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Shell-modified Sikarex calorimeter as a screening tool for runaway reactions[1]

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Abstract

Adiabatic or accelerating rate calorimetry and differential scanning calorimetry (DSC) are both used for the study of runaway reactions. The application of DSC is limited to the study of solids and homogeneous liquid mixtures and generally no information is obtained on pressure development. Adiabatic calorimetry is laborious and time consuming. This paper describes the development of the Shell-modified Sikarex calorimeter as a versatile screening tool for runaway reactions, combining advantages of both techniques. Its construction facilitates the study of multiphase systems. A case history on the treatment of an organic mixture with nitric acid demonstrates a few of the unique properties of the instrument.

Keywords: DSC; Multiphase; Runaway; Screening; Sikarex

1. Introduction

Runaway reactions have led to major accidents in the processing industry. Various experimental methods are available to check the thermal stability or runaway potential of pure compounds or mixtures [1,2].

It is generally accepted that adiabatic, or accelerating rate, calorimeters are of great value for the study of runaway reactions. Under runaway conditions, large chemical reactors, due to their large volume-to-surface ratio, are almost adiabatic. Hence, translation of results obtained from small-scale adiabatic experiments to commercial-

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sized reactors is fairly straightforward for homogeneous systems. For heterogeneous multiphase systems, careful attention should be given to the scale-up of the mass- and heat–transfer characteristics.

Accelerating rate calorimeters that are readily available commercially include the ARC, Phi–Tec and VSP. A practical disadvantage of these calorimeters is, however, that the experiments are relatively time–consuming due to either the handling of the fragile test cells that must be wired to heat them to the desired onset temperature, or to the introduction of the reaction mixtures through the thin tubing required to reduce the reactor heat capacity. Assembly of the test cells into a pressure compensation vessel adds to the experimental time. The thin-walled reactors, required to reduce heat losses from the reaction mixture (ϕ factor), cannot be easily cleaned for re–use and are relatively costly. For these reasons and because only small samples are required, a technique like Differential Scanning Calorimetry (DSC) is widely used as a screening tool [1]. In the case of pure compounds or single–phase mixtures this provides an attractive alternative, although generally no information on pressure development is obtained. A further limitation is the study of multiphase systems where mixing is an important process parameter. In such a case DSC does not give meaningful results.

Therefore, we have further developed the Sikarex calorimeter from Systag System Technik A.G., Switzerland [3], into a quick and easy screening tool that does not have the shortcomings of the DSC with respect to multiphase systems.

Our main goal was to develop an instrument that could be used for the screening of large amounts of samples under close to actual process conditions. The experimental results should enable us to answer the following qualitative questions:

- are there any unknown reactions over the temperature range investigated?
- what are their temperature and pressure effects?
- is it necessary to follow– up with adiabatic experiments for a more quantitative description of the observed phenomena?

If the answer to the last question is affirmative, adiabatic experiments are carried out in an accelerating rate calorimeter. From these experiments, we gather the information required for the design of a process safeguarding system.

This paper describes the basic features of the Shell–modified Sikarex equipment and gives some examples of experiments carried out.

2. Equipment description

Originally, the Sikarex instrument was equipped with an open glass container [3]. As this considerably limited its application range, we decided to design a steel reactor that would fit in the existing Sikarex oven.

The Shell-modified Sikarex calorimeter basically consists of an 80-ml steel autoclave placed inside a convective oven (Fig. 1). The reactor is designed for a maximum operating temperature and pressure of 350°C and 75 bar, respectively. It is equipped with a safety valve or bursting disc set at a relief pressure of 60 bar. The entire top of the reactor can be disconnected, allowing easy access for the addition of solids and for cleaning purposes.

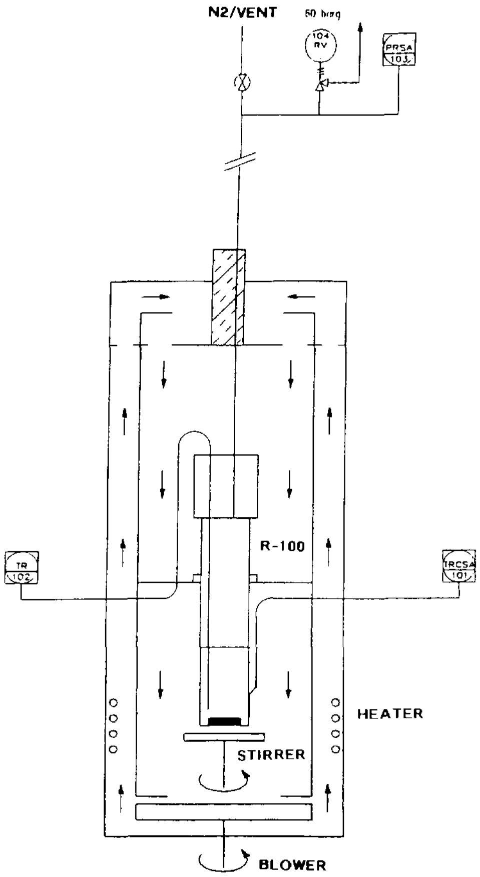

Fig. 1. Schematic drawing of the Shell-modified Sikarex.

Two Pt-100 resistance thermometers are placed inside and at the outside reactor wall. The pressure is measured by a pressure transducer (0–60 bar). The remaining connection may be used for the introduction of chemicals and/or for (de)pressurizing the reactor for pressure testing or blanketing with a variety of gasses.

The blower for the circulation of hot air is placed at the bottom of the oven. A second shaft, driven by a separate motor, is mounted with a permanent magnet that drives the magnetic stirrer bar inside the reactor. The reactor is normally operated at a low hold-up of approximately 25 ml. The Pt-100 is positioned off-centre to ensure that it is inserted in the liquid and not in the gas cap in case of a vortex. Its position also ensures some baffle action that may further improve the mixing. When multiphase and/or strongly viscous systems are studied we usually study the mixing performance of the system at ambient temperature in a glass vessel with identical geometry before carrying out the screening test.

The circulating air is heated by heating elements attached to the oven wall. The oven lay-out is such that direct radiation from the heating elements to the reactor wall is avoided. The radiation shields also serve to direct the circulation of air in the oven in the way shown in Fig. 1.

In the set-up used in our laboratory, the temperature and pressure signals are sent to an A/D converter and stored on disc by the data-acquisition programme. The electronics were developed by Systag A.G. to our specifications. The set-point for the temperature controller is generated by a control programme and compared with the outside reactor wall temperature. Consequently, the temperature ramp is forced upon the outside reactor wall rather than on the oven itself.

The ramp rate can be adjusted at any level between 0 and 20°C min^{-1}. Typically, a temperature ramp of 1°C min^{-1} is used for screening experiments. Due to the heavy construction of the oven wall, the thermal inertia of the oven becomes determining at ramp rates in excess of 20°C min^{-1}.

Figure 2 gives an example of the experimental results for the decomposition of a solution of di-tertiary butyl peroxide in toluene, a widely used test reaction for reaction calorimetry. In the screening or linear heat-up experiment, the setpoint of the outside wall temperature was increased at 1°C min^{-1} from ambient to 300°C. Inside and outside temperatures and the pressure are recorded as a function of time, together with the difference between the inside and outside temperature. This temperature difference can be compared with the output that would have been obtained from a DSC experiment. The outside wall temperature in the Sikarex can be considered as the equivalent of the temperature of the reference cup in DSC for moderately exothermal

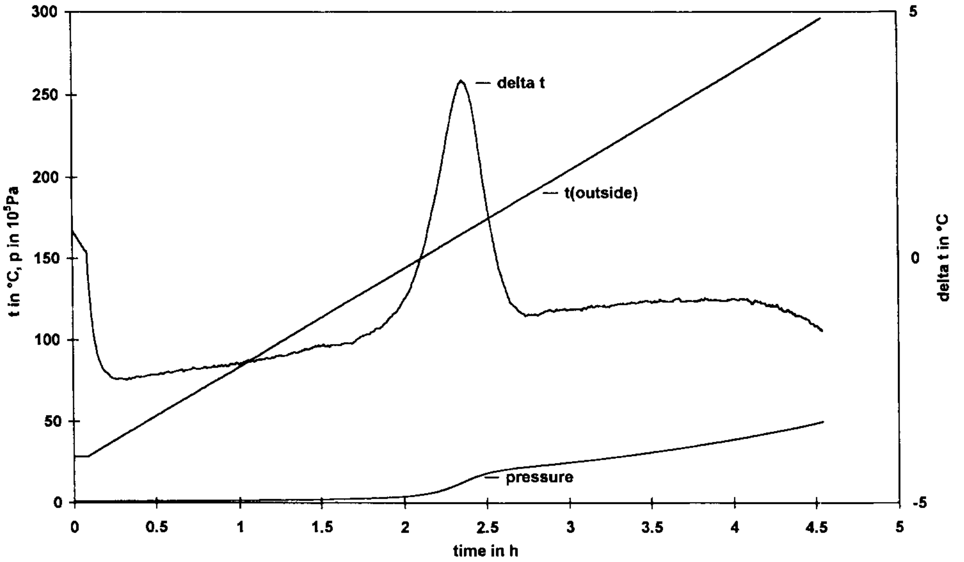

Fig. 2. Experimental results of the decomposition of 20% m/m di-tertiary butyl peroxide in toluene.

reactions. In the case of strongly exothermal reactions, the wall temperature may be affected by the temperature of the reaction mixture, as will be shown in the examples. Most of the information is extracted from this Δt versus time curve. It shows that the decomposition of the peroxide started at a temperature of approximately 130°C and that the maximum in the reaction rate occurred at a temperature of 170°C. The peak caused by the exothermal decomposition reaction is superimposed on a baseline that would have been obtained without any reaction occurring.

The temperature ramp that is forced on the outside reactor wall causes a heat flow directed inwards which causes a negative Δt over the reactor wall, Δt being defined as the inside reactor temperature minus the outside reactor wall temperature. Generally, Δt will vary slightly with temperature as the heat transfer coefficient inside the reactor will be a function of the temperature. The absolute value of Δt will gradually decrease with increasing temperature as the heat transfer improves.

Apart from the temperature, the heat transfer will also be affected by for example, stirrer speed and reactor hold-up (surface-to-volume-ratio). Comparison of the absolute values of Δt is therefore only meaningful if these process variables are kept constant between experiments. Fig. 3 shows the results of three experiments with pure toluene and *n*-hexadecane to illustrate a phenomenon that may be observed when using low boiling point solvents. The first experiment with toluene was carried out without the addition of inert gas. At a temperature of 220°C, there was a sharp drop in the Δt curve. This suggests that an endothermal process took place, withdrawing heat from the reaction mixture. In this case, however, the phenomenon can be explained by the refluxing of toluene in the tubing protruding from the oven. This effect could mask other effects occurring in the same temperature range. Although it is very difficult to

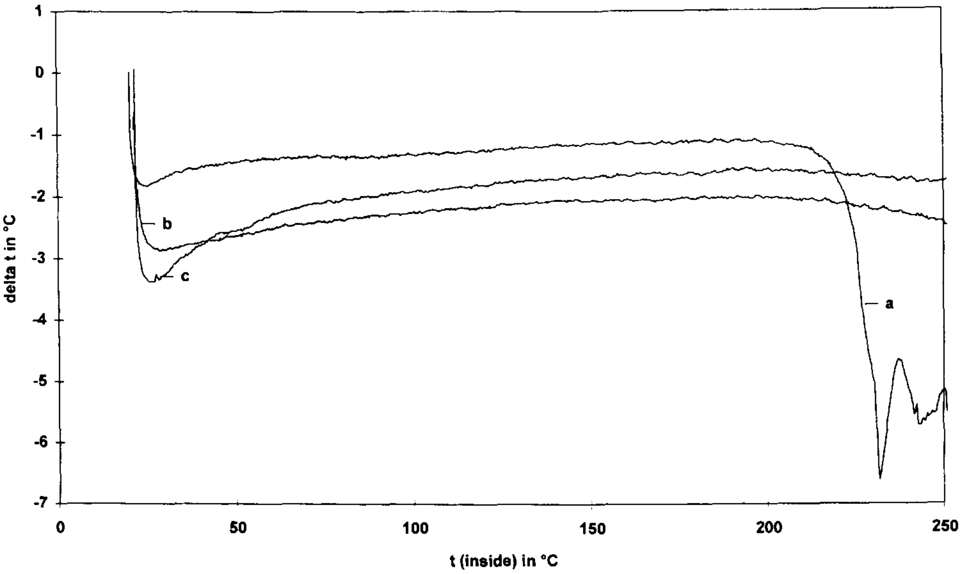

Fig. 3. Effect of boiling point on Δt curves: a, toluene b, toluene with 10^6 Pa N_2; c, *n*-hexadecane.

completely eliminate refluxing, it can be suppressed to a very large extent by adding an inert gas as shown in the second toluene experiment where we added 10 bar of nitrogen.

The experiment with *n*-hexadecane (boiling point 287°C) confirmed that the endothermal effect was related to the boiling point of the reactor contents.

As mentioned before, the ramp rate can be chosen between 0 and 20°C min^{-1}. Fig. 4 shows the effect of the ramp rate on the Δt signal. In this case, Δt is plotted as a function of the inside temperature for easy comparison. As expected, a higher ramp rate resulted in a larger signal. Both the onset and the temperature of maximum rate were shifted towards higher temperatures, a phenomenon well-known from DSC experiments. From this, it can be understood that at higher ramp rates and, consequently, larger heat flows, the baseline of the Δt curve will generally become more negative.

The choice of a ramp rate will depend largely on the requirements with respect to experiment time, sensitivity and peak resolution. In our screening work, we use 1°C min^{-1} as we put the main emphasis on the detection of consecutive reactions.

Currently, four of the described calorimeters are operational in our laboratory in a single train using one PC for the control and data– acquisition. Running in parallel, more than 800 screening tests may be easily carried out annually by one laboratory technician.

3. Case history

In this section, we will describe a case history which highlights a few of the unique properties of the Shell–modified Sikarex calorimeter.

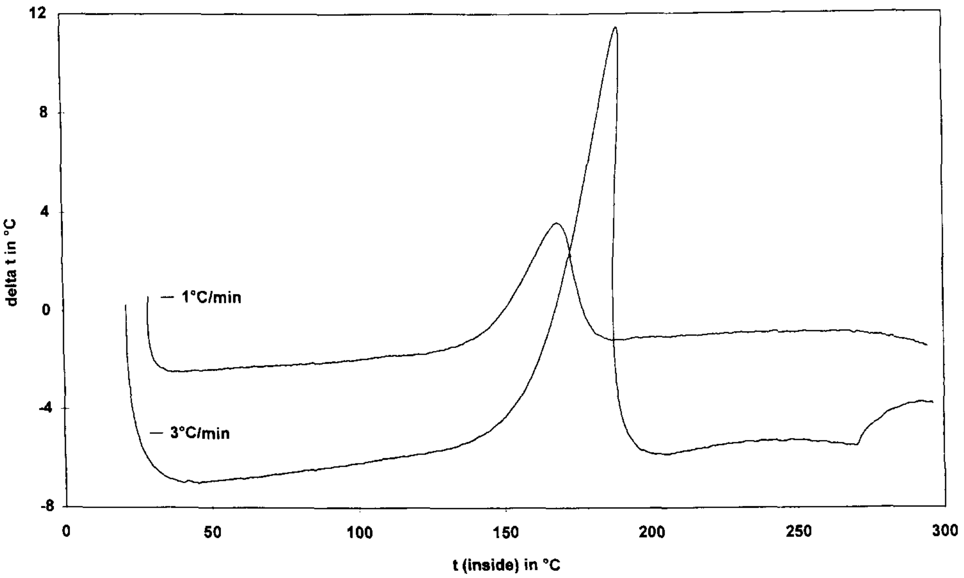

Fig. 4. Decomposition of di-tertiary butyl peroxide; effect of ramp rate.

In one of our subsidiaries, a process for the removal of iron compounds from an acidic aqueous mixture was evaluated for further process development. In the process, the aqueous mixture was extracted with a three–compound organic mixturte consisting of: a hydrocarbon solvent mixture in the kerosene boiling range; an organic phosphoric ester; and a high boiling alcohol.

After phase separation the extract was treated with 10 N nitric acid at a temperature of approximately 60°C to remove the iron compound. The regenerated organic extraction mixture was recycled.

Our group was requested to assess the runaway potential of the nitric acid treatment.

We started our investigation with a few screening tests in the Shell–modified Sikarex. At the phase ratio employed of 60/40 organic/aqueous, the mixing was found to be adequate. The results of the first test of the organic extract and nitric acid are shown in Fig. 5. It can be seen that at very moderate temperatures an exotherm developed, accompanied by a fairly steep increase in the pressure. From the Δt curve, at least three different reactions can be distinguished, the first reaction starting at a temperature of approximately 30°C.

In view of the anticipated operating temperature of 60°C, these results were rather worrying. It was decided to investigate which of the three organic constituents was responsible for the low temperature reaction. This might have instigated a search for a more stable replacement. The results of the screening experiments for the separate components are given in Figs. 6–8. Fig 6 shows that the kerosene solvent started to react at temperatures just above ambient. This might be explained by the presence of small amounts of unsaturated or aromatic compounds in the kerosene. A small

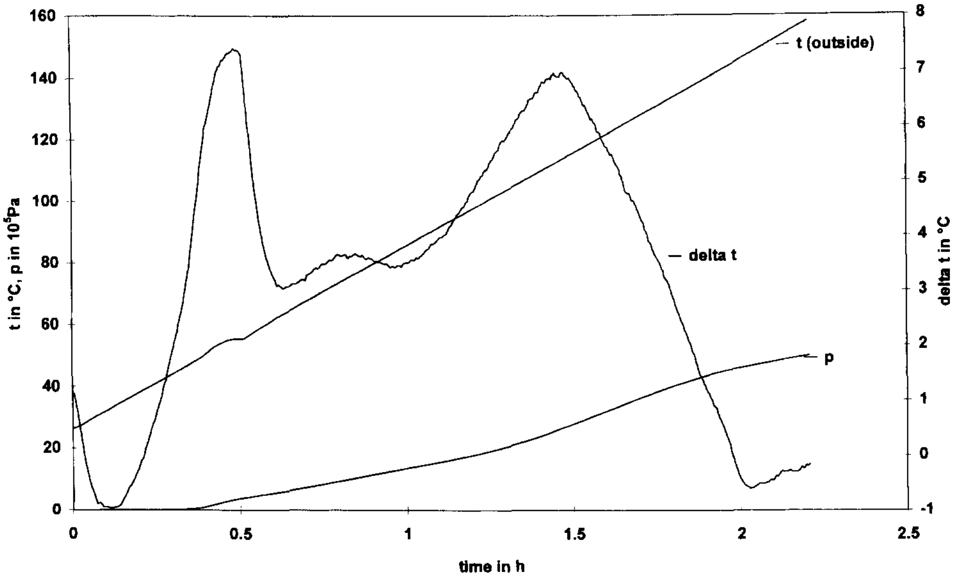

Fig. 5. Screening test of organic extraction mixture.

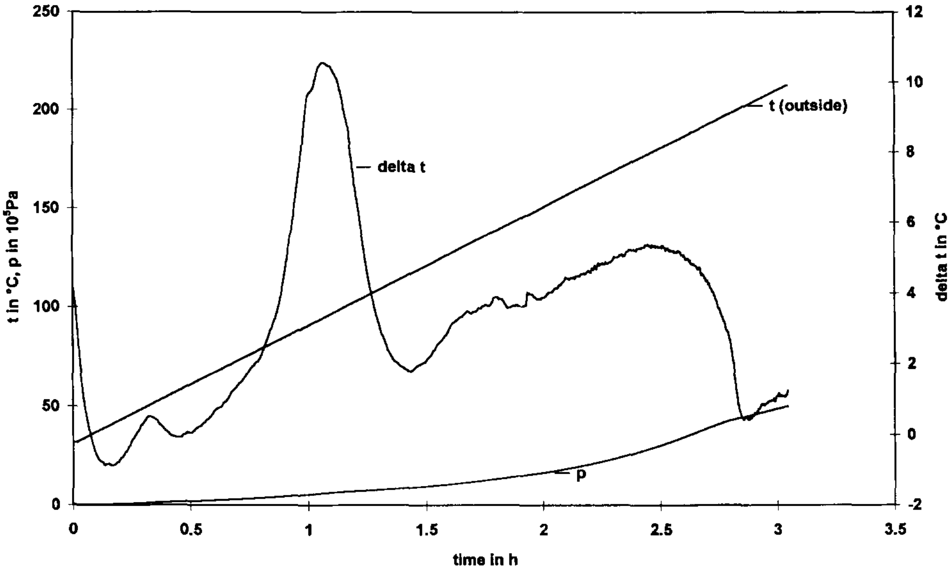

Fig. 6. Screening test of kerosene solvent.

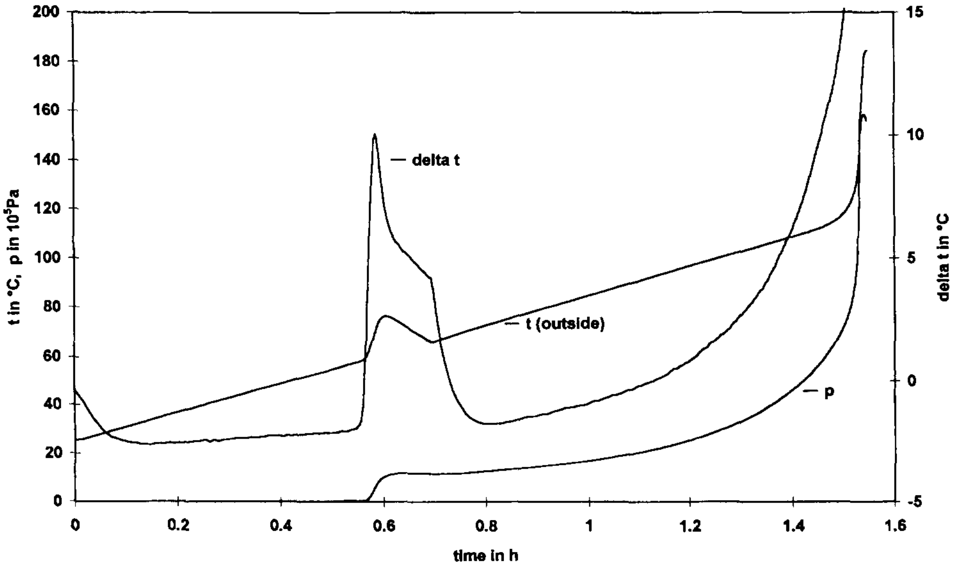

Fig. 7. Screening test of organic phosphoric ester.

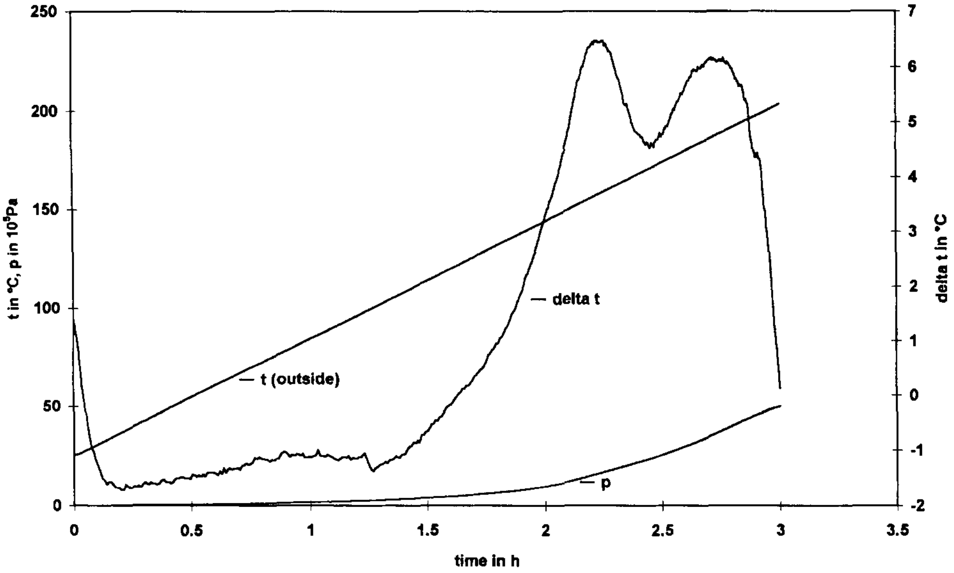

Fig. 8. Screening test of high boiling alcohol.

exotherm starting at approximately 40°C might generate enough heat trigger a second starting at around 50°C.

The phosphoric ester compound (Fig. 7) proved to have an onset temperature of approximately 50°C. The first large exotherm was immediately followed by a second which, at temperatures of around 100°C, was accompanied by a severe pressure rise. In this experiment the rate of heat developed by the first exotherm was so high that it exceeded the heat transfer rate at the outside reactor wall. Consequently, the reactor wall was temporarily heated above its setpoint as can be seen from Fig. 7.

The alcohol (Fig. 8) proved to be the most stable compound of the mixture, although the continuous rise in the pressure does indicate that in this case also, decomposition started at fairly low temperatures.

The screening tests had shown that there was considerable potential for runaway reaction at the envisaged operating temperature and it was decided to proceed with an adiabatic test of the complete extraction mixture.

The test in an accelerating rate calorimeter (Fig. 9) showed that the Time to Maximum Rate at the operating temperature of 60°C amounted to approximately 80 min (Fig. 10). Although safeguarding systems can be designed for such a case, the measured heat rate of 0.15–0.2°C min at 60°C indicated a relatively rapid decomposition of the organic extractant. This would have meant a heavy burden on the variable costs of the process.

The combination of variable cost penalty and safeguarding requirements finally led to the rejection of the use of this particular organic mixture for the extraction process.

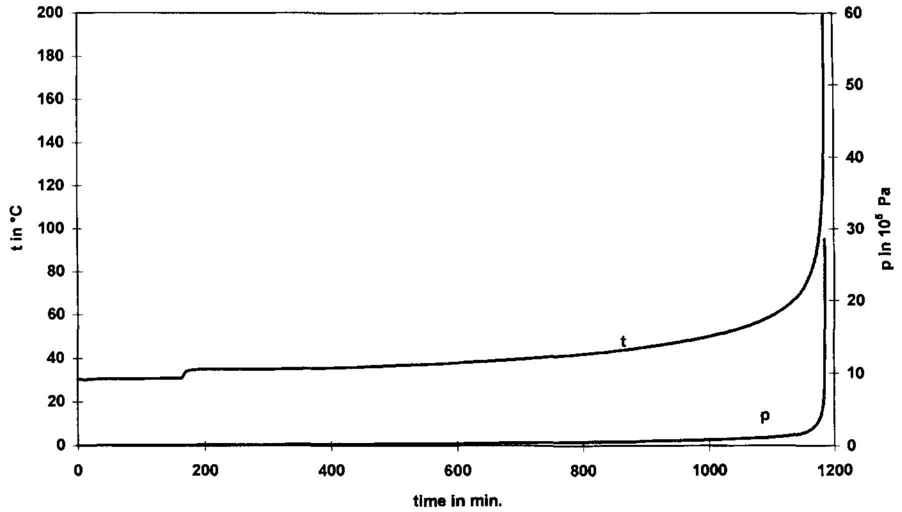

Fig. 9. Adiabatic test of the organic extraction mixture.

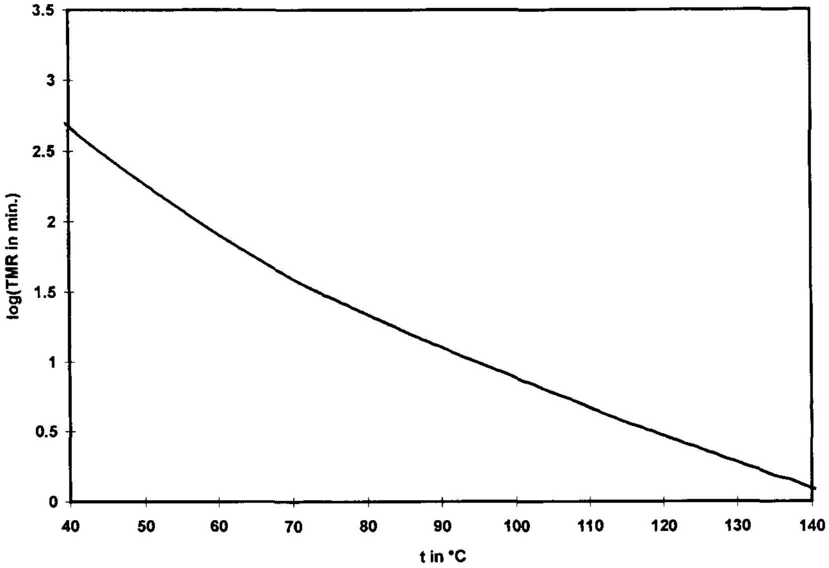

Fig. 10. Time to maximum rate as a function of operating temperature.

4. Conclusions

The Shell-modified Sikarex calorimeter has proven to be a versatile instrument for the screening of runaway reactions. Its reactor design facilitates the study of complex multiphase reaction mixtures, provided that careful attention is given to mixing phenomena. The "linear heat–up" operating mode gives the opportunity to distinguish between consecutive reactions which may give additional insight into the chemistry involved.

The combined information of temperature and pressure development may help in the interpretation of the observed phenomena, a feature that cannot easily be realized with standard DSC equipment.

References

[1] S. Tharmalingam, The Chemical Engineer, August (1983) 33.
[2] R.L. Rogers and J.A. Barton (Eds.), Chemical Reaction Hazards, Institution of Chemical Engineers, 1993.
[3] L. Hub, Ph.D. Thesis no. 5577, ETH Zürich, 1975.