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Determination of Accurate Specific Heat Capacities of Liquids in a Reaction Calorimeter, by Statistical Design

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ABSTRACT: A method using statistical design is proposed to determine the measurement error of specific heat capacities (Cp) of liquids in any reaction calorimeter. This method only takes into account the experimental specific heat of the liquid, its volume and the reactors stirring rate. With the RC1e calorimeter used in this study, the Cp measured by its QuickCal mode was overestimated by up to 0.4 $J\cdot g^{-1}\cdot K^{-1}$, whereas with its RTCal mode, more accurate values of Cp ($\pm$ 0.2 $J\cdot g^{-1}\cdot K^{-1}$) were obtained. The statistical model obtained based on the QuickCal mode predicts experimental conditions which improve the accuracy of Cp, and could also be used to correct the value of Cp in the rest of the experimental domain. The corrected values of Cp for test solvents using this model were close to those cited in literature ($\leq$5%). As an application, the specific heat capacities at 25 °C of less well documented solvents were determined: anisole, ethyl-tertiobutylether, methyl-tetrahydrofurane, diethoxymethane, dimethyl-ethyleneurea and dimethylpropyleneurea.

INTRODUCTION

Reaction calorimetry is widely used to determine the potential hazard of a chemical process. The heat generated by the desired reaction (Q_r) is measured close to the process temperature (T_{Process}) and this value is used to calculate the temperature rise in the event of uncontrolled process conditions, often referred to as the adiabatic temperature rise (ΔT_{adiab}). This situation can arise if all the reactant, instead of being dosed regularly, is abruptly introduced into the reaction mixture. Combined with an inadequate vessel cooling capacity, the reaction mixture will evolve uncontrolled in a nearly adiabatic manner (no heat exchanged with the environment). The resulting final temperature of the reaction mixture (MTSR = maximal temperature of synthesis reaction), in the absence of any decomposition, is given by the formula:[1]

$$\text{MTSR} = T_{\text{Process}} + \Delta T_{\text{adiab}}$$

MTSR is a theoretical value: if it is higher than the boiling point of the solvent, MTSR will never be reached by the reaction mass because ebullition will tend to limit the increase in temperature. On the other hand, if the reaction mixture begins to decompose at a temperature lower than MTSR, the runaway of the desired reaction will initiate additional undesired reactions and the temperature of the mixture may exceed MTSR. The comparison of MTSR with the boiling point of the solvent and the temperature of decomposition of either reaction mass or its products is a criterion in assessing the criticality of a process.[1]

The adiabatic temperature increase depends on the mass of the reaction mixture (m, in kg), the heat produced by the reaction (Q_r, in kJ), and the specific heat capacity at constant pressure of the mixture (C_p, in $kJ\cdot kg^{-1}\cdot K^{-1}$ or $J\cdot g^{-1}\cdot K^{-1}$):

$$\Delta T_{\text{adiab}} = Q_r/(m \times C_p)$$

The specific heat capacity reflects the ability of a medium to accumulate energy when exposed to heat: it is the amount of energy in Joules needed to raise by one Kelvin one gram of material. Typical Cp values for solvents range from 4.2 for water to 1.0 for some chlorinated solvents. As a consequence, an undesired and exothermic event in these chlorinated solvents will be more hazardous than in water, because the resulting increase in temperature will be four times higher.

The specific heat capacity is temperature dependent, but in the liquid range this can often be neglected. For example, the Cp of water only varies from 4.18 to 4.21 $J\cdot g^{-1}\cdot K^{-1}$ in the range 5−95 °C.[2]

Nonadiabatic reaction calorimeters used in process safety laboratories are based on three main types of technologies, all of which can be used in combination: heat-flow, power compensation and heat balance.[3−5]

In heat flow calorimeters, the heat exchanged between the mixture and the fluid in the double jacket is continuously calculated. This heat flow (q, in W) is proportional to the temperature difference between the reaction mass (Tr) and the jacket fluid (Tj) and as well as to the heat transfer surface (A, in m^2):

$$q = UA(T_r - T_j)$$

In this equation, U is the heat transfer coefficient, in $W.m^{-2}\cdot K^{-1}$, which is considered constant over a small temperature range.

Integration of the heat flow (q) as a function of time over the reaction event gives the energy (Qe, in J) exchanged between the reaction mixture and the fluid in the jacket:

$$Q_e = UA\int_0^t (T_r - T_j)dt$$

However, Q_e is not equal to the heat produced by the reaction (Q_r). In order to determine the latter with any accuracy, one has to take into account additional terms such as the heat capacities

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of the vessel, stirrer and probes (inserts), the energy dissipated by the stirrer, heat losses, and so on. The heat-flow technology is used under either isothermal (e.g., Reaction Calorimeter RC1e from Mettler[6]) or isoperibolic[7] conditions (e.g., Differential Reaction Calorimeter[8−10] (DRC) from SETARAM[11]). In an isothermal reaction calorimeter, the temperature of the fluid in the jacket is continuously adjusted by cooling or heating in order to keep the reaction mixture at constant temperature. Under isoperibolic conditions on the contrary, the system maintains the jacket fluid at constant temperature, leaving the reaction mixture to evolve.

The accuracy of the measurement of the heat flow is high: for energetic exothermic reactions (with Q_r in the range of 60 kJ/mol) the error is lower than 5%.[10,12]

In a power-compensation reaction calorimeter, an electrical resistance in the reaction mixture maintains the reactor temperature constant by continuously compensating either the heat removed from the reactor mixture by the colder double jacket, or that which is lost to the surroundings. The heat produced by an exothermic reaction for example is directly measured by the decrease in the electrical power consumption during the reaction.

In a heat-balance reaction calorimeter, the temperature of the reaction mixture is controlled by varying the temperature of the cooling fluid in the jacket. Unlike the RC1e, in which the temperature of the fluid is considered as homogeneous as a result of its high flow rate, in the heat-balance reaction calorimeter, the instantaneous heat of the reaction is calculated from the fluid temperature difference between the inlet and outlet of the jacket. Peltier elements can also be used to control the temperature of the reaction mixture. In this case, it is the electric power exchanged between the elements and the reactor which is integrated to measure the heat-flow.

■ C_P MEASUREMENT MODES

In the heat-flow calorimeter used in this study (Mettler RC1e), there are three modes which can be used to measure the specific heat capacity of the mixture and the exchange transfer coefficient UA. These methods take into account the inserts heat capacity (C_{pi}) which are predetermined.[13]

- The more widely used mode applied by Mettler is called "QuickCal". This measurement employs the Joule effect: a resistance inside the mixture dispenses a known amount of energy. The curve Tr versus time is used to calculate the heat capacity of the reaction mixture in a similar way as with the DRC.[9] With the RC1e used in this study, around 5 W are injected into the mixture for 5 min under isoperibolic conditions, raising the reactor through several K, depending on the solvent and the fill volume. UA and C_p are determined simultaneously.
- More recently, Mettler has developed another approach to the measurement of heat exchange, using horizontal and vertical heat sensors between the reactor and the jacket (Figure 1). This system, called "RTCal", is independent of the properties and behavior of the reaction mass. The accuracy of the heat flow measured is very high. According to our experience, the two methods QuickCal and RTCal give differences in measured heats of reactions lower than 5%. In the measurement by RTCal, the reactor contents are heated regularly at 0.3 K/min by the jacket through 3 K regardless of the solvent and the volume, while the heat flow q(RTCal) exchanged with the jacket is calculated from the heat flow measured by the heat sensors. The C_p of the mixture and of the inserts are determined by resolution of the equation:

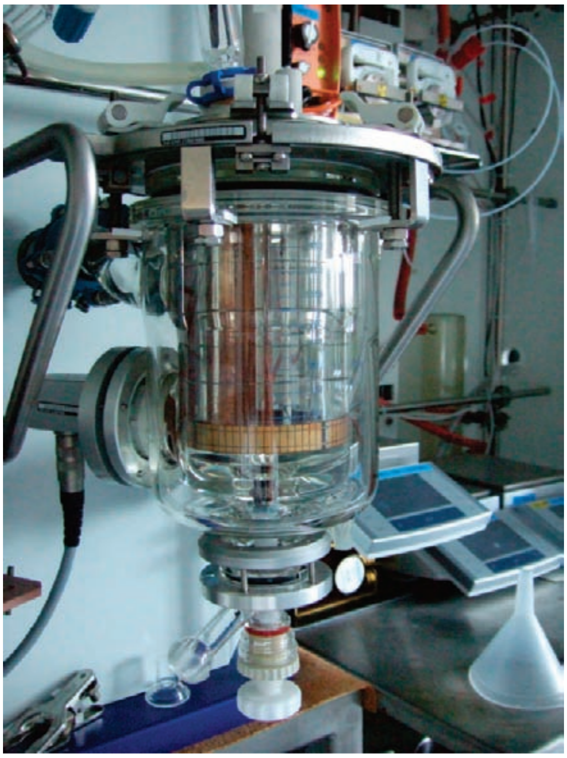

Figure 1. RC1e calorimeter with horizontal (ring) and vertical (back) heat-flow sensors.

$$\int_0^t q(\mathrm{RTCal})\,\mathrm{d}t = (mC_p + C_{pi})\Delta T_r$$

- The "standard" measurement mode consists of a reaction mixture temperature ramp of 0.3 K/min for 10 min by heating via the jacket, during which C_p is determined by the following equation, between two isothermal modes (regression area):

$$UA\int_0^t (T_r - T_j)\,\mathrm{d}t = (mC_p + C_{pi})\Delta T_r$$

A preliminary calibration by Joule effect is necessary to determine the UA term. This mode is relatively time-consuming (approximately one hour per measurement) and therefore not often used.

■ EXPERIMENTAL ERROR IN THE MEASUREMENT OF C_P

With regard to the calculation of the adiabatic increase in temperature, which permits an assessment of the hazard of the reaction ($\Delta T_{adiab} = Q_r/(m \times C_p)$), if the heat of reaction (Q_r) can often be calculated with confidence, the measurement of the specific heat capacity can sometimes give erratic results. As errors on both the heat flow and the C_p equally affect the calculation of the adiabatic temperature increase, it is important to know the experimental error of the determination of C_p, and which factors influence it. The measurement of the error on C_p has been described as being less than 0.5% by differential scanning calorimetry[14] and 4 to 10.5% by temperature oscillation calorimetry,[15] but to the best of our knowledge, the error on C_p in a RC1e has hitherto not been published.

Furthermore, our RC1e was fitted with a modified double-impeller stirrer, each with three blades at 315°, in order to offer a good coverage of the probes and an efficient stirring in a large range of volume fill. We also wanted to check the potential of this agitator.

The specific heat of a material is an intrinsic property, and cannot be easily correlated to other parameters. During calibration and experimentation, many factors can affect the accuracy of the measurement, such as the temperature, the stirring rate, the volume, the specific gravity and the viscosity. In fact, most of these factors affect either the system's heat loss term or the term *UA*, which are directly related to dynamic transfer and heat distribution in the reactor. The variation of C_p with temperature can be neglected on a first approach. In this study, the C_p was measured at 25 °C, a temperature of reference in the literature.

Our aim was to analyze the parameters which could influence the experimental error ΔC_p, defined as the difference between the actual value of specific heat (given in the literature for most pure solvents) and the measured value:

$$\Delta C_p = C_{p_{lit}} - C_{p_{exp}}$$

In order to describe this error over a complete operating range, the methodology of Statistical Design was applied to lower the number of experiments and facilitate the statistical treatment of the response.[16−19]

For the sake of simplification, we only considered parameters which are immediately available when conducting any calorimetric experiment: the volume (V) of the liquid, the stirring rate (R), and the value of C_p given by the calorimeter ($C_{p_{exp}}$). With these three factors, a response surface design could be proposed, which if validated could provide a model of ΔC_p as a second order polynomial function of the factors, and thus a prediction of the error everywhere in the experimental domain.

The limits of the experimental domain were determined as follows:

- Volume: in the 500 mL vessel used, after preliminary experiments the lowest practical volume was determined to be 150 mL and the upper limit was 450 mL.[20]
- Stirring rate: again, after preliminary experiments, the rate was allowed to vary between 200 and 700 rpm.[20]
- C_p: chloroform is the solvent with the lowest C_p: 0.95 $J\cdot g^{-1}\cdot K^{-1}$.[21,22] Water has the highest C_p: 4.18 $J\cdot g^{-1}\cdot K^{-1}$. For the center point of the domain, a liquid with a C_p equal to the mean of these limits (2.57 $J\cdot g^{-1}\cdot K^{-1}$) was ideally needed, but we were reluctant to use a mixture of solvents. We preferred to use a pure solvent, the C_p of which was also given with an accuracy of 0.01 $J\cdot g^{-1}\cdot K^{-1}$. Methanol with a C_p of 2.53 $J\cdot g^{-1}\cdot K^{-1}$ [21,23] was selected as a reference for the central point of this domain. These three solvents also offer a wide diversity in terms of polarity, viscosity, and density.

The design selected was a three-factor Central Composite Design with three levels per factor (−1, 0, +1 in coded values). In this design, the experiments are distributed in a cube (Figure 2). These three levels were best adapted to the constraint

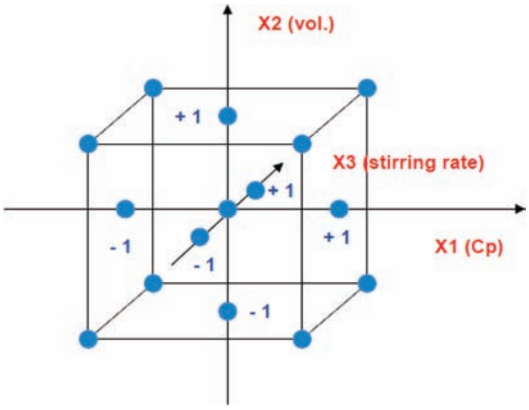

Figure 2. Central Composite Design with α = 1.

Table 1. Error on C_p with the QuickCal method depending on $C_{p_{exp}}$, volume and stirring rate[a]

solvent	$C_{p_{exp}}$ ($J\cdot g^{-1}\cdot K^{-1}$)	X_1	volume (mL)	X_2	rate (rpm)	X_3	$\Delta C_p(Q_c)$ ($J\cdot g^{-1}\cdot K^{-1}$)
$CHCl_3$ C_p = 0.95 $J\cdot g^{-1}\cdot K^{-1}$	1.102	−0.808	150	−1	200	−1	−0.152
	1.247	−0.732	150	−1	700	1	−0.297
	1.020	−0.851	300	0	450	0	−0.070
	0.949	−0.889	450	1	200	−1	0.001
	1.000	−0.862	450	1	700	1	−0.050
MeOH C_p = 2.53 $J\cdot g^{-1}\cdot K^{-1}$	2.909	0.142	150	−1	450	0	−0.379
	2.575	−0.034	300	0	200	−1	−0.045
	2.627	**0 (ref)**	**300**	**0**	**450**	**0**	**-0.097**
	2.684	**0 (ref)**	**300**	**0**	**450**	**0**	**-0.154**
	2.627	**0 (ref)**	**300**	**0**	**450**	**0**	**-0.097**
	2.617	**0 (ref)**	**300**	**0**	**450**	**0**	**-0.087**
	2.673	**0 (ref)**	**300**	**0**	**450**	**0**	**-0.143**
	2.609	**0 (ref)**	**300**	**0**	**450**	**0**	**-0.079**
	2.747	0.057	300	0	700	1	−0.217
	2.568	−0.038	450	1	450	0	−0.038
water C_p = 4.18 $J\cdot g^{-1}\cdot K^{-1}$	4.410	0.931	150	−1	200	−1	−0.230
	4.542	1 (ref)	150	−1	700	1	−0.362
	4.290	0.868	300	0	450	0	−0.110
	4.179	0.809	450	1	200	−1	0.001
	4.317	0.882	450	1	700	1	−0.137

[a] Centre points in bold.

Table 2. Error on C_p with the RTCal method depending on $C_{p_{exp}}$, volume and stirring rate[a]

solvent	$C_{p_{exp}}$ ($J \cdot g^{-1} \cdot K^{-1}$)	X_1	volume (mL)	X_2	rate (rpm)	X_3	$\Delta C_p(RTc)$ ($J \cdot g^{-1} \cdot K^{-1}$)
$CHCl_3$ $C_p = 0.95\ J \cdot g^{-1} \cdot K^{-1}$	1.067	−0.667	150	−1	200	−1	−0.117
	0.962	−0.719	150	−1	700	1	−0.012
	0.928	−0.736	300	0	450	0	0.022
	0.992	−0.704	450	1	200	−1	−0.042
	0.974	−0.713	450	1	700	1	−0.024
MeOH $C_p = 2.53\ J \cdot g^{-1} \cdot K^{-1}$	2.653	0.126	150	−1	450	0	−0.123
	2.420	0.010	300	0	200	−1	0.111
	2.394	**0 (ref)**	**300**	**0**	**450**	**0**	**0.136**
	2.440	**0 (ref)**	**300**	**0**	**450**	**0**	**0.090**
	2.394	**0 (ref)**	**300**	**0**	**450**	**0**	**0.136**
	2.369	**0 (ref)**	**300**	**0**	**450**	**0**	**0.161**
	2.428	**0 (ref)**	**300**	**0**	**450**	**0**	**0.102**
	2.375	**0 (ref)**	**300**	**0**	**450**	**0**	**0.155**
	2.418	0.009	300	0	700	1	0.112
	2.501	0.050	450	1	450	0	0.029
water $C_p = 4.18\ J \cdot g^{-1} \cdot K^{-1}$	4.400	1 (ref)	150	−1	200	−1	−0.220
	4.066	0.833	150	−1	700	1	0.114
	4.131	0.866	300	0	450	0	0.049
	4.241	0.920	450	1	200	−1	−0.061
	4.156	0.878	450	1	700	1	0.024

[a] Centre points in bold.

Table 3. Analysis of variance of the models

response	$\Delta C_p(Q_c)$ in $J \cdot g^{-1} \cdot K^{-1}$	$\Delta C_p(RTc)$ in $J \cdot g^{-1} \cdot K^{-1}$
model (in real values)	$-0.3537 - 0.1008\ C_p + 2.5778 \times 10^{-3}\ V - 2.3915 \times 10^{-4}\ R + 5.0472 \times 10^{-5}\ C_p \cdot V - 2.8687 \times 10^{-5}\ C_p \cdot R + 2.4481 \times 10^{-7}\ V \cdot R + 0.0151\ C_p^2 - 3.398 \times 10^{-6}\ V^2 - 9.84 \times 10^{-9}\ R^2$	$-0.6886 + 0.0795\ C_p + 4.2212 \times 10^{-3}\ V - 6.3154 \times 10^{-5}\ R - 8.16.10^{-7}\ C_p \cdot V - 8.2615 \times 10^{-5}\ C_p \cdot R - 1.0767 \times 10^{-6}\ V \cdot R - 0.0216\ C_p^2 - 5.9167 \times 10^{-6}\ V^2 + 4.2628 \times 10^{-7}\ R^2$
Fischer's test (model)	F value = 16.0 (significant)	F value = 8.31 (significant)
Fischer's test (lack of fit)	F value = 2.07 (not significant)	F value = 5.14 (significant)

of C_p distribution of common solvents, as the experiments could be conducted with only three of them. A centered composite design necessitates at least 15 experiments, but it is necessary to reproduce the centre points at least three times in order to assess experimental variations. Twenty experiments were carried out, which included six centre points.

It is worth noting that our design is not an ideal cube, first of all because, as already stated, the C_p of methanol is not strictly the mean of the C_p of chloroform and that of water, and second because the value of C_p is experimental and not theoretical. It is possible to build a less deformed design using the theoretical values of C_p, but this model would give the experimental error with respect to a theoretical value of C_p, which is of little use when conducting a calorimetric experiment in an actual mixture whose C_p is unknown. A prediction of the error based on the experimental value of C_p is by far more useful. Besides, this lack of symmetry has little significance in the overall efficiency of the model, as long as a reasonable evaluation of the pure error, necessary in assessing the validity of the model, can be obtained from repeated centre points.

The response modeled was the error of C_p for each measurement method: QuickCal ($\Delta C_p(Q_c)$; Table 1) and RTCal ($\Delta C_p(RTc)$; Table 2). The error of the standard method was also studied, but the results will not be presented here, because the trends were very similar to that of the QuickCal method, and the standard method is more time-consuming.

The experimental results show that the QuickCal mode overestimates the C_p by up to 0.4 $J \cdot g^{-1} \cdot K^{-1}$ (Table 1), whereas the RTCal mode gives more accurate values (± 0.2 $J \cdot g^{-1} \cdot K^{-1}$) (Table 2). These values are significantly higher than the standard deviation determined by the repetition of the center points (0.03 $J \cdot g^{-1} \cdot K^{-1}$ in both cases).

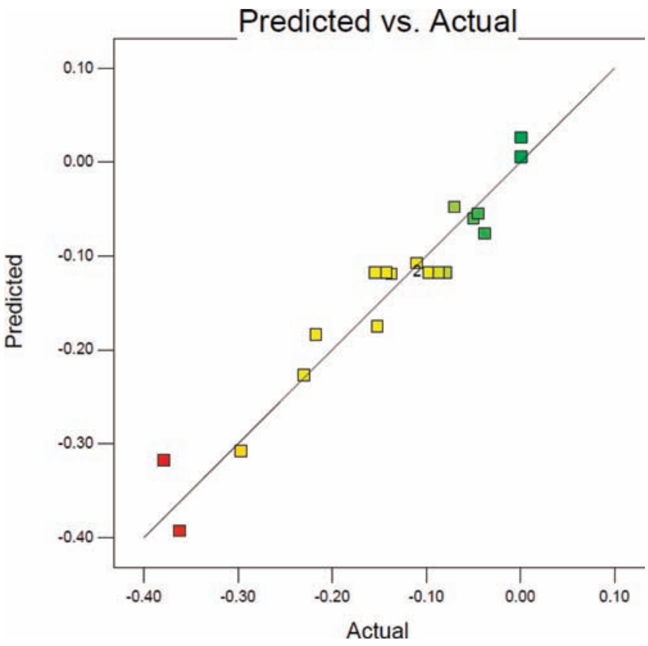

Figure 3. Prediction of the model $\Delta C_p(Q_c) = f(C_p(Q_c), V, R)$.

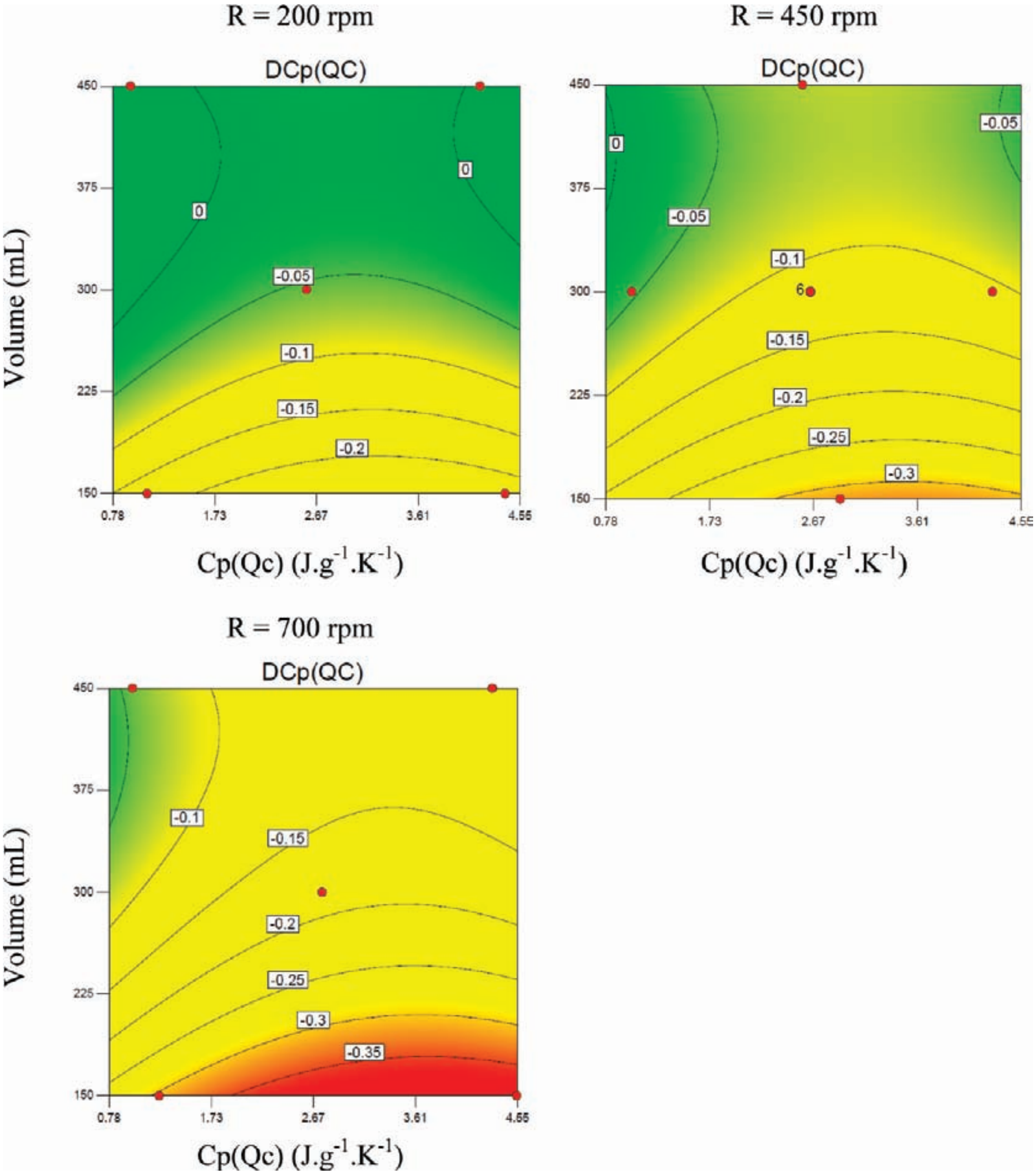

Figure 4. Contour maps of the model $\Delta C_p(Q_c) = f(C_p(Q_c), V, R)$.

The results were analyzed using NEMRODW[24] (version 2007-03) and Design Expert[25] (version 8.0) software. Both gave exactly the same models (Table 3).

For the QuickCal mode, the polynomial model proposed complies with the two tests of analysis of variance (ANOVA): the mean square of the regression is significantly higher than the mean square of the residues (Fischer's test of model), and the mean square of the lack of fit is not significantly different from the mean square of the experimental error (Fischer's test of lack of fit; Table 3). Thus, the model represents well the error on C_p on the experimental points. The predicted value of $\Delta C_p(Q_c)$ differs by 0.06 $J \cdot g^{-1} \cdot K^{-1}$ to the experimental value only in one experiment (figure 3), which is acceptable. The contour maps displaying the predicted error on C_p with respect to the experimental specific heat capacity, the volume and the stirring rate (figure 4) can be used to navigate in the experimental domain.

On the other hand, the model of prediction of C_p error with RTCal mode is not well adjusted: there is a significant lack of fit (Table 3). As the experimental error is small using this mode of measurement ($\pm$ 0.2 $J \cdot g^{-1} K^{-1}$; up to 11% for chloroform in one point) the model cannot improve it efficiently. The predicted contour maps generated by this model can therefore not be used with confidence. In the rest of the paper, the experimental values of C_p by RTCal will not be corrected.

The contour maps (figure 4) show the zones in which the QuickCal mode estimates the C_p with a high accuracy (<0.1 $J \cdot g^{-1} \cdot K^{-1}$: high volume, low stirring rate), and the zones with the highest error. Low volumes and high stirring rates can result in a significant overestimation of the specific heat capacity, up to 0.3 $J \cdot g^{-1} \cdot K^{-1}$ as in the case of chloroform, which represents 30%.

It is not quite surprising that low volumes affect the measurement of C_p by QuickCal: as heat dissipated by the electric resistance is always the same regardless of the reactor contents,

Table 4. Test of the model with other solvents[a]

		method		
		QuickCcal		RTCal
solvent	C_p literature	C_p measured	C_p corrected	C_p measured
pyridine	1.68[21,23]	**1.76 (+5%)**	1.65 (−2%)	1.63 (−3%)
NMP	1.68[26,27]	**1.83 (+9%)**	1.71 (+2%)	1.72 (+2%)
toluene	1.70[21,23,26]	1.76 (+3%)	1.65 (−3%)	**1.62 (−5%)**
chlorobutane	1.72[23,28,29]	**1.83 (+6%)**	1.72 (0%)	1.70 (−1%)
THF	1.72[21,23,26]	**1.83 (+6%)**	1.71 (−1%)	1.67 (−3%)
AcOnPr	1.92[21,23,26]	**2.02 (+5%)**	1.89 (−2%)	1.87 (−3%)
diisopropyl ether	2.12[23,26]	**2.23 (+5%)**	2.10 (1%)	2.07 (−2%)
TEA	2.16[22,23,29]	**2.29 (+6%)**	2.16 (0%)	2.11 (−2%)
ethylene glycol	2.40[21,30]	2.38 (−1%)	**2.25 (−6%)**	2.39 (0%)
2-butanol	2.66[21,23,31]	2.73 (+3%)	2.59 (−3%)	2.69 (+1%)
40% glycol	3.57[21,30]	3.56 (0%)	3.42 (−4%)	**3.39 (−5%)**

[a] C_p in $J \cdot g^{-1} \cdot K^{-1}$. The figures are the average of four measurements, generally done at 225 and 375 mL and 325 and 575 rpm. Figures in bold indicate an error higher than 4% with respect to the literature value. Numbers in parentheses represent the relative error with respect to the literature value.

this method is sensitive to volume fill and the solvent nature. Besides, the surface exchange is smaller at low volume fill, and the heat losses are more important.

The RTCal system is less dependent on the volume effect. The horizontal heat sensors used by this system are situated at a level corresponding to 80 mL and are not affected by the variations of volume above 150 mL. With this system, the error on C_p never exceeds 11%, which is quite acceptable for reaction calorimetry.

Using the calorimeter only in the zone of confidence is too restrictive for the current work in process safety. It is feasible to act on the stirring rate, but not on the C_p, and not always on the volume: variations of volumes by 300% are common during a dosing in a process. The polynomial model generated for QuickCal mode gives at any point in the experimental domain the error on C_p (ΔC_p) which can be added to the experimental value in order to get a more accurate value: $C_{p_{corr.}} = C_{p_{exp.}} + \Delta C_p$. This is particularly useful if the relative error on C_p is higher than 10%.

In summary, in a very simple and fast set of experiments (3 solvents, 20 measurements, approximately 4 days work), a model could be generated, which enabled us to establish the zone of confidence of the calorimeter regarding the determination of specific heat capacity of the QuickCal mode and, if necessary, to correct the experimental value.

VALIDATION OF THE MODEL WITH OTHER SOLVENTS

The model generated is not useful if it applies only to water, methanol, and chloroform. We therefore compared the experimental and corrected values of heat capacities of some solvents obtained by QuickCal with those given by the literature. The experimental values obtained by RTCal were also compared. These solvents were selected to cover as much as possible the range of C_p , including a 6/4 (m/m) mixture of water and ethylene glycol with a C_p of 3.57 $J \cdot g^{-1} \cdot K^{-1}$. The volumes and stirring rates were fixed at the levels ±0.5 (in coded values) in order to explore the zones of the domain not covered by experiments in the initial matrix. Four measurements of C_p were conducted per solvent, one for each volume and stirring rate level. The mean value of experimental C_p and that of the corrected C_p were compared to the value given in the literature (Table 4). With the QuickCal method, the crude experimental value often differs from the literature value by more than 4%, whereas the corrected value is always accurate (4% error at most), except in the case of ethylene glycol (6% error). On the other hand, with the RTCal method, the experimental value is always acceptable (5% error at most). Besides, these test points confirmed that the experimental error on C_p is negligible at high volumes (375 mL, level +0.5), but significant at low volumes (225 mL, level −0.5).

As a conclusion, these test points confirm the validity of the model used to correct the C_p measured with the QuickCal method, and the contour maps given in figure 4 can be used for any solvent or homogeneous reaction mixture near 25 °C. Moreover, the corrected value of C_p(QuickCal) is always very close to the experimental value of C_p(RTCal).

DETERMINATION OF C_P OF ADDITIONAL SOLVENTS

The validation performed enables us to correct with confidence the crude measurement of specific heat capacity of any homogeneous mixture. As an application, other solvents were selected because the values of their C_p are either not confirmed, or missing. The results are given in Table 5. Again, four measurements per solvent were carried out, each corresponding to the levels ± 0.5 of volume and stirring rate. The experimental value of C_p reported is the mean of these measurements, and the corrected value of C_p is the mean of the four corrected values. The relative error was taken to be the maximum error on the corrected value of C_p by QuickCal (with the exception of ethylene glycol), and that on the experimental value by RTCal, on the test points: 5% in both cases (Table 4). This is all the more acceptable, as the C_p of solvents in Table 5 are in the same range of C_p as those in Table 4, and measured under the same conditions.

Again, the value of C_p by QuickCal method corrected by the model is always very close to the experimental value by RTCal. We therefore propose the average of both figures for the specific heat capacity of the following solvents at 25 °C: anisole (1.77 $J \cdot g^{-1} \cdot K^{-1}$), methyl-tetrahydrofuran (1.77 $J \cdot g^{-1} \cdot K^{-1}$), diethoxymethane (2.07 $J \cdot g^{-1} \cdot K^{-1}$), ethyl-*tert*-butylether (2.13 $J \cdot g^{-1} \cdot K^{-1}$), dimethyl-ethyleneurea (1.73 $J \cdot g^{-1} \cdot K^{-1}$) and dimethyl-propylene-urea (1.70 $J \cdot g^{-1} \cdot K^{-1}$).

Table 5. Determination of C_p[a] with RC1e

		method		
		QuickCal		RTCal
solvent	C_p literature	C_p exp.	C_p corr.	C_p exp.
anisole	–	1.87	1.75 ± 0.09	1.79 ± 0.09
Me-THF	1.80[32]	1.90	1.78 ± 0.09	1.76 ± 0.09
ETBE	2.16[33]	2.27	2.14 ± 0.11	2.12 ± 0.11
diethoxymethane	–	2.21	2.08 ± 0.10	2.06 ± 0.10
DMEU	–	1.85	1.73 ± 0.09	1.73 ± 0.09
DMPU	–	1.80	1.69 ± 0.09	1.72 ± 0.09

[a] C_p in $J \cdot g^{-1} \cdot K^{-1}$. The figures are the average of four measurements, done at 225 and 375 mL and 325 and 575 rpm.

Table 6. Origin and grade of solvents

solvent	CAS no.	supplier	grade
chloroform	67-66-3	Acros	99+%, stabilized with ethanol
methanol	67-56-1	SDS	99.8%
pyridine	110-86-1	Acros	99+%
NMP	872-50-4	Acros	99+%
toluene	108-88-3	SDS	99.8%, anhydrous
THF	109-99-9	SDS	99.9%, stabilized with BHT
AcOnPr	109-60-4	Acros	99%
diisopropyl ether	108-20-3	SDS	>98.5%, anhydrous
TEA	121-44-8	Acros	99%
ethylene glycol	107-21-1	SDS	>99%
2-butanol	78-92-2	Acros	99+%
1-chlorobutane	106-69-3	Acros	99+%
anisole	100-66-3	Acros	99%
Me-THF	96-47-9	Acros	99+%, anhydrous, stabilized with BHT
ETBE	637-92-3	TCI	99%
diethoxymethane	462-95-3	Acros	99%, stabilized with BHT
DMEU	80-73-9	Acros	98%
DMPU	7226-23-5	Acros	97%

CONCLUSION

By a simple design involving only 20 rapid experiments and using easily available solvents (chloroform, methanol and water), a model could be generated, capable of determining the experimental error in the measurement of specific heat capacities (C_p) on a RC1e calorimeter using the QuickCal mode. The predicted error depends only on the C_p measured, the volume of liquid and the stirring rate.

As a first application, this permitted us to establish the experimental zone in which the error is acceptable for process safety purposes (usually 10%). If the experiment is run outside this zone, or if a more accurate value of C_p is needed, the model can correct the experimental C_p value. As a result, the maximal adiabatic temperature increase of a process is calculated with more confidence.

The model thus generated on the RC1e with the QuickCal mode allowed us also to calculate with an accuracy of 5% the C_p of solvents which have not been widely established. These values were confirmed by the measurement of C_p with the RTCal mode.

Of course a model is only valid with a given system (calorimeter, inserts and method of C_p determination). The contour maps thus generated are valid as long as the inserts are not changed, which is the most common situation. Anyone can reproduce the methodology with its own calorimeter and establish, after a couple of days of experiments, and using classical Statistical Design software, its own zone of confidence. Even if the model is not valid, a rough estimation of the error of C_p determination, based on the experimental values, can be established.

All this work was done at 25 °C, the classical temperature for C_p. As the specific heat capacity varies with the temperature, it will be interesting to investigate the evolution of the experimental error in this fourth dimension. The case of heterogeneous mixtures of solvents also merits some investigation.

EXPERIMENTAL SECTION

General. The experiments were carried out in a 500 mL calorimeter Mettler RC1e AP01-0.5-5W fitted with two three blade turbines, inclined at 315°. These blades are situated at the bottom and at midlevel. As with new fittings, the Cp of this insert was determined as a function of volume and entered into the operating software using standard Mettler procedure involving the determination of the volume of the insert by a displacement method.

Origin and Grade of Solvents. The solvents were taken from nonopened bottles, and were not further purified. The origin and grades are given in Table 6. Demineralized water was used.

Measurement of C_p. For the Central Composite Design, the acquisition of experimental C_p was grouped by category of solvents. All experiments were conducted at 25 °C.

Separate volumes of solvents were used to additively constitute the three levels chosen by the design. After the experiment, the reactor was emptied and the collected solvent was weighed to check the accuracy of the final volume. The centre points (measurement of C_p of 300 mL of methanol at 450 rpm) were repeated regularly during the Central Composite Design then during the determination of the C_p of alternative solvents, in order to obtain a better prediction of the pure error associated with the measurement.

The QuickCal and RTCal modes were applied one after the other for each point. The standard mode was used only during the centered composite design. For the QuickCal mode, *UA* and C_p were determined simultaneously without using any correction for the virtual volume, i.e. without any visual correction to compensate for the increased wetted surface due to agitation.

In order to ensure that the parameters are weighed equally during model regression, the domain is coded into dimensionless values X_i which vary from −1 to +1 and are equal to zero in the centre of the domain.

X_1 is the coded value for $C_{p_{exp}}$, $X_1 = 0$ corresponds to the mean C_{p0} of the values of C_p measured at the centre of the domain for each method (QuickCal or RTCal). The level +1 of X_1 was fixed arbitrarily at the highest value of C_p measured with water in the set of experiments ($C_{p_{max}}$). For each method of calibration, the value of X_1 is therefore given by the formula:

$$X_1 = (C_{p_{exp}} - C_{p_0})/(C_{p_{max}} - C_{p_0})$$

The coded value X_2 for the volume is:

$$X_2 = (V(\text{in mL}) - 300)/150$$

The coded value X_3 for the stirring rate is:

$$X_3 = (R(\text{in rpm}) - 450)/250$$

In coded values, the polynomial models are (coefficients in $J \cdot g^{-1} \cdot K^{-1}$):

$$\begin{aligned}\Delta C_p(Q_c) = & -0.12 - 0.036X_1 + 0.12X_2 - 0.063X_3 \\ & + 0.014X_1X_2 - 0.014X_1X_3 + 0.009X_2X_3 \\ & + 0.055{X_1}^2 - 0.076{X_2}^2\end{aligned}$$

$$\Delta C_p(\mathrm{RTc}) = 0.11 + 0.026X_1 + 0.028X_2 - 0.049X_3 + 0.041X_1X_3 - 0.04X_2X_3 - 0.086{X_1}^2 - 0.13{X_2}^2 + 0.027{X_3}^2$$

Coefficients below 10^{-3} J·g^{-1}·K^{-1} are neglected.

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(6) (a) www.mt.com. (b) The isothermal mode is more widely used, but the RC1e can also be used in isoperibolic mode.

(7) "Isoperibolic" means that the temperature of the surroundings (the jacket) is maintained constant.

(8) The DRC consists of two vessels, one devoted to the reaction and the other serving as a reference. In the DRC, the heat flow is not measured using the temperature of the jacket fluid but that of the reference vessel (T_{ref}): $q = UA\ (T_r - T_{ref})$.

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