Journal of Thermal Analysis and Calorimetry, Vol. 84 (2006) 2, 317–323

'EXTREMELY DILUTED SOLUTIONS' AS MULTI-VARIABLE SYSTEMS
A study of calorimetric and conductometric behaviour as a function of the parameter time

V. Elia[1,*], *L. Elia*[2], *P. Cacace*[1], *E. Napoli*[1], *M. Niccoli*[1] *and F. Savarese*[1]

[1]Department of Chemistry, University 'Federico II' of Naples, Complesso Universitario di Monte S. Angelo, via Cintia 80126 Naples, Italy
[2]Department of Physics, University 'Federico II' of Naples, via Coroglio 156, 80126 Naples, Italy

A large number of thermodynamic and transport measurements were conducted on 'extremely diluted solutions' (EDS). The physico-chemical results presented here allow us to hypothesize that the process of iterated dilutions and succussions is capable of modifying in a permanent way the features of water. A really intriguing phenomenon was the evolution of two physico-chemical properties with time. The calorimetric and conductometric measures were carried out as a function of the age of the samples. We found a good linear correlation between these two independent parameters, also as a function of time. A careful study of the phenomenon puts in evidence that these solutions are characterised by multiple independent variables. The EDS behave as complex systems, influenced by peculiar aspects of the preparation technique and also by the storage conditions. The EDS are far-from-equilibrium systems, capable of auto-organising themselves as a consequence of little perturbations.

Keywords: *calorimetry, conductivity, extremely diluted aqueous solutions, far-from-equilibrium system, temporal evolution*

Introduction

In preceeding papers [1–6] we studied the 'extremely diluted solutions', EDS, putting in evidence the fundamental importance of the preparation technique. The EDS have been described as solutions obtained through a special process in which the dilution and succussion operations are repeated in every step [1–6]. The process is carried out until extreme dilutions are reached, namely until the composition of the solution is identical to that of the solvent used. The EDS were studied through chemical-physical measurements to verify whether these particular solutions are characterized by an alteration of the 'structure' of the solvent. The calorimetric and conductometric measurements, in particular, have strongly confirmed this hypothesis.

The reported results have shown that every preparation is characterized by numerous factors also related to the storage of the solutions. In each physico-chemical measurement, only one factor was varied. By studying one factor of preparation at a time we have evaluated the contribution of each parameter to the properties of the EDS. This way we evidenced some key factors: nature of solute, degree of dilution, presence of electrolytes [3], number of strokes during succussion and especially the age of samples [5, 6]. We prepared and studied the EDS using always the same active principles as solute, and using as solvent some solutions with a low and known concentrations of sodium bicarbonate or silicic acid [3–6]. This study has also shown that even controlling the parameters affecting a preparation, the quantitative reproducibility of the phenomenon is poor.

The results of the paper of Samal and Geckeler are in line with this behaviour [7]. In the article, they observed that the size of clusters of molecules in several substances (e.g. fullerene, cyclodextrines, NaCl, …) increased with decreasing concentration and that the results depend on the variation of the initial conditions.

The behaviour of EDS is characteristic of a complex system, in far-from-equilibrium conditions. In these systems the sum of the parts does not correspond to the whole. Therefore studying and analysing the single parts of the system does not guarantee an understanding of the system and its evolution. A far-from-equilibrium system can introduce non linear behaviours. This means that with even a slight change in the conditions, the system can evolve. A far-from-equilibrium system can persist for a long time in steady state but can also change for a small perturbation, leading to the auto-organization of its structure. Similar conclusions are reached by Lobyshev *et al.* [8]. These authors state that, as a result of perturbations due to the very low concentrations and electromagnetic fields, water and aqueous solutions can

---

[*] Author for correspondence: elia@chemistry.unina.it

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

evolve as complex systems, capable of auto-organising by producing long-scale realignments.

In addition, Rey [9] states that 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 this paper we report a study on the EDS carried out at different ages of the samples, since we noticed that time is the factor influences mostly the value of the measured parameters.

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 contact with atmospheric carbon dioxide by means of suitable traps. The EDS were prepared using as solvent a solution of low and known concentration ($5\cdot10^{-5}$–$10\cdot10^{-5}$ mol L^{-1}) of sodium bicarbonate and, in two cases, silicic acid.

Procedures

The EDS were prepared by iterating two steps: dilution and dynamization. The dilution can be centesimal or korsakovian. For a centesimal dilution, the starting point is a 1% in mass solution [10]; for example, to prepare a 2,4-dichlorophenoxyacetic acid (2,4-D) solution, 1 g of 2,4-D gets added to 99 g of solvent. After the mechanical treatment, plain 'dynamization', the solution so obtained is called '1 centesimal hahnemannian' or 1CH in short, and the name of the solution begins with the name or formula of the solute, or a simple abbreviation of it. So in the preceding example, 2,4-D 1CH is obtained. In order to prepare the 2 centesimal hahnemannian (2,4-D 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, when carrying out the dilutions, the bottle containing the solution to dilute is never changed: each dilution step consists of disposing 99% of the liquid from the bottle, and then refilling to 100% with pure water, before moving to the 'dynamization' step. The solution so obtained is called '1 centesimal korsakovian' or 1CK in short (e.g. NaCl 1CK).

The process of 'dynamization' consists of either a violent shaking (succussion) of the solution by means of a mechanical apparatus (DYNA HV 1 by Debofar N.V.S.A. Belgium), or of shaking obtained by a vortex (Inter Continental equipment). In a single succussion process 50–500 vertical strokes were 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 was a solution with known contents of sodium bicarbonate or silicic acid. After their preparation, the EDS were stored at room temperature. The samples were then tested at different ages, varying from several months to several years.

Samples of two different solutes were prepared: Arsenicum Sulphuratum Rubrum, (As_4S_4, ASR) and 2,4-dichlorophenoxyacetic acid (2,4-D). 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 (mol L^{-1}); a solution of sodium bicarbonate $6.0\cdot10^{-5}$ M (mol L^{-1}); a solution of sodium bicarbonate $7.5\cdot10^{-5}$ M (mol L^{-1}); a solution of sodium bicarbonate $10\cdot10^{-5}$ M (mol L^{-1}). In some preparations the initial solution contained only the solvent and no 'active principle'. Such preparations are known as potentized water (*W*).

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 to mix 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 $3\cdot10^{-3}$ 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 [11]:

$$\Delta H_{mix}(m_x^i, m_y^i \rightarrow m_x^f, m_y^f) = (dQ/dt)/P_w \qquad (1)$$

where d*Q*/d*t* is the heat flux (Watt), 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.

According to the previous papers [12–18], 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:

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

where h_{xx}, h_{yy} and h_{xy}, the enthalpic interaction coefficients, are adjustable parameters. The *h* coefficients appearing in Eq. (2) represent the enthalpic contributions to the Gibbs free energy coefficients characterising the interaction between pairs, triplets or higher order 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 EDS is less than $1\cdot10^{-5}$ mol kg^{-1}, while the concentration of solute x (NaOH) is $1\cdot10^{-2}$ mol kg^{-1}, the only contribution in the previous equation is that due to x, namely the heat of dilution of solute x.

Conductivity

Systematic measures of electrical conductivity (μS cm^{-1}) were performed on the EDS. Conductivity data were collected with an YSI conductivity instrument, model 3200, using a cell with a cell constant=1.0 cm^{-1}. The cell constant was periodically measured, using a standard KCl solution. The values of conductivity were temperature corrected to 25°C using a pre-stored temperature compensation for pure water [19]. Hence, the electrical conductivity of the EDS should depend solely on the presence of the electrolytes.

Results and discussion

In Table 1 we report the results of the study on the EDS performed with two experimental techniques: mixing-flow microcalorimetry and electrical conductivity. In Table 1 we report the active principle, the degree of dilution, the excess heats of mixing, $Q^{\mathrm{E}}_{\mathrm{mix}}$ (J kg^{-1}) and the excess conductivity, χ^{E} (μS cm^{-1}). Each EDS was analysed on several successive occasions (i.e. different portions of a single sample were employed in different experimental measures), to put in evidence the calorimetric and conductometric behaviour as a function of the age of the samples.

We determined the heats of mixing of sodium hydroxide with the EDS, and almost always found an excess heat of mixing. $Q^{\mathrm{E}}_{\mathrm{mix}}$ defined as the heat of mixing of sodium hydroxide with the EDS, minus the heat of mixing of the same NaOH when mixed with the untreated solvent. It follows that the chemical contributions due to CO_2 and sodium bicarbonates or silicic acid are removed and do not affect the value of $Q^{\mathrm{E}}_{\mathrm{mix}}$. On the same EDS we measured the electric conductivity. Similarly to the previous case, we define the excess conductivity, χ^{E}, as the conductivity, χ, of the EDS minus the conductivity, χ_{w}, of the untreated solvent. The chemical contributions due to CO_2 and sodium bicarbonate were removed in this case too.

The actual concentration of sodium was determined through atomic absorbance, and the silicic acid concentration by measuring the UV absorption of complexes with ammonium molybdate.

The results obtained through the analytical measurements characterize the untreated solvent and were employed to obtain the values of the excess heats of mixing and excess conductivity [3–6].

In the last few years the ‘extremely diluted solutions’, EDS, have been the target of a systematic study [1–9]. The experimental results have shown an anomalous thermodynamic picture. The EDS have a chemical composition that is not different from that of the solvent used for the preparation. The central point of the preparation technique is the repetition of the dilution process, to which the mechanical shaking process follows, in every step. We conducted thermodynamic and transport measurements of the solutions and of the interaction of those solutions with acids and bases [1–3, 5, 6]. The results of the experiments performed on the EDS have been unexpected. The heats of mixing of sodium hydroxide with the EDS have allowed us to hypothesize a variation in the distribution of hydrogen bonds with respect to the solvent. A relevant exothermic excess heat of mixing has been measured in most of the measures. To explain these results we have hypothesized that the EDS exhibit a larger number of aggregates of water molecules than untreated water. These aggregates are characterized by an increase of the number and/or energy of the hydrogen bonds. Two possible interaction mechanisms can be used for explaining the calorimetric behaviour of the EDS. First mechanism: in the mixing with the EDS, the Na^{+} and OH^{-} ions would more efficiently hydrate than in water. The ions present in probe solutions probably use in a preferential way the aggregates of water molecules found in the EDS solvent to build their hydration sphere, with a consequent increase of the heat of mixing. In the mixing process an increase of the average number of water molecules of hydration accounts for the exothermic effect [20]. Second mechanism: the increase of pH during the mixing with NaOH solutions could induce a reduction or a disruption of the aggregates of water molecules [1]. To explain the exothermic excess heat of mixing we need to invoke the effect of destructured hydration spheres of hydrophilic solutes [11]. We suppose that the hydration sphere of water molecules aggregates is less ordered than that of the solvent. In the mixing process, the aggregates are disrupted by the increase of pH and this produces two opposite contributions. The net result is an exothermic effect.

A very effective kind of measurements has been that of electrical conductivity, at 298 K. Such measures put in evidence a systematic higher value of the specific conductivity with respect to that attributable to the presence of electrolytes, determined through atomic absorbance [3–6]. The χ^{E} is substantially posi-

Table 1 Thermodynamic and transport properties for extremely diluted solutions of Arsenicum Sulphuratum Rubrum, (ASR: As_4S_4), 2,4-dichlorophenoxyacetic acid (2,4-D) and potentized water (*W*), at 298 K

System	$-Q^{\mathrm{E}}_{\mathrm{mix}}$[1]	$\chi^{\mathrm{E},2}$	System	$-Q^{\mathrm{E}}_{\mathrm{mix}}$[1]	$\chi^{\mathrm{E},2}$
	20–750 days[3]			800–1400 days[4]	
ASR 7CH[a]	2.10	3.3	2,4-D 3CH[l]	0.58	3.6
ASR 12CH[a]	0.52	4.8	2,4-D 4CH[l]	3.51	20.0
ASR 14CH[a]	1.07	3.3	2,4-D 6CH[l]	1.38	7.9
ASR 18CH[a]	0.59	10.4	2,4-D 8CH[l]	1.88	10.2
ASR 22CH[a]	0.47	3.8	2,4-D 10CH[l]	2.97	15.5
ASR 27CH[a]	0.29	3.2	2,4-D 12CH[l]	0.58	4.5
ASR 29CH[a]	0.21	5.3	2,4-D 8CH[m]	1.90	6.5
ASR 8CH[b]	0.79	3.6	2,4-D 4CH[m]	1.97	13.6
ASR 9CH[b]	1.01	5.5	2,4-D 9CH[m]	1.27	4.6
ASR 10CH[b]	0.76	4.9	2,4-D 10CH[m]	2.29	15.8
ASR 12CH[b]	0.54	4.6	2,4-D 5CH[n]	0.38	0.6
ASR 13CH[b]	0.18	4.9	2,4-D 6CH[n]	0.79	2.6
ASR 14CH[b]	0.69	4.0	2,4-D 9CH[n]	0.58	2.2
ASR 15CH[b]	0.63	4.9	2,4-D 11CH[n]	0.18	0.3
ASR 16CH[b]	2.11	9.0	2,4-D 12CH[n]	0.38	1.7
ASR 18CH[b]	0.73	5.2	2,4-D 4CH[n]	0.42	4.2
ASR 20CH[b]	0.46	4.7	2,4-D 6CH[n]	1.74	5.1
ASR 22CH[b]	0.42	3.4	2,4-D 7CH[n]	1.08	1.9
ASR 24CH[b]	0.59	2.8	2,4-D 8CH[n]	0.33	1.1
ASR 28CH[b]	0.95	6.6	2,4-D 9CH[n]	0.57	2.2
ASR 29CH[b]	0.50	3.9	2,4-D 12CH[n]	2.89	17.7
ASR 30CH[c]	0.96	5.0	2,4-D 6CH[o]	0.79	0.5
ASR 9CH[c]	1.37	6.7	2,4-D 9CH[o]	0.59	0.7
ASR 30CH[c]	1.11	5.9	2,4-D 12CH[o]	0.90	1.9
2,4-D 6CH[d]	0.49	2.4	ASR 18CH[a]	0.81	5.3
2,4-D 9 CH[d]	0.48 0.51	2.1 2.4	ASR 25CH[a]	1.22	6.7
ASR 25CH[e]	0.18	0.3	ASR 5CH[a]	1.60	9.0
W 9CH[f]	0.51	2.5	ASR 7CH[a]	1.72	8.7
W 12CH[f]	1.15 0.64 0.60	5.3 3.1 2.6	ASR 17CH[a]	1.14	5.2
W 30CH[f]	2.83 2.25 1.18	10.5 8.4 1.4	W 30CH[f]	0.38	1.7
W 6CH[g]	0.87	3.5	W 9CH[g]	1.28	3.1
W 9CH[g]	0.61	2.5			
W 12CH[g]	0.25 0.36 0.25	1.5 1.5 1.5			
W 30CH[g]	0.42 0.08 0.10 0.50	2.3 0.4 0.5 2.1			
W 12CH[h]	1.13 1.43	4.0 4.0			

Table 1 Continued

System	$-Q^{E}_{mix}$[1]	χ^{E}[2]	System	$-Q^{E}_{mix}$[1]	χ^{E}[2]
	20–750 days[3]			20–750 days[3]	
W 30CH[h]	0.63 0.90	4.0 4.9	ASR 17CH[b]	1.15	3.9
W 1CK[i]	0.49	3.5	ASR 7CH[b]	1.29	3.8
W 3CK[i]	0.33	3.1	ASR 12CH[c]	0.77	5.0
W 5CK[i]	0.19	2.2	ASR 30CH[c]	1.40	10.0
W 7CK[i]	0.09	2.0	2,4-D 6CH[d]	0.49	1.2
W 9CK[i]	0.35	2.9	2,4-D 12CH[d]	0.23	1.2
W 12CK[i]	0.15 0.13 0.42 0.19 0.41	1.9 2.3 2.8 2.2 2.8	W 30CH[f]	2.22 0.00 0.15	10.0 3.9 1.6
W 30CK[i]	0.51	4.1	W 9CH[f]	0.92	2.5
2,4-D 3CH[l]	0.03	0.5	W 12CH[g]	0.77 1.08	3.4 3.3
2,4-D 4CH[l]	0.03	0.5	W 30CH[g]	1.10 2.20	3.6 6.6
2,4-D 6CH[l]	0.03	0.5	W 12CH[h]	2.13	8.8
2,4-D 8CH[l]	0.03	0.5	W 30CH[h]	0.12 0.57 0.10 0.10	1.6 2.5 2.5 2.8
2,4-D 10CH[l]	0.03	0.5	W 3CK[i]	0.40	1.2
2,4-D 12CH[l]	0.03	0.5	W 5CK[i]	0.00	0.2
2,4-D 8CH[m]	0.06	0.0	W 7CK[i]	0.00	0.1
2,4-D 4CH[m]	0.05	0.0	W 12CK[i]	0.14 0.30 0.41 0.35 0.47	0.8 1.7 0.8 1.5 0.7
2,4-D 8CH[m]	0.05	0.0	W 30CK[i]	0.51 0.25	1.9 1.3
2,4-D 9CH[m]	0.10	0.0	W 30CH[i]	0.10	1.3
2,4-D 10CH[m]	0.05	0.0	W 3CK[i]	0.63	3.2
ASR 13CH[a]	1.01	3.4	W 7CK[i]	0.45	1.5
ASR 8CH[b]	0.61	2.9	W 12CK[i]	0.12	1.5
ASR 13CH[b]	2.70	12.3	W 30CK[i]	0.45 0.71	2.1 2.4
ASR 14CH[b]	1.06	4.5			
ASR 20CH[b]	0.80	3.0			
ASR 25CH[b]	0.61	3.2			

[1] Excess heat of mixing in J (kg of solvent in final solution)$^{-1}$. [2] Excess conductivity in μS cm^{-1}. [3] Samples with an age between 20 and 750 days. [4] Samples with an age between 800 and 1400 days. [a] Active principle: Arsenicum Sulphuratum Rubrum. Solvents: 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. [e] Active principle: Arsenicum Sulphuratum Rubrum. Solvent: aqueous solution of $NaHCO_3$ $1\cdot10^{-4}$ M. Dynamization method: vortex. [f] Active principle: none. Solvent: aqueous solution of $NaHCO_3$ $7.5\cdot10^{-5}$ M. Dynamization method: succussion. [g] Active principle: none. Solvent: aqueous solution of $NaHCO_3$ $7.5\cdot10^{-5}$ M. Dynamization method: vortex. [h] Active principle: none. Solvent: aqueous solution of $NaHCO_3$ $1\cdot10^{-4}$ M. Dynamization method: succussion. [i] Active principle: none. Solvent: aqueous solution of $NaHCO_3$ $6\cdot10^{-5}$ M. Dynamization method: succussion. [l] Active principle: 2,4-dichlorophenoxyacetic acid. Solvent: aqueous solution of $NaHCO_3$ $5\cdot10^{-5}$ M. Dynamization method: succussion. [m] Active principle: 2,4-dichlorophenoxyacetic acid. Solvent: aqueous solution of H_4SiO_4 $5\cdot10^{-5}$ M. Dynamization method: succussion. [n] Active principle: 2,4-dichlorophenoxyacetic acid. Solvent: aqueous solution of $NaHCO_3$ $5\cdot10^{-5}$ M. Dynamization method: succussion. [o] Active principle: 2,4-dichlorophenoxyacetic acid. Solvent: aqueous solution of H_4SiO_4 $5\cdot10^{-5}$ M. Dynamization method: succussion

tive and increases with the age of samples [4, 6]. Therefore the excess heat of mixing and excess conductivity have shown that the EDS have different physico-chemical features with respect to the solvent.

The whole picture is more articulated, because the physical quantities that influence the phenomenon are numerous and the properties exhibited by each sample turn out to be characterised by several factors. Quantitatively the most important factor is time. As described in previous papers [4–6], the values of the physico-chemical parameters increase with the age of samples, with different laws. To acquire information on the hypothesized supramolecular structures of water, we have analyzed the influence of time on the properties of EDS. The excess heat of mixing, $Q^{\mathrm{E}}_{\mathrm{mix}}$, and the excess conductivity, χ^{E}, turn out to be linearly correlated, as both of them also increase with the age of samples. Figure 1 reports the excess conductivity *vs*. the excess heat of mixing. The values of two sets of data are presented. In one set, samples have an age ranging from 20 to 700 days; in the other set the age range is 800–1400 days. A linear trend is found for both sets, but with different slopes.

The excess heat of mixing and excess conductivity variation as a function of time can be explained as an increase in the number or size of the aggregates or both. Figure 2 reports the excess conductivity and excess heat of mixing *vs*. the age of the samples. This graph shows the distribution for every age at which the conductometric and calorimetric measurements have been performed. The distribution is a further evidence that the EDS are complex systems, influenced by numerous factors. Our systematic study underlines the key factors affecting the solutions under examination. Nature of solute, degree of dilution, presence of electrolytes, succussion and time are very important factors on the physico-chemical properties of the EDS. All the aforementioned parameters contribute to determine the complexity of the EDS and the distribution values.

Despite the EDS complexity, the $Q^{\mathrm{E}}_{\mathrm{mix}}$ and χ^{E} values regularly increasing time. This shows that time is the most important factor from the quantitative point of view. In particular, it can be observed that the excess conductivity increases more than the excess heat. Figure 3 reports the minimum, maximum and average $Q^{\mathrm{E}}_{\mathrm{mix}}$ and χ^{E} values as a function of age.

A quantitative analysis of Fig. 3 shows that:

- the minimum, maximum and average $Q^{\mathrm{E}}_{\mathrm{mix}}$ and χ^{E} values of the distribution for every age regularly increase with the samples age.
- The temporal evolution of the excess conductivity is faster than that of the excess heat of mixing.

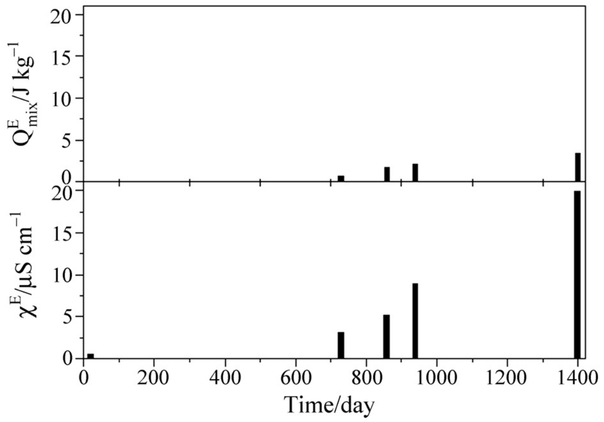

Fig. 2 Excess heat of mixing, $Q^{\mathrm{E}}_{\mathrm{mix}}$, and excess conductivity, χ^{E}, *vs*. the age of the samples

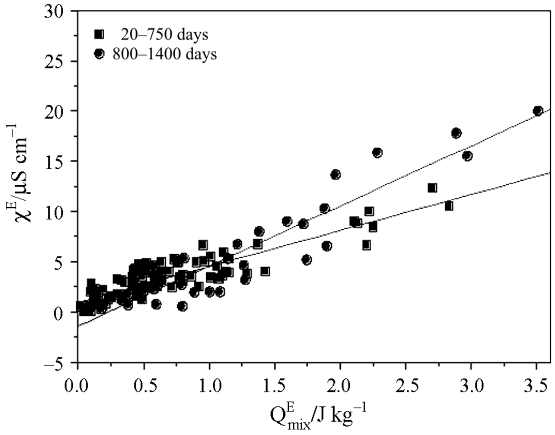

Fig. 1 Excess conductivity *vs*. excess heat of mixing. Samples with an age between 20–750 and 800–1400 days are shown. For the first set, the line $y=a+bx$ gives as values: $a=0.9\pm0.1$; $b=3.6\pm0.1$ and $R=0.91$, while for the second one, gives as values: $a=-1.4\pm0.7$; $b=6.0\pm0.3$ and $R=0.93$

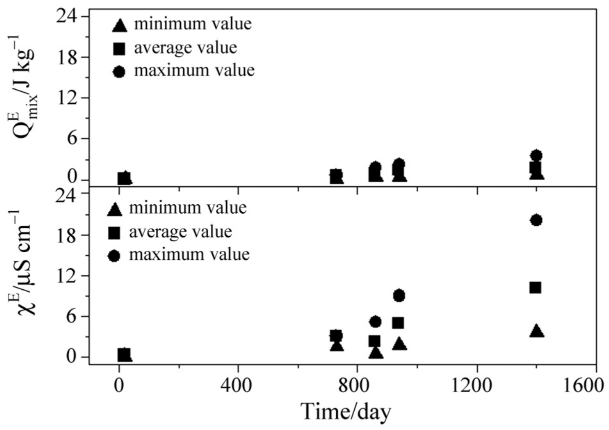

Fig. 3 The minimum, average and maximum $Q^{\mathrm{E}}_{\mathrm{mix}}$ value and the minimum, average and maximum χ^{E} value *vs*. the age of the samples

Conclusions

This evolution could depend on the variation of the molecular aggregates that characterize the supramolecular structure of water. As we have previously stated, the temporal evolution can depend on an increase in the number or size of the aggregates or both. The conductometric evolution could be due to an increase in the dimension of the aggregates of water molecules, rather than to an increase of their number. In fact it is well known that protons can move in aqueous solutions through a rapid hopping mechanism [21]. Therefore the ions migration is strongly associated to clusters of water molecules made through hydrogen bonds. A structuring of the solvent in a linear fashion could favour the conduction mechanism, and explain a higher value for the conductivity in the EDS.

The excess heat of mixing would probably be influenced mostly by an increase in the number of aggregates, according to the hypothesis of more efficient hydration rather than the destructive one.

We are working to confirm this interpretation model and to obtain further information about the parameters that influence the properties of the EDS.

Acknowledgements

This work was financied by Regione Campania with funds for Non-Conventional Medicines Cap.7100.

References

1 V. Elia and M. Niccoli, Ann. New York Acad. Sci., 879 (1999) 241.
2 V. Elia and M. Niccoli, J. Therm. Anal. Cal., 61 (2000) 527.
3 V. Elia and M. Niccoli, J. Therm. Anal. Cal., 75 (2004) 815.
4 V. Elia, S. Baiano, I. Duro, E. Napoli, M. Niccoli and L. Nonatelli, Homeopathy, 93 (2004) 144.
5 V. Elia, E. Napoli, M. Niccoli, L. Nonatelli, A. Ramaglia and E. Ventimiglia, J. Therm. Anal. Cal., 78 (2004) 331.
6 V. Elia, M. Marchese, M. Montanino, E. Napoli, M. Niccoli, L. Nonatelli and A. Ramaglia, J. Sol. Chem., 34 (2005) 947.
7 S. Samal and K. E. Geckeler, Chem. Commun., (2001) 2224.
8 V. I. Lobyshev, R. E. Shikhlinskaya and B. D. Ryzhikov, J. Molecular Liquids, 82 (1999) 73.
9 L. Rey, Physica A, 323 (2003) 67.
10 S. Hahnemann, Organon, VI Edizione, RED, 1985.
11 G. Castronuovo, V. Elia and F. Velleca, Curr. Top. Solution Chem., 2 (1997) 125.
12 W. G. McMillan Jr. and J. E. Mayer, J. Chem. Phys., 13 (1945) 276.
13 H. L. Friedman and C. V. Krisnann, J. Solution Chem., 2 (1973) 119.
14 F. Franks and M. D. Pedley, J. Chem. Soc. Faraday Trans I, 79 (1983) 2249.
15 J. J. Kozac, W. S. Knight and W. Kauzmannn, J. Chem. Phys., 48 (1968) 675.
16 I. R. Tasker and R. H. Wood, J. Solution Chem., 11 (1982) 469.
17 C. Jolicoeur and G. Lacroix, Canad. J. Chem., 54 (1976) 624.
18 M. Fujisawa, M. Maeda, S. Takagi and T. Kimura, J. Therm. Anal. Cal., 69 (2002) 841.
19 T. S. Light and S. L. Licht, Anal. Chem., 59 (1987) 2327.
20 G. Barone, G. Castronuovo, V. Crescenzi, V. Elia and E. Rizzo, J. Solution Chem., 3 (1978) 197.
21 C. J. T. de Grotthus, Ann. Chim. LVIII, 1806, 54.

Received: July 27, 2005
Accepted: October 29, 2005

DOI: 10.1007/s10973-005-7266-7