

Characteristic performances of a Thermometric (LKB) multichannel microcalorimeter and its use for determination of heats of mixing of concentrated electrolytes

Mirjana M. Marković and Slobodan K. Milonjić

Chemical Dynamics Laboratory, The Boris Kidrič Institute of Nuclear Sciences, P.O. Box 522, 11001 Belgrade (Yugoslavia)

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Abstract

Characteristic parameters, such as base-line noise, base-line stability over eight hours and time constant, of a multichannel microcalorimetry system (Thermal Activity Monitor, Thermometric (LKB), model 2277) have been determined for different measuring cylinder types and standard reaction vessels at a water thermostat temperature of 298.15 K. The standard thermochemical test-reaction of protonation of tris(hydroxymethyl)aminomethane (TRIS) solution (0.20 M) by HCl (0.04 M) at 298.15 K was performed in a flow-mix measuring cell. The enthalpy of TRIS protonation was calculated to be $\Delta H_p = -(47.97 \pm 0.74)$ kJ mol⁻¹. Application of the flow-mix measuring cell for determination of the heats of mixing of concentrated electrolytes was demonstrated using isomolal NaCl and KCl aqueous solutions in the molality range 0.1–4.0 *m*.

INTRODUCTION

The Thermometric (LKB) thermal activity monitor (TAM), model 2277, is a multichannel microcalorimetry system designed to monitor a wide range of chemical and biological reactions. Thermal events producing fractions of a microwatt can be observed using this instrument. This means that temperature differences of less than 10⁻⁶ °C can be detected [1,2].

The TAM works on the heat flow or heat leakage principle, where the heat generated in a thermally defined vessel flows away in an effort to establish a thermal equilibrium with its surroundings. The thermal stability of the system is achieved by a 25 liter water thermostat which surrounds the reaction measuring vessels and acts as an infinite heat sink. Reactions can be studied within the range 278–353 K, the working temperature range of the thermostat.

Samples are introduced into measuring cylinders which are housed in the water thermostat and kept there at a constant temperature to within $\pm 2 \cdot 10^{-4}$ °C. Each cylinder, together with its individual signal amplifier, forms a complete measuring channel. Up to four measuring channels can operate at the same time in the monitor.

Different standard reaction vessels are available, also including a perfusion cell. The perfusion cell can operate in two alternative modes (perfusion or titration) [3]. In the perfusion mode a liquid can be continuously perfused through the cell, while in the titration mode the sample, liquid or solid, is loaded into an ampoule where it can be titrated through a steel tube. A variety of stirrer configurations allows liquids and suspensions to be mixed continuously or intermittently during the experiment.

Heat energy from an active sample in the reaction vessel is channelled through extremely sensitive thermopile blankets, Peltier elements, before escaping to the heat sink. Peltier elements are bimetal devices made of semiconductor materials, and these highly sensitive detectors convert the thermal energy produced by the sample into a voltage signal proportional to the heat flow. The output signal from the thermal event in the measuring cylinder is led directly to the appropriate channel amplifier and the amplified signal can be monitored on a digital voltmeter or recorder. The results are quantified by electrical calibration where known power values pass through built-in precision resistors.

In order to test the new instrument, characteristic system parameters, such as base-line noise, base-line stability over eight hours and time constant, were determined for all the built-in measuring cylinders and for different standard reaction vessels. The system functioning reliability was confirmed by comparing the obtained values with those given in the Technical Specifications.

Protonation of tris(hydroxymethyl)aminomethane (TRIS) solution by HCl solution at 298.15 K was performed as a standard thermochemical test reaction using the flow-mix measuring technique. This technique of mixing two solutions in a specially designed measuring cup inside the flow-mix measuring cylinder is quite different from the well known, frequently used, titration technique.

The measurement of heats of mixing of electrolyte solutions (ΔH_m) is an excellent way to study the interactions of ions in aqueous solution [4]. In comparison with other thermodynamic functions, the heat of mixing is the most sensitive parameter describing the mixing process of electrolyte solutions. Because the common-ion electrolyte heats of mixing are quite small (in the range 0–300 J per kilogram of solvent), a high-precision microcalorimeter must be used for their determination. The heats of mixing of isomolal aqueous NaCl and KCl solutions were measured in the 0.1–4.0 *m* (molality) region by the flow-mix cell and the data obtained were compared with the literature values.

EXPERIMENTAL

Two combination measuring cylinders (Thermometric (LKB), model 2277-202) were installed in channels 1 and 2. A cylinder accepts two 5 ml stainless steel ampoules or two disposable 2.5 ml glass ampoules, as well as the perfusion cell. It also incorporates gold tubing for flow-through measurements.

An ampoule measuring cylinder, Thermometric (LKB), model 2277-201, mounted in channel 3, accepts 5 ml stainless steel ampoules and 2.5 ml glass ampoules. Because of its stability, it is recommended that this cylinder is used with the perfusion cell accessory.

Channel 4 is equipped with a combination measuring cylinder, Thermometric (LKB), model 2277-204, which accommodates stainless steel and glass ampoules, as well as the perfusion cell. It also incorporates a gold flow-through tube and a gold flow-mix cell in which two different liquids can be mixed.

All experiments were performed at 298.15 K, the water thermostat working temperature.

The temperature of an external thermostatic circulator (LKB BROMMA, model 2219) was maintained at 295.6 K, thus providing a constant cooling effect.

As recommended [1], the calorimeter was installed in a room where the ambient temperature was kept constant within 295–300 K using an electric calorifer with a thermostat.

The flow-through and flow-mix experiments were performed by a pair of LKB BROMMA, model 2132, microperspex peristaltic pumps. The water used to fill the tubes was doubly distilled and freshly boiled. The output signals were recorded by an LKB BROMMA 2210 2-channel recorder.

The TRIS used (Aldrich) was of 99.9% reagent grade. It was oven-dried for 24 h at 383 K and stored in a desiccator over calcium chloride. The TRIS solution (0.20 mol dm^{-3}), as well as the HCl solution ($0.0409 \text{ mol dm}^{-3}$), were prepared with freshly boiled, doubly distilled water.

The reagent grade NaCl and KCl salts were also thermally pre-treated at 383 K for 24 hours and 4 *m* stock solutions were prepared with freshly boiled, doubly distilled water. All the other solutions in the 0.1–3.0 *m* range were made by diluting the stock solutions.

Protonation of TRIS by HCl was performed in channel 4 using the flow-mix measuring cell. Solutions were introduced by peristaltic pumps, previously calibrated with the same solutions, at flow rates of 5 ml h^{-1} . The amplifier range was $3000 \mu\text{W}$. Nine experimental runs were performed, so that the uncertainty interval was calculated as twice the standard deviation of the mean value [5].

Mixing of NaCl and KCl solutions took place in the flow-mix cell with flow rates of $10 + 10 \text{ ml h}^{-1}$. For each isomolal salt solution pair, five experimental runs were performed and the mean value was calculated.

To prevent air bubbles from entering the flow-mix cell, a bubble trap [3] was used between the pump and the cell.

RESULTS AND DISCUSSION

Results of the base-line stability examinations for different experimental conditions are presented in Tables 1–3. The numbers in parentheses (Table 1) are the values given in the instrument technical specifications. The stability parameters for channel 1 (Table 2) are omitted because both channel 1 and channel 2 are equipped with the same measuring cylinder type (2277–202). The stability parameters obtained (Table 1) are in good agreement with the manufacturer's values, showing that the whole system functions properly. Somewhat higher values obtained for the base-line stability over eight hours are the consequence of an electrical circuit voltage instability.

Comparing the results from Tables 1 and 2, one can conclude that the system is more stable when the flow tubes are filled with distilled water.

TABLE 1

Stability parameters for various measuring cylinders when the flow tubes are not filled with distilled water; numbers in parentheses are values given by the manufacturer; amplifier range: 10 μW

	Measur. cyl. 2277–202 (channel 1)		Measur. cyl. 2277–202 (channel 2)		Measur. cyl. 2277–201 (channel 3)		Measur. cyl. 2277–204 (channel 4)	
	a ^a	b ^b	a ^a	b ^b	a ^a	b ^b	a ^a	b ^b
Empty	± 0.2 (± 0.2)	± 0.4 (± 0.2)	± 0.2 (± 0.2)	± 0.4 (± 0.2)	± 0.05 (± 0.2)	± 0.1 (± 0.2)	± 0.25 (± 0.3)	± 0.4 (± 0.5)
With empty glass ampoules	± 0.2	± 0.3	± 0.2	± 0.4	± 0.1	± 0.1	± 0.3	± 0.3
With glass ampoules filled with 1 ml H ₂ O	± 0.2	± 0.3	± 0.2	± 0.3	± 0.1	± 0.1	± 0.2	± 0.3
With glass ampoules filled with 2 ml H ₂ O	± 0.2	± 0.3	± 0.2	± 0.3	± 0.06	± 0.1	± 0.2	± 0.4
With glass ampoules filled with 3 ml H ₂ O	± 0.2	± 0.25	± 0.15	± 0.2	± 0.05	± 0.1	± 0.25	± 0.45

^a Base-line noise less than (μW).

^b Base-line stability over eight hours (μW).

TABLE 2

Stability parameters for measuring cylinders 2277-202 and 2277-204 when the flow tubes are filled with distilled water and left to thermostat over a weekend. Amplifier range, 10 μW

	Measur. cyl. 2277-202 (channel 1)		Measur. cyl. 2277-204 (channel 4)	
	a ^a	b ^b	a ^a	b ^b
Empty	± 0.1	± 0.2	± 0.8	± 0.1
With empty glass ampoules	± 0.06	± 0.2	± 0.06	± 0.1
With glass ampoules filled with 1 ml H ₂ O	± 0.08	± 0.2	± 0.8	± 0.2
With glass ampoules filled with 2 ml H ₂ O	± 0.06	± 0.2	± 0.05	± 0.2
With glass ampoules filled with 3 ml H ₂ O	± 0.01	± 0.1	± 0.09	± 0.2

^a Base-line noise less than (μW).

^b Base-line stability over 8 h (μW).

Base-line stability inspection in the case of different distilled water flow rates through the flow tubes of the measuring cylinder 2277-202 (channel 1, Table 3) indicates that the base line remains stable up to 20 ml h⁻¹. For the higher flow rates, one can notice a considerable drift from the base line obtained at zero flow rate.

The time constant values, τ (s), the time to reach 63% of the full-scale deflection from the beginning of electrical calibration when the uncorrected signal is used [6,7], for different experimental conditions, are presented in Tables 4-6. The results obtained are in fair agreement with the manufacturer's values in parentheses, except for measuring cylinder 2277-204 (channel 4) with the flow-mix cell (Table 4). This deviation can be

TABLE 3

Base-line stability for empty measuring cylinder 2277-202 (channel 1) and for different distilled water flow rates F (ml h⁻¹) through the flow-through tube. Amplifier range, 10 μW

F (ml h ⁻¹)	Deviation from the baseline at $F = 0$ ml h ⁻¹ (μW)
5	0.3
10	0.4
15	0.4
20	0.5
30	3.1
40	5.7

TABLE 4

Time constant τ (s) values for various measuring cylinders and glass ampoules (flow-through tubes are filled with distilled water)

	τ (s)		
	Measur. cyl. 2277-202 (channel 2)	Measur. cyl. 2277-201 (channel 3)	Measur. cyl. 2277-204 (channel 4)
Empty	123 (110-130)	86 (80-100)	114 (90-100)
With empty glass ampoules	146	120	138
With glass ampoules filled with 1.0119 g H ₂ O	181	156	160
With glass ampoules filled with 2.0147 g H ₂ O	209	196	189
With glass ampoules filled with 3.0086 g H ₂ O	228	217	198

Numbers in parentheses are values given by the manufacturer: electrical calibration range, 30 μ W; amplifier range, 100 μ W.

TABLE 5

Time constant, τ (s), values for measuring cylinder 2277-202 (channel 2) and stainless steel ampoules (flow-through tubes are filled with distilled water)

Measuring cylinder with	τ (s)
Empty s.s. ampoules	201
S.s. ampoules filled with 0.9993 g H ₂ O	224
S.s. ampoules filled with 1.9986 g H ₂ O	256
S.s. ampoules filled with 3.0092 g H ₂ O	300
S.s. ampoules filled with 3.9987 g H ₂ O	314

Time constant for cylinder 2277-202 and water-filled stainless steel ampoule given by the manufacturer is approx. 390 s; electrical calibration range 30 μ W; amplifier range, 100 μ W.

TABLE 6

Time constant τ (s) values for measuring cylinder 2277-201 (channel 3)

m_w (g)	τ (s)
0.9897	278
2.0021	279
3.0169	319
3.9596	321

Side A, perfusion cell with 3.5 ml stainless steel ampoule and water flow rate of 20 ml h⁻¹ through the cell; side B, static reference 5 ml stainless steel ampoule with different amounts of distilled water m_w (g): electrical calibration range, 100 μ W; amplifier range, 300 μ W.

explained by the fact that the time constant values in parentheses represent flow rates of $20 + 20 \text{ ml h}^{-1}$ through the flow-mix cell, while the results from Table 4 are obtained at zero flow rates.

The value of the time constant for the perfusion cell with 3.5 ml stainless steel ampoule was determined from a rectilinear function, $\tau = f(m_w)$ (Table 6), treated by the least-squares method. The value obtained, 316 s, is within the perfusion cell time constant range given by the manufacturer (140–330 s).

The time constant value for the stainless steel ampoule filled with distilled water (4.3871 g H_2O) was also obtained by the least-squares method (Table 5); it is 331 s (manufacturer's value, approx. 390 s).

Tris(hydroxymethyl)aminomethane (TRIS) is a solid, water-soluble organic base of considerable interest both as an acidimetric standard [8] and as a biological buffer [9]; its relatively non-toxic character even permits its use *in vivo* [10]. The reaction of TRIS with hydrochloric acid is widely used as a convenient, moderately exothermic, standard test-reaction in both solution and titration calorimetry. The principal purpose of such a standard reaction comparison is to eliminate the systematic errors sometimes associated with new equipment or with alterations made to existing apparatus [11].

The enthalpy values for the TRIS protonation at 298.15 K for nine experimental runs are presented in Table 7; the calculated mean value is $\Delta H_p = -48.39 \pm 0.74 \text{ kJ mol}^{-1}$. The enthalpy of dilution of the TRIS solution was taken to be 0.42 kJ mol^{-1} [2], so that the corrected enthalpy value is $\Delta H_p = -47.97 \pm 0.74 \text{ kJ mol}^{-1}$. For the HCl solution, the enthalpy of dilution can be neglected [2]. The TRIS protonation enthalpy value, obtained using the flow-mix measuring cell, is in satisfactory agreement with the literature ΔH_p values (-47.40 [9], -47.48 [12] and $-47.44 \text{ kJ mol}^{-1}$ [13]) measured using a calorimeter specially designed for the titration technique. The enthalpy of TRIS protonation, determined at 310 K

TABLE 7

Enthalpy change $-\Delta H_p$ (kJ mol^{-1}) values for the protonation of TRIS solution (0.20 M) by HCl (0.04 M): amplifier range, 3000 μW

Run No.	$-\Delta H_p$ (kJ mol^{-1})
1	47.80
2	48.26
3	48.21
4	48.08
5	48.21
6	48.59
7	48.66
8	48.70
9	48.99

TABLE 8

Heats of mixing (ΔH_m) of NaCl and KCl solutions for different salt molalities m at 298 K

$m_{\text{NaCl}} = m_{\text{KCl}}$	$-\Delta H_m$ (J (kg H ₂ O) ⁻¹)	$-\Delta H_m$ (J mol ⁻¹)
0.1	0.36 ± 0.01 (0.42 [4])	3.54 ± 0.09
0.2	1.27 ± 0.03 (1.67 [4])	6.36 ± 0.11
0.5	8.00 ± 0.17 (9.67 [4])	16.05 ± 0.32 (20.63 [4])
1.0	31.49 ± 0.84 (40.08 [4])	31.74 ± 0.82 (40.08 [16]; 40.25 [14])
2.0	122.9 ± 2.0	61.94 ± 1.30 (74.06 [14])
3.0	283.9 ± 3.6	95.30 ± 1.14 (105.0 [14])
4.0	525.9 ± 6.2	131.4 ± 0.4

Values in parentheses are the literature data

using the same calorimeter type and identical flow-mix cell as in our experiment [2], was calculated to be $\Delta H_p = -46.67 \pm 0.10$ kJ mol⁻¹. Disregarding the temperature difference, we can conclude that this value and our result are compatible.

Because the system functioning reliability is confirmed by the standard TRIS + HCl reaction, there is no need to standardize the instrument again before each measurement. Results can be quantified by electrical calibration before and after each measurement; therefore, we can conclude that, using the calorimeter, the heats of reaction in solutions can be determined with a high precision.

The heats of mixing ($-\Delta H_m$) of isomolal KCl and NaCl solutions are summarized in Table 8. The uncertainty interval was calculated as twice the standard deviation of the mean value. In order to compare our results with the literature values [4,14–16], the heats of mixing are given both for the total number of NaCl and KCl moles present in the flow-mix cell during the mixing process, and for one kilogram of water as solvent (the second and the third column in Table 8). The algebraic sign of the ΔH_m value reflects the cation hydration character during the mixing process. For systems with ions that influence the water structure in the same way (the Li⁺–Na⁺ ion pair), ΔH_m is positive and the mixing process is endothermic; in contrast, in systems of ions with opposite influences on water structure (the Li⁺–K⁺ and Na⁺–K⁺ ion pairs), ΔH_m is negative and the mixing process is exothermic. Experimentally obtained negative ΔH_m values for the system NaCl–KCl (Table 8) confirm this classification, which is in agreement with the literature data [4,14–16]. The results presented in Table 8 show an approximately linear change of ΔH_m with molality m (at

the solute mole fraction $x = 0.5$) for the whole molality range, which agrees very well the results of other authors [4,14]. Although the ionic strength (I) of the solution was not kept constant (all experiments were performed at solute mole fraction $x = 0.5$) and the mixing process was performed in the flow-mix cell using a different procedure, not the one reported in the literature, we can say that the agreement between our data and those in the literature is satisfactory.

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