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CONDUCTOMETRIC AND CALORIMETRIC STUDIES OF THE SERIALLY DILUTED AND AGITATED SOLUTIONS

On the combined anomalous effect of time and volume parameters

P. Belon[1], *V. Elia*[2*], *L. Elia*[3], *M. Montanino*[2], *E. Napoli*[2] *and M. Niccoli*[2]

[1]Boiron, 21 rue de la Libération 60110 Sainte-Foy France
[2]Department of Chemistry, University 'Federico II' of Naples, Complesso Universitario di Monte S'Angelo, via Cintia, 80126 Naples, Italy
[3]Department of Physics, University 'Federico II' of Naples, Via Coroglio 156, 80126 Naples, Italy

We systematically analysed the experimental data related to the specific conductivities and heats in excess of several serially diluted and agitated solutions (SDA for short). For all of the analysed samples, we found that both the excess conductivity, χ^E (μS cm^{-1}), and excess heat, Q^E_{mix} (J kg^{-1}), varied with the age of the sample (up to 2 years of ageing). Furthermore, we found that after a certain period of ageing, small volume samples exhibited a much higher excess than large volume ones. The results we report in this paper are the product of a systematic study, during which we operated on known and constant volumes across the life of the samples. The incidence of volume on χ^E and Q^E_{mix} turned out to be overwhelming when compared with that of time. The temporal evolution of the smaller samples was found significantly higher than that of the larger volume ones. A careful numerical analysis of the results uncovered an extraordinary and unexpected correlation, of exponential kind, between the excess parameters and the volume of the solution in the container. As for the temporal evolution of these systems, we found that the measured excess heats and conductivity often reach a maximum. That led us to the conclusion that the temporal evolution of the physico-chemical parameters is not caused by the slow process of equilibrium attainment; on the contrary, these systems are far from equilibrium systems, dissipative structures, whose experimental behaviour is certainly due to the variation of the super-molecular structure of the solvent, water. The agitation phase during the preparation could be the trigger for the formation of dissipative structures and the emergence of the novel behaviour. We put forth a simple rationalizing hypothesis, based on the general idea of water as an auto-organizing system that, when elicited by even small perturbations, can enter a far from equilibrium state, sustained by the dissipation of the electromagnetic energy coming from the environment. (Dissipative Structures).

Keywords: *calorimetry, conductometry, dissipative structures, homeopathic dilution, SDA*

Introduction

Recent years have witnessed a renewed interest, by researchers, in the study of water. As a consequence, its properties appear increasingly unexpected, as they are found to clash with current theories [1–11]. Water constitutes a key element to the existence of all biological systems and behaves as a complex system, capable of auto-organizing as a consequence of small perturbations [12, 13]. Some papers, published in the last few years [14–21], involve a physico-chemical study of aqueous solutions obtained through an iterative process, of successive dilutions and violent agitations in the vertical direction, called succussions, that produces 'extremely diluted solutions' or SDA for short (serially diluted and agitated solutions). The chemical composition of solutions obtained through such a protocol is exactly that of the solvent used to dilute. It follows that an SDA should behave as its solvent, at least from a physico-chemical point of view. Actually, since the glass containers release alkaline oxides, it is also necessary to know the contents of Na^+ of these solutions, because sodium oxide, by interacting with the environmental CO_2, gives rise to sodium bicarbonate. Other works also have dealt with the physico-chemical properties of aqueous solutions that underwent a series of dilutions [12, 13, 22, 23]. As a whole, the cited studies back up the concept of water as a complex system, led to auto-organization by perturbations of small entity (dilution, succussion, electromagnetic fields, etc.), a process that alters the physico-chemical properties of the liquid, in a way that can be either permanent, temporary or oscillating. In particular it has been shown that conductivity and heat of mixing with alkaline solutions are affected by time and samples volume in the same way. Prompted by those previous results, we conducted a new systematic study, this time operating on known and constant volumes across the life of the samples.

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

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

Experimental

Materials

An SDA is prepared by iterating two steps: dilution and dynamization. The process of dynamization consists of a violent agitation (succussion) of the solution by means of a mechanical apparatus. To obtain what is called a centesimal dilution, the starting point is a 1% in mass solution [24]; to prepare, for example, a magnesium muriaticum (MM) solution, 1 g of $MgCl_2$ is added to 99 g of solvent. After the mechanical treatment, plain succussion, the resulting solution is called 1 centesimal hahnemannian or 1CH in short, and the solution is labelled with the name or formula of the solute, or a simple abbreviation of it. So in the previous example, MM 1CH is obtained. In order to prepare the 2 centesimal hahnemannian (MM 2CH), 1 g of the 1CH solution is added to 99 g of solvent, and the resulting solution is dynamized.

The SDA we employed were supplied by Cemon (Italy) or prepared by us. Just after their preparation, in some cases, or many months later, each SDA was divided into several samples, varying in volume from several hundred to 1 mL, that were stored at room temperature. These samples were then tested at different ages, ranging from several months to several years.

Methods

Calorimetry

The SDA were studied by means of two experimental techniques: mixing-flow microcalorimetry and conductometry. 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 sends the solutions into the calorimeter through Teflon tubes. The exact experimental procedure is detailed in previous papers [14–21]. The heat of mixing, Q_{mix}, is given by the following formula:

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

where $\mathrm{d}Q/\mathrm{d}t$ 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. Q_{mix} is given in J kg^{-1} of solvent in the final solution. All the measures of the heats of mixing were performed at 25°C. We determined the heats of mixing of probe solutions with the SDA, and found an excess heat of mixing in about the totality of the studied samples. The excess heat of mixing, Q_{mix}^E, is defined as: the heat of mixing of the probe solution with the SDA, Q_{mix}, minus the heat of mixing of the same probe solution with the untreated solvent, containing the same contents of chemical impurities.

Conductivity measurements

We performed systematic measurements of the specific conductivity of the SDA, using a conductometer, model 3200 by YSI, employing a conductivity cell with constant equal to $1.0\ \text{cm}^{-1}$. Before measuring the conductivity of the sample, the cell has to be calibrated by determining the cell constant K (cm^{-1}). The specific conductivity χ ($\mu\text{S cm}^{-1}$), is the product of the cell constant and the conductivity of the solution. For a given cell, the cell constant is determined by measuring the conductivity of a KCl solution with a specific conductivity that is known with great accuracy for several concentrations and temperatures. All the values of conductivity were temperature corrected for 25°C, using the built-in temperature compensation for pure water [25].

Analytical determination of impurities

Sodium concentration was determined through atomic absorption spectroscopy, with a Spectra A Varian instrument. Before measuring the samples, we obtained the necessary calibration curve, using standard solutions: NaCl dissolved in water and diluted to 1 L, to obtain $1000\ \mu\text{g mL}^{-1}$ Na. The working conditions were [26]: Lamp current: 5 mA; Fuel: acetylene; Support: air; Flame stoichiometry: oxidizing. We used a wavelength of 589.6 nm, chosen on the basis of the concentration range of sodium. Since sodium is partially ionised in the air-acetylene flame, some potassium chloride solution was added in, to suppress the ionisation, producing a final concentration of $2000\ \mu\text{g mL}^{-1}$ for every solution, including the blank.

Results and discussion

We conducted a systematic experimental study, to determine the specific electrical conductivities and the heats of mixing of ‘serially diluted and agitated solutions’ (SDA), prepared according to the procedure described in the Procedures section. The resulting measures put in evidence systematically higher specific conductivities and heats of mixing of the SDA compared to the solvent i.e. an aqueous solution of the same chemical composition of the SDA studied. For practical reasons, the measures of χ and sodium concentration can rarely be simultaneous. So, to obtain the actual sodium concentration of the sample at the time of the conductivity measure, we linearly interpolate between two successive measures of sodium concentration, performed before and after the conductivity measure. The conductivity of sodium bicarbonate as a function of molarity, M (mol L^{-1}), is given by the

Table 1 Electrical conductivities (χ_t) for SDA of arsenicum album (AA) and magnesium muriaticum (MM) at 298 K

System	V/mL[a]	$\chi_{t=28}$[b]	$\chi_{t=115}$[b]	$\chi_{t=192}$[b]	$\chi_{t=252}$[b]	$\chi_{t=330}$[b]	$\chi_{t=414}$[b]	$\chi_{t=555}$[b]	$\chi_{t=683}$[b]	$\chi_{t=735}$[b]	$\chi_{t=878}$[b]
H_2O	–	1.2±0.1[c]									
AA 5CH	200	7.9	7.9	8.6	9.3	12.8	20.6	27.8			
	3				9.3	22.8	13.9	15	14.3	14	13.2
	5				9.3	22.9	12.6	12.9	13.3	13.1	14.4
	10				9.3	17.3	23.1	14.7	10.4	10.1	10.5
AA 6CH	200	7.6	8.2	8.2	8.1	7.2	7.5	7.7			7.6
	3				8.1	14.8	15.9	17.5	17.9	16.9	17.7
	5				8.1	7.6	8.1	8.3	8.6	8.3	8.9
	10				8.1	7.4	8	8	8.1	7.9	8.2
AA 9CH	200	7.7	7.9	7.8	7.9	7.3	7.3	7.4			7.4
	5				7.9	9.1	9.4	9.8	10	9.8	10.6
	10				7.9	7.8	8.1	8.2	8.3	8	8.3
AA 12CH	200	7.6	7.9	7.9	7.9	7.3	7.5	7.5			7.5
	3				7.9	9.5	9.9	10.3	11.3	10.3	10.6
	5				7.9	9.4	9.9	9.9	10	9.5	10.2
	10				7.9	7.5	7.9	7.8	8	7.7	8.1
AA 30CH	200	7.4	7.7	7.7	7.7	7.1	7.3	7.2			7.2
	3				7.7	8	8.2	8.1	8.4	8.1	8.3
	5				7.7	8.2	9.2	8.9	9	8.6	9.1
	10				7.7	7.2	7.4	7.4	7.5	7.1	7.3
AA 10DH	200	7.8	7.9	8	8	7.5	7.5	7.6			8.2
	3				8	15.1	21	20.8	17.9	14.7	9.6
	5				8	7.9	11.9	16.4	12.6	9.1	9.5
	10				8	9.1	10.4	9	9.1	8.9	9
AA 12DH	200	7.5	7.7	7.3	7.5	7.2	7.5	7.3			7.5
	3				7.5	7.7	8	8	8.3	8.3	9.6
	5				7.5	8	9.2	9.3	9.5	9.2	9.9
	10				7.5	7.1	7.2	7.2	7.5		7.4
AA 24DH	200	7.5	7.6	7.5	7.2	8.6	7	7.5			7.8
	3				7.2	9	9.9	10.1	10.2	10.1	11.9
	5				7.2	13.9	22.2	22.9	22.8	22.2	22.6
	10				7.2	9	10	9.7	9.9		9.6
AA D45	200	7.4	7.5	7.9	9.2	9.1	9.4	9.1			
	3			7.9	12.4	10.5	9.8	10	10.5	10.5	
	5			7.9	9.2	8.9	10.4	9.6	9.5	9.6	
	10			7.9	8.3	8.3	8.8	8.6	8.8	8.1	
AA D45	200	7.5	7.5	7.8	9	9.5	9.8				9.6
	3			7.8	11	9.3	8.4	8.4	8.5	8.1	8.8
	5			7.8	9.3	9.4	9.3	9.1	9.2	8.8	9.7
	10			7.8	8.8	8.4	8.6	8.8	8.6	8.4	9.1
AA D45	200	7.6	7.6	7.9	8.8	8.4	8.6	8.3			
	3			7.9	15.2	15.7	14.4	12.9	11.8	11.4	12.5
	5			7.9	9	9.3	9.2	9xd.2	9.6	9.2	10.3
	10			7.9	8.9	8.7	8.8	8.9	8.6	8.4	9.2

Table 1 Continued

System	V/mL[a]	$\chi_{t=28}$[b]	$\chi_{t=115}$[b]	$\chi_{t=192}$[b]	$\chi_{t=252}$[b]	$\chi_{t=330}$[b]	$\chi_{t=414}$[b]	$\chi_{t=555}$[b]	$\chi_{t=683}$[b]	$\chi_{t=735}$[b]	$\chi_{t=878}$[b]
H_2O	–	1.2±0.1[c]									
AA D45	200	7.6	7.8	7.9	8.0	8.1	8.1	8.1			
	3			7.6	13.3	12.6	11.5	11	10.5	10	11
	5			7.6	8.3	8.1	8.2	8.1	8.4	8	9.2
	10			7.6	8.4	7.9	8.3	8	8.1	8	8.9
AA D45	200	7.6	7.6	7.9	8.5	8.3	8.5	8.4			
	3			7.9	11	10.2	9.8	9.9	9.9	9.4	10.6
	5			7.9	10.3	10.2	10	9.5	9.9	9.5	10.1
	10			7.9	8.4	8.1	9	7.2	7.7	7.7	8.6
AA D45	200	7.5	7.6	7.7	9.5	8.8	8.8	8.8			
	3			7.7	17.9	17.1	13.5	12.5	11.5	11.3	11.1
	5			7.7	9.1	8.9	8.7	8.6	8.8	8.4	9.1
	10			7.7	8.9	8.3	8.8	8.8	8.4	8.4	9.1
AA D45	200	7.7	7.7	8.2	8.9	8.2	8.9	8.4			
	3			8.2	11	11.8	10.6	10.2	10.3	9.8	11.2
	5			8.2	8.4	8.4	8.3	8.1	8.2	7.8	8.4
	10			8.2	8.6	8.2	8.3	8.1	8.1	7.9	8.9
AA D45	200	7.4	7.7	7.6	8.4	8.2	8.6	8			
	3			7.6	9.7	9.4	9.3	9.4	9.4	9	10.2
	5			7.6	8	8.1	8.1	8.1	8	7.6	8.2
	10			7.6	10.3	9.6	9.7	9.4	9.6	9.4	10
AA D45	200	7.4	7.6	7.6	8.2	7.8	7.8	7.8			
	3			7.6	7.8	7.9	7.4	7.5	7.4	7.1	7.8
	5			7.6	8.7	7.9	8.1	8	8.1	7.6	8.4
	10			7.6	7.9	7.5	7.8	7.9	8.2	7.9	8.8
AA 60DH	200	7.5	7.5	7.3	7.5	7.1	7.1	7.1			7.5
	3				7.5	7.8	8	8.1	8.1	7.9	8.6
	5				7.5	9.6	9.8	10.5	11	10.5	11.5
	10				7.5	7	7.3	7.2	7.5		7.9
MM 5CH	200	7.4	7.4	7.5	7.7	7.3	7.4	6.9			7.5
	3				7.7	8.3	9.2	9.5	9.4		10
	5				7.7	10.1	10.7	11.4	11.7		12.4
	10				7.7	8.1	7.7	7.7	7.6		8.4
MM 6CH	200	7.4	7.6	8.2	7.8	7.7	7.3	7.1			7.5
	3				7.8	13.2	11.8	14	12.9		20.6
	5				7.8	9.7	7.6	67.5	65.3		67.4
	10				7.8	7.7	7.5	7.6	7.7		8.1
MM 9CH	200	7.3	7.5	7.6	7.5	7.3	7.1	7			7.4
	3				7.5	9.2	9.7	11	11.6		13.9
	5				7.5	7.9	7.4	10.6	13.4		12.0
	10				7.5	7.2	8.3	8.4	8.4		9.0
MM 12CH	200	7.6	7.8	7.5	7.8	7.3	7.6	7.3			7.7
	3				7.8	8.1	8.1	10.4	10.9		11.5
	5				7.8	9	8.6	9.9	9		8.6
	10				7.8	9.7	9.7	12	12.5		12.4

Table 1 Continued

System	V/mL[a]	$\chi_{t=28}$[b]	$\chi_{t=115}$[b]	$\chi_{t=192}$[b]	$\chi_{t=252}$[b]	$\chi_{t=330}$[b]	$\chi_{t=414}$[b]	$\chi_{t=555}$[b]	$\chi_{t=683}$[b]	$\chi_{t=735}$[b]	$\chi_{t=878}$[b]
H_2O	–	1.2±0.1[c]									
MM 30CH	200	7.3	7.8	7.5	7.7	7.5	7.4	7.1			7.3
	3				7.7	8.3	8.2	7.9	9.1		10.8
	5				7.7	7.6	7.1	7.1	7.2		7.6
	10				7.7	7.5	7.3	7.4	7.5		8.0
MM 10DH	200	7.8	7.9	8.4	8.2	7.6	7.7	7.6			7.9
	3				8.2	8	7.5	7.8	7.9		8.7
	5				8.2	18.8	19.8	22.6	28.2		34.3
	10				8.2	8	7.6	7.7	7.9		8.4
MM 12DH	200	8.1	7.7	7.9	7.1	7.7	7.6	7.3			7.6
	3				7.1	19.5	18.8	20	19.7		19.9
	5				7.1	9.1	9	9	9.1		9.3
	10				7.1	8.3	8.5	8.6	8.6		9.0
MM 24DH	200	7.5	7.7	7.6	8	7.7	7.5	7.3			
	3				8	21.9	25.4	38.2	60.5		
	5				8	8.8	10.3	11.2	11.8		
	10				8	7.6	7.3	7.3	7.3		
MM 60DH	200	7.5	7.6	7.5	8.1	7.5	7.6	7.2			7.6
	3				8.1	13.8	13.1	13.1	14.1	12.9	12.1
	5				8.1	12.4	14.2	14.9	21.3	21	22.3
	10				8.1	7.7	7.5	7.7	7.9	7.8	7.9

[a] Volume of the solution in the container
[b] Electrical conductivity (μS cm^{-1});
[c] Average and standard deviation determined using 60 experimental measurements of water

following linear trend: χ=0.29±0.17+0.932±0.003 M, R=0.999, as experimentally determined in [21].

Table 1 reports the conductometric experimental data: active principle; degree of dilution; volume of the SDA (mL); electrical conductivity (μS cm^{-1}) measured at several ages of the sample.

Table 2 reports, for the same samples of Table 1, both the conductometric and calorimetric data: excess conductivity χ^E (μS cm^{-1}) i.e. the difference between the SDA conductivity and the conductivity of an aqueous solution of $NaHCO_3$ at the same concentration of the SDA; excess heats of mixing Q^E_{mix} (J kg^{-1}) i.e. the difference between the heat of mixing of the SDA and the heat of mixing of an aqueous solution of $NaHCO_3$ at the same concentration of the SDA.

Table 3 reports conductometric and calorimetric data: active principle; degree of dilution; volume of the SDA (mL); excess heats of mixing Q^E_{mix} (J kg^{-1}); electrical conductivity and excess conductivity, χ^E (μS cm^{-1}) measured at several ages of the sample. The concentration of sodium was determined through atomic absorption measures.

Figure 1 is about two SDA that were partitioned in several smaller volumes immediately after the preparation, and shows how the excess conductivities of the different volumes evolve through time. In this case, time 0 is both the time of preparation and when the partitioning took place. It can be seen that the smaller volumes increase their conductivity more rapidly than the larger ones.

Figure 2 represents the behaviour of two 'old' samples, aged for several months with a large volume

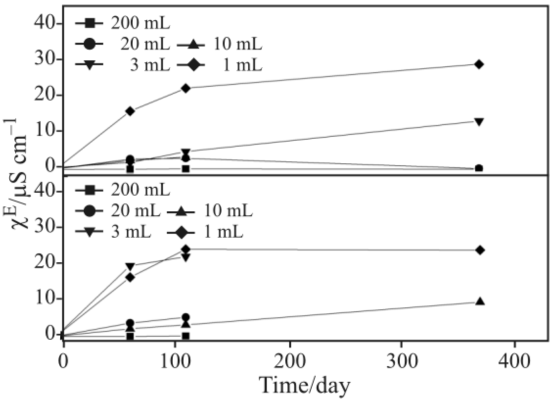

Fig. 1 Excess conductivities for two samples, a – AM 6 CH and b – AM 9 CH, *vs.* age of the SDA

Table 2 Excess conductivities (χ_t^E) and heats of mixing (Q_{mix}^E) for SDA of arsenicum album (AA) and magnesium muriaticum (MM) at 298 K

System	V/mL[a]	$\chi_{t=28}^{E}$[b]	$\chi_{t=115}^{E}$[b]	$\chi_{t=192}^{E}$[b]	$\chi_{t=252}^{E}$[b]	$\chi_{t=330}^{E}$[b]	$\chi_{t=414}^{E}$[b]	$\chi_{t=555}^{E}$[b]	$\chi_{t=683}^{E}$[b]	$\chi_{t=735}^{E}$[b]	$\chi_{t=878}^{E}$[b]	Q_{mix}^{E}[c]
AA 5CH	200	0.9	0.9	1.5	2.0	5.4	13.0	19.9				
	3				1.6	14.7	5.4	5.9	4.5	4.0	3.2	0.53
	5				1.6	14.9	4.2	3.8	3.6	3.2	3.8	0.86
	10				1.6	9.4	14.9	6.1	1.3	0.9	0.8	1.76
AA 6CH	200	0.4	1	1	0.9	0	0.3	0.5			0.4	
	3				0.9	6.9	7.2	7.5	6.6	5.2	4.6	1.89
	5				0.9	0.3	0.7	0.8	0.9	0.6	1.0	
	10				0.9	0.04	0.5	0.2	0.1	0	0	0.76
AA 9CH	200	0.4	0.6	0.5	0.6	0	0	0.1			0.1	
	5				0.6	1.7	1.8	2.0	2.0	1.7	2.2	0.97
	10				0.6	0.4	0.6	0.6	0.5	0.1	0.3	1.04
AA 12CH	200	0.3	0.6	0.6	0.6	0	0.2	0.2			0.2	0.22
	3				0.6	1.8	1.7	1.4	1.7	0.5	0	
	5				0.6	2.0	2.5	2.4	2.4	1.8	2.4	0.70
	10				0.6	0.1	0.4	0.1	0.1	0	0	0.18
AA 30CH	200	0.2	0.5	0.5	0.5	0	0.1	0			0	
	3				0.5	0.7	0.8	0.5	0.6	0.2	0.2	
	5				0.5	0.8	1.7	1.1	1.0	0.5	0.7	
	10				0.5	0	0.1	0.1	0.2	0	0	
AA 10DH	200	0.6	0.7	0.8	0.8	0.3	0.3	0.4			1	
	3				0.8	7.7	13.4	12.8	9.6	6.3	0.8	1.02
	5				0.8	0.6	4.4	8.7	4.7	1.1	1.3	0.62
	10				0.8	1.7	2.8	1.0	0.7	0.4	0.1	
AA 12DH	200	0.8	1.0	0.5	0.7	0.4	0.6	0.3			0.4	
	3				0.7	0.6	0.6	0.1	0	0	0.5	
	5				0.7	0.9	1.8	1.4	1.1	0.6	0.7	
	10				0.7	0.2	0.2	0.1	0.3		0	
AA 24DH	200	0.5	0.6	0.5	0.2	1.6	0	0.5			0.8	
	3				0.2	1.6	2.1	1.5	0.9	0.5	1.6	
	5				0.2	5.9	13.0	11.8	9.9	8.6	7.1	2.74
	10				0.2	1.7	2.4	1.5	1.2		0.1	0.70
AA D45	200	0	0.1	0.1	1.8	1.7	2	1.7				
	3			0.1	4.5	2.3	1.6	1.7	1.0	0.3		1.33
	5			0.1	1.3	0.8	1.4	1.1	0.9	0.5		0.43
	10			0.1	0.4	0.3	0.4	0.5	0.6	0.5		0
AA D45	200	0	0	0	0.3	0.7	0.9				0.4	
	3			0	2.3	0.6	0	0	0	0	0	
	5			0	0.6	0.6	0.5	0.2	0.1	0	0.4	0.73
	10			0	0	0	0	0	0	0	0.3	0.37
AA D45	200	0	0	0	0.9	0.5	0.7	0.4				
	3			0	7.0	7.1	5.4	3.4	1.4	0.8	1.2	
	5			0	1.0	1.2	0.9	0.8	0.8	0.3	1.1	0.53
	10			0	0.9	0.6	0.6	0.6	0.1	0	0.4	0

Table 2 Continued

System	V/mL[a]	$\chi^{E}_{t=28}$ [b]	$\chi^{E}_{t=115}$ [b]	$\chi^{E}_{t=192}$ [b]	$\chi^{E}_{t=252}$ [b]	$\chi^{E}_{t=330}$ [b]	$\chi^{E}_{t=414}$ [b]	$\chi^{E}_{t=555}$ [b]	$\chi^{E}_{t=683}$ [b]	$\chi^{E}_{t=735}$ [b]	$\chi^{E}_{t=878}$ [b]	Q^{E}_{mix} [c]
AA D45	200	0.1	0.3	0.1	0.5	0.6	0.6	0.6				
	3			0.1	5.5	4.4	3.0	1.9	0.5	0	0	
	5			0.1	0.7	0.3	0.3	0	0	0	0.3	0.33
	10			0.1	0.8	0.2	0.4	0	0	0	0.3	0
AA D45	200	0	0	0.3	0.9	0.7	0.9	0.8				
	3			0.3	3.4	2.5	1.9	1.9	1.6	1.0	2.0	
	5			0.3	2.7	2.5	2.1	1.5	1.6	1.1	1.5	1.07
	10			0.3	0.8	0.4	1.1	0	0	0	0	0.29
AA D45	200	0	0.1	0.2	2	1.3	1.3	1.3				
	3			0.2	10.0	8.8	4.9	3.3	1.4	0.9	0	
	5			0.2	1.5	1.2	0.9	0.7	0.7	0.2	0.7	0.39
	10			0.2	1.3	0.6	1.0	0.9	0.3	0.3	0.8	0.48
AA D45	200	0	0	0.5	1.2	0.5	1.2	0.7				
	3			0.5	3.1	3.7	2.3	1.6	1.2	0.6	1.6	
	5			0.5	0.6	0.6	0.4	0.1	0	0	0	0.35
	10			0.5	0.8	0.2	0.2	0	0	0	0	0.40
AA D45	200	0	0.3	0.2	1	0.8	1.2	0.6				
	3			0.2	2.2	1.8	1.6	1.6	1.4	1.0	2.0	
	5			0.2	0.5	0.5	0.4	0.3	0	0	0	0.14
	10			0.2	2.9	2.1	2.2	1.8	1.9	1.7	2.2	0.69
AA D45	200	0.2	0.2	0.2	0.8	0.4	0.4	0.4				
	3			0.2	0.4	0.4	0	0	0	0	0	
	5			0.2	1.2	0.4	0.5	0.3	0.3	0	0.4	0.09
	10			0.2	0.5	0	0.2	0.3	0.4	0.1	0.9	0.74
AA60DH	200	0.4	0.4	0.2	0.4	0	0	0			0.4	
	3				0.4	0.5	0.5	0.3	0	0	0	
	5				0.4	2.3	2.3	2.6	2.7	2.1	2.7	0.89
	10				0.4	0	0.2	0.1	0.3		0.7	0.50
MM5CH	200	0	0	0.1	0.3	0	0	0			0.1	
	3				0.3	0.7	1.5	1.6	1.2		1.5	
	5				0.3	2.2	2.6	2.7	2.4		2.2	
	10				0.3	0.7	0.3	0.3	0.2		1	
MM6CH	200	0	0.2	0.8	0.4	0.3	0	0			0.1	0.06
	3				0.4	5.3	3.7	5.3	3.6		10.4	0
	5				0.4	0.4	0.4	41.7	31.3		21.5	0
	10				0.4	0.2	0	0	0		0	0.03
MM9CH	200	0	0.2	0.3	0.2	0	0	0			0.1	
	3				0.2	1.6	2.0	3.0	3.3		5.1	1.27
	5				0.2	0.1	0	2.0	4.2		2.0	
	10				0.2	0	0.9	1.0	0.9		1.4	
MM12CH	200	0.2	0.4	0.1	0.4	0	0.2	0			0.3	0
	3				0.4	0.5	0.4	2.5	2.7		3.0	
	5				0.4	1.4	1.0	2.1	1.0		0.3	
	10				0.4	1.9	1.7	3.5	3.5		2.7	0.6

Table 2 Continued

System	V/mL[a]	$\chi^{\mathrm{E}\ \mathrm{b}}_{\mathrm{t=28}}$	$\chi^{\mathrm{E}\ \mathrm{b}}_{\mathrm{t=115}}$	$\chi^{\mathrm{E}\ \mathrm{b}}_{\mathrm{t=192}}$	$\chi^{\mathrm{E}\ \mathrm{b}}_{\mathrm{t=252}}$	$\chi^{\mathrm{E}\ \mathrm{b}}_{\mathrm{t=330}}$	$\chi^{\mathrm{E}\ \mathrm{b}}_{\mathrm{t=414}}$	$\chi^{\mathrm{E}\ \mathrm{b}}_{\mathrm{t=555}}$	$\chi^{\mathrm{E}\ \mathrm{b}}_{\mathrm{t=683}}$	$\chi^{\mathrm{E}\ \mathrm{b}}_{\mathrm{t=735}}$	$\chi^{\mathrm{E}\ \mathrm{b}}_{\mathrm{t=878}}$	$Q^{\mathrm{E}\ \mathrm{c}}_{\mathrm{mix}}$
MM30CH	200	-0.1	0.4	0.1	0.3	0.1	0	0			0	
	3				0.3	0.7	0.6	0.1	1.1		2.5	
	5				0.3	0.2	0	0	0		0.2	
	10				0.3	0.1	0	0	0.1		0.6	
MM10DH	200	0.4	0.5	1	0.8	0.2	0.3	0.2			0.5	
	3				0.8	0.6	0	0.3	0.4		1.1	
	5				0.8	8.6	8.3	7.7	9.7		10.8	
	10				0.8	0.6	0.2	0.3	0.4		0.9	
MM12DH	200	0.7	0.3	0.5	0	0.3	0.2	0			0.2	
	3				0	11.1	9.9	9.8	8.2		6.6	
	5				0	1.6	1.4	1.3	1.2		1.2	
	10				0	0.9	1.0	1.1	1.0		1.3	
MM24DH	200	2.5	2.7	2.6	3	2.7	2.5	2.3				
	3				3	16.9	20.4	33.2	55.5			
	5				3	3.8	5.3	6.2	6.8			
	10				3	2.6	2.3	2.3	2.3			
MM60DH	200	0.4	0.5	0.4	1.0	0.4	0.5	0.1			0.5	
	3				1.0	6.2	5.3	4.6	5.0	3.6	2.1	
	5				1.0	4.2	5.6	5.0	10.0	9.4	9.1	
	10				1.0	0.6	0.3	0.5	0.6	0.5	0.5	

[a] Volume of the solution in the container;
[b] Excess conductivity (μS cm^{-1}), namely the difference between the conductivity of the SDA and the conductivity of a sodium bicarbonate solution at the same concentration of the SDA;
[c] Excess heat of mixing (J kg^{-1}), namely the difference between the heat of mixing of the SDA and the heat of mixing of a sodium bicarbonate solution at the same concentration of the SDA

(200 mL), then subdivided into different smaller volumes. It shows how the smaller volumes evolved in a case where the partitioning took place after the time of preparation (time 0). The qualitative trend is very similar to that in Fig. 1.

Figure 3 reports the excess conductivity curves in function of the volume, for all the samples of Tables 2 and 3. This figure highlights an unexpected correlation, of exponential kind, between the excess parameter and the volume of the solution [27]. Figure 4 shows the linear correlation between the two excess parameters: excess conductivity χ^{E} (μS cm^{-1}) and excess heat of mixing $Q^{\mathrm{E}}_{\mathrm{mix}}$ (J kg^{-1}).

It is interesting to note that, especially for smaller volumes, the trends of χ^{E} (μS cm^{-1}) *vs.* age show a common, distinctive feature: they reach a

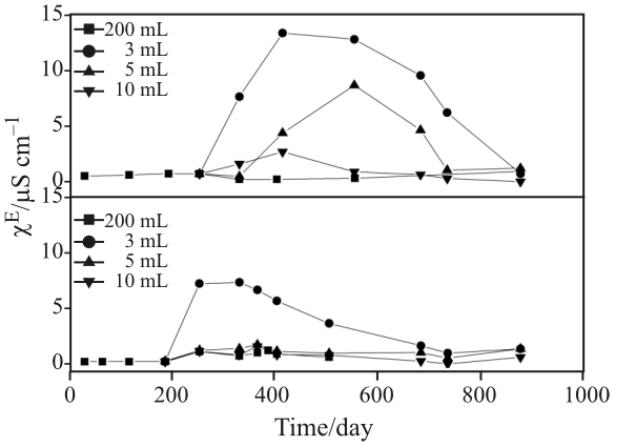

Fig. 2 Excess conductivities for two samples, AA10 DH and AA 45 DH, *vs.* age of the SDA

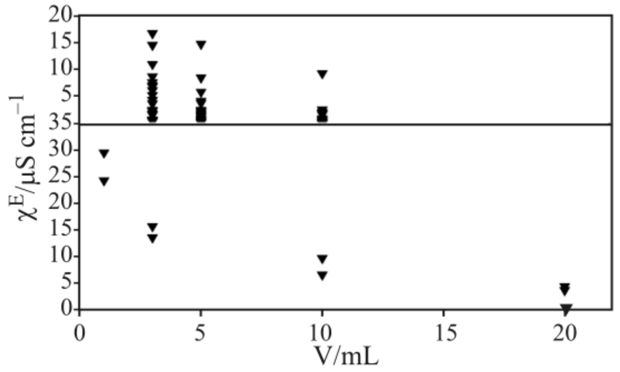

Fig. 3 Excess conductivity curves *vs.* volume, for all the samples about 300 days old

Table 3 Conductivities (χ_t) and heats in excess Q^E_{mix} (J kg^{-1}) for SDA of Arnica Montana (AM) at 298 K

System	V/mL[a]	$\chi_{t=1}$ [b]	$\chi_{t=64}$ [b]	$\chi_{t=113}$ [b]	$\chi_{t=372}$ [b]	$\chi^E_{t=1}$ [c]	$\chi^E_{t=64}$ [c]	$\chi^E_{t=113}$ [c]	$\chi^E_{t=372}$ [c]	Q^E_{mix} [d]
AM 6CH	200	5	5	5.1		0	0	0.1		–
	20	5.1	9.4	11.5		0.1	3.8	5.4		–
	10	5.1	7.6	9.1	20.8	0.1	2.2	3.3	9.7	–
	3	5.7	25.7	28.9		0.7	19.9	22.4		–
	1	5.6	23.7	33.1	45.6	0.6	16.7	24.5	24.3	18.1
AM 7CH	200	4.9	5	5.1	5.1	0	0	0.1	0.1	–
	20	5.2	8.8	9.2	11.5	0.2	3.5	3.6	4.4	3.38
	10	5.2	6.5	8.2	16	0.2	1.1	2.4	6.6	6.56
	3	5.4	9	11		0.4	3.1	4.3		–
	1	5.7	20.2	36		0.7	13.4	27.6		–
AM 9CH	200	4.9	5	5.1	5	0	0	0.1	0	
	20	5.2	8.3	8.9	7.9	0.2	2.9	3.1	0.2	4.63
	10	5.2	8	9.3		0.2	2.5	3.4		–
	3	5.5	7.8	11.5	24.7	0.5	1.9	5.0	13.6	11.90
	1	5.5	23.2	31.2	48.3	0.5	16.4	22.8	29.5	19.0
AM 12CH	200	5	5	5	4.9	0	0	0	0	
	20	5	7.5	7.8	11.4	0	2.1	2.0	3.7	2.43
	10	5	8.2	9.3		0	1.3	0.9		–
	3	5.5	10.2	15.3	26.8	0.5	4.2	8.5	15.7	10.30
	1	5.6	18	30.7		0.6	11.1	22.3		–

[a]Volume of the solution in the container; [b]Electrical conductivity (μS cm^{-1}); [c]Excess conductivity (μS cm^{-1}), namely the difference between the conductivity of the SDA and the conductivity of a sodium bicarbonate solution at the same concentration of the SDA; [d]Excess heat of mixing (J kg^{-1}), namely the difference between the heat of mixing of the SDA and the heat of mixing of a sodium bicarbonate solution at the same concentration of the SDA

maximum. This has deep implications, since such a behaviour is markedly different from that of near-equilibrium systems as described by classical thermodynamics. It must be stressed that the increase of excess conductivity and excess heat of mixing as a function of time and volume can't be attributed to chemical agents (e.g. impurities, carbon dioxide, etc.) given the outstanding variations measured. For example, the excess conductivity of a sample of 200 mL and that of a sample of 1 mL, measured at the same age of the samples, differ by an order of magnitude, and thus cannot be attributed to impurities, by definition. At any rate, we did systematically check the sodium bicarbonate concentration, the substance that gets most abundantly released from the glass of the containers. It can be noted that we performed more conductometric measures than calorimetric ones. That was because the latter measurements irreversibly consume the SDA under study, while the former do not, and are therefore preferable. This is not a problem though, considering the linear correlation between specific conductivity and heat of mixing with alkaline solutions (Fig. 4).

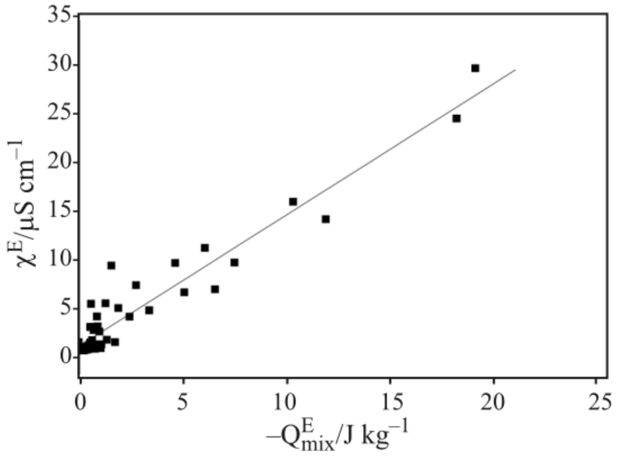

Fig. 4 Excess conductivity χ^E (μS cm^{-1}) *vs.* excess heats of mixing Q^E (J kg^{-1}), for all the samples of Tables 2 and 3

Conclusions

In this article we described how conductivity and heat of mixing of an SDA sample are affected by the volume of the sample and its age. Each studied SDA sample had a constant volume throughout its lifetime.

It is worth noting that a different volume also means a different surface-volume ratio. The measures we carried out seem to indicate that the variation of the contact surface between solid and liquid, and hence of the surface–volume ratio, is more important than the variation of volume. Obviously, as volume decreases, the surface–volume ratio increases, i.e. smaller volumes have higher surface-volume ratios. Prompted by this insight, we have started a further systematic study, in order to gather data on systems whose volume and surface–volume ratio are known with precision, and kept constant in time. Conductometry will be the main technique, since it is not destructive (as opposed to calorimetry, for instance). The linear correlation between calorimetric data and conductometric data (Fig. 4) will enable us to extend the current results.

The fact that the electrical conductivity trend with time depends on the volume being aged, is made apparent by Figures 1 and 2, showing χ^E *vs.* age of the samples. The measured conductivity values increase as the sample volumes get smaller, and the correlation is of exponential kind (Fig. 3) [27]. That leads us to think that the volume of the ageing sample is the most important parameter affecting the temporal evolution.

The abundant experimental data reported fits the peculiar behaviour just described, and produces a statistical significance that violently clashes with what predicted by the Thermodynamics of near-equilibrium systems for an intensive parameter such as χ^E (μS cm^{-1}). Since the systems under study cannot be described by the thermodynamics of equilibrium, it seems natural to base their interpretation on the thermodynamics of far from equilibrium, dissipative processes [27].

A first hypothesis to try and rationalize the experimental results is this: the SDA, after the strong agitation (succussions), enter a far from equilibrium state and remain there, or get even farer from the equilibrium, by dissipating energy in the form and amount necessary to stay in that state. In an oversimplified picture, some radiating energy (probably at extremely low frequencies, ELF) is the source of the energy that gets dissipated. Let us further hypothesize that, for a given flux of dissipated energy (W cm^{-2}), the same number of dissipative structures would be present in a sample, regardless of its volume. Thus, in average, at any given age, small volumes would exhibit a higher 'concentration' of dissipative structures than large volumes. This hypothesis resolves the apparent inconsistency of an intensive parameter, χ^E that depends on the volume of the ageing sample, and brings the SDA back to a known paradigm. The physico-chemical parameters suitable to reveal these dissipative structures, i.e. χ^E (μS cm^{-1}) and Q^E_{mix} (J kg^{-1}) are, not surprisingly, those affected by concentration, size and shape of the dissipative structures [28].

The hypothesis of the involvement of extremely low frequency electromagnetic fields is backed up by a series of studies, conducted by us over a period of 18 months, to evaluate the influence on the SDA of the electromagnetic fields of the environment in our laboratories. The studies consisted in comparing the temporal evolution of the χ^E parameter for a series of twin samples, where one sample from a couple of identical samples would be stored in an ordinary laboratory cabinet, and the other in a container made of Mumetal. The Mumetal container, of about 0.5 m^3 in volume, is an excellent shield to high frequency radiations, as well as to the terrestrial magnetic field. Only ELF radiations are able to penetrate the container. We found out an extremely similar temporal evolution of the specific conductivity in the two storage environments. It is therefore reasonable to suppose that extremely low frequency radiations are indeed exploited by the dissipative systems to keep far from the equilibrium.

One would expect the systematic increase of the physico-chemical parameters to be linked to a trend towards an equilibrium condition, characterized by an energetic minimum. But the very long period needed to reach the hypothetical equilibrium condition is not favourable to this rationalization. The new and unexpected trend observed, characterized by a maximum of excess conductivity is in stark contrast with the idea of attainment of an equilibrium. At the same time, the decrease of the parameters after the maximum has been reached, excludes the presence of unknown chemical impurities, released by the glass containers, because their presence must be permanent. The reduction of the physico-chemical parameters after the maximum should be attributable to the occurrence of environmental conditions, at the studied volume, such that the dissipation of energy, necessary to stay in a far from equilibrium condition, can no longer be carried out in an efficient way. However, these are multi-variable systems, and as such it is very difficult to determine which one of the several involved parameters acts as the most important driving force. For example, if the high concentration of dissipative structures would cause the energy dissipation to cease, the smaller volumes would reach the maximum in a shorter time. On the other hand, each volume could have a characteristic temporal evolution and the two effects, time and volume, could be roughly compensated. At any rate, we can conclude that:

- The excess parameters are certainly due to the variation of the super-molecular structure of the water solvent.
- The temporal evolution of said parameters is not a trend towards an energetic minimum.
- A self consistent interpretation could be the presence of dissipative structures.

The succussion step could be the trigger for the formation of dissipative structures, and the emergence of the novel behaviour. The temporal evolution could be connected with the variation of the number and/or dimension and/or shape of the dissipative structures, during their permanence in a far from equilibrium state.

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