 7 Emulsions stabilized with Optigel CK (transmission profiles after 2 h at 1200*g*)

could be traced with the separation analyzer despite no visual changes occurring upon the emulsions standing (at 1*g*) over a period of several months. The transmission profiles are compared after 15 h of centrifugation at 1200*g* in Fig. 6. Only the values of the top layer (overall sample length 20 mm) are presented. In the top zone of about 0.5–1 mm a clearing up, i.e. separation of an oil phase, takes place. The stability is enhanced by increasing the water content in the range 30–60 wt% water. The overall results prove the high emulsion stability of the corresponding w/o emulsions.

The emulsions stabilized with Optigel CK (15–70 wt% castor oil) were less stable. Upon the emulsions standing over a period of several days, oil or water separated. The transmission profiles obtained after 2 h at 1200*g* are displayed in Fig. 7 as a function of oil content. For comparison a sample of the corresponding Optigel CK dispersion without oil is also shown. The sections of profiles with high transmission values have clear liquid phases; however, the transmission in the region of the oil phases is lowered by the higher optical density of the oil. Different regions of transparency could be observed. The dispersion without oil separated into a clear aqueous phase and a swollen sediment. On adding 15 wt% oil the separation stability of the aqueous clay dispersion is enhanced considerably. In the range 20–40 wt% oil centrifugation resulted in a settled clay layer, an aqueous phase, a w/o emulsion and an oil phase, whereas at 60 and 70 wt% oil content only two regions, i.e. oil and swollen clay sediment, formed.

As documented in the upper part of Fig. 7 the transmission profiles reflect the distribution of different phases, i.e. the transmission profiles can be used to evaluate the relative amount of layers separated.

Conclusions

A novel type of separation analyzer – the LUMiFuge 114 – has been used for fast characterization of the sedimentation and swelling behavior of organoclays in binary solvent mixtures (toluene/cyclohexane) as well as for stability evaluation of o/w and w/o emulsions stabilized by clay derivatives.

The automatic measuring system is based on a special centrifuge with an integrated optoelectronic sensor system which allows the measuring of spatial and temporal changes of light transmission during the rotation at a predefined centrifugal acceleration (12–1200*g*).

Besides fast and reproducible measurements of settling behavior and stability, the new technique provided additional information on the heterogenity of the separation process, the sample transparency and the elastic behavior of the sediment as a function of alternating centrifugal force.

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