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NEW PHYSICO-CHEMICAL PROPERTIES OF EXTREMELY DILUTED AQUEOUS SOLUTIONS
A calorimetric and conductivity study at 25°C

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Abstract

The ‘extremely diluted solutions’, anomalous solutions prepared through the iteration of a process of dilution and succussion, have been studied with the aim of obtaining information about the influence of the preparation method on the water structure of the solutions. We measured the heats of mixing of basic solutions with such ‘extremely diluted solutions’, and their electrical conductivity, comparing with the analogous heats of mixing, electrical conductivity of the solvent. We found some relevant exothermic excess heats of mixing, and higher conductivity than those of the untreated solvent.

The heats of mixing and electrical conductivity show a good correlation, underlining a single cause for the behaviour of the extremely diluted solutions.

Keywords: calorimetry, conductivity, extremely diluted aqueous solutions

Introduction

Recent studies on the physico-chemical properties of water put in evidence that the most studied liquid by far, water, still exhibits totally unexpected properties [1–12]. The peculiar characteristics of the water liquid derive from the presence of the hydrogen bond, that is characterized by a very directional intermolecular potential. Through very precise measurements of the refraction index, it is becoming evident that this liquid, on average, is composed of dynamically interconverting microdomains of two different structural types [4]. Even a femtosecond mid-infrared pump-probe study suggests that, with respect to orientational dynamics, two distinct molecular species exist in liquid water [5].

Lobyshev and co-workers have shown that the effect of very low concentrations and electromagnetic fields elicit long-scale realignments of the structure of the liq-

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uid, that can either be reversible or irreversible [13]. Recently, an important paper concerning the effect of dilution on molecules has been published [14]. Samal and Geckeler have observed that the clusters size of fullerene–cyclodextrin, β-cyclodextrin, sodium chloride, sodium guanosine monophosphate, and a DNA oligonucleotide, increased with decreasing concentration [14]. Rey [15] has shown that, even though they should be identical, the structures of hydrogen bonds in pure water and in an extremely diluted solution, obtained by an iterative procedure of successive dilutions and succussions, are very different.

In preceding papers [16–18], we reported on the interaction of the 'extremely diluted solutions' with acids or bases. The 'extremely diluted solutions' were studied to test the validity of the hypothesis that the particular preparation technique, and the initial presence of molecules of solutes, of various nature, could lead to an alteration of the 'structure' of the solvent. To get a complete physico-chemical characterization, the 'extremely diluted solutions' have been submitted to numerous measures of experimental parameters. The approach used for this study has been to identify an experimentally accessible parameter and to compare the measured value with the characteristic value in the solvent, under the same experimental conditions. The performed measures have been selected as to highlight a possible different structural organization of the solvent, through the hydrogen bonds.

Our present contribution further develops our long term goal of understanding the properties of solutions that underwent the dilution and succussion cycle. In fact, despite an intense research, a single coherent description of the anomalous behaviour of the 'extremely diluted solutions' is still lacking.

A preceding paper stressed the importance of the presence of electrolytes in solution, as that produces the chance of determining a different physico-chemical behaviour of the 'extremely diluted solutions' with respect to the solvent. A possible interpretation of the phenomenon is that those substances allow the solvent, probably due to succussion process, to acquire a varied structural organisation.

Because of that, we have prepared the 'extremely diluted solutions' using as solvent some solutions with a low and known contents of sodium bicarbonate or silicic acid ($5\cdot10^{-5}$ M), and as containers laboratory bottles made of a glass that does not release significant quantities of alkaline oxide or silicic acid. This way the contents of chemical impurities does not change as a function of time, and the probability to spot a difference between the physico-chemical behaviour of the untreated solvent and that of the 'extremely diluted solutions' is greatly enhanced. Here, we thus report a physico-chemical study that employs as techniques: mixing-flow microcalorimetry and electrical conductivity: these measures allow to discriminate among the solutions under examination and the untreated solvent. The observed phenomenon provides new information on the physical nature of the liquid state of water and leads to conclude that the structure of the solvent can be permanently altered by the procedure used in preparing the solutions. One could deduce from those studies that water and aqueous solutions are complex systems, capable of auto-organising themselves as a consequence of little perturbations of various nature [13].

Methods

Calorimetry

The heats of mixing were monitored using a thermal activity monitor (TAM) model 2227, by Thermometric (Sweden) equipped with a flow mixing vessel. A P3 peristaltic pump from Pharmacia envoys the solutions into the calorimeter through Teflon tubes. The flow rates of the two 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 $3\cdot 10^{-3}$ g s^{-1}: it was the same for all the experiments.

The values of the mixing enthalpies, $\Delta_{\text{mix}}H$, were obtained using the following formula [19]:

$$\Delta_{\text{mix}} H(m_x^i, m_y^i \rightarrow m_x^f, m_y^f) = \frac{\mathrm{d}Q/\mathrm{d}t}{P_w}$$

where $\mathrm{d}Q/\mathrm{d}t$ is the heat flux (W), P_w is the total mass flow-rate of the solvent (kg s^{-1}) and m_x^i, m_y^i and m_x^f, m_y^f are the initial and final molalities. $\Delta_{\text{mix}}H$ is given in J kg^{-1} of solvent in the final solution.

Molecular interactions can be studied through the analysis of the excess thermodynamic properties, that are defined as the difference between the values of that function, referred to a real and an ideal solution. According to the treatment of the properties of solutions proposed by McMillan–Mayer [20] and modified by other authors [21–26], an excess thermodynamic property, J^E, of a solution containing n solutes, can be expressed as a virial expansion of pairwise molalities and higher order interaction coefficients, j, as follows:

$$J^E = \sum_{i=1}^{n} \sum_{k=1}^{n} j_{ik} m_i m_k + \text{higher order terms} \tag{1}$$

In the case of the excess enthalpy for binary and ternary solutions, the virial coefficients can be easily obtained from the dilution enthalpy, $\Delta_{\text{dil}}H$, which is related to the corresponding excess enthalpy, H^E, as follows:

$$\Delta_{\text{dil}} H = H^E(m_x^f, m_y^f, \ldots) - \frac{m_x^f}{m_y^f} H^E(m_x^i, m_y^i, \ldots) \tag{2}$$

where x, y,...... are the solutes, m_x^f and m_x^i, m_y^f and m_y^i are the molalities of solute x and y after and before the dilution process, respectively.

Thus the mixing enthalpy 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:

$$\Delta_{\text{mix}} H = h_{xx} m_x^f (m_x^f - m_x^i) + h_{xy} m_x^f m_y^f + h_{yy} m_y^f (m_y^f - m_y^i) + \text{higher order terms} \tag{3}$$

where h_{xx}, h_{yy} and h_{xy}, the enthalpic interaction coefficients, are adjustable parameters. The h coefficients appearing in Eq. (3) represent the enthalpic contributions to the Gibbs free energy coefficients, characterising the interaction between pairs, triplets or higher order interactions. They implicitly account also for all variations of solvent–solvent and solute–solvent interactions.

Their values fall in the range $1\cdot10^{2}$–$1\cdot10^{4}$ J kg mol^{-2}. Consequently, when the concentration of solute y of an 'extremely diluted solution' is less than $1\cdot10^{-5}$ mol kg^{-1}, while the concentration of solute x (NaOH) is $1\cdot10^{-2}$ mol kg^{-1}, the sole contribution in the previous equation is that due to x, namely the heat of dilution of solute x.

It takes about three successive 1:100 dilutions of the y solution (3CH) to reach a point where the y solute cannot produce any significative contribution to the heat of mixing and the previous equation reduces to:

$$\Delta_{\text{mix}} H = h_{xx} m_x^f (m_x^f - m_x^i) + \text{higher order terms}$$

Conductivity measurements

Systematic measures of the electrical conductivity, χ (μS cm^{-1}) were performed on the 'extremely diluted solutions'. Conductivity data were collected with an YSI conductivity instrument, model 3200, using a cell of cell constant = 1.0 cm^{-1}. The cell constant has been periodically measured, using a KCl standard solution. The values of conductivity were temperature corrected to 25°C using a pre-stored temperature compensation for pure water [27].

The migration of the ions under the action of a gradient of electric potential can happen with two typical mechanisms, the viscous motion and the hopping mechanism. In the case of the 'extremely diluted solution', the electrical conductivity is in practice determined by the mobility of the ions H_3O^+ and OH^- in solution and, accordingly, it's based also the hopping mechanism. The proton can jump from a molecule of water to the other, only if the two molecules are directed in a favourable way. The mobility of the hydrogen ion depends on the rate of reorientation of the molecules of water, and this behaviour is influenced by the strength of the hydrogen bonds.

Experimental

Materials

The solutes were Carlo Erba, Sigma or Fluka products, of the highest purity commercially available. The solutions of the various solutes (NaOH, $NaHCO_3$, SiO_2) were prepared by mass using twice distilled water. NaOH solutions were protected from the contact with atmospheric carbon dioxide by means of suitable traps. The 'extremely diluted solutions' were prepared using as solvent a solution of sodium bicarbonate or/and silicic acid, at low and known contents ($5\cdot10^{-5}$ mol L^{-1}). The container of laboratory glass were treated with a $H_2SO_4/K_2Cr_2O_7$ mixture.

Procedures

The 'extremely diluted solutions' are obtained through the process of dilution and 'dynamization'. The dilution can be centesimal hahnemannian or korsakovian. In the case of the centesimal dilution, the starting point is a 1% in mass solution [28]; to prepare, for example a sodium chloride solution, 1 g of NaCl is added to 99 g of solvent. After the mechanical treatment, simple 'dynamization', the solution so obtained is called '1 centesimal hahnemannian' or 1CH in short, and the name of the solution starts with the name or formula of the solute, or a simple abbreviation of it. So in the preceding example, NaCl 1CH is obtained. In order to prepare the 2 centesimal hahnemannian (NaCl 2CH), 1 g of the 1CH solution is added to 99 g of solvent, and the resulting solution is 'dynamized'.

The korsakovian preparations are characterized by the fact that the dilution is not effected changing bottle to every passage, but voiding the container every time, filled and again submitted to 'dynamization' up to the desired dilution. Just the quantity of substance between a dilution and the other one that sticks to the walls of the container is considered constant. In the case of korsakovian preparations, the solution so obtained is called '1 centesimal korsakovian' or 1CK in short, and the name of the solution starts with the name or formula of the solute, or a simple abbreviation of it.

The process of 'dynamization' consists of either a violent shaking of the solution by means of a mechanical apparatus (succussion), or of a shaking obtained by a vortex. The apparatus used in the 'dynamization' step is a DYNA HV 1 by Debofar N.V.S.A. Belgium or a vortex of Inter Continental equipment. In a single succussion process 50–500 vertical strokes are given to the vessel containing the solution, at the frequency of 0.83 Hz. In the case of the vortex the time varied from 20 to 120 s.

In this paper, the solvent employed for dilution is a solution with known contents of sodium bicarbonate or silicic acid. After their preparation, the 'extremely diluted solutions' and the solvent used for preparing them were stored at room temperature. Samples from nine different preparations, obtained throughout the 2002–2003 years, were studied starting from the 3CH to 30CH (Hanhemannian Centesimal Dilution). Two different 'active principles' were used: arsenicum sulphuratum rubrum, (As_4S_4, ASR) and 2,4-dichlorophenoxyacetic acid (2,4D). The solvents used were: a solution of sodium bicarbonate and of silicic acid, both at $5\cdot10^{-5}$ M (mol L^{-1}); a solution of sodium bicarbonate $5\cdot10^{-5}$ M; a solution of sodium bicarbonate $6.0\cdot10^{-5}$ M; a solution of sodium bicarbonate $7.5\cdot10^{-5}$ M; a solution of sodium bicarbonate $10\cdot10^{-5}$ M. Some of the preparation procedures started with the solvent alone and no 'active principle', leading to what is known as potentiated water (W). The containers were in laboratory glass to avoid the release of alkaline oxide and silica from the walls in the 'extremely diluted solutions', that is otherwise expected with bottles of dark glass that are normally used in the preparation procedures.

Table 1 Thermodynamic and transport properties for 'extremely diluted solutions' of arsenicum sulphuratum rubrum, (ASR: As_4S_4), and 2,4-dichlorophenoxyacetic acid (2,4D) at 298 K

System	N.S.$^{(1)}$	$-Q_{\text{Mix}}^{(2)}$	$\chi^{(3)}$	$-Q_{\text{Mix}}^{\text{E}\,(4)}$	$\chi^{\text{E}(5)}$
H_2O	–	1.05±0.05$^{(6)}$	1.2±0.1$^{(7)}$	–	–
ASR 7 CH[a]	20	4.07	7.8	1.85	2.6
ASR 12 CH[a]	20	2.55	9.6	0.33	4.4
ASR 14 CH[a]	20	2.98	7.5	0.75	2.3
ASR 18 CH[a]	20	2.72	15.7	0.50	10.5
ASR 22 CH[a]	20	2.44	8.3	0.23	3.1
ASR 27 CH[a]	20	2.22	7.5	–0.01	2.3
ASR 29 CH[a]	20	2.07	9.3	–0.15	4.1
ASR 8 CH[b]	18	2.76	8.1	0.54	2.9
ASR 9 CH[b]	18	3.04	10.3	0.82	5.1
ASR 10 CH[b]	18	2.66	9.1	0.44	3.9
ASR 12 CH[b]	18	2.45	8.8	0.22	3.6
ASR 13 CH[b]	18	2.11	9.2	–0.11	4.0
ASR 14 CH[b]	18	2.60	8.2	0.37	3.0
ASR 15 CH[b]	18	2.60	9.4	0.37	4.2
ASR 16 CH[b]	18	4.22	14.2	2.00	9.0
ASR 18 CH[b]	18	2.70	9.7	0.48	4.5
ASR 20 CH[b]	18	2.45	9.3	0.23	4.1
ASR 22 CH[b]	18	2.30	7.5	0.08	2.3
ASR 24 CH[b]	18	2.47	6.9	0.25	1.7
ASR 28 CH[b]	18	2.96	11.3	0.73	6.1
ASR 29 CH[b]	18	2.43	8.2	0.20	3.0
ASR 30 CH[c]	12	3.19	10.8	0.45	3.2
ASR 30 CH[c]	12	3.42	12.1	0.69	4.5
2,4D 6 CH[d]	12	3.05	9.8	0.21	1.8
2,4D 9 CH[d]	12	3.06	9.6	0.22	1.6

[1]) Dynamization time in s; [2]) Heat of mixing, in J (kg of solvent in final solution)$^{-1}$; [3]) Electrical conductivity in μS cm^{-1}; [4]) Excess heat of mixing in J (kg of solvent in final solution)$^{-1}$; [5]) Excess conductivity in μS cm^{-1}; [6]) Average and standard deviation determined using 60 experimental heats of mixing of NaOH 0.01 mol kg^{-1} with water; [7]) Average and standard deviation determined using 60 experimental measurements of water.

[a]) Active principle: arsenicum sulphuratum rubrum. Solvent: aqueous solution of $NaHCO_3$ and H_4SiO_4 both $5\cdot10^{-5}$ M. Dynamization method: vortex.

[b]) Active principle: arsenicum sulphuratum rubrum. Solvent: aqueous solution of $NaHCO_3$ and H_4SiO_4 both $5\cdot10^{-5}$ M. Dynamization method: succussion.

[c]) Active principle: arsenicum sulphuratum rubrum. Solvent: aqueous solution of $NaHCO_3$ $7.5\cdot10^{-5}$ M. Dynamization method: succussion.

[d]) Active principle: 2,4-dichlorophenoxyacetic acid. Solvent: aqueous solution of $NaHCO_3$ $1\cdot10^{-4}$ M. Dynamization method: succussion

Table 2 Thermodynamic and transport properties for 'extremely diluted solutions' of potentiated water, (W), at 298 K

System	N.S.(1)	$-Q_{\mathrm{Mix}}$(2)	χ(3)	$-Q^{\mathrm{E}}_{\mathrm{Mix}}$(4)	χ^{E}(5)
H_2O	–	1.05±0.05(6)	1.2±0.1(7)	–	–
W 9 CH[d]	12	2.68	8.0	–0.05	0.4
W 12 CH[d]	12	3.38	11.1	0.65	3.5
W 12 CH[d]	12	2.89	9.0	0.10	1.4
W 12 CH[d]	12	2.89	8.7	0.16	1.1
W 30 CH[d]	12	5.43	18.1	2.70	10.5
W 30 CH[d]	12	4.72	15.4	1.99	7.8
W 30 CH[d]	12	3.66	11.2	0.93	3.6
W 6 CH[e]	20	3.34	10.5	0.92	4.4
W 6 CH[e]	20	3.08	9.5	0.65	3.4
W 12 CH[e]	20	2.72	8.5	0.29	2.4
W 12 CH[e]	20	2.83	8.5	0.40	2.4
W 12 CH[e]	20	2.72	8.5	0.29	2.4
W 30 CH[e]	20	2.89	9.3	0.46	3.2
W 30 CH[e]	20	2.55	7.4	0.13	1.3
W 30 CH[e]	20	2.57	7.5	0.15	1.4
W 30 CH[e]	30	2.97	9.1	0.55	3.0
W 9 CH[f]	12	4.65	12.9	1.82	4.9
W 12 CH[f]	12	3.59	10.9	0.76	2.9
W 12 CH[f]	12	3.95	11.2	1.11	3.2
W 30 CH[f]	12	3.10	10.7	0.27	2.7
W 30 CH[f]	48	3.73	12.9	0.90	4.9

1) Dynamization time in s; 2) Heat of mixing, in J (kg of solvent in final solution)$^{-1}$; 3) Electrical conductivity in μS cm^{-1}; 4) Excess heat of mixing in J (kg of solvent in final solution)$^{-1}$; 5) Excess conductivity in μS cm^{-1}; 6) Average and standard deviation determined using 60 experimental heats of mixing of NaOH 0.01 mol kg^{-1} with water; 7) Average and standard deviation determined using 60 experimental measurements of water.

d) Active principle: none. Solvent: aqueous solution of $NaHCO_3$ $7.5\cdot 10^{-5}$ M. Dynamization method: succussion.

e) Active principle: none. Solvent: aqueous solution of $NaHCO_3$ $7.5\cdot 10^{-5}$ M. Dynamization method: vortex.

f) Active principle: none. Solvent: aqueous solution of $NaHCO_3$ $1\cdot 10^{-4}$ M. Dynamization method: succussion.

g) Active principle: none. Solvent: aqueous solution of $NaHCO_3$ $6\cdot 10^{-5}$ M. Dynamization method: succussion

Table 2 Continued

System	N.S.(1)	$-Q_{\mathrm{Mix}}$(2)	χ(3)	$-Q^{\mathrm{E}}_{\mathrm{Mix}}$(4)	χ^{E}(5)
W 1 CK[g]	48	2.56	8.5	0.34	3.3
W 3 CK[g]	48	2.36	7.9	0.14	2.7
W 5 CK[g]	48	2.20	6.9	0.00	1.7
W 7 CK[g]	48	2.12	6.7	–0.10	1.5
W 9 CK[g]	48	2.42	7.9	0.20	2.7
W 12 CK[g]	48	2.22	6.9	0.00	1.7
W 12 CK[g]	60	2.14	7.0	–0.08	1.8
W 12 CK[g]	72	2.43	7.5	0.21	2.3
W 12 CK[g]	90	2.22	7.0	0.00	1.8
W 12 CK[g]	120	2.44	7.6	0.28	2.4
W 30 CK[g]	54	2.52	8.8	0.30	3.6
W 30 CK[g]	72	2.29	7.1	0.07	1.9
W 30 CK[g]	90	2.29	6.9	0.07	1.7
W 30 CK[g]	120	2.29	7.0	0.07	1.8

[1]) Dynamization time in s; [2]) Heat of mixing, in J (kg of solvent in final solution)$^{-1}$; [3]) Electrical conductivity in μS cm^{-1}; [4]) Excess heat of mixing in J (kg of solvent in final solution)$^{-1}$; [5]) Excess conductivity in μS cm^{-1}; [6]) Average and standard deviation determined using 60 experimental heats of mixing of NaOH 0.01 mol kg^{-1} with water; [7]) Average and standard deviation determined using 60 experimental measurements of water.

[d]) Active principle: none. Solvent: aqueous solution of $NaHCO_3$ $7.5\cdot10^{-5}$ M. Dynamization method: succussion.

[e]) Active principle: none. Solvent: aqueous solution of $NaHCO_3$ $7.5\cdot10^{-5}$ M. Dynamization method: vortex.

[f]) Active principle: none. Solvent: aqueous solution of $NaHCO_3$ $1\cdot10^{-4}$ M. Dynamization method: succussion.

[g]) Active principle: none. Solvent: aqueous solution of $NaHCO_3$ $6\cdot10^{-5}$ M. Dynamization method: succussion

Results

The heats of mixing of sodium hydroxide solutions with the solvent, as well as with the ‘extremely diluted solutions’, were determined.

As reported in preceding papers [16–18], we sought the concentration of the test solute (x) most suitable to put in evidence the existence of the heat in excess in the experimental conditions. Increasing the concentration of NaOH solutions from $1\cdot10^{-5}$ to $1\cdot10^{-2}$ M, the detected heat of mixing in excess increases and then turns out to be constant for concentrations of NaOH higher than about $5\cdot10^{-3}$ M. Therefore, to obtain the largest thermal effect, the most suitable concentration of NaOH is $1\cdot10^{-2}$ M.

In about the totality of the cases we found an exothermic heat of mixing higher than the heat of mixing obtained when mixing the same reagents with untreated solvent. By excess heat of mixing, $Q^{\mathrm{E}}_{\mathrm{Mix}}$, we simply mean the following difference between experimental values: the heat of mixing, Q_{Mix}, expressed in J (kg of water in the final solution)$^{-1}$, of some reagent *x* with the 'extremely diluted solutions', minus the heat of mixing, expressed in the same unit, of the same reagent x when mixed with the untreated solvent. In the same way, by excess conductivity, χ^{E}, we mean the difference between the conductivity, χ, of the 'extremely diluted solutions' minus the conductivity, χ, of the untreated solvent.

In Tables 1–2 we report: the experimental heats of mixing, Q_{Mix} (J kg^{-1}), and the excess heats of mixing, $Q_{\mathrm{Mix}}^{\mathrm{E}}$, of the studied 'extremely diluted solutions' with NaOH 0.01 M; the electrical conductivity, χ (μS cm^{-1}); and the excess conductivity, χ^{E} (μS cm^{-1}). The values, once corrected to account for the contents of sodium bicarbonate and silicic acid, result systematically higher than those of the reference solvent. The excess heat of mixing $Q_{\mathrm{Mix}}^{\mathrm{E}}$ and the excess conductivity, χ^{E}, are of the same order of magnitude of measured parameters, Q_{Mix} and χ.

From the results obtained it can be inferred that, in 100% of the preparations, the procedure of successive dilutions and 'dynamizations' modified the physico-chemical properties of water.

Discussion and conclusions

Calorimetry has been used for the determination of the heat of mixing. The heats of mixing of the 'extremely diluted solutions' with solutions of strong electrolytes, sodium hydroxide solutions, provide information on a hypothesized different structural organization of the solvent, determining the coefficients of the virial of the excess enthalpy.

As mentioned in the Results section, when mixing the 'extremely diluted solutions' with aqueous solutions of sodium hydroxide 0.01 M, the measures reveal an excess heat of mixing. Every experimentally measured excess heat turned out to be exothermic. The heat of mixing of sodium hydroxide, experimentally measured, is exothermic. Thus, sodium hydroxide behaves phenomenologically as a structure-making solute. Remembering that the 'extremely diluted solutions' have the same composition of the reference solvent, the pairwise enthalpic interaction coefficient of NaOH in the 'extremely diluted solutions' could be higher than that of the solvent. In the dilution process, an increase of the average number of water molecules of hydration accounts for the exothermic effect in this process [29].

The behaviour of the 'extremely diluted solutions' suggests that the excess heat of mixing is linked to an increase in the number and/or energy of hydrogen bonds, with respect to the reference solvent, in the examined systems. During the mixing with the 'extremely diluted solution', the $\mathrm{Na^+}$ and $\mathrm{OH^-}$ ions would more efficiently hydrate than in water, probably exploiting, the aggregates of water molecules found in the solvent, with a consequent increase of the pairwise enthalpic interaction coefficient and producing an exothermic excess heat.

Past studies from this laboratory on the 'extremely diluted solutions' enable us to establish that every sample of a preparation turns out to be characterised by a different factor. These factors are linked to the preparation technique as well as the storage conditions. The main parameters that characterize the 'extremely diluted solutions' we employed in this work are:

- Nature of solute
- Nature of solvent (presence of electrolytes)
- Degree of dilution
- Number of strokes and frequency during "dynamization"
- Age of samples

Through calorimetric and conductometric measurements we can now strongly confirm the results obtained in the past. We examined the nature of the initially present solute, the dilution degree and the quantity of mechanical energy during the succussion or the vortex procedure. We obtained 'extremely diluted solutions' originating from different solutes, with dilutions ranging from 3CH to 30CH, and different quantities of mechanical energy. A correlation between those three factors, initial solute, dilution, mechanical energy, and the physico-chemical behaviour is not yet suggested by our data as a whole. It is noteworthy that the solutions that underwent the dilution cycle, but not the succussion one, do not differ from the reference solvent at all. It must be stressed that the iterative procedure of dilutions and succussions works also in the absence of an 'active principle'. As a consequence, the 'dynamization' (succussion or vortex process) stands out as fundamental, in order to activate the different behaviour of the 'extremely diluted solutions'.

By controlling every parameter affecting a preparation, it will hopefully be possible in the future to better the qualitative and/or quantitative reproducibility of the phenomenon under examination. Electrical conductivity measures were performed on the studied samples, at 25°C. Such measures put in evidence a systematically higher value of conductivity with respect to that of the solvent. In this case too, our discussion of the 'extremely diluted solutions' behaviour takes into account the sodium bicarbonate: its presence alone cannot explain the increase in electrical conductivity for the samples, with respect to the solvent, just like it could not explain the whole excess heat found. For the solutions under study, measures of excess heat and excess conductivity, turn out to be correlated, pointing at a presumably single cause of the exhibited behaviour. Plotting the electric conductibility *vs*. the heat of mixing minus heat of mixing of water, $Q^{\mathrm{E}}_{\mathrm{Mix}}$ (Fig. 1) a linear relationship can be noticed between these two independent chemical parameters. In water, the high mobility of H^+ and OH^- ions under a gradient of electrical potential is explained through the hopping mechanism, as proposed by Grotthus [30]. The migration of ions is strongly associated to clusters of water molecules through hydrogen bonds. Thus, a higher structuring of the solvent could favour the aforementioned mechanism, leading to a higher value for the conductivity in the 'extremely diluted solutions', and explaining the correlation with the heat in excess.

The thermodynamic picture here presented allows to make the hypothesis that the procedure of dilutions and succussions, even if there are no convincing theoretical explanations yet, is capable of modifying in a permanent way the physico-chemical features of water.

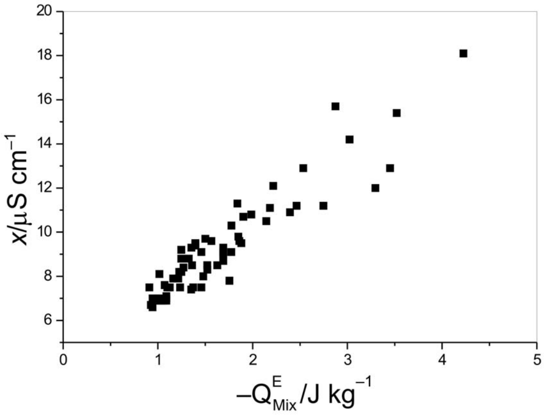

Fig. 1 The electric conductivity *vs*. the heat of mixing minus heat of mixing of water studied 'extremely dilute solutions'

A necessary condition, to be able to experimentally ascertain variations of the physico-chemical properties of such dilutions, is the presence of structural variations in the solvent, via water molecules aggregates, in number and size suitable to be revealed by a thermodynamic technique. Experimental evidence leads to conclude that there is an increase of these structural variation in the solvent as a function of time. The latter fact could be one of the causes of so many failures in this research field: when a too short period of time elapses from the preparation to the measurements the effects are negligible, leading to failures that conjure in keeping this field too "mysterious" still. It is however our hope that the frame outlined in this, and in the three preceding works [16–18], will elicit enough scientific concern as to induce other researches to repeat this kind of experiments. Should those repetitions yield positive results, then the models of water will probably have to be revised in order to account for these latest experimental results.

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