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CONDUCTOMETRIC AND CALORIMETRIC STUDIES OF SERIALLY DILUTED AND AGITATED SOLUTIONS: THE DEPENDENCE OF INTENSIVE PARAMETERS ON VOLUME

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ABSTRACT

We systematically analysed the experimental data related to the specific conductivities (χ^{E}) and heats of mixing ($Q^{\mathrm{E}}_{\mathrm{mix}}$) of a series of more than a thousand serially diluted and agitated (SDA) solutions. The results show systematically higher specific conductivities and heats of mixing for SDA solutions with sodium hydroxide than for NaOH with the reference solvents at the same chemical composition. The analysis of the results yielded an extraordinary and unexpected correlation, of an exponential kind, between the two excess parameters and the volume of the solution in the container. In other words, when the specific conductivity of samples of the same preparation that differ in volume (1–200 ml) were measured, the conductivity values were found to increase as the sample volumes decrease. As the influence of volume on the physicochemical properties of the SDA solution was unexpected, the volumes and time of stay at a given volume are not known exactly but are estimates. A new systematic study based on known and constant volumes across the life of the samples is underway. The influence of volume on χ^{E} (μS cm^{-1}) and $Q^{\mathrm{E}}_{\mathrm{mix}}$ (J kg^{-1}) turned out to be overwhelming compared with that of time, and is therefore statistically very significant despite the uncertainty in terms of the exact volume value. A simple rationalizing hypothesis is put forth which is consistent with the more general idea of water as a system that is capable of auto-organizing, even in the presence of small perturbations, and is then able to sustain a far from equilibrium state (dissipative structures).

Keywords: dissipative structures, homeopathic dilution, SDA.

1 INTRODUCTION

Recent years have witnessed a renewed interest by researchers in studying the properties of water, which appear increasingly unpredictable and are hardly framed within the current theories [1–5]. Water constitutes a key element for the existence of all biological systems and it behaves as a complex system that is capable of auto-organizing as a result of small perturbations [6]. Some papers published in the last few years [7–14] have undertaken a physicochemical study of aqueous solutions prepared by an iterative process of successive dilutions and violent agitations in the vertical direction, called succussions, which produce 'extremely diluted solutions' or 'serially diluted and agitated' (SDA) solutions. The chemical composition of the solutions obtained by this process is exactly similar to that of the solvent used for dilution. It follows that the SDA solution should behave as the solvent, at least from a physicochemical point of view. Other studies have also dealt with the physicochemical properties of aqueous solutions that underwent a series of dilutions [6, 15, 16]. As a whole, those studies back-up the theory of water as a complex system that is capable of auto-organization owing to small entity perturbations (dilution, succussion, electromagnetic fields, etc.), with variations in physicochemical properties that can be either permanent, temporary or oscillating.

The study carried out on our SDA systems has shown the paramount importance of two parameters, among the others: time and volume. Time refers to the age of the samples, whereas volume indicates the sample volume at the time of measurement of specific conductivity or heat of mixing. The fact that time is among the parameters that are capable of modifying the physicochemical properties, and therefore the supramolecular structure, of these solutions seems to suggest that the SDA solutions are far from equilibrium systems that are capable of forming dissipative structures. The number, the dimension and/or the shape of these dissipative structures are responsible for the variation of the

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physicochemical parameters. We have already described the temporal evolution of these systems, at a phenomenological level, in previous papers [10, 13, 14].

2 EXPERIMENTAL PROCEDURE

An SDA solution is prepared by a two-step iterative process: dilution and 'dynamization'. The process of 'dynamization' consists of violent agitation (succussion) of the solution using a mechanical apparatus. For centesimal dilution, the starting point is a 1% mass solution [17]; for example, to prepare a Magnesium Muriaticum (MM) solution, 1 g of $MgCl_2$ is added to 99 g of solvent. After mechanical treatment, plain succussion, the solution obtained is called '1 centesimal hahnemannian' or 1CH, and the name of the solution begins 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 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 involves in disposing of 99% of the liquid in the bottle and then refilling to 100% with pure water before moving to the dynamization step. The solution obtained is called '1 centesimal korsakovian' or 1CK (i.e. MM 1CK).

The SDA solutions used were supplied by Cemon (Italy). After their preparation, the SDA solutions were stored at room temperature.

3 METHODS

3.1 Calorimetry

The heats of mixing were monitored using a Thermal Activity Monitor model 2227 (Thermometric, Sweden) equipped with a flow-mixing vessel. A P3 peristaltic pump (Pharmacia) conveys the solutions into the calorimeter through Teflon tubes. The exact experimental procedure is detailed in previous papers [8–10, 18–22]. The value of the heat of mixing, Q_{mix}, was obtained using the following formula:

$$Q_{\mathrm{mix}}\left(m_x^{\mathrm{i}}, m_y^{\mathrm{i}} \rightarrow m_x^{\mathrm{f}}, m_y^{\mathrm{f}}\right) = \frac{(\mathrm{d}Q/\mathrm{d}t)}{P_{\mathrm{w}}}, \tag{1}$$

where $\mathrm{d}Q/\mathrm{d}t$ is the heat flux (W), P_{w} is the total mass flow rate of the solvent ($\mathrm{kg\,s^{-1}}$), and m_x^{i}, m_y^{i} and m_x^{f}, m_y^{f} are the initial and final molalities, respectively. Q_{mix} is given in $\mathrm{J\,kg^{-1}}$ of the solvent in the final solution. We determined the heats of mixing of probe solutions with the SDA, and found an excess heat of mixing in almost all the studied samples. The excess heat of mixing, $Q^{\mathrm{E}}_{\mathrm{mix}}$, is defined as the heat of mixing of the probe solution with the extremely diluted solution, Q_{mix}, minus the heat of mixing of the same probe solution when mixed with the untreated solvent, having the same contents of chemical impurities [11].

3.2 Conductivity measurements

Systematic measurements of the specific conductivity were performed on the SDA solution using a conductometer, YSI model 3200, with a conductivity cell having a cell constant equal to $1.0\,\mathrm{cm^{-1}}$. Before measuring the conductivity of the sample, the cell has to be calibrated by determining the cell constant K ($\mathrm{cm^{-1}}$). The specific conductivity χ ($\mu\mathrm{S\,cm^{-1}}$) is then given by the product of the cell constant and the conductivity of the solution. For a chosen conductivity-measuring 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 to 25°C, using a prestored temperature compensation for pure water.

4 RESULTS

A systematic experimental study has been carried out to determine the excess heat of mixing and the specific electrical conductivities of SDA solutions, prepared according to the procedure described in Section 2. The results show systematically higher specific conductivities and heats of mixing of the SDA solutions with the reference solvents.

Tables 1–3 report the age of the SDA solution (days); the specific conductivity χ (μS cm^{-1}); the excess conductivity χ^E (μS cm^{-1}), i.e. the difference between the conductivity of the SDA solution and that of the solvent employed for preparation; the active principle; the degree of dilution for the

Table 1: Electrical conductivity for SDA solutions of Arnica Montana (AM) at 298 K (age: 503 days).

System	Dilution degree	V (ml)[a]	χ[b]	χ^{E}[c]
H_2O	–	–	1.1 ± 0.2[d]	0
AM[e]	5K	8	59	38
AM[e]	6K	7	66	26
AM[e]	12K	20	49	9
AM[e]	30K	3	131	43
AM[e]	200K	7	56	16
AM[e]	5K	20	44	13
AM[e]	6K	25	40	11
AM[e]	12K	15	52	16
AM[e]	30K	25	44	12
AM[e]	200K	20	45	11
AM[e]	5K	20	43	9
AM[e]	6K	15	49	13
AM[e]	12K	20	50	13
AM[e]	30K	20	47	13
AM[e]	200K	40	37	8
AM[e]	5K	115	29	11
AM[e]	6K	120	26	3
AM[e]	30K	105	28	6
AM[e]	200K	118	26	2
AM[e]	5K	45	32	10
AM[e]	6K	115	23	3
AM[e]	12K	115	27	2
AM[e]	30K	115	28	6
AM[e]	200K	100	25	4
AM[e]	5K	150	24	3

Continued

Table 1: *Continued*

System	Dilution degree	V (ml)[a]	χ^{b}	$\chi^{E\ c}$
AM[e]	6K	115	27	5
AM[e]	12K	115	29	5
AM[e]	30K	100	26	4
AM[e]	200K	115	26	4
AM[e]	5K	120	24	2
AM[e]	6K	115	27	5
AM[e]	12K	115	28	5
AM[e]	30K	120	26	4
AM[e]	200K	120	26	4
AM[e]	5K	115	24	3
AM[e]	6K	115	24	4
AM[e]	12K	115	27	4
AM[e]	30K	115	29	3
AM[e]	200K	120	26	4
AM[e]	5K	120	24	3
AM[e]	6K	120	27	4
AM[e]	12K	115	27	5
AM[e]	30K	120	27	5
AM[e]	200K	115	26	4

[a] Volume (ml) of SDA solutions at the time of the measurement.
[b] Electrical conductivity in μS cm^{-1}.
[c] Excess conductivity in μS cm^{-1}.
[d] Average and standard deviation determined using 60 experimental measurements of water.
[e] Active principle: Arnica Montana; solvent: deionized water; preparation method: Korsakovian; dynamization method: succussion.

Table 2: Electrical conductivity for SDA solutions of Magnesium Muriaticum (MM) at 298 K (age: 503 days).

System	Dilution degree	V (ml)[a]	χ^{b}	$\chi^{E\ c}$
H_2O	–	–	1.1 ± 0.2[d]	0
MM[e]	5K	24	45	9
MM[e]	5K	26	46	10
MM[e]	5K	24	47	10
MM[e]	6K	24	46	10
MM[e]	6K	24	47	13
MM[e]	6K	4	83	34
MM[e]	12K	35	40	9
MM[e]	12K	35	41	8

Continued

Table 2: *Continued*

System	Dilution degree	*V* (ml)[a]	χ[b]	χ^E[c]
MM[e]	12K	24	48	20
MM[e]	30K	24	45	10
MM[e]	30K	35	39	10
MM[e]	30K	50	39	13
MM[e]	200K	24	44	11
MM[e]	200K	12	69	14
MM[e]	200K	50	39	10
MM[e]	5K	135	27	9
MM[e]	5K	135	26	7
MM[e]	5K	120	27	7
MM[e]	5K	115	26	4
MM[e]	5K	135	27	8
MM[e]	5K	115	26	5
MM[e]	6K	140	27	6
MM[e]	6K	135	26	6
MM[e]	6K	140	27	7
MM[e]	6K	140	27	6
MM[e]	6K	115	27	7
MM[e]	6K	110	27	7
MM[e]	12K	115	26	6
MM[e]	12K	125	26	6
MM[e]	12K	115	28	8
MM[e]	12K	110	28	8
MM[e]	12K	115	27	7
MM[e]	12K	115	28	8
MM[e]	30K	120	28	9
MM[e]	30K	115	28	8
MM[e]	30K	110	29	8
MM[e]	30K	110	28	8
MM[e]	30K	120	28	7
MM[e]	30K	120	28	7
MM[e]	200K	110	29	8
MM[e]	200K	45	34	13
MM[e]	200K	110	28	8
MM[e]	200K	150	27	8
MM[e]	200K	115	29	8

[a] Volume (ml) of SDA at the time of the measurement.

[b] Electrical conductivity in μS cm^{-1}.

[c] Excess conductivity in μS cm^{-1}.

[d] Average and standard deviation determined using 60 experimental measurements of water.

[e] Active principle: Magnesium Muriaticum; solvent: deionized water; preparation method: Korsakovian; dynamization method: succussion.

Table 3: Electrical conductivity for SDA solutions of Silicea at 298 K (age: 503 days).

System	Dilution degree	V (ml)[a]	χ^{b}	$\chi^{E\ c}$
H_2O	–	–	1.1 ± 0.2^{d}	0
S^{e}	5K	7	68	10
S^{e}	5K	8	62	11
S^{e}	5K	40	43	10
S^{e}	6K	20	56	9
S^{e}	6K	25	46	7
S^{e}	12K	10	62	10
S^{e}	12K	20	53	3
S^{e}	12K	10	61	5
S^{e}	30K	20	46	9
S^{e}	30K	30	41	7
S^{e}	200K	40	42	8
S^{e}	200K	25	40	6
S^{e}	200K	25	41	8
S^{e}	5K	142	27	4
S^{e}	5K	140	27	4
S^{e}	5K	150	27	5
S^{e}	5K	140	27	4
S^{e}	5K	140	27	5
S^{e}	5K	40	37	5
S^{e}	6K	150	28	10
S^{e}	6K	145	27	5
S^{e}	6K	145	26	4
S^{e}	6K	150	26	5
S^{e}	6K	140	26	7
S^{e}	6K	150	25	6
S^{e}	12K	145	25	5
S^{e}	12K	140	26	5
S^{e}	12K	145	26	5
S^{e}	12K	140	25	6
S^{e}	12K	165	24	5
S^{e}	30K	150	25	5
S^{e}	30K	140	24	3
S^{e}	30K	24	24	3
S^{e}	30K	150	24	5
S^{e}	30K	150	25	6

[a] Volume (ml) of SDA at the time of the measurement.

[b] Electrical conductivity in μS cm^{-1}.

[c] Excess conductivity in μS cm^{-1}.

[d] Average and standard deviation determined using 60 experimental measurements of water.

[e] Active principle: S, solvent: deionized water. preparation method: korsakovian, dynamization method: succussion.

three active principles: Arnica Montana (AM), Magnesium Muriaticum (MM), Silicea (S); and the volume of the SDA solution (ml). The actual concentration of sodium was determined by atomic absorption measurements. The values, once corrected to account for the sodium bicarbonate content, are systematically higher than those due to the presence of electrolytes.

In Figs 1–3, the excess conductivities of the three preparations as a function of the SDA solution volumes are plotted. It is clear from the figures, albeit unexpected, that the values of χ^E are exponentially correlated with the values of volume.

To confirm the analogy between the behaviour of excess heat and excess conductivity, measurements of the heat of mixing with 0.01 m NaOH were carried out as a function of the volume of the SDA solution. The excess heat of mixing, Q^E_{mix} (J kg^{-1}), is defined as the heat of mixing of NaOH with the SDA solution minus the heat of mixing of the same NaOH when mixed with the untreated solvent. The actual concentration of sodium was determined by atomic absorption measurements and the actual silicic acid concentration was determined by measuring the UV absorption of complexes with ammonium molybdate. From this definition, the chemical contributions due to CO_2 and sodium bicarbonate or silicic acid are eliminated and do not affect the value of Q^E_{mix}. The values, once corrected to account for the sodium bicarbonate and silicic acid content, are systematically higher than those due to the presence of electrolytes, and are of the same order of magnitude of the measured parameters Q_{mix} and χ [11–14].

Table 4 contains the age of the SDA solution, the heats of mixing Q_{mix} (J kg^{-1}), the excess heat Q^E_{mix} (J kg^{-1}), the active principle 2,4-dichlorophenoxyacetic acid (2,4-D), the degree of dilution and the volume of the samples. These results once again confirm the exponential correlation with the volume of the SDA solution, as can be seen from Fig. 4.

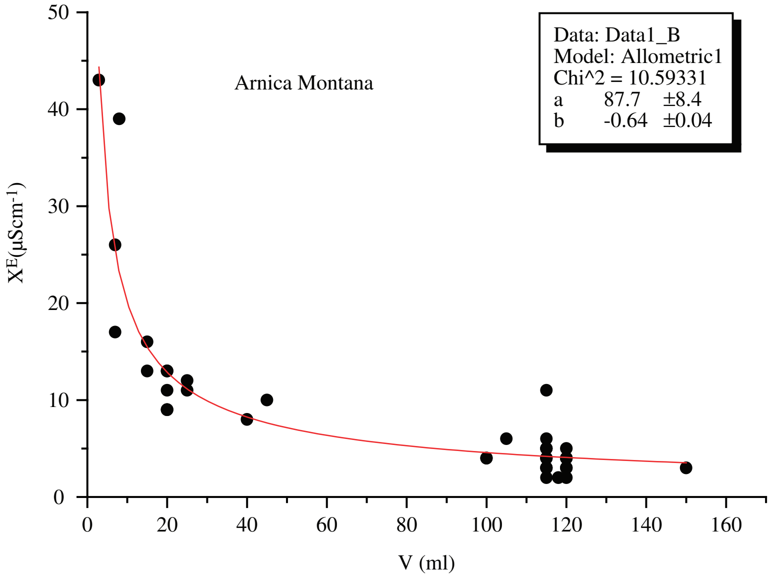

Figure 1: Excess conductivities of Arnica Montana vs. the SDA solution volumes (age: 503 days). The interpolating function is $Y = aX^b$. The values of a and b and their errors and χ^2 are given in the figure.

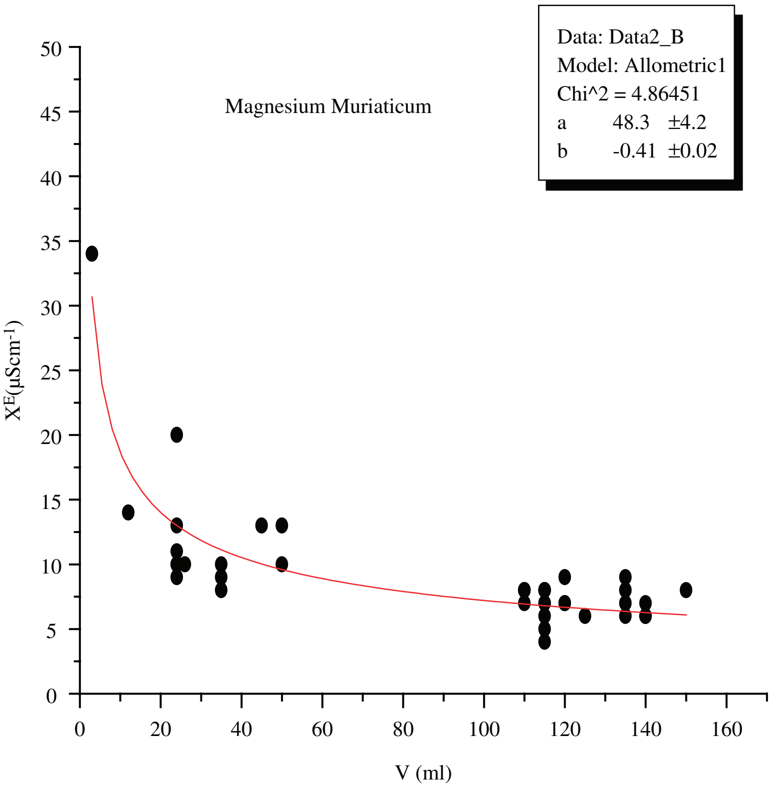

Figure 2: Excess conductivities of Magnesium Muriaticum vs. the SDA solution volumes (age: 503 days). The interpolating function is: $Y = aX^b$. The values of a and b and their errors and χ^2 are given in the figure.

5 DISCUSSION AND CONCLUSIONS

In this paper, we described the phenomena related to the dependence of conductivity and heats of mixing of samples stored in different volumes. Every SDA solution has been studied at different and randomly scattered volume values. The randomness is related to the consumption connected to the use of the solutions in various experimental measurements.

It is worth noting that a different volume also means a different surface–volume ratio. The measurements performed seem to indicate that the variation in the contact surface between the solid and the liquid, and hence in the surface–volume ratio, is more important than the variation in volume itself. On the basis of this insight, a systematic study has been initiated to collect data on systems whose volume and surface–volume ratio are accurately known and kept constant with time. Conductometry will be the main viable technique, as it is not destructive whereas calorimetry is destructive. The linear correlation between the calorimetric data and the conductometric data [11] will allow us to extend the current results. The amount of time for which a given solution has been stored at a given volume is not known, as solutions were used in experiments dealing with electromotive force and heat of mixing to explore their physicochemical properties. The latter experiments caused a series of random and not programmed volume decrements, without a record of the temporal evolution of volumes. Furthermore, the volumes were estimates and not precisely measured. One of the causes of

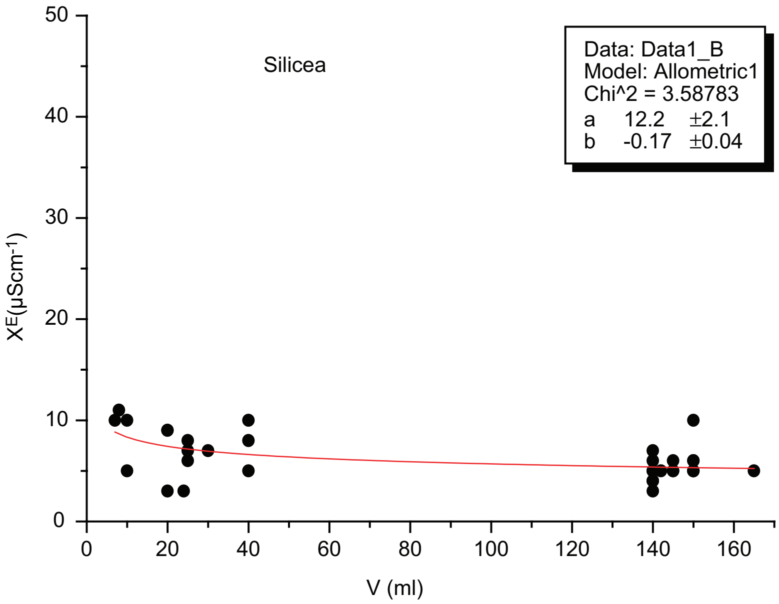

Figure 3: Excess conductivities of Silicea vs. the SDA solution volumes (age: 503 days). The interpolating function is: $Y = aX^b$. The values of a and b and their errors and χ^2 are given in the figure.

the scattering in the experimental data was attributed to such uncertainty, whose influence is greater for smaller volumes.

The excess conductivity or the excess heat of mixing, as functions of the volume of the solution, refers to the volume at the time of the measurement (503 days) rather than to the time of permanence at that volume. Meanwhile, new data are being collected to form a critical mass that will help improve and refine the conclusions drawn so far.

When observing the experimental values of χ^E for the thousand or so solutions studied, it is evident that SDA solutions aged at small volumes (a few millilitres) show a much faster temporal evolution than systems with a larger volume (unpublished data).

In Figs 1–3, the χ^E values for AM, MM and S preparations as a function of the SDA solution volumes are reported. These samples show the different trends of electrical conductivity with respect to volumes. This behaviour confirms, for the first time, a possible correlation between the physico-chemical parameters and the nature of the active principle. The correlation between conductivity and volume, leads us to think that, despite the aforementioned issues, the volume of the ageing sample is the most important parameter driving the temporal evolution. Figure 4 reports the values of Q^E_{mix} as a function of the volume at the time of the measurement (1,400 days).

Such an abundance of experimental data is in accord with the peculiar behaviour we have just described and produces a statistical significance that strongly disagrees with what is predicted for the intensive parameters, χ^E (μS cm^{-1}) and Q^E_{mix} (J kg^{-1}), by the thermodynamics of nearly-in-equilibrium systems. The systems do not fit in the thermodynamics of equilibrium framework, and it thus seems natural to base the interpretation of their behaviour on the thermodynamics of far from equilibrium dissipative processes [23].

Table 4: Excess heats of mixing for SDA solutions of 2,4-dichlorophenoxyacetic acid (2,4-D) in $NaHCO_3$ or H_4SiO_4 solvent at 298 K (age: 1,400 days).

System	Dilution degree	V (ml)[a]	$-Q_{\mathrm{mix}}$[b]	$-Q^{\mathrm{E}}_{\mathrm{mix}}$[c]
H_2O	–	–	1.05 ± 0.05[d]	0
2,4-D[e]	3CH	100	1.64	0.6
2,4-D[e]	4CH	15	6.39	3.5
2,4-D[e]	6CH	40	2.44	1.4
2,4-D[e]	8CH	35	2.90	1.9
2,4-D[e]	10CH	15	4.68	3.0
2,4-D[e]	12CH	30	3.65	2.0
2,4-D[f]	3CH	40	4.10	2.0
2,4-D[f]	8CH	80	2.04	1.9
2,4-D[e]	8CH	70	1.33	0.6
2,4-D[f]	9CH	30	1.97	1.3
2,4-D[f]	10CH	15	2.98	2.3
2,4-D[g]	6CH	250	1.78	0.8
2,4-D[g]	9CH	250	1.60	0.6
2,4-D[g]	11CH	250	1.20	0.2
2,4-D[g]	12CH	250	1.40	0.4
2,4-D[g]	6CH	20	2.80	1.7
2,4-D[g]	7CH	20	2.10	1.1
2,4-D[g]	8CH	20	2.61	1.4
2,4-D[g]	12CH	20	3.90	2.9

[a] Volume (ml) of SDA solution at the time of the measurement.
[b] Heat of mixing in J kg^{-1} of solvent in final solution with 0.01 m NaOH.
[c] Excess heat of mixing in J kg^{-1} of solvent in final solution with 0.01 m NaOH.
[d] Average and standard deviation determined using 60 experimental heats of mixing of 0.01 m NaOH with water.
[e] Active principle: 2,4-D; solvent: aqueous solution of 5×10^{-5} M $NaHCO_3$; preparation method: centesimal Hahnemannian; dynamization method: succussion.
[f] Active principle: 2,4-D; solvent: aqueous solution of 5×10^{-5} M H_4SiO_4; preparation method: centesimal Hahnemannian; dynamization method: succussion.
[g] Active principle: 2,4-D; solvent: aqueous solution of 5×10^{-5} M $NaHCO_3$; preparation method: centesimal Hahnemannian; dynamization method: succussion.

The first hypothesis to try and rationalize the experimental results is that these extremely diluted solutions, i.e. the SDA solutions, after the strong agitation (succussion), enter a far from equilibrium state and remain there or get even farther by dissipating energy in the form and amount necessary to stay in a far from equilibrium state. Thinking of some radiating energy as the source of energy dissipated, probably at extremely low frequencies (ELFs), it is further hypothesized that, for a given flux of dissipated energy (W cm^{-2}), the same number of dissipative structures would be present in different volumes. Thus, on average, at any given age, small volumes would exhibit a higher ‘concentration’ of dissipative structures than large volumes do. The physicochemical parameters that are suitable to reveal these structures, χ^{E} (μS cm^{-1}) and $Q^{\mathrm{E}}_{\mathrm{mix}}$ (J kg^{-1}), are in fact themselves functions of the number, size and shape of the dissipative structures [8–14].

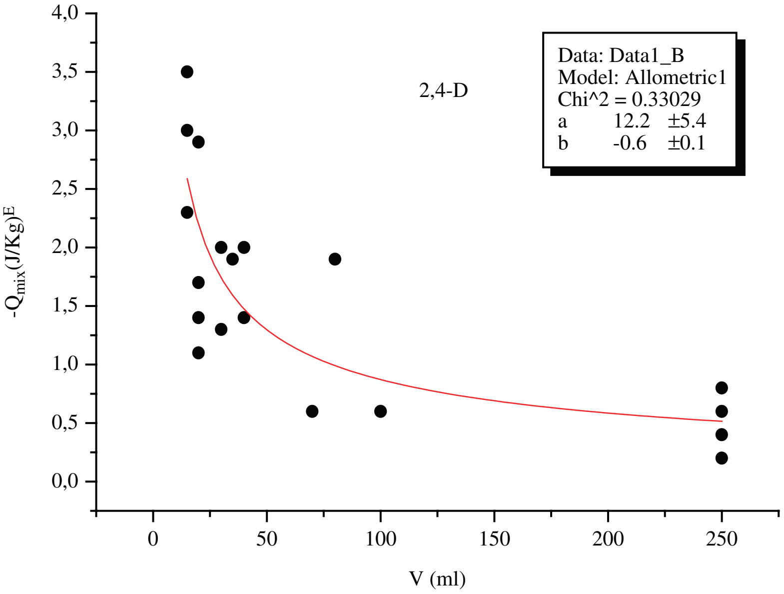

Figure 4: Excess heat of mixing of 2,4-dichlorophenoxiacetic acid vs. the SDA solution volumes (age: 1,400 days) The interpolating function is: $Y = aX^b$. The values of a and b and their errors and χ^2 are given in the figure.

The hypothesis of ELF electromagnetic fields is backed up by a series of studies conducted in our laboratories over a period of 18 months to evaluate the influence of the electromagnetic fields of the environment on the SDA solutions. The studies involved comparison of the temporal evolution of the parameter χ^E 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 Mumetal container. The Mumetal container, of about $0.5\,m^3$ in size, is an excellent shield against high-frequency radiations as well as the terrestrial magnetic field. Only ELF radiations are able to penetrate inside the container. The study of the twin samples shows an extremely similar temporal evolution of the specific conductivity in the two storage environments. It is therefore reasonable to suppose that ELF radiations are indeed exploited by the dissipative systems to stay far from equilibrium.

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