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A VERSATILE AND HIGH-PRECISION SOLUTION–REACTION ISOPERIBOL CALORIMETER

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A new solution–reaction isoperibol calorimeter was developed to measure enthalpies of solution and reaction. A new system of sample cell was developed to avoid the breaking of glass ampoules, hence making the sample cell reusable. The system is suitable for measuring molar enthalpies of solid-liquid and liquid-liquid interactions at different temperatures. The reproducibility and accuracy of the apparatus were tested by measuring the enthalpy of solution of KCl in water at 298.15 K and the enthalpy of protonation of THAM in HCl (0.1 M) at 298.15 K. The results showed the uncertainty taken as the reproducibility was ±0.3% and the difference with the literature values was within ±0.5%.

Keywords: *enthalpy of protonation, enthalpy of solution, solution–reaction isoperibol calorimeter, temperature measurements*

Introduction

The isoperibol solution-reaction calorimetry is a versatile technique widely used to measure enthalpies of solution, reaction, dilution, mixing, adsorption, formation and of excess [1–9]. The isoperibol calorimetry is in particular used to determine the molar enthalpies of solution and transfer. By determining these properties, information about the interactions inside the solution, interactions of the type solute–solute, solute–solvent and solvent–solvent, is found.

In our research on thermodynamic properties of solutions of symmetrical and unsymmetrical quaternary ammonium salts, we have determined apparent molal volumes [10] and activity coefficients [11]. In order to complete the study of solvation for these solutes, it is necessary to determine the molar enthalpies of solution in aqueous and non-aqueous solvents.

For this purpose, we have built an isoperibol solution reaction calorimeter which is characterized by its great versatility, high precision and low cost. This calorimeter possesses a novel system of sample cell, which avoids breaking glass ampoules, thus making the sample cell reusable.

Experimental

Description of the apparatus

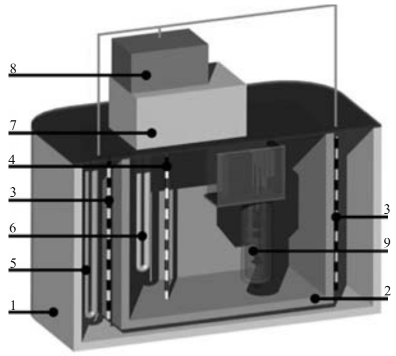

Fig. 1 The complete experimental setup. 1 – External tank (cooling system); 2 – internal tank; 3 – external tank temperature sensor; 4 – internal tank temperature sensor; 5 – external tank heater; 6 – internal tank heater; 7 – internal tank temperature control; 8 – external tank temperature control; 9 – solution-reaction isoperibol calorimeter (Fig. 2 for details)

The isoperibol solution reaction calorimeter consists on a Dewar vessel, an electric stirring system, a sample cell, a temperature measuring circuit, a heater circuit for calibration and equilibration purposes, and the temperature controlling system. The schematic diagram of the isoperibol solution-reaction calorimeter is shown in Fig. 1.

Dewar vessel and electric stirring system

The Dewar vessel was built of Pyrex glass. Its dimensions are: 30 and 38 mm of internal and external diameter respectively, with a depth of 63 mm, and an internal volume of 50 mL. The internal walls of the jacket were silvered and evacuated to a pressure of $1\cdot10^{-3}$ Pa in order to reduce heat leakage from the heat

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conduction and air convection to a minimum level. We have found that our Dewar vessel has a leakage modulus of $3\cdot10^{-4}$ s^{-1}. This value shows the low level of heat losses, which is comparable to other Dewar vessels used in isoperibolic calorimetry [6, 12]. The stirrer was built using 2 mm stainless steel rod, and it rotates at a 250 rev min^{-1}.

Sample cell

Special attention has been given to the sample cell, which is the system is novel contribution because the rupture of glass ampoules is no longer needed, making the cell reusable. The cell consists of a Teflon hollow cylinder, 2 cm high with an internal radius of 0.9 cm, for a total capacity around 1.5 mL. The sample is enclosed in the sample cell with Teflon caps as shown in Fig. 2. The sample cell is placed on a stainless steel support, and is fixed by means of a griping system. To trigger the reaction the caps are removed using a remotely controlled servomotor allowing the solution or reaction process to trigger.

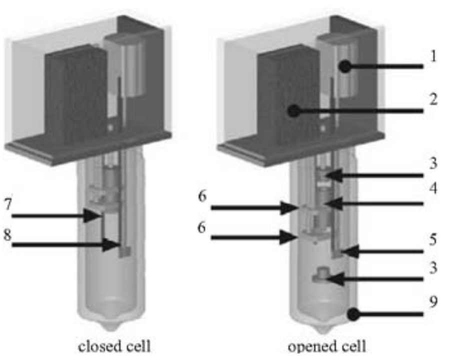

Fig. 2 The solution-reaction isoperibol calorimeter. 1 – Sample cell; 2 – teflon caps; 3 – servomotor; 4 – Dewar vessel; 5 – thermistor probe; 6 – electrical heater; 7 – stirrer; 8 – electric motor; 9 – cap openers

Temperature measuring circuit

The temperature measuring circuit consists of a DC Wheatstone bridge arrangement using a thermistor as the temperature sensing element. The thermistor, PTC, has a nominal resistance 3 kΩ at 298.15 K and constitutes one of the four arms of the Wheatstone bridge circuit. The other resistors in the bridge circuit are thermostated to avoid voltage fluctuations resulting from temperature variation. A 2.5 V constant voltage is applied to the Wheatstone bridge. The signal is recorded every 1 s using an Agilent 34401A multimeter providing 6–1/2 digit readings and interfaced through a personal computer using the program Agilent Intuilink for Multimeters, version 1.0. The unbalanced voltage signal of the bridge has a linear response to temperature change in the range from 298.15 to 303.15 K. The temperature data were compared with data obtained from a 5 K Beckmann thermometer with divisions spaced 0.01 K. The variation of temperature as a function of the potential, E, can be calculated as dT/dE=202.532 K V^{-1}. Figure 3 shows the relationship between the temperature and the potential.

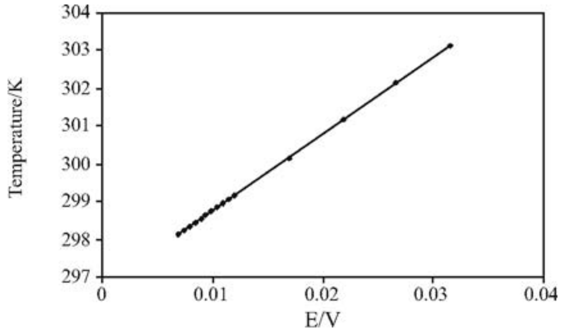

Fig. 3 Calibration of the thermistor. Relationship between the temperature and the potential

Heater circuit

The heater circuit consists of an electrical heater of 75 Ω and a precision power supply of 6.00 V, both built in the laboratory. The voltage on the heater is measured with a multimeter like the one described above. A computer controls the heating duration with a time resolution of 0.01 s.

Temperature controlling system

The calorimeter is immersed in a double water bath to provide isothermal surroundings during the tests. The inner bath consists of tank 35 cm long, 17 cm wide and 20 cm high made of 0.5 cm acrylic sheets. This tank is immersed on a bigger tank built of stainless steel, with a refrigeration system able to cool the contents below the room temperature. The outer tank is 45 cm large and 25 cm both wide and depth. An electronic circuit using a LM35 temperature transducer regulates the outer tank temperature at a constant temperature in the ±0.2 K range. The inner tank temperature is controlled by a Julabo temperature control which sets a constant temperature in the ±0.001 K range at 298.15 K. This bath is supported on four legs which raise it 2 cm above the bottom of the outer tank and place its top 1 cm above the water level in the outer tank. Both tanks used an air stirring system to homogenize the water temperature. The temperatures were verified with a regular thermometer, previously checked against a NIST certified thermometer. Additionally the temperature variation for the bath was measured using a 1 K Beckmann differential thermometer with 0.002 K. The maximum variation of temperature was found to be ±0.001 K at 298.15 K.

Results and discussion

Operational procedure and calibration

For the calorimetric test to take place, it is necessary that the solvent reaches the equilibrium temperature. Once equilibrium has been reached, calibration measurements of temperature, voltage, and time indicated that the maximum variation the system has ±0.0003 K, and the time constant of the calorimeter is about 3 s. Figure 4 shows the relationship between the potential and time for the aforementioned setup.

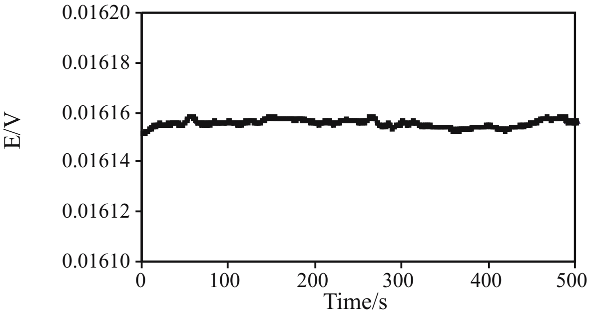

Fig. 4 Stability of the temperature measuring circuit

The test is divided in two phases: solution or reaction, and electric calibration. The first phase lasts for 2–5 min and it is then the measurement of temperature variation is made, the second phase lasts 2–5 min during which calibration takes place. The calibration is made keeping the range of variation similar to the one found during the measurements.

The temperature variation is directly related to the voltage on the thermistor. In order to eliminate the effect of the stirring on the Dewar vessel and heat transfer between the vessel and its sourroundings, the Dickinson's method [13] was used. The heat of solution is then calculated from the Eq. (1)

$$Q_S = \frac{Q_C}{\Delta E_C}\Delta E_S \qquad (1)$$

where Q_S is the heat of solution or reaction, Q_C is the heat supplied by the electric calibration, ΔE_S and ΔE_C are the voltage changes in the solution or reaction process and in the electric calibration, respectively.

Both the reproducibility and accuracy of the calorimetric system were tested by measuring the molar enthalpy of solution of KCl in double distilled water at 298.15 K and the molar enthalpy of protonation of THAM (tris(hydroxymethyl)aminomethane) in HCl (0.1 M) at 298.15 K. The concentrations used were the recommended values given in [1] and [14], respectively.

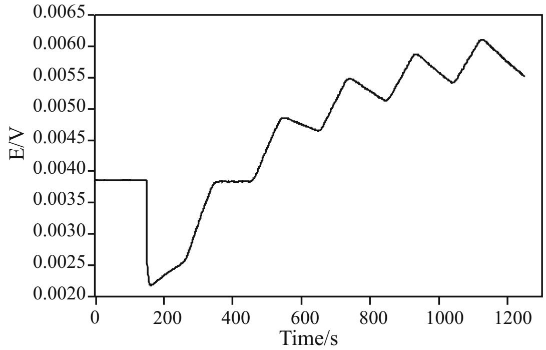

Fig. 5 The potential-time curve for the dissolution of KCl in water at 298.15 K

Reproducibility

The reproducibility was determined from four electric calibration tests for the same sample of KCl. Figure 5 shows the complete calorimetric test and the potential–time curve for the dissolution of KCl in water at 298.15 K. The reproducibility of the method was found to be ±40 J mol^{-1}.

The accuracy was verified by means of five independent experiments on both systems: KCl and THAM, and the results are presented in Tables 1 and 2. The molar enthalpy solution of KCl in water was 17.54±0.08 kJ mol^{-1} at 298.15 K and the molar enthalpy of protonation of THAM was –29.75±0.08 kJ mol^{-1} at 298.15 K. These values were in good agreement with the literature values: 17.584±0.017 kJ mol^{-1} [14] and –29.76±0.02 kJ mol^{-1} [1], respectively. This shows that

Table 1 The molar enthalpy of solution of KCl in water at 298.15 K

No.	m/g	$\Delta_S H_m$/kJ mol^{-1}
1	0.37480	17.50
2	0.38906	17.60
3	0.37201	17.56
4	0.38203	17.62
5	0.37001	17.43
Mean		17.54±0.08

Table 2 The molar enthalpy of protonation of THAM in 0.1 M HCl at 298.15 K

No.	m/g	$\Delta_S H_m$/kJ mol^{-1}
1	0.26004	29.80
2	0.26321	29.67
3	0.27001	29.75
4	0.26482	29.84
5	0.26922	29.65
Mean		29.74±0.08

our apparatus is of good quality: the uncertainty in molar enthalpies, by reproducibility, was ±0.3% and the uncertainty between the literature values and the measured value was within ±0.5%.

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