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Influence of solids (crud) on the separation of liquid two-phase systems

ABSTRACT

Batch-settling experiments have been conducted to investigate the cause for crud formation in an industrial system of a solvent extraction process. Particles cause the stabilisation of crud in such a system. A well-established batch-settling cell, which can be applied to design gravity settlers, is used for the experiments. To show the applicability of the experimental setup, the effects occurring in the industrial system have been reproduced using the model system methyl isobutyl ketone (MiBK) + water + Aerosil 200. Factors influencing the formation and stabilisation of crud, like the amount of particles in the system and the dispersion direction, were investigated in the model and the industrial system. The strong influence that trace impurities can have upon the formation of crud is demonstrated. It is shown how batch-settling experiments can be used to support a basic understanding about the stabilisation of dispersions by solid particles and as a practical approach to test the possible methods to treat and avoid crud formation. This experimental setup is the basis of a heuristic approach to deal with crud problems in solvent extraction. The heuristic supports the systematic solution of crud problems in industrial solvent extraction processes.

INTRODUCTION

In liquid-liquid separation processes, a phenomenon occurs that is commonly known as crud. Crud is a stable dispersion layer that forms in most cases at the interface and has in the past been attributed to the presence of small solid particles [1]. The underlying mechanisms of the stabilisation of dispersion droplets by small solid particles have been extensively studied [2]. The stabilisation is in general attributed to the adsorption of the particles at the interface between drops of the disperse phase and the surrounding continuous phase. Depending on the application, a stable dispersion consisting of two liquid phases and small solid particles is a desired product, for example in cosmetics. Therefore research activity in this field often focuses on factors leading to more stable dispersions. A key concept to explain and understand stabilisation is the wetting behaviour of the particles as expressed by Young's equation:

$$\sigma_{ow} \cos \theta = \sigma_{sd} - \sigma_{sc} \quad (1)$$

Where σ_{ow} is the oil-water interfacial tension, σ_{sd} and σ_{sc} are the interfacial tensions between the solid and the dispersed and the solid and the continuous phase, respectively, and θ is the contact angle. Other research activities dealing with solids at interfaces focus on the measurement of the rheological properties of the particle laden interfaces in order to explain the stabilisation of dispersion by particles [3]. The partition and the structure of the particles at a liquid-liquid interface is another factor contributing to the stabilisation of the droplets. In the field of emulsion science and physical chemistry, these concepts and ideas are widely known.

In order to deal with crud problems in industrial processes, a more practical approach is needed, as the determination of contact angles and rheological properties of the interfaces require sophisticated measurement techniques that are difficult to handle, especially in industrial systems. The aim of the current research activities is the development of a physically based understanding of particle-induced crud formation and to establish suitable batch-settling experiments [4]. This experimental setup is used to characterise the settling behaviour of liquid-liquid systems and to design horizontal gravity settlers [5]. The applicability of the batch-settling experiments is extended to the investigation of crud formation in industrial processes. Based upon this, a heuristic approach for the treatment of crud problems in solvent extraction will be deduced.

METHODOLOGY

Materials

Water was passed through a deionising unit first and then distilled twice. MiBK of purity greater than 99% and sodium chloride were purchased from Merck KGaA, Darmstadt, and used as received. Hydrophilic silica particles (Aerosil 200) were supplied by Evonik Degussa. The industrial system was supplied by BASF. It consists of a heavy organic phase, an intermediate crud layer and a light aqueous phase as shown in **Figure 1**. The physical properties of the industrial system at 35 °C are given in **Table 1**.

Table 1 Properties of the industrial system at 35 °C

Property	Organic phase	Aqueous phase
Density	1.178 g/cm ³	1.009 g/cm ³
Viscosity	7.6 mPas	0.79 mPas
Interfacial tension	3.4 mN/m	

Methods

Batch-settling experiments were conducted in pure liquid-liquid systems and in systems containing solid particles. The settling cell that was used in all experiments is shown in Figure 1 and described in detail in [5].

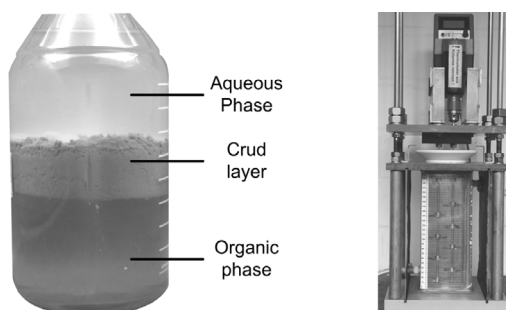


Figure 1 Industrial system with crud (left) and batch-settling cell (right) [5]

The two phases are filled into the glass cylinder to a total height of 210 mm. The agitator consists of two counter-rotating shafts, each bearing four stirrers with inclined stirrer blades. The top of the glass cylinder is closed by a PTFE-cover. The two phases are saturated by stirring the system for 5 minutes at 800 rpm. The dispersion for the settling experiments is created by stirring at 800 rpm for 30 seconds. After the stirrer is turned off, the dispersion starts to settle. The principle result of the experiment is shown in **Figure 2**. Two distinct processes lead to the separation of the system. First, the droplets settle due to buoyancy forces. Second, the drops coalesce and form a coherent phase. The sedimentation and the coalescence interfaces are visible as distinct lines in the experiment. The separation process is recorded by a video camera and the sedimentation and the coalescence curve are evaluated as a function of time. The settling experiment ends when 50% of the interface between the formerly dispersed and the continuous phase remain covered by a single layer of droplets. This time t_E is defined as settling time. Before solid particles are added to the system, the settling time for the liquid-liquid system is measured three times to assure that the system and the experimental setup are clean.

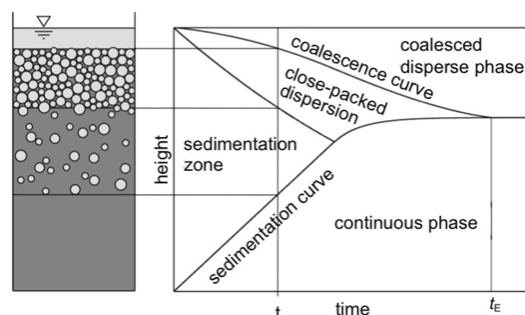


Figure 2 Batch-settling experiment and heights of the sedimentation and the coalescence interface

The method of adding the solid particles differs for the model system and the industrial system. For the model-crud system a 60 ml sample of the aqueous phase is taken from the cell. The desired amount of solid particles is added to that sample and the particles are dispersed using an IKA Ultra Turrax T18 equipped with an 18 mm head, at 10 000 rpm for 3 minutes. The particle suspension is then added to the liquid in the settling cell. The dispersion with particles present is then produced by stirring at 800 rpm for 20 minutes. For the industrial system, the particles are weighed and added directly to the liquid in the cell without being dispersed before. The dispersion is then produced by stirring at 800 rpm for 20 minutes. The experiments are recorded for 60 min if crud is formed. The accuracy of the measured crud height and the sedimentation and coalescence lines is ± 2.5 mm.

RESULTS AND DISCUSSION

The liquid phases of the industrial system have been separated from the crud phase and investigated in the batch-settling cell. For a phase ratio of organic to aqueous phase of 5:1, the settling time of the industrial system is 49 s. The aqueous phase is dispersed. The solids previously removed by centrifugation, were then added stepwise and the separation behaviour was again observed in order to investigate the effects on the formation of the crud layer. The liquid system without solids separates completely and does not form crud. Addition of the solids leads to incomplete phase separation and the formation of a crud layer. **Figure 3** shows the height of the stable dispersion layer as a function of the solid load of the dispersed phase. The results in **Figure 3** show that increasing the solid load of the system increases the amount of crud that is formed. The results prove that solid particles induce the formation of a stable crud layer in this industrial system. One can see from **Figure 3** that the same solid load of the dispersed phase leads to a smaller amount of crud, if the aqueous phase is dispersed.

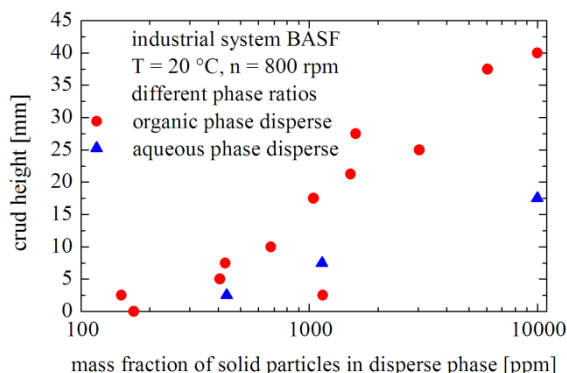


Figure 3 Crud height as a function of solid content of the dispersed phase in the industrial system

In order to derive a physically founded heuristic for the treatment of crud problems, the factors influencing the formation and stabilisation of crud were investigated in the model system MiBK + water + Aerosil 200 using the batch-settling setup. A model system was chosen for it can be characterised more easily and industrial systems are usually not produced with reproducible composition. The organic phase was dispersed and the settling time of the system is 11 s. As was expected, the system separates completely. Addition of Aerosil 200 particles leads to the formation of a stable dispersion layer at the interface, comparable to the results in the industrial system. **Figure 4** shows the height of crud measured for the case that the organic phase is dispersed as a function of the concentration of solid particles in the dispersed phase.

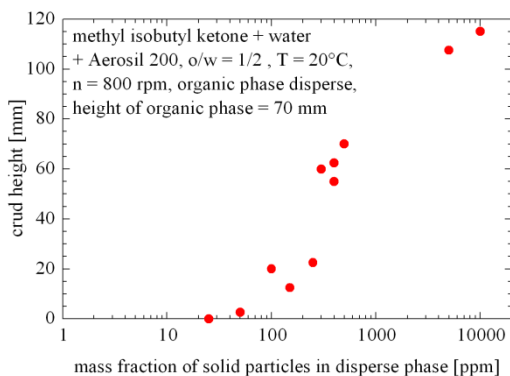


Figure 4 Crud height as a function of solid content in MiBK + water + Aerosil 200

From **Figure 4** one can see that increasing the amount of solids in the system increases the amount of crud that is stabilised. Furthermore, the results show that a small amount of particles in the system up to roughly 12 ppm, does not lead to crud formation. In both systems, the industrial system from BASF and the model system, particles induce crud. Thus, the model system is used as a characteristic system for crud formation to systematically study influencing factors.

A factor that is known to influence the phase separation of liquid-liquid systems is the presence of electrolytes. NaCl was added to the methyl isobutyl ketone + water system and the phase separation was observed. The settling time increases with increasing salt concentration up to 800 mmol l⁻¹. No significant change in settling time can be observed below a concentration of 1 mmol l⁻¹. In order to investigate the influence of electrolytes on the crud formation, NaCl was added to MiBK + water + Aerosil 200. **Figure 5** shows the amount of crud that is formed as a function of the amount of sodium chloride that was added to the aqueous phase. Without any added sodium chloride, the resulting crud height in the experiment is 12.5 mm. The solid load is 150 ppm. Stepwise addition of up to 0.21 mmol NaCl/l aqueous phase results in a six-fold increase in crud formation. The initial height of the organic phase in this experiment was 70 mm. The addition of 1 mmol l⁻¹ NaCl does not affect the settling time, while the crud formation is strongly influenced. This increase of crud that is formed upon the addition of an electrolyte indicates that electrostatic effects play a major role in crud formation in the model system. These results indicate furthermore that batch-settling experiments in solid contaminated systems are more sensitive to trace impurities than pure liquid-liquid systems.

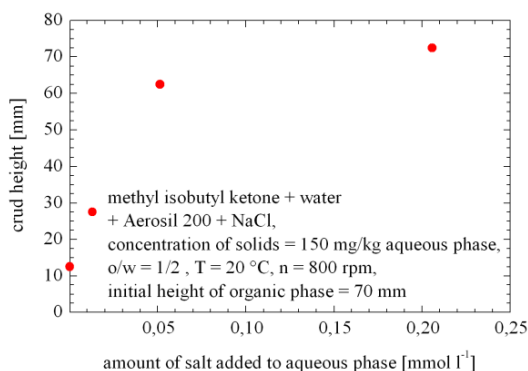


Figure 5 Crud height as a function of added electrolyte in MiBK + water + Aerosil 200

The high sensitivity to trace impurities and the ability to form particle induced crud make the batch-settling setup a beneficial method to investigate crud problems in solvent-extraction processes. A heuristic approach has been developed which is based on the batch-settling experiments. The general structure is shown in **Figure 6**. The starting point of the heuristics is a system comparable to the industrial system shown in **Figure 1**. The kind of system that can be treated with the methods described in this paper consists of three phases: two immiscible liquid phases and a crud phase. First, the crud phase must be separated from the two liquids. The liquid phases are then filtered to remove any solid particles. The solid constituents of the crud layer can often be separated by centrifugation and analysed to identify chemical elements constituting the particles. The separation behaviour of the liquid-liquid system is characterised by performing the described batch-settling experiments. Both directions of dispersion should be investigated. If a complete phase separation can be observed, it can be concluded that the removal of the crud layer suppresses the formation of a new crud phase. The solid constituents of the crud layer are

then added to system. Again, the phase separation is characterised by performing the batch-settling experiment. If the system forms crud upon the addition of the solid particles, these are clearly the cause for the crud formation in the system. Otherwise, other constituents of the crud phase are responsible for the crud formation. For particle-induced crud, the batch-settling experiments can be used to investigate influencing factors, like dispersion direction or presence of other contaminants like electrolytes or surfactants on the crud formation in order to develop methods to treat crud in the solvent extraction process. A possible method to decrease the formation of crud in the industrial system found in this work is the choice of the aqueous phase as the disperse phase, as can be seen in **Figure 3**.

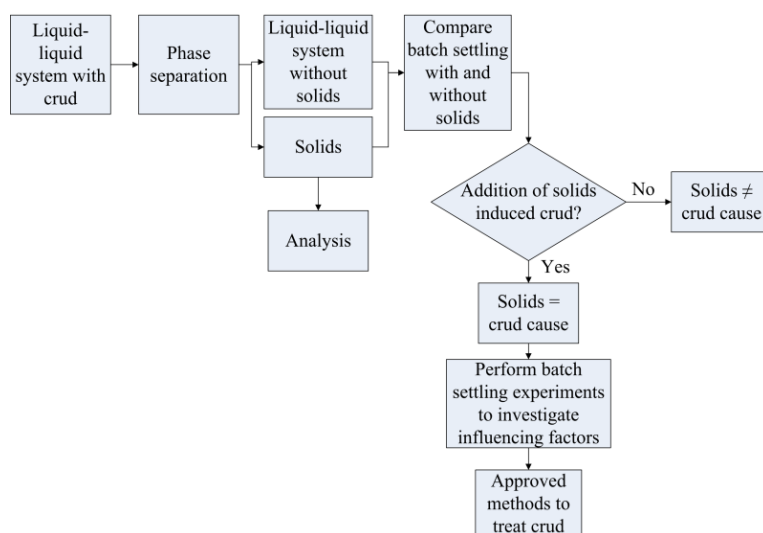


Figure 6 Structure of the heuristic approach for the treatment of crud in solvent extraction

CONCLUSION

Experimental results with an industrial crud system from a solvent extraction process prove that solid particles are the cause of the crud formation in this system. Batch-settling experiments can be used to investigate influencing factors on crud formation, e.g., dispersion direction or amount of solids in the system. The experiments conducted in a model system show that model crud can be produced by adding solid particles of hydrophilic silica to methyl isobutyl ketone + water. Particle contaminated systems have a significantly higher sensibility to traces of salt than pure liquid-liquid systems. The influence of the electrolyte can be quantified using batch-settling experiments. Based on this experimental setup, a heuristic approach can be followed to identify solids as crud cause and to investigate possible methods to avoid and treat crud problems in solvent extraction.

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