Some applications of mixing calorimetry

INTRODUCTION

Mixing calorimetry cells aim at putting in contact two or more substances in the sensitive part of the calorimeter after having stabilized them to the same test temperature. The heat release linked with the interaction between the substances is then measured from the very first moments. Such a setup allows determining thermodynamic and kinetic parameters of processes such as a chemical reaction, an adsorption, or a dissolution.

Samples type	Mixing Method	Cell type
Liquid vs. Liquid	Batch	Reversal or membrane
	Semi-batch	Flow 1 inlet or mini-reactor
	Continuous	HP flow 2 inlets
Solid vs. Liquid	Batch	Reversal, membrane or ampoule
	Semi-batch	Flow 1 inlet or mini-reactor
	Continuous	Percolation
Liquid vs. Gas	Continuous	HP flow 2 inlets
Solid vs. Gas	Continuous	Flow 1 inlet or mini-reactor

Table 1 – Review of the different mixing calorimetric methods

Figure 1 – Some of the most typically used calorimetric mixing cells (from left to right: reversal, membrane, ampoule and percolation mixing)

1. Determination of the heat of mixing of polymers – Hess cycle

EXPERIMENT

Direct measurement of the heat of mixing of polymers may not feasible due to their high viscosity. A convenient indirect approach can consist in measuring the heat of dissolution of the individual polymers and of their blend into the same organic solvent by the batch mixing method. A Hess's Law cycle is used to determine the heat of mixing from the individual heats of solution.

$$\Delta H_s^A + \Delta H_s^B + \Delta H_s^S + \Delta H_m + \Delta H_s^{AB}$$

With ΔH_s^A, ΔH_s^B and ΔH_s^{AB} the heat of dissolution of polymers A and B, and of the blend AB into the solvent S respectively.

ΔH_s^S is the heat of mixing of the solution of A and B in the solvent S, and ΔH_m is the heat of mixing.

RESULTS AND CONLUSION

With this method the heat of mixing of a 75 / 25 (% by wt) poly(dimethyl) phenylene oxide/polystyrene alloy has been determined by the SETARAM CALVET calorimeter as 4.9 +/- 0.2 J/g

For more information see application note AN 089 or the following reference paper:
[1] P.N. Aukett and C.S Brown, J. of Thermal Analysis, Vol 33, 1079-1084, (1988).

2. Heat of wetting of activated carbon powders by solvents – ampoule mixing

EXPERIMENT

The interactions of the surface of solids with different solvents can be studied by wetting (or immersion) assays. In the present example, a series of activated carbon powders were tested against water and benzene, two solvents with drastically different polarities.
The tests were run at 30°C with 60-100mg of powder mixed with volumes of solvent of 5mL. The powders were initially degassed under vacuum and sealed in glass ampoules.

RESULTS AND CONCLUSION

According to their degree of activation, the powders developed particular affinities with the different solvents, leading to high or lower heat of wetting. AC1 is the less activated sample, and thus leads to low heat effects. Both AC2 and AC3 lead to higher exotherms with benzene, i.e. more or stronger interactions with this solvent.

This study was run with the Latvian State Institute of Wood Chemistry, Riga, Latvia.

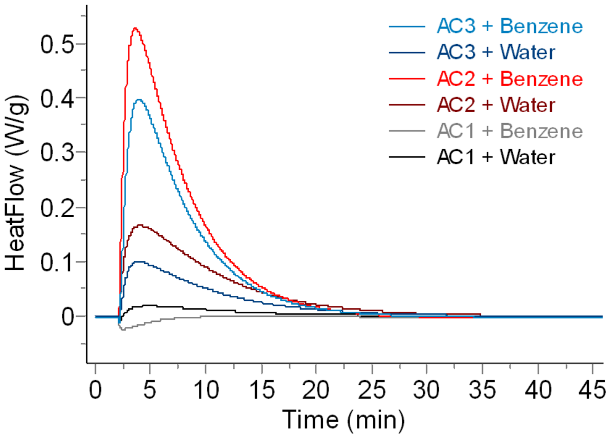


Figure 2 – Heatflow during wetting of the activated carbon samples with water or benzene. The data are plotted in watts per gram of powder.

3. Interaction of sulphur containing molecules on a solid sorbent under flow conditions

EXPERIMENT

Many investigations are realized on the desulphurization of transportation fuels to avoid poisoning platinum (in catalysts, electrodes, etc). For example, the adsorption of sulphur containing chemicals present in gas oil can be studied using a liquid phase flow calorimetric technique with hexadecane as a solvent to mimic the fuel and a zeolite such as NaY.
Experiments were conducted on a CALVET calorimeter at 30°C with two identical percolation vessels, one for the sample and another for the reference. At time zero, the liquid is changed from pure hexane to a solution of hexadecane and sulfur-containing compound..

RESULTS AND CONCLUSION

The exothermic heat of adsorption decreases and the kinetics of adsorption gets faster with increasing aromatic rings, meaning that very rapid adsorption occurs at the beginning of the experiments in spite of the size of the S compound.

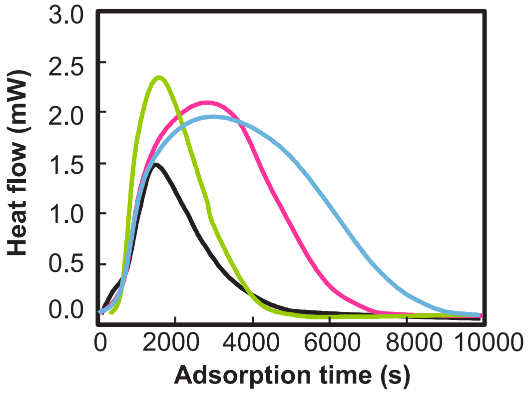


Figure 3 – Heatflow during adsorption of sulfur compounds in hexadecane on NaY at 30 °C.
After integration, the heats of adsorption are determined equal to -39.65 J/g (Thiophene), -31.63 J/g (Benzothiophene), -18.73 J/g (Dibenzothiophene), -12.12 J/g (Dimethyldibenzothiophene)
– Adapted from [3]

For more information see application note AN542 or the following reference paper:
[3] Flora T.T. Ng, Ataur Rahman, Tomotsugu Ohasi, Ming Jiang, Applied Catalysis B: Environmental 56 (2005) 127–136

4. Chemical reaction under batch mixing conditions – biodiesel from vegetable oil

EXPERIMENT

The interactions of Biodiesels are synthesized from a transesterification reaction of triglycerides by low molecular weight alcohols leading to the formation of fatty acid alkyl esters with the use of a catalyst. The base-catalyzed ethanolysis of colza oil was studied by isothermal microcalorimetry.
CALVET calorimeter was used under isothermal conditions at 30°C, 40°C and 50°C with membrane mixing vessels as shown on Figure 1. Commercial colza oil (~1.3g / test) was mixed with 3.4w% NaOH in EtOH (~0.45g / test).

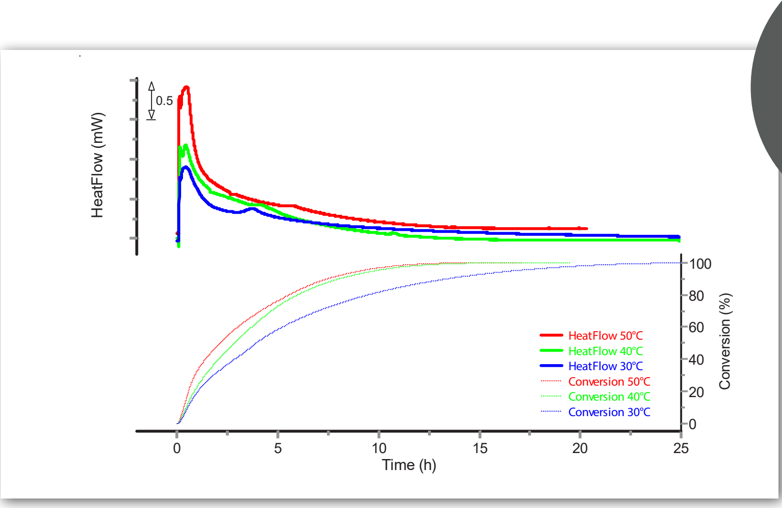


Figure 4 - Heat release data vs. time during the reactions are integrated in order to reach the reaction enthalpy. It is equal to -10.9 ± 0.6J/g of ethanolate (NaOH + EtOH solution).

RESULTS AND CONCLUSION

Thermal conversion α is obtained from partial integration. Both maximum heat release rate and conversion data confirm the acceleration of the reaction with increasing temperature. The thermal conversion reaches 98% after 10.8h at 50°C, 11.7h at 40°C and 20.0h at 30°C.

For more information see poster PO026.

5. High pressure flow mixing calorimetry - Investigation of CO2 capture in amine solutions

EXPERIMENT

The use of the chemical sorbents is today one of the most popular absorption technique for the CO2 capture in post combustion techniques. In such an industrial process, the amine solution reacts with the gas to reversibly form the corresponding carbamate. Enthalpies of absorption are key data to design the process.
Flow mixing calorimetry is here applied to simulate the continuous process and avoid effects of vapour pressure by minimizing the dead volumes. Both fluids are inserted continuously in the cell and mixed at its bottom. The formed carbamate is also continuously removed from the calorimeter. The CO2 / amine solution ratio is controlled by the flow rates of each fluid.
The flow mixing vessel operates from room temperature to 200°C and for a range of fluid pressure from 0.1 to 20 MPa. The fluid flow rates vary from 50 to 1500 µ.min-1.

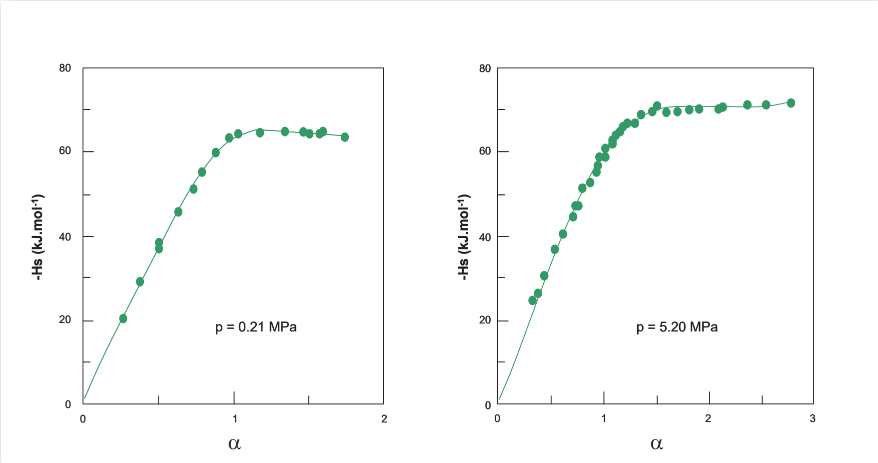


Figure 5 - Enthalpy of solution per mole of amine vs CO2 loading for aqueous solution of AMP 15 wt% at 322.5 K - Adapted from [4]

RESULTS AND CONCLUSION

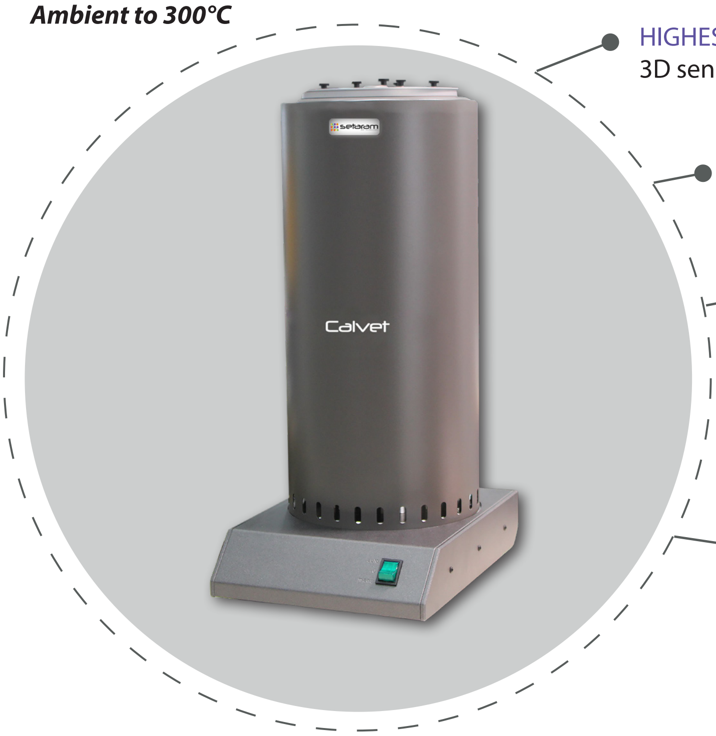
An example is given for the enthalpy of solution of CO2 in a primary amine AMP (2-amino-2-methyl-1-propanol).

For more information see application note AN638 and AN557 [4] H. Arcis, L. Rodier, J-Y. Coxam, J. Chem. Thermodynamics 39 (2007) 878-887

INSTRUMENT

CALVET

Ambient to 300°C



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