

## **NEW PHYSICO-CHEMICAL PROPERTIES OF WATER INDUCED BY MECHANICAL TREATMENTS A calorimetric study at 25°C**

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### **Abstract**

An extensive thermodynamic study has been carried out on aqueous solutions, obtained through the iteration of two processes: a dilution 1:100 in mass and a succussion. The iteration is repeated until extreme dilutions are reached (less than  $1 \cdot 10^{-5}$  mol kg<sup>-1</sup>) to the point that we may call the resulting solution an ‘extremely diluted solution’. We conducted a calorimetric study, at 25°C, of the interaction of those solutions with acids or bases. Namely, we measured the heats of mixing of acid or basic solutions with bidistilled water and compared them with the analogous heats of mixing obtained using the ‘extremely diluted solutions’. Despite the extreme dilution of the latter solutions, we found a relevant exothermic excess heat of mixing, excess with respects to the corresponding heat of mixing with the untreated solvent. Such an excess has been found in about the totality of measurements, and of a magnitude being well beyond one that could arise any issue of sensibility of the instrumental apparatus. Here we thus show that successive dilutions and succussions can permanently alter the physico-chemical properties of the solvent water. The nature of the phenomena here described still remains unexplained, nevertheless some significant experimental results were obtained.

**Keywords:** aqueous solution, calorimetry, extremely diluted solutions, mechanical treatments

### **Introduction**

We can notice a great, increasing interest towards the therapeutic effects of the remedies used by the homeopathic medicine, and that induced us to begin a physico-chemical study on the very object of this alternative medicine, namely the ‘extremely diluted solutions’. Those solutions have the same composition of the solvent used, thus it is very difficult to understand how they can work as remedies.

Such ‘extremely diluted solutions’ are usually prepared through the technique proposed by Hahnemann [1], which essentially implies the iteration of two processes: dilution and succussion. The iteration of these two processes yields the ‘extremely diluted solutions’ used by the homeopathic medicine. Each dilution step is called ‘centesimal hannemian’, CH in short: a 1 CH solution underwent one 1:100 dilution

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and succussion, a 2 CH solution underwent two steps of 1:100 dilution and succussion, and so forth. The dilution of these solutions is an extreme one, such that they can be considered, from the chemical point of view, as pure water. Thus, their physico-chemical properties should not differ from those of the solvent: pure, untreated water. On the other hand, Davenas *et al.* [2] claimed that the property of releasing histamine, due to degranulation of human basophils interacting with antibodies of the immunoglobulin E (IgE), is kept by the anti-IgE extremely diluted solutions, that are obtained with the same procedure that we just described.

In the present paper we studied calorimetrically, at 25°C, ‘extremely diluted solutions’ of sodium chloride (NaCl 3 CH and 30 CH, remember the CH number is a dilution measure) and samples of ‘treated waters’ (H<sub>2</sub>O 1 CH, 3 CH and 30 CH). This paper accounts for the systematic study of the heats of mixing of acids or bases – aqueous solutions of NaOH or HCl 0.01 mol kg<sup>-1</sup> – with the ‘extremely diluted solutions’ or with the ‘treated waters’. We also investigated the interaction of those ‘extremely diluted solutions’ or ‘treated waters’ with solutions of various solutes (ethanol, lactose, glucose, urea, sodium, potassium or lithium chlorides), used as reagents at a finite concentration (0.01 mol kg<sup>-1</sup>). It’s known that procedures, for the calorimetric determination of the heat of dilution or mixing, are well developed [3]. The experimental results are normally treated according to the MacMillan–Mayer approach [4], modified by Friedman and Krishnan [5].

It’s worth noting, instead, that no work of this kind, concerning the study of the physico-chemical properties of this ‘anomalous solutions’, with significative results, are known in current literature. Our present contribution aims at proving that the structure of the solvent could be permanently altered by the procedure used in preparing the solutions.

## Experimental

### Materials

The solutes were Carlo Erba or Sigma products: they were of the highest purity commercially available. The solutions of the various solutes (NaOH, HCl, ethanol, lactose, glucose urea, sodium, potassium or lithium chlorides), were prepared by mass using doubly distilled water. NaOH solutions were protected from the contact with atmospheric carbon dioxide by means of suitable traps.

The ‘extremely diluted solutions’ or ‘treated waters’ were supplied by Sifra O. (Florence, Italy): they were prepared using doubly distilled water, from Carlo Erba, only. The way that such ‘extremely diluted solutions’ are obtained is the following: the starting point is a 1% in mass solution; to prepare, for example, the sodium chloride solutions (NaCl 3 CH and 30 CH), 1 g of NaCl is added to 99 g of water. After a mechanical treatment, simple succussion, the solution that is obtained is called ‘1 centesimal hahnemannian’, or 1 CH in short, and the name of the solution starts with the name or formula of the solute. So in the preceding example, NaCl 1 CH is obtained. The process of succussion consists in a violent shaking of the solution by

means of a mechanical apparatus, while the solution are kept in vessels of dark glass or polypropylene. In order to prepare the 2 centesimal hahnemannian (NaCl 2 CH), 1 g of the 1 CH solution, that we just talked about, is added to 99 g of water and the resulting solution is succussed. This two processes, dilution 1:100 and succussion, are iterated many times. In a wholly similar way, the 'treated waters' (H<sub>2</sub>O 1 CH, 3 CH and 30 CH) are prepared following this procedure:

- 1 H<sub>2</sub>O 1 CH: 100 g of bidistilled water are succussed
- 2 H<sub>2</sub>O 2 CH: 1 g of H<sub>2</sub>O 1 CH is added to 99 g of bidistilled water and succussed
- 3 H<sub>2</sub>O 3 CH: like step 2 but using H<sub>2</sub>O 2 CH.

The iteration of this process yields the solution H<sub>2</sub>O 30 CH.

One of the apparatuses used in the succussion step is a: DYNA HV 1 from 'debofar' N.V.S.A. Belgium. In a single succussion process 100 vertical strokes in six s are given to the vessels containing the solutions or bidistilled water. After preparation, the 'extremely diluted solutions' and the 'treated waters' were stored in a thermostated room at 25±2°C.

The samples were tested at different ages, varying from several days to several weeks. During this long time the equilibrium with dissolved gases was certainly reached, for both samples and blank water. We can in fact note that such a procedure allows us to experimentally subtract the contribution coming from impurities or dissolved gases.

### *Calorimetry*

The heats of mixing were monitored using a Thermal Activity Monitor (TAM) from Thermometric (Sweden), equipped with a flow-mixing vessel. Two peristaltic pumps envoy the solutions into the calorimeter through Teflon tubes. The flow rates of the liquids are the same, and are constant in the inlet tubes, so that the solution coming out of the calorimeter has a concentration half the initial one. The mass flow-rate, constant within 1%, amounts to 3·10<sup>-3</sup> g s<sup>-1</sup>: it was the same for all the experiments. The heats of mixing,  $Q_{\text{mix}}$ , were obtained using the following formula:

$$Q_{\text{mix}}(m_x^i, m_y^i \rightarrow m_x^f, m_y^f) = (dQ/dt) / P_w \quad (1)$$

where (dQ/dt) is the heat-flux (Watt),  $P_w$  is the total mass flow-rate of the solvent (kg s<sup>-1</sup>) and  $m_x^i, m_y^i$  and  $m_x^f, m_y^f$  are the initial and final molalities, respectively, of the solutes before and after the mixing procedure.  $Q_{\text{mix}}$  is expressed in J (kg of solvent in the final solution)<sup>-1</sup>.

### *Treatment of the data*

The heats of mixing of two binary solutions, due to the contribution of the heats of dilution of the two solutes, x and y, and to the interaction of the two solutes, can be expressed as follows:

$$Q_{\text{mix}} = h_{xx} m_x^f (m_x^f - m_x^i) + 2h_{xy} m_x^f m_y^f + h_{yy} m_y^f (m_y^f - m_y^i) + \text{higher terms}$$

where  $Q_{\text{mix}}$ , J (kg of solvent in the final solution)<sup>-1</sup>, is the heat of mixing,  $m_x^f$ ,  $m_y^f$ ,  $m_x^i$ ,  $m_y^i$  are the molalities (mol kg<sup>-1</sup>) after and before the mixing process, respectively, and  $h_{xx}$ ,  $h_{yy}$  and  $h_{xy}$ , the enthalpic interaction coefficients, are adjustable parameters. Their values fall in the range  $1 \cdot 10^2$ – $1 \cdot 10^4$  J kg mol<sup>-2</sup>. Consequently, when the concentration of solute y of an ‘extremely diluted solution’ is less than  $1 \cdot 10^{-5}$  mol kg<sup>-1</sup>, while the concentration of solute x is  $1 \cdot 10^{-2}$  mol kg<sup>-1</sup>, the sole contribution in the previous equation is that due to x, namely the heat of dilution of the solute x. It takes about three successive 1:100 dilution of the y solution (3 CH) to reach a point where the y solute cannot produce any significant contribution to the heat of mixing.

## Results

We conducted a preliminary study with test solutions 0.01 mol kg<sup>-1</sup>, containing different x solutes (ethanol, lactose, glucose, urea, sodium, potassium or lithium chlorides, sodium hydroxide, and hydrochloric acid). This study put in evidence that only in the latter two cases (sodium hydroxide, and hydrochloric acid) it was possible to detect a heat, when mixing with the ‘extremely diluted solutions’, larger than that obtained when mixing the same test solution with bidistilled, untreated water. In other words, the interaction of the ‘extremely diluted solutions’, or the ‘treated waters’, with reactants other than acids or bases does not exhibit a thermal excess.

For this reason we decided to measure the heats of mixing using the ‘extremely diluted solutions’, or the ‘treated waters’, and acid or basic solutions. In about the totality of the cases we found an excess exothermic heat of mixing, in comparison with the heat of mixing that is obtained mixing the same reagents with the bidistilled, untreated water. By excess heat of mixing, we simply mean the difference between the former and the latter experimental values: the heat of mixing – J (kg of water in the final solution)<sup>-1</sup> – of the reagent with the extremely diluted solutions, minus the heat of mixing – J (kg of water in the final solution)<sup>-1</sup> – of the same reagent mixed with untreated, bidistilled water. The solvent used for the blank experiments, bidistilled untreated water, was stored in the same type of vessels (dark glass) that the ‘extremely diluted solutions’ or the ‘treated waters’ were stored in, and for the same time. The blank tests were performed immediately before any measurement with the ‘extremely diluted solutions’ or ‘treated waters’. It’s worth noting that the heats in excess obtained using HCl solutions were systematically lower than those concerning NaOH solutions. It must as well be stressed that the excess heats of mixing are of the same order of magnitude or higher than the heats of dilution of the 0.01 m acid or basic solutions used. We sought the concentration of the test solute (x) most suitable to unequivocally put in evidence the existence of the heat in excess in the described experimental conditions. To that purpose we performed the mixing experiments that are reported in Table 1.

**Table 1** Excess heats of mixing of H<sub>2</sub>O 3 CH<sup>a</sup> with HCl and NaOH aqueous solutions as reagent

| Reagent solutions | $m^b/\text{mol kg}^{-1}$ | $-Q^c/\text{J kg}^{-1}$ |
|-------------------|--------------------------|-------------------------|
| HCl               | $1 \cdot 10^{-2}^d$      | $0.82 \pm 0.01^e$       |
|                   | $1 \cdot 10^{-3}^d$      | $0.82 \pm 0.01^e$       |
|                   | $1 \cdot 10^{-4}^d$      | $0.32 \pm 0.01^e$       |
|                   | $1 \cdot 10^{-5}^d$      | $0 \pm 0.01^e$          |
| NaOH              | $5 \cdot 10^{-2}^d$      | $2.9 \pm 0.1^f$         |
|                   | $1 \cdot 10^{-2}^d$      | $3.0 \pm 0.1^f$         |
|                   | $1 \cdot 10^{-3}^d$      | $1.8 \pm 0.1^f$         |
|                   | $5 \cdot 10^{-4}^d$      | $0.6 \pm 0.1^f$         |
|                   | $2 \cdot 10^{-4}^d$      | $0.5 \pm 0.1^f$         |
|                   | $1 \cdot 10^{-5}^d$      | $0.3 \pm 0.1^f$         |

<sup>a</sup>The treated waters H<sub>2</sub>O 3 CH are of two different lots: F1022UL and F1120UL.

<sup>b</sup>Initial concentration of the reagent solution. The concentration of the final solution is half the initial one.

<sup>c</sup>Excess heat of mixing J (kg of water in the final solution)<sup>-1</sup>: difference between the heat of mixing of the reagent solutions with the 'treated water' H<sub>2</sub>O 3 CH and the heat of mixing with untreated bidistilled water (blank experiment).

<sup>d</sup>These solutions were prepared diluting the most concentrated one.

<sup>e</sup>The reported error is the standard deviation calculated using 30 experimental heats of mixing of HCl solutions 0.01 mol kg<sup>-1</sup> with bidistilled water used as blank experiment. The heat of mixing is:  $0.85 \pm 0.01$  J (kg of water in the final solution)<sup>-1</sup>.

<sup>f</sup>The reported error is the standard deviation calculated using 30 experimental heats of mixing of NaOH solutions 0.01 mol kg<sup>-1</sup> with bidistilled water used as blank experiment. The heat of mixing is:  $2.1 \pm 0.1$  J (kg of water in the final solution)<sup>-1</sup>.

The excess heat detected turns out to be a constant value for a given concentration of the x solute. Therefore, to obtain the largest thermal effect in both cases, the most suitable concentration of NaOH or HCl is 0.01 mol kg<sup>-1</sup>.

In Tables 2–3 we report the experimental excess heats of mixing of the 'extremely diluted solutions' or the 'treated waters' studied with NaOH and HCl 0.01 mol kg<sup>-1</sup>.

**Table 2** Excess heats of mixing of NaOH 0.01 m with 'treated waters' (H<sub>2</sub>O 1 CH, 3 CH and 30 CH) or with 'extremely diluted solutions' (NaCl 3 CH and 30 CH)

| Bidistilled untreated water | $-Q_{\text{mix}}/\text{J kg}^{-1}$ |                           |         |
|-----------------------------|------------------------------------|---------------------------|---------|
|                             | $2.1 \pm 0.1^a$                    |                           |         |
| H <sub>2</sub> O 1 CH Lot   | $-Q^b$                             | H <sub>2</sub> O 1 CH Lot | $-Q^b$  |
| G0212UL M                   | $1.1^c$                            | G0212UL M                 | $1.3^c$ |
| G0212UL M                   | $0.9^c$                            | G0212UL M                 | $1.1^c$ |
| G0212UL M                   | $0.8^c$                            | G0127UL A                 | $0.6^c$ |
| G0212UL M                   | $0.8^c$                            | G0306UL M                 | $0.7^c$ |
| G0212UL M                   | $0.9^c$                            |                           |         |

**Table 2** Continued

| Bidistilled untreated water |                   | $-Q_{\text{mix}}/\text{J kg}^{-1}$ |                  |
|-----------------------------|-------------------|------------------------------------|------------------|
|                             |                   | 2.1±0.1 <sup>a</sup>               |                  |
| H <sub>2</sub> O 3 CH Lot   | $-Q^b$            | H <sub>2</sub> O 3 CH Lot          | $-Q^b$           |
| F1022UL M                   | 0.5 <sup>c</sup>  | F1202UL A                          | 1.6 <sup>c</sup> |
| F1022UL M                   | 1.7 <sup>c</sup>  | F1209UL A                          | 1.0 <sup>c</sup> |
| F1022UL A                   | 0.8 <sup>c</sup>  | F1217UL M                          | 1.4 <sup>c</sup> |
| F1022UL A                   | 8.5 <sup>c</sup>  | F1217UL M                          | 1.1 <sup>c</sup> |
| F1120UL M                   | 0.9 <sup>c</sup>  | F1217UL M                          | 0.7 <sup>c</sup> |
| F1120UL M                   | 2.9 <sup>c</sup>  | F1217UL M                          | 0.5 <sup>c</sup> |
| F1120UL M                   | 5.0 <sup>c</sup>  | G0127UL A                          | 0.3 <sup>c</sup> |
| F1120UL A                   | 1.8 <sup>c</sup>  | G0127UL A                          | 0.2 <sup>c</sup> |
| F1125UL M                   | 2.2 <sup>c</sup>  | G0127UL A                          | 0.6 <sup>c</sup> |
| F1125UL M                   | 7.9 <sup>c</sup>  | G0212UL M                          | 0.8 <sup>c</sup> |
| F1125UL M                   | 19.0 <sup>c</sup> | G0212UL M                          | 1.1 <sup>c</sup> |
| F1125UL M                   | 0.7 <sup>c</sup>  | G0212UL M                          | 0.8 <sup>c</sup> |
| F1125UL M                   | 0.5 <sup>c</sup>  | G0212UL M                          | 1.1 <sup>c</sup> |
| F1125UL A                   | 2.8 <sup>c</sup>  | G0212UL M                          | 0.8 <sup>c</sup> |
| F1125UL A                   | 4.5 <sup>c</sup>  | G0212UL M                          | 1.3 <sup>c</sup> |
| F1202UL M                   | 1.3 <sup>c</sup>  | G0306UL M                          | 1.1 <sup>c</sup> |
| H <sub>2</sub> O 30 CH Lot  | $-Q^b$            | H <sub>2</sub> O 30 CH Lot         | $-Q^b$           |
| F1022UL M                   | 0.5 <sup>c</sup>  | F1125UL A                          | 4.3 <sup>c</sup> |
| F1022UL M                   | 1.4 <sup>c</sup>  | F1202UL M                          | 0.3 <sup>c</sup> |
| F1022UL A                   | 0.8 <sup>c</sup>  | F1202UL M                          | 0.4 <sup>c</sup> |
| F1022UL A                   | 7.9 <sup>c</sup>  | F1202UL A                          | 2.0 <sup>c</sup> |
| F1120UL M                   | 0.5 <sup>c</sup>  | F1209UL A                          | 0.9 <sup>c</sup> |
| F1120UL M                   | 0.6 <sup>c</sup>  | F1217UL M                          | 0.4 <sup>c</sup> |
| F1120UL A                   | 2.2 <sup>c</sup>  | F1217UL M                          | 0.8 <sup>c</sup> |
| F1125UL M                   | 1.0 <sup>c</sup>  | F1217UL M                          | 0.7 <sup>c</sup> |
| F1125UL M                   | 0.7 <sup>c</sup>  | F1217UL M                          | 0.5 <sup>c</sup> |
| F1125UL M                   | 0.9 <sup>c</sup>  | G0306UL M                          | 1.4 <sup>c</sup> |
| F1125UL A                   | 1.1 <sup>c</sup>  |                                    |                  |

**Table 2** Continued

| Bidistilled untreated water |                  | $-Q_{\text{mix}}/\text{J kg}^{-1}$ |                  |
|-----------------------------|------------------|------------------------------------|------------------|
|                             |                  | 2.1±0.1 <sup>a</sup>               |                  |
| NaCl 3 CH Lot               | $-Q^b$           | NaCl 3 CH Lot                      | $-Q^b$           |
| F1022UL M                   | 0.6 <sup>c</sup> | F1202UL M                          | 0.6 <sup>c</sup> |
| F1022UL M                   | 1.9 <sup>c</sup> | F1202UL M                          | 0.6 <sup>c</sup> |
| F1022UL A                   | 1.9 <sup>c</sup> | F1202UL A                          | 2.7 <sup>c</sup> |
| F1022UL A                   | 8.7 <sup>c</sup> | F1209UL A                          | 1.4 <sup>c</sup> |
| F1120UL M                   | 0.9 <sup>c</sup> | F1217UL M                          | 0.0 <sup>c</sup> |
| F1120UL A                   | 2.9 <sup>c</sup> | F1217UL M                          | 0.0 <sup>c</sup> |
| F1125UL M                   | 0.5 <sup>c</sup> | F1217UL M                          | 0.2 <sup>c</sup> |
| F1125UL M                   | 1.1 <sup>c</sup> | F1217UL M                          | 0.4 <sup>c</sup> |
| F1125UL M                   | 1.2 <sup>c</sup> | F1217UL M                          | 0.4 <sup>c</sup> |
| F1125UL M                   | 0.6 <sup>c</sup> | F1217UL M                          | 0.5 <sup>c</sup> |
| F1125UL A                   | 2.4 <sup>c</sup> | G0306UL M                          | 0.8 <sup>c</sup> |
| F1125UL A                   | 3.9 <sup>c</sup> |                                    |                  |
| NaCl 30 CH Lot              | $-Q^b$           | NaCl 30 CH Lot                     | $-Q^b$           |
| F1022UL M                   | 0.4 <sup>c</sup> | F1125UL A                          | 4.3 <sup>c</sup> |
| F1022UL M                   | 0.9 <sup>c</sup> | F1202UL M                          | 0.6 <sup>c</sup> |
| F1022UL A                   | 0.8 <sup>c</sup> | F1202UL M                          | 0.5 <sup>c</sup> |
| F1022UL A                   | 7.9 <sup>c</sup> | F1202UL A                          | 2.2 <sup>c</sup> |
| F1120UL M                   | 1.0 <sup>c</sup> | F1209UL A                          | 1.4 <sup>c</sup> |
| F1120UL A                   | 2.9 <sup>c</sup> | F1217UL M                          | 0.0 <sup>c</sup> |
| F1125UL M                   | 0.6 <sup>c</sup> | F1217UL M                          | 0.0 <sup>c</sup> |
| F1125UL M                   | 1.3 <sup>c</sup> | F1217UL M                          | 0.6 <sup>c</sup> |
| F1125UL M                   | 2.7 <sup>c</sup> | F1217UL M                          | 0.6 <sup>c</sup> |
| F1125UL M                   | 0.6 <sup>c</sup> | F1217UL M                          | 0.7 <sup>c</sup> |
| F1125UL A                   | 1.9 <sup>c</sup> | G0306UL M                          | 0.8 <sup>c</sup> |
| F1202UL M                   | 0.6 <sup>c</sup> |                                    |                  |

M=succussion in vessels of dark glass;

A=succussion in vessels of polypropylene, storage in vessels of dark glass.

<sup>a</sup>Standard deviation determined using 30 experimental heats of mixing of NaOH solutions 0.01 mol kg<sup>-1</sup> with bidistilled untreated water used as blank experiment. The concentration of NaOH in the final solution is half the initial one.

<sup>b</sup>Excess heats of mixing J (kg of water in the final solution)<sup>-1</sup>: difference between the heat of mixing of the NaOH reagent solution at 0.01 mol kg<sup>-1</sup> with the samples and the one with untreated bidistilled water.

<sup>c</sup>The standard deviation was not reported because the result is dependent on the age of the sample (see text)

**Table 3** Excess heats of mixing of HCl 0.01 m with 'treated waters' (H<sub>2</sub>O 1 CH, 3 CH and 30 CH) or with 'extremely diluted solutions' (NaCl 3 CH and 30 CH)

| Bidistilled untreated water |                   | $-Q_{\text{mix}}/\text{J kg}^{-1}$ |                   |
|-----------------------------|-------------------|------------------------------------|-------------------|
| $0.85 \pm 0.01^{\text{a}}$  |                   |                                    |                   |
| H <sub>2</sub> O 1 CH Lot   | $-Q^{\text{b}}$   | H <sub>2</sub> O 1 CH Lot          | $-Q^{\text{b}}$   |
| G0212UL M                   | 0.21 <sup>c</sup> | G0212UL M                          | 0.26 <sup>c</sup> |
| G0212UL M                   | 0.20 <sup>c</sup> | G0212UL M                          | 0.27 <sup>c</sup> |
| G0212UL M                   | 0.23 <sup>c</sup> | G0127UL A                          | 0.30 <sup>c</sup> |
| G0212UL M                   | 0.24 <sup>c</sup> | G0127UL A                          | 0.16 <sup>c</sup> |
| G0212UL M                   | 0.21 <sup>c</sup> | G0127UL A                          | 0.21 <sup>c</sup> |
| H <sub>2</sub> O 3 CH Lot   | $-Q^{\text{b}}$   | H <sub>2</sub> O 3 CH Lot          | $-Q^{\text{b}}$   |
| F1022UL M                   | 0.05 <sup>c</sup> | F1202UL M                          | 0.20 <sup>c</sup> |
| F1022UL M                   | 0.29 <sup>c</sup> | F1202UL M                          | 0.14 <sup>c</sup> |
| F1022UL A                   | 0.02 <sup>c</sup> | F1202UL A                          | 0.93 <sup>c</sup> |
| F1022UL A                   | 1.60 <sup>c</sup> | F1217UL M                          | 0.10 <sup>c</sup> |
| F1120UL M                   | 0.11 <sup>c</sup> | F1217UL M                          | 0.13 <sup>c</sup> |
| F1120UL A                   | 0.27 <sup>c</sup> | G0127UL A                          | 0.08 <sup>c</sup> |
| F1120UL M                   | 0.00 <sup>c</sup> | G0127UL A                          | 0.24 <sup>c</sup> |
| F1120UL A                   | 1.40 <sup>c</sup> | G0212UL M                          | 0.13 <sup>c</sup> |
| F1125UL M                   | 0.37 <sup>c</sup> | G0212UL M                          | 0.19 <sup>c</sup> |
| F1125UL M                   | 0.96 <sup>c</sup> | G0212UL M                          | 0.30 <sup>c</sup> |
| F1125UL M                   | 0.11 <sup>c</sup> | G0212UL M                          | 0.19 <sup>c</sup> |
| F1125UL M                   | 0.27 <sup>c</sup> | G0212UL M                          | 0.27 <sup>c</sup> |
| F1125UL M                   | 0.00 <sup>c</sup> | G0212UL M                          | 0.19 <sup>c</sup> |
| F1125UL A                   | 0.42 <sup>c</sup> | G0212UL M                          | 1.20 <sup>c</sup> |
| F1125UL A                   | 1.00 <sup>c</sup> |                                    |                   |
| H <sub>2</sub> O 30 CH Lot  | $-Q^{\text{b}}$   | H <sub>2</sub> O 30 CH Lot         | $-Q^{\text{b}}$   |
| F1022UL M                   | 0.13 <sup>c</sup> | F1125UL A                          | 0.24 <sup>c</sup> |
| F1022UL M                   | 0.22 <sup>c</sup> | F1202UL M                          | 0.02 <sup>c</sup> |
| F1022UL A                   | 0.18 <sup>c</sup> | F1202UL M                          | 0.13 <sup>c</sup> |
| F1022UL A                   | 1.20 <sup>c</sup> | F1202UL A                          | 0.32 <sup>c</sup> |
| F1120UL M                   | 0.08 <sup>c</sup> | F1217UL M                          | 0.14 <sup>c</sup> |
| F1120UL M                   | 0.00 <sup>c</sup> | F1217UL M                          | 0.14 <sup>c</sup> |
| F1120UL A                   | 2.90 <sup>c</sup> | G0127UL A                          | 0.40 <sup>c</sup> |
| F1125UL M                   | 0.10 <sup>c</sup> | G0127UL A                          | 0.08 <sup>c</sup> |
| F1125UL M                   | 0.08 <sup>c</sup> |                                    |                   |



**Table 3** Continued

| Bidistilled untreated water |                   | $-Q_{\text{mix}}/\text{J kg}^{-1}$ |                   |
|-----------------------------|-------------------|------------------------------------|-------------------|
|                             |                   | 0.85±0.01 <sup>a</sup>             |                   |
| NaCl 3 CH Lot               | $-Q^b$            | NaCl 3 CH Lot                      | $-Q^b$            |
| F1022UL M                   | 0.18 <sup>c</sup> | F1125UL M                          | 0.14 <sup>c</sup> |
| F1022UL M                   | 0.19 <sup>c</sup> | F1125UL M                          | 0.00 <sup>c</sup> |
| F1022UL A                   | 0.32 <sup>c</sup> | F1125UL A                          | 0.35 <sup>c</sup> |
| F1022UL A                   | 1.60 <sup>c</sup> | F1202UL M                          | 0.13 <sup>c</sup> |
| F1120UL M                   | 0.13 <sup>c</sup> | F1202UL M                          | 0.13 <sup>c</sup> |
| F1120UL M                   | 0.43 <sup>c</sup> | F1202UL A                          | 0.57 <sup>c</sup> |
| F1120UL A                   | 0.05 <sup>c</sup> | F1217UL M                          | 0.11 <sup>c</sup> |
| F1125UL M                   | 0.00 <sup>c</sup> | F1217UL M                          | 0.08 <sup>c</sup> |
| NaCl 30 CH Lot              | $-Q^b$            | NaCl 30 CH Lot                     | $-Q^b$            |
| F1022UL M                   | 0.14 <sup>c</sup> | F1125UL M                          | 0.00 <sup>c</sup> |
| F1022UL M                   | 0.26 <sup>c</sup> | F1125UL A                          | 0.21 <sup>c</sup> |
| F1022UL A                   | 0.19 <sup>c</sup> | F1202UL M                          | 0.08 <sup>c</sup> |
| F1022UL A                   | 1.30 <sup>c</sup> | F1202UL M                          | 0.13 <sup>c</sup> |
| F1120UL M                   | 0.08 <sup>c</sup> | F1202UL A                          | 0.38 <sup>c</sup> |
| F1120UL M                   | 0.00 <sup>c</sup> | F1217UL M                          | 0.13 <sup>c</sup> |
| F1120UL A                   | 0.29 <sup>c</sup> | F1217UL M                          | 0.11 <sup>c</sup> |
| F1125UL M                   | 0.08 <sup>c</sup> | G0127UL A                          | 0.40 <sup>c</sup> |
| F1125UL M                   | 0.10 <sup>c</sup> |                                    |                   |

M=succussion in vessels of dark glass;

A=succussion in vessels of polypropylene, storage in vessels of dark glass.

<sup>a</sup>Standard deviation determined using 30 experimental heats of mixing of HCl solutions 0.01 mol kg<sup>-1</sup> with untreated bidistilled water used as blank experiment. The concentration of HCl in the final solution is half the initial one.

<sup>b</sup>Excess heats of mixing J (kg of water in the final solution)<sup>-1</sup>: difference between the heat of mixing of the HCl reagent solution at 0.01 mol kg<sup>-1</sup> with the samples and the one with untreated bidistilled water.

<sup>c</sup>The standard deviation was not reported because the result is dependent on the age of the sample (see text)

## Discussion

Tables 2–3 clearly show a very surprising finding, but stemming from a nevertheless ‘objective’ instrumental response, and this latter fact allows us to state that there is a new phenomenon that is occurring. Two points must be stressed: we obtained a very good qualitative reproducibility of the excess heat, but the quantitative reproducibility was rather poor. This is usually the case when one is facing a new phenomenon: while the good qualitative reproducibility is there to confirm that a new phenomenon is indeed occurring, the poor qualitative reproducibility is the prize to pay for the lack

of knowledge both of the nature itself of the parameters affecting it and their relevance in terms of the influence that they may have on the experimental results. In fact the nature and relative importance of these parameters for this phenomenon in particular is not (yet) well known. One parameter that we found is the age of the samples, in that we found that this age can influence the quantitative reproducibility of our experiments. For example, when the same sample is tested again after a time lapse of a week (that is: different portions of the same sample are used in different experiments) it usually gives an excess heat that is greater than the one obtained in the first experiment, while if the two measurements on the same sample are conducted during the same day, they give the same result (within of the experimental errors). Since we can state that the solute is absent in the solutions that we study, we are forced to focus our attention on the solvent, bidistilled water. It can be indeed inferred that the physico-chemical properties of the solvent have been permanently altered by the procedure of successive dilutions (1:100) and succussions, used to prepare the 'extremely diluted solutions'. The overall features lead to retain that succussions and dilutions can alter the physico-chemical properties of water, and this fact is probably due to the transfer of mechanical energy to water, through a yet unknown mechanism. Those alterations can be detected by commercial scientific apparatuses (microcalorimeters), through experimental measurements of the heats evolved when mixing the solutions under examination with acids or bases. We must underline the very good qualitative reproducibility of the detected effects and their statistical relevance, facts that suggest a systematic study the phenomenon.

The heats of mixing in excess are all exothermic. Given the chemical composition of the solutions used, that is pure water, the excess heats ought to depend on the variation of the number and/or on the energy of the H-bonds in this 'modified' water, in comparison with the bidistilled water used as blank. If we suppose that the reagents (NaOH or HCl aqueous solutions) totally or in part (as it is probable in the case of HCl) destroy the domains of this new state of water, leading to a water that is more similar to the untreated bidistilled one, we could infer from the sign of the excess heat, that this new state should be less rich of H-bonds than the bidistilled untreated water. From this point of view, this is a more 'disordered state'. Lo [6, 7] has put in evidence the presence of water aggregates in a 'treated water' obtained with a procedure that is partially similar to that used in this work. Using this model, we could infer that the formation of domains of different water structure, or water molecules aggregates, involves a reduced number of H-bond and/or a reduced value of energy of the H-bond per molecule with respects to the mean value of those of the untreated water. The hypothesis of disorder-order transition, induced by the pH variation, as a consequence of the addition of the acid or basic reagent, would be a self-consistent one.

Through this extensive study we could assess that it is possible to qualitatively distinguish the behaviour of the pure solvent from that of the 'extremely diluted solutions', despite the fact that the chemical composition of the latter solutions is the same as that of the solvent used, with aqueous solutions of acids or bases as reagents.

The exact nature of the phenomena just described is yet to be explained, but the experimental results obtained are significant and strongly support the statement that a

new phenomenon has been discovered: a phenomenon that depends on the unusual procedure used in preparing what we have called the 'extremely diluted solutions'. At present, the current theories concerning the properties of liquid water at room temperature [8] are not in agreement with this phenomenon and consequently, the need for new appropriate theoretical studies urges.

Work is in progress, in fact, aiming at exploring the role and importance of the three factors acting in the preparation of the 'extremely diluted solutions', namely: succession, degree of dilution and nature of the initially present solute.

The measurements of other physico-chemical parameters (NMR  $T_2$  and  $T_1$  relaxation time, viscosity, pH, electrical conductivity,  $\Delta H$  of fusion, procedures of calorimetric titrations, etc.) are also in progress. Preliminary results show a very good correlation between independently measured parameters (heat in excess, pH, electrical conductivity). They also reveal the possibility of characterising this 'anomalous water' using other experimental techniques.

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We thank Dr. Filomena Velleca and Prof. Salvatore Andini for the help in the experimental measurements; Prof. Liberato Ciavatta for helpful suggestions and discussions.

This work was financially supported by Ministry for University and Scientific and Technological Research-Italy (MURST), Rome, Cofin. MURST 97 CFSIB.

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