

Barium sulfate precipitation as model reaction for segregation studies at pilot scale

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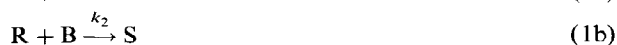
Abstract

The precipitation of barium sulfate from a basic EDTA-complex upon addition of a small volume of acid in a stirred tank reactor has been used as a model reaction to study the local state of micromixing. Limitations and modifications of this reaction are presented here and its application on an industrial pilot scale is realized. A higher reaction rate is used in order to decrease the reaction time using different concentrations of reactants which modify the stability of the precipitate. A study of this stability is presented here.

Introduction

Micromixing can be defined as the contact and mixing of fluids at the molecular scale. The characterization and understanding of these phenomena are of special importance for industrial processes: micromixing may control the yield and selectivity of chemical reactors in which mixing and reactions occur simultaneously with comparable rates. Examples are polymerisation in high viscous medium, precipitation or fast combustions.

To characterize segregation in homogeneous systems several authors [1–3] propose consecutive competing reactions. The reactants are fed separately into the reactor in order to create initially high concentration gradients. The first reaction forming the intermediate product should be fast compared to the second one, which has a rate comparable to the micromixing process.



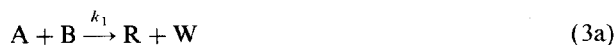
$$k_1 \gg k_2, \quad (n_{A0} > n_{B0})$$

If a limited amount of B (n_{B0}) is added to an excess of A (n_{A0}), the intermediate R is immediately formed and B is totally consumed at the end of the reaction. Under ideal micromixing conditions, the formation of S is

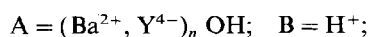
quite insignificant owing to the instantaneous dispersion of B and its stoichiometric deficit. On the contrary, if the fluid is partially segregated, B is locally in stoichiometric excess in contact with R which is thus converted to the final product S. Therefore, the amount of S formed is a measure of the degree of segregation. For the practical use of a model reaction, a trace of the history of mixing must be kept in the system in form of the stable end product. In this way the system retains a memory of the micromixing process which takes place during the lifetime of segregated eddies. As proposed by Bourne *et al.* [4, 5], the yield of S may be considered as a segregation index for the system:

$$X_s = \frac{2C_s}{(2C_s + C_R)} \quad (2)$$

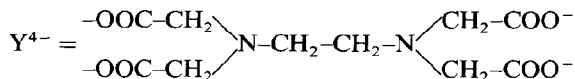
Besides the well studied azo-coupling of 1-naphthol with diazotised sulfanilic acid [1, 6], the precipitation of barium sulfate (S) from a basic EDTA-complex (A) under the influence of acid (B) has been proposed by Barthole *et al.* [2] and Villermaux [7]. The reaction scheme can be summarized as follows [3, 8]



with



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The alkaline solution is prepared using BaCl_2 , NaOH , Na_2SO_4 , and the sodium salt of EDTA. Protons are added in the form of a dilute (0.1N) HCl solution.

To use the proposed model reaction for different mixing devices and varying micromixing time (t_m), the characteristic reaction time (t_r) has to be modified to get $t_r \approx t_m$. Barthole *et al.* [2, 10] studied the reaction under defined experimental conditions, giving a characteristic reaction time of approximately $t_r = 3$ s [9], thus limiting the use of the test reaction to mixers with mixing times in the same order of magnitude. The present study will focus on changing reactant concentrations in order to decrease t_r . The upper limit, due to instabilities of the reactant solutions will be shown. Finally local micromixing intensities were measured in an industrial pilot reactor of 0.160 m^3 volume for various mixer types.

Kinetics of the model reaction

The first step of reaction 3 is a neutralization reaction and can be considered as instantaneous ($k_1 = 1.8 \times 10^8 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$, [3]) compared to the second one [3].

$$r_2 = k_2 C_R C_U \quad \text{with } k_2 = k_0 C_0^{2/3} \quad (4)$$

$$k_0 = 1.9 \times 10^{-2} \text{ m}^5 \text{ mol}^{-5/3} \text{ s}^{-1} \quad (5)$$

C_0 is the concentration of available sites for the crystallization of BaSO_4 :

$$C_0 = C_{S0} + \frac{1}{2}(nC_{A0} + nC_{U0} - |nC_{A0} - nC_{U0}|) \quad (6)$$

The characteristic reaction time is defined as

$$t_r = (k_0 C_{U0} C_0^{2/3})^{-1} \quad (7)$$

Thus the reaction time t_r can be adjusted to the actual mixing system by changing the concentration of Barium- and/or Sulfate-ions as shown in Fig. 1.

Unfortunately, a stoichiometric amount of EDTA is not sufficient to prevent BaSO_4 precipitation in the complex mixture even before adding protons. The prepared solutions become turbid and are no longer suitable for the segregation measurements.

On the contrary, if the chosen EDTA concentration is too high, the once precipitated BaSO_4 after injection of the acid is redissolved and the reaction system loses its memory.

Therefore a compromise has to be found in order to prevent precipitation and redissolution in a reasonable time interval needed for the experimental studies. This time interval was fixed to about one hour.

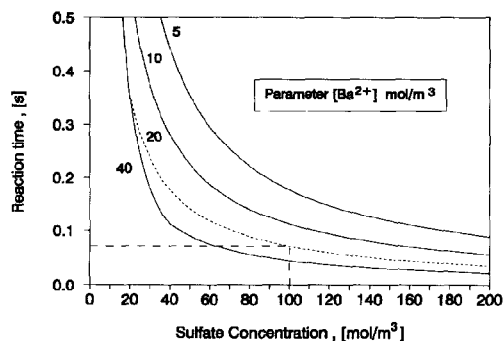


Fig. 1. Reaction time of the test reaction.

For the planned experiments a characteristic reaction time of $t_r \leq 0.1$ s was necessary. According to Fig. 1 the following concentrations were used:

$$[\text{Ba}^{2+}] = 20 \text{ mol m}^{-3}, \quad [\text{SO}_4^{2-}] = 100 \text{ mol m}^{-3}$$

Adding a small amount of HCl-solution induced BaSO_4 precipitation. The concentration of the precipitate was determined by light absorption in a spectrophotometer. In Fig. 2 the absorbance is shown as function of time for different concentrations of EDTA.

Three fields can be distinguished:

$[\text{EDTA}] < 38 \text{ mol m}^{-3}$ The absorbance is growing with the time, the precipitation is going on without any additional acid.

$38 < [\text{EDTA}] < 42 \text{ mol m}^{-3}$ The absorbance is quite constant, the maximal variation in one hour is 5%.

$[\text{EDTA}] > 42 \text{ mol m}^{-3}$ A large decrease in absorbance is measured signifying a redissolution of the precipitate.

As a consequence, the EDTA-concentration was fixed to 40 mol m^{-3} . This condition allows a sufficient stability of the suspensions formed and reproducible results for the segregation index (X_s).

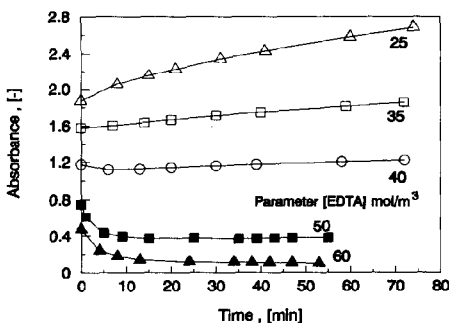


Fig. 2. Stability of the formed precipitate as a function of time.

For solutions with higher concentrations of Ba^{2+} and SO_4^{2-} satisfactory conditions for the test reaction could not be found. The minimal characteristic reaction time obtained for segregation measurement is therefore in the order of $t_r = 0.1$ s.

Experimental determination of segregation

The test reaction is used to study the segregation characteristic of a pilot plant stirred tank with a volume of $V_r = 0.160 \text{ m}^3$ equipped with two types of stirrer, an anchor and a three stages Intermig. The rotation speed can be varied between $N = 45\text{--}115$ and $N = 100\text{--}290$ RPM respectively.

The tank initially contains an aqueous Barium-EDTA solution under basic conditions and a small amount of barium sulfate crystals. This solution is prepared in a 2 m^3 tank (see Fig. 3, zone A). The experimental conditions are summarized in Table 1.

At a specified point in the tank a solution of 2 N hydrochloric acid is pumped for a limited time. The injection tube has an inner diameter of 2.5 mm. To be sure that the measured phenomena is due to micromixing, the injection time for the acid is varied in a broad range from 3–15 minutes. The flow rate is adapted to maintain the total amount of acid injected to 600 g. After the injection a sample of 250 ml is taken to determine the precipitated BaSO_4 by light absorption at a wave length of 650 nm. The absorbance measurement of the same sample is repeated about six times over a

time interval of 20 min to check the stability of the solution.

After an experiment the used solution is pumped to a precipitation tank to eliminate the barium sulfate as a solid waste. The EDTA containing solution is sent to the biological waste water treatment (Fig. 3, zone C).

Results and discussion

Typical segregation data are shown in Figs. 4 and 5 for the anchor stirrer at a stirrer speed of 45 rpm. The segregation index depends on the location of the injection point and varies from 1.9%–6.1%. The highest mixing intensity is on the upper point of the anchor. Injection of the reactant on the surface or in the lower parts of the reactor is less favourable.

As expected, the segregation depends strongly on the stirrer speed as shown in Fig. 6. For three different angles of $\beta = 123, 135$ and 180 the dependence of X_s as a function of the stirrer speed is represented. Similar results are obtained for the Intermig which can not be published. High mixing intensities are observed near the edge of the blade of the stirrer and just behind or before the baffles.

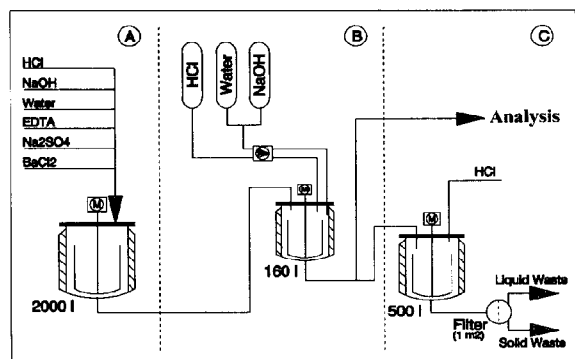


Fig. 3. Experimental set-up.

TABLE 1. Experimental conditions.

$[\text{Ba}^{2+}]_0 = 20 \text{ mol m}^{-3}$	$[\text{BaSO}_4]_0 = 10^{-4} \text{ mol m}^{-3}$
$[\text{EDTA}]_0 = 40 \text{ mol m}^{-3}$	$[\text{H}^+]_0 = 2\text{N}$
$[\text{SO}_4^{2-}]_0 = 100 \text{ mol m}^{-3}$	pH = 12
$t_r = 0.07 \text{ s}$	

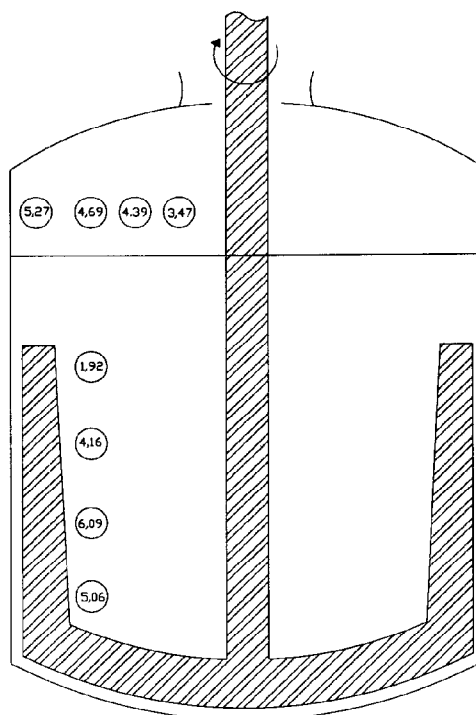


Fig. 4. Segregation index in % for the anchor stirrer at $N = 45$ rpm.

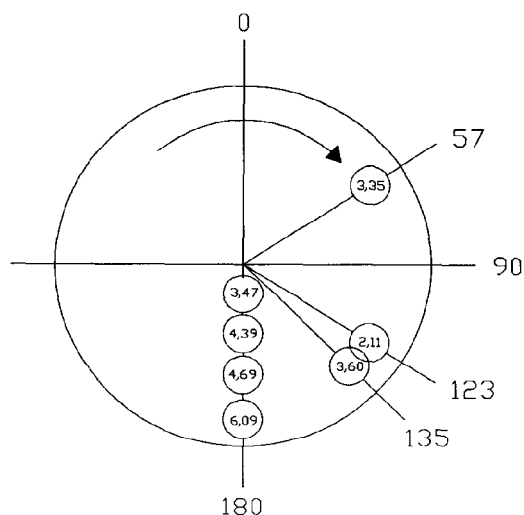


Fig. 5. Segregation index in % for the anchor stirrer at $N = 45$ rpm, horizontal plane. $\beta = 90$ corresponds to the position of the inner baffle.

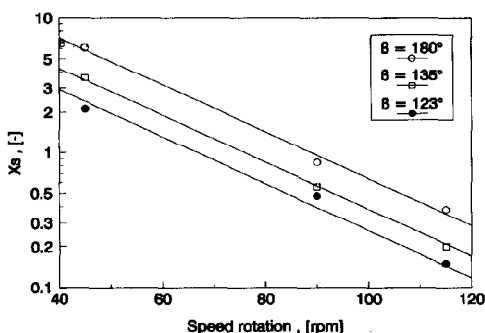


Fig. 6. Effect of the stirrer speed on the segregation index.

Conclusion

The precipitation of BaSO_4 in the presence of EDTA by adding an acid is a simple method for measuring local states of micromixing in a stirred tank. The great advantage of this method is the potential low cost of the products and the ease to measure the segregation index. Nevertheless, the limit of the test reactions is due to the stability of the basic sulfate solution at high concentration and to the redissolution of the crystals after precipitation. The goal of the present communica-

tion is therefore to show the extreme conditions and the shortest characteristic reaction time (0.07 s) obtained without experimental difficulties.

Nomenclature

ABS	absorbance
C	concentration, mol m^{-3}
k	reaction rate constant, variable dimension
l	length, m
n	stoichiometric coefficient
N	rotation speed, rpm
t_m	mixing time
t_r	reaction time
V	volume, m^3
X_s	segregation index
ε	extinction coefficient

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