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FLOW MICROCALORIMETRY AND THERMOKINETICS OF LIQUID MIXTURES

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The identification of the calorimetric curves corresponding to liquid mixtures for different injection flows, given by a flow microcalorimeter, permits to classify in a kinetic way the studied mixtures. For this purpose, it is determined the establishment time constant of the mixture (τ_{mix}) that allows us to estimate the length occupied by the dissipation (through the parameter λ_{mix}) and thus to justify the sensitivity variation obtained in different chemical calibrations.

Keywords: *calibration, flow microcalorimetry, kinetic, liquid mixtures, sensitivity*

Introduction

Flow microcalorimeters are used to determine the energies of liquid mixtures. The enhancement of these instruments has simplified a lot their handling and this fact has produced an increase in their use these years. The operation principle consists in a simultaneous injection of the two liquids that are wanted to mix in a mixture zone. The thermopiles detector system provides the experimental output (in V), when this reaches the stationary state, it is supposed that the mixture is homogeneous and then the power developed in the mixture process (in W) is proportional to the experimental response, the proportionality factor is the sensitivity (in V W^{-1}) [1].

The calibration of these instruments consists in the determination of the sensitivity, this is determined by means of electrical and chemical calibrations. As a final result of the calibration, it is assumed a sensitivity value for an operating margin which is limited by the value of $(\rho c_p f)_T=(\rho c_p f)_1+(\rho c_p f)_2$ (ρc_p is the volumetric heat capacity of the injected liquid and f is the injection flow). For example, for a TAM2277-204 by Thermometric, it is obtained a sensitivity of 0.313±0.004 V W^{-1} for $(\rho c_p f)_T<15$ mW K^{-1} [2]; besides, considering a coverage factor similar to 2, it can be said that the instrument allows to obtain thermal measures with an uncertainty of 3% [3].

The uncertainty of the sensitivity is mainly produced by two factors. The first one is due to the power $\rho c_p f\Delta T$ derived from the injection of the liquids (ΔT is the difference between the mixture temperature and the thermostat temperature). The second aspect refers to the fact that the electrical calibration and the different chemical calibrations provide distinct sensitivity values because the dissipation location is different in each case, even for the different mixtures carried out [4, 5].

In order to classify the mixtures kinetically, we utilize in this article the results obtained in different chemical calibrations. This study is based on the recent works [6, 7] in which it is shown that the dissipation location of the mixture in these flow microcalorimeters increases with the injection flow.

The structure of this study is as follows: firstly, it is made a brief description of the experimental system and the Transference Function showing the operation of the instrument. Next, it is described the utilized experimental measures, the method of analysis and the obtained results. The studied mixtures have been ‘water+methanol’, ‘cyclohexane+benzene’ and ‘cyclohexane+hexane’.

Experimental system and transference function

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 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 Δt=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; by programming the number of steps in every sampling period the desired injection flow is obtained.

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The calibration of these thermal instruments consists in determining the parameters that define the model which represents the calorimeter and relates the power developed in the calorimeter to the experimental output or curve. In this case, it has been chosen a simple model given by a transference function (TF) of two poles:

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

where $Y(s)$ and $W(s)$ are Laplace transforms of the output and the power, K is the sensitivity (in V W^{-1}), τ_1 and τ_2 are the time constants. In this study, K_{elect} is the sensitivity obtained in the electrical calibrations and K_{mix}, the sensitivity obtained in the chemical or mixture calibrations. Supposing that the time constants only depend on the heating capacity of the used liquids and the injection flow; however, the sensitivity also depends on the dissipation location [2].

For electrical calibration, we dissipate a known power in a resistance placed very near the mixture location. In Fig. 1a, it is shown the dissipated power and the corresponding experimental output, the baseline noise was ±1 μV.

As time constants depend on the heating capacity, the thermograms have been identified by using different liquids. In Fig. 1b, it can be observed the linear variation of the first time constant with the volumetric heat capacity of the liquids used. Thus, the first time constant varies from τ_1=99.69 s for cyclohexane to τ_1=110.15 s for water, the second time constant has been fixed for all the liquids in τ_2=24 s. In order to do so, it has been used the simplex search algorithm method by Nelder and Mead [8] using the software MatLab [9]. In the adjustment, it has been utilized 1000 experimental dots and the standard deviation between the experimental and calculated values has been 1 μV.

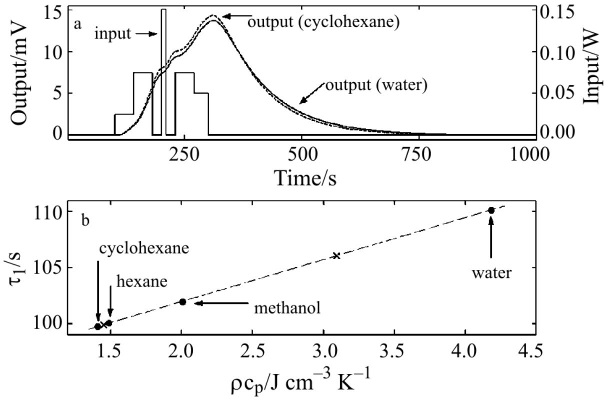

Fig. 1 a – Curves corresponding to the electrical calibration (input and output), b – first time constant *vs*. the volumetric heat capacity

Space-time evolution of the mixture energy

The experimental measures have already been described in previous works [2, 4–6], the injection flows have ranged from 2·0.75 to 2·8.25 μL s^{-1}, the liquid mixtures used in this study have been ‘water+methanol’, ‘cyclohexane+benzene’ and ‘cyclohexane+hexane’, and the enthalpies of reference (for 25ºC) have been, respectively, 875.0, 796.2 and 220.3 J mol^{-1} [10–12].

The mixtures provide an experimental output of the type represented in Fig. 2. In the identification, it is necessary to know the entrance power, for this task, it is supposed that the energetic dissipation due to the mixture does not take place instantly, but it follows an exponential law:

$$W_{\mathrm{mix}}=W_{\mathrm{ref}}(1-\mathrm{e}^{-t/\tau_{\mathrm{mix}}})\ [\mathrm{W}] \qquad (2)$$

where τ_{mix} is the stabilization time constant of the mixture energy.

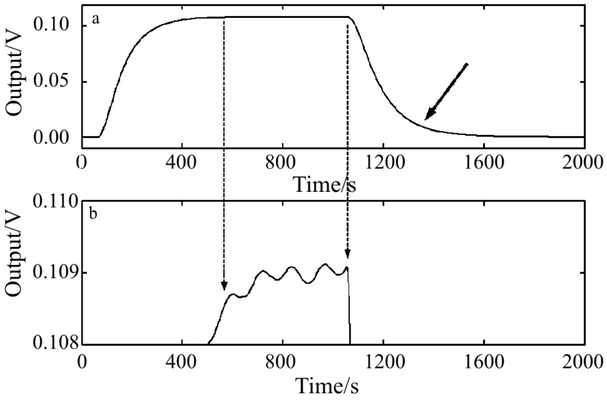

Fig. 2 a – Calorimetric curves corresponding to a simultaneous water+methanol injection. The injection flow was $2f$=12 μL s^{-1} and the reference power was W_{ref}=425 mW. The arrow indicates the curve zone used in the identification, b – extension of the mixture curve

The reference power W_{ref} is given by the expression:

$$W_{\mathrm{ref}}=H^{\mathrm{E}}_{\mathrm{ref}}(\dot{n}_1+\dot{n}_2)\ [\mathrm{W}] \qquad (3)$$

where $H^{\mathrm{E}}_{\mathrm{ref}}$ is the reference enthalpy in J mol^{-1}, $\dot{n}_1$ and $\dot{n}_2$ are the injection flows in mol s^{-1}.

It is also supposed that the mixture dissipation has an exponential spatial distribution characterized by the typical length λ_{mix}. For a constant injection velocity ν, we make $\lambda_{\mathrm{mix}}=\tau_{\mathrm{mix}}\nu$ [7]. In short, it is being considered a space-time function of the mixture power per unit of length that follows an expression of the type:

$$w_{\mathrm{mix}}(x,t)=\frac{W_{\mathrm{ref}}}{\lambda_{\mathrm{mix}}}\mathrm{e}^{-x/\lambda_{\mathrm{mix}}}(1-\mathrm{e}^{-t/\tau_{\mathrm{mix}}})\ [\mathrm{W\ m^{-1}}] \qquad (4)$$

For the identification, it has utilized the zero return position of the signal (see area marked by an arrow in Fig. 2a). The time constants of the TF are obtained from the electrical calibration; for example, for the mixture water+methanol we obtain τ_1=106.04 s (Fig. 1b) and τ_2=24 s. Once the time constants have been fixed, the identification in the curves corresponding to the mixtures will consist in obtaining τ_{mix} and the sensitivity K_{mix}. In order to do so, it has been used the simplex search algorithm method by Nelder and Mead [8, 9].

The high-frequency noise (of the baseline) is ±1 μV, but the mixture curves have a low-frequency oscillation (Fig. 2b) which depends on the mixture type. For instance, it has an oscillation of ±0.3 mV in the case of the 'water+methanol' and ±0.03 mV in the case of the 'cyclohexane+hexane' mixture. However, considering the amplitudes of the signals, this oscillation produces in both cases an uncertainty in the calculation of the sensitivity that varies from 1.5% for the lowest velocity to 0.2% for the highest velocity.

Results and discussion

The results are summarized in Figs 3 and 4. In Fig. 3a the values of τ_{mix} are shown for every mixture and for every injection flow. It can also be observed that this time constant diminishes with the injection flow in all cases; that is to say, the reaction is faster when increasing the concentration of the constituents. On the other hand, it can be compared the kinetics of the three studied mixtures showing that the 'water+methanol' mixture is slower than the other two, as its corresponding value of τ_{mix} is greater.

In Fig. 3b, it is shown the values of the characteristic length of every mixture, λ_{mix}, in terms of the injection flow. The obtained values are approximate since, in the mixture zone, the pipes have a narrowing point and it has been considered a mean diameter of 0.75 mm. The results point out that the faster the mixture dissipation ('cyclohexane+hexane' case), the lesser the characteristic length is, that is to say, the mixture dissipation occupies less pipe length.

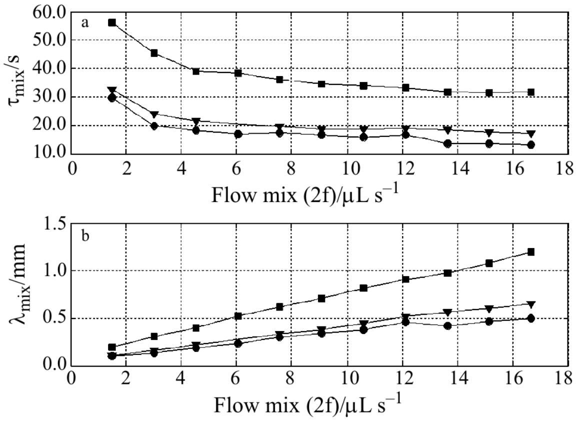

Fig. 3 Parameters τ_{mix} and λ_{mix} *vs*. flow mix. Results for the mixtures ■ – water+ methanol, ▲ – cyclohexane+benzene and ● – cyclohexane+hexane

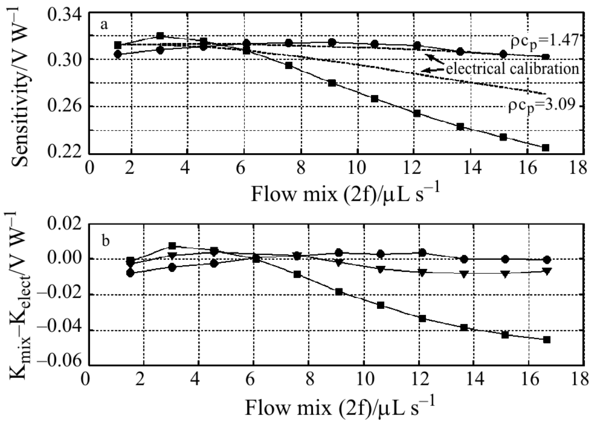

Fig. 4 a – Comparison of the sensitivity obtained in the chemical calibrations and the sensitivity inferred from the electrical calibrations (in discontinuous line) for every volumetric heat capacity (ρc_p in J cm^{-3} K^{-1}), b – difference between the mixture sensitivity and the electrical sensitivity corresponding to the same heating capacity as that of the mixture. Results for the ■ – water+methanol, ▲ – cyclohexane+benzene and ● – cyclohexane+hexane mixtures

Apparently, it should not exist connection between the value of τ_{mix} and the sensitivity, as the first one only affects the transitional state and the second one can be obtained directly from the signal stationary state. However, through the λ_{mix} parameter, the connection is evident as the sensitivity depends clearly on the dissipation location and, when increasing the characteristic length λ_{mix}, the dissipation location also increases and, consequently, there is a change in the experimental response of the calorimeter through the sensitivity (K_{mix}) of the TF (Eq. (1)).

In order to analyze the sensitivity obtained in the chemical calibrations (K_{mix}) we propose to make a comparison with the sensitivity obtained in the electrical calibrations (K_{elect}). For this purpose, it has been carried out an electrical calibration by injecting water through the two pipes and, simultaneously, a power is dissipated by using the Joule effect of the type represented in Fig. 1a. The sensitivity for each injection flow is determined and the electrical sensitivity curve is adjusted in terms of $\rho c_p f$ obtaining the following adjustment:

$$K_{elect}=A_0+A_1\rho c_p f+A_2(\rho c_p f)^2+ \\ +A_3(\rho c_p f)^3+A_4(\rho c_p f)^4 \quad [\mathrm{V\ W^{-1}}] \qquad (5)$$

where A_0=3.113·10^{-1}, A_1=5.827·10^{-4}, A_2=–5.477·10^{-5}, A_3=7.213·10^{-7}; A_4=–3.406·10^{-9}, $\rho c_p f$ is in mW K^{-1}.

From the discussion on λ_{mix}, we conclude that the fastest mixture occupies less dissipation length. According to this, we can say that the ideal case would be represented by an electrical dissipation in which τ_{mix}=0 and the dissipation length does not change when increasing the injection flow.

The adjustment of K_{elect} given by the Eq. (5) allows to represent the sensitivity of the electrical calibration for every volumetric heat capacity and for every injection flow (Fig. 4a). As it has been said before, these curves represent a mixture dissipation that is located in a point and whose mixture length does not change with the injection velocity. In a real mixture, the mixture length increases with the injection flow and, as a consequence of it, there would be a difference between K_{mix} and K_{elect}.

In Fig. 4a it is represented the sensitivity curves of the mixtures (K_{mix}) 'cyclohexane+hexane' and 'water+methanol' in terms of the injection flow, and, in discontinuous line, it is represented the electrical sensitivity curves (K_{elect}) corresponding to the same volumetric heat capacities (ρc_p). A clearer representation is given in Fig. 4b in which it is shown the difference K_{mix}–K_{elect} for the same ρc_p. In this figure it is observed that the mixture 'water+methanol' is the slowest and, as a consequence, is the farthest from the zero line; on the other hand, the mixture 'cyclohexane+hexane' is the fastest mixture and this is the reason why it is the nearest one to the zero line, that is to say, its dissipation is similar to the one of the electrical calibration.

Finally, it is necessary to point out that, if the mixture enthalpies are not known a priori, τ_{mix} can be determined for every injection flow and the mixtures that are desired to study can be compared kinetically. The extent of this work is justified because we have wanted to use all our knowledge about the mixtures (reference enthalpies) and about the calorimetric instrument.

Conclusions

Through the adequate treatment of the calorimetric signal, it can be determined the temporal evolution of the mixture energy produced in a flow microcalorimeter, this fact permits to compare kinetically the different mixtures. In the studied mixtures, we can talk about 'fast' mixtures (cyclohexane+hexane, τ_{mix}=19.8 s for 2·3 μL s^{-1}), 'medium' (cyclohexane+benzene, τ_{mix}=23.9 s for 2·3 μL s^{-1}) and 'slow' (water+methanol, τ_{mix}=45.2 s for 2·3 μL s^{-1}).

Kinetics changes with the injection velocity, showing a reduction of the establishing time constant of the mixture (τ_{mix}) when increasing the injection velocity. Besides, this time constant τ_{mix} is directly related to the length occupied by the mixture dissipation through the characteristic length ($\lambda_{mix}=\tau_{mix}\nu_{mix}$) and, as a consequence, with the calorimeter sensitivity.

If the calibration electrical resistance is very near the mixture location, the results of a chemical calibration using very fast mixtures are very similar to those of an electrical calibration (for the same value of ρc_p). However, if the chemical calibration utilizes a very slow mixture, the results from the electrical and chemical calibrations diverge (for the same value of ρc_p). This experimental matter can also be used to compare the mixtures kinetically through the values of the sensitivity obtained in the different chemical calibrations.

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