

NEW PHYSICO-CHEMICAL PROPERTIES OF EXTREMELY DILUTED AQUEOUS SOLUTIONS

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Abstract

The 'extremely diluted solutions' are anomalous 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⁻¹) to the point that we may call the resulting solution an extremely diluted solution, namely the composition of the solution is identical to that of the solvent used (e.g. twice distilled water). We conducted thermodynamic and transport measurements of the solutions and of the interaction of those solutions with acids or bases. The purpose of this study is to obtain information about the influence of successive dilutions and succussions on the water structure of the solutions under study. We measured the heats of mixing of acid or basic solutions with such 'extremely diluted solutions', their electrical conductivity and pH, comparing with the analogous heats of mixing, electrical conductivity and pH of the solvent. We found some relevant exothermic excess heats of mixing, higher electrical conductivity and pH than those of the untreated solvent. The measurements show a good correlation between independent physico-chemical parameters. Care was taken to take into account the effect of chemical impurities deriving from the glass containers. Here we thus show that successive dilutions and succussions can permanently alter the physico-chemical properties of the water solvent. The nature of the phenomena here described still remains unexplained, nevertheless some significant experimental results were obtained.

Keywords: aqueous solution, calorimetry, conductivity, pH, solute-solvent interaction, solutions

Introduction

Since time immemorial water has attracted the scientists' attention. The studies carried out on this system revealed that this substance, despite its apparent simplicity, behaves in a fascinating, often surprising manner. A number of explanations of the complex behaviour of water have been published, many quite recently. A large number of models for water have been developed in an attempts to discover the structure of water [1], based on the premise that if the model can successfully predict the physical properties of water then the structure of water is determined [2–4]. Recent stud-

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ies on the physico-chemical properties of water put in evidence that the most studied liquid by far, water, still exhibits totally unexpected properties [5–12]. Rey [5] has shown that even though they should be identical, the structure of hydrogen bonds in pure water is very different from that of an, extremely diluted solution obtained by an iterative procedure of successive dilutions and succussions. 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]. Lobyshev and co-workers have shown that the effect of very low concentrations and electromagnetic fields are long-scale realignments of the structure of the liquid, which can be of either 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].

A noteworthy issue is that of the hypothetical therapeutic power of the ‘extremely diluted solutions’ of homeopathic medicine that employs ‘medicines without molecules’ that should thus exhibit no healing properties. Still, sometimes behind ‘popular beliefs’ lie actual physical properties, not yet fully investigated. The very absence of molecules in the active principle obviously excludes the possibility of them taking part in any action. Scant attention has been paid to the solvent, water, the structure of which is still subject to numerous studies and not fully clarified yet. We thus reckoned right and useful to try and yield a scientific contribution to such issue without, however, touching the therapeutic aspects in any way, but remaining strongly rooted in the physico-chemical aspects. In preceding papers [15, 16], we have 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.

Our present contribution continues the program aimed at understanding the properties of solutions that underwent the dilution and succussion cycle. Here, we report a physico-chemical study that employs as techniques: mixing-flow microcalorimetry, electrical conductivity and potentiometry for pH measurements.

Care was taken to account for impurities released by the glass containers, that can affect the measures of the physico-chemical parameters because of, respectively, the heat of neutralisation of alkaline bicarbonates and silicic acid with the employed acid and basic reactives, the presence of electrolytes, bicarbonates, and the presence of amphoteric electrolytes, bicarbonates. Sodium bicarbonate and silicic acid can derive from the alkaline oxides and silica in the glass of the containers. The concentration of sodium was determined, through atomic absorbance measures, as well as the silicic acid concentration, by measuring the UV absorption of complexes with ammonium molybdate.

The analyses we brought forth allowed to confirm the different physico-chemical behaviour of the ‘extremely diluted solutions’ with respect to that of untreated, bidistilled water at the same level of impurity. This approach also showed

that the presence of that kind of impurities is very important in determining a different physico-chemical behaviour after the preparation procedure we described. Because of that, some 'extremely diluted solutions' were prepared using as solvent some solutions with a low and known contents of sodium bicarbonate or silicic acid ($5 \cdot 10^{-5}$ M). This way the probability to differentiate between the physico-chemical behaviour of the mixed untreated solvent and that of the 'extremely diluted solutions' was greatly increased.

It's worth noting that no work of this kind, concerning the study of the physico-chemical properties of these 'anomalous solutions', namely the 'extremely diluted solutions', with significative results, is known in current literature. 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 could be permanently altered by the procedure used in preparing the solutions.

Experimental

Materials

The solutes were Carlo Erba, Sigma or Fluka products, of the highest purity commercially available. The solutions of the various solutes (NaOH, NaHCO₃, SiO₂) 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 twice distilled water or using as solvent a solution of sodium bicarbonate or/and silicic acid at low and known content ($5 \cdot 10^{-5}$ mol L⁻¹).

Procedures

The procedure by which such 'extremely diluted solutions' are obtained is the following [17]: the starting point is a 1% in mass solution; to prepare, for example, the sodium chloride solutions (NaCl 3CH to 12CH), 1 g of NaCl is added to 99 g of water. After the mechanical treatment, simple succussion, the solution so obtained is called '1 centesimal hahnemannian' or CH 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 CH is obtained. The process of succussion consists in a violent shaking of the solution by means of a mechanical apparatus, while the solutions are kept in vessels of glass. In order to prepare the 2 centesimal hahnemannian (NaCl 2CH), g of the CH solution 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. The apparatus used in the succussion step is a DYNA HV 1 by Debofar N.V.S.A. Belgium. In a single succussion process 50 vertical strokes in 6 s are given to the vessel containing the solution.

The same procedure is used for the preparation of the 'extremely diluted solutions' in NaHCO₃ or H₄SiO₄ solutions. In this case, 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 (twice distilled water; NaHCO_3 or H_4SiO_4 in twice distilled water) were stored at room temperature. The samples and the solvent were then tested at different ages, varying from several days to several months.

Samples of 4 different solutes were prepared:

NaCl: sodium chloride; GLP: *n*-(phosphonomethyl)-glycine; IAA: indole-3-acetic acid; 2,4-D dichlorophenoxyacetic acid.

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 $3 \cdot 10^{-3} \text{ g s}^{-1}$: it was the same for all the experiments.

The values of the mixing enthalpies, ΔH_{mix} , were obtained using the following formula [18]:

$$\Delta H_{\text{mix}}(m_x^i, m_y^i \rightarrow m_x^f, m_y^f) = \frac{dQ}{dt} P_w$$

where (dQ/dt) 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. ΔH_{mix} 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, which 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 [19] and modified by other authors [20–25], 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:

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

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:

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

where x, y, \dots are the solutes, and m_x^f, m_x^i and m_y^f, 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:

$$\Delta H_{\text{mix}} = h_{xx} m_x^f (m_x^f - m_x^i) + 2h_{xy} m_x^f m_y^f + h_{yy} m_y^f (m_y^f - m_y^i) + \text{higher order terms} \quad (3)$$

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 $1 \cdot 10^2 - 1 \cdot 10^4$ (J kg mol⁻²). Consequently, when the concentration of solute y of an extremely diluted solution is less than $1 \cdot 10^{-5}$ mol kg⁻¹, while the concentration of solute x (NaOH) is $1 \cdot 10^{-2}$ 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:

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

Based upon statistical mechanics considerations, also Pitzer [26] adopted a virial expansion of the terms in molality, with the second coefficient dependent upon ionic strength. By measuring the enthalpy of dilution it is thus possible to obtain the pairwise enthalpic interaction coefficient for solute x . The integral yielding this coefficient contains, as factors, the potential of mean force and the pairwise correlation function, both averaged over every possible orientation of the solvent. In a solvent with a local structure like water, the potential of mean force and the pairwise correlation function depend on the distribution of local configurations of the molecules in the solvent. Hence, by measuring the ΔH_{mix} in the mixing of the sodium hydroxide solution with the ‘extremely diluted solutions’ it is possible to acquire information on the solvent through both solute–solute and solute–solvent interactions.

pH measurements

Systematic measures of pH were performed on the ‘extremely diluted solutions’. pH potentiometric data were collected with a Crison pH ion meter (model microPH 2002), with 0.1 mV or 0.001 pH units of resolution for measurements of voltage and pH, respectively. A combined glass electrode (suitable for low ionic strength systems), containing 3M KCl as the reference electrolyte solution, and an external temperature probe were used. The asymmetrical potential and the Nernst slope of the combined glass electrode were determined by calibrating the electrode daily with two Crison standard buffer solutions of pH 4 and 7.

Conductivity measurements

Systematic measures of electrical conductivity ($\mu\text{S cm}^{-1}$) were performed on the 'extremely diluted solutions'. Conductivity data were collected with an YSI conductivity instrument, model 3200, using a cell for low ionic strength systems (cell constant = 0.1 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].

Analytical determination of impurities

Sodium concentration was determined by the spectroscopic method of atomic absorption using a Spectra A Varian instrument. Before measuring the samples, a calibration curve is necessary, obtained using standard solutions. To prepare the standard solutions, NaCl has been dissolved in water and diluted to 1 L to obtain $1000 \mu\text{g mL}^{-1}$ Na. The working conditions are [28]: lamp current: 5 mA; fuel: acetylene; support: air; flame stoichiometry: oxidizing. The used wavelength depends on the concentration range of sodium. For our samples the wavelength of 589.6 nm has been used. Sodium is partially ionised in the air-acetylene flame. To suppress the ionisation, some potassium chloride solution has been added to produce a final concentration of $2000 \mu\text{g mL}^{-1}$ in all solutions, including the blank.

Silicon is determined as silica (SiO_2) through a colorimetric method [29]. Ammonium molybdate at approximately pH 1.2, reacts with silica present in solution to produce heteropolyacids, yellow coloured. The colour intensity is proportional to the concentration of silica. This complex is photometrically determinable using a wavelength of 410 nm. To determine the concentration of silica a calibration curve is needed. To prepare the standard solutions, sodium metasilicate nonahydrate, $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$, has been dissolved in water and diluted to 1 L. Six standard solutions were prepared, to cover the optimal range of concentration.

The concentrations of impurities are of the order of magnitude of several ppm.

Results

The heats of mixing with the solvent as well as with the 'extremely diluted solutions', were determined.

As reported in preceding papers [15, 16], 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 $1 \cdot 10^{-5}$ to $1 \cdot 10^{-2}$ m, the detected heat of mixing increases and then turns out to be constant for concentrations of NaOH higher than about $5 \cdot 10^{-3}$ m. Therefore, to obtain the largest thermal effect, the most suitable concentration of NaOH is $1 \cdot 10^{-2}$ m.

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 when mixing the same reagents with twice distilled, untreated water. By excess heat of mixing, we simply

mean the following difference between experimental values: the heat of mixing [J (kg of water in the initial solution)⁻¹] of some reagent x with the ‘extremely diluted solutions’, minus the heat of mixing [J (kg of water in the initial solution)⁻¹] of the same reagent x mixed with untreated, twice distilled water. In the case of a calibration curve (Figs 3–5) the same procedure works, namely Q^E is the difference between the heat of mixing of some reagent x with the solutions of NaHCO₃ and/or H₄SiO₄ at the various concentrations minus the heat of mixing of the same reagent x mixed with the untreated twice distilled water. In this way the contribution deriving by dissolved CO₂ was instrumentally eliminated.

In Tables 1–9, we report: the experimental excess heats of mixing of the studied ‘extremely diluted solutions’ with NaOH 0.01 m (the experimental conditions were such that the concentration of the NaOH solution after the mixing procedure was half the initial one), the pH, the electrical conductivity ($\mu\text{S cm}^{-1}$), the concentration of sodium and of SiO₂ experimentally determined (see Method), for the extremely dilute solutions obtained using as solvent: twice distilled water, NaHCO₃ or H₄SiO₄ solutions $5 \cdot 10^{-5}$ M in twice distilled water.

In Tables 10 and 11 the thermodynamic and transport parameters for NaHCO₃ or H₄SiO₄ solutions used as standard solutions are reported. Of those we measured the heat of mixing with NaOH 0.01 m, pH and electrical conductivity that represent the calibration curves needed to correct for ‘chemical impurities’.

In Tables 12 and 13 are brought the excess heats of mixing in function of the age of the samples prepared using NaHCO₃ or H₄SiO₄ solutions as solvent. As it can be seen the Q^E for the samples increase at increasing the age while that of the reference do not. In the following Tables (14 and 15), the analytical determination of the chemical impurities is reported. As the value of these impurities can be observed it does not increase to increase some time.

In two preparations all the dilutions, from 3CH to 12CH, are ‘inactive’: the measured parameters are the same as with twice distilled water (Tables 1 and 5). In the remaining eight preparations, the dilutions behave as ‘active’. For those ‘extremely diluted solutions’ we take into account the contribute to the heat of mixing deriving from chemical impurities (the alkaline oxides and silica in the glass of the containers). The values, once corrected to account for chemical impurities, result systematically higher than those of the reference solvent. The excess heat of mixing is of the same order of magnitude of the heat of dilution of the 0.01 m basic solution that was used.

Thus, in 83% of the preparations the procedure of successive dilutions and succussions modified the physico-chemical properties of water. In 50% of the samples the heat is in excess; in 35% of the samples pH was higher and in 38% of the samples the electrical conductivity was higher too.

Discussion

The heat of dilution of sodium hydroxide, experimentally measured, is exothermic. According to the McMillian and Mayer theory, the second coefficient of the virial of the excess enthalpy for NaOH is greater than zero [19]. Thus, sodium hydroxide be-

Table 1 Thermodynamic and transport properties and impurity contents (mol L⁻¹) for, extremely diluted solutions^a of indole-3-acetic acid, IAA, at 25°C

System	$-Q^{E,a,b}$	pH ^c	$\mu\text{S cm}^{-1c}$	M_{Na^+}	$M_{\text{Ca}^{2+}}$	M_{SiO_2}
H ₂ O bid.	2.1±0.1	5.8±0.2	1.2±0.1	–	–	–
IAA 4 CH	0	6.0	1.0			
IAA 5 CH	0	6.0	1.1			
IAA 6 CH	0	6.0	1.0			
IAA 7 CH	0	6.0	1.1			
IAA 8 CH	0	6.0	1.2			
IAA 9 CH	0	6.0	1.0			
IAA10 CH	0	6.1	1.0			
IAA 11 CH	0	6.0	1.3			
IAA12 CH	0	6.0	1.2			
IAA 7 CH	0	5.9	1.1			
IAA 8 CH	0	6.0	1.2			
IAA 9 CH	0.7	6.3	2.4	6·10 ⁻⁶	N.D.	N.D.
IAA 10 CH	0	5.8	1.1	N.D.	N.D.	N.D.
IAA 11 CH	1.4	6.4	6.5	1·10 ⁻⁵	1·10 ⁻⁵	N.D.
IAA12 CH	0	6.0	1.2	N.D.	N.D.	N.D.

Table 2 Thermodynamic and transport properties and impurity contents (mol L⁻¹) for, extremely diluted solutions^a of sodium chloride, NaCl, at 25°C

System	$-Q^{E,a,b}$	pH ^c	$\mu\text{S cm}^{-1c}$	M_{Na^+}	$M_{\text{Ca}^{2+}}$	M_{SiO_2}
H ₂ O bid.	2.1±0.1	5.8±0.2	1.2±0.1	–	–	–
NaCl 4 CH	2.0	7.1	11.9			
NaCl 5 CH	1.1	7.0	10.5			
NaCl 6 CH	1.5	7.0	11.3			
NaCl 7 CH	1.9	6.4	6.8	1·10 ⁻⁵	8·10 ⁻⁶	N.D.
NaCl 8 CH	1.6	6.3	6.7	1· 0 ⁻⁵	6·10 ⁻⁶	N.D.
NaCl 9 CH	1.7	6.3	6.7	1·10 ⁻⁵	7·10 ⁻⁶	N.D.
NaCl 10 CH	2.0	6.4	6.5	2·10 ⁻⁵	9·10 ⁻⁶	N.D.
NaCl 11 CH	2.1	7.3	12.4			
NaCl 12 CH	1.7	7.1	11.4			

^aExcess heat of mixing, in J (kg of solvent in initial solution)⁻¹. ^bAverage and standard deviation determined using 60 experimental heats of mixing of NaOH 0.01 m with water. ^cAverage and standard deviation determined using 60 experimental measurement of water. The error in the determination of Na⁺, Ca²⁺ and SiO₂ is 5·10⁻⁶ mol L⁻¹. N.D. – not detected. The value of concentration is below the detection limit of apparatus employed. Namely, the concentration in the solution is equal to that in the blank solution, i.d. twice distilled water in polyethylene containers

Table 3 Thermodynamic and transport properties and impurity contents (mol L⁻¹) for ‘extremely diluted solutions’ of 2,4-dichlorophenoxyacetic acid, 2,4-D, at 25°C

System	$-Q^{E,a,b}$	pH ^c	$\mu\text{S cm}^{-1c}$	M_{Na^+}	$M_{\text{Ca}^{2+}}$	M_{SiO_2}
H ₂ O bid.	2.1±0.1	5.8±0.2	1.2±0.1	–	–	–
2,4-D 3 CH	1.8	6.6	4.7	N.D.	2·10 ⁻⁵	N.D.
2,4-D 4 CH	2.1	6.7	5.3	N.D.	2·10 ⁻⁵	N.D.
2,4-D 5 CH	0	6.0	1.2	N.D.	N.D.	N.D.
2,4-D 6 CH	0.4	6.5	1.1	N.D.	N.D.	N.D.
2,4-D 7 CH	1.5	6.7	4.2	2·10 ⁻⁵	N.D.	N.D.
2,4-D 8 CH	0.6	6.6	2.3	N.D.	N.D.	N.D.
2,4-D 9 CH	4.0	6.9	10.2	2·10 ⁻⁵	2·10 ⁻⁵	N.D.
2,4-D 10 CH	0	6.1	1.2	N.D.	N.D.	N.D.
2,4-D 11 CH	0	5.9	1.1	N.D.	N.D.	N.D.
2,4-D 12 CH	0.7	6.4	2.3	N.D.	N.D.	N.D.

Table 4 Thermodynamic and transport properties and impurity contents (mol L⁻¹) for ‘extremely diluted solutions’ of sodium chloride, NaCl, at 25°C

System	$-Q^{E,a,b}$	pH ^c	$\mu\text{S cm}^{-1c}$	M_{Na^+}	$M_{\text{Ca}^{2+}}$	M_{SiO_2}
H ₂ O bid.	2.1±0.1	5.8±0.2	1.2±0.1	–	–	–
NaCl 4 CH	1.4	6.4	3.8	N.D.	1·10 ⁻⁵	N.D.
NaCl 5 CH	1.4	6.3	4.0	N.D.	N.D.	N.D.
NaCl 6 CH	0.4	6.1	2.1	N.D.	N.D.	N.D.
NaCl 7 CH	0	5.8	1.0	N.D.	N.D.	N.D.
NaCl 8 CH	0.5	6.1	2.1	N.D.	N.D.	N.D.
NaCl 9 CH	3.8	7.0	12.4	N.D.	4·10 ⁻⁵	N.D.
NaCl 10 CH	0	5.8	1.4	N.D.	N.D.	N.D.
NaCl 12 CH	0.4	6.0	2.7	N.D.	N.D.	N.D.

^aExcess heat of mixing, in J (kg of solvent in initial solution)⁻¹. ^bAverage and standard deviation determined using 60 experimental heats of mixing of NaOH 0.01 m with water. ^cAverage and standard deviation determined using 60 experimental measurement of water. The error in the determination of Na⁺, Ca²⁺ and SiO₂ is 5·10⁻⁶ mol L⁻¹. N.D. – not detected. The value of concentration is below the detection limit of apparatus employed. Namely, the concentration in the solution is equal to that in the blank solution, i.d. twice distilled water in polyethylene containers

has phenomenologically as a structure-maker solute. The ion–dipole interaction between dissolved ions and water molecules can affect a number of bulk properties of water. The high electric fields exerted by these ions can polarise the water molecules, producing additional order beyond the first hydration layer. The introduction of Na⁺ and OH⁻ ions in solution is capable of producing an extensive perturbation zone

Table 5 Thermodynamic and transport properties and impurity contents (mol L^{-1}) for ‘extremely diluted solutions’ of indole-3-acetic acid, IAA, at 25°C

System	$-Q^{\text{E,a,b}}$	pH ^c	$\mu\text{S cm}^{-1}$ ^c	M_{Na^+}	$M_{\text{Ca}^{2+}}$	M_{SiO_2}
H ₂ O bid.	2.1±0.1	5.8±0.2	1.2±0.1	–	–	–
IAA 3 CH	0	5.9	1.0	N.D.	N.D.	N.D.
IAA 4 CH	0	6.0	1.1	N.D.	N.D.	N.D.
IAA 5 CH	0	6.0	1.0	N.D.	N.D.	N.D.
IAA 6 CH	0	6.0	1.0	N.D.	N.D.	N.D.
IAA 7 CH	0	5.9	1.0	N.D.	N.D.	N.D.
IAA 8 CH	0	5.9	1.0	N.D.	N.D.	N.D.
IAA 9 CH	0	6.0	1.0	N.D.	N.D.	N.D.
IAA 10 CH	0	5.9	1.0	N.D.	N.D.	N.D.
IAA 11 CH	0	6.0	1.0	N.D.	N.D.	N.D.
IAA 12 CH	0	5.9	1.1	N.D.	N.D.	N.D.
IAA 4 CH	0	5.9	1.1	N.D.	N.D.	N.D.
IAA 5 CH	1.4	6.7	4.3	$7 \cdot 10^{-6}$	$7 \cdot 10^{-6}$	$1 \cdot 10^{-5}$
IAA 6 CH	1.2	6.7	4.1	$5 \cdot 10^{-6}$	$8 \cdot 10^{-6}$	$1 \cdot 10^{-5}$
IAA 7 CH	0.4	6.5	2.2	N.D.	N.D.	N.D.
IAA 8 CH	0.3	6.2	1.2	N.D.	N.D.	$5 \cdot 10^{-6}$
IAA 9 CH	4.9	7.1	12.8	N.D.	$4 \cdot 10^{-5}$	N.D.
IAA 10 CH	0.2	6.0	1.2	N.D.	N.D.	N.D.
IAA 11 CH	0.3	6.0	1.6	N.D.	N.D.	N.D.
IAA 12 CH	0.2	6.0	1.4	N.D.	N.D.	N.D.

^aExcess heat of mixing, in J (kg of solvent in initial solution)⁻¹. ^bAverage and standard deviation determined using 60 experimental heats of mixing of NaOH 0.01 m with water. ^cAverage and standard deviation determined using 60 experimental measurement of water. The error in the determination of Na⁺, Ca²⁺ and SiO₂ is $5 \cdot 10^{-6}$ mol L⁻¹. N.D. – not detected. The value of concentration is below the detection limit of apparatus employed. Namely, the concentration in the solution is equal to that in the blank solution, i.d. twice distilled water in polyethylene containers

within the net of hydrogen bonds of water, in accordance with theoretical studies that employ ab initio computational techniques [30].

As mentioned in the Results section, when mixing the ‘extremely diluted solutions’ with aqueous solutions of sodium hydroxide NaOH 0.01 m, the measures reveal an excess heat of mixing. Every experimentally measured excess heats turned out to be exothermic. Remembering that the ‘extremely diluted solutions’ have the same composition of pure water or of 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 [31].

Table 6 Thermodynamic and transport properties and impurity contents (mol L⁻¹) for 'extremely diluted solutions' of *n*-(phosphonimethyl)-glycine, GLP, at 25°C

System	$-Q^{E,a,b}$	pH ^c	$\mu\text{S cm}^{-1 c}$	M_{Na^+}	$M_{\text{Ca}^{2+}}$	M_{SiO_2}
H ₂ O bid.	2.1±0.1	5.8±0.2	1.2±0.1	–	–	–
GLP 4 CH	0.2	6.0	1.1	N.D.	N.D.	N.D.
GLP 5 CH	0.3	6.0	1.6	N.D.	N.D.	N.D.
GLP 6 CH	0.2	6.0	1.2	N.D.	N.D.	N.D.
GLP 7 CH	0.8	6.1	2.8	N.D.	8·10 ⁻⁶	N.D.
GLP 8 CH	0.1	5.9	1.2	N.D.	N.D.	N.D.
GLP 9 CH	3.2	7.0	8.4	2·10 ⁻⁵	2·10 ⁻⁵	N.D.
GLP 10 CH	0.2	6.0	1.2	N.D.	N.D.	N.D.
GLP 12 CH	1.7	6.4	4.5	9·10 ⁻⁶	1·10 ⁻⁵	N.D.

Table 7 Thermodynamic and transport properties and impurity contents (mol L⁻¹) for 'extremely diluted solutions' of 2,4-dichlorophenoxyacetic acid, 2,4-D, in NaHCO₃ 5·10⁻⁵ M as solvent

System	$-Q^{E,a,b}$	pH ^c	$\mu\text{S cm}^{-1 c}$	M_{Na^+}	M_{SiO_2}
H ₂ O bid.	2.1±0.1	5.8±0.2	1.2±0.1	–	–
[1]	1.9	6.8	5.3	4.8·10 ⁻⁵	N.D.
[2]	1.9	6.8	5.3	4.9·10 ⁻⁵	N.D.
[3]	1.9	6.8	5.3	4.7·10 ⁻⁵	N.D.
[4]	1.9	6.8	5.4	4.7·10 ⁻⁵	N.D.
2,4-D 4 CH	2.1	6.8	5.2	4.8·10 ⁻⁵	N.D.
2,4-D 5 CH	2.1	6.9	5.2	4.8·10 ⁻⁵	N.D.
2,4-D 6 CH	2.0	7.1	5.3	4.8·10 ⁻⁵	N.D.
2,4-D 7 CH	2.0	7.0	5.3	4.7·10 ⁻⁵	N.D.
2,4-D 8 CH	2.0	6.9	5.3	4.7·10 ⁻⁵	N.D.
2,4-D 9 CH	2.8	7.1	5.3	4.7·10 ⁻⁵	N.D.
2,4-D 10 CH	1.9	6.8	5.2	4.7·10 ⁻⁵	N.D.
2,4-D 11 CH	2.3	6.8	5.4	4.7·10 ⁻⁵	N.D.
2,4-D 12 CH	1.9	6.8	5.3	4.7·10 ⁻⁵	N.D.

^aExcess heat of mixing, in J (kg of solvent in initial solution)⁻¹. ^bAverage and standard deviation determined using 60 experimental heats of mixing of NaOH 0.01 m with water. ^cAverage and standard deviation determined using 60 experimental measurement of water. The error in the determination of Na⁺, Ca²⁺ and SiO₂ is 5·10⁻⁶ mol L⁻¹. N.D. – not detected. The value of concentration is below the detection limit of apparatus employed. Namely, the concentration in the solution is equal to that in the blank solution, i.d. twice distilled water in polyethylene containers

Table 8 Thermodynamic and transport properties and contents (mol L^{-1}) for 'extremely diluted solutions' of 2,4-dichlorophenoxyacetic acid, 2,4-D, in H_4SiO_4 $1 \cdot 10^{-5}$ M as solvent

System	$-Q^{\text{E,a,b}}$	pH ^c	$\mu\text{S cm}^{-1}$ ^c	M_{Na^+}	M_{SiO_2}
H ₂ O bid.	2.1±0.1	5.8±0.2	1.2±0.1	–	–
[1]	0.4	5.9	1.0	N.D.	$1 \cdot 10^{-5}$
[2]	0.4	6.1	1.0	N.D.	$1 \cdot 10^{-5}$
[3]	0.5	6.1	2.3	N.D.	$1 \cdot 10^{-5}$
[4]	0.4	5.9	1.0	N.D.	$1 \cdot 10^{-5}$
2,4-D 4 CH	0.4	5.9	1.0	N.D.	$1 \cdot 10^{-5}$
2,4-D 5 CH	0.4	6.0	1.0	N.D.	$1 \cdot 10^{-5}$
2,4-D 6 CH	7.2	6.2	1.8	$5 \cdot 10^{-6}$	$4 \cdot 10^{-5}$
2,4-D 7 CH	0.4	6.1	1.0	N.D.	$1 \cdot 10^{-5}$
2,4-D 8 CH	0.4	6.1	1.0	N.D.	$1 \cdot 10^{-5}$
2,4-D 9 CH	0.6	6.2	1.1	N.D.	$1 \cdot 10^{-5}$
2,4-D 10 CH	0.4	6.0	1.0	N.D.	$1 \cdot 10^{-5}$
2,4-D 11 CH	0.5	6.1	1.0	N.D.	$1 \cdot 10^{-5}$
2,4-D 12 CH	0.4	6.1	1.0	N.D.	$1 \cdot 10^{-5}$

^aExcess heat of mixing, in J (kg of solvent in initial solution)⁻¹. ^bAverage and standard deviation determined using 60 experimental heats of mixing of NaOH 0.01 m with water. ^cAverage and standard deviation determined using 60 experimental measurement of water. The error in the determination of Na⁺, Ca²⁺ and SiO₂ is $5 \cdot 10^{-5}$ mol L⁻¹. N.D. – not detected. The value of concentration is below the detection limit of apparatus employed. Namely, the concentration in the solution is equal to that in the blank solution, i.d. twice distilled water in polyethylene containers

The 'extremely diluted solutions' behaviour suggests that the excess heat of mixing is linked to an increase in the number and/or energy of the hydrogen bonds in the examined systems, with respect to the reference solvent. During the mixing with the extremely diluted solution, the Na⁺ and OH⁻ ions would more efficiently hydrate than in water, exploiting, probably, 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.

Mixing with strong acids or bases seems to be a necessary condition in order to differentiate between the calorimetric behaviour of the solution under study and the reference solvent. The suggestive hypothesis that H⁺ and OH⁻ ions, characterising acids and bases, and water are a necessary condition for obtaining the heats in excess, is not to be excluded.

Every sample of a preparation turns out to be characterised by different factors, linked to the preparation technique as well as with the storage conditions. The main pa-

Table 9 Thermodynamic and transport properties and impurity contents (mol L⁻¹) for, extremely diluted solutions^a of 2,4-dichlorophenoxyacetic acid, 2,4-D, in H₄SiO₄ 5·10⁻⁵ M as solvent

System	$-Q^{E,a,b}$	pH ^c	$\mu\text{S cm}^{-1 c}$	M _{Na⁺}	M _{SiO₂}
H ₂ O bid.	2.1±0.1	5.8±0.2	1.2±0.1	–	–
[1]	1.5	5.9	1.0	N.D.	5·10 ⁻⁵
[2]	1.5	6.1	1.0	N.D.	5·10 ⁻⁵
[3]	1.5	6.1	1.3	N.D.	5·10 ⁻⁵
[4]	1.5	5.9	1.0	N.D.	6·10 ⁻⁵
2,4-D 4 CH	1.5	5.9	1.0	N.D.	5·10 ⁻⁵
2,4-D 5 CH	1.9	6.0	1.0	N.D.	5·10 ⁻⁵
2,4-D 6 CH	2.7	6.0	1.5	5·10 ⁻⁶	6·10 ⁻⁵
2,4-D 7 CH	1.6	6.1	1.0	N.D.	5·10 ⁻⁵
2,4-D 8 CH	1.5	6.1	1.0	N.D.	5·10 ⁻⁵
2,4-D 9 CH	1.8	6.2	1.1	N.D.	6·10 ⁻⁵
2,4-D 10 CH	1.5	6.0	1.0	N.D.	5·10 ⁻⁵
2,4-D 11 CH	1.5	6.1	1.0	N.D.	5·10 ⁻⁵
2,4-D 12 CH	1.5	6.1	1.0	N.D.	5·10 ⁻⁵

^aExcess heat of mixing, in J (kg of solvent in initial solution)⁻¹. ^bAverage and standard deviation determined using 60 experimental heats of mixing of NaOH 0.01 m with water. ^cAverage and standard deviation determined using 60 experimental measurement of water. The error in the determination of Na⁺, Ca²⁺ and SiO₂ is 5·10⁻⁵ mol L⁻¹. N.D. – not detected. The value of concentration is below the detection limit of apparatus employed. Namely, the concentration in the solution is equal to that in the blank solution, i.d. twice distilled water in polyethylene containers

rameters that characterise the ‘extremely diluted solutions’ we employed in this work are:

- Nature of solute
- Degree of dilution
- Number of strokes and frequency during succussion
- Age of samples
- The nature of the containers, employed in both preparation and storage, can be considered an additional factor, because of the nature and quantity impurities they release.

Each of those factors influences the ‘extremely diluted solutions’ in different ways and amount.

When an, extremely diluted solution is tested at different times (that’s to say different portions of a single sample are employed in different experimental measures) the excess heat turns out to be larger as the age of the sample grows, with increases of more than 100%. This temporal evolution can be slow, requiring months since the

Table 10 Thermodynamic and transport properties for solutions of sodium bicarbonate, NaHCO₃, at 25°C

System	$-Q^E/J\text{ kg}^{-1}$ ^{a,b}	pH ^c	$\mu\text{S cm}^{-1}$ ^c
H ₂ O bid.	2.1±0.1	5.8±0.2	1.2±0.1
NaHCO ₃ 1.0·10 ⁻⁵	0.3±0.1	6.0±0.2	1.6±0.2
NaHCO ₃ 1.5·10 ⁻⁵	–	6.2±0.2	2.0±0.2
NaHCO ₃ 2.0·10 ⁻⁵	–	6.3±0.2	2.5±0.2
NaHCO ₃ 2.5·10 ⁻⁵	–	6.4±0.2	2.8±0.2
NaHCO ₃ 3.0·10 ⁻⁵	–	6.4±0.2	3.2±0.2
NaHCO ₃ 3.5·10 ⁻⁵	–	6.5±0.2	3.5±0.2
NaHCO ₃ 4.0·10 ⁻⁵	–	6.5±0.2	4.1±0.2
NaHCO ₃ 4.5·10 ⁻⁵	–	6.6±0.2	4.6±0.2
NaHCO ₃ 5.0·10 ⁻⁵	1.7±0.1	6.7±0.2	5.0±0.2
NaHCO ₃ 6.0·10 ⁻⁵	–	6.7±0.2	6.1±0.2
NaHCO ₃ 7.0·10 ⁻⁵	–	6.7±0.2	6.9±0.2
NaHCO ₃ 8.0·10 ⁻⁵	–	6.8±0.2	7.9±0.2
NaHCO ₃ 1.0·10 ⁻⁴	4.1±0.1	6.9±0.2	9.8±0.2
NaHCO ₃ 2.5·10 ⁻⁴	11.1±0.1	7.5±0.2	24.1±0.2
NaHCO ₃ 5.0·10 ⁻⁴	20.4±0.1	7.7±0.2	47.1±0.2
NaHCO ₃ 7.5·10 ⁻⁴	30.6±0.1	7.9±0.2	71.6±0.2
NaHCO ₃ 1.0·10 ⁻³	40.7±0.1	8.1±0.2	93.6±0.2

^aExcess heat of neutralisation (J kg⁻¹) in the titration of NaHCO₃ solutions with sodium hydroxide.

^bAverage and standard deviation determined using 60 experimental heats of mixing of NaOH 0.01 m with water. ^cAverage and standard deviation determined using 60 experimental measurement of water

Table 11 Thermodynamic and transport properties for solutions of silicic acid, H₄SiO₄, at 25°C

System	$-Q^E/J\text{ kg}^{-1}$ ^{a,b}	pH ^c	$\mu\text{S cm}^{-1}$ ^c
H ₂ O bid.	2.1±0.1	5.8±0.2	1.2±0.1
H ₄ SiO ₄ 1.9·10 ⁻³	58.4±0.1	5.8±0.2	1.2±0.1
H ₄ SiO ₄ 9.6·10 ⁻⁴	29.7±0.1	5.8±0.2	1.1±0.1
H ₄ SiO ₄ 5.1·10 ⁻⁴	14.5±0.1	5.9±0.2	1.2±0.1
H ₄ SiO ₄ 2.7·10 ⁻⁴	7.2±0.1	5.9±0.2	1.1±0.1
H ₄ SiO ₄ 1.2·10 ⁻⁴	3.6±0.1	5.8±0.2	1.0±0.1

^aExcess heat of neutralisation (J kg⁻¹) in the titration of H₄SiO₄ solutions with sodium hydroxide.

^bAverage and standard deviation determined using 60 experimental heats of mixing of NaOH 0.01 m with water. ^cAverage and standard deviation determined using 60 experimental measurement of water

Table 12 Extremely diluted solutions of 2,4-dichlorophenoxyacetic acid, 2,4-D, in NaHCO_3 $5 \cdot 10^{-5}$ M as solvent. The excess heats of mixing are reported in function of the age of sample

t/day	Ref. 1 ^{a,b}	4CH ^{a,b}	5CH ^{a,b}	6CH ^{a,b}	7CH ^{a,b}	8CH ^{a,b}	10CH ^{a,b}	11CH ^{a,b}	12CH ^{a,b}
20	1.9±0.1	1.9±0.1	1.9±0.1	1.9±0.1	1.9±0.1	1.9±0.1	1.9±0.1	1.9±0.1	1.9±0.1
90	1.9±0.1	2.1±0.1	2.1±0.1	2.0±0.1	2.0±0.1	2.0±0.1	1.9±0.1	2.3±0.1	1.9±0.1
300	1.9±0.1	2.6±0.1	2.9±0.1	2.8±0.1	2.1±0.1	2.4±0.1	2.4±0.1	3.0±0.1	2.0±0.1

^aExcess heat of mixing, in J (kg of solvent in initial solution)⁻¹.^bThe excess heat of mixing of the solvent used for preparation do not vary with time while that of the samples does**Table 13** Extremely diluted solutions of 2,4-dichlorophenoxyacetic acid, 2,4-D, in H_4SiO_4 $5 \cdot 10^{-5}$ M as solvent. The excess heats of mixing are reported in function of the age of sample

t/day	Ref. 1 ^{a,b}	4CH ^{a,b}	5CH ^{a,b}	6CH ^{a,b}	7CH ^{a,b}	8CH ^{a,b}	10CH ^{a,b}	11CH ^{a,b}	12CH ^{a,b}
20	1.5±0.1	1.5±0.1	2.7±0.1	1.6±0.1	1.5±0.1	1.8±0.1	1.5±0.1	1.5±0.1	1.5±0.1
180	1.6±0.1	1.9±0.1	4.5±0.1	2.2±0.1	1.6±0.1	2.5±0.1	1.7±0.1	1.7±0.1	1.7±0.1

^aExcess heat of mixing, in J (kg of solvent in initial solution)⁻¹.^bThe excess heat of mixing of the solvent used for preparation do not vary with time while that of the samples does

Table 14 Extremely diluted solutions of 2,4-dichlorophenoxyacetic acid, 2,4-D, in NaHCO_3 $5 \cdot 10^{-5}$ M as solvent. The contents (mol L^{-1}) of sodium are reported in function of the age of sample

t/day	Ref. 1 ^a	4CH ^a	5CH ^a	6CH ^a	7CH ^a	8CH ^a	10CH ^a	11CH ^a	12CH ^a
20	$4.7 \cdot 10^{-5}$	$4.8 \cdot 10^{-5}$	$4.8 \cdot 10^{-5}$	$4.8 \cdot 10^{-5}$	$4.7 \cdot 10^{-5}$	$4.7 \cdot 10^{-5}$	$4.7 \cdot 10^{-5}$	$4.7 \cdot 10^{-5}$	$4.7 \cdot 10^{-5}$
300	$4.4 \cdot 10^{-5}$	$4.4 \cdot 10^{-5}$	$4.5 \cdot 10^{-5}$	$4.5 \cdot 10^{-5}$	$4.5 \cdot 10^{-5}$	$4.3 \cdot 10^{-5}$	$4.5 \cdot 10^{-5}$	$4.7 \cdot 10^{-5}$	$4.3 \cdot 10^{-5}$

^aThe error in the determination of Na^+ is $5 \cdot 10^{-6}$ mol L^{-1}

Table 15 Extremely diluted solutions of 2,4-dichlorophenoxyacetic acid, 2,4-D, in H_2SiO_4 $5 \cdot 10^{-5}$ M as solvent. The contents (mol L^{-1}) of sodium are reported in function of the age of sample

t/day	Ref. 1 ^a	4CH ^a	5CH ^a	6CH ^a	7CH ^a	8CH ^a	10CH ^a	11CH ^a	12CH ^a
20	$5 \cdot 10^{-5}$	$5 \cdot 10^{-5}$	$5 \cdot 10^{-5}$	$6 \cdot 10^{-5}$	$5 \cdot 10^{-5}$	$5 \cdot 10^{-5}$	$5 \cdot 10^{-5}$	$5 \cdot 10^{-5}$	$5 \cdot 10^{-5}$
180	$5 \cdot 10^{-5}$	$5 \cdot 10^{-5}$	$5 \cdot 10^{-5}$	$6 \cdot 10^{-5}$	$5 \cdot 10^{-5}$	$5 \cdot 10^{-5}$	$5 \cdot 10^{-5}$	$5 \cdot 10^{-5}$	$5 \cdot 10^{-5}$

^aThe error in the determination of SiO_2 is $5 \cdot 10^{-6}$ mol L^{-1}

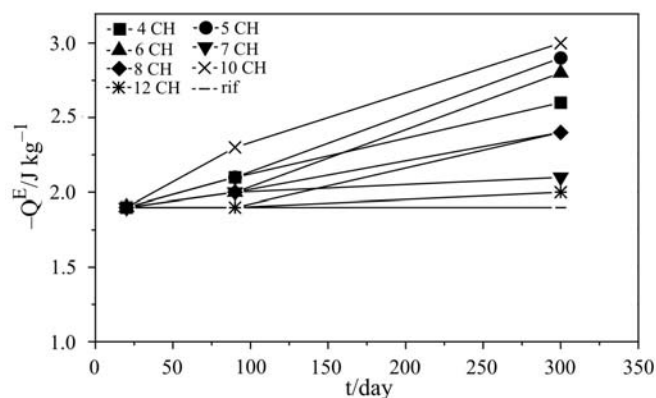


Fig. 1 Excess heats of mixing of 'extremely dilute solutions' vs. the age of the samples. Preparation of 2,4-dichlorophenoxyacetic acid in NaHCO_3 $5 \cdot 10^{-5}$ M as solvent

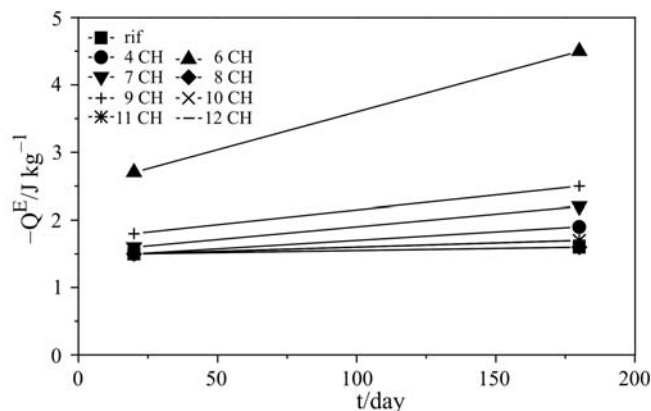


Fig. 2 Excess heats of mixing of 'extremely dilute solutions' vs. the age of the samples. Preparation of 2,4-dichlorophenoxyacetic acid in H_4SiO_4 $5 \cdot 10^{-5}$ M as solvent

preparation. As Figs 1 and 2 show, the varying value of the thermodynamic parameters as a function of time is a feature of the extremely diluted solutions only, those that underwent the succession–dilution cycle, and is not detected in the references (Tables 12 and 13). For the samples reported in graphic, the analytical determination of impurities has been effected in function of the age. This analysis has not underlined an increase of the content of chemical impurities.

We examined the nature of the initially present solute and the dilution degree. We obtained 'extremely diluted solutions' originating from different solutes and with dilution ranging from 4CH to 12CH. A correlation between those two factors, initial solute and dilution, and the thermodynamic behaviour is not yet suggested by our data as a whole. It is noteworthy that those solutions that underwent the dilution cycle, but not the succession one, do not differ from the reference solvent. It must be

underlined that the iterative procedure of dilutions and succussions works also in the absence of the initial solute. The succussion phenomenon thus appears as fundamental in order to activate the different behaviour of the extremely diluted solutions.

Since the containers employed to prepare and store the ‘extremely diluted solutions’ are made of glass, we performed measures of atomic absorbance to determine the released quantity of sodium oxide, appearing as bicarbonate in solution, as well as spectrophotometric measures (UV-VIS) to determine the presence of silica under the form of undissociated silicic acid. Solutions of sodium bicarbonate and silicic acid in known quantities were prepared, to produce the calibration curves needed to compensate for chemical impurities in the ‘extremely diluted solutions’.

The obtained data put in evidence a differing behaviour, with respect to the reference water with the same amount of impurities, when gradually increasing the concentration of impurities as shown in Figs 3–5. For the ‘extremely diluted solutions’ the experimentally obtained values differ from that attributable to the sole impurities; those solutions exhibit a different physico-chemical picture to that of the reference solvent, as can be seen in Tables 10 and 11.

Such results seem to suggest that substances released by the glass of the containers, found as traces, are able to ‘activate’ the ‘extremely diluted solutions’ in the sense that they exhibit a different thermodynamic picture from that of the solvent, the chemical composition of which is identical. A possible interpretation of the phenomenon is that those substances allow the solvent, probably due to the succussion process, to acquire a varied structural organisation. By controlling every parameter af-

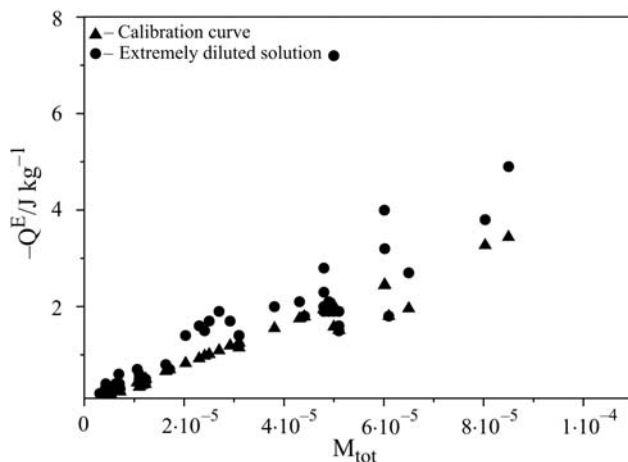


Fig. 3 Comparison between the experimentally measured excess heats and the computed ones. ● – experimentally measured, ▲ – computed taking into account the experimentally measured contents of sodium, calcium and silicic acid. In this figure we report the Q^E of all samples studied without taking into account the nature of the solutes nor the degree of dilution. The difference between the values of Q^E of the samples and those of the calibration curve, that takes into account the chemical contribution due to the analytically determined impurities, is attributable to the new phenomenon

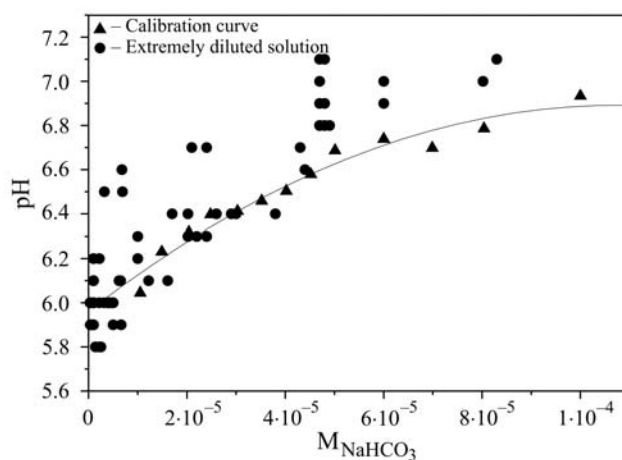


Fig. 4 Comparison between the experimentally measured pH values and the calibration curve. ● – experimentally measured, ▲ – measured for solutions of NaHCO_3 at known content. In this case the contribution the H_4SiO_4 is not influent because the very low degree of dissociation. In this figure we report the pH of all samples studied without taking into account the nature of the solute nor the degree of dilution. The difference between the values of pH of the samples and those of the calibration curve, that takes into account the chemical contribution due to the analytically determined impurities, is attributable to the new phenomenon

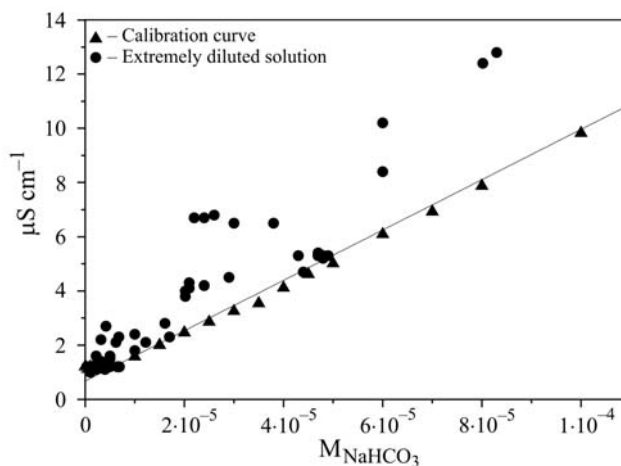


Fig. 5 Comparison between the experimentally measured electrical conductivity values and the computed ones. ● – experimentally measured, ▲ – measured for solutions of NaHCO_3 at known content. In this figure we report the electrical conductivity of all samples studied without taking into account the nature of the solute nor the degree of dilution. The difference between the values of the electrical conductivity of the samples and those of the calibration curve, that takes into account the chemical contribution due to the analytically determined impurities, is attributable to the new phenomenon

fecting a preparation maybe it will be possible in the future to better the qualitative and/or quantitative reproducibility of the phenomenon under examination.

The thermodynamic picture of the 'extremely diluted solutions' has been made even richer by pH and electrical conductivity measures.

pH measures reveal a statistically higher value than that of the reference solvent with the same degree of impurities coming from the glass of the containers. The difference between the measured value and that calculated according to the contents of impurities has been attributed also to a variation of the activity of the solvent, probably due to a different structural organisation of the solvent itself. To confirm the hypothesis of a variation of activity of the solvent, caused by structural variations, measures of e.m.f. in suitable galvanic cells are planned, to estimate the variation of activity of a solute (NaCl, NaClO₄) dissolved in it in ponderal quantities. This would put in evidence the variation of activity in the solvent that has undergone the dilutions and succussions procedure.

Electrical conductivity measures were performed on the studied samples, at 25°C. Such measures put in evidence a systematic higher value of the specific conductivity with respect to that of the solvent. In this case too our discussion of the 'extremely diluted solutions' behaviour keeps track of sodium bicarbonate, the amount of which is determined through atomic absorbance. The presence of bicarbonate alone cannot explain the increase in electrical conductivity for the samples, with respect to the solvent at an equal concentration of 'chemical impurities', just like it could not explain the whole excess heat found in pH measures.

For the solutions under study, measures of excess heat and electrical conductivity turn out to be correlated, pointing at a presumably single cause of the exhibited behaviour. 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 [32]. The migration of ions results 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.

Conclusions

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. There is no doubt that, from a strictly chemical point of view, the 'extremely diluted solutions' are exactly identical to the solvent employed in their preparation: twice distilled water, with a certain amount of chemical impurities deriving from the dissolution of modest quantities of alkaline oxides and silica from the glass containers. Even when accounting for the contributions to the studied parameters that come from the latter substances, the conclusion is that the behaviour of the 'extremely diluted solutions' is measurably different from that of the control solutions. What's more, a really intriguing phenomenon is that of the evolution of some

physico-chemical parameters with time, that hints at the hypothesis of a trigger effect on the formation of molecular aggregates, following the succussion procedure, a not easily reproducible effect, but one that once established would permit a slow growing of the thermodynamic parameters, probably following the increase of the number of aggregates or of their size or of both.

Hence, a necessary condition to be able to experimentally ascertain variations of the thermodynamic 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. The latter fact could be one of the causes of so many failures in this research field, failures that conjure in keeping it too 'mysterious' still. It is however our hope that the frame outlined in this and in the two preceding works [15, 16], will elicit enough scientific concern as to induce other researches to repeat this kind of experiments. Should those repetitions yield positive results, then our models of water will probably have to be revised in order to account for these latest experimental results.

* * *

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