MICRO-EFFECTS ON CONTINUOUS-INJECTION HEAT CONDUCTION CALORIMETRY

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Abstract

A localized-constant model involving two capacities reliably describes two injection calorimeters: a mass-variation calorimeter and a constant-volume calorimeter (TAM 2277 by Thermometric). The model distinguishes the place and the types of dissipation, and its parameters depend on the rates and on the heat capacities of the liquids. In the case of the TAM 2277 calorimeter, the dependence between the detected heat of mixing and the injection rate is revealed. The proposed model permits the inclusion of perturbations on the baseline originating from the temperature variation of the thermostat.

Keywords: conduction calorimetry, flow calorimetry, liquid mixtures, low concentration, modeling, signal processing, time-dependent systems

Introduction

Continuous-injection heat conduction calorimeters are used for the thermodynamic study of liquid mixtures. Identification of the calorimetric model and appropriate signal processing of the experimental measurements permit the determination of thermodynamic properties of mixtures and solutions. Starting from a localized-constant model, we try to explain some perturbations in two injection calorimeters: a mass-variation calorimeter [1] and a constant-volume calorimeter [2] (TAM 2277 by Thermometric). The former provides good results for the overall mole fraction domain (0.001 ≤ x ≤ 0.999), the low concentration zone being especially interesting; the latter is suitable for intermediate concentrations (0.15 ≤ x ≤ 0.85).

The principle of performance of injection and mass-variation calorimeters consists in the continuous injection of a liquid into another one situated in the laboratory cell. The heat of mixing is in relation to the dissipation W(t), supposing that, at each instant, equilibrium is reached and the mixture is perfectly homogeneous. The thermodynamic property under consideration is obtained as a continuous function of the concentration [3] and its accuracy will depend on the precision of n1, n2 and the model chosen to determine W(t) from the experimental data.
curve. Models with three and six heat capacities with variable parameters have been proposed [4–6], the injection effect has been demonstrated [7, 8] and there are even works that consider the variation in the sensitivity with the level of liquid in the cell [8]; recently, due to improvements in temperature control, non-differential calorimeters have been proposed [9]. Here we will prove that a two-capacity model is sufficient to describe the typical phenomena of the variability of the system and the micro-effects detected in the calibration:

a) The injection causes an increase in the heat capacity of the contents of the laboratory cell, and as a consequence an increase in the main time constant. The thermal coupling and the detection surface grow larger with the volume, causing a variation in the sensitivity.

b) An additional energetic term appears, due to the temperature difference between the injected liquid and the mixture.

c) If volatile liquids are used, then the vaporization heat included in the power $W(t)$ will produce a certain imprecision in the determination of $n_1$ and $n_2$.

d) In this calorimeter, the calibration resistance is situated in the liquid, and the difference between the electric and the chemical calibrations is not appreciated (it is presumed that the dissipated power does not perceptibly modify the temperature of the thermostat)

In the injection and constant-volume calorimeter (TAM 2277 by Thermometric), the reaction zone has three orifices: two for injecting the liquid in continuous form, and one as exit. The heat of mixing is calculated when the experimental output reaches the permanent state. Now we do not obtain a continuous function, but distinct values for each molar fraction $x$ that match up to the programmed rates of each injector. The detection surface of these instruments is constant and no vapour space is present. Nowadays, this device provides reliable thermodynamic results of excess enthalpies of liquid mixtures [10, 11]; the calibrations are based on determination of the sensitivity as function of the injection rates and the heat capacities of the liquids used [12–14]; instruments are now being constructed in which the reaction zones are of higher volume and in which the influence of the rate is less [15]. This calorimeter (TAM 2277) has also been used for the determination of heat capacities $C_p$; in this case, a second-order model was chosen [16]. Here, we consider that a two-capacity model adequately describes the performance of the device; three micro-effects are taken into account:

a) energetic terms due to friction and to the temperature difference between the injected liquid and the mixture;

b) the difference between the chemical and the electric calibration (this is because the Joule dissipation is not produced in the same place as the mixing);

c) the mixing could continue out of the detection zone, due to the increasing injection rate.