MODELLIZATION OF THE MIXTURE DISSIPATION IN A FLOW MICROCALORIMETER

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The signal processing of the experimental output produced by simultaneous injection of two liquids in a flow microcalorimeter allows, besides the determination of the mixture energy, to obtain information about the mixture thermokinetics. Starting from this information, a model of space-time behaviour of the mixture dissipation is proposed. The simulations carried out explain that an increase of the injection flow produces an increase in the dissipation length which could be located out of the detection zone.

Keywords: flow microcalorimetry, kinetic, liquid mixtures

Introduction

The use of flow microcalorimeters has increased these years due to the fact that the handling of these devices is very simple and the determination of the mixture energy is immediate.

In general, the calibration of these instruments consists in the determination of the sensitivity through electrical and chemical calibrations. The sensitivity uncertainty is mainly due to two factors. The first one is originated by the power $\rho c_p f \Delta T$ due to the injection of liquids, where ρc_p is the injected liquid capacity, f is the injection flow, and ΔT is the temperature difference between the mixture temperature and the thermostat. The second aspect refers to the fact that the electrical calibration and the different chemical calibrations provide different sensitivity values because the dissipation place is different in each case, even for the different liquid mixtures carried out [1–3].

In previous works, the experimental curves corresponding to chemical calibrations have been studied in order to look for some parameters to provide information on the spatial location of the mixture dissipation [4, 5]. As a result from these studies, it has been defined an establishment time constant of the homogeneous mixture that provides information about the mixture thermokinetics [6].

In this work, the experimental conditions of the mixture zone are compared with the results obtained from the analysis of the experimental curves corresponding to the liquid mixtures dissipations. As a result of this comparative study, it is proposed a space-time model of the mixture dissipation that allows to determine its spatial location and to evaluate the percentage of mixture power that is developed in the detection zone.

Experimental

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 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 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.

The experimental method consists in the simultaneous injection of two liquids in the mixture zone (see detail of the mixture cell in Fig. 1). The detector system of thermopiles provides the experimental output (in mV); when this reaches the stationary state, it is supposed that the mixture is homogeneous and the power dissipated in the mixture $W_{mix}(t)$ is proportional to the experimental output; the reverse of the proportionality constant is called sensitivity (in mV/W). In this stationary situation and, for the case of a molecular mixture of two pure liquids, the power dissipated by the mixture will be:

$$W_{mix}(t) = \frac{dQ}{dt} = (H_1 \dot{n}_1 + H_2 \dot{n}_2) - (H_1^* \dot{n}_1 + H_2^* \dot{n}_2) = \quad (1)$$
$$(H_1^E \dot{n}_1 + H_2^E \dot{n}_2) = H^E (\dot{n}_1 + \dot{n}_2)$$

being H_1 and H_2 the partial molar enthalpies of each component, H_1^* and H_2^* the molar enthalpies of each pure component, H_1^E and H_2^E the excess partial molar

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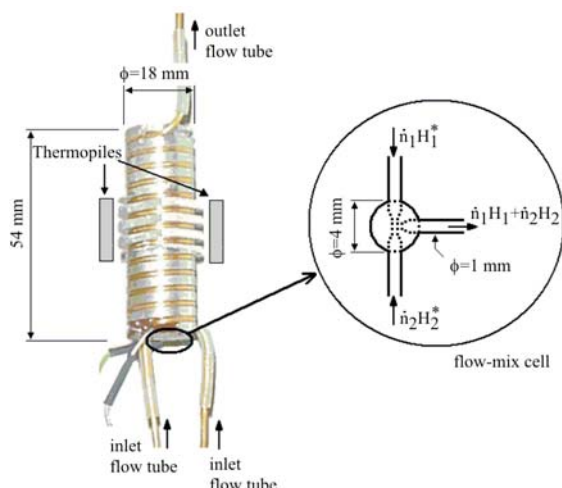
Fig. 1 Diagram of a flow-mix measuring cup in a TAM 2277-204 flow microcalorimeter by thermometric. In the figure, it is shown the thermopiles location and a flow-mix cell detail

enthalpies of each component, H^E the excess molar enthalpy of the mixture. The determination of the mixture enthalpy is carried out for a molar fraction $x_1 = \dot{n}_1/(\dot{n}_1 + \dot{n}_2)$, being $\dot{n}_1$ and $\dot{n}_2$ the molar rate of injection.

The experimental measures have already been described in previous works [2, 3], the injection flows have ranged from $2 \cdot 0.75$ to $2 \cdot 8.25$ μL s^{-1}, the liquid mixtures used in this study have been 'water+methanol', 'cyclohexane+benzene' and 'cyclohexane+hexane', and the reference enthalpies (for 25ºC) have been, respectively, 875.0, 796.2 and 220.3 J mol^{-1} [7–9].

Results and discussion

Signal processing

The electrical calibration allows to model the experimental system with a Transfer Function of two poles [2–3]. The sensitivity obtained in the electrical calibration depends mainly on the term $\rho c_p f$ (ρc_p is the injected liquid capacity and f is the injection flow). It has also been tested that the main time constant τ_1 increases with the volumetric heat capacity of the injected liquids; in this case and without liquid flow ($f = 0$ μL s^{-1}) τ_1 ranges from 99.8 s for $\rho c_p \approx 1.5$ J cm^{-3} K^{-1} (hexane) to 110.4 s for $\rho c_p \approx 4.2$ J cm^{-3} K^{-1} (water).

In order to approach the experimental situation of mixture, the same pure liquid is injected in each injection tube during the electrical calibration, and a reduction of the first time constant is observed when the injection flow increases; in this case and, for the case of injecting water in both tubes, the first time constant τ_1 ranges from $\tau_1 = 110.4$ s for a total injection flow $f_T = 2 \cdot 0$ μL s^{-1} to $\tau_1 = 82.9$ s for $f_T = 2 \cdot 8.25$ μL s^{-1}. The

second time constant can be kept constant for each liquid and for each injection flow: $\tau_2 \approx 24$ s.

Figure 2 shows experimental curves corresponding to the simultaneous injection of cyclohexane and benzene. In these curves, it can be observed the way in which the experimental output reaches the stationary state and increases the experimental output value when the injection flows are increased. For the treatment of these curves, two zones have been differentiated:

- Initial zone: from the beginning of the injection to the point when the signal reaches the stationary state.
- End zone: from the interruption of the injection to the point where the output returns to experimental zero.

The dynamic response of the curve end zone is characterized by a first time constant that only depends on the injected liquids, not on the injection flow, and by a second time constant that has been kept the same for 24 s. However, to rebuild the experimental curve, it is necessary a third constant called τ_{mix} which is related to the establishment time of the homogeneous mixture or, in this case, it is related to the mixture weakening.

The initial parts of the curves have been identified taking into account that the first time constant diminishes with the injection flow and when keeping constant $\tau_2 = 24$ s. At this point, it is also necessary a third time constant (τ_{mix}) to be able to rebuild the experimental signal.

For the determination of the time constants, it has been utilized the optimization technique by Nelder and Mead [10] and used the MatLab software [11].

It has been tested the equivalence between the τ_{mix} obtained at the initial part of the curve and the one obtained at the end part of the curve. Figure 3 shows
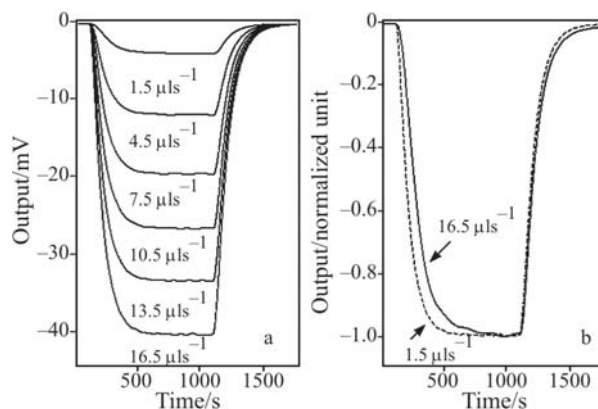
Fig. 2 a – Experimental curves corresponding to the simultaneous injection of cyclohexane and benzene for different injection flows. b – Experimental curves of the same liquid mixture with the vertical axis normalized in order to compare the dynamic responses of the cases with lesser and greater injection flow

the values obtained in terms of the injection flow for each studied mixture. In this Fig. 3, it is also represented the adjustment carried out through an exponential function:

water+methanol
$$\tau_{mix} = 32.6 + 42.2 \exp(-0.39 f_T)$$
cyclohexane+benzene
$$\tau_{mix} = 17.9 + 24.6 \exp(-0.39 f_T) \quad (in \quad s) \tag{2}$$
cyclohexane+hexane
$$\tau_{mix} = 14.3 + 25.7 \exp(-0.39 f_T)$$

being f_T the total injection flow in $\mu L\ s^{-1}$ ($f_T = f_1 + f_2$).

In the adjustment, the three curves have been forced to have the same coefficient $\gamma = 0.39$ of the exponential function is not related to the mixture kinetics but with the geometry of the mixture location. However, the highest or lowest value of τ_{mix} is directly related to the mixture kinetics. Thus, observing the curves, it is possible to say that the mixture water+methanol has a superior value of τ_{mix} and it needs more time to reach the stationary state and, therefore, it is slower than the other two.

Simulation of the mixture dissipation

When two liquids are mixed in a flow microcalorimeter, the experimental output has the form that is represented in Fig. 2; the analysis of the experimental measures for the studied mixtures and for different injection flows shows that the energetic dissipation due to the mixture does not take place instantaneously, on the contrary, it follows an exponential law characterized by an establishing time constant of the mixture τ_{mix} that has been evaluated and whose values are shown in Fig. 3 and in the expressions of the Eq. (2).

Also supposing that the mixture dissipation has a spatial distribution in an exponential way characterized by the characteristic length λ_{mix} proportional to the injection flow and to the constant τ_{mix} [6, 12]; for a constant injection velocity, it is:

$$\lambda_{mix} = \tau_{mix} v = \tau_{mix} \frac{f_T}{A} \tag{3}$$

where v is the constant injection velocity, f_T is the total injection flow ($f_T = f_1 + f_2$) and A is the internal section of the mixture tube, in this case $A \approx 1\ mm^2$.

In short, it is being supposed a space-time function of the mixture power per unit of length that follows an expression of the type:

$$w_{mix}(x,T) = \frac{W_{mix}}{\lambda_{mix}} e^{-x/\lambda_{mix}} (1 - e^{-t/\tau_{mix}}) \quad (in\ W\ m^{-1}) \tag{4}$$

where W_{mix} comes from the energy balance stated in Eq. (1).

In Fig. 4, it is shown the simulations carried out for the studied mixtures and for two injection flows: $f_T = 3$ and $f_T = 6\ \mu L\ s^{-1}$. It is also indicated in this Fig. 4 the tube total length of the mixture coil ($L = 720$ mm) and the zone where the thermopiles are located ($T = 240$ mm).

The calibration of this instrument is based on the sensitivity obtention from different chemical calibrations; for this instrument, it was determined a sensitivity of 313 ± 4 mV W^{-1} for $(\rho c_p f)_T < 15$ mW K^{-1} [2, 3]. It was looked for a parameter easy to calculate that will determine the validity margin of the calibration. The chosen
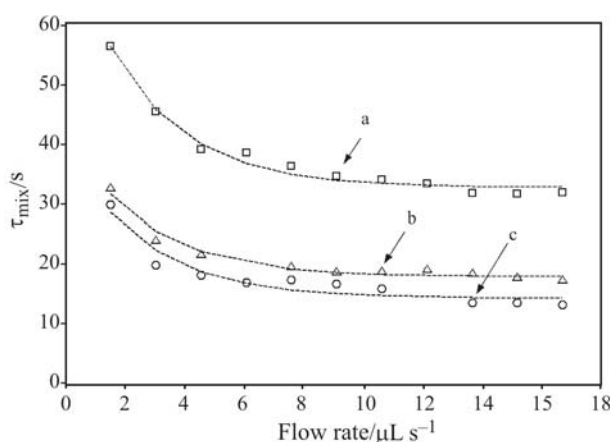
Fig. 3 Establishment time constant of the homogeneous mixture (τ_{mix}) *vs.* flow rate $f_T = f_1 + f_2$, where $f_1 = f_2$ are the injection flows of each component. Results for the mixtures a – 'water+methanol', b – 'cyclohexane+benzene' and c – 'cyclohexane+hexane', the dashed line corresponds to an exponential adjustment (Eq. (2))
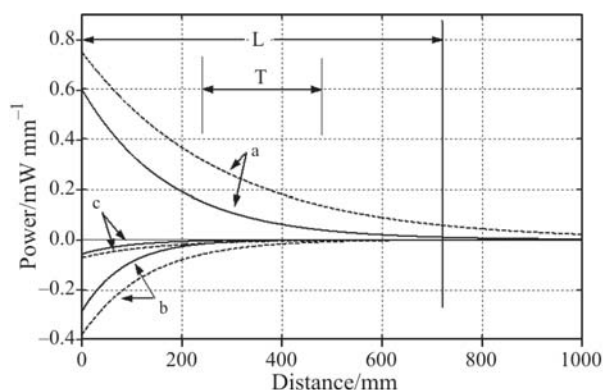
Fig. 4 Simulation of the dissipated power in terms of the distance to the starting point of the mixture: a – 'water+methanol', b – 'cyclohexane+benzene' and c – 'cyclohexane+hexane'. The solid lines correspond to 3 $\mu L\ s^{-1}$, and the dashed line corresponds to 6 $\mu L\ s^{-1}$. L indicates the tube length of the mixture coil, and T indi-

Table 1 Values of the characteristic length λ_{mix} and percentages of the mixture energy developed in the mixture coil zone for each total injection flow ($f_T = f_1 + f_2$). Results obtained from Eqs (3) and (4). It is indicated in boldface the acceptable maximum values for each liquid mixture

Flow rate	Water+methanol		Cyclohexane+benzene		Cyclohexane+hexane	
$f_T/\mu L\ s^{-1}$	λ_{mix}/mm	W/W_{mix}/%	λ_{mix}/mm	W/W_{mix}/%	λ_{mix}/mm	W/W_{mix}/%
3	174.6	98.38	97.5	99.94	85.3	99.98
6	280.3	92.34	154.8	99.05	128.5	99.63
9	388.3	84.34	213.4	96.58	173.1	98.44
12	504.4	76.01	276.7	92.59	222.7	96.06
15	625.3	68.38	342.9	87.75	275.2	92.69
18	748.4	61.79	410.3	82.70	329.1	88.78

parameter was the volumetric heat capacity of the mixture per time unit: $(\rho c_p f)_T = (\rho c_p f)_1 + (\rho c_p f)_2$.

Now, with the space-time modellization of the mixture dissipation, the calibration validity margin can be extended having the same uncertainty in the sensitivity. In the used microcalorimeter, to obtain an uncertainty of ±4 mV W^{-1} in the sensitivity, it would be sufficient to dissipate in the mixture zone at least 92% of the mixture power and this is equivalent to $\lambda_{mix} < 285$ mm. Table 1 shows some values of the characteristic length λ_{mix} and of the power percentage of the mixture developed in the detection zone for each studied liquid system.

For a not well known mixture, measures with different injection flows can be carried out to determine the evolution of the constant τ_{mix} and to determine λ_{mix} for each injection flow. Afterwards, the injection flows must be selected, trying not to extend the mixture dissipation in a more than acceptable way. The superior limit of the injection flows that will be fixed will depend on the desired accuracy of the measures.

Conclusions

From the experimental curves corresponding to mixture dissipations, the establishment time constants of the mixtures τ_{mix} have been obtained. This time constant allows to compare kinetically different liquid mixtures. Besides, it is obtained from τ_{mix} the characteristic length λ_{mix} that informs about the tube length in which the mixture dissipation takes place.

It has been simulated the mixture dissipation produced in a flow microcalorimeter for different injection flows, this simulation, apart from giving information about the liquid mixture thermokinetics, allows to determine the adequate injection flows for the correct determination of the mixture energy in this type of microcalorimeter, avoiding an unacceptable percentage of the mixture dissipation to take place out of the detection zone.

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