Thermochimica Acta 639 (2016) 10–13

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Short communication

A procedure for calibration of differential scanning calorimeters

I.A. Sedov*, T.A. Muhametzyanov, B.N. Solomonov

Chemical Institute, Kazan Federal University, 420008, Kremlevskaya 18, Kazan, Russia

ARTICLE INFO

Article history:
Received 1 June 2016
Received in revised form 7 July 2016
Accepted 12 July 2016
Available online 14 July 2016

Keywords:
Differential scanning calorimetry
DSC
Heat capacity
Calibration

ABSTRACT

A new approach to calibration of differential scanning calorimeters based on the difference in heat capacities of heavy and light water is described. The advantages of heavy water over salt solutions currently used for the same purpose are described. Sources of uncertainties in measurements and possible ways to reduce these are discussed.

1. Introduction

Differential scanning calorimetry (DSC) of solutions [1–3] is a method allowing determination of the enthalpies of conformational changes and phase transitions in solutions of polymers and biopolymers, and formation and decomposition of complexes in the liquid phase. DSC is also a very simple way to measure the isobaric heat capacities of liquids and solutions over a broad range of temperatures in a single experiment.

A very high precision of the measured values of heat capacities is required to determine accurately the partial molar heat capacities of dissolved proteins, which reflect the changes in protein structure with temperature and upon unfolding, especially at low concentrations. The same is true for the partial or apparent heat capacities of any solutes in dilute solutions. However, it is impossible to make the sample and reference cells identical and fill with exactly equal volumes of liquid. Introduction of a temperature-dependent calibration coefficient related to the difference in the volumetric heat capacities of the cells filled with standard samples can reduce the error of measured heat capacity and enthalpy values.

A previously suggested calibration procedure for a twin, fixed-cell, temperature-scanning calorimeter [4,5] is based on measuring the difference in heat capacities of 1 M NaCl and pure water. The present work suggests using heavy water (D_2O) in one cell and pure light water (H_2O) in the other. The difference in heat capacities is larger than for 1 M or even 6 M NaCl, which reduces the relative error of the calibration coefficient. There is no need to prepare a solution with exact concentration. There is no risk of changing concentration during degassing of the samples or adsorption and crystallization of the salt. A minimum requirement for calibration is only 1 ml of pure D_2O. Choosing another pure liquid for calibration is difficult because the difference in volumetric heat capacities between water and other pure liquids is too large and the signal goes off scale at usual scanning rates.

2. Experimental

The calorimeter was a TA Instruments NanoDSC with two 300 μl capillary cells. Water was distilled, deionized, and degassed while stirring under vacuum. The measured resistance at 298 K was 18.2 MOhm cm. Heavy water purchased from Prikladnaya himiya was degassed while stirring under vacuum. Infrared spectrum shows the light water content is less than 0.1% (determined using the dependence of absorption at 3400 cm^{-1} corresponding to O—H stretching vibrations on addition of small portions of light water).

DSC curves for the sample pairs H_2O (cell1)–H_2O (cell 2), D_2O–H_2O, H_2O–D_2O, and D_2O–D_2O were recorded at constant pressure 3.5 bar in the temperature range 278.15–393.15 K repeating the heating and cooling cycle 4 times for each pair of samples. The scanning rate was 1 K min^{-1}. The cells were cleaned with Contrad 70 solution before the experiments, and a balance scan with both cells filled with H_2O was done. The experiment was repeated 2 more times with the new samples. After that, the same procedures were repeated at a scanning rate of 2 K min^{-1}.

To remove the initial part of the curve corresponding to non-steady heating or cooling, the DSC curves were truncated; the

* Corresponding author.
E-mail address: igor_sedov@inbox.ru (I.A. Sedov).

http://dx.doi.org/10.1016/j.tca.2016.07.010
0040-6031/

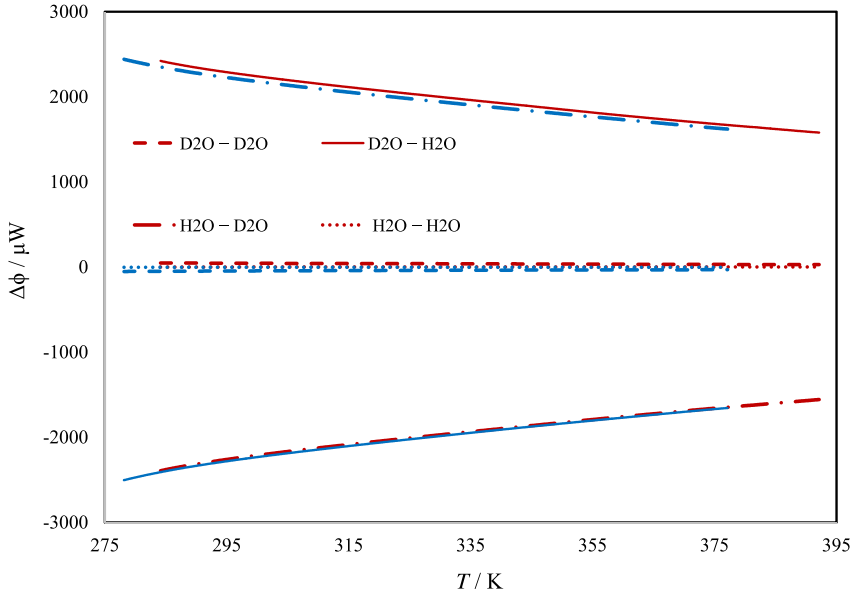

Fig. 1. DSC curves of heating (red curves) and cooling (blue curves) of different combinations of heavy and light water samples. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

parts from 278.15 to 283.15 K for heating curves and from 393.15 to 357.15 K for cooling curves were discarded. In raw curves, the temperature difference between neighbouring data points is always a little different. Thus, we calculated the values each 0.1 K using spline interpolation. The first scan for each sample pair was abandoned, while scans 2–4 were compared, and no significant difference is observed. The difference is <0.05% of the signal intensity at the same temperature for D_2O–H_2O pair. At the same time, after refilling the cells with the same pair of samples, the signal can change by up to 2% (for D_2O–H_2O pair), which is likely due to small random changes in the volumes of the samples in measurement cells. The maximum relative uncertainty of the values of calibration coefficient k (see below) will be the same (2%) if one determines it from a single experiment. However, we averaged the results for each sample pair over 3 repetitive experiments with new samples, which reduces the uncertainty. Averaged values referred to as "experimental data" or "DSC curve" were used in further analysis.

In the experiment with potassium chloride solution, the calorimetric signal between this solution and pure light water was measured in the temperature range 278.15–393.15 K, repeating the heating and cooling cycle 4 times and averaging over the last 3 cycles.

3. Results and discussion

The DSC curves for each of the sample pairs are shown in Fig. 1a (heating) and 1b (cooling).

In the ideal case, the difference of volumetric heat capacities of the samples (1 and 2) put into two absolutely identical cells will be proportional to the differential calorimetric signal from the cells:

$$C_{p(1)}\rho_{(1)} - C_{p(2)}\rho_{(2)} = k\Delta\phi, \quad (1)$$

where C_p is the mass heat capacity of the sample, ρ is the mass density, $\Delta\phi$ is the calorimetric signal, which reflects the difference of the heat flows through the cells. If $\Delta\phi$ is expressed in watts and equals the total heat flow between the cells, then the coefficient k is given by:

$$k/\left(s\cdot ml^{-1}\cdot K^{-1}\right) = 1/\left(\left(V/ml\right)\cdot\left(v/\left(K\cdot s^{-1}\right)\right)\right), \quad (2)$$

where v is the temperature scanning rate, V is the volume of each cell.

The output signal of a real calorimeter is the temperature-dependent heat flow $\Delta\phi$ between the cells. This differential signal from two cells filled with the same sample can differ from zero because of different cell volumes or non-synchronous heating. In current calorimeter software, this is corrected with a balance scan with two cells filled with the samples of pure water, which is below denoted as a temperature-dependent function $\Delta\phi_0$. However, the balance scan is not very stable over time. We observed small deviations of $\Delta\phi$ from zero even with light water in both cells. With two identical samples other than light water, the values of $\Delta\phi$ can be much larger.

Assuming that some of the systematic errors, e.g. inequality of the cell volumes, can be taken into account by multiplying the volumetric heat capacity of one of the cells by a factor x:

$$C_{p(1)}\rho_{(1)} - xC_{p(2)}\rho_{(2)} = k(\Delta\phi + \Delta\phi_0). \quad (3)$$

Both k and x may be temperature-dependent in real calorimeters, but we presume these to be stable in time and not to depend significantly on the nature of the samples.

A correction of the experimental data can be made by subtracting a DSC curve of compound 2 against compound 2 (which can be viewed as a baseline) from the DSC curve of compound 1 against compound 2:

$$C_{p(1)}\rho_{(1)} - C_{p(2)}\rho_{(2)} = k(\Delta\phi_{1-2} - \Delta\phi_{2-2}). \quad (4)$$

Using this method, evaluating x is unnecessary, but an additional scan for the baseline needs to be done (even if measured against pure water, because the baseline changes slightly in time and the balance scan made once is not sufficient for correction). However, the value of x is of interest to determine for a particular instrument, because x is close, but a little bit different from 1.

Denoting the calorimetric signal $\Delta\phi_{H-H}$ for the pair H_2O–H_2O, $\Delta\phi_{D-H}$ for the pair D_2O–H_2O, $\Delta\phi_{H-D}$ for the pair H_2O–D_2O, $\Delta\phi_{D-D}$ for the pair D_2O–D_2O, according to Eq. (4),

$$C_{p(D_2O)}\rho_{(D_2O)} - C_{p(H_2O)}\rho_{(H_2O)} = k(\Delta\phi_{D-H} - \Delta\phi_{H-H}), \quad (5)$$

$$x\left(C_{p(D_2O)}\rho_{(D_2O)} - C_{p(H_2O)}\rho_{(H_2O)}\right) = k(\Delta\phi_{H-H} - \Delta\phi_{H-D}), \quad (6)$$

$$(1-x)\left(C_{p(D_2O)}\rho_{(D_2O)} - C_{p(H_2O)}\rho_{(H_2O)}\right) = k(\Delta\phi_{D-D} - \Delta\phi_{H-H}), \quad (7)$$