Calorimetric determination of the neutralization of tham-HCl from 0⁰C to 50⁰C using a new isothermal calorimeter connected to an automated temperature transducer

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ABSTRACT

At our laboratory, we developed a new cell type for the batch isothermal calorimetry of dissolution enthalpies to determine small amounts of easily soluble or slightly soluble solids. An innovative mixing system aimed at minimizing errors related to the common brittle point breakage effect has been coupled with a pneumatic valve, thus allowing it to work as a cell within an environment involving automatic information management done with software and electronics. The calorimetric cell has a capacity of 20 mL and the sample valve can handle solid samples between 5.0 and 30.0 mg. The experimental conditions suggested in specialized literature were maintained. Values of $-\Delta H°$ of 33.4134 ± 0.0005, 32.1248 ± 0.0012, 30.7357 ± 0.0014, 30.2754 ± 0.0017, 30.2691 ± 0.0007, 29.3395 ± 0.0023, 28.7232 ± 0.0032 and 26.0705 ± 0.0028 Kjoul./mole at 0, 10, 10, 15, 20, 25, 30, 40, and 50°C, respectively, are reported. The results of the study are then compared with existing studies in calorimetrics, and confirm the results of the standard THAM-HCl calorimetric system.   © 2008 Trade Science Inc. - INDIA

1. INTRODUCTION

Calorimetric investigations for determining dissolution enthalpies, ΔH_{sol}, of pure chemical compounds (gases, liquids and solids) are mainly aimed at researching solute-solvent interactions. In order to obtain data on in?nite dilution, these determinations are sometimes complemented by measuring dilution enthalpies. To obtain the value for the molecule transfer from the aqueous phase to in?nite dilute solutions (for liquid and solid compounds), it is necessary to know their vaporization enthalpy($?H_{vap.}$). However, such data are rarely available, particularly for solids.

The temperature derived for the dissolution enthalpy at in?nite dilution, i.e. the change in heat capacity, $C_{p(sol)}\infty$, is a remarkable property, especially for aqueous solutions, including biochemical systems. Such values, in conjunction with then heat capacity for the corresponding pure compound, C_p*, will yield the partial molar heat capacity of the compound in an infnitely dilute solution, $C\infty_{p,2}$ given by:

$$C\infty_{p,2} = C*_p + C_{p(sol)}\infty \tag{1}$$

In research on the aqueous solutions of simple, partially hydrophobic compounds, the function $C\infty_{p,2}$ has

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been used extensively(e.g. in discussions on 'hydrophobic hydration')[1–9].

The precise calorimetric determination of the dissolution enthalpies of solid compounds has recently become of significant interest, particularly for the pharmaceutical industry. This procedures represents a viable alternative for characterizing solid materials with respect to their polymorphic content[10-12] or degree of crystallinity[13]. Such measurements may not be sufficiently accurate when in fact very precise determinations are often needed. Many substances of interest are slightly soluble in water and methods requiring suitable organic solvents are therefore important. In the past, most determinations of $\Delta H_{m(sol)}$ have been made using semi-adiabatic "macro-solution calorimeters". Typically, such measurements require about 100 mL of solvent and 0.5g of solute in each experiment. For compounds with high solubility, such determinations can usually be made accurately, better than 0.1%[14], provided that the dissolution process is short, less than about 30 min. For slow processes, adiabatic calorimeters are recommended. In cases where relatively small quantities of material are available, microcalorimetric techniques are preferred. In many cases, such methods are suitable both for fast and slow processes. For solid and liquid solutes, measurements can be done at the mg level; however, the accuracy is much lower than that obtained using the macro-level.

In some cases, the Twin Heat Conduction Principle has been employed; nevertheless, here a single cell has been used with a simple isothermal calorimeter. This device allows measurements to be taken at the μW level over long periods of time (24hrs), and the design can be applied to both liquids and solids. Liquids can be easily found for slightly soluble hydrophobic compounds[15,16]. The instrument used for these solids and liquids requires easily soluble solutes[17]. Using the method in the present report, a batch technique, both easily and slightly soluble compounds can be studied. Other equipment used to take the microcalorimetric measurement of solid dissolution includes the device described by Roque-Malherbe and Seibold[18,19] and commercial vessels available from Setaram[20].

There is a definite need to define a single reaction that could be used as an interlaboratory comparison standard for solution calorimetry. The principal purpose

of such a comparison standard would be to eliminate the systematic errors sometimes associated with new equipment or with changes made to existing apparatus. The requirements for this kind of comparison standard as outlined by Sunner[20] are so numerous and demanding that most materials are excluded from even a cursory consideration. However, a few reactions have been identified that meet all or most of the requirements.

Many researchers have suggested that KCl could be a heat solution, but the reported[21] values differ by as much as 1%, and both Sunner[20] and Wadso, Moreno and others[21-24] have concluded that the system is unsatisfactory. The heat produced by the neutralization of a strong base with strong acid has also been recommended as a possible comparison standard. The heat neutralization of $HClO_4$ with NaOH, for example, has been proposed as a comparison standard but does not meet all of the requirements outlined by Gunn, such as being nonreactive with the atmosphere and having a low temperature coefficient. On the basis of work by Sunner[20], the heat of the neutralization of H_2SO_4 with excess NaOH appears to be an excellent way to compare calorimeters in the same laboratory, since the reproducibility between batches of H_2SO_4 is not better than that reported between batches of the solid compound known as THAM (tris(hydroxymethyl)-aminomethane or 2-amino-2-(hydroxymethyl)-1,3,-propanediol.

All things considered, there is clearly an advantages to working with a non-corrosive solid. THAM has already been used as a primary acidimetric standard and appears to meet most of the requirements for a solution calorimetric standard. The heat produced by the reaction of THAM(s) with HCl solution combines the endothermic heat solution and the exothermic heat protonation of THAM; the resulting overall reaction is exothermic. The protonation reaction is presented in the equation:

$$(HOCH_2)_3CHH_2 \; H^+ \leftrightarrow (HOCH_2)_3CNH_3^+ \tag{2}$$

It should be noted that there is no change in the solution's ionic strength during the reaction. During the calorimetric run, the temperature variation of the cell, T_C, needs to be closely monitored given that heat generated by the studied process in question depends on the ease with which electronic thermometers can be

handled with a previous calibration according to the temperature.

Thermistors are frequently used in calorimetry and are made using semiconductor ceramic materials with powder mixtures of metallic oxides treated at high pressures and temperatures. In thermistors, the electric resistance signal does not depend on the temperature and in many cases, there is an inverse relationship. Thus, they are referred to as thermistors with negative temperature coefficient, NTC. A relationship between these two parameters is as follow:

$$R_T = R\infty e^{(B/T)} \tag{3}$$

where T is the system temperature (°C); R_T, resistance of the thermistor at temperature (T) and $R\infty$ and B are constants which depend on the characteristics of the thermistor[9].

In this work, an isothermal calorimetric cell has been developed and then connected to a temperature transducer based on montage NTC thermistors that have had broad applications as reported in existing literature; the cell was then adapted to this equipment[25]. This is used for measuring the solution heats of liquids and solids at different temperatures in order to determine those which present minor changes in the temperature magnitude.

The values for the heat of the reaction of THAM(s) with 0.100 M HCl at 10, 25, 30, 35 and 40^0C are reported here together with a summary of published historic data from other laboratories.

2. MATERIALS AND METHOD

2.1. Device design and operation

The instrument is a single isothermal micro-calorimeter that uses a specially constructed thermistor system which produces a voltage proportional to the heat ?ow between the dissolution cell and the surroundings. The calorimeter is laid out in a water bath, where the temperature is maintained at $\pm6\times10^{-40}$C. The water bath, temperature controller and all peripheral units were built in our laboratory. The built calorimeter is shown on figure 1. The cell consists of a dewar-type glass (1) that has been vacuum-sealed (10^{-6} mBar) and whose volume is 25 mL. The cell possesses a flange containing a channel fit for an o-ring, thus ensuring a perfect hermetic seal with the top lid that contains the elements
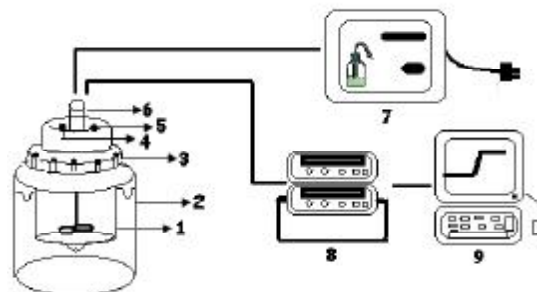

Figure 1: Dissolution isoperibol microcalorimeter: General scheme
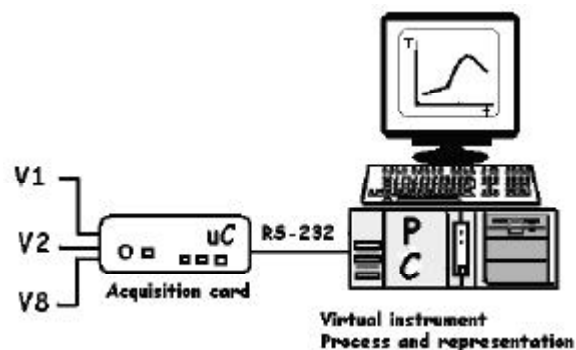
Figure 2 : General structure of the environment with all peripheral units

that communicate with the peripheries. A coating has been especially elaborated for this machine that allows the reflux of water at 25^0C. The coating was manufactured with carbon fiber (2), which not only provides insulation but converts it into a robust machine. This unit is fit with a glass lid and also covered with at carbon fiber lid, affixed by a set of precision screws (3).

The machine has a platinum resistance to convey 25 ohm electric calibrations (4) and the temperature sensor system is based on the thermistor system described below (5).

The mixture system consists of two parts: a pneumatic valve externally controlled by a computer and whose solution is kept at a temperature of $\pm 0.0001^0$C that allows one of the mixture solvents in question to be injected and the mixing system, which is a counterclockwise blade made of stainless steel (6).

2.2 Electronic system for measuring thermal effect[25]

A complete system was designed and implemented by closely following the work of Oleagordia et al.[25],

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Figure 3 : Operational scheme of the proposed system

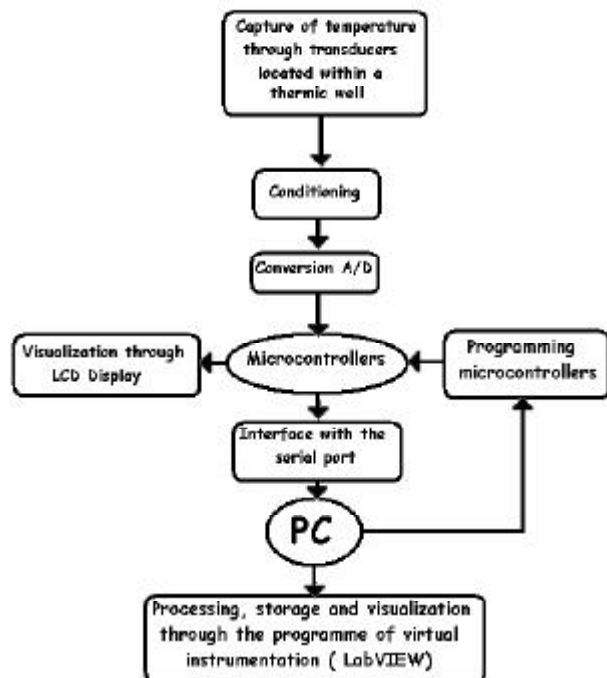I.J.Urrtabizacaya, R.Rodríguez P as described at http://www.euitt.upm.es/taee06/papers/S7/p64.pdf. Only certain elements have been adapted to our calorimetric machine, which consists of a data acquisition card and a PC that controls the system's operation. This system, represented on figure 2, encompasses hardware features such as the data acquisition card based on a microcontroller connected to a PC via RS232 through a serial port. In figure 3 the block diagram that represents the operation of the system is shown.

The digitalization of the thermometric signal is performed as per the literature, while leaving room to allow for a basic system to perform virtual treatments, which is new for this type of experiments. The system could be programmed by the user in order to capture the signals and apply certain mathematical equations to the signals to obtain the required information.

2.2.1 Operation of the NTC-type temperature transducers

In terms of the NTC (Negative Temperature Coefficient) and PTC (Positive Temperature Coefficient) thermistors, the NTC has been more commonly used. A brief description of this coefficient will be provided. The easiest mathematical model of a NTC thermistor is:

Where R_T is the thermistor resistance at a T temperature in °K, β is the thermistor sensitivity quotient in °K and R_0 is the T_0 temperature resistance. Equation (4) might be used in a program to calculate the temperature when the resistive value of the NTC is known:

$$R_T = R_o \cdot e^{\beta\left(\frac{1}{T} - \frac{1}{T_0}\right)} \tag{4}$$

Where R_T is the thermistor resistance at a T temperature in K, β is the affinity quotient of the thermistor in K and R_0 is the T_o. temperature resistance. The equation may be used in a program to calculate the temperature knowing the resistive value of the NTC:

$$T = \left(\frac{\beta.T_o}{\beta + T_o.\ln\frac{R_T}{R_o}}\right) \tag{5}$$

With this equation as a reference (1), the relation between the T temperature and the R_T resistance may be expressed as:

$$\frac{1}{T} = A_0 + A_1.\ln(R_T) + A_2.\ln\left((R_T)A_2\right) + \\ ....A_N.\ln(\ln(R_T).A_N)^N \tag{6}$$

Where T is the temperature in Kelvin, $(A_0, A_1, A_2, ...A_N)$ with the quotients of the polynomial. It is generally accepted that a third degree polynomial provides an accurate temperature measurement when the term $(\ln(R_T))^2$ is not considered. In this case, the equation is reduced to:

$$\frac{1}{T} = A + B.\ln(R) + C.(\ln(R))^3 \tag{7}$$

The equation (4) is known as the Steinhart-Hart equation and is used by most of the NTC thermistor manufacturers. The A, B and C quotients are known as the Steinhart-Hart quotients, with t as the K temperature. From the equation (4) the analytic function that determines the R_T resistance of the NTC for a specified temperature may be obtained:

$$R_T = \exp$$

$$\left[\left(-\frac{x}{2} + \left(\frac{x^2}{4} + \frac{y^3}{27}\right)^{1/2}\right)^{1/2} + \left(-\frac{x}{2} - \left(\frac{x^2}{4} + \frac{y^3}{27}\right)^{1/2}\right)^{1/2}\right] \tag{8}$$

where $x = \dfrac{A - 1/T}{C}$ and $V = \dfrac{B}{C}$

Several customized electronic circuits have been implemented to replicate the interface between the thermistor system that we have implemented in our work (an interface which consists of a Wheatstone bridge in which two of the arm resistances have been replaced by two thermistors), and to effect the analysis and reproduce the acquisition system.

The basic circuit used is the same as reported in the literature as departure circuits[25]; in this case, the NTC potential is:

$$V_T = \frac{R_T}{R + R_T}.V_{cc} \tag{9}$$

Once normalized, it appears as follows:

$$\frac{V_T}{V_{cc}} = \frac{R_T}{R + R_T} \tag{10}$$

Signals are taken from the Wheatstone bridge circuit and the signals are then captured by means of the system development in our laboratory. Such experimental data, apart from being processed and graphically represented, are stored in a data file for their subsequent processing in the same mathematical environment or another environment.

The censor system has been optimized to linearize it by accurately choosing the R value. For example, from the experimental point of view, the method that best linearizes V_T/VV_{CC} consists of:

Determining the temperature range of the calorimeter

Determining the NTC resistance value at the extremes, $(R_{T1}.R_{T2})$ and the central point R_{TDM} of the temperature range. These date might be obtained through experiments or taken from the manufacturers' technical data sheets. These values are designed by: RT_1: NTC resistance to the lowest temperature (T_1) of the operative range, RT_2: NTC resistance to the highest temperature (T_2) of the operative range, RTM: NTC resistance to the mean temperature TM of the operative range, $(T_M = (T_1 + T_2)/2)$. With these considerations, the Rx value that optimizes the $V_T/V_{CC.}$ linearity is

$$R_X = \frac{R_{T1}.R_{TM}.R_{T2} - 2.R_1.R_2}{R_{T1} + R_{T2} - 2.R_{TM}} \tag{11}$$

This equation has been applied to the temperature ranges from 10^0C to 50^0C ($T_1 = 10^0C$, $T_2 = 50^0C$, $T_M = 30^0C$). From the data sheet, we can conclude that
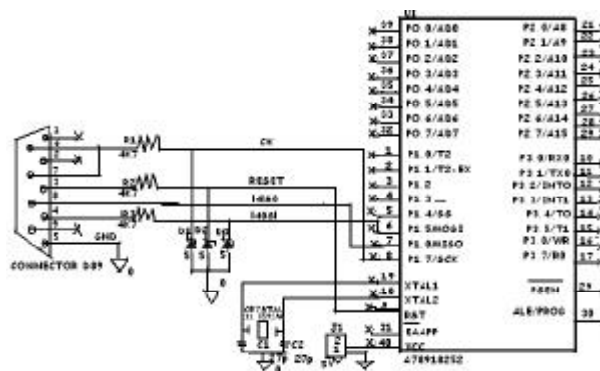
Figure 4 : ISP programming circuit of the μC AT89S8252

$RT_1 = 19.903\Omega$, $RT_2 = 3.601\ \Omega$, $R_{TM} = 8.056\Omega$.

2.2.2 Acquisition card

The acquisition card is basically comprised of three blocks: the microcontroller, the analogical-digital converter and the LCD. Among the options available of microcontrollers compatible with the MCS51 family, the AT89S8252 was preferred over the T89C51AC2 that incorporates the ADC. The criterion was based on potentiating the didactic slope when making the interface between the μC and the ADC0808. The μC AT89S8252 is ISP and the scheme implemented for its programming with the PonyProg2000 program is shown on figure 4 (www.lancos.com/prog.html). The μC coordinates the analogical digital conversion, data visualization in the LCD and the communication via RS232 with the PC. The ADC is connected to the signal conditioner outlet which is being used at that moment (dependant on the temperature transducer type). It has 8 analogical entrances with a range of tension from 0-5 volts. Externally, it uses an oscillator at a frequency of 640 KHz. When the conversion of each channel is complete, the ADC activates the EOC signal which, in turn, provokes an external interruption (INT0) in the μC, so that the reading is done in the associated ISR through the P_0 port of the chosen channel

ADC uses P1.2, P1.1 and P1.0 lines to choose the analogical channel, whose address is stored in the codifier by means of the ALE signal (P1.3 of the μC). The START signal is activated (P1.4 of the μC) so the analogical/digital conversion may start. On figure 5, a constructive detail is attached, together with the description of the interconnection of DAC and μC pins.

The system has two user interfaces, one on the cor-

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Figure 5 : Interconnection ADC- μC figure 9

responding PC screen corresponding to the virtual instrument and the other in LCD field located on the acquisition card. The chosen LCD measures 16x2, and the 4-bit hardware configuration is used to visualize the information. The P2.3, P2.2, P2.1 and P2.0 lines are used for the data and P2.4 y P2.5 are used for the RS (record selection) control signals and E (habilitation).

To perform the essays with the NTC thermistors, the calorimeter was used and the thermal effects have been dissipated through its electric resistance. Temperature control was performed from the PC through the front panel/user interface of the virtual instrument.

2.2.3 Design of the virtual instrument

The virtual instrument, implemented in LabVIEW 7.0 within a MATHLAB programming environment, allows all the system operations to be controlled from the front panel, including both sample injection and software. Basically, the instrument consists of a recorder whose functions include acquisition, monitoring, the data file on the hard disk, and the subsequent analysis and processing of the data stored on the disk. This function is achieved with two modules: the acquisition and the analysis modules.

For both the acquisition and analysis module, we have followed the module proposed by Oleagordia, et al.[25]. I.J., Urrtabizacaya, R., Rodríguez, as described on http://www.euitt.upm.es/taee06/papers/S7/p64.pdf

2.3 Materials

Reagent grade hydrochloric acid (Merck) and the water used in the dissolution measurements were produced through Milli-Q fltration. The system was used to prepare a stock solution of 0.10047 M HCl. This

solution was standardized with THAM (Merck, Analytic Reagent, 99.999%) and then checked with standard sodium hydroxide solutions; g in each case, a pH meter was used to detect end points.

To compare the results of this work, the samples were prepared as described in the literature and especially taking into account the suggestions of the Standards Committee of the U.S. Calorimetry conference, as reported Christensen[24] for the purpose of determining the heat solution the heat of reaction of THAM(s) with HCl using specific experimental conditions including:

- The reaction temperature should be stored at 25°C.
- The concentration of THAM should be 5 g/l.
- The concentration of the HCl solution should be 0.100 mol/L.
- The THAM sample should be stored with no further crushing or grinding in an atmosphere of 50% relative humidity, weighed in air, and bsealed in a glass ampoule with atmospheric pressure.
- A blank determination should be made.

These conditions were followed in this study. The values for the heat of the reaction of THAM(s) with 0.100 M HCl was measured at 0, 10,15, 20, 25, 30, 35, 40 and 50°C.

The THAM used to measure the heat reaction was prepared following the previous procedure; this sample was spread across a thin layer on a watchglass and stored at 25°C in a desiccator over a satured magnesium nitrate solution which provides an atmosphere of about 50% relative humidity.

2.4 Method

THAM samples (approximately 0.1025 g) were weighed in air and sealed with a small membrane of paraffin at atmospheric pressure and coupled to the valves system dual-pneumatic (for the dosing of liquids or solids) of the high-precision design in this work. For comparison, some ampoules were carefully sealed in the same shape to simulate the opening of the valve and the system of the mixture. Each sample was mixed in a solution of 20 ml of HCl leaving a final solution concentration in THAM of 5 g/l and the mixture was controlled from the exterior using the computer of the developed system.

The initial temperatures were $0,0000 \pm 0,0005$°C ;

TABLE 1: Heat of reaction of THAM(s) with 0.100 M HCl at various temperature

Temperature	-ΔH (Kcal/mole) others authors	- ΔH (Kcal/mole) this study
0	8.112[8]	7.9860
10	7.644[24]	7.6780
15	7.524[24]	7.3460
20	7.306[9]	7.2360
25	7.104[24], 7.109[8],7.104[9], 7.111[10], 7, 112[11], 7,1070[1], 7.109[12], 7.123[13],7.125[14],7.114[15]	7.2345
30	6.9049	7.0123
40	6.5552[4]	6.8650
50	6.055[8]	6.2310
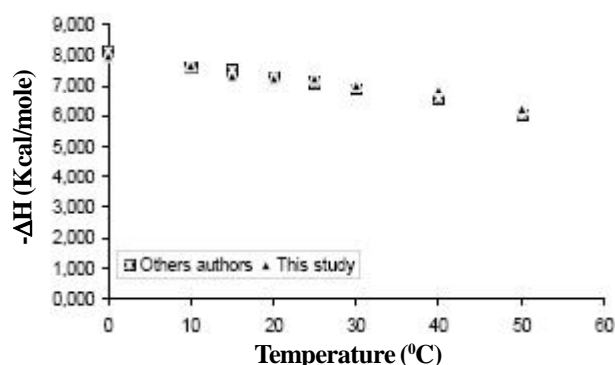
Figure 6 : Plot of heat reaction of THAM(s) in 0.1MHCl solutions versus temperature

$10,0000 \pm 0,0005\,^0C$; $15,0000 \pm 0,0005\,^0C$; $20,0000 \pm 0,0005\,^0C$; $25,0000 \pm 0,0005\,^0C$, $30,0000 \pm 0,0005\,^0C$, $35,0000 \pm 0.0005\,^0C$;$40,0000 \pm 0.0005\,^0C$ and $50,0000 \pm 0.0005\,^0C$, for the runs 0, 10, 15, 20, 25, 30, 35, 40 and 50 respectively. The balance of the procedure followed was the same as that previously described. Blank determinations showed that the heat effect was < 0.01%. This effect was assumed to be negligible in comparison to the total heat that evolved in the reaction.

3. RESULTS AND DISCUSSION

Experimental data and the values obtained in this study for the reaction of THAM(s) with HCl solution are given on TABLE 1 for greater clarity. The value determined in this study for the heat of reaction at 25^{0}C of THAM(s) with HCL solution concurs with previously reported values at this temperature and under similar experimental conditions within a range of to ± 0.01%.

The values obtained in this study for the heat of

reaction at 0, 10, 15, 20, 25, 30, 40 and 50^{0}C of THAM(s) with the HCl solution together with other reported values including those at the same values reported for other published studies.

The uncertainty interval for each of the values reported in this study is given as twice the standard deviation of the mean:

$$2\sqrt{\Sigma\left(d^2\right)\Big/n(n-1)}$$

Figure 6 is a plotting of temperature versus ΔH value for the reaction of THAM(s) with HCl obtained in this study and compared with others published studies.

These works show that the system used does not contribute in a significant way to the measurements of the neutralization calorimetry, thus evidencing the importance of using a mixed system in solution calorimetry. This is an advance in terms of the designs described in existing literature: here, the use of electronics connected to the system calorimeter reduces experimental errors. The relative humidity of 47% (controlled in these works) in the pneumatic valves to a temperature of 25^{0}C contains about 10^{-4} g/ml of water vapor, a small portion of which may condense at 10^{0}C on the inside of the valve during the opening, that contain of THAM. Some of the THAM is thus dissolved, but really with these new system electronics, the amount is minimal, thus representing an improvement on the systems previously described in existing literature. Nevertheless, as mentioned before, experimental errors are minimal.

For this very reason, quantity in this work is not calculated before the dissolution of the reagent since this is not necessary. It is clear that with high system mixing precision, errors such as the breakage of glass ampoules are avoided and therefore, there is no need to make up for the variations owed to such experimental errors. This makes experiments more precise, specifically the calorimetric experimentation.

4. ACKNOWLEDGMENTS

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5. REFERENCES

[1] F.Franks; 'Water a Comprehensive Treatise', Plenum Press, New York, **(1972)**.

[2] M.Bastos, G.Bai, E.Qvarnstron, I.Wadso; Therm.Chim.Acta, **405**, 21-30 **(2003)**.

[3] N.F.Nicohls, R.Skold, C.Spink, J.Suurkuusk, I.Wadso; J.Chem.Thermodyn, 8, 1081-1089 **(1976)**.

[4] G.Olofsson, I.Wadso; J.Chem.Thermodyn, **23**, 95-104 **(1991)**.

[5] S.Cabani, P.Gianni, V.Mollica, L.Lepori; J.Sol. Chem., **10**, 563-569 **(1981)**.

[6] I.Wadso, R.N.Goldberg; Pure and Appl.Chem., **73**, 1625-1639 **(2001)**.

[7] G.Ojelund, I.Wadso; Acta, Chem.Scan., **21**, 1838-1840 **(1967)**.

[8] J.O.Hill, G.Ojelund, I.Wadso; J.Chem.Thermodyn, **1**, 111-116 **(1969)**.

[9] M.Bastos, T.Kimura, I.Wadso; J.Chem.Thermodyn, **23**,1069-1073 **(1991)**.

[10] S-O.Nilsson, I.Wadso; J.Chem.Thermodyn, **18**, 673-679 **(1986)**.

[11] D.Hallen, S.O.Nilsson, W.Rotschild, I.Wadso; J.Chem.Thermodyn., **18**, 429-436 **(1986)**.

[12] H.Naghibi, D.W.Ownby, S.J.Gill; J.Phys.Chem., **91**, 245-251 **(1987)**.

[13] K.Lindner, W.Saenger; Biochem.Biophys.Res. Commun., **92**, 933-942 **(1980)**.

[14] D.Hallen, I.Wadso; J.Chem.Thermodyn., **21** , 519-524 **(1989)**.

[15] I.Wadso; Thermochim.Acta, **347**, 73-77 **(2000)**.

[16] W.Backman, M.Bastos, L-E.Bringgner, S.Hagg, D. Hallen, P.Lonnbro, S-O Nilsson, G.Olofsson, A. Schon, J.Suurkuusk, C.Teixeira, I.Wadso; Pure and Appl.Chem., **66(3)**, 375-381 **(1994)**.

[17] P.Backman, M.Bastos, D.Hallen, L.Lonnbro, I. Wadso; J.Biochem.Biophys Methods, **28**, 85-92 **(1994)**.

[18] R.Roque-Malherbe, A.Berazain, J.A.del Rosario; J.Therm.Anal.Calorim., 949-951 **(2005)**.

[19] S.J.Gill, M.L.Seibold; Rev.Sci.Inst., **47**, 1399-1406 **(1976)**.

[20] Setaram; Calure, France, Application notes M117-v1 and M256-v1.

[21] S.Sunner, I.Wadso; Acta Chem.Scand, **13**, 97-105 **(1959)**.

[22] D.Hallen, S-O.Nilsson, I.Wadso, J.Chem. Thermodyn, **21**, 529-1630 **(1989)**.

[23] J.C.Moreno-Piraján, L.Giraldo-Gutierrez, A.Gomez-Ordonez; Thermochim.Acta, **290**, 1-12 **(1997)**.

[24] J.J.Christensen,L.G.Kimbal, R.M.Izatt; Thermo chim.Acta, **5**, 293-301 **(1973)**.

[25] I.J.Oleagordia, R.Urrtabizacaya, P.Rodríguez; http://www.euitt.upm.es/taee06/papers/S7/p64.pdf, **(2008)**.