Journal of Thermal Analysis and Calorimetry, Vol. 93 (2008) 3, 1003–1011

PHYSICO-CHEMICAL PROPERTIES OF AQUEOUS EXTREMELY DILUTED SOLUTIONS IN RELATION TO AGEING

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An extensive study has been carried out on aqueous 'extremely diluted solutions' (EDS). The employed experimental methodologies were well established physico-chemical techniques: flux calorimetry, conductometry, pH-metry, e.m.f. of suitable galvanic cell. The obtained results show that the preparation procedure significantly alters the physico-chemical behaviour of such solutions. Moreover, the analysis of the experimental data *vs.* the 'arrow of time' turned out to be astonishingly important. In fact some measured physico-chemical parameters evolve with time. Some experimentally measurable physico-chemical properties of the solvent water were largely affected by both time and the 'life path' of the samples. In particular, we evidenced two new experimental phenomena characterizing the EDS: the presence of a series of maximums in the measured electrical conductivity *vs.* the sample age; the dependence of said maximums on the volume of the EDS during its ageing.

All of these new experimental results clearly suggest the presence of an extended and 'ordered' dynamics involving the whole of the water molecules in the liquid. A temporal evolution, featuring three maximums in the course of four years of ageing and the dependence on the ageing volumes do not fit the framework of classical thermodynamics. It therefore seems appropriate to interpret these phenomena on the basis of the thermodynamics of dissipative structures, which are far from equilibrium systems.

Keywords: *age of EDS, dissipative structures, EDS, electrical conductivity, extremely diluted solutions, oscillating systems, volume of EDS, water*

Introduction

In the last decade, we have been trying to give an answer to the following question: is water, treated according to the peculiar procedure that makes 'extremely diluted solutions', from the physico-chemical point of view, a 'new water', really different from the initial one? The answer to this question turns out to be positive, with the support of a wealth of experimental results and the use of established scientific paradigms. The EDS have been systematically studied [1–11]. We showed that the physico-chemical properties of the aqueous EDS are different from those of the solvent used to dilute, despite the identical chemical composition of the two liquids [1–11]. The experiments draw an anomalous thermodynamic picture: similar conclusions were reached by Lo [12, 13]. Likewise, Rey [14] showed that the structure of hydrogen bonds in pure water is very different from that of aqueous EDS obtained by an iterative procedure of dilution and succussion and not identical as expected.

These studies of aqueous EDS reveal some unexpected new properties of water. Recent studies on the physico-chemical properties of water also confirmed that water still has unexpected properties [15–24]. The studies by Lobyshev on low concentrations and electromagnetic fields, as well as the results of Samal and Geckeler on the effect of dilution on the size of clusters of e.g. fullerene-cyclodextrin, β-cyclodextrin and sodium chloride, suggest that water and aqueous solutions are complex systems [25–27].

In our previous studies we measured the heats of mixing of basic and acid solutions with EDS and their electrical conductivity and compared them with the analogous heats of mixing and electrical conductivity of the solvent. We found some relevant exothermic excess heats of mixing, as well as higher electrical conductivities than those of the untreated solvent. We highlighted a net exothermic effect, when mixing aqueous EDS with solutions of sodium hydroxide at different concentrations. The peculiar results of calorimetric titration suggested a transition from order to disorder, induced by pH variations [1]. Based on those calorimetric and conductometric measurements it was hypothesized that the particular preparation technique could lead to an alteration of the 'structure' of the solvent, namely to the development of dissipative structures [28].

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1388–6150/$20.00

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Here we report a transport study in which the electrical conductivity of aqueous EDS was measured in relation to the age of the solutions. We confirmed the importance of the time parameter, i.e. the age of the samples.

In water, the high mobility of the H^+ and OH^- ions under a gradient of electrical potential is related to the presence of clusters of water molecules, held together by hydrogen bonds (the hopping mechanism [29, 30]). Our view is that the aqueous EDS are far-from-equilibrium systems, capable of forming dissipative structures. That view is supported by the fact that time modifies their physico-chemical picture and hence their supermolecular structure.

The conductivity of the EDS shows a linear correlation with the heats of mixing with sodium hydroxide solutions. This linear correlation between two independent physico-chemical parameters hints at a single cause for both behaviours. By virtue of this correlation, when we measure the conductivity we also acquire the calorimetric information. This is important, since conductometry makes long-term studies possible, since the solutions are not consumed by the measurements, whereas calorimetric techniques are disruptive. The variations in these physico-chemical parameters would therefore be caused by variation of the number, size and/or shape of the dissipative structures. The observed phenomena provide new information on the physical nature of the liquid state of water, suggesting that water is a complex system, induced to self-organize by small perturbations (succussion, dilution, electromagnetic fields, etc.) and exhibiting variations in its physico-chemical properties that may be permanent, temporary or oscillating [1–11, 14, 25, 26].

Experimental

Background

Aqueous EDS are prepared by iterating two steps: dilution and dynamization. The process of dynamization consists in a violent agitation (succussion) of the solution by means of a mechanical apparatus. The process of dilution used in this study is the Korsakovian one. For example, to prepare a solution of Arnica Montana (AM), 1 g of an extract of Arnica Montana is added to 99 g of solvent. After the mechanical treatment (succussion), the resulting solution is called ‘1 centesimal Korsakovian’ or 1CK and is named after the formula of the solute (or a simple abbreviation of it). In our example, AM 1CK is obtained. In order to prepare the 2 centesimal Korsakovian (AM 2CK), the AM 1CK solution is diluted 1:100 (in volume) with the solvent and then successed. That is, each dilution step consists in disposing of 99% of the liquid in the bottle, refilling to 100% with deminerilized water and then dynamizing. According to the protocol, the bottle containing the solution to dilute is never changed while carrying out the dilutions.

Procedures

The EDS were supplied by Cemon (Italy) and were prepared in the Korsakovian mode. The solvent used for the preparations was demineralized water. First, samples of Arnica Montana were prepared (AM, an extract of Arnica Montana in a water–alcohol mix). There were used three different processes of dynamization given 100, 400 and 600 stokes in succussion procedures. After preparation, the EDS were stored at room temperature for several months (aged) in bottles of dark glass. Since these bottles may release impurities, a systematic analytical study of the samples was carried out. This made it possible to subtract from the measured conductivities the ‘chemical’ contribution. We found that the physico-chemical properties of the solutions were different from those of the solvent water, despite the identical chemical composition.

Methods

Conductivity measurements

Systematic measurements of specific conductivity were performed on the EDS, using a YSI mod-3200 conductometer with a conductivity cell, having a constant of 1.0 cm^{-1}. Before measuring the conductivity of a sample, the cell had to be calibrated by determining the cell constant K (cm^{-1}). The specific conductivity, χ ($\mu S\ cm^{-1}$), was then obtained as the product of the cell constant and the conductivity of the solution. For a given conductivity measuring cell, the cell constant was determined by measuring the conductivity of a KCl solution with a specific conductivity known with great accuracy, at several concentrations and temperatures. All conductivities were temperature corrected to 298 K, using a pre-stored temperature compensation for pure water [31].

Analytical determination of impurities

Care was taken to account for impurities, released by the glass containers, that can affect the electrical conductivity results. The glass may release alkaline oxides, that get converted to sodium bicarbonate in contact with the atmospheric CO_2. Therefore, the sodium concentration was determined, through atomic absorption spectrometry carried out with a Varian Spectra A instrument. Before measuring the samples with the instrument, a calibration curve was obtained using standard solutions.

To prepare the standard solutions, NaCl was dissolved in water and diluted to 1 L to obtain 1000 μg mL^{-1} Na. The working conditions were: lamp current: 5 mA; fuel: acetylene; support: air; flame stoichiometry: oxidizing. The wavelength used depends on the concentration range of sodium. For our samples it was 589.6 nm. Sodium is partially ionised in the air–acetylene flame. To suppress ionisation, some potassium chloride solution was added to produce a final concentration of 2000 μg mL^{-1} in all solutions, including the blank [32]. Impurities were in the ppm range.

Due to the release of sodium oxide by the glass containers, the chemical composition of the solvent varies with the age of the solutions, while the other components of the dark glass of the bottles have very low solubility and cannot contribute appreciably to the conductivity.

Results and discussion

Tables 1–3 show, for all the samples: the name of the substance (system) and their degree of dilution, CK; the number of strokes in the succussion procedure, n_s; the time at which we measured the conductivity of the EDS, $t\chi$/day , expressed in days; the conductivity χ/μS cm^{-1}; the concentration of sodium [Na$^+$]/mol L^{-1}, determined as described in Analytical determination of impurities; the excess conductivity χ^E/μS cm^{-1}, namely the difference between the conductivity of the sample and that of the solvent. For practical reasons, often the measurements of conductivity and sodium concentration could not be simultaneous. The time at which we measured the sodium concentration of the EDS is reported in the table as $t_{[\mathrm{Na}^+]}$/day. So, in order to know the sodium concentration of the sample at the age for which we measured its conductivity, we used a linear interpolation between the values of the sodium concentration measured before and after the conductivity measure. The conductivity of sodium bicarbonate as a function of the molarity, M/mol L^{-1}, was determined experimentally in the range $1\cdot10^{-5}$–$1\cdot10^{-3}$ M and showed a linear trend: $\chi=0.29(\pm0.17)+0.932(\pm0.003)M$, $R=0.999$ [9].

Table 1 Electrical conductivity χ/μS cm^{-1}, excess conductivity, χ^E/μS cm^{-1} and sodium concentration, [Na$^+$]/mol L^{-1} for extremely dilute solutions of Arnica Montana (AM, n_s=100 strokes)

System	t_χ	χ	χ^E	$t_{[\mathrm{Na}^+]}$	[Na$^+$]·10^5	System	t_χ	χ	χ^E	$t_{[\mathrm{Na}^+]}$	[Na$^+$]·10^5
AM 5CK[a]	0	24.0	0.0	0	25.4	AM 12CK[a]	503	49.0	9.0	844	90.3
AM 5CK[a]	69	26.0	3.3	83	23.8	AM 12CK[a]	608	49.9	2.8	963	141
AM 5CK[a]	161	27.0	4.4	161	23.9	AM 12CK	839	102	18		
AM 5CK[a]	459	83.3	64.8	494	19	AM 12CK	953	151	23		
AM 5CK[a]	503	59.4	38.5	619	62	AM 30CK[a]	0	24.0	0.0	0	25.4
AM 5CK[a]	608	61.5	6.9	844	78.3	AM 30CK[a]	69	27.0	2.3	83	26.4
AM 5CK	839	96	23	963	98.2	AM 30CK[a]	161	28.2	3.2	161	26.5
AM 5CK	953	104	14	1062	98.4	AM 30CK[a]	459	75.0	–3.0	494	90
AM 5CK	1062	110	18	1187	113	AM 30CK[a]	503	131.3	43.2	619	149
AM 5CK	1183	139	34	1289	142	AM 30CK[a]	608	156.0	21.7	844	241
AM 5CK	1391	168	19	1394	160	AM 30CK	839	331	108	963	306
AM 6CK[a]	0	24.0	0.0	0	25.4	AM 30CK	953	339	58.6		
AM 6CK[a]	69	28.4	3.6	83	26.5	AM 200CK[a]	0	24.0	0.0	0	25.4
AM 6CK[a]	161	29.0	4.4	161	26.1	AM 200CK[a]	69	27.4	2.9	83	26.1
AM 6CK[a]	459	54.8	18.6	494	40	AM 200CK[a]	161	26.5	3.1	161	24.8
AM 6CK[a]	503	66.2	26.2	619	76	AM 200CK[a]	256	28.7	1.7	390	34
AM 6CK[a]	608	79.0	10.8	844	102	AM 200CK[a]	372	35.2	3.9	494	41
AM 6CK	839	122	25			AM 200CK[a]	459	45.0	8.7	619	61
AM 12CK[a]	0	24.0	0.0	0	25.4	AM 200CK[a]	503	56.4	16.5	844	69.8
AM 12CK[a]	69	28.8	3.3	83	27.4	AM 200CK[a]	608	59.1	3.6	963	84.3
AM 12CK[a]	161	28.4	4.4	161	25.4	AM 200CK	839	80	14.8	1062	95.7
AM 12CK[a]	372	35.9	2.1	494	42	AM 200CK	953	88.1	10.4		
AM 12CK[a]	459	46.0	8.2	619	51	AM 200CK	1062	112	22.5		

[a] [10]

Table 2 Electrical conductivity χ/µS cm^{-1}, excess conductivity, χ^E/µS cm^{-1} and sodium concentration, [Na$^+$]/mol L^{-1} for extremely dilute solutions of Arnica Montana (AM, n_s=400 strokes)

System	t_χ	χ	χ^E	$t_{[Na^+]}$	[Na$^+$]·10^5	System	t_χ	χ	χ^E	$t_{[Na^+]}$	[Na$^+$]·10^5
AM 5CK[a]	0	24.0	0.0	0	25.4	AM 12CK[a]	372	35.8	3.6	494	38
AM 5CK[a]	69	24.2	2.1	83	23	AM 12CK[a]	459	43.1	8.3		
AM 5CK[a]	161	26.2	4.4	161	23.1	AM 12CK[a]	503	51.8	15.8		
AM 5CK[a]	256	26.5	2.0	494	33	AM 12CK[a]	608	53.3	14.5		
AM 5CK[a]	372	31.6	3.9	619	44	AM 30CK[a]	0	24.0	0.0	0	25.4
AM 5CK[a]	459	40.0	9.9	844	45.7	AM 30CK[a]	69	28.2	3.1	83	26.9
AM 5CK[a]	503	44.4	12.6	963	55.3	AM 30CK[a]	161	28.4	4.7	161	25.1
AM 5CK[a]	608	44.6	4.2	1062	57	AM 30CK[a]	256	30.1	4.0	494	34
AM 5CK	839	54.6	11.7	1187	62	AM 30CK[a]	372	35.0	6.1	619	46
AM 5CK	953	59.4	8.3	1289	66.6	AM 30CK[a]	459	41.5	10.4	844	50.3
AM 5CK	1062	63	9.6	1394	77.2	AM 30CK[a]	503	44.4	11.6	963	56.7
AM 5CK	1183	75.9	17.9			AM 30CK[a]	608	45.2	3.0	1062	58.1
AM 5CK	1286	81.2	18.9			AM 30CK	839	88	41	1289	69
AM 5CK	1391	83.7	11.7			AM 30CK	953	63.1	11	1394	80.7
AM 6CK[a]	0	24.0	0.0	0	25.4	AM 30CK	1062	65.1	11		
AM 6CK[a]	69	24.6	1.9	83	23.7	AM 30CK	1183	77.1	17		
AM 6CK[a]	161	23.6	1.7	161	23.2	AM 30CK	1286	85.5	21		
AM 6CK[a]	372	30.9	5.0	494	30	AM 30CK	1391	89	14		
AM 6CK[a]	459	38.0	10.4	619	42	AM 200CK[a]	0	24.0	0.0	0	25.4
AM 6CK[a]	503	39.8	10.7	844	47.2	AM 200CK[a]	69	27.6	3.2	83	25.9
AM 6CK[a]	608	41.2	2.7	953	56.2	AM 200CK[a]	161	26.9	3.6	161	24.7
AM 6CK	839	58.4	14	1062	59.5	AM 200CK[a]	372	33.5	3.5	494	36
AM 6CK	953	58.7	6.7	1187	64	AM 200CK[a]	459	40.2	7.5	619	47
AM 6CK	1062	67.5	12	1289	74	AM 200CK[a]	503	45.3	10.7	844	55.4
AM 6CK	1183	76.6	17	1394	87.5	AM 200CK[a]	608	46.6	3.4	963	67
AM 6CK	1286	88	19			AM 200CK	839	66.9	15.1	1062	70.9
AM 6CK	1391	95.9	14			AM 200CK	953	73.6	11.8	1187	74.7
AM 12CK[a]	0	24.0	0.0	0	25.4	AM 200CK	1062	77.4	11	1289	82.4
AM 12CK[a]	69	24.3	–0.8	83	26.8	AM 200CK	1183	87.8	18	1394	102
AM 12CK[a]	161	28.9	5.0	161	25.3	AM 200CK	1286	103.1	26.1		
AM 12CK[a]	256	28.7	1.1	390	35	AM 200CK	1391	108	13.2		

[a] [10]

As we have shown in a preceding article [10], after 60–240 days the excess conductivity χ^E reached values higher than the experimental error and, in some cases, as time went by, the experimental conductivity, χ, become more than 5 times the initial one. All of the systems increased their excess conductivity with a low slope, up to an age of about 500 days, when they reached a maximum, sometimes a very pronounced one. After the maximum, several systems returned to the initial conditions. Here we report the study of those same samples of Arnica Montana, in the following two years of age. As shown by the Tables 1–3 and Figs 1–3, in which the results are grouped by protocol of succussion (100, 400 or 600 strokes), after about 350 days after the first maximum, the systems reached a new maximum. Furthermore, several systems after returning near the initial state, as in the previous case, underwent a new increase of conductivity towards a third maximum, reached about 450 days after the second one. Again, they returned near the initial state afterwards. There does not seem to be a clear correlation between the peculiarities of a given dilution and the trend of its excess conductivity as a function of time.

That is, we did not find e.g. the same trend in the intensities of the maximums or in their sequence. Each system acted differently, except for a common temporal behaviour, i.e. the frequency of the maximums was the same. In some cases the highest maxi-

Table 3 Electrical conductivity χ/μS cm^{-1}, excess conductivity, χ^E/μS cm^{-1} and sodium concentration, [Na$^+$]/mol L^{-1} for extremely dilute solutions of Arnica Montana (AM, n_s=600 strokes)

System	t_χ	χ	χ^E	$t_{[Na^+]}$	$[Na^+]\cdot 10^5$	System	t_χ	χ	χ^E	$t_{[Na^+]}$	$[Na^+]\cdot 10^5$
AM 5CK[a]	0	24.0	0	0	25.4	AM 12CK	839	72.8	18.5	1187	76.5
AM 5CK[a]	69	24.6	2.1	83	23.5	AM 12CK	953	79	16.1	1289	90.6
AM 5CK[a]	161	26.0	4	161	23.3	AM 12CK	1062	83.3	14	1394	106
AM 5CK[a]	372	31.0	1.5	494	36	AM 12CK	1183	93.3	21.8		
AM 5CK[a]	459	38.5	5.9	619	45	AM 12CK	1286	115	30.5		
AM 5CK[a]	503	43.2	8.7	844	42.8	AM 12CK	1391	121	22.3		
AM 5CK[a]	608	44.2	2.7	963	63.2	AM 30CK[a]	0	24.0	0	0	25.4
AM 5CK	746	52.8	11.7	1062	66	AM 30CK[a]	69	27.8	3.5	83	25.8
AM 5CK	839	61.5	21.3	1187	73.9	AM 30CK[a]	161	26.8	3.5	161	24.7
AM 5CK	953	66	8.4	1289	80.6	AM 30CK[a]	256	29.2	3.1	494	35
AM 5CK	1062	73	11.2	1394	94.2	AM 30CK[a]	372	34.5	5.1	619	48
AM 5CK	1183	88.8	19.8			AM 30CK[a]	459	41.4	9.5	844	57.3
AM 5CK	1286	102.9	27.6			AM 30CK[a]	503	46.7	12.9	963	66.3
AM 5CK	1391	106	18.3			AM 30CK[a]	608	47.4	3.4	1062	66
AM 6CK[a]	0	24.0	0	0	25.4	AM 30CK	746	53.1	8.4	1187	71.8
AM 6CK[a]	69	28.0	3.3	83	26.3	AM 30CK	839	66.3	13.1	1289	77.8
AM 6CK[a]	161	27.8	3.8	161	25.4	AM 30CK	953	69	7.6	1394	91.4
AM 6CK[a]	256	29.4	2.1	494	38	AM 30CK	1062	74.5	12.7		
AM 6CK[a]	372	35.2	3.8	619	52	AM 30CK	1183	90.1	23		
AM 6CK[a]	459	43.9	9.4	844	59.1	AM 30CK	1286	93	20.3		
AM 6CK[a]	503	49.4	12.7	963	74.4	AM 30CK	1391	102	16.4		
AM 6CK[a]	608	51.2	3.6	1062	83.5	AM 200CK[a]	0	24.0	0	0	25.4
AM 6CK	746	58.8	9.2	1187	98.5	AM 200CK[a]	69	27.6	2.9	83	26.3
AM 6CK	839	74.9	19.8	1289	103	AM 200CK[a]	161	27.0	3.6	161	24.8
AM 6CK	953	82	13.6	1394	137	AM 200CK[a]	256	28.4	3.6	494	30
AM 6CK	1062	95.3	17.2			AM 200CK[a]	372	31.7	5.2	619	36
AM 6CK	1183	122.5	30.7			AM 200CK[a]	459	36.4	8.6	844	40.5
AM 6CK	1286	136.1	39.9			AM 200CK[a]	503	36.7	8	963	47.4
AM 6CK	1391	151	23.9			AM 200CK[a]	608	37.5	4.1	1062	48.5
AM 12CK[a]	0	24.0	0	0	25.4	AM 200CK	746	41.1	10.4	1187	48.5
AM 12CK[a]	69	28.5	3.4	83	26.9	AM 200CK	839	48.8	11.1	1289	51.7
AM 12CK[a]	161	26.8	2.6	161	25.6	AM 200CK	953	48.1	4.2	1394	57.8
AM 12CK[a]	372	36.8	5.3	494	38	AM 200CK	1062	50.5	5		
AM 12CK[a]	459	45.5	11	619	52	AM 200CK	1183	58.2	12.7		
AM 12CK[a]	503	50.1	13.4	844	58.1	AM 200CK	1286	63.3	14.9		
AM 12CK[a]	608	51.2	3.6	963	68	AM 200CK	1391	63.3	9.3		
AM 12CK	746	57.8	5.8	1062	74						

[a][10]

mum occurred at about 500 days and the second and third was lower than the first; while in other cases the highest maximum was the second and so on, as we can see in Figs 1–3 that summarize the main kinds of behaviour. Some regularity does appear when grouping all the dilutions prepared with the same succussion protocol, namely with the same number of strokes. For all the solutions prepared using 600 succussions, we notice that each maximum is higher that the previous one, in a regular fashion as the age increases (Fig. 3). Furthermore, the value of the third maximum follows the degree of dilution,

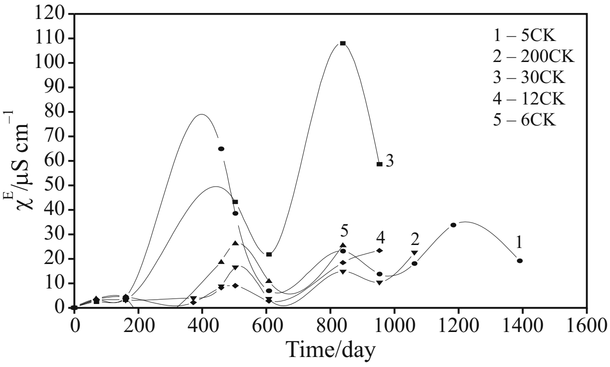

Fig. 1 Excess conductivity *vs.* time (days) of Arnica Montana 5, 6, 12, 30 and 200CK, prepared using a protocol of 100 succussions

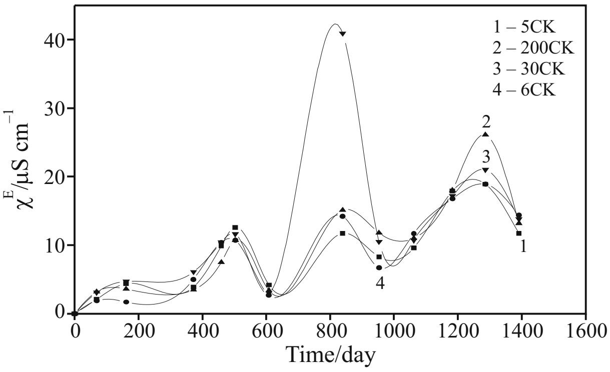

Fig. 2 Excess conductivity *vs.* time (day) of Arnica Montana 5, 6, 30 and 200CK, prepared using a protocol of 400 succussions

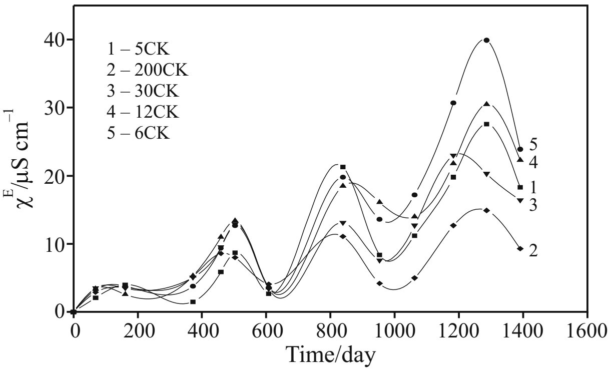

Fig. 3 Excess conductivity *vs.* time (day) of Arnica Montana 5, 6, 12, 30 and 200CK, prepared using a protocol of 600 succussions

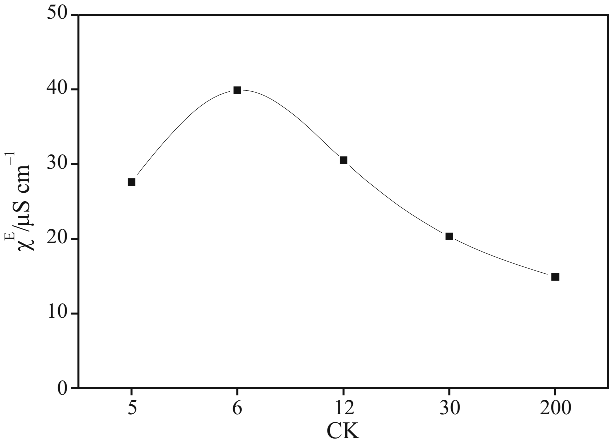

Fig. 4 Values of the excess conductivity for the third maximums *vs.* the degree of dilution of Arnica Montana 5, 6, 12, 30 and 200CK, prepared using a protocol of 600 strokes in the succussion procedure

with the most diluted solutions exhibiting the smallest maximums (200<30<5<12<6 CK), while for the second and first maximums the sequence of dilutions is less characterized (Fig. 4). For the protocol employing 400 stokes there is no such simple correlation, but we notice that the 30 CK solution features a pronounced maximum for the second of the three ones (Fig. 2). This just goes to show how difficult it is to obtain regular behaviours studying these far from equilibrium systems, as their history affects their following temporal evolution during ageing. Indeed, these are typical not reproducible systems, because they are multivariable. The protocol making use of 100 succussions produces solution with a much less regular sequence of maximums, compared to the previous two protocols: for example the AM 30K reaches its highest maximum of about 115 μS cm^{-1} at roughly 800 days; whereas the AM 5K has its highest maximum at about 400 days, with an intensity of 80 μS cm^{-1} (Fig. 1). The latter dilution also shows a very interesting behaviour, in that the second and third maximums are lower than the first. In the previous work in this field [10], we did not keep track of the volumes of the ageing samples, since we had not yet discovered the unexpected role of that parameter in measures of intensive variables i.e. variables that should be independent of the volume.

In another work, published in the International Journal of Ecodynamics [7], we found out that the lower the volume of the sample is the higher the excess conductivity. That conclusion is not confirmed here, at least for systems at different ages, because, as we just saw, in some cases the second maximum is lower than the first and/or the third maximum is lower than the second. But the volume of a sample cannot increase with time and it actually always decreases, since each measure consumes some of the sample. So, the systems behave very differently from one another, probably because of the several variables affecting them and depending on their own particular history and on the initial conditions. Fortunately though, the decrease of conductivity after each maximum excludes the possibility that undetected impurities would be the cause of the unexpected behaviours: the contribution to conductivity stemming from chemical impurities cannot diminish. So we can state that the impurities are correctly determined and the oscillating behaviour that we witnessed is that of far from equilibrium systems that produce dissipative structures.

These systems are oscillating! This is a clear outcome of the experiments on 15 different solutions, studied at different ages, for a total of 181 conductivity measurements. There is no simple correlation between this behaviour and the degree of dilution (CK) or the protocol of succussion. However, it is possible to infer from our results that a protocol of 600 strokes produces a more regular behaviour with respect to time. We cannot exclude the need for additional studies in order to find the best protocol for the succussion procedure. It is otherwise clear that much more work is needed to begin to understand these very complexes, far from equilibrium systems.

Conclusions

The present results on conductivity reinforce the hypothesis of the role played by the aggregates of water molecules, as well as the role played by H^+ and OH^-, in explaining the higher conductivity of the EDS compared to the solvent. This new phenomenon evidenced, the variation of conductometric data with time, seems to be a distinctive feature of aqueous EDS.

The new phenomena of a slow increase of conductivity with time and of an unexpected trend towards a maximum of excess conductivity, appear to be in stark contrast with the thermodynamics of systems near the equilibrium and moving towards it. It therefore seems appropriate to interpret them on the basis of the thermodynamics of dissipative structures, which are far-from-equilibrium systems. These systems need to dissipate energy to stay far from the equilibrium. For reasons not yet clarified, the modified environmental conditions periodically prevent the necessary energy dissipation, so the systems tend to return to the initial conditions. But the peculiar feature to dissipate environmental energy seems to be present in each of these systems and to be affected by the history of the system itself.

The temporal evolution of the EDS also happens to be affected by small magnitude perturbations. In some cases we had a highly diluted aqueous system that at a certain age got divided in smaller volumes. We found a deeply changed behaviour of the smaller volumes *vs.* time, compared to that of the bigger volume [7]. Whereas the bigger volume did not exhibit relevant modifications *vs.* time, every new sample of smaller volume, apart from the common feature of having maximums, 'chose' its own different way to evolve.

This finding can be related to the collisions of molecules against the walls: there is a non zero probability of transition to any of a continuum of microstates and due to the unstable character of the trajectories in phase space, all microstates possible a priori become accessible.

If our system is going through an obligatory succession of microstates, $b_i \rightarrow b_{i+1} \rightarrow b_{i+2} \rightarrow \ldots$, the transition from one microstate to the next is caused by an elastic collision between two molecules. When the system is in microstate b_{i+k}, there comes a moment when one of its molecules collides with a wall of the container. The inelastic collision causes a transition to another obligatory succession of microstates, $c_1 \rightarrow c_2 \rightarrow \ldots$, completely independent of the former succession and microstate c_1 will be chosen randomly on the basis of the laws of probability from a continuous range of possible microstates. The most probable choice is a microstate belonging to the macrostate richest in microstates (disorder) in the range. Of course this analysis is completely in line with classical statistical Thermodynamics and with the classical related concept of probability. Whereas, if we deal with water self-organization plays a completely different fundamental role: in this case irreversibility is related to the origin of life and the capability of dissipative living structures to self-organize. Self-organization leads to ordered macrostates poor in microstates [33].

This means that the evolution with time depends on the initial state (in this case: large or small volume) and that the system, in a certain sense, 'has a memory' i.e. the starting point is so relevant as to determine a very different maximum of the measured parameter (conductivity).

Another example of different temporal evolutions can be had by producing the simple perturbation of adding to the systems some water (without succussion) at different dilution ratios [9]. Again, the systems evolutions are much affected by their specific initial conditions and produce very different values of the maximums and different slopes too, in line with our findings for oscillating BZ (Belousov–Zhabotinsky) reactions [34], where Turing structures are formed which may explain the initial stages of aggregation and development, according to the following generic reaction-diffusion system:

$$\frac{\partial C_i}{\partial t} = D_i \nabla^2 C_i + f_i(\ldots, C_i, \ldots, C_j, \ldots)$$

where C_i is the concentration of the i^{th} species participating in the reaction, f_i is the non-linear kinetics equation describing the reaction and D_i is the diffusion coefficient of species i [34].

Thus, it is once again evident that the past influences the evolution of the 'pure water' system. The EDS are non-equilibrium systems in which irreversible processes occur: a new supermolecular order may appear whereby a giant fluctuation is stabilized through the exchange of energy with the outside world. This is the order associated with the dissipative structures, in which the role of water is fundamental [34]. As pointed out by Prigogine [35], non-equilibrium may be a source of order.

In general, there is a complete agreement among scientists, that a Dissipative Structure is a thermodynamically open system that maintains itself far from thermodynamic equilibrium through a continuous dissipation of low quality energy to the external environment. Through an inflow of high quality energy, matter or information, a Dissipative System gives rise to spontaneous appearance of symmetry breaking, both spatial and temporal and the formation of complex structures and behaviour, where interacting particles exhibit long range correlations. The nonlinear processes that regulate the balance between the negentropy inflow and the entropy outflow, allow the self-organization of the system.

A dissipative structure is a system that, far from thermodynamic equilibrium, efficiently dissipates the low quality energy generated to sustain it and has the capacity of changing to higher levels of orderliness, i.e. to produce self-organization.

It contains subsystems that continuously fluctuate.

At times a single fluctuation or a combination of them may become so magnified by possible feedback, that it shatters the pre-existing organization. At such ‘bifurcation points’, according to Prigogine, it is impossible to determine in advance whether the system will disintegrate into ‘chaos’ or leap to a new, more differentiated, higher level of ‘order’. The latter case defines dissipative structures so termed because they need more energy to sustain them than the simpler structures they replace and are limited in growth by the amount of low quality energy they are able to disperse.

Self-organization is normally triggered by internal variation processes, which are usually called fluctuations. Prigogine noted that a self-organizing system which also decreases its thermodynamical entropy must necessarily (because of the second law of thermodynamics) export (‘dissipate’) such entropy to its surroundings, according to the following equations:

$$\mathrm{d}S_s+\mathrm{d}S_i\geq 0$$

where S_s is the entropy of source+sink and S_i is the entropy of our intermediate system. The flow of energy from the source to the sink will always involve an increase in entropy:

$$\mathrm{d}S_s>0$$

whereas the only restriction placed by the second law of thermodynamics on $\mathrm{d}S_i$ is that:

$$-\mathrm{d}S_i\leq \mathrm{d}S_s$$

so that the entropy of the intermediate system (in our case the EDS) can decrease if there is an energy flow.

Dissipative structures cannot be created in isolated systems (no exchange of matter and energy) where entropy can only increase. However, in closed systems (exchange of energy but not matter) and open systems (exchange of matter and energy), dissipative structures can be created and entropy may decrease, provided a flux of energy of some type is present and that the system is capable of self-organizing, as is water, with its own intermolecular structures (i.e. hydrogen bonds) giving rise to dissipative structures at supermolecular level. Prigogine underlines that to extend thermodynamics to non-equilibrium processes we need an explicit expression for entropy production (entropy production per unit time, P):

$$P=\mathrm{d}_iS/\mathrm{d}t=\Sigma_\rho \mathrm{J}_\rho \mathrm{X}_\rho\geq 0$$

where J_ρ are the rates of the various irreversible processes involved (chemical reactions, heat flow, diffusion) and X_ρ are the corresponding generalized forces (affinities, temperature gradients, chemical potential gradients). This is Prigogine’s basic formula for the macroscopic thermodynamics of irreversible processes.

We conclude that the conductometric behaviour of the EDS should stem from the variation of the supermolecular structure of the solvent water, because of the linear correlation between excess conductivity and excess heat of mixing with alkaline solution. A self-consistent interpretation of this phenomenon could involve the formation of dissipative structures (a variation of the supermolecular structure of the solvent water via H-bonds). The oscillating phenomena could depend on a yet undetermined variation of the energy available from the environment, that gets dissipated to maintain the far from equilibrium condition. The temporal evolution could be related to a variation in the number, size or shape of these dissipative structures.

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Received: October 19, 2007
Accepted: January 15, 2008

DOI: 10.1007/s10973-007-8843-8