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BASELINE CHANGES IN AN ISOTHERMAL TITRATION MICROCALORIMETER

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Isothermal titration microcalorimeters are submerged in an ambience at constant temperature and, this is the reason why there should not be variations in the baseline; but the experimental measures show that, in some cases, it is produced a jump in the baseline after the liquid injection. In this paper, it is studied the origin of this variation of the baseline in order to avoid it, if it is possible, or correct it and thus, to determine with the minimum error the amounts of energy or power developed in the energetic process that is being studied. The experimental results that are shown support the hypothesis that states that the cause of the baseline jump in an isothermal microcalorimeter is the variation of the thermal coupling between the content of the mixture cell and the axis of the stirrer, which is coupled, at the same time, with an area with a temperature slightly lower (in this case) than the thermostat temperature. This jump is independent from the dissipation and it always has the same sign. The magnitude of the baseline jump is variable and it mainly depends on the volume that the liquid content in a cell reaches and the placement of the stirrer within the cell, that can be changed in the handling process.

Keywords: *baseline, baseline correction, isothermal titration microcalorimeter, liquid injection calorimeter*

Introduction

Isothermal titration microcalorimeters (ITC) are utilized to study solid–liquid and liquid–liquid processes (enthalpies of solution, enthalpies of dilution, enthalpies of reaction in solution, enthalpies of mixing, etc.). In general, with these instruments, it is determined the total energy developed and, in some cases, it is also determined the total power developed at every instant in a liquid mixture process. For the latter, it is necessary for the mixture to be homogeneous constantly, that is the reason why the stirring must be adequate and, the liquid injection must also be well controlled in a way that permits to know the injected liquid at every sampling period. When these two experimental conditions take place, it is possible to determine the power developed at every instant by using a signal treatment that necessarily includes the identification of the calorimetric system.

There are certain studies on the identification of isothermal calorimeters of both types, injection and variable mass, in which the methods for signal treatment are proposed in order to obtain the thermogenesis or developed power [1, 2], other studies show the relationship between the thermogenesis and the thermodynamical properties adequate for every type of mixture [3]. Till now, attention has only been paid to three effects caused by the injection in a calorimetric signal. They are as follow:

- Increase of the main time constant during the injection as the heat capacity of the content increases in the mixture cell.
- Possible variation of the sensitivity due to the increase of the liquid level in the laboratory cell.
- Effect produced by the injection of a liquid which is at the thermostat temperature (T_0) on the mixture area which is at a temperature (T). The corresponding power is equal to $\rho c_p f(T-T_0)$ where ρc_p is the volumetric heat capacity of the injected liquid and f is the injection flow.

These effects that are produced by the injection have been analysed in some continuous liquid injection calorimeters [4, 5] and their study must be necessarily carried out at the initial calibration of these types of instruments. However, there is a fourth aspect that appears in some cases and that is the target of this paper. We are referring to the baseline jump that takes place after the injection process.

In this paper, it is studied the cause that produces this baseline variation in order to avoid it if it is possible; otherwise, it must be corrected to determine, with the minimum error, the energies or powers developed in the energetic process that is being measured.

The development of this work begins with the explanation of the calorimetric model proposed that explains how the baseline variation is produced, next the experimental measures that support the hypotheses considered in the model are studied, and, finally, a final discussion on the studied problem is made.

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Calorimetric model

To model the calorimeter, we utilize the method called 'localized constants' [6] that has been used in several calorimetric instruments and it has shown that it is a very useful tool to explain the characteristic and particular functioning of every calorimeter [7–9].

To explain the baseline variation, we propose a very simple model of the calorimeter, based on four bodies that represent four zones of it: the first body (with a capacity C_1) represents the place where the electric resistance of calibration is located, the second body (with a capacity C_2) represents the place where the mixture is carried out, the third body (with a capacity C_3) represents the detector system, and the fourth body (with a capacity C_4) represents the upper part of the stirrer (Fig. 1).

The considered hypothesis is that the jump in the baseline is due to the small differences of temperature that exist in the inner part of the thermostat and that, when a liquid is injected, the liquid level in the laboratory cell increases and it is produced a variation in the thermal coupling of the liquid with the stirrer that, at the same time, is in contact with thermostat areas that are at a slightly higher or lower temperature. This is the reason why, in the model, we have thermally coupled the stirrer with an area of the thermostat that is at a temperature $T_0^{'}$ while the detector system is placed between the reaction area and another thermostat area at a temperature T_0 (Fig. 1).

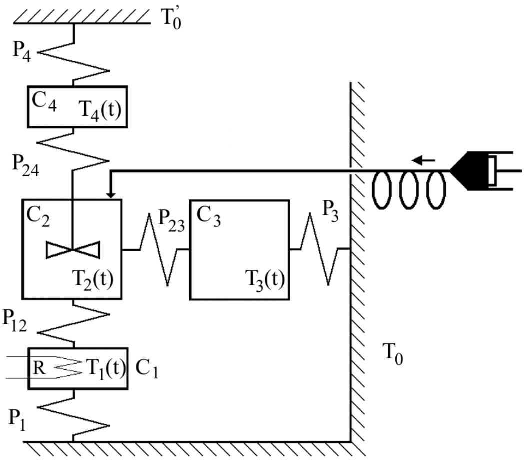

Fig. 1 Representative model of the calorimeter. The first body (with a capacity C_1) represents the place where the calibration resistance is located, the second body (with a capacity C_2) represents the place where the mixture is carried out, the third body (with a capacity C_3) represents the detector system, the fourth body (with a capacity C_4) represents the upper part of the stirrer. P_{ik} and P_i represent the thermal conductivities between the different bodies and with the thermostat. $W_1(t)$ is the dissipated power in the calibration resistance (R). $W_2(t)$ is the power corresponding to the mixture process. $T_i(t)$ is the temperature of each body and T_0 and $T_0^{'}$ are the temperatures in two different places of the thermostat

We apply the energetic balance for every domain making the developed power, W_i, to be equal to the stored power, $C_i\mathrm{d}T_i/\mathrm{d}t$, plus the losses by conduction to the nearby domains, $P_{ij}(T_i-T_j)$. The term $g(T_2-T_0)$ that appears in the second equation represents the power due to the liquid injection that enters at a thermostat temperature (T_0) different from the temperature of the mixture (T_2). Thus, we have:

$$
\begin{aligned}
W_1 &= C_1\frac{\mathrm{d}T_1}{\mathrm{d}t}+P_1(T_1-T_0)+P_{12}(T_1-T_2)\\
W_2 &= C_2\frac{\mathrm{d}T_2}{\mathrm{d}t}+P_{12}(T_2-T_1)+P_{23}(T_2-T_3)+\\
&+P_{24}(T_2-T_4)+g(T_2-T_0) \qquad (1)\\
0 &= C_3\frac{\mathrm{d}T_3}{\mathrm{d}t}+P_3(T_3-T_0)+P_{23}(T_3-T_2)\\
0 &= C_4\frac{\mathrm{d}T_4}{\mathrm{d}t}+P_4(T_4-T_0^{'})+P_{24}(T_4-T_2)
\end{aligned}
$$

The power W_1 is the one that dissipates in the calibration resistance and the power W_2 is the one developed in the mixture. Given the relationship signal/noise of the calorimetric measures (72 dB in the electrical calibrations), it is difficult to determine more than three time constants and, as the capacity of the body where the calibration resistance is also very small with regard to the others, we make: $C_1\approx 0$.

We also make: $\theta_i=T_i-T_0$; $\Delta T_0=T_0^{'}-T_0$. With all these, the equations are as follow:

$$
\begin{aligned}
W_1 &= (P_1+P_{12})\theta_1-P_{12}\theta_2\\
W_2 &= C_2\frac{\mathrm{d}\theta_2}{\mathrm{d}t}+(P_{12}+P_{23}+P_{24}+g)\theta_2-\\
&-P_{12}\theta_1-P_{23}\theta_3-P_{24}\theta_4 \qquad (2)\\
0 &= C_3\frac{\mathrm{d}\theta_3}{\mathrm{d}t}+(P_3+P_{23})\theta_3-P_{23}\theta_2\\
P_4\Delta T_0 &= C_4\frac{\mathrm{d}\theta_4}{\mathrm{d}t}+(P_4+P_{24})\theta_4-P_{24}\theta_2
\end{aligned}
$$

To obtain only one differential equation that relates the developed power, $W(t)$, with the output, $y(t)$, we make $W(t)=\alpha W_1(t)+W_2(t)$; $y(t)=\theta_2(t)$, by making operations we obtain only one differential equation that relates the input $W(t)$ with the output $y(t)$:

$$
\begin{aligned}
& b_1\frac{\mathrm{d}W}{\mathrm{d}t}+b_0W+\gamma\Delta T_0=\\
&=a_3\frac{\mathrm{d}^3y}{\mathrm{d}t^3}+a_2\frac{\mathrm{d}^2y}{\mathrm{d}t^2}+a_1\frac{\mathrm{d}y}{\mathrm{d}t}+a_0y
\end{aligned}
\qquad (3)
$$

If there is no injection, as in the case of electric calibration, there is no baseline modification and this is corrected by making $y'(t)=y(t)-\gamma\Delta T_0$. However, when injecting, the effect due to the modification of the thermal conductivity, P_{24}, of the liquid with the stirrer comes before the dissipation corresponding to the mixture process, since the contact surface increases; this results in a change of the γ that produces a modification of the baseline that will be positive or negative depending on the sign of ΔT_0.

On the other hand, if the thermal coupling P_{24} is very small ($P_{24}\approx 0$), the differential equation that relates the input $W(t)$ with the output $y(t)$ is reduced to a differential equation of the type:

$$b_0 W = a_2 \frac{\mathrm{d}^2 y}{\mathrm{d}t^2} + a_1 \frac{\mathrm{d}y}{\mathrm{d}t} + a_0 y \tag{4}$$

Equations (3) and (4) will be the ones that will model the calorimeter before (Eq. (4)) and after the injection (Eq. (3)); in the first case the coupling P_{24} is very small, and in the second case, it will have increased enough as to have to be considered. In the following section, the experimental measures that justify the hypotheses considered in the proposed model are shown.

Experimental measures

The instrument utilized in this study is a calorimetric cylinder TAM2277-201/2250 by Thermometric, this calorimetric cylinder is submerged in a thermostatic bath (TAM2277) that keeps a constant temperature with an accuracy of ±0.001 K in stationary state. The injection device and the measure and control system is the same as the one for the flow-microcalorimeter described in previous works [10, 11]. The measures have been carried out for a thermostat temperature T_0=298.15 K and the sampling period in data acquisition has been Δt=0.989 s.

As an example of the phenomenon explained, it is shown the case of a continuous injection of 2 cm^3 of methanol on initial 1 cm^3 of water, the injection flow rate was of 1.5 $\mu\mathrm{L\ s}^{-1}$ and the stirring was of 120 rpm; in Figs 2a and b it is represented the corresponding experimental output, where it is noticed a baseline jump $\Delta y\approx 120$ μV.

To ascertain when and how this jump is produced, we have injected in a continuous way methanol on methanol with the same injection flow rate (1.5 $\mu\mathrm{L\ s}^{-1}$) and in the same initial conditions of volume, i.e., with initial 1 cm^3 of methanol in the cell (Fig. 2c). In this measure, it is checked that the injection does not leave any signal, that is to say, both the injected liquid and the content in the cell are at the same thermostat temperature; in fact, a coil has been arranged in order to make the injected liquid be previously at the thermostat temperature (see diagram on Fig. 1). It is also observed that, from a given instant on, a small but appreciable baseline jump takes place, deriving the signal in order to determine the instant in which it is produced, we observe that this happens when the liquid volume in the cell reaches approximately 2.70 cm^3.

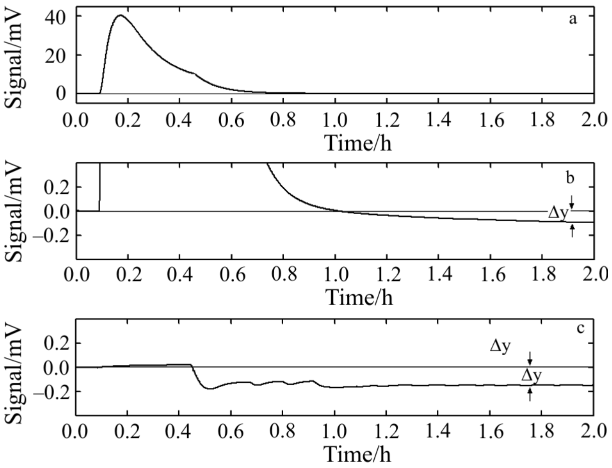

Fig. 2 a – Calorimetric curve or experimental output corresponding to the continuous injection (1.5 $\mu\mathrm{L\ s}^{-1}$) of methanol on initial 1 cm^3 of water, b – extension of the previous curve; c – curve corresponding to the continuous injection (1.5 $\mu\mathrm{L\ s}^{-1}$) of methanol on initial 1 cm^3 of methanol

Before and after every mixture process, it is made an electrical calibration that consists in a rectangular pulse with a power of 17.67 mW during 590 s. The noise in the baseline with the activated stirring (120 rpm) is ±1.5 μV, and the relationship signal/noise of these curves is of 72 dB. These electrical calibrations maintain the stated hypothesis because they show a significant change of the transference function (TF) of the system: before the injection, we can identify the system with a TF of two poles, while after the injection it is necessary to introduce a third pole and a zero.

According to Eq. (3), the TF is represented by the expression:

$$\begin{aligned} \mathrm{TF}(s) &= \frac{b_1 (s+s_1^*)}{a_3 (s+s_1)(s+s_2)(s+s_3)} = \\ &= K \frac{(1+s\tau_1^*)}{(1+s\tau_1)(1+s\tau_2)(1+s\tau_3)} \end{aligned} \tag{5}$$

where K is the sensitivity or static gain, s_i are the poles, s_i^* are the zeroes, $\tau_\mathrm{i}=-1/s_\mathrm{i}$, $\tau_\mathrm{i}^* = -1/s_\mathrm{i}^*$.

In Table 1, it is shown the results of the identification. These results show that the coupling P_{24}, that represents the thermal conductivity between the body 2 and the stirrer has increased. Initially, its value is very low and the TF is simplified and corresponds to a differential equation of the type Eq. (4); however, when it is increased the value of the coupling P_{24}, the TF responds to a differential equation Eq. (3). The stirrer is made of Teflon, and initially the conductiv-

Table 1 Parameters of the TF (Eq. (5)) obtained in the electrical calibrations before and after the injections of methanol on water and of methanol on methanol (the curves corresponding to the injections are represented in Fig. 2)

Case of injection of methanol on water	K_{elec}/mV W^{-1}	τ_1/s	τ_2/s	τ_3/s	τ_1^*/s
Before the injection (1 cm^3 water)	393	257	13	–	–
After the injection (3 cm^3 water+methanol)	393	300	13	18	24
Case of injection of methanol on methanol	K_{elec}/mV W^{-1}	τ_1/s	τ_2/s	τ_3/s	τ_1^*/s
Before the injection (1 cm^3 methanol)	393	236	13.5	–	–
After the injection (3 cm^3 methanol)	393	277	12.0	18	24

ity is very low, but when the liquid level goes up, this reaches the metallic axis, from this moment on the conductivity changes sharply, originating the baseline jump Δy observed in the Figs 2b and c.

The identification has been carried out by reconstructing the input signal (rectangular pulse) through a method based on the technique of Inverse Filtering [12], this method becomes more efficient than the techniques of minimizing. These techniques consist of searching the parameters of the model that reconstruct the output signal, while the technique of Inverse Filtering is based on the application of derivative filters and/or integrals that reconstruct the input signal.

Other observation that supports the hypotheses considered in the model is that the baseline jump has the same sign in the cases of an injection that provokes an exothermic or endothermic mixture. In Figs 2 and 3, it is shown the cases of injection of methanol on water (exothermic) and of injection of cyclohexane on benzene (endothermic). In both cases, the jump is produced below experimental zero, this is due to the fact that the thermostat temperature is T_0=25ºC and the room temperature is 23ºC, as a consequence $T_0^{'}$ must be something lower than T_0, i.e.: $\Delta T_0<0$ (Eq. (3)).

The experimental measure shown in Fig. 3 corresponds to a cyclohexane injection of 2 cm^3 (1.5 μL s^{-1}) on initial 1 cm^3 of benzene. Before and after the mixture, the corresponding electrical calibrations are carried out. In Fig. 3a the experimental output is shown, in Fig. 3b an extension is made where it is observed a baseline jump of $\Delta y \approx 200$ μV. In Fig. 3c it is shown the reconstruction of the input (developed power), this reconstruction has been carried out through an inverse filtering technique. We have to point out that the baseline has not been corrected, the filter has simply been applied and the sensitivity corrected; the jump produced is of 0.1 mW, and corresponds to a 10% of the minimum value of the developed power.

In the study of the zones with low concentrations or infinite dilution, the injection flow is usually reduced, this makes the developed power be lower and the baseline jump would have a percentage higher than 10%, for the considered mixture; this is the reason why the adequate correction of the baseline is essential to obtain correct energetic results.

The electrical calibration helps to understand the performance of the instrument, but does not replace the chemical calibration as, in each case, the dissipation takes place in different places and the sensitivity obtained in each calibration (electrical and chemical) is slightly different. This is a rather complex topic to be studied in this paper because there are other effects that have to be evaluated, only to indicate that the data of references of both mixtures shown correspond to the ones obtained by Marongiu *et al*. [13] and Stokes *et al*. [14]; the sensitivity values obtained in the chemical calibrations are K_{mix}=391 mV W^{-1} for the first case, and K_{mix}=397 mV W^{-1} for the second case.

The sensitivity values obtained in the electrical calibrations are K_{elec}=393 mV W^{-1} for water+methanol, and K_{elec}=400 mV W^{-1} for the measure corresponding to cyclohexane+benzene.

We do not have to be surprised with the difference between the sensitivity values obtained in the measures of methanol on water with the ones obtained in the measures of cyclohexane on benzene, because the assembling and installation of the measuring cell

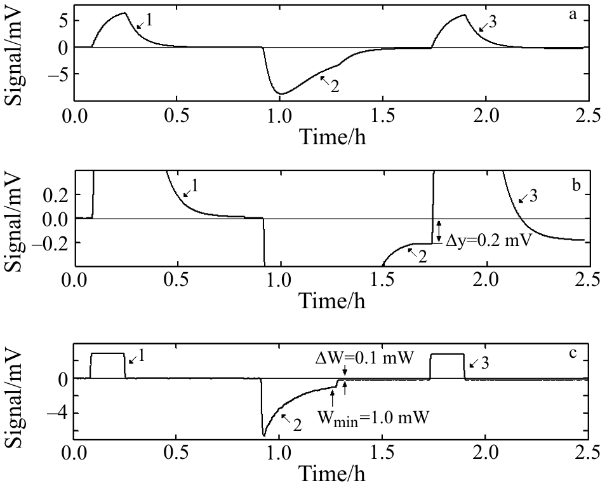

Fig. 3 a – Calorimetric curve or experimental output corresponding to a continuous injection (1.5 μL s^{-1}) of cyclohexane on initial 1 cm^3 of benzene (curve 2), the curves 1 and 3 correspond to the electrical calibrations; b – extension of the previous curve, Δy is the baseline jump; c – power developed in terms of time obtained by applying an inverse filtering on the experimental output (the baseline jump ΔW has not been corrected)

is never the same, so the configuration may change; but it is possible to observe that K_{mix} is slightly lower than K_{elec} obtained in electrical calibrations carried out before and after the mixture.

Final discussion and conclusions

The experimental results that are presented support the hypothesis that the baseline jump in an isothermal microcalorimeter is the variation of the thermal coupling between the content in the mixture cell and the axis of the stirrer, which is coupled, at the same time, to a zone with a temperature slightly lower (in our case) than the thermostat temperature. This jump is independent from the dissipation and it has always the same sign. The magnitude of the baseline jump is variable and depends mainly on the volume that reaches the liquid content in the cell and on the stirrer location inside the cell, that may change in the handling process.

With the modification of the thermal coupling, two effects are produced: the first one is the baseline jump itself, and the second one is a modification of the TF.

As for the baseline jump, its magnitude has to be evaluated and it has to be ascertained how and when it is produced. For the physical location of the stirrer in the calorimeter utilized and in the experiences shown, the jump is of 0.1 mW, it is produced when the volume of the cell reaches 2.7 cm^3 (from a total of 3 cm^3) and its evolution takes place in time $t \approx 4$ min, for an injection velocity of 1.5 $\mu L\ s^{-1}$.

As for the modification of the TF, the appearance or increasing of the thermal coupling inserts a pole and a zero in the TF that models the operation of the calorimeter in its invariant situations. This is an inconvenience when the intermediate signal corresponding to the mixture has to be filtered.

In short, it would be desirable to work with liquid volumes in the cell that did not surpass the minimum volume for which the baseline jump started to take place, for this case V_{min}=2.7 cm^3. If it was not possible, it would be advisable to insulate thermally the stirrer axis in order to reduce this jump that is necessary to evaluate, checking how and when it is produced, for the purpose of realizing the adequate correction and guarantee the right determination of the powers developed in the mixture process; powers that will result subsequently in the thermodynamic properties searched for.

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