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INJECTION EFFECT ON THE SENSITIVITY IN AN ISOTHERMAL TITRATION CALORIMETER[*]

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By using electrical calibrations and with the injection of liquids with very different heating capacities (water and cyclohexane), it is made a thorough evaluation of the 'injection effect' in terms of the parameter $\rho c_p f$ (ρc_p – volumetric heat capacity, f – injection flow) in an isothermal titration calorimeter. This effect can be evaluated accurately in the case of non-volatile liquids, however, when dealing with volatile liquids, the uncertainty in their determination increases because of the vaporization heat.

Keywords: *injection effect, isothermal titration calorimeter, liquid injection calorimeter, liquid mixture*

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, by using these instruments, it is determined the total energy developed in the process being studied. These instruments also allow to determine the power developed at every time in the processes of liquid mixtures provided that it has a controlled liquid injection system and an adequate stirring system that assures a homogeneous mixture at every time [1, 2].

The calibration of conduction calorimeters is always a problem to solve that has to establish the margin of validity of the calibration carried out; in practice, the calibration of ITC is accomplished by using reference mixtures [3]; in this chemical calibration, it is included, without a differentiated study, the microeffects that could take place in the instrument.

The accuracy of the energy results depends on the consideration of all those aspects that could affect the previous working hypothesis; in previous works, it has been enumerated and described some aspects that could alter the final energetic result; for the case of calorimeters with heat conduction, isothermal, with continuous injection and variable mass, (isothermal titration calorimeter) it is possible to point out the following aspects [4–7]:

- Increase of the main time constant when increasing the mass of the mixture cell and as a consequence of the heating capacity of the content in the mixture cell.
- Variation of the sensitivity due to the increase of the liquid level in the laboratory cell. This variation can be significative in some cases.
- Effect produced by the liquid injection that is at the thermostat temperature on the mixture area which is at a different temperature.
- Variation of the baseline due to the modification of the thermal coupling between the mixture area and the thermostat through the stirrer.

These effects and others, which could appear due to the inherent characteristics of the manufactured calorimeter, must be analyzed in the initial calibration. In this paper, special attention is paid to the third enumerated aspect. For this reason, it is made a thorough study of the effect produced by the injection using two liquids with very different heating capacities: water and cyclohexane, and carrying out electrical calibrations by dissipating different powers.

The aim of every measuring instrument is to measure with the minimum error. This study intends to evaluate the order of power magnitude due to this effect in terms of the injection flow and the heating capacity of the injected liquid. Once this effect has been evaluated, it will be able to correct it and to determine, with the minimum error, the energies or powers developed in the energy process under study.

Experimental

The instrument used in this study is an isothermal heat conduction calorimeter TAM2277-204/2250 by Thermometric. The calorimetric signal or curve is directly read by a digital multimeter HP3457A (10 nV resolution). The Joule calibration is carried out through a resistance of 50 Ω placed in the base of a cell and the feeding is done through a programmable source HP6633A; the dissipated power is determined at ev-

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ery time by measuring the tension in the terminals of a standard 10 Ω resistance located in series with the Joule calibration resistance, this voltage is measured with a multimeter HP3478A (100 nV resolution). The injection system allows to inject, step by step, 0.0832 μL per step of the motor, which, through a micrometric screw moves a billet that pushes the piston of a Hamilton syringe of 50 mL; programming the number of steps of the motor at every sampling period (Δt) we obtain the injection flow; in this case, the injection flows used have been: 0.5, 1.0, 1.5 and 2.0 $\mu L\ s^{-1}$ (Δt=1.0 s). All the described elements are connected to a PC through the GPIB bus.

In order to assure that the injected liquid acquires the thermostat temperature, it has been disposed a coil previous to the mixture cell, the coil capacity is 1.5 cm^3. The stirring system (120 rpm) assures a homogeneous mixture at every time.

To study the injection effect, electrical calibrations have been carried out by inserting in the system a Heaviside signal of different powers (10.5, 22.2 and 45.3 mW) and when the output reaches the stationary state, it is injected 1.5 cm^3 of liquid on initial 1 cm^3 of the same liquid, with different velocities; the chosen liquids for this study have very different heating capacities: water (c_p=4.18 J K^{-1} cm^{-3}) and cyclohexane (c_p=1.43 J K^{-1} cm^{-3}). Figure 1 shows three curves corresponding to every dissipated power and for the case of injecting water on water with a flow of 1.5 $\mu L\ s^{-1}$. Figures 2 and 3 show an extension of the injection zones for the cases of injecting water (Fig. 2) and cyclohexane (Fig. 3). The injection flows used are: 2.0, 1.5, 1.0 and 0.5 $\mu L\ s^{-1}$.

Results and discussion

In order to understand the performance of every measuring instrument, it is necessary to model it. As in this case we want to study how the sensitivity of a calorimeter is affected by the liquid injection, we assimilate the calorimeter to a linear input-output system, where the input is the developed power and the output or curve the one given by the thermopiles detector system. With this hypothesis, the sensitivity can be defined as the output value in stationary state to a Heaviside input (unitary step). That is to say, the sensitivity will be given by $S=y/W$, where y is the response to the stationary state and W is the constant power that is being dissipated. When there is injection, we obtain a new sensitivity $S'=y'/W$, and the effect produced by the injection can be quantified in $\Delta y=y-y'$ (Fig. 2). The relative variation of the sensitivity will be $\Delta S/S=\Delta y/y$. The experimental measures show how the experimental response is affected by the injection (Figs 1–3).

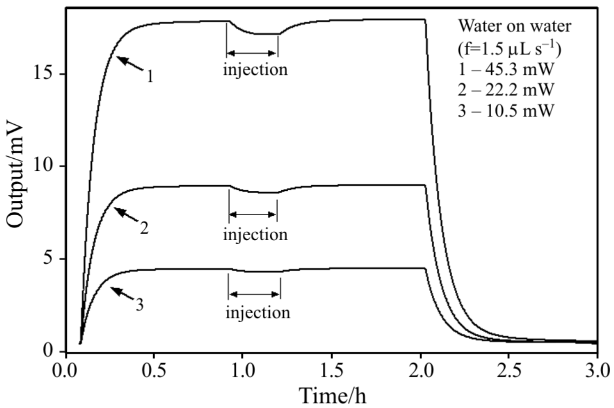

Fig. 1 Curves corresponding to Joule dissipations of different powers (45.3, 22.2 and 10.5 mW). During the dissipation, 1.5 cm^3 of water was injected to 1 cm^3 of water. The injection flow rate was of 1.5 $\mu L\ s^{-1}$

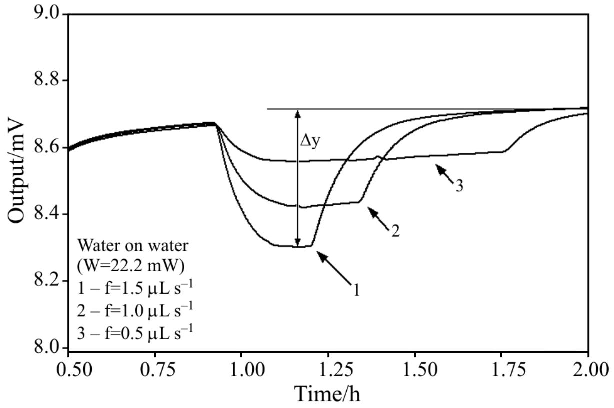

Fig. 2 Extension of the injection zone of the curves corresponding to a Joule dissipation of 22.2 mW (Fig. 1). During the Joule dissipation, 1.5 cm^3 of water was injected to 1 cm^3 of water with different flow rates: 1.5, 1.0 and 0.5 $\mu L\ s^{-1}$. The injection effect is quantified by Δy

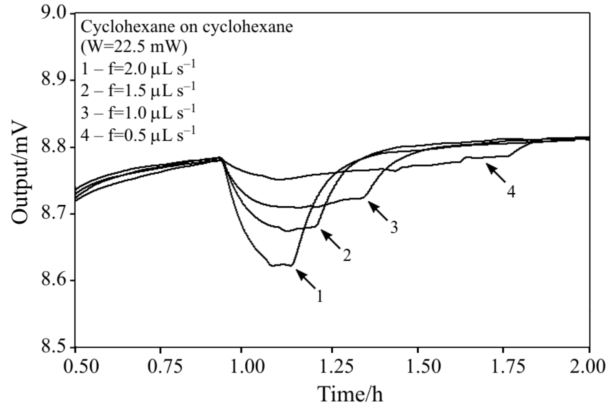

Fig. 3 Extension of the injection zone of the curves corresponding to a Joule dissipation of 22.2 mW (Fig. 1). During the Joule dissipation, 1.5 cm^3 of cyclohexane was injected to 1 cm^3 of cyclohexane with different injection flow rates: 2.0, 1.5, 1.0 and 0.5 $\mu L\ s^{-1}$

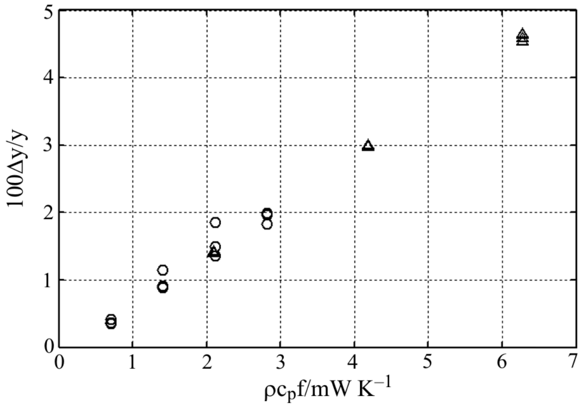

Fig. 4 Injection effect on the sensitivity *vs.* $\rho c_p f$ (ρc_p – volumetric heat capacity, f – injection flow). $100\Delta y/y$ – percentage of the relative variation of the sensitivity. △ – in case of injecting water, ○ – in case of injecting cyclohexane

It is known that the power due to the liquid injection is proportional to $\rho c_p f \Delta T$, where ρc_p is the volumetric heat capacity, f is the injection flow and ΔT is the difference between the temperatures of the injected liquid (T_0) and the mixture zone (T_m). If we suppose that the experimental output is also proportional to this difference in temperatures ΔT (the thermopiles are located between the thermostat and the sample), we can say that $\Delta y/y$ is proportional to $\rho c_p f$. In order to check it, it has been carried out the experimental measures described in the previous section. A summary of all obtained experimental results is shown in Fig. 4, in which it is represented the relative variation of the sensitivity in terms of $\rho c_p f$.

In Fig. 4, it is observed a clear proportionality between the relative variation of the sensitivity and the parameter $\rho c_p f$. Besides, the experimental results show that this injection effect is independent of the power which is being dissipated and only depends on $\rho c_p f$. It is also observed a greater dispersion in the evaluation of this effect in the case of being injecting cyclohexane, we interpret that this is due to the vaporization heat of the liquid, effect which has not been taken into account in the previous reasoning.

Conclusions

As conclusions of this paper, we indicate the following ones:

- The injection effect can be quantified in a relative variation of the sensitivity. This relative variation is proportional to $\rho c_p f$ where ρc_p is volumetric heat capacity and f is the injection flow. This will be certain if all the injected liquid has acquired the thermostat temperature before entering in the mixture zone.
- This effect is independent of the developed power, provided that the developed power does not affect in a significant way the temperature control of the calorimeter; that is to say, if the developed power is within the working domain of the calorimeter.
- This effect can be evaluated accurately if we deal with non volatile liquids, in the case of volatile liquids, the uncertainty of measurement increases due to their vaporization heat.

References

1 H. Tachoire and V. Torra, Thermochim. Acta, 110 (1987) 163.
2 F. Socorro, M. Rodríguez de Rivera, J. P. Dubès, H. Tachoire and V. Torra, Meas. Sci. Technol., 1 (1990) 1285.
3 R. Sabbah, A. Xu-Wu, J. S. Chickos, M. L. Planas Leitão, M. V. Roux and L. A. Torres, Thermochim. Acta, 331 (1999) 93.
4 C. Rey, J. R. Rodríguez, V. Pérez Villar, J. Ortín, V. Torra, J. P. Dubes, R. Kechavarz and H. Tachoire, Thermochim. Acta, 81 (1984) 97.
5 M. Rodríguez de Rivera, H. Tachoire and V. Torra, J. Thermal Anal., 41 (1994) 1392.
6 F. Socorro and M. Rodríguez de Rivera, J. Thermal Anal., 52 (1998) 729.
7 F. Socorro, I. de la Nuñez, L. Alvarez and M. Rodríguez de Rivera, Thermochim. Acta, 420 (2004) 163.

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