

A THERMAL MODEL OF A FLOW CALORIMETER

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Abstract

This work shows the difference between the results obtained in the electrical calibration and those corresponding to the chemical calibration in a TAM2277-204 flow-calorimeter by Thermometric. This difference is due to the fact that the mixture and the electrical dissipation do not occur in the same place. There are other additional aspects inherent to the mixture dissipation: the mixture does not take place instantaneously and extends in space. The physical model that has been calculated in this work explains the characteristics that are proper to a mixture dissipation and the effects of the injection in a qualitative and quantitative way.

Keywords: conduction calorimetry, flow calorimetry, liquid mixtures, modelling, signal processing, thermal measurement

Introduction

In this work the performance of a TAM 2277-204 conduction calorimeter by Thermometric AB [1] has been studied. This calorimeter is used to measure the energy produced when mixing two liquids. This energy is related to the thermodynamic properties of the mixture. The simultaneous injection of two pure liquids (*A* and *B*) provides an output $y(t)$, that reaches the stationary state, y_s , when the mixture is homogeneous, then the excess enthalpy is given by:

$$H^E(x_A) = \frac{1}{(\dot{n}_A + \dot{n}_B)} \frac{y_s}{K} \quad (\text{J mol}^{-1}) \quad (1)$$

where the molar fraction is calculated with the expression $x_A = \dot{n}_A / (\dot{n}_A + \dot{n}_B)$, being $\dot{n}_A = dn_A/dt$ and $\dot{n}_B = dn_B/dt$ the injection flows in mol s⁻¹. K is the sensitivity of the instrument in V W⁻¹.

The users of these instruments base the calibration just on the calculation of the sensitivity and propose empirical expressions of the sensitivity as a function of the volumetric heat capacity and also of the flow rate of the injected liquids [2, 3]. A model with physical image that adequately represents the performance of the instrument and which provides an expression of the sensitivity as a function of $\rho c_p f$ (ρ is the density, c_p is the heat capacity and f is the flow rate of the injected liquid) has already been proposed in a previous study [4]. However, that model was obtained start-

ing from electrical calibrations and did not sufficiently represent the results of the chemical calibrations due to the fact that the mixture does not occur in the same place where the calibration resistance is located. In this work we incorporate the results provided by the chemical calibration.

The objective is to study the static and dynamic performance of the device, to relate both (electrical and chemical) calibration results and to show that they are complementary. For this, we first make a short description of the experimental equipment and of the measures accomplished for the calibration. After this, we expose the model and the identification method of the parameters of the model. Finally, we make an analysis of the obtained results.

The modelling presented in this work is very simple and is mainly based on the application of the equations for heat flow by conduction. We affirm that the model has 'physical image' because each element of the model represents a particular part of the calorimeter, and this permits the model to adapt to the different configurations and particularities of each instrument.

Experimental measures

The calorimetric output of TAM 2277-204 calorimeter is directly digitized by a Hewlett Packard HP3457A multimeter (10 nV resolution). The electrical calibration is made by the dissipation of a known power in a 50 Ω resistance located inside the calorimeter, the resistance is connected to a HP6284A source controlled by a HP59501B. The system is controlled through the GPIB bus by a PC and the readings are stored for the subsequent analysis; the sampling interval used is $\Delta t=1.0989$ s.

The injection system is constituted by two Hamilton syringes of 50 cm³ which are pushed by a stepper motor MT-160-250 by Microcontrole, producing an injection of 0.0184 mm³ per step. The wanted injection flow is obtained by programming the number of steps in every sampling period.

Chemical calibration consists of the determination of the calorimetric model using the experimental results obtained by mixing liquids, the mixture energies of which are well known. A cyclohexane (A)+benzene (B) liquid mixture has been chosen as work standard. The reference power is:

$$W_{\text{ref}} = H_{\text{ref}}^E (\dot{n}_A + \dot{n}_B) \quad (2)$$

where $H_{\text{ref}}^E(x_A) = 796.20 \text{ J mol}^{-1}$ ($x_A = 0.4527$) for 298.15 K [5]. In all measurements used in this work the two syringes injected at equal rate, that is: $f_A = f_B$. Because of this, though total injection flow might change, the concentration and the mixture enthalpy stay the same.

In order to study the injection effect different flows have been tested: from 0.756 to 8.318 mm³ s⁻¹. The reference power changes with the total injection flow (Table 3). The experimental output corresponding to the mixture process reaches the stationary state (Fig. 1), so, a homogeneous mixture is supposed to have been obtained from that moment on. The mixture is not instantaneous and we cannot associate the mixture

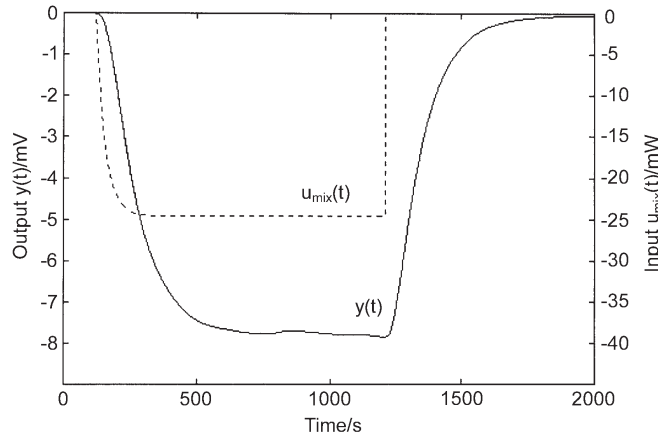


Fig. 1 Estimated input power, $u_{mix}(t)$, and experimental output, $y(t)$, for the cyclohexane (A)+benzene (B) mixture. In this case: $f_A=f_B=1.512 \text{ mm}^3 \text{ s}^{-1}$; $W_{ref}=24.62 \text{ mW}$; $\tau_{mix}=33.7 \text{ s}$; $\Delta_{mix}=10 \text{ s}$. The injection of the liquids starts at point $n=100$ and ends at point $n=1100$, $\Delta t=1.0989 \text{ s}$

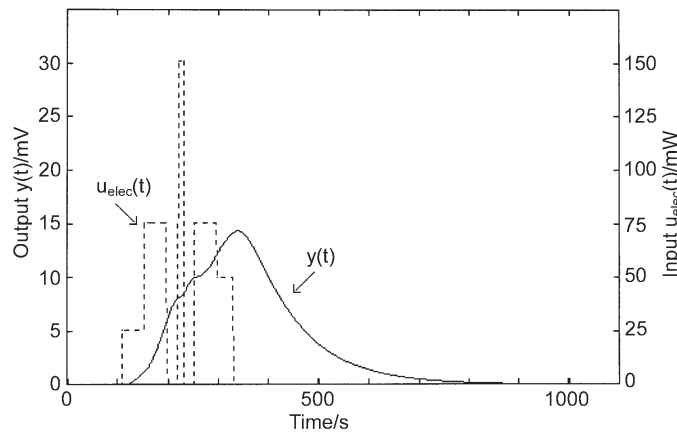


Fig. 2 Input power, $u_{elec}(t)$, and experimental output, $y(t)$, corresponding to an electrical calibration measure

power (system’s input) to a Heaviside-type signal, therefore, and as a first approximation, we suppose that the input power (u_{mix}) matches an exponential function with a time-constant (τ_{mix}) that will depend on the injection flow and on its own characteristics of the mixture:

$$u_{mix}(t) = W_{ref} \{1 - \exp[-(t - \Delta_{mix})/\tau_{mix}]\} \quad (3)$$

Δ_{mix} is a temporary lag in the accomplishment of the mixture that is due to the relative situation of the pure liquids within the injection pipes.

In the electrical calibration the input power consists of a train of pulses of different power and duration (Fig. 2). During the measurement (before, during and after the electrical dissipation) the same pure liquid is injected through each syringe, and with the same injection flow ($f_A=f_B$). The measurements have been accomplished for different injection flows: from 0 to $8.318 \text{ mm}^3 \text{ s}^{-1}$, and the used liquids are the same that were used in the chemical calibration: cyclohexane and benzene.

Model with physical image. Identification

In order to model the calorimeter we opt for the localized-constants model [4, 6, 7] which consists of decomposing the calorimeter in N domains of heat capacity C_i connected to its neighbouring through coupling contacts of thermal conductivity P_{ik} . The temperature T_i of each domain is a function of the time but not of the space since we consider that each domain has infinite thermal conductivity. Considering that heat is mainly transmitted by conduction, the energetic balance for each domain looks like follows:

$$W_i = C_i \frac{dT_i}{dt} + \sum_{k \neq i}^N P_{ik} (T_i - T_k) + P_i (T_i - T_0) + g_{ij} (T_i - T_j) \quad (4)$$

The power developed in each domain is W_i , this can be due to a Joule dissipation in the calibration resistance, $u_{\text{elec}}(t)$, or to the energetic process that is under study, $u_{\text{mix}}(t)$. The heat stored per time unit in each domain is $C_i dT_i/dt$ and the power transmitted by conduction to the neighboring domains and to the thermostat are $P_{ik}(T_i - T_k)$ and $P_i(T_i - T_0)$ respectively. Finally, $g_{ij}(T_i - T_j)$ represents the calorific power due to the liquid injection; as a first approach and for low rates, we consider that the injected liquid acquires the temperature of the body which it passes through (T_i and T_j).

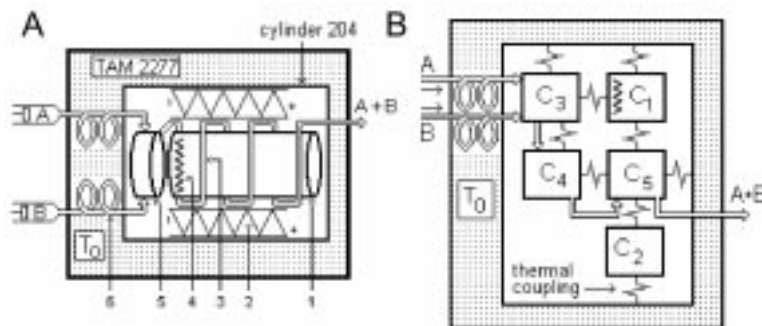


Fig. 3 Scheme of the flow calorimeter (A). TAM 2277 thermostatic bath and cylinder 204 by Thermometric AB (just the mixture cell is represented, not the reference cell). 1: cell-holder, 2: thermocouple detector, 3: mixture coil, 4: electrical calibration resistance, 5: flow-mix cell, 6: heat exchanger. Scheme of the model with physical image (B). C_1 represents the cell-holder, C_2 the detector system, C_3 the flow-mix cell, C_4 and C_5 the first and second part of the mixture coil. T_0 it is the thermostat

The chosen model for the instrument under study is a model of 5 bodies, where C_1 represents the cell-holder (includes the calibration resistance), C_2 represents the detector system, C_3 represents the flow-mix cell, C_4 and C_5 represent the mixture coil that has been decomposed in two parts. Figure 3 shows a scheme of the flow-calorimeter and of the model. The equations of the model are the following:

$$\begin{aligned}
 u_{\text{elec}} &= C_1 \frac{dT_1}{dt} + P_{13}(T_1 - T_3) + P_{15}(T_1 - T_5) + P_1(T_1 - T_0) \\
 0 &= C_2 \frac{dT_2}{dt} + P_{25}(T_2 - T_5) + P_2(T_2 - T_0) \\
 \alpha_1 u_{\text{mix}} &= C_3 \frac{dT_3}{dt} + P_{13}(T_3 - T_1) + P_{34}(T_3 - T_4) + P_3(T_3 - T_0) + g_3(T_3 - T_0) \\
 \alpha_2 u_{\text{mix}} &= C_4 \frac{dT_4}{dt} + P_{34}(T_4 - T_3) + P_{45}(T_4 - T_5) + g_{34}(T_4 - T_3) \\
 \alpha_3 u_{\text{mix}} &= C_5 \frac{dT_5}{dt} + P_{15}(T_5 - T_1) + P_{45}(T_5 - T_4) + P_{25}(T_5 - T_2) + P_5(T_5 - T_0) + g_{45}(T_5 - T_4)
 \end{aligned} \tag{5}$$

The electrical dissipation occurs in the first element where the calibration resistance is located, and the power obtained from the mixture is produced with different percentages in elements 3, 4 and 5 ($\alpha_1 + \alpha_2 + \alpha_3 \leq 1$). The experimental output is proportional to the temperature difference between the bodies that represent the detector system and the thermostat: $y(t) = \varepsilon(T_2 - T_0)$, where ε is the Seebeck coefficient and T_0 is the temperature of the thermostat.

We generally consider capacities C_1 and C_2 to be constant, but C_3 , C_4 and C_5 depend on the heat capacities of the used liquids, since their domains are crossed by the injected liquids. Concerning the thermal couplings we consider that they are all constant except the coupling to the thermostat of the element where the liquids start to get mixed (P_3). Parameters g_3 , g_{34} and g_{45} will also depend on the heat capacity of the injected liquids and of its injection rate.

When the injection flow is constant, the parameters of the model are invariant in time and we can apply the Laplace transform to the equation system of the model:

$$U_i(s) = \left[sC_i + \sum_{k \neq i}^N P_{ik} + p_i + g_{ij} \right] \Theta_i(s) - \sum_{k \neq i}^N P_{ik} \Theta_k(s) - g_{ij} \Theta_j(s) \tag{6}$$

We suppose the thermostat temperature to be constant, that is $dT_0/dt = 0$. The Laplace transform of the temperature difference ($T_i(t) - T_0$) is $\Theta_i(s)$ and the transform of the power $u_i(t)$ is $U_i(s)$. For the specific model of 5 bodies characterized by the equation system (5) and represented in Fig. 3, we have:

$$\begin{aligned}
 U_{elec} &= (sC_1 + P_{13} + P_{15} + P_1)\Theta_1 - P_{13}\Theta_3 - P_{15}\Theta_5 \\
 0 &= (sC_2 + P_{25} + P_2)\Theta_2 - P_{25}\Theta_5 \\
 \alpha_1 U_{mix} &= -P_{13}\Theta_1 + (sC_3 + P_{13} + P_{34} + P_3 + g_3)\Theta_3 - P_{34}\Theta_4 \\
 \alpha_2 U_{mix} &= -(P_{34} + g_{34})\Theta_3 + (sC_4 + P_{34} + P_{45} + g_{34})\Theta_4 - P_{45}\Theta_5 \\
 \alpha_3 U_{mix} &= -P_{15}\Theta_1 - P_{25}\Theta_2 - (P_{45} + g_{45})\Theta_4 + (sC_5 + P_{15} + P_{45} + P_{25} + P_5 + g_{45})\Theta_5
 \end{aligned}
 \tag{7}$$

$\Theta_2(s)$ is obtained using Cramer:

$$\Theta_2(s) = U_{elec}(s) \frac{-\Delta_{12}(s)}{\Delta(s)} + U_{mix}(s) \frac{-\alpha_1 \Delta_{32}(s) + \alpha_2 \Delta_{42}(s) - \alpha_3 \Delta_{52}(s)}{\Delta(s)}
 \tag{8}$$

$\Delta(s)$ is the determinant of the coefficients of the equation system (7), and $\Delta_{ij}(s)$ is the corresponding adjoint of the element 'ij'.

The output of the system is $y(t) = \epsilon(T_2(t) - T_0)$, then $Y(s) = \epsilon\Theta_2(s)$. Making $\epsilon = 1 \text{ VK}^{-1}$, the transfer functions for each independent input are the following:

$$\begin{aligned}
 H_{elec}(s) &= \left. \frac{Y(s)}{U_{elec}(s)} \right|_{U_{mix}(t)=0} = -\frac{\Delta_{12}(s)}{\Delta(s)} = \sum_{i=1}^5 \frac{a_i \tau_i}{1 + s\tau_i} \\
 H_{mix}(s) &= \left. \frac{Y(s)}{U_{mix}(s)} \right|_{U_{elec}(t)=0} = \frac{-\alpha_1 \Delta_{32}(s) + \alpha_2 \Delta_{42}(s) - \alpha_3 \Delta_{52}(s)}{\Delta(s)} = \sum_{i=1}^5 \frac{a'_i \tau_i}{1 + s\tau_i}
 \end{aligned}
 \tag{9}$$

The impulsional outputs will be:

$$h_{elec}(t) = \sum_{i=1}^5 a_i e^{-t/\tau_i}; \quad h_{mix}(t) = \sum_{i=1}^5 a'_i e^{-t/\tau_i}
 \tag{10}$$

The program for identification of the parameters of the model has been written in Fortran and is supported by three main subprograms: the Marquardt algorithm, the program Modcal [6], and the program Simula. These programs have been adapted for the case under study and coupled as the scheme of Fig. 4 shows. The first program (Marquardt), that has been extracted of the routines facilitated

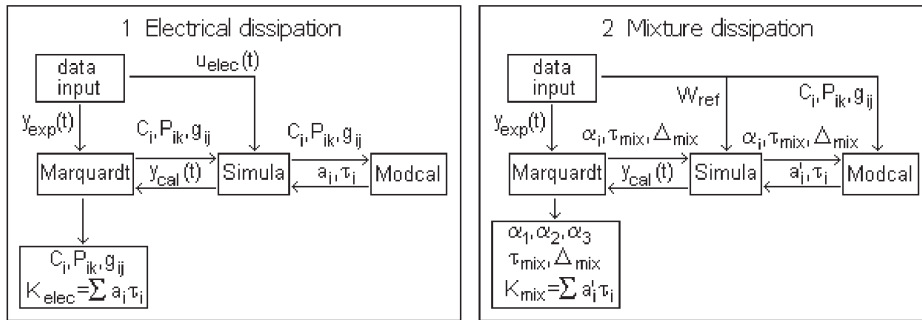


Fig. 4 Scheme of the identification method

by Numerical Recipes in Fortran [8], uses a non-linear adjustment method by minimal squares based on the Marquardt algorithm [9]. The second program (Modcal) attends the calculation of the amplitudes and time constants of the impulsional output corresponding to the considered model given by the equation system (5). The third program (Simula) determines the calculated output $y_{\text{cal}}(t)$ through the convolution integer between impulsional output and the corresponding system input. The partial derivatives of the output with respect to parameters C_i , P_{ik} , P_i , g_{ij} , α_i are numerically made by the program Modcal, and the partial derivatives of the output with respect to Δ_{mix} and τ_{mix} are mathematically made using Eq. (3).

Results

The results are shown in the same order that was used during the identification. In the first place, the model with signals that proceed from electrical dissipations and injection flow zero is identified by determining the parameters C_i , P_{ik} , P_i for each liquid. Table 1 shows the obtained values for the heat capacities from each body and the values for the thermal couplings to the thermostat and between neighbouring bodies. Capacities C_3 , C_4 and C_5 change with the real heat capacity of the liquid that is inside the pipes.

Table 1 Invariant parameters of the model for injection flow zero. Parameter P_3 depends on the liquid and of the injection flow (see Table 2). The output is $y(t)=\varepsilon(T_2-T_0)$, $\varepsilon=1 \text{ V K}^{-1}$

	Heat capacities/ J K^{-1}		Thermal coupling/ W K^{-1}	Thermal coupling/ W K^{-1}
	Cyclohexane	Benzene		
C1	38.50	38.50	$P_1=0.9660$	$P_{13}=0.2680$
C2	92.50	92.50	$P_2=0.5380$	$P_{15}=0.7170$
C3	2.780	2.880	$P_3=(*)$	$P_{25}=0.4863$
C4	3.280	3.380	$P_4=0.0000$	$P_{34}=0.1400$
C5	19.62	20.02	$P_5=0.2420$	$P_{45}=0.1720$

Remaining parameters: P_3 , g_3 , g_{34} and g_{45} are identified by using the electrical calibration measures for the different liquids and different injection flows. The values of the parameters shown in Table 1 are maintained constant during this identification. Table 2 shows the results, the sum P_3+g_3 is given since these parameters are always together in the equations of the model. We have also forced g_{34} to be equal to g_{45} . In all cases curves of $N=1000$ points have been used and the standard deviation (δ_d) of the adjustment has always been less than $21 \mu\text{V}$,

$$\delta_d = \sqrt{\sum (y_{\text{exp}} - y_{\text{cal}})^2 / (N-1)} \quad (11)$$

Table 2 Parameters P_3 , g_3 , g_{34} and g_{45} of the model that depend on the liquid and of the injection flow and first time constant (τ_1) calculated from the model

Flow-rate in each pump ($f_A=f_B$)	Cyclohexane injection/ $\rho c_p \approx 1.41 \text{ J cm}^{-3} \text{ K}^{-1}$			Benzene injection/ $\rho c_p \approx 1.52 \text{ J cm}^{-3} \text{ K}^{-1}$		
	$f_A/\text{mm}^3 \text{ s}^{-1}$	$P_3+g_3/$ W K^{-1}	$g_{34}=g_{45}/$ W K^{-1}	τ_1/s	$P_3+g_3/$ W K^{-1}	$g_{34}=g_{45}/$ W K^{-1}
0.000	0.194	0.000	101.1	0.201	0.000	101.3
0.756	0.189	0.012	100.7	0.190	0.004	101.4
1.512	0.186	0.019	100.5	0.191	0.017	100.9
2.269	0.191	0.030	100.0	0.197	0.029	100.4
3.025	0.201	0.045	99.4	0.208	0.042	99.7
4.537	0.237	0.072	97.8	0.240	0.078	97.8
6.806	0.287	0.134	94.7	0.299	0.139	94.6
8.318	0.327	0.176	92.5	0.340	0.182	92.4

Table 3 Results of chemical calibration for the cyclohexane (A)+benzene (B) mixture.

Reference power W_{ref} . Parameters τ_{mix} and Δ_{mix} of input function $u_{\text{mix}}(t)$. Dissipation percentages (α_1 , α_2 , α_3) in each body (per unit). First time constant (τ_1) obtained from the model. The percent error is $100 \delta_i/y_{\text{max}}$, where y_{max} is the maximum value of the corresponding experimental output, and δ_i is calculated by Eq. (11)

$f_A/\text{mm}^3 \text{ s}^{-1}$ $f_A=f_B$	W_{ref}/mW	$\Delta_{\text{mix}}/\text{s}$	$\tau_{\text{mix}}/\text{s}$	α_1	α_2	$\alpha_1+\alpha_2$ ($\alpha_3 \approx 0$)	τ_1/s	Error/ %
0.756	12.310	10.4	62.0	0.863	0.137	1.000	101.0	0.69
1.512	24.620	10.0	33.7	0.893	0.107	1.000	100.7	0.36
2.269	36.931	8.6	24.4	0.909	0.086	0.995	100.2	0.29
3.025	49.241	8.4	21.0	0.909	0.069	0.978	99.5	0.24
4.537	73.861	6.8	16.8	0.909	0.036	0.945	97.8	0.21
6.806	110.792	5.5	13.6	0.860	0.002	0.862	94.7	0.15
8.318	135.412	3.8	13.4	0.820	0.002	0.822	92.5	0.12

For the identification of the model by chemical calibration we use the parameters of the model given in Table 1, and as values of C_3 , C_4 and C_5 we take the arithmetic mean of those corresponding to the cyclohexane and to the benzene. The parameters P_3 , g_3 , g_{34} and g_{45} are also calculated from those obtained in the electrical calibrations by their arithmetic mean for each liquid and for each injection flow. After having calculated these parameters in this way and using the identification program the parameters Δ_{mix} , τ_{mix} , α_1 , α_2 y α_3 (Table 3) are determined.

The sensitivities obtained in the electrical and chemical calibrations are determined by the expressions: $K_{\text{elec}} = \sum a_i \tau_i$ and $K_{\text{mix}} = \sum a'_i \tau_i$. In Fig. 5 these values are represented as function of $\rho c_p f$.

Analyzing the results we make the following comments:

a) The time constant τ_{mix} diminishes when increasing the injection flow, that is, the stationary state of the input power is reached sooner when increasing the injection rate.

b) The amplitudes and time constants of the transfer function (expressions 9) change with $\rho c_p f$, this produces a dynamical and static behavioural variation of the system.

c) The sensitivity shows the static behaviour of the system, this depends on $\rho c_p f$ and on the place of dissipation, see the variation of K_{elec} and the difference between K_{elec} and K_{mix} in Fig. 5.

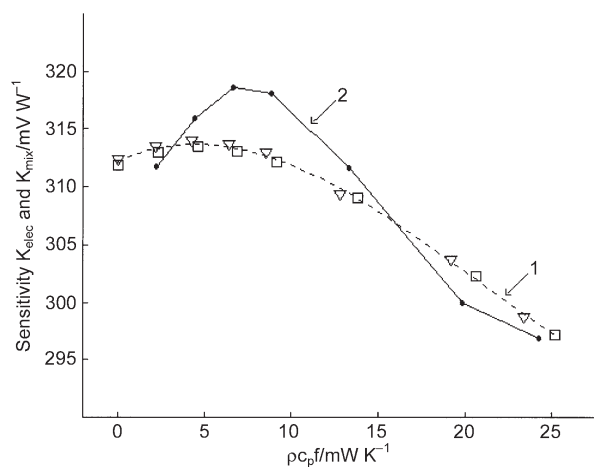


Fig. 5 Comparison between the sensitivities K_{elec} and K_{mix} as function of $\rho c_p f$ ($f=f_A+f_B$). Sensitivity K_{elec} for cyclohexane injection (triangles) and benzene injection (squares), fit curve (curve 1). Sensitivity K_{mix} for cyclohexane+benzene mixture (points of curve 2)

d) The different dynamical behaviour of the system for the different injection rates can be observed in the main time constant (τ_1 in Table 3), while the injection rate increases the system answers faster: the main time constant reduces; its variation is not very important since the mass of liquid is very small in comparison with the mass of the calorimeter, this is, of cylinder 204.

e) The major part of the mixture is accomplished in domain C_3 , that is represented by the flow-mix cell ($\alpha_1 \gg \alpha_2$, Table 3).

f) The injected liquids are supposed to get mixed in the flow-mix cell and in the mixture coil (detection zone), but if the injection rate increases the sum $\Sigma \alpha_i$ diminishes, this means that the liquids keep on mixing outside of the established 'detection' zone.

Conclusions

A model with physical image has been proposed, which is capable of reproducing the performance of the calorimeter satisfactorily. An advantage of the model is that the representative equations and the identification method are very simple. The model explains the effect of the injection on the static and dynamical behaviour of the system. It also explains the effect of the spatial location of the dissipation which is put in manifest by the difference between the sensitivities obtained from the electrical and chemical calibrations. Furthermore, the proposed model provides a macroscopic information about the mixture through the parameters τ_{mix} and α_i . In addition, the models with physical image constitute a very useful tool in designing new equipment and to propose improvements in the current ones.

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