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Catalytic reaction performed in the liquid–liquid system at batch and semibatch operating mode

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Abstract

Hydrolysis of the propionic anhydrite catalysed with sulphuric acid at batch and semibatch operating conditions has been investigated using the reaction calorimeter RC1 Mettler Toledo. Due to a limited solubility of the anhydrite in the aqueous phase where the reaction takes place, mass transfer with simultaneous chemical reaction has to be considered. Contributions of both phases to the reaction mixture change during the reaction progress, so that a complex, strongly non-linear behaviour of the reactor has been noticed. Influence of the concentration of the catalyst, the reaction temperature as well as the initial volume fraction of the organic phase in the reaction mixture and the stirrer speed on the overall conversion rate have been determined directly from calorimetric measurements. Some indications related to the safe and efficient performance of the investigated process as well as to a simplified experimental kinetic model have been formulated.

Keywords: Catalytic reaction; Liquid–liquid reaction; Reaction calorimeter

1. Introduction

Catalytic chemical reactions performed in heterogeneous liquid–liquid systems are frequently encountered in the industrial practice. Such systems include the well-known processes, e.g. such as aromatic nitrations in mixed acids, hydrolysis of organic compounds slightly soluble in water, etc. Elaboration of a trustworthy and universal model for these processes is of a great significance from the performance point of view. However, other aspects — e.g. those related to safe execution of these reactions — should also be taken into account. In particular, an elaboration of practical criteria to avoid runaway events and methods to minimise the amount of waste materials is very important.

Despite of the fact that reactions performed in the heterogeneous liquid–liquid systems have been carried out in practice for many years, a lot of problems related to the kinetics, reaction mechanisms, etc. remain still unsolved. In such liquid–liquid dispersions the chemical reactions and mass transfer phenomena occur simultaneously. Also determination of fluid properties and equilibrium expressions, indispensable to accurate characterisation of the processes, becomes rather a complex task. Additionally, for the fast reaction regime the overall conversion rate is affected by the interfacial area — i.e. by hydrodynamic conditions as well as by mechanical and geometrical characteristics of the equipment. Thus the dynamic behaviour of batch and semibatch reactors is difficult to predict, particularly for reactions with significant heat effect. Because of their complexity, modelling of such liquid–liquid reaction systems requires a great experimental, theoretical and computational effort.

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Nomenclature

a	interfacial area (m^2/m^3)
c	concentration (mol/m^3)
C_{PT}	total heat capacity (J/K)
d_{32}	Sauter diameter (m)
D_a	stirrer diameter (m)
D_A	diffusivity coefficient (m^2/s)
ΔH_A	reaction enthalpy (J/mol)
ΔH_T	total heat generated (J)
Ha	Hatta number, $Ha = \sqrt{k_2 c_W^{L2} D_A}/k_{L2}$ (–)
k_2	kinetic rate constant (m^3/mol s)
m	solubility (–)
m_i	mass of the ith reactant (kg)
n_A	number of moles (mol)
N	stirrer speed (s^{-1})
Q_R	power generated due to the reaction (W)
R_A	overall conversion rate (mol/s)
ΔT_{ad}	adiabatic temperature rise (K)
t	time (s)
x	molar fraction (–)
V_R	reactor content volume (m^3)
We	Weber number, $We = \rho_c N^2 D_a^3/\sigma$ (–)

Greek symbols

α_A	conversion of the anhydrite (–)
β	relative concentration of the propionic acid , $\beta = m_C/m_W$ (–)
ρ_c	density of the continuous phase (kg/m^3)
σ	interfacial tension (N/m)
φ_A	dosing rate (mol/s)
Φ	volumetric fraction of the organic phase (–)

Subscripts

acc	accumulation
A	anhydrite
C	propionic acid
i2	interface (aqueous side)
L1	organic phase
L2	aqueous phase
o	initial
w	water

In this paper detailed investigations of the hydrolysis of the propionic anhydrite catalysed with sulphuric acid have been carried out. All the experiments have been performed in an RC1 Mettler Toledo Reaction Calorimeter. An extensive experimental programme has been executed at isothermal and isoperibolic (at a constant temperature of the cooling liquid) conditions following batch or semibatch operating mode. The influence of conditions such as: the reactor temperature, the catalyst concentration, the initial volume fraction of the anhydrite in the reaction mixture, the stirrer speed and the dosing rate (for semibatch operating mode) on the reactor performance have been investigated.

2. Experimental

The hydrolysis reaction chosen for this study can be described by the following stoichometric equation:

$$A + H_2O \xrightarrow{H^+} 2C \tag{1}$$

where A is the propionic anhydrite ($C_2H_5COOCOC_2H_5$) and C the propionic acid (C_2H_5COOH), respectively. Because of the limited solubility of the anhydrite in the aqueous phase (being a mixture of water and propionic acid), at some conditions the reacting mixture forms a heterogeneous liquid–liquid system. Propionic anhydrite of a purity better than 97 wt.% supplied by Aldrich and the redistilled water have been used in experiments. The sulphuric acid having a concentration of 96–98 wt.%, supplied by Merck, has been used as a catalyst. In one experiment the propionic acid of a purity 99 wt.%, supplied by Aldrich, has been used instead of H_2SO_4 as a source of H^+ ions at the start of the reaction.

All experiments have been performed in an RC1 Mettler Toledo Reaction Calorimeter. A simplified diagram of this installation is shown in Fig. 1. The experimental runs have been carried out at the isothermal and isoperibolic (at a constant temperature of the cooling liquid) conditions following batch or semibatch operating mode, in the reactor having a total volume of 2 dm^3, equipped with four baffles and a downward propeller stirrer. All experiments performed as well as the main operating conditions are listed in Table 1.

Due to the use of the RC1 reaction calorimeter a performance of the accurate measurements of the reaction progress was possible, even at the fast reaction regime. For each experimental run the power generated due to the reaction progress, $Q_R(t)$, has been estimated from

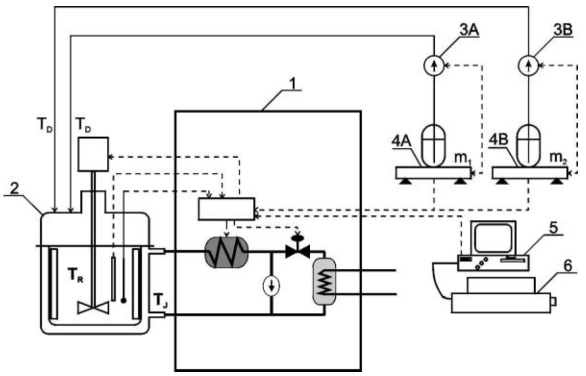

Fig. 1. Simplified schematic diagram of the RC1 Mettler Toledo Reaction Calorimeter. 1: Basic unit; 2: reactor; 3A and 3B: pumps; 4A and 4B: weights; 5: computer; 6: printer.

the reactor heat balance. Then the total heat generated during the process, ΔH_T, can be estimated as follows:

$$\Delta H_\mathrm{T} = \int_0^{t_\mathrm{R}} Q_\mathrm{R}\,\mathrm{d}t \tag{2}$$

where t_R is the total reaction time until the reaction is completed. Then, the heat of reaction (the reaction enthalpy) can be evaluated from:

$$\Delta H_\mathrm{A} = \frac{\Delta H_\mathrm{T}}{n_\mathrm{Ao}} \tag{3}$$

where n_Ao is the number of moles of the converted anhydrite.

Directly from the calorimetric measurements also the overall conversion rates of the anhydrite, R_A, have been estimated as

$$R_\mathrm{A} = \frac{Q_\mathrm{R}(t)}{\Delta H_\mathrm{A}} \tag{4}$$

while the conversion of the anhydrite is given by the following relationship:

$$\alpha_\mathrm{A}(t) = \frac{\int_0^t Q_\mathrm{R}(t)\,\mathrm{d}t}{\Delta H_\mathrm{T}} \tag{5}$$

Then, from the mass balance the molar content of anhydrite in the reactor can be calculated as a function of time, which reads for the semibatch operating mode as

$$n_\mathrm{A}(t) = \int_0^t \varphi_\mathrm{A}\,\mathrm{d}t - \int_0^t R_\mathrm{A}\,\mathrm{d}t \tag{6}$$

where φ_A is the molar dosing rate of the anhydrite. In the case of a constant dosing rate the first integral in Eq. (6) can be replaced by the product ($\varphi_\mathrm{A} t$). For a batch operating mode Eq. (6) is modified by replacing the first integral with the initial number of moles of the anhydrite in the reactor, n_Ao. The molar contents of the second substrate (water) as well as the product C

Table 1
Experiments performed and the main operating conditions

Run	Code[a]	T_R or T_J (°C)	N (s^{-1})	x_So (–)	Φ_o (–)	Dosing time (s)
R1	B-IT	40	10	0.0110	0.457	–
R2	B-IT	40	6.67	0.0110	0.457	–
R3	B-IT	40	13.33	0.0110	0.457	–
R4	SB-IT	40	10	0.0118	0	1000
R5	SB-IT	40	10	0.0118	0	2000
R6	B-IT	20	10	0.0110	0.457	–
R7	B-IT	40	10	0.0114	0.200	–
R8	B-IT	15	10	0.0110	0.457	–
R9	B-IT	40	10	0.0113	0.300	–
R10	B-IT	40	10	0.0112	0.380	–
R11	B-IP	40	10	0.0110	0.457	–
R12	B-IP	30	10	0.0110	0.457	–
R13	B-IT	40	10	0.0071	0.457	–
R14	SB-IT	40	10	0.0118	0	2000
R15	B-IT	40	10	0	0.444	–
R16	B-IT	40	10	0.0113	0.330	–
R17	B-IT	40	10	0.0219[b]	0.431	–

[a] B: batch, SB: semibatch, IT: isothermal, IP: isoperibolic.

[b] Propionic acid used instead of the sulphuric acid as an initial source of the ions H^+.

in the reactor have been estimated taking into account the overall stoichiometric equation of Eq. (1).

3. Results

A quite consistent value of the reaction enthalpy can be observed for all the performed experimental runs, while they are calculated following Eqs. (2) and (3), in spite of a large diversity of the operating conditions. The average reaction enthalpy $\Delta H_A = 53.35 \pm 1.66\,\mathrm{kJ/mol}$ has been determined from these measurements.

The overall conversion rate, the anhydrite conversion and the molar content of the anhydrite in the reactor measured at a batch operating mode are plotted in Fig. 2 as a function of the reaction time. The obtained results indicate that the reaction accelerates as it proceeds, until it is completed due to an exhaust of one of the substrates. It has been proved in the next section that this observed "autocatalytic effect" is apparent.

From the performed measurements (Runs R1–R3), it is observed that at the stirrer speeds $N \geq 10\,\mathrm{s}^{-1}$, practically no dependence of the overall conversion rate on this parameter is observed.

A distinct influence of the initial volume fraction of the anhydrite Φ_o, the reaction temperature T_R as well as the concentration of the catalyst (H_2SO_4) on the overall reaction rate R_A is visible in Figs. 3–5.

The experiments shown in Fig. 3 have been performed at the same total volume of the reaction mixture, following isothermal and batch operating conditions, hence if the value of Φ_o decreases, the amount of water in the reactor at the start of the process correspondingly increases. Because the studied reaction takes place in the aqueous phase the measured overall conversion rates of the anhydrite are the higher the lower is the Φ_o.

In Fig. 4 it is clearly visible that the rate R_A significantly increases as the reactor temperature increases.

An influence of the catalyst concentration shown in Fig. 5 is more complex. The conversion rate R_A increases with the increase of the concentration of the sulphuric acid. It has been checked that a replacement of the sulphuric acid by a chemically equivalent amount of the propionic acid accelerates the reaction, but the observed increase of the conversion rate is not so significant as for H_2SO_4 — compare in Fig. 5 lines at $x_{So} = 0.011$ and $x_{Co} = 0.022$, respectively. It means the sulphuric acid acts specifically in the investigated system, not only being simply a source of the H^+ ions.

The results obtained performing the process at semibatch conditions are shown in Fig. 6. During the semibatch experiments (Runs: R4 and R5) the anhydrite

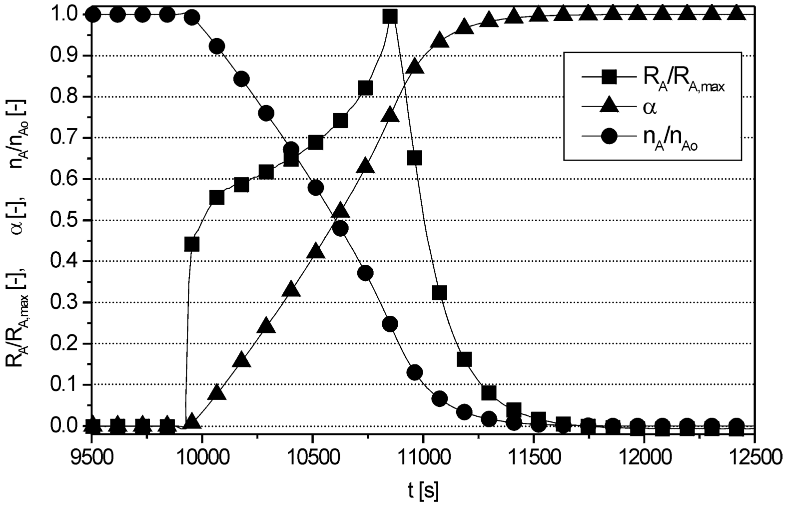

Fig. 2. The normalised overall conversion rate R_A, the anhydrite conversion α_A and the molar content of the anhydrite in the reactor n_A — Run: R15.

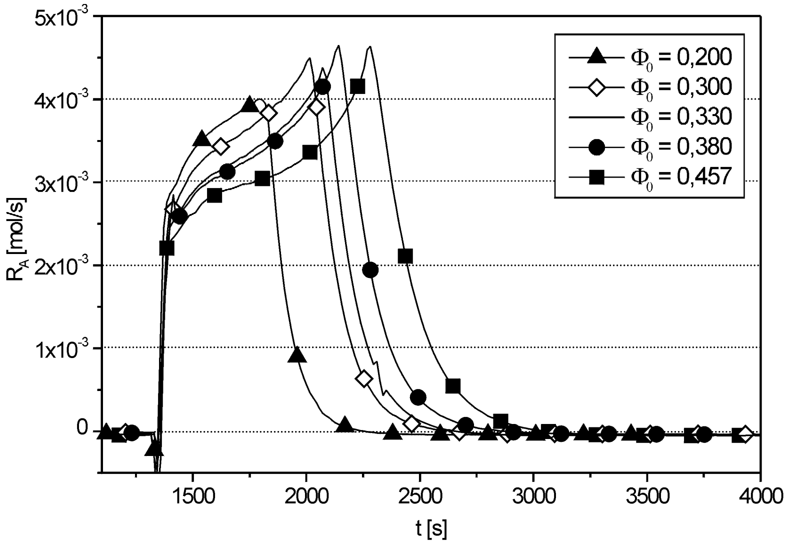

Fig. 3. Influence of the initial volume fraction of the organic phase Φ_o on the overall conversion rate R_A (T_R, x_{So} = const.) — Runs: R7, R9, R16, R10, R1.

(A) has been poured at a constant dosing rate, φ_A, into the reactor containing the solution of H_2SO_4 in water. Also an experiment with two dosing streams (R14), being the anhydrite and aqueous sulphuric acid solution, respectively, has been carried out. A comparison of the molar dosing rate and the overall conversion rate R_A for each run is shown in Fig. 6, so the accumulation of the unreacted anhydrite in the reactor could be determined as a function of time. Because the investigated hydrolysis reaction is strongly exothermic, accumulation of the anhydrite in some cases (e.g. damage of the cooling or mixing systems) can lead to loss of control and thermal runaway. Knowing the amount of the anhydrite accumulated in the reactor, $n_{A,acc}$, the

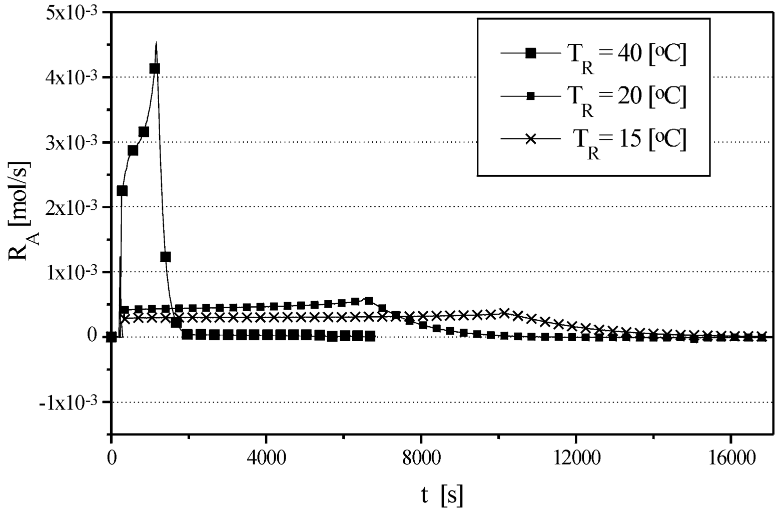

Fig. 4. Influence of the reactor temperature T_R on the overall conversion rate R_A — Runs: R1, R6, R8.

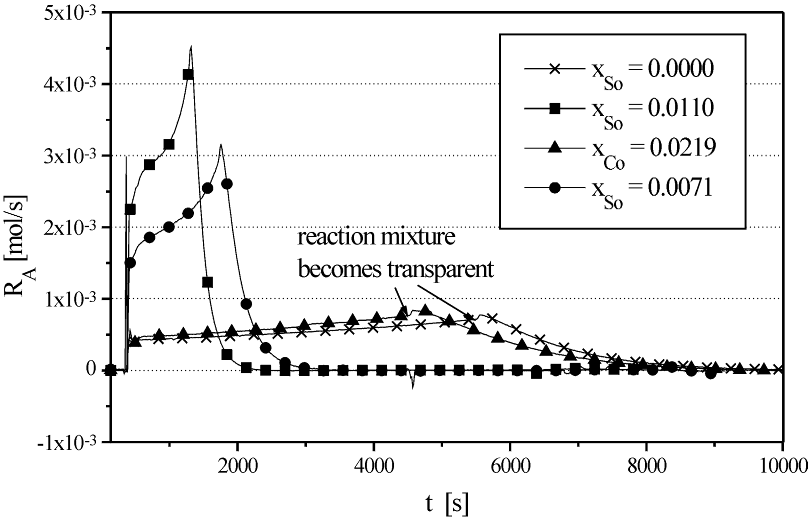

Fig. 5. Influence of the catalyst concentration x_{So} on the overall conversion rate R_{A} — Runs: R15, R13, R17 and R1.

adiabatic temperature rise at any moment of the process can be calculated as

$$\Delta T_{\mathrm{ad}} = \frac{n_{\mathrm{A,acc}} \Delta H_{\mathrm{A}}}{C_{\mathrm{PT}}} \tag{7}$$

where C_{PT} is the heat capacity of the reactor content. The presented analysis can be very helpful to determine safe and efficient operating conditions for the process performed at the semibatch mode.

Safe performance of a batch process can be investigated executing isoperibolic runs (performed at a constant temperature of the cooling liquid). Such conditions simulate a failure of the temperature control system, when the reactor is cooled by the liquid

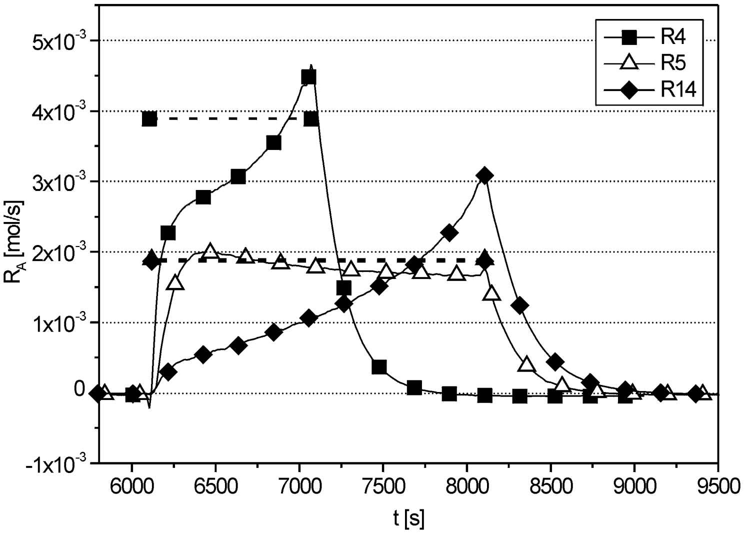

Fig. 6. The overall reaction rates R_{A} obtained at the semibatch conditions — Runs: R4, R5 and R14. Continuous lines: the experimental conversion rates; dashed lines: the appropriate dosing rates.

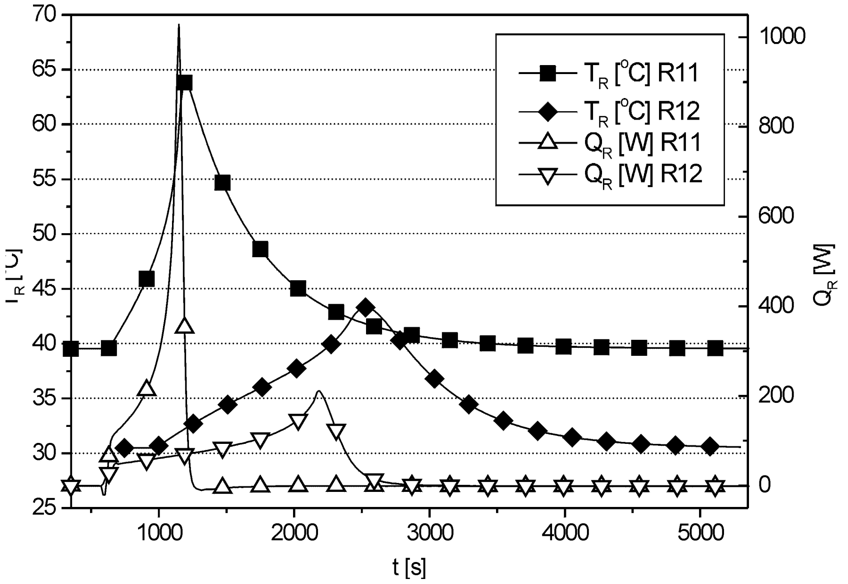

Fig. 7. Reactor temperature rise and the heat generated during batch and isoperibolic runs — R11 and R12.

taken from the emergency tank. The results obtained at batch and isoperibolic conditions (Runs R11 and R12 performed at two different temperatures of the cooling liquid) are shown in Fig. 7. A significant reactor temperature rise as well as the power generated due to acceleration of the reaction can be observed in this diagram. Depending on the temperature of the cooling liquid, safe and efficient operating conditions can be indicated from such kind of measurements.

4. Discussion

4.1. Mass transfer with simultaneous catalytic chemical reaction

Despite the fact that the investigated system can be described with a very simple overall stoichiometric reaction scheme, a detailed mechanism is quite complex and a few possible reaction pathways are considered in the literature, particularly for a process carried out at the presence of the catalyst (H_2SO_4) (e.g. see [1]). Anyway, even for the assumed mechanism a quantitative description of the reaction kinetics remains uncertain due to a specific influence of the catalyst on the overall conversion rate. Among others, for systems similar to the hydrolysis reaction a description of the catalyst transformation with the acidity function is proposed in the literature (see [2]).

In our previous work [3] neural networks has been successfully applied for fast modelling of the reaction kinetics and mass transfer. The hybrid first principle-neural network model, proposed in the cited paper, makes possible an effective prediction of the system behaviour without any prior knowledge about the reaction mechanisms and kinetics.

In this study some principal conclusions related to the mass transfer with simultaneous chemical reaction have been drawn from the performed calorimetric measurements.

The hydrolysis of propionic anhydrite occurs in the aqueous phase, therefore the anhydrite diffuses to the interface and then into the aqueous phase; at the same time in that phase it reacts. Since in the investigated system, the following assumption hold.

- mass transfer resistances in the organic phase can be neglected (this phase consists of pure propionic anhydrite only);
- no depletion of water is observed (because of its great excess; $c_{\mathrm{W}}^{\mathrm{L2}} \approx$ const.);

- the reaction is sufficiently fast to consume all A in the film ($Ha=\sqrt{k_2 c_{\mathrm{W}}^{\mathrm{L2}} D_{\mathrm{A}}}/k_{\mathrm{L2}} > 3$);

then, according to the general theory of mass transfer accompanied with a second-order chemical reaction (see [4]), the overall conversion rate of the anhydrite can be calculated as follows:

$$R_{\mathrm{A}} = c_{\mathrm{A}}^{\mathrm{i2}}\sqrt{k_2 c_{\mathrm{W}}^{\mathrm{L2}} D_{\mathrm{A}}}(aV_{\mathrm{R}}) \tag{8}$$

Eq. (8) demonstrates that for the runs performed at the isothermal and batch conditions, an increase of the conversion rate R_{A} during the progress of the process can result from: changes of the kinetic constant k_2 (which for the considered system contains also the influence of the catalyst concentration), changes of the solubility of the anhydrite in the aqueous phase, m (because $c_{\mathrm{A}}^{\mathrm{i2}} = mc_{\mathrm{A}}^{\mathrm{L1}}$) and changes of the contact surface area between the organic and the aqueous phases, aV_{R} during the singular run.

To check which of the listed parameters plays the most significant role, the following considerations have been carried out.

4.2. Influence of the contact surface area (aV_R)

Due to the limited solubility of the anhydrite in the aqueous phase and simultaneously good solubility of the reaction product in that phase, a contribution of the organic phase to the reaction mixture decreases significantly during the process performed at the batch and semibatch conditions. To estimate the interfacial area in the considered system the correlation obtained for the same geometry of the reactor and for a similar liquid–liquid system in the previous studies, see [5], has been adopted. The interfacial area has been estimated as a function of the volume fraction of the organic phase, according to the following relationship:

$$a = \frac{6\Phi}{d_{32}} \tag{9}$$

where the Sauter mean diameter of droplets has been calculated as

$$d_{32} = 0.0210\,(1+2\Phi)\,We^{-0.6} \tag{10}$$

Then the surface contact area, $F = aV_{\mathrm{R}}$, could be estimated at any time of the process taking the actual values of Φ. The experimental values of R_{A} divided by the product (aV_{R}) are plotted in Fig. 8 — see line 2. It is evident from the diagram that the conversion rate recalculated per unit of the surface contact area still increases during the reaction progress, so that other parameters also play a significant role.

4.3. Influence of the solubility of anhydrite, m

From the independently performed solubility measurements it has been found that the solubility of anhydrite in the aqueous phase strongly increases if a content of the propionic acid in this phase increases. The relationship obtained for the solubility of the anhydrite in the aqueous solution of the propionic acid reads as follows:

$$m = 0.02546 + 0.3406\beta^{1.751} \tag{11}$$

where $\beta = m_{\mathrm{C}}/m_{\mathrm{W}}$ is the concentration of the propionic acid expressed as the mass ratio (propionic acid to water).

Eq. (11) is valid for the water–propionic acid solutions only, because for solutions containing the sulphuric acid the reaction is too fast to be able to determine the solubility with a reasonable accuracy. So, as a first attempt it has been assumed that a presence of the sulphuric acid does not influence the solubility m.

The values of the expression $R_{\mathrm{A}}/C_{\mathrm{A}}^{\mathrm{i2}}(aV_{\mathrm{R}})$ plotted in Fig. 8 (line 3) as a function of the reaction time indicate, taking into account Eq. (8), that changes in the contact surface area as well as in the solubility does not fully compensate the increase of the anhydrite conversion rate observed during the reaction progress.

4.4. Influence of the kinetic constant, k_2

It is seen in Fig. 8 (line 3) that the expression $R_{\mathrm{A}}/c_{\mathrm{A}}^{\mathrm{i2}}(aV_{\mathrm{R}}) = \sqrt{k_2 c_{\mathrm{W}}^{\mathrm{L2}} D_{\mathrm{A}}}$ slightly changes during the reaction progress. Similar dependencies has been obtained for other experimental runs. It means that or during the presented analysis, all inaccuracies are lumped into the kinetic term $\sqrt{k_2 c_{\mathrm{W}}^{\mathrm{L2}} D_{\mathrm{A}}}$, either a complex or unknown contribution of the sulphuric acid and the propionic acid to this term is demonstrated. Notice that with the proposed approach the parameter k_2 is not strictly a kinetic constant, but an experimental process parameter describing the reaction kinetics. On the

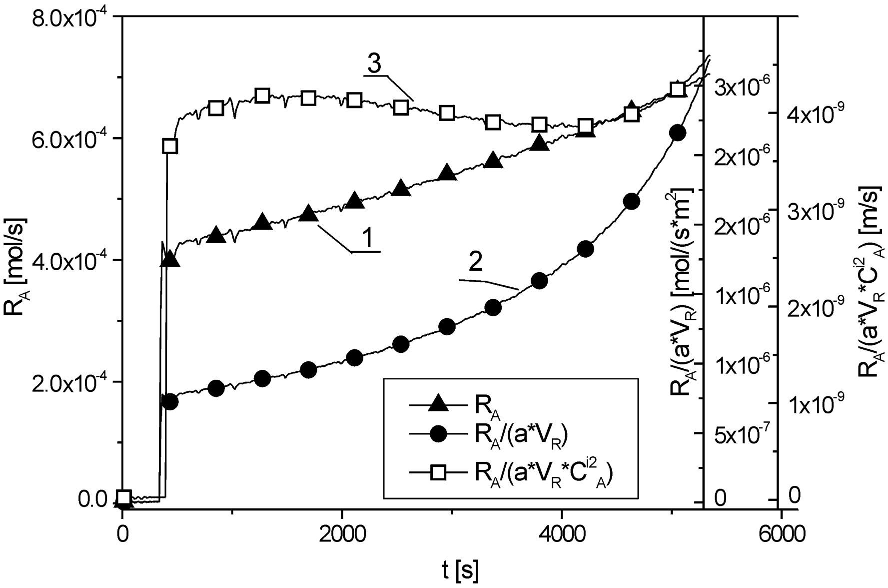

Fig. 8. The overall conversion rate as a function of the reaction time, R_A — line 1, that rate recalculated per unit of the contact surface area, R_A/aV_R, — line 2, the expression: $R_A/c_A^{i2}(aV_R)$ — line 3. Presented results are for Run R15.

basis of the performed calorimetric experiments, it was not possible to anticipate accurately the expression for k_2 in terms of the concentrations of the sulphuric acid and the propionic acid, respectively. Additional kinetic measurements, e.g. performed in a stirred cell with well-defined interfacial area, are needed.

5. Summary

The experimentally determined overall conversion rates for hydrolysis of the propionic anhydrite performed at different, batch and semibatch, operating conditions have been presented and discussed. Influence of process parameters such as: the reaction temperature, the concentration of the catalyst (sulphuric acid), the initial volume fraction of the organic phase have been investigated. Also the reactor performance at the batch and semibatch as well as at the isothermal and isoperibolic conditions has been discussed. Based on the general theory of mass transfer with simultaneous chemical reaction the expression for the overall conversion rate has been proposed. Analysis of the significance of such parameters as: the contact surface area, the solubility of the anhydrite in the organic phase and the kinetic constant has been performed. Some indications for further studies on the reaction kinetics have been formulated.

Acknowledgements

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