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EXTRAPOLATION OF LABORATORY REACTION KINETIC DATA FOR RELIEF VENT DESIGN IN THE CASE OF A HETEROGENEOUS RUNAWAY REACTION

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Abstract

The relief area sizing of safety devices in the case of a postulated thermal runaway condition requires reaction kinetic data, usually measured in dedicated adiabatic calorimeters. In the course of the design, it is then assumed that the same reaction kinetic data prevail on the laboratory and production scale. This assumption seems to be valid in the case of homogeneous reaction systems. In contrast to this the results of experiments with a heterogeneous system have shown that the stirring intensity and the reactor size have a considerable influence on the reaction progress.

Keywords: mixing, runaway reaction, scale-up

Introduction

In the course of the relief area design of safety devices on chemical reactors as a prerequisite, the reaction kinetic data under runaway conditions are needed. These include for example the self-heat rate which is used in the simplified stationary methods or the pre-exponential factor and the activation energy during the dynamic simulation of the pressure relief process. These data are generally measured in dedicated adiabatic reaction calorimeters. For the design of the large scale pressure relief device it is then generally assumed that the same reaction kinetic data in laboratory and production scale prevail. Only corrections for the heat losses and the heating of the thermally inert test vessel structure are taken into consideration [1].

In the case of homogeneous reaction systems, the reaction rate is only a function of the concentration of the agents and the temperature. Therefore, this kind of extrapolation of the reaction kinetic data is suitable during the design if the laboratory experiment has been carried out in a calorimeter test cell with a relative thermal inert mass similar to that of the large scale vessel. Indeed if the relative thermal inert mass of the calorimeter test cell is larger than that of the production vessel, a higher final temperature during the runaway reaction in the vessel can be attained than that measured in the calorimeter. So far also the extrapolation of the measured reaction kinetic data beyond the maximum measured temperature in the calorimeter is formally

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only valid for single exothermic reactions [2], where the decrease in concentration of the agent is directly related to the increase of the mixture temperature. Whereas for multiple reactions, which in practice are the norm, there is no such direct relation between the concentrations and the temperature. It is conceivable that other reactions may also occur at a temperature higher than that measured in the calorimeter. Therefore in this latter case, the straightforward extrapolation of the reaction kinetics may be questionable. In contrast to this, the reaction rate of heterogeneous reaction systems can be influenced by additional parameters. For example in situations where mass transfer is the conversion rate limiting reaction step, the reaction rate can depend on the size of the interfacial area. Further on, it is also possible that due to a deviating mixing intensity in the laboratory and production reactor, as in the case of an emulsion polymerisation system, different amounts of loci are existent in which the reaction takes place ultimately leading to discrepancies in measured reaction rates. Also, other volumetric reactant distributions in the reaction mixture can lead to different reaction rates. All these effects have in common that due to a different mixing quality during the laboratory test and later in the production unit, varied reaction rates are conceivable. In the end, this can result in an under- or overdesign of the necessary relief area when extrapolating the reaction kinetics.

The usual procedure in chemical process engineering is to derive the scaling rules by performing identical experiments in several plant sizes. In the case of the postulated thermal runaway reactions this is not practicable. In the literature, there are also no scaling rules for the reaction kinetics of heterogeneous runaway reactions included. In order to achieve a solution for this extrapolation problem, from a physical point of view, it is conceivable that as a basic condition besides of equal reaction starting conditions also an identical mixing quality in the laboratory and production reactor must (initially) be present. For the validation of this assumption, experiments in a small and large scale have been performed.

As an example of a heterogeneous liquid/liquid reaction system, the emulsion polymerisation of vinyl acetate has been selected. For preliminary investigations, the size of the specific interfacial area of the non-reacting vinyl acetate/water emulsion was characterised by stopping the agitation and measuring the time required for the initially homogeneously mixed emulsion to separate as a function of reactor size, applied stirrer speed for emulsion generation and stirrer type. In spite of the possibility to measure directly the drop size distribution with an image analysing system only in the smallest reactor, the indirect characterisation of the specific interfacial area size is indispensable because the determination of the drop size distribution in the large reactors is not possible with the usual devices available.

Based on these results it should be possible to develop a scaling rule for the specific interfacial area of reaction systems where the mass transfer limits the reaction rate and to propose a scale-up rule for the reaction kinetics for other heterogeneous reaction systems. For the validation, the reaction mixture temperature course of the runaway system has been measured as a function of the reactor size and the stirrer speed.

As a first step, the size of the interfacial area between the organic and the aqueous phase has been characterised in several reactor sizes by measuring the phase separation time.

Characterisation of the interfacial area size

The experiments on the self-adjusting interfacial area as a function of the stirrer speed have been performed in reactors with volumes of 10 and 100 litres and in an adiabatic calorimeter with a test cell volume of 0.1 litre, Fig. 1. Each reactor is equipped with a close-clearance anchor stirrer and with baffles placed in the reactor core. The reactors and the stirrers are geometrically similar, the ratio of the reactor height to diameter is about two. Normally, anchor stirrers are not suited to producing emulsions. Indeed, the determination of the anchor stirrer efficiency was not the objective of these examinations. Rather, the anchor stirrer has been selected due to the viscosity increase during the course of the runaway experiment, and therefore, to provide a sufficient mixing of the reaction system at a later stage.

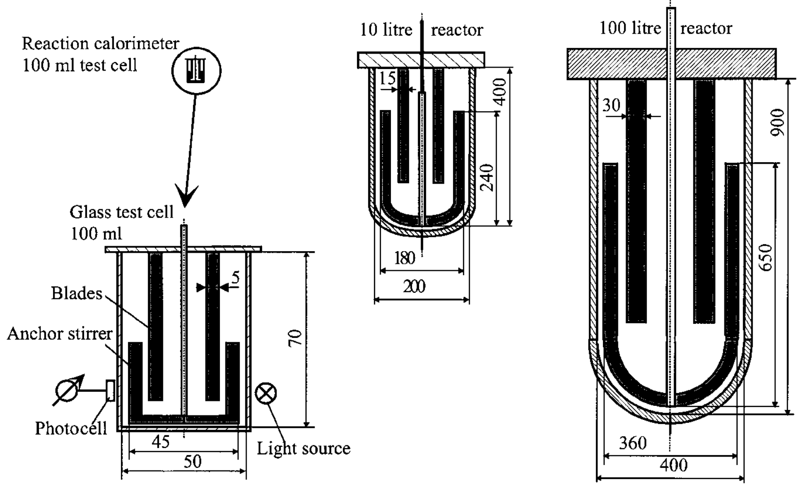

Fig. 1 Device for the characterisation of the initial interfacial area in the reactors via measurement of the phase separation time

The basic assumption underlying the experiments is that the applied mixing quality defined by the obtained specific interfacial area is characterised by the separation time of the emulsion after the stirring is stopped. For validation a homogeneously mixed emulsion has been produced in a glass test cell with the same geometric size as the calorimeter test cell and equipped with a geometrically identical stirrer. After stopping the agitation of the emulsion, the generated vinyl acetate drops, due to their lower density, start to rise in the water phase with a velocity dependent on their size. As a consequence, the light transparency of the remaining water phase, measured as a function of time by using a light source and a photocell, increases. The resulting plot of such a light transparency measurement is shown in Fig. 2. It is comparable to the cumulative curve for the drop size distribution in a normal particle size analysis. Analogously to the derivation of the equivalent mean particle diameter, the time at the turning point of the phase separation curve has been chosen as a characteristic value of the interfacial area for the further analysis. Additionally, the separation time

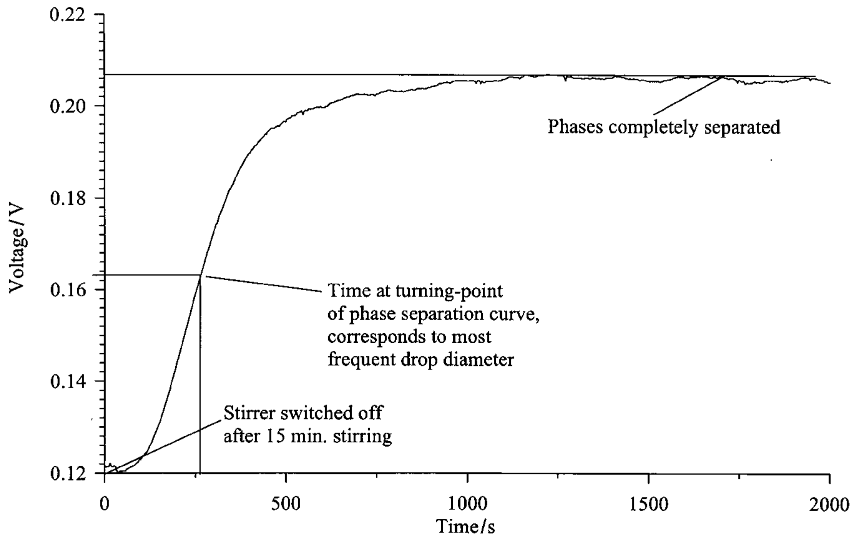

Fig. 2 Measured voltage during the phase separation of a non-reacting vinyl acetate/water emulsion from an experiment in a 100 ml test cell with an initial stirrer speed of 550 l min^{-1}

of the emulsion in the larger reactors has been measured by analysing a sample of the homogeneously mixed emulsion in the glass test cell, because a direct measurement of the separation times in the reactors was not possible. Further, the separation time of emulsions produced with a pitched-blade stirrer in the glass test cell have been tracked for comparative purposes. By this, also the influence of the stirrer type on the final interfacial area of a homogeneously mixed emulsion has been checked. The monitoring of the power requirement of the stirrer, however, was not possible.

For an assessment of the physical meaning of the measured phase separation times, in parallel the particle size distributions of the emulsions produced in the glass test cell have been measured via an image analysis. In Fig. 3 are shown the measured most frequent drop diameters as a function of the separation time at the turning point of the separation time curve. Additionally, the sizes of these drop diameters have been calculated by applying a force balance on the vinyl acetate drops, rising in the water phase at a constant velocity, e.g. according to Brauer [3]:

$$d_T = \left(\frac{18\eta_c \Delta H}{g(\rho_c - \rho_d)} (1 - \varphi_d)^{-4.6} \right)^{0.5} 1/\sqrt{\Delta t}$$

In this equation d_T denotes the drop diameter, η_c the dynamic viscosity of the continuous (water) phase, ΔH the height a particle ascends during the time Δt, ρ_c and ρ_d respectively the density of the continuous and the dispersed phase, and φ_d the volume fraction of the dispersed phase. With the latter one takes into consideration the hindered ascending of the vinyl acetate drops due to their high concentration.

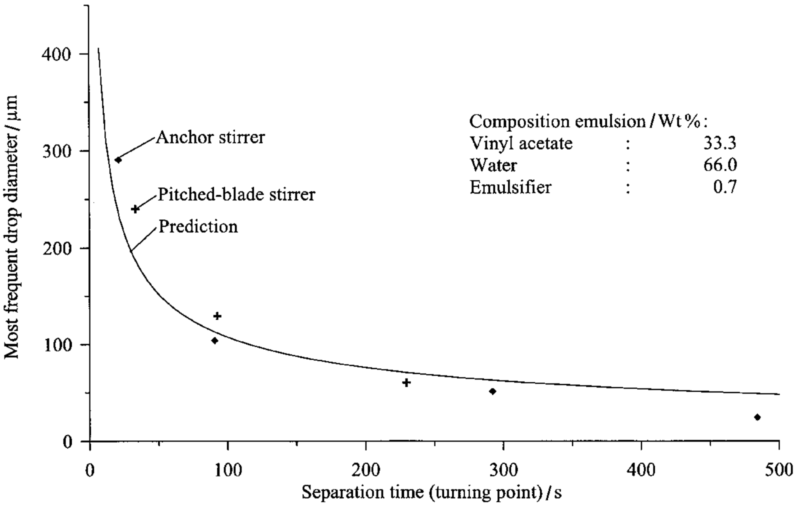

Fig. 3 Predicted and measured (via image analysis) most frequent drop diameter as a function of the separation time at the turning point of the separation curve for emulsions produced with anchor and pitched-blade stirrers

From Fig. 3 it is evident that the predictions of this equation practically coincide with the measured results. Also it becomes clear that the relation between the drop diameter and the separation time is independent of the stirrer type, if the composition of the emulsion is retained.

In the following sections the separation time of the emulsion at the turning point will be used a) to characterise the initial size of the specific interfacial area and b) to check the suitability of scaling rules for an equal mixing quality.

Scaling rules for the mixing quality

For the retention of the (initial) mixing quality in different reactor sizes, amongst other criteria an equal agitation power input in case of geometrically similar stirrers is used. In Fig. 4 is shown the separation time at the turning points obtained from experiments in the 0.1, 10 and 100 litre vessels as a function of the specific stirrer power, calculated from mixture density, stirrer diameter, number of rotations and drag coefficient of the stirrer. It is obvious that an identical specific stirrer power does not lead to the same separation time if the reactor volume is changed and, therefore, an identical initial specific interfacial area in each reactor is not obtainable in this way. So far, this criterion seems not to be suitable as a scaling rule for the specific interfacial area of the emulsion.

Another common criterion for maintaining an identical initial mixing quality is to retain a constant anchor stirrer tip circumference speed in each reactor. Evidently, at an equal circumference speed nearly the same separation time (at the turning point) in the three reactors is obtained, Fig. 5. Consequently, this criterion seems to be more appropriate for scaling the initial specific emulsion interfacial area. This would be explicable by the fact that in general the drop formation or break up is caused by the pressure differences in the turbulent flow nearby the stirrer blade [4]. Indeed, in the case of agitation by an anchor stirrer the induced turbulence depends on the circumference speed of the relatively thin blades. On the other hand, also for this reason this scaling criterion is probably not suitable in the case of agitator types

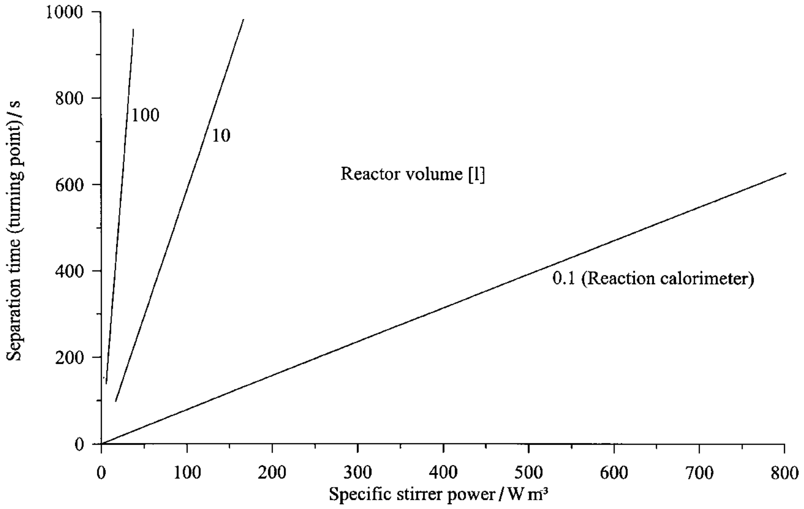

Fig. 4 Experimental separation time of a vinyl acetate/water emulsion as a function of the specific stirrer power in geometrically similar reactors with volumes of 0.1, 10 and 100 litres

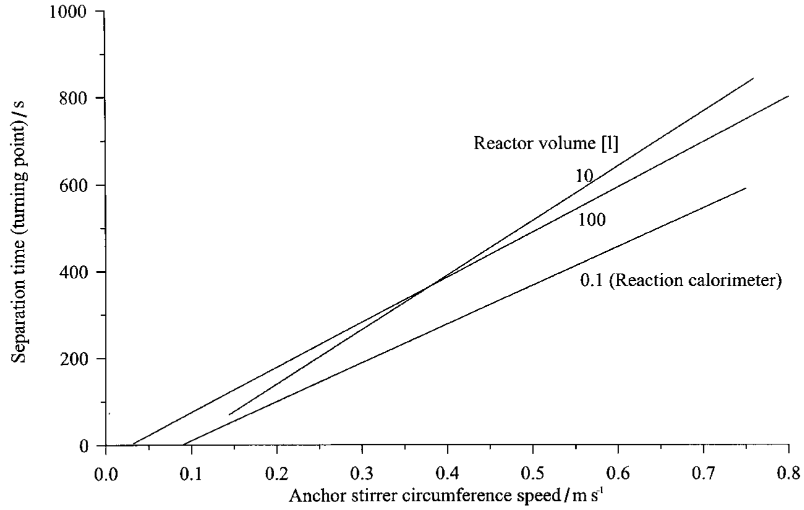

Fig. 5 Experimental separation time of a vinyl acetate/water emulsion as a function of the anchor stirrer circumference speed in geometrically similar reactors with volumes of 0.1, 10 and 100 litres

other than an anchor stirrer. On a general basis, this finding indicates that this criterion is not generally valid and that for each stirrer type, and for different properties of the reaction system, another scaling criterion must be validated. Nevertheless, is what follows the effect of the stirrer speed on the runaway reaction progress is analysed.

Influence of the anchor stirrer speed on the runaway reaction

The runaway reaction experiments have been performed in parallel in the reaction calorimeter and in the 10 litre reactor. The stirrer speeds in the calorimeter were 100 and 200 rpm and in the large reactor 50 and 100 rpm. In view of the experimental procedure with the non-reacting mixtures the course of the tests is different: in the runaway experiments the stirrer is running for the entire duration of the experiment in order to maintain a homogeneously mixed reaction mixture and uniformly distributed (chemical) reaction sites, while in the preliminary investigations with the non-reacting mixture the agitation ended after the establishment of a homogeneously mixed emulsion, i.e. a stationary drop size distribution. In Fig. 6 are depicted the measured self-heat rates as a function of the reaction mixture temperature. It is obvious that the stirrer speed drastically effects the runaway reaction progress. The maximum adiabatic self-heat rate at a rotation speed of 100 rpm in the calorimeter is 1 K min^{-1}. If the stirrer speed is doubled, a maximum self-heat rate of 40 K min^{-1} is measured. The same effect is exhibited by the experiments in the 10 litre reactor. The augmentation of the stirrer speed from 50 to 100 rpm leads to an increase of the maximum self-heat rate from 3 to 100 K min^{-1}.

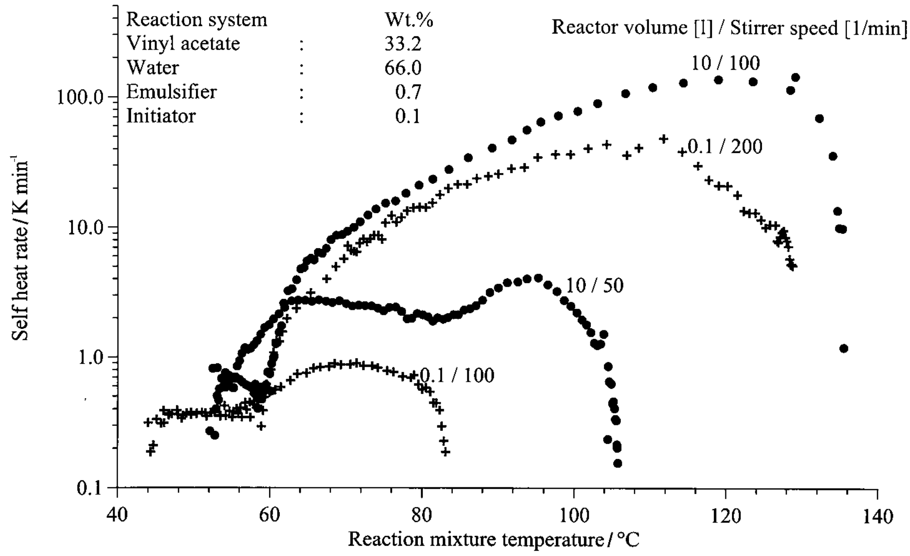

Fig. 6 Measured self-heat rate as a function of the reaction mixture temperature during a runaway vinyl acetate emulsion polymerisation in geometrically similar reactors with volumes of 0.1 and 10 litres

The variation of the stirrer speed also leads to different final reaction mixture temperatures. In the reaction calorimeter tests with 100 and 200 rotations per minute respectively, maximum temperatures of 84 and 128°C were established. In the 10 litre reactor experiments with 50 and 100 rpm analogous figures of 105 and 135°C were recorded. With a reaction enthalpy for the vinyl acetate polymerisation of 88 kJ mol^{-1} [5] an adiabatic temperature difference of 97°C would be calculated based on a mean specific heat of the reaction mixture of 2.85 kJ kg^{-1} K^{-1}. By taking into account the thermal inert mass of the calorimeter test cell, arithmetically a final temperature of approximately 135°C should be attainable in the case of the calorimeter experiments. This indicates that a complete conversion of the monomer has not been achieved in the calorimeter experiments. The back calculation of the monomer conversion degree in the 10 litre reactor from the final temperature in the course of the self-heat rates is not immediately possible due to the heat exchange with the surrounding heating jacket. However, further experiments are necessary to check whether higher stirrer speeds can lead to a further increase of the self-heat rates and monomer conversion.

The immediate comparison of the results obtained from the calorimeter and 10 litre reactor experiments *vs.* each other is not permissible as long as the thermal inert mass of the reaction calorimeter test cell, characterised by the so-called Φ-factor, and the heat losses to the surroundings are not considered. The Φ-factor of the calorimeter test cell amounted to 1.3, the 10 litre reactor on the other hand was equipped with a jacket heater, the temperature of the heating oil being about 75°C during the experiment. Therefore, a definition of a Φ-factor for this reactor is not meaningful. Indeed, when considering equal reaction starting conditions in the form of mixture composition, identical reaction starting temperature and equal initial mixing quality, then it would only be allowed, according to the deduced scaling criterion, to compare the experimental results in the calorimeter with a number of stirrer revolutions of 200 l min^{-1} and in the 10 litre reactor with 50 l min^{-1} *vs.* each other. In both experiments the product of the anchor stirrer diameter and the number of revolutions is equal. For making the experimental results comparable then only the different heat losses have to be considered. This can be achieved by using the formal reaction kinetics deduced from the experiment in the calorimeter and predicting the measured self-heat rates from the experiment in the 10 litre reactor with these kinetics by taking into consideration the heat exchange and the thermal inert mass of the 10 litre reactor, Fig. 7. Here, the calculation of the self-heat rates has been carried out with the relationship for autocatalytic reactions according to Yin [6]:

$$\frac{\mathrm{d}c_\mathrm{M}}{\mathrm{d}t} = -k_\mathrm{o}\exp\left\{-\frac{E_\mathrm{a}}{RT}\right\}\alpha c_\mathrm{M}^\mathrm{n}\left(\frac{c_\mathrm{I}}{\alpha} + c_\mathrm{M,o} - c_\mathrm{M}\right)$$

In this equation c_M, $c_\mathrm{M,o}$ and c_I, denote the monomer, initial monomer and the initiator concentration. The pre exponential factor amounted to 326.1 m^3 kmol^{-1} s^{-1}, the activation energy E_a is 32.6 kJ mol^{-1}, the autocatalytic factor reads 1.15, and the reaction order is 1.

Evidently, with this equation and the deduced parameters an adequate reproduction of the measured self-heat rates in the reaction calorimeter is possible. When ap-

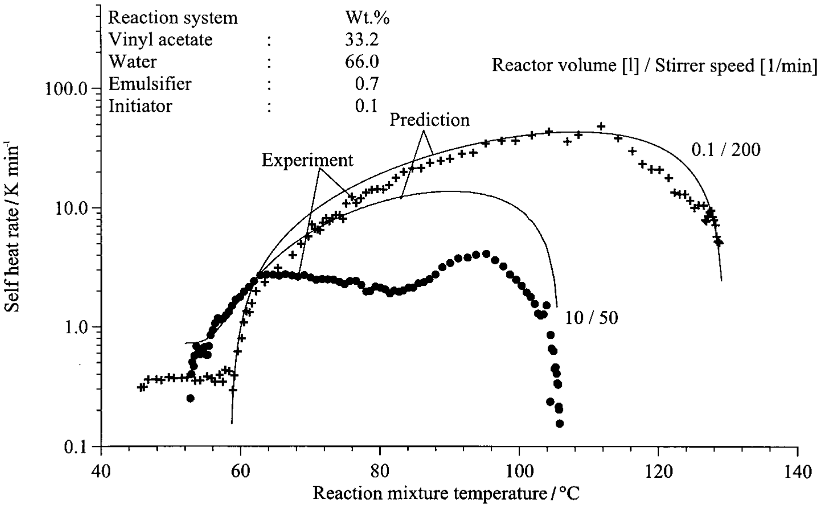

Fig. 7 Measured and predicted self-heat rate as a function of the reaction mixture temperature during a runaway vinyl acetate emulsion polymerisation in geometrically similar reactors with volumes of 0.1 and 10 litre

plying the formal kinetics to the 10 litre reactor and considering the heat losses, then only the measured self-heat rates in the initial period of the reaction between temperatures of 52 and 64°C can be reproduced. At higher temperatures larger self-heat rates are predicted by a factor of about three. This implies that only at the beginning of the reaction in both stirred reactors the same reaction rates are established and that the mass transfer of the agents can not be the only reason for the differences in the reaction rate at later stages and higher temperatures.

The reaction rate in emulsion polymerisations is also controlled by the amount of available free radicals and therefore, by the amount of latex particles which have been developed at the beginning of the reaction in which the polymerisation takes place [7]. Due to a greater stirrer speed and thus a higher turbulence, smaller latex particles remain suspended in the water phase and, therefore, more single and small latex particles are present. Whereas at lower stirrer speeds in the same reactor a coalescence of the latex particles can occur so that only a smaller amount of latex particles with a larger size is existent. This leads to a comparatively slower reaction rate and also to a lower final temperature because more monomer is in existence in the swollen larger latex particles which do not react completely due to the high viscosity of the monomer/polymer mixture within the particles. This large viscosity hinders the diffusion of the monomer to the radicals.

The preliminary resumee is that an identical initial monomer drop size distribution, characterised by the specific interfacial area, is not at all sufficient to ensure an identical reaction rate in different reactor sizes in the case of emulsion polymerisations as examples of heterogeneous reactions. However, if the process of stabilising the latex particles in the water phase is the same as the mechanism of drop formation resp. break up, the formerly derived scaling criterion for the initial interfacial area could also be used a) for the scale-up of the amount and, therefore, b) also of the size of the latex particles during the reaction which is much smaller in contrast to the size of the monomer drops. Indeed, it is conceivable that a coalescence of the latex particles takes place during the reaction leading to a size equal to that of the smallest monomer drops so that their particle size distribution is also influenced by the turbulence due to the stirring.

Conclusions

A scaling criterion based on a constant anchor stirrer tip circumference speed leads in the case of a vinyl acetate emulsion polymerisation nearly to essentially the same initial interfacial area and hence mixing quality in different reactor sizes. Together with the same reaction starting conditions, a reasonable prediction of the initially measured self-heat rates from an experiment in the 10 litre reactor with the formal reaction kinetics from the reaction calorimeter experiment is possible. In the further course of the runaway reaction, higher reaction rates will be predicted. For the fluid dynamic design of the safety relief device this means that maintaining the same initial mixing quality in the calorimeter and the production reactor leads to a conservative design of the necessary relief diameter. From the point of view of an integrated design of the pressure relief system, inclusive of the downstream containment, this procedure still leads to an oversizing of these devices too. For improving the design quality, further experiments in the adiabatic reaction calorimeter, especially at high stirrer speeds are indispensable to confirm the results and to check the assumed influence of the initial amount of latex particles in the reaction system.

Nomenclature

c	concentration/kmol m^{-3}
d_T	drop diameter/m
E_a	activation energy/J mol^{-1}
H	height/m
k_0	pre-exponential factor/m^3 $kmol^{-1}$ s^{-1}
n	reaction order/–
t	time/s
T	temperature/K
α	autocatalytic factor/–
η	dynamic viscosity/Pas
φ	volume fraction/–
ρ	density/kg m^{-3}

Subscripts

0	initial
c	continuous phase
d	dispersed phase
I	initiator
M	monomer

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