ELSEVIER

Thermochimica Acta 347 (2000) 3–7

thermochimica acta

www.elsevier.com/locate/tca

Calibration of a fixed-cell temperature-scanning calorimeter to measure precise solution heat capacities from 275 to 398 K at 0.35 MPa

K. Ballerat-Busserolles[1], M.L. Origlia, E.M. Woolley*

Department of Chemistry and Biochemistry, Brigham Young University, Provo, UT 84602-5700, USA

Received 2 August 1999; accepted 26 August 1999

Abstract

A procedure was developed to calibrate the Calorimetry Sciences Corporation Models 5100 and 6100 Nano-DSCs to measure more precisely volumetric heat capacities of liquids and solutions. These calorimeters are small-volume, twin fixed-cell, power-compensation, differential-output instruments that can scan temperature upward or downward between 263 and 398 K at pressures up to 0.4 MPa. The calibration procedure leads to volumetric heat capacities that have a relative precision and accuracy of 3×10^{-6} to 5×10^{-5} for aqueous solutions at concentrations between ca. 0.001 and 1 mol kg^{-1}. The Nano-DSCs operate on the principle that the volumetric heat capacity of a solution or liquid is proportional to the difference between the calorimetric outputs for two separate experiments: one when both the cells contain a reference liquid (usually water), and one when the reference cell contains the reference liquid and the sample cell contains the solution or some other liquid of interest. The volumetric heat capacity of the reference liquid must be known precisely and accurately at the temperatures and pressures of the experiment. The calibration constant is determined from measurements on a second reference liquid whose volumetric heat capacity is also known precisely and accurately: 1-mol kg^{-1} NaCl(aq). Results of calibration and other experiments are used as examples to illustrate the advantages of the calibration procedure described in this paper. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Calibration; Differential scanning calorimetry (DSC); Heat capacities; Nano-DSC

1. Introduction

The determination of thermodynamic properties of solutions over wide ranges of temperature and pressure is of great interest in various systems to better understand and describe solute–solute and solute–solvent interactions. Precise volumetric heat capacities of solutions have generally only been determined near room temperature and ambient pressure. The precision of these measurements generally decreases at temperatures and/or pressures that differ significantly from the ambient [1]. Important progress has been made recently in the design of calorimeters for use at extended temperatures and pressures to measure solution heat capacities. In this paper, we report a procedure to calibrate and use twin fixed-cell temperature-scanning calorimeters to obtain solution and

---

* Corresponding author.

E-mail address: earl_wooley@byu.edu (E.M. Woolley).

[1] Current address: C.N.R.S., Institut de Chimie des Surfaces et Interfaces, B.P. 2488, Mulhouse Cedex, France, 68057.

PII: S0040-6031(99)00428-1

liquid volumetric heat capacities with equal or superior precision and accuracy to the best previous results available, while also increasing significantly the efficiency of performing the experiments.

We have used the Model 5100 and 6100 Nano-DSCs from Calorimetry Sciences Corporation (Provo, UT) to determine precise and accurate volumetric heat capacities of aqueous solutions from 278 to 393 K at 0.35 MPa. The Nano-DSC is a twin fixed-cell, power-compensation, differential-output, temperature-scanning calorimeter that can scan temperatures upward or downward between 263 and 398 K at pressures up to 0.4 MPa. The calibration procedure that we have developed for the Nano-DSC leads to solution volumetric heat capacities with relative precision and accuracy between 3×10^{-6} and 5×10^{-5} for aqueous solutions containing nonvolatile electrolyte solutes at concentrations between ca. 0.001 and 1 mol kg^{-1} [2].

2. Experimental

Twin capillary cells in the Model 5100 Nano-DSC instrument each hold 0.9 cm^3, and they were each filled through permanently attached platinum capillaries. Twin chamber cells in the Model 6100 instrument each hold 0.38 cm^3, and they were each filled through a single, permanently attached platinum capillary. The cells are filled at room temperature. The reference cell was filled with a reference liquid (usually water), and the other cell was filled with the liquid or solution of interest. After the cells were filled, the space above the cells was decreased so that the pressure in the cells increased to ca. 0.35 MPa. This prevents bubble formation and minimizes evaporation from the capillaries in the head space above the cells. This pressure was fixed at the beginning of an experiment, but it was not controlled during the experiment in these calorimeters. Thus, there was a small increase in pressure from the starting 0.35 MPa to about 0.37 MPa in the Model 5100 Nano-DSC and to about 0.36 MPa in the Model 6100 Nano-DSC at 393 K. A pressure increase from 0.35 to 0.37 MPa causes changes in density of 1×10^{-5} g cm^3 for both, water and 1-mol kg^{-1} NaCl(aq) at 393 K, and a change in apparent molar heat capacity $C_{p,\phi}$ from −40.68 to −40.67 J K^{-1} mol^{-1} at 393 K for 1-mol kg^{-1} NaCl(aq) [3].

The cell temperature in the Models 5100 and 6100 Nano-DSCs is controlled by Peltier elements, while temperature is scanned at a constant scan rate during an experiment. The temperature scan rate is controlled and monitored by measurement of the resistance of a calibrated platinum resistance thermometer placed in the thermal control block. Semiconductor thermobatteries are placed in thermal contact with the two cells to sense differences in their temperatures. Any temperature differences are kept as close to zero as possible by application of a current to electric heaters attached to the cells. That difference in power applied to the two cells is a proportional measure of the difference in heat capacities of the two cells and their contents. A diagram of the cells, sensors, and controls is given in the Model 5100 and 6100 Users Manuals, and it has also been published for the Model 5100 cell design [4]. The cells in both the Model 5100 and the Model 6100 have response half-times of about 5 s and the sensitivity of both the models is ca. 50 nW at a scan rate of 1 K min^{-1}. In our laboratory, consecutive scans at a rate of 1 K min^{-1} were generally reproducible to within ca. ±1–2 μW with the Model 5100 and ±0.2–0.5 μW with the Model 6100. All results described in this paper were obtained at a scan rate of 1 K min^{-1}.

3. Results

The calibration procedure we have developed is based on the principle that the volumetric heat capacity of a solution or liquid of interest is proportional to the difference between the calorimetric power output from the Nano-DSC for two separate experiments. In a ‘baseline’ experiment, temperature scans are made when both the cells contain water (or some other reference liquid with a well-known volumetric heat capacity). If the calorimeter were ideal, this experiment would give zero differential power output to the cells during the scan over the complete range of temperatures. Since it is not possible to make cells, thermobatteries, heaters, and other components that are identical physically and thermally, ‘baseline’ experiments give a non-zero differential power output. A ‘baseline’ experiment is performed before, and after, each measurement on a solution of interest so that any possible drift or change in the response of the cells and thermal components over time can be observed and compensated for.

In the second or 'solution' experiment, the reference cell is again filled with water (or with the same other reference liquid used in the 'baseline' experiment) and the sample cell is filled with the solution or liquid of interest. The volumetric heat capacity ($c_{p,s}$ ρ_s) of the solution is then given by the Eq. (1).

$$c_{p,s}\rho_s = k(\Delta P_s - \Delta P_w) + c_{p,w}\rho_w \qquad (1)$$

In Eq. (1), k is the temperature-dependent and scan-rate-dependent calibration constant of the calorimeter, $c_{p,w}$ the gravimetric heat capacity of water, ρ_s and ρ_w the densities of the solution and water, respectively, and ΔP_w and ΔP_s the differences in power applied to the heaters on the two cells to maintain them at the same temperature during the 'baseline' and 'solution' experiments, respectively.

The calibration constant k was determined from Eq. (1) at temperatures varying from 278.15 to 393.15 K at 5-K intervals at a scan rate of 1 K $\min^{-1}$ from results of 'baseline' and 'solution' measurements on reference liquids whose volumetric heat capacities are well known. We used water and 1-mol kg^{-1} NaCl(aq) for these reference liquids because their specific heat capacities and densities are known with high precision and accuracy, and also because of our current interest in the determination of heat capacities of aqueous solutions. We used values of $c_{p,s}$ and ρ_s from the equations given by Archer [3] and values of $c_{p,w}$ and ρ_w from the equations given by Hill [5]. The sodium chloride used for calibration was a dried analytical reagent, and solutions were prepared by mass with distilled, deionized, degassed water. We have used water as the reference liquid for 'baseline' experiments and in the reference cell in 'solution' experiments.

Each experiment was performed by scanning temperature upward and downward at least four times each. Examples of power outputs from experiments are illustrated in Figs. 1 and 2. The reproducibility and stability of calorimetric signals are illustrated in plots of the differences between the signals for successive scans for a given experiment as shown in Figs. 3 and 4. Differences are largest for the first scan up and down, and those largest initial differences are probably caused by the presence of very small bubbles in the cells or capillaries that apparently dissolve during the first scan cycle. Consequently, results from the first scans up and down are usually not included in the averages of calorimetric signals ΔP_w and ΔP_s that are used to determine the calibration constant k and solution heat capacity $c_{p,s}$ with Eq. (1).

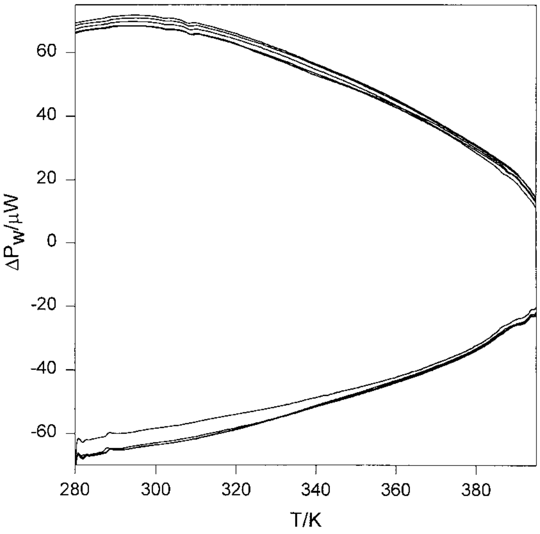

Fig. 1. Differential power output for a 'baseline' experiment with water in both cells of the Model 5100 Nano-DSC.

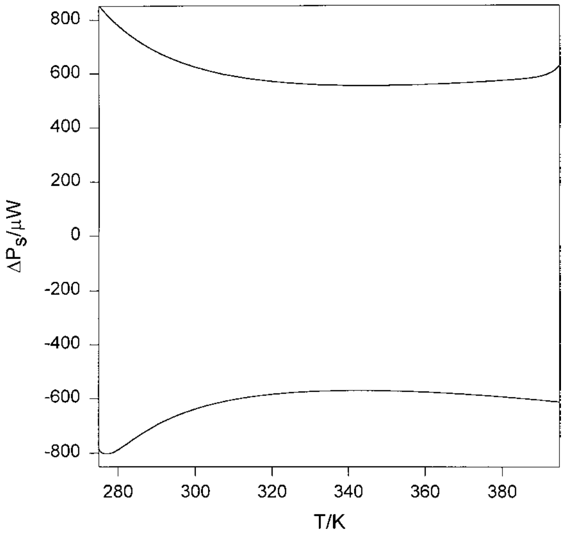

Fig. 2. Differential power output for a 'solution' experiment with water in the reference cell and 0.9979_4 mol kg^{-1} NaCl(aq) in the sample cell of the Model 6100 Nano-DSC.

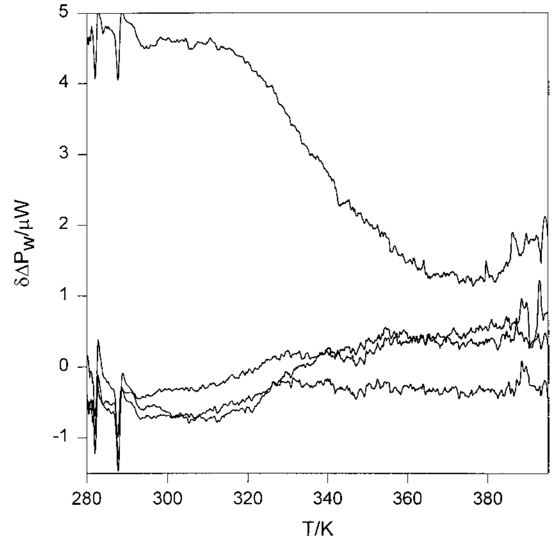

Fig. 3. Differences in differential power outputs (output for the final scan down subtracted from the output for each scan down) for the 'baseline' experiment in Fig. 1 with water in both cells of the Model 5100 Nano-DSC. The results for first scan down are the top curve.

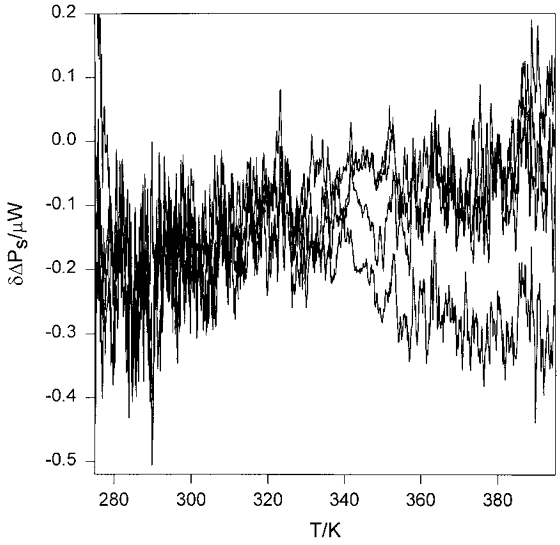

Fig. 4. Differences in differential power outputs (output for the final scan up subtracted from the output for each scan up) for the 'solution' experiment in Fig. 2 with water in the reference cell and 0.9979_4 mol kg^{-1} NaCl(aq) in the sample cell of the Model 6100 Nano-DSC.

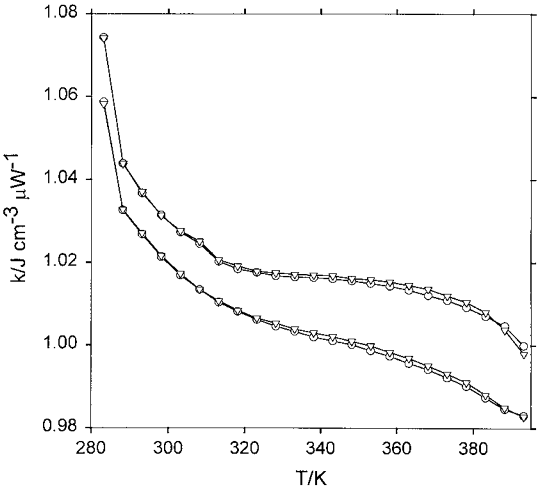

Fig. 5. Calibration constant for the Model 5100 Nano-DSC obtained from experiments about 6 weeks apart with 0.98900-mol kg^{-1} NaCl(aq). The upper two curves are for scanning up, and the lower two curves are for scanning down: (○), initial calibration; and (▽) calibration 6 weeks later.

Fig. 5 shows the calibration constants for the Model 5100 Nano-DSC as a function of temperature determined from our experiments on water and 1-mol kg^{-1} NaCl(aq). These calibration constants were determined periodically and were found to be reproducible with a relative precision of ca. 1×10^{-3} at all temperatures between 278 and 393 K. Thus, differences in volumetric heat capacities between reference liquids and the solutions or liquids being investigated can be determined with a relative precision $\{\delta\ (c_{p,w}\rho_w - c_{p,s}\rho_s)/(c_{p,w}\rho_w)\}$ of between 3×10^{-6} and 5×10^{-5}.

The apparent molar heat capacity of a solution that contains a solute with molar mass M at molality m is given by Eq. (2).

$$C_{p,\phi} = Mc_{p,s} + \frac{1000 \times (c_{p,s} - c_{p,w})}{m} \qquad (2)$$

Fig. 6 shows a surface plot of (root-mean-square deviation in $C_{p,\phi}$ vs. $m^{1/2}$ vs. T) for NaCl(aq) at m from 0.001 to 0.3 mol kg^{-1} obtained from multiple scans and multiple experiments with our Model 5100 Nano-DSC. [2] These results show clearly the excellent precision possible at m as low as 0.01 mol kg^{-1}.

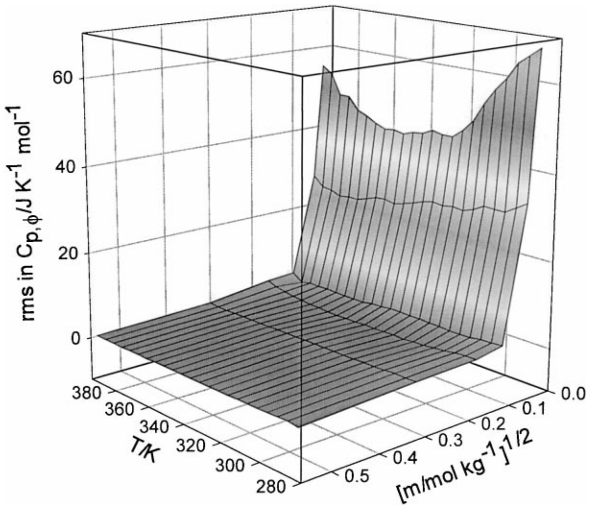

Fig. 6. Root-mean-square deviations of apparent molar heat capacities $C_{p,\phi}$ of 0.001–0.3-mol kg^{-1} NaCl(aq) from multiple scans up and down and independent experiments using the Model 5100 Nano-DSC [2].

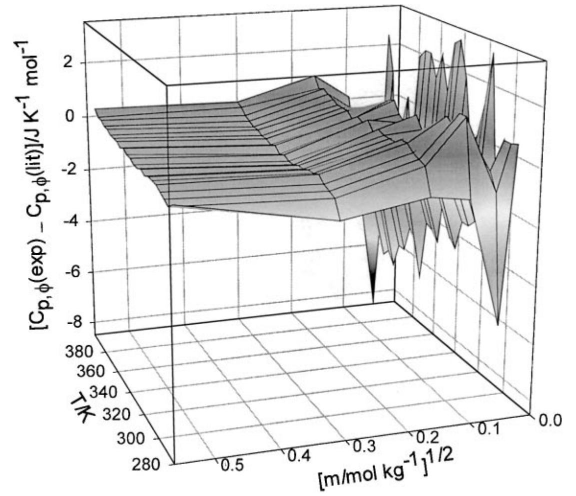

Fig. 7. Difference between experimental and literature [3] values for apparent molar heat capacities $C_{p,\phi}$ of 0.001–0.3-mol kg^{-1} NaCl(aq). Experimental values were obtained from measurements with the Model 5100 Nano-DSC [2].

A measure of the accuracy of $C_{p,\phi}$ values for NaCl(aq) obtained from our experiments with the Model 5100 Nano-DSC is given in Fig. 7, which shows a surface plot of (difference between experimental [2] and literature [3] values of $C_{p,\phi}$ vs. $m^{1/2}$ vs. T). These results show clearly that acceptably accurate values of solution heat capacities can be obtained at m as low as 0.001 mol kg^{-1}.

We have recently published heat capacity results obtained with the Model 5100 Nano-DSC for aqueous sodium acetate, acetic acid, HCl, and NaOH [6] and for the aqueous ionic surfactant *n*-dodecylpyridinium chloride [7]. These results, along with those more recently obtained with the Model 6100 Nano-DSC for aqueous 2-amino-2-hydroxymethyl-propan-1,3-diol (tris or tham) [8], and for β-D-glucose and β-D-galactose [9], illustrate the sensitivity, precision, and accuracy possible for solution heat capacities obtained through calibration of, and measurements with, twin fixed-cell temperature-scanning calorimeters by the procedures outlined in this paper.

References

[1] J.M. Simonson, R.E. Mesmer, in: K.N. Marsh, P.A.G. O'Hare (Eds.), Solution Calorimetry: Experimental Thermodynamics, vol. IV, IUPAC Chemical Data Series No. 39, Blackwell, Oxford, 1994, Chap. 11.

[2] E.M. Woolley, J. Chem. Thermodyn. 29 (1997) 1377–1385.

[3] D.G. Archer, J. Phys. Chem. Ref. Data 21 (1992) 793–829.

[4] G. Privalov, V. Kavina, E. Freire, P.L. Privalov, Anal. Biochem. 232 (1995) 79–85.

[5] P.G. Hill, J. Phys. Chem. Ref. Data 19 (1990) 1233–1274.

[6] K. Ballerat-Busserolles, T.D. Ford, T.G. Call, E.M. Woolley, J. Chem. Thermodyn. 31 (1999) 741–762.

[7] K. Ballerat-Busserolles, C. Bizzo, L. Pezzini, K. Sullivan, K.E.M. Woolley, J. Chem. Thermodyn. 30 (1998) 971–983.

[8] T.D. Ford, T.G. Call, M.L. Origlia, M.A. Stark, E.M. Woolley, J. Chem. Thermodyn. 22 (2000) in press.

[9] M.L. Origlia, T.G. Call, E.M. Woolley, J. Chem. Thermodyn. 22 (2000) in press.