Journal of Thermal Analysis and Calorimetry, Vol. 80 (2005) 763–767

EFFECT OF THE INJECTION VELOCITY ON THE SPATIAL LOCALIZATION OF THE MIXTURE DISSIPATION IN A FLOW MICROCALORIMETER

F. Socorro and M. R. de Rivera[*]

Departamento Física, Universidad de Las Palmas, 35017 Las Palmas de Gran Canaria, Spain

The effect of the injection velocity in the chemical calibration of a flow microcalorimeter is studied in this article. The experimental measures show a parabolic variation of the sensitivity in terms of the injection flow. The considered hypothesis is that the maximum of the sensitivity curve is produced when the spatial area in which the mixture dissipation takes place is centred with regard to the detector system. When increasing the injection flow, this mixture zone moves till it goes out of the detection area making the sensitivity diminish. It has been defined a time constant τ_{mix} which is related to the establishment time of the homogeneous mixture and with the length occupied by the mixture dissipation. A study has been carried out with three liquid mixtures that have different behaviours; within these mixtures, τ_{mix} has been determined in terms of the injection flow and the considered hypothesis has been confirmed.

Keywords: *chemical calibration, flow microcalorimeter, injection calorimeter, isothermal conduction calorimeter, liquid mixtures, sensitivity*

Introduction

Flow microcalorimeters are isothermal heat conduction calorimeters that are used to determine the energy developed in a liquid mixture process [1]. The basic principle of operation consists in injecting two liquids continuously in a mixture zone; when the mixture is homogeneous, the experimental response reaches the stationary state. In this situation the power developed by the mixture is equal to the experimental output divided by the sensitivity of the calorimeter. The concentration of the mixture is determined from the injection flows, new mixture concentrations are obtained by changing the injection flows. The improvement of the instruments and, above all, their automation have facilitated their handling, these are the reasons why their use have increased considerably in the last years.

Among the most interesting works within the large bibliography about the calibration of these instruments, we want to point out the articles by Monk and Wadsö and Harsted and Thomsen [2, 3] in which they propose empirical expressions about the sensitivity in terms of the injection flow, and the work by Tanaka *et al*. [4] in which he adds the dependence of the heat capacity of the injected liquids in the sensitivity. Subsequently, a methodology of calibration has been established for these instruments [5–7] with the help of some models that try to explain their static and dynamic operation. In these last works, a clear difference between the sensitivity obtained in the electrical calibrations and the one obtained in the chemical calibrations can be observed; besides, these differences are also extensive to the different chemical calibrations. This uncertainty in the sensitivity is justified because the energetic dissipation does not always happen in the same place. Faced with the impossibility of establishing a sensitivity function that could be applied for any kind of mixture, it is proposed to establish, after a thorough experimental study, a validity domain of the calibration carried out; this domain is defined with the parameter $\rho c_p f$ (ρc_p: volumetric heat capacity, f: injection flow). Thus, for the established domain, a sensitivity value is proposed with an uncertainty that has to be calculated in the calibration.

In this article, the causes by which the distinct chemical calibrations of a flow microcalorimeter provide different sensitivity values will be studied. The preliminary working hypothesis is that these differences are due to the fact that the mixture dissipation does not always occur in the same area and that each mixture shows a different behaviour. The need for a thorough study is increased because, nowadays, very small new devices [8] whose operating principle is similar and, probably, with the same calibration problems are being developed.

This work will be exposed according to the following order: firstly, the experimental system and the experimental measures will be briefly described; secondly, our work will centre upon the study of the sensitivity in terms of $\rho c_p f$ and the injection flow, also de-

---

[*] Author for correspondence: mrodriguez@dfis.ulpgc.es

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

fining. the time constant τ_{mix}; and finally, it will take place a final discussion presenting the hypothesis about how the mixture dissipation is produced in each one of the three studied mixtures.

Device and experimental

The utilized experimental system is a flow microcalorimeter TAM 2277-204 by Thermometric AB. The detector system of thermopairs provides the experimental output that is directly read by a Hewlett Packard HP3457A multimeter (10 nV of resolution). The system is controlled through the bus GPIB by a PC and the readings are stored for the subsequent analysis. The sampling interval used is $\Delta t \approx 1.0989$ s. The injection system is composed of two Hamilton syringes of 50 cm^3 pushed by a stepper motor MT-160-250 by Microcontrole producing an injection of 0.0831 μL per step of the motor; the desired injection flow is obtained by programming the number of steps in every sampling period [5, 6].

For this study, it has been used the measures of chemical calibration provided by the liquid mixtures water+methanol, cyclohexane+benzene and cyclohexane+hexane. Different injection flows have been tested: from $2\cdot 0.75$ to $2\cdot 8.25$ $\mu L\ s^{-1}$ and, in all cases, both mixed liquids are injected with the same flow (f_1=f_2). As a consequence, the concentration and the enthalpy per mol of mixture is the same although the total injection flow was changed. The enthalpies of reference for the working temperature T_0=298.15 K and for the concentration in which f_1=f_2, are the following ones:

water(1)+ methanol(2)	H^E_{ref}=875.0 J mol^{-1}	x_1=0.6926 [9]
cyclohexane(1)+ benzene(2)	H^E_{ref}=796.2 J mol^{-1}	x_1=0.4527 [10]
cyclohexane(1)+ hexane(2)	H^E_{ref}=220.3 J mol^{-1}	x_1=0.5472 [11]

As a sample of the measures utilized in this work, the experimental outputs corresponding to the mixture of cyclohexane+benzene for three different injection flows are shown in Fig. 1: $2\cdot 0.75$, $2\cdot 1.5$ and $2\cdot 2.25$ $\mu L\ s^{-1}$; the powers developed in each case are –12.379, –24.758 and –37.137 mW, respectively. Although the noise of the baseline is of ±1 μV, when the mixture dissipation begins, it appears some low frequency oscillation (≈0.01 Hz) that makes the relationship signal/noise of these curves be between 40 and 500 (32 and 54 dB, respectively).

The measures of electrical calibration consist in the dissipation of a known power in the calibration resistance when the same pure liquid is being injected for each pipe; the liquids and flows used in the electrical calibration are the same used in the chemical calibration, in these curves the relationship signal/noise is of 5600 (≈75 dB).

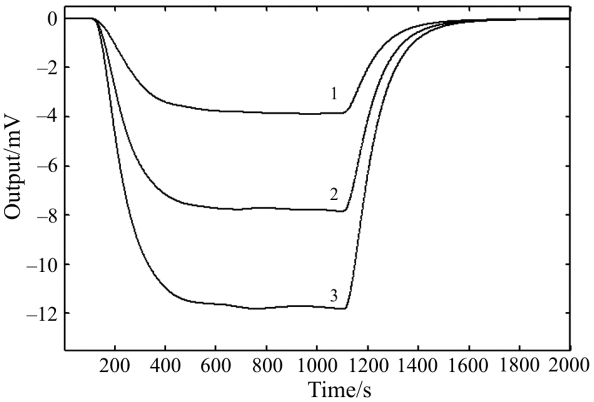

Fig. 1 Curves corresponding to the mixture cyclohexane+benzene for different injection flows: 1 – $2\cdot 0.75$, 2 – $2\cdot 1.5$ and 3 – $2\cdot 2.25$ $\mu L\ s^{-1}$. The powers developed in each case are –12.379, –24.758 and –37.137 mW

Sensitivity of the calorimeter *vs.* $\rho c_p f$

To model the device, it is necessary to calibrate the system with dissipations of the Joule type in order to obtain results that permit to determine the size and complexity of the model required by the calorimeter. The measures of electrical calibration carried out on this system [5, 6] show that the system remains well identified with a transference function (*TF*) of two poles:

$$TF(s) = \frac{Y(s)}{W(s)} = \frac{K}{(1+s\tau_1)(1+s\tau_2)} \qquad (1)$$

where s is the Laplace variable, $Y(s)$ is the output Laplace transform or curve, $W(s)$ is the input Laplace transform or developed power, K is the sensitivity, τ_1 and τ_2 are the time constants. These parameters have been evaluated and it has been checked that the sensitivity changes with the heat capacity and with the injection flow of the injected liquids [2–7] and that the main time constant, τ_1, increases with the heat capacity of the liquids and decreases with the injection flow [5–7].

An analysis of all the calibration measures carried out suggests to impose a maximum limit in the injection flow that guarantees that the injected liquids have acquired, through the homogeniser coil, the thermostat temperature before arriving at the mixture zone. The limit chosen for our calorimeter is of a maximum volumetric flow, for each pipe, 7 $\mu L\ s^{-1}$ and a flow in heat capacity units, for each pipe, $\rho c_p f$<12.5 mW K^{-1} (ρc_p is the volumetric heat capacity and f is the injection flow). With these limits, the measures of chemical calibration used in this study have dissipations that goes from 50 to 250 mW in the case of the mixture water+methanol (exothermic), and from –2 to –120 mW in the case of endothermic mixtures (cyclohexane+benzene and cyclohexane+hexane).

In Fig. 2, it is shown the result of the sensitivity obtained in the chemical calibrations compared with the sensitivity obtained in the electrical calibrations. It is observed that the sensitivity obtained in the electrical calibrations can be expressed in terms of the heat capacity of the injected liquids and the injection flow, curve 1 in Fig. 2 shows the polynomial carried out following the subsequent function:

$$K_{\text{elect}} = a_0 + a_1(\rho c_{\text{p}} f)_{\text{T}} + \\ +a_2(\rho c_{\text{p}} f)_{\text{T}}^2 + a_3(\rho c_{\text{p}} f)_{\text{T}}^3 \ \ [\text{mV W}^{-1}] \qquad (2)$$

where $(\rho c_p f)_T=(\rho c_p f)_1+(\rho c_p f)_2$ is in mW K^{-1}; ρc_p is the volumetric heat capacity and f is the injection flow; the polynomial coefficients have the following values: a_0=311.98; a_1=0.818; a_2=–99.2·10^{-3}; a_3=1.96·10^{-3}.

In this adjustment, there is an acceptable maximum dispersion of 1.98 mV W^{-1} (0.64%) that can be justified by the different thermal conductivities and viscosities of the injected liquids.

However, the results of the chemical calibration do not follow a function of $(\rho c_p f)_T$. The dispersion that is obtained in the chemical calibration with regard to the electrical calibration (9 mV W^{-1}) and between both chemical calibrations is mainly due to two causes: the first one refers to the different place where the mixture dissipation is developed, and the second one to the spatial extension that occupies. In order to support these hypotheses, we are going to carry out an analysis of the sensitivity obtained in the chemical calibration in terms of the injection flow.

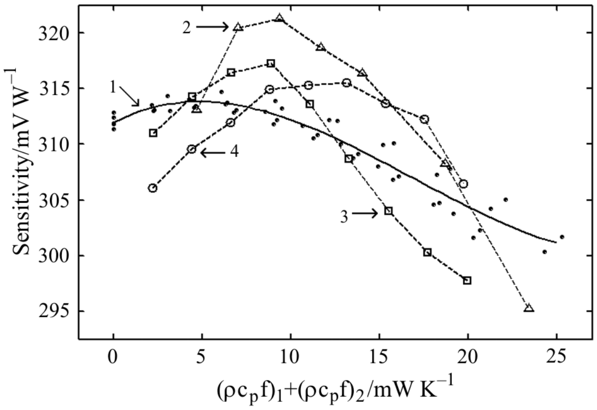

Fig. 2 Sensitivity in terms of $(\rho c_p f)_1+(\rho c_p f)_2$. Curve 1 is an adjustment on the sensitivity values obtained in the electrical calibrations by 1 – injecting water, methanol, benzene, hexane and cyclohexane, curves 2–4 correspond to the sensitivity values obtained in the chemical calibrations: 2 – water+methanol, 3 – benzene+cyclohexane and 4 – cyclohexane+hexane

Sensitivity of the calorimeter *vs.* flow rate f_T

To explain the results obtained in the chemical calibration, it is introduced an additional time constant (τ_{mix}) that is related to the establishment time of the homogeneous mixture and that will also be associated with the spatial length of the mixture dissipation. With this hypothesis, the real power of mixture in terms of time, $W_{\text{mix}}(t)$, would be represented by:

$$W_{\text{mix}}(t) = (\dot{n}_1 + \dot{n}_2)H_{\text{ref}}^{\text{E}}[1 - \exp(-t/\tau_{\text{mix}})] \qquad (3)$$

where $H_{\text{ref}}^{\text{E}}$ is the enthalpy of reference; $\dot{n}_1$ and $\dot{n}_2$ are the injection flows in mol s^{-1}.

In previous works, this time constant has been determined starting from a complex process of calculation that requires to suppose some time constants that have been previously obtained in electrical calibrations [5, 6]. In this work, it is presented a simpler way for its determination consisting in identifying the return to zero of the mixture curve; this situation has two advantages:

- as there is no injection, the first and second time constants of the *TF* (Eq. (1)) are invariant for the utilized mixture
- as there is no injection, the low frequency oscillations characteristic of the mixture dissipation are not present, so the relationship signal/noise is better

Supposing that the establishment time of the homogeneous mixture is the same as the disappearance time of that mixture; i.e., Eq. (3) is considered not only valid for the establishment of the mixture but also for the end of its dissipation.

Figure 3 shows two curves corresponding to the mixture cyclohexane+benzene for two different injection flows: f_1+f_2=1.5 μL s^{-1} (curve 1) and f_1+f_2=13.5 μL s^{-1} (curve 2), where $f_1=f_2$. The vertical scale has been normalized to compare the dynamical response of the two curves, in this comparison it is observed that, in the initial part of the curve, the first time constant has diminished as the injection flow is increased (the response is faster); however, in the final part of the curves there is a slight difference in the dynamics of both curves that is supposed to be only due to the different value of τ_{mix} in each one of the mixtures.

For the final section of the considered curve, it is supposed that it follows a transference function whose time constants (τ_1 and τ_2) are invariant for every type of mixtures and that they do not change with the injection flow. In the determination of the three time constants (τ_1, τ_2 and τ_{mix}), a non-linear adjustment method by minimal squares based on Marquardt's algorithm [12] is used and, for this method, we use the routine 'mrqmin' provided by numerical recipes in Fortran [13]. In the adjustment of every experimental curve it has been used 1000 dots, the value of the stan-

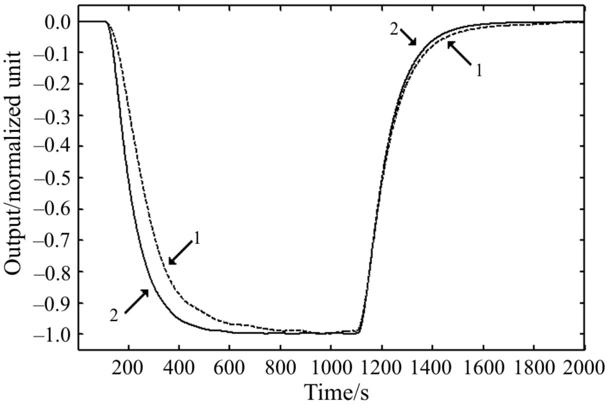

Fig. 3 Curves corresponding to the mixture cyclohexane+benzene curve 1 – for $f_1+f_2=1.5$ μL s^{-1} and curve 2 – for $f_1+f_2=13.5$ μL s^{-1}, where $f_1=f_2$. The vertical scale has been normalized to compare the dynamical response of the curves

dard deviation (σ_d) depends on the amplitude of the signal and, in the calculations carried out, its value relative to the maximum value of the curve (y_{max}) has not been over 0.8%, that is to say: $100\sigma_d/y_{max}<0.8$.

In the case of the mixtures water+methanol, the first obtained time constant is $\tau_1=115$ s, and for the other two mixtures (cyclohexane+benzene and cyclohexane+hexane) is $\tau_1=103$ s. The second obtained time constant remains invariant in the three cases: $\tau_2=24$ s.

The value of τ_{mix} depends on the mixture type and the injection flow. Figure 4 shows the values obtained for each studied mixture; in Fig. 5 it is represented the sensitivity, K_{mix}, in terms of the total injection flow. In these figures (Figs 4 and 5) it is observed a relationship between the situation of the maximum of the curve K_{mix} and the value of τ_{mix}: the greater the time constant τ_{mix}, the lesser the injection flow for which the maximum of the sensitivity curve takes place. In this case, the τ_{mix} of the mixture water+methanol (M1) is the highest and the maximum of the sensitivity curve of the other two mixtures is produced for a lesser total flow ($f_T=3.16$ μL s^{-1}), while the maximum of the sensitivity curves of the other two mixtures is produced for greater injection flows $f_T=4.64$ μL s^{-1} for the mixture cyclohexane+benzene (M2) and $f_T=8.36$ μL s^{-1} for the mixture cyclohexane+hexane (M3); this is coherent with the order $(\tau_{mix})_{M1}>(\tau_{mix})_{M2}>(\tau_{mix})_{M3}$.

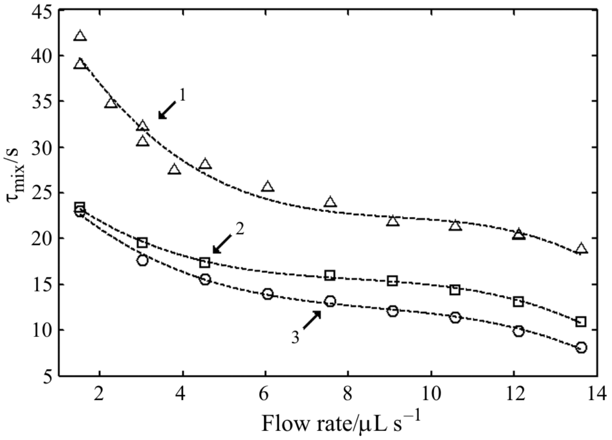

Fig. 4 Values of τ_{mix} in terms of the total injection flow. Cases: 1 – mixture water+methanol, 2 – mixture benzene+cyclohexane and 3 – mixture cyclohexane+hexane

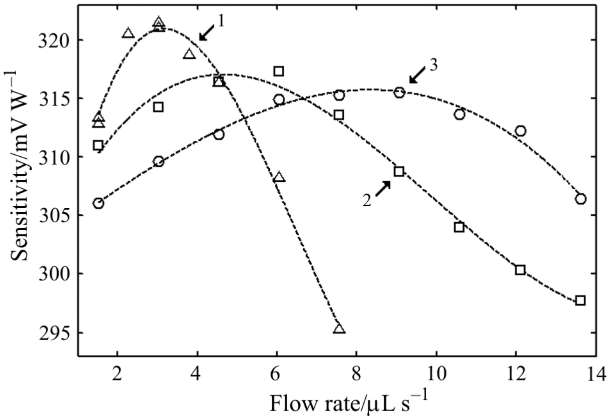

Fig. 5 Sensitivity values K_{mix} in terms of the total injection flow. Cases: 1 – mixture water+methanol, 2 – mixture benzene+cyclohexane and 3 – mixture cyclohexane+hexane

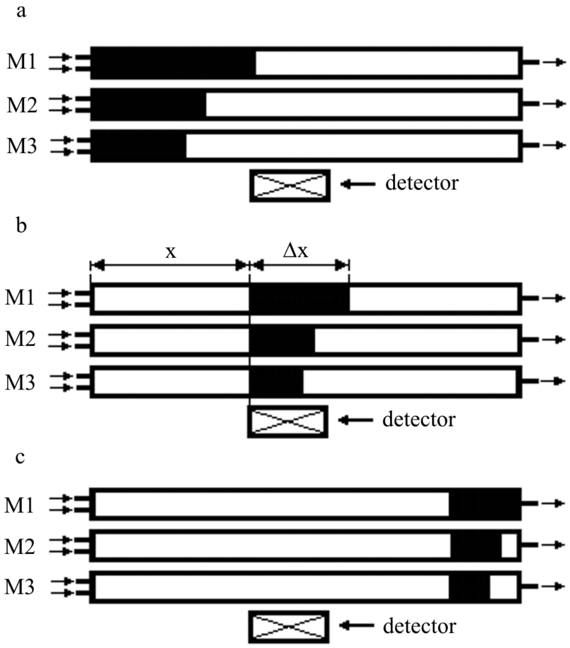

Fig. 6 Hypothesis considered about the relative situation of the dissipation area for each injection flow ($f_1<f_2<f_3$) and for each studied mixture: water+methanol (M1), benzene+cyclohexane (M2), cyclohexane+hexane (M3)

Conclusions

As a summary, it can be said that the maximum of each sensitivity curve is obtained when the dissipation area is centred upon the detector system; when increasing the injection flow, the mixture moves till it goes out of the detection area making the sensitivity decrease.

The considered hypothesis is described in Fig. 6, in which a diagram represents the relative place where the mixture dissipation is located for every studied mixture and for three injection flows ($f_1<f_2<f_3$). It is supposed that the extension of the mixture is proportional to the value of τ_{mix}. Thus, for the case of the mixture water+methanol (M1) this length is always greater than that for the other two because its τ_{mix} is also greater. For the flow f_1 the mixture M1 has a greater extension, it is nearer the detector system and provides a signal with regard to the power developed (greater sensitivity) which is greater than the other two mixtures. For the flow f_2 the dissipation of the mixture M1 is placed centred in the detector system, it can be said for that flow that there is a sensitivity maximum, and this maximum takes place before in the other two mixtures. As the injection flow increases, the sensitivity diminishes because we go off the detection area.

In this discussion, it would also have to take into account the effect that is produced by the liquid flow given by the term $\rho c_p f \Delta T$, that represents the power due to the liquid flow between two areas that are at a temperatures difference ΔT. Knowing that, in general, when increasing the value of $\rho c_p f$ the sensitivity diminishes, a preliminary evaluation of this effect has been made and the function K_{mix}–K_{elec} has been studied for every analyzed mixture and for every value of $\rho c_p f$, and three curves very similar to those represented in Fig. 5, and with the same order in the maximum values of the curves are observed. This fact supports the hypothesis shown in Fig. 6, but this preliminary evaluation is not enough because in the electrical calibration the dissipation is located in a fixed place and in the real measures of mixture the dissipation is carried out along the coil of the mixture. This is the reason why it is considered necessary the production of a model capable of relating the parameters K_{mix} and τ_{mix} with the localization and extension of the mixture (values x and Δx of the Fig. 6), model that has to be corroborated by enough experimental measures.

References

1 R. B. Kemp, Chap. 14. Nonscanning Calorimetry, Handbook of Thermal Analysis and Calorimetry, Vol. 1: Principles and Practice. Edited by M. E. Brown, Elsevier, 1998.
2 P. Monk and I. Wadsö, Acta Chem. Scand., 22 (1968) 1842.
3 B. S. Harsted and E. S. Thomsen, J. Chem. Thermodyn., 6 (1974) 549.
4 R. Tanaka, P. J. D'Arcy and G. C. Benson, Thermochim. Acta, 11 (1975) 163.
5 F. Socorro, I. de la Nuez and M. R. de Rivera, Measurement, 33 (2003) 241.
6 F. Socorro and M. R. de Rivera. J. Therm. Anal. Cal., 72 (2003) 47.
7 F. Socorro M. R. de Rivera and Ch. Jesus, J. Therm. Anal. Cal., 64 (2001) 357.
8 J. Michael Köhler and M. Zieren, Thermochim. Acta, 310 (1998) 25.
9 B. Marongiu, I. Ferino and R. Monaci, J. Mol. Liq., 28 (1984) 229.
10 R. H. Stokes, K. N. Marsh and R. P. Tomlins, J. Chem. Thermodyn., 1 (1969) 211.
11 K. N. Marsh and R. H. Stokes. J. Chem. Thermodyn., 1 (1969) 223.
12 D. W. Marquardt, Appl. Math., 11 (1963) 431.
13 W. H. Press (Editor), S. A. Teukolsky, W. T. Vetterling and B. P. Flannery, Numerical Recipes in Fortran, Cambridge University Press, 1992.