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MODELLIZATION OF THE SPATIAL LOCALIZATION EFFECT OF THE MIXTURE DISSIPATION ON THE SENSITIVITY IN A FLOW MICROCALORIMETER

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It is proposed a calorimetric model that helps to understand the dependence on the sensitivity of a flow microcalorimeter with the spatial localization of the energetic dissipation. The model allows to compare the spatial localization of different studied mixtures and permits us to conclude that in the ‘rapid’ mixtures, the length that the mixture dissipation occupies and the sensitivity remain nearly constant; however, in the mixtures called ‘slow’, the mixture length increases with the injection flow. This fact produces, at the same time, a clear variation of the sensitivity.

Keywords: *calibration, flow microcalorimeter, liquid mixtures, sensitivity, thermal model*

Introduction

Flow microcalorimeters are isothermal heat conduction calorimeters that are used to determine the energy developed in a liquid mixture process [1–2]. The operating principle consists in injecting simultaneously two liquids in a continuous way in a mixture zone: when the experimental output reaches the stationary state, we suppose that the mixture is homogeneous and the power dissipated or absorbed by the mixture is equal to the experimental output divided by the sensitivity of the calorimeter. The improvement of the equipments and, above all, their automation have made easier their handling, this is the reason why their use has increased considerably these years.

The calibration of these instruments consists in the determination of the sensitivity: the trouble is that the sensitivity is not constant and depends mainly on three factors: a) the injection flow, b) the volumetric heat capacity of the injected liquids and c) the dissipation area. The two first aspects can be evaluated with relative easiness but the dissipation area can change for every studied liquid mixture, so, because of the impossibility of establishing a function of the sensitivity that could be applied for every type of mixture, it is proposed a validity domain of the calibration; this domain is defined with the parameter $\rho c_p f$ (ρc_p: volumetric heat capacity, f: injection flow), for example, for a TAM2277-204 by Thermometric, the sensitivity is determined with an uncertainty of ±3% for values of $\rho c_p f < 15$ mWK^{-1} [3, 4].

The aim of this paper is to propose a model capable of explaining the dependence on the sensitivity with the three mentioned factors. Besides, we think that the model has an added interest because, together with the experimental calorimetric measures, it can give information about the mixture dissipation localization. The necessity of deepening in this study is increased by the development of minute new devices [5, 6] whose operating principle is similar and that, probably, have the same calibration problems.

Nowadays new mixture cells are being built in which the dependence on the sensitivity with $\rho c_p f$ has been reduced as the input and output tubes are so close one another that the injected liquid acquires a temperature nearer the one of the mixture (new Flow-Mix Insertion Vessel 2250-007 by Thermometric, AB); however, in this new configuration there is still a dependence between the sensitivity and the dissipation area.

The proposed model combines the modellization based on the discretization of the experimental system (RC-representative model [7]) with the use of the equation of thermal diffusivity for the domain represented by the mixture coil.

The presentation of this work will be made with the following order: firstly, it will be briefly described the system and the experimental measures; next, it will be exposed the proposed model and the simulation carried out, and lately, it will be made a final discussion in which it will be shown the hypotheses on where the mixture dissipation is produced in each of the three studied mixtures.

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Experimental method

The utilized experimental system is a flow microcalorimeter TAM 2277-204 by Thermometric AB. The detector system of thermopiles provides the experimental output that is directly read by a Hewlett Packard HP3457A multimeter (10 nV 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 50 cm^3 Hamilton syringes pushed by a stepper motor MT-160-250 by Microcontrole producing an injection of 0.0831 μL per step of the motor; by programming the number of steps in every sampling period the desired injection flow is obtained.

The experimental method have already been described in previous works [3, 4, 8], the injection flows have ranged from 2×0.75 to 2×6.75 μL s^{-1}, the liquid mixtures used in the chemical calibration were water+methanol, cyclohexane+benzene and cyclohexane+hexane, and the reference enthalpies (for 25°C) have been, respectively, 875.0, 796.2 and 220.3 J mol^{-1} [9–11]. Electrical calibration measures have also been used in this work, consisting in the dissipation of a known power in the calibration resistance when it is being injected the same pure liquid through each duct; the liquids and flows used in the electrical calibration are the same utilized in the chemical calibration.

Model

The proposed model combines the modellization based on the discretization of the calorimetric system in heating capacities and contact thermal resistances (R–C representative model) with the use of the equation of thermal diffusivity for the domain which represents the mixture coil.

It is proposed a simple model with three bodies because, in the electrical calibrations, it can be identified up to three time constants. We suppose that the first body is in contact with the thermostat and with the mixture coil, and is crossed by the injection tubes. The second body represents the mixture coil, the liquid goes through its inner part and the mixture takes place; besides, the Joule calibration resistance has been placed in this domain (Fig. 1). And the third body represents the detector system so that the experimental output or calorimetric signal is proportional to T_3 (Eq. 16).

The equations of the model for each domain are the following ones:

Domain 1:

$$0 = C_1 \frac{\mathrm{d}T_1}{\mathrm{d}t} + P_1(T_1 - T_0) + \rho c_\mathrm{p} f (T_1 - T_0) + \\ + P_{12}(T_1 - T_{20}) \tag{1}$$

Domain 2:

$$w(x)\mathrm{d}x = c_2 \frac{\partial T_2}{\partial t} S\mathrm{d}x - \lambda S \frac{\partial^2 T_2}{\partial x^2}\mathrm{d}x + \\ + \frac{P_{23}}{L}(T_2 - T_3)\mathrm{d}x + \rho c_\mathrm{p} f \frac{\partial T_2}{\partial x}\mathrm{d}x \tag{2}$$

Domain 3:

$$0 = C_3 \frac{\mathrm{d}T_3}{\mathrm{d}t} + P_3(T_3 - T_0) + P_{23}(T_3 - \overline{T}_2) \tag{3}$$

Equations (1) and (3) are based on the R–C representative model, the energetic balance is as follows: the power developed in the domain, W_i, is equal to the stored power, $C_\mathrm{i}T_\mathrm{i}/\mathrm{d}t$, plus the losses towards the thermostat and towards the neighbouring domains: $\Sigma P_\mathrm{ik}(T_\mathrm{i} - T_\mathrm{k})$. In this case, the powers W_1 and W_2 are

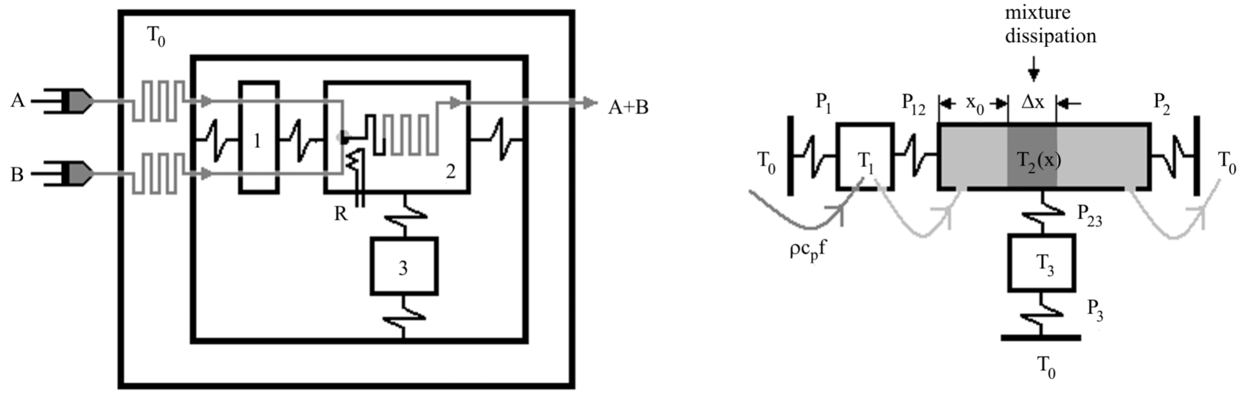

Fig. 1 Diagram of the proposed model with three bodies. ρc_p is the volumetric heat capacity of the injected liquid and f is the injection flow. P_i and P_ik: contact thermal conductivities between domains. T_1, T_2 and T_3: temperatures of each domain, and T_0: temperature of thermostat. Supposing that the Joule dissipation and the mixture dissipation are produced in the second domain and that the calorimetric signal is proportional to the temperature T_3

zero; besides, in the first domain it appears the term $\rho c_p f(T_1-T_0)$ which is the power due to the liquid ranging from the thermostat temperature (T_0) to the temperature of the first domain (T_1); for the injection flows used in this simulation ($f_i<7$ μL s^{-1}, $f_T=2f_i$), it is supposed that the injected fluid acquires the temperature of the domain through which it goes.

Equation (2), corresponding to the second domain, presents the energetic balance for a differential element. In this simulation, we have considered a one-dimensional model for the mixture coil, that is to say: $T_2=T_2(x)$. In the balance, the different contributions participate, these are: the developed power: $w(x)$, the heating: $c_2S\delta T_2/\delta t$, the losses at the third domain $(P_{23}/L)(T_2-T_3)$, the contribution by heat conduction within the domain: $\lambda S\delta^2T_2/\delta x^2$, and the contribution due to the pass of liquid fluid: $\rho c_p f\delta T_2/\delta x$. The boundary conditions considered for this domain are the following ones:

For $x=0$,

$$-\lambda S\frac{\partial T_2}{\partial x}=(P_{12}+\rho c_p f)(T_2-T_1) \qquad (4)$$

For $x=\mathrm{L}$,

$$-\lambda S\frac{\partial T_2}{\partial x}=P_2(T_2-T_0) \qquad (5)$$

With this model, it is intended to study the sensitivity of the device, this is the reason why the simulation is made for the stationary state ($\delta T_i/\delta t=0$). Finding T_3 from the Eq. (3) and substituting in the Eq. (2), we obtain only one differential equation for T_2. The boundary conditions for T_2 are obtained by taking as reference temperature $T_0=0$ and finding T_1 from the Eq. (1) and substituting in the Eq. (4). The following expressions are a result of them:

Domain 2:

$$\begin{aligned}-\lambda S\frac{\mathrm{d}^2T_2}{\mathrm{d}x^2}+\rho c_p f\frac{\mathrm{d}T_2}{\mathrm{d}x}+\frac{P_{23}}{L}T_2&=\\=\frac{P_{23}^2}{L(P_{23}+P_3)}\overline{T}_2+w(x)&\end{aligned} \qquad (6)$$

For $x=0$,

$$\lambda S\frac{\mathrm{d}T_{20}}{\mathrm{d}x}+(P_{12}+\rho c_p f)\frac{P_1+\rho c_p f}{P_1+\rho c_p f+P_{12}}T_{20}=0 \qquad (7)$$

For $x=\mathrm{L}$,

$$\lambda S\frac{\mathrm{d}T_{2\mathrm{L}}}{\mathrm{d}x}+(P_2+\rho c_p f)T_{2\mathrm{L}}=0 \qquad (8)$$

As a first approach and for the simulation carried out, we suppose that $w(x)$ has a rectangular shape (Fig. 2), and the dissipation is produced in a spatial domain Δx, starting from $x=x_0$. In order to solve the differential Eq. (6), we split up the power $w(x)$ in harmonic functions through a representation of Fourier series:

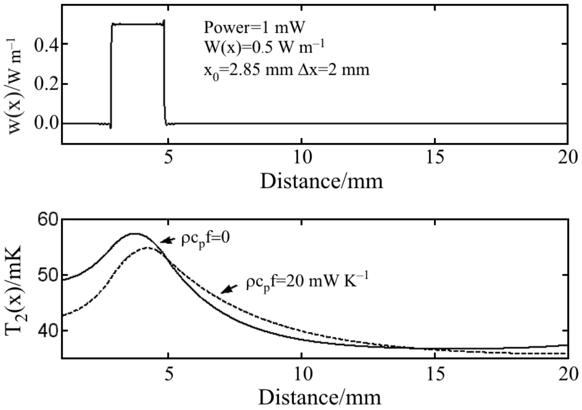

Fig. 2 Simulation for the stationary state. Dissipated power and temperature *vs.* distance of the domain that represents the mixture coil

$$w_{\mathrm{mix}}(x)=\sum_{\mathrm{n}=1}^{\infty}a_{\mathrm{n}}\sin(w_{\mathrm{n}}x) \qquad (9)$$

where

$$\begin{aligned}w_n=\frac{n\pi}{L};\ a_{\mathrm{n}}&=\frac{H_{\mathrm{ref}}^{\mathrm{E}}(\dot{n}_1+\dot{n}_2)}{\Delta x}\frac{2}{n\pi}\\&[\cos(w_{\mathrm{n}}x_0)-\cos(w_{\mathrm{n}}(x_0+\Delta x))]\end{aligned} \qquad (10)$$

The solution to the differential Eq. (6) belongs to the following type:

$$\begin{aligned}T_2(x)&=\frac{P_{23}}{P_{23}+P_3}\overline{T}_2+K_1\exp(\alpha_1x)+\\&+K_2\exp(\alpha_2x)+\sum_{\mathrm{n}=1}^{\infty}A_{\mathrm{n}}\sin(w_{\mathrm{n}}x-\varphi_{\mathrm{n}})\end{aligned} \qquad (11)$$

The simulated calorimetric output for the stationary state (y) will be proportional to T_3, and as we have supposed an input step, the (S) will be the output value in stationary state divided by the constant input power:

$$S=\frac{y}{w(x)\Delta x}=\frac{kT_3}{w(x)\Delta x}=\frac{k}{w(x)\Delta x}\frac{P_{23}\overline{T}_2}{P_{23}+P_3} \qquad (12)$$

In Fig. 2, it is shown a simulation example; in this case, the total dissipated power is 1 mW along a domain $\Delta x=2$ mm, that is to say, $w(x)=0.5$ Wm^{-1}. It is presented the temperature $T_2(x)$ for that constant dissipation and for two different cases: without liquid flow ($\rho c_p f=0$) and with liquid flow ($\rho c_p f=20$ mWK^{-1}); the sensitivity obtained in each case is 312.6 and 303.7 mV W^{-1} respectively.

Table 1 Values of the model parameters

Model parameters	Thermal coupling/mW K^{-1}
L=25 mm	P_1=88.70
k=8.6032 mV W^{-1} K^{-1}	P_{12}=38.90
λS=0.050 mW m K^{-1}	P_2=74.20
Joule dissipation: x_0=2.85 mm Δx=2.00 mm	P_{23}=221.85
Mixture dissipation: x_0 and Δx in Fig. 5	P_3=34.10

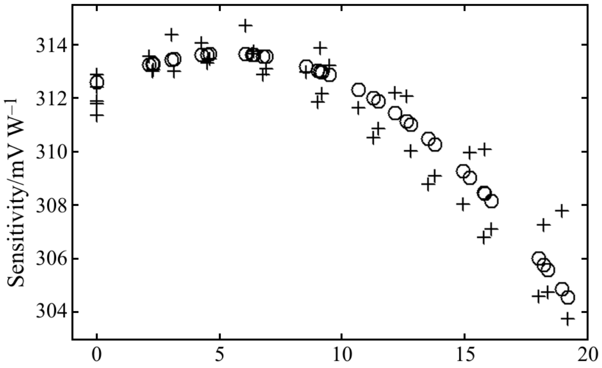

Fig. 3 Sensitivity obtained in the electrical calibrations in terms of $\rho c_p f$ (different liquids and different injection flows). In this case the dissipation is always produced in the same place and it only depends on $\rho c_p f$. Experimental values (crosses), values obtained with the proposed model (circles)

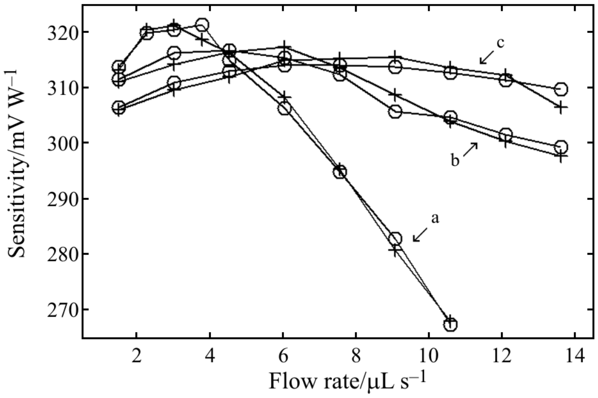

Fig. 4 Sensitivity obtained in the chemical calibration: a – mixture water+methanol, b – cyclohexane+benzene and c – cyclohexane+hexane. The experimental values (crosses) and values obtained with the model (circles)

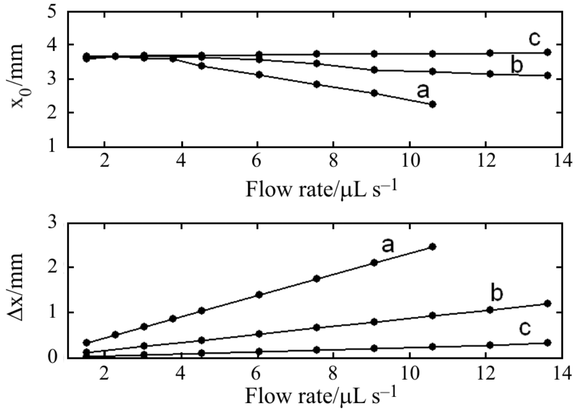

Fig. 5 Results given by the model on the place (x_0) and length of the mixture dissipation (Δx). Cases: a – mixture water+methanol, b – cyclohexane+benzene and c – cyclohexane+hexane

Results and discussion

As it is usual, to obtain the model parameters we utilize the measures of electrical calibration in which the dissipation takes place in a fixed place allowing to obtain easily the parameters. In order to do so, it has been used the simplex search algorithm method by Nelder and Mead [12] using the software MatLab [13].

In Table 1, it is shown the model parameters and, in Fig. 3, it is presented the experimental values of the sensitivity obtained in the electrical calibrations in terms of $\rho c_p f$, and the values obtained with the model. The standard deviation in this adjustment has been 1 mVW^{-1}. The dispersion of the experimental values of the sensitivity is due mainly to a different thermal conductivity of the utilized liquids, this variable has not been taken into account in the model proposed in this paper.

In the electrical calibrations, the dissipation always takes place in the same location; however, in the liquid mixtures, the dissipation may change its location. The proposed model allows to determine the place where the dissipation starts (x_0) and its length (Δx). Keeping fixed the parameters of the model obtained from the electrical calibration measures, it is studied each one of the three liquid mixtures used in the chemical calibration.

Figures 4 and 5 show the results of this work. In Fig. 4, it is represented the experimental and simulated values of the sensitivity for each mixture in terms of the total injection flow, the standard deviation between the experimental and simulated values has been ≈1.5 mVW^{-1}.

The most important effect which is observed is the increase of the spatial dissipation area (Δx) when the injection flow increases. This proportionality is different for each studied mixture, the increase of Δx with the injection flow is much lesser in the mixture cyclohexane+hexane than in the other two. This suggests to think that this mixture is produced more rapid in time than the other two. As a consequence, and observing the three curves in Fig. 5, we can classify the mixtures into three types: 'rapid' (cyclohexane+hexane), 'medium' (cyclohexane+benzene) and 'slow' (water+methanol).

In the curves corresponding to the mixtures, it is observed that, apart from the time constants typical of the experimental system, there is another additional time constant that corresponds to the establishment time of the mixture that we have called τ_{mix}. This time constant has been evaluated in previous works [3, 4, 8] and seems to support the hypothesis relative to the differentiation between 'rapid', 'medium' and 'slow' mixtures. In this case: τ_{mix}(cyclohexane+hexane)<τ_{mix}(cyclohexane+benzene)<τ_{mix}(water+methanol).

Conclusions

The proposed model is the first approach to the study of how the sensitivity of a flow microcalorimeter is affected by the spatial localization of the dissipation. To conclude this study, it is necessary to point out that the sensitivity of a flow microcalorimeter depends mainly on two factors:

- The parameter $\rho c_p f$; the closer the injected liquid temperature be to the temperature at which the mixture is produced, the lesser this effect will be. However, this effect can be evaluated experimentally through electrical calibrations.
- The dissipation area for the case of liquid mixtures; the sensitivity depends mainly on the length that occupies the mixture dissipation. We have classified the studied mixtures into rapid ones, medium ones, and slow ones. In the rapid mixtures there is very little variation of the sensitivity with the injection flow as the length that occupies the mixture dissipation remains nearly constant; on the contrary, in the slow mixtures there is a great dependence on the sensitivity with the injection flow.

Abbreviations

$T_1(t)$, $T_2(t,x)$ and $T_3(t)$	temperatures for each domain
$T_{20}(t)$	the temperature T_2 in x=0
$T_{2L}(t)$	the temperature T_2 in x=L
$\overline{T}_2(t)$	the average temperature in the second domain (from x=0 to x=L)
T_0	the constant temperature of the thermostat
C_1, C_3	the heat capacities for the domains 1 and 3
c_2	the heat capacity per unit of volume for the domain 2
P_{12}	the thermal coupling between the domains 1 and 2
P_{23}	the thermal coupling between the domains 2 and 3
P_1, P_2, P_3	the thermal coupling for the domains 1, 2 and 3 with the thermostat
ρc_p	the volumetric heat capacity of the injected liquid
f	the injection flow
λ	the thermal conductivity for the domain 2
S	the mixture coil section (through which the heat is transmitted)
L	the mixture coil length (domain 2)
$w(x)$	the power per unit of length
Δx	the spatial domain where the dissipation is produced
x_0	the point where the dissipation starts
H^E_{ref}	the reference enthalpy (J mol^{-1})
$\dot{n}_1$, $\dot{n}_2$	the injection flows (mol s^{-1})
w_n, a_n	see Eq. 10
y	the simulated output
k	the proportionality constant between the out put and T_3
S	sensitivity

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