Thermodynamic parameters for the binding process of the OH⁻ ion with the dissipative structures. Calorimetric and conductometric titrations

V. Elia · E. Napoli · M. Niccoli

Abstract Conductometric and calorimetric titrations of Extremely Diluted Solutions (EDS) were performed by adding HCl or NaOH solutions. The aim of this study is to obtain further confirmation of the hypothesized presence, in the EDS, of molecular aggregates of water molecules. The measurements on the EDS evidenced some relevant differences compared to those on solutions with just water as solvent. The conductivity and the pH caused by adding the titrant, namely NaOH or HCl, were markedly different to those of the control solutions. We suppose that the preparation procedure of the EDS could produce non-equilibrium changes in the supramolecular structure of water. The experimental results were interpreted by considering the interactions that can take place between the OH⁻ or H_3O^+ and the hypothesized molecular aggregates of water molecules i.e. dissipative structures. A comparison was made about the nature of the driving force that leads to the formation of the complexes between the two ions deriving from probes and the molecular aggregates of water molecules (dissipative structures). In this study, we have determined the thermodynamic parameters of association between molecular aggregates of water molecules (dissipative structures) in the EDS and OH⁻ or H_3O^+ probe ions. The experimental results were interpreted by considering a favorable interaction between the H_3O^+ and OH⁻ ions and the dissipative structures, due, probably, to steric hindrance and chemical affinity with the aggregates.

Keywords EDS · Calorimetric titration · Conductometric titration · Complex systems · Dissipative structures

V. Elia (✉) · E. Napoli · M. Niccoli
Department of Chemistry University "Federico II" of Naples,
Complesso Universitario di Monte S'Angelo, Via Cintia,
80126 Naples, Italy
e-mail: vittorio.elia@unina.it

E. Napoli
e-mail: elena.napoli@unina.it

M. Niccoli
e-mail: marcella.niccoli@unina.it

Introduction

In our recent articles [1, 2], we put forth a new interpretation of conductometric and pHmetric titrations, performed on EDS, using HCl or NaOH as titrants. Based on those conductometric and pHmetric measurements, it was hypothesized that the particular preparation technique of EDS could lead to an alteration of the structure of the solvent [3–12]. The obtained results enable us to treat the EDS as complex systems that, under the action of perturbations of various natures, are capable of assuming a structural organization characterized by a variation of the local order, through the formation of dissipative structures [13–15] or aqueous nanostructures [16]. The titration curves differ according to the acidic or basic nature of the probe. All the conductometric titrations of sodium bicarbonate solutions at different concentrations, using an HCl solution as titrant, show equivalent points in good agreement with the analytic concentrations. The conductometric titrations of an EDS with HCl exhibit the same shape as that of a titration of a weak base with a strong acid [1]. Within such similitude, we also observe something like an equivalent point for EDS, which we prefer to indicate as a "break point" (b.p). The value of the "break point" is always higher than the equivalent point due to the presence of sodium bicarbonate. The difference between the two values represents the concentration of dissipative structures [1]. The higher the initial conductivity

of the EDS, the higher the value of the "break point" [1]. Conductometric titrations of the EDS, using NaOH, exhibit a monotonic trend, linear for lower concentrations of the titrant, but with a slope that increases for higher concentrations. The higher the initial conductivity is the lower the slopes are [2]. It seems that to a higher initial conductivity corresponds a higher capability to buffer the increase of conductivity coming from the successive additions of the alkaline solution. Despite their differences, the observed trends can be ascribed to a single cause: the presence within the EDS of something that reduces the mobility of the added ions. We put forth the hypothesis that the H_3O^+ or OH^- ions from the probes are able to form complexes with the supramolecular structures in the EDS, i.e., the dissipative structures. Acids and bases would differ in their capability of interaction with such structures, thus producing different titration curves. The whole phenomenology hints at the presence of dissipative structures with a "concentration" that can be determined using conductometric titrations with strong acids [1, 2].

That new molecular interpretation, also explains the calorimetric titrations done in the past, employing a flow-mix microcalorimetry technique [17–20]. In both kinds of titrations (acids or bases as titrants), a strong interaction with the dissipative structures is supposed, because of the measured exothermic effect. The experimental results were interpreted by considering a favorable interaction between the H_3O^+ and OH^- ions and the dissipative structures, due, probably, to steric hindrance and chemical affinity with the aggregates. It is in fact well known that isothermal calorimetry is widely used to characterize association complexes.

Experimental

Materials

The solutes, produced by Carlo Erba, Sigma, or Fluka, were of the highest purity commercially available. The "extremely diluted solutions" were prepared using, as solvent, a solution of sodium bicarbonate and/or silicic acid, at low and known concentrations ($5 \times 10^{-5} \div 1 \times 10^{-4}$ mol L^{-1}). The EDS were prepared and stored in laboratory glass containers treated with a $H_2SO_4/K_2Cr_2O_7$ solution. After that treatment, the containers were rinsed with twice distilled water, until the electric conductivity of the rinsing water reached a value of 1.2 ± 0.2 μS cm^{-1}, the same as twice distilled water.

EDS preparation

The EDS preparation follows the typical technique of Homeopathic Medicine proposed by Hahnemann [21],

which essentially implies the iteration of two steps: dilution (centesimal or decimal) and "dynamization." The process of "dynamization" consists of violent agitations (succussions) of the solution, by means of a mechanical apparatus. For a centesimal dilution, the starting point is a 1% in mass solution: as an example, to prepare a centesimal dilution of Sodium Chloride (NaCl), 1 g of NaCl is added to 99 g of solvent (dilution step). The solution is then subjected to the process of "dynamization" (succussion step) involving a violent shaking by means of a mechanical apparatus (DYNA HV 1 by Debofar N.V.S.A. Belgium). The final solution is called "1 centesimal hahnemannian" or 1 CH for short. Therefore, in the preceding example, NaCl 1 CH was obtained. In order to prepare the 2 centesimal hahnemannian (NaCl 2 CH), 1 g of the 1 CH solution is added to 99 g of solvent, and the resulting solution is "dynamized." The dilution and succussion steps are iterated until the desired degree of dilution is met. Because in 3 CH the concentration of solutions is less than 1×10^{-5} mol L^{-1} of solute, it follows that an EDS should behave as its solvent, at least from a physicochemical 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, during interaction with the environmental CO_2, gives rise to the sodium bicarbonate.

Procedures

The studied EDS were a mix of many solutions with different active principles and dilution degrees (from 3 CH to 30 CH). The conductometric titrations were performed measuring the specific electrical conductivity of a solution of EDS (1–3 mL) as a function of the volume of added HCl, and thus of the concentration of the added probe in the final solution (the molarity of HCl indicated with M_{HCl}^f/mol L^{-1}). The procedure for calorimetric titrations was similar, and involved mixing the EDS with solutions of increasing concentration of acid or base (the molality of HCl or NaOH indicated with m_{HCl}^f or m_{NaOH}^f/mol kg^{-1}). The same procedure was employed for the control solutions, namely, solutions of sodium bicarbonate at the same concentration of the EDS solutions. Samples of four different solutes were used: AA: Asernicum Album (As_2O_3); 2,4D: Dichlorophenoxicacethic acid; AM: Arnica Montana, Mother Tincture; and MM: Magnesium Muriaticum ($MgCl_2$). The EDS that we employed are labeled $Tmix_1$, $Tmix_2$, Mix_3, and Mix_{122}: each one is a mix of different volumes of the above solutions at different CHs. This choice is a consequence of the fact that large quantities of EDS are needed to perform the conductometric and calorimetric titrations and furthermore, and from a precedent article [19], we know that there is no correlation between the initial solute and dilution, and the thermodynamic

behavior of EDS. The EDS need to exhibit high initial conductivities and this property can be usually obtained using small volumes of EDS, aged for a prolonged period of time, i.e., years. Recently, we devised an alternative method to obtain relatively large volumes to carry out the two kinds of titrations, from many small volume samples aged for as long a time as that of the same active principle and dilution degree (CH). Further study is in progress to obtain more information regarding the influence of the nature of active principle and their dilution degree.

Calorimetry

The EDS were studied by means of two experimental techniques: mixing-flow microcalorimetry and electrical conductivity.

The heats of dilution and mixing were carried out using a Thermal Activity Monitor (TAM) model 2227, by Thermometric (Sweden) equipped with a flow mixing vessel. A P3 peristaltic pump from Pharmacia conveys the solutions into the calorimeter through Teflon tubes.

The values of the experimental heats (of dilution or mixing) can be obtained from the equation:

$$\Delta H = (dQ/dt)/P_w \qquad (1)$$

where dQ/dt/Watt is the heat flux, P_w/kg s⁻¹ is the total mass flow-rate of the solvent through the calorimeter. ΔH is given in J kg⁻¹ of solvent in the final solution. We determined the heats of dilution and mixing of probe solutions with the solvent and the EDS, respectively. Aqueous solutions of NaOH or HCl at different concentrations were used as probe solutions.

The following three experiments were performed:

(i) the determination of the heat of dilution, ΔH_{dil} ($m^i \rightarrow m^f$), from the initial, m^i, to the final, m^f, molality of binary aqueous solutions of NaOH or HCl, at the different concentrations employed.

(ii) the determination of the neutralization heat of the NaHCO₃, ΔH_{neutr}, contained in the EDS with binary aqueous solutions of NaOH or HCl, at the different concentrations employed.

(iii) The determination of the heat of mixing, ΔH_{mix} [$(m_x^i)(m_x^i) \rightarrow m_x^f, m_y^f$], of EDS with binary aqueous solutions as probes.

The enthalpies of mixing two solutions are given by the following equation:

$$\Delta H_{mix}[(m_x^i)(m_y^i) \rightarrow m_x^f, m_y^f] = \Delta H^* + \Delta H_{dil}(m_x^i \rightarrow m_x^f)$$
$$+ \Delta H_{dil}(m_y^i \rightarrow m_y^f) \qquad (2)$$

The enthalpy of mixing two binary solutions, ΔH_{mix}, is related to the enthalpy of formation of a complex, or in general to the enthalpy of interaction between solutes, ΔH^*, and to the heats of dilution experienced by the two solutes, ΔH_{dil}. The EDS, because of the practical absence of the solute, cannot produce any contribution to the heat of dilution and mixing via the y component, i.e., the active principle. Consequently, ΔH_{mix} [$(m_x^i)(m_y^i) \rightarrow m_x^f, m_y^f$] should coincide with ΔH_{dil} ($m_x^i \rightarrow m_x^f$) $+ \Delta H^*$, i.e., the dilution enthalpy of the probe plus am interaction term. The latter interaction enthalpy, ΔH^*, can in turn be expressed as the sum of two contributions as follows:

$$\Delta H^* = \Delta H_{neutr} + \Delta H^E \qquad (3)$$

where ΔH_{neutr} accounts for the neutralization heat of the acid or base solution with the bicarbonate at the same concentration as the EDS used in the titration; ΔH^E represents the excess enthalpy of the mixing of EDS and probe. The latter is the contribution attributed to the dissipative structures presence. The hypothesis is that some strong favourable interactions take place between the OH⁻, or H₃O⁺ ions and the supposed dissipative structures (DS). The existence of a strong interaction between a water molecule's aggregate and one of the two ions deriving from the water dissociation, could lead to the formation of a complex.

Assuming that a 1:1 complex is formed when mixing an EDS with NaOH or HCl solutions, the association process can be represented as follows:

$$DS + L = DSL$$
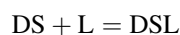
with L = H₃O⁺ or OH⁻ and DS that indicated the molecular aggregate, i.e., the dissipative structure.

ΔH^E, normalized to the total molality of the DS, m_{DS}, is a linear function of the actual molality of the titrant, m_L^f, of the standard molar enthalpy of association, ΔH_a°, and of the apparent association constant, K_a', as follows [22]:

$$m_{DS}\Delta H^E = 1/\Delta H_a^\circ + 1/\left(\Delta H_a^\circ K_a' m_L^f\right) \qquad (4)$$

For each value of ΔH^E, the actual concentration of the probe is given by:

$$m_L^f = m_L - (\Delta H^E/\Delta H_{sat}^E)m_{DS} \qquad (5)$$

where m_L is the total stoichiometric molality of the probe. The standard enthalpy and the constant are obtained from Eqs. 4 and 5 by an iterative least-squares fitting. The iterations are continued until two successive values of ΔH_a° differ by less then 2%. The values of the free energy and entropy are obtained through the usual thermodynamic relations. The absence of any information about the activity coefficients leads to evaluation of the association parameters that are thermodynamically not exactly defined. Only an apparent constant, K_a', can be determined, and consequently the standard free energy and entropy; $\Delta G_a^{\circ\prime}$ and $\Delta S_a^{\circ\prime}$, suffer from the same limitations.

Conductometric measurements

Systematic measurements of specific conductivity were performed on the EDS, using a Radiometer CDM 210 conductometer, with a conductivity cell having a constant of 0.1 cm^{-1}. Before measuring the conductivity of a sample, the cell was calibrated by determining the cell constant K/cm^{-1}. The conductometric titrations were performed in a thermostatic room (25 ± 1 °C) using samples whose temperature was conditioned in a measuring cell by a thermostat–cryostat (Grant LTD6) to be within ± 0.1 °C.

Analytic determination of impurities

The sodium concentration, M_{Na+}/mol L^{-1}, of EDS was determined through the spectroscopic method of atomic absorption, using a Spectra A Varian instrument. Before measuring the samples, the necessary calibration curve was obtained using standard solutions. In order to prepare the standard solutions, NaCl was dissolved in water and diluted to 1 liter, to obtain 1000 µg/mL Na. The working conditions were Lamp current: 5 mA; Fuel: acetylene; Support: air; and Flame stoichiometry: oxidizing. The wavelength

Table 1 Corrected conductivity, χ_r analytic concentration of HCl or NaOH in the final volume, ΔH^E of mixing the EDS with NaOH or HCl

M^f_{HCl}/mol L^{-1}	χ_r/µS cm^{-1}	m^f_{HCl}/mol kg^{-1}	$-\Delta H^E$/J kg^{-1}	m^f_{NaOH}/mol kg^{-1}	$-\Delta H^E$/J kg^{-1}	$-\Delta H^E$/m_{DS} kJ mol^{-1}
0	0.0	0	0	0	0	0
6.6×10^{-5}	1.2	2.5×10^{-5}	0.008	6.6×10^{-5}	0.60	10.8
1.3×10^{-4}	3.4	5.0×10^{-5}	0.07	1.9×10^{-4}	2.31	42.0
2.0×10^{-4}	5.6	1.0×10^{-4}	0.29	3.1×10^{-4}	3.98	72.4
2.6×10^{-4}	9.9	1.5×10^{-4}	0.41	4.3×10^{-4}	5.63	102.4
3.2×10^{-4}	25.1	5.0×10^{-4}	0.41	5.4×10^{-4}	6.60	120.0
3.8×10^{-4}	50.3	2.5×10^{-4}	0.41	6.9×10^{-4}	7.18	130.6
4.5×10^{-4}	74.5	4.0×10^{-4}	0.41	8.3×10^{-4}	7.74	140.8
5.1×10^{-4}	93.7	5.0×10^{-4}	0.41	9.8×10^{-4}	7.87	143.1
5.7×10^{-4}	117.9			9.2×10^{-4}	7.87	143.1
6.2×10^{-4}	144.1			1.2×10^{-3}	7.87	143.1
				1.5×10^{-3}	7.87	143.1
				1.8×10^{-3}	7.87	143.1
				2.0×10^{-3}	7.87	143.1

Tmix$_1$: a mix of different EDS, prepared starting from different initial solutes or dilution degrees. $\chi^i = 34$ µS cm^{-1}; $M^+_{Na} = 1.6 \times 10^{-4}$ mol L^{-1}; m_{DS}/mol kg$^{-1} \equiv M_{DS}$/mol L$^{-1} = 1.1 \times 10^{-4}$

Table 2 Corrected conductivity, χ_r; analytical concentration of HCl or NaOH in the final volume, ΔH^E of mixing the EDS with NaOH or HCl

M^f_{HCl}/mol L^{-1}	χ_r/µS cm^{-1}	m^f_{HCl}/mol kg^{-1}	$-\Delta H^E$/J kg^{-1}	m^f_{NaOH}/mol kg^{-1}	$-\Delta H^E$/J kg^{-1}	$-\Delta H^E$/m_{DS}/kJ mol^{-1}
0	0	0	0	0	0	0
6.6×10^{-5}	0.33	2.5×10^{-5}	0.03	1.0×10^{-4}	1.55	10
1.3×10^{-4}	3.7	3.7×10^{-5}	0.04	2.0×10^{-4}	3.1	20
2.0×10^{-4}	6.0	5.0×10^{-5}	0.1	3.5×10^{-4}	4.6	30
2.6×10^{-4}	8.3	1.0×10^{-4}	0.15	5.0×10^{-4}	6.2	40
3.2×10^{-4}	11.6	1.5×10^{-4}	0.49	1.0×10^{-4}	8.3	53.3
3.8×10^{-4}	13.9	2.5×10^{-4}	0.69	1.5×10^{-4}	8.9	57.2
4.5×10^{-4}	18.2	5.0×10^{-4}	0.93	2.0×10^{-4}	9.2	59.4
5.1×10^{-4}	35.5	1.0×10^{-3}	0.93	2.5×10^{-4}	9.2	59.4
5.7×10^{-4}	77.0	2.0×10^{-3}	0.93	3.0×10^{-4}	9.2	59.4
6.2×10^{-4}	104.1	2.5×10^{-3}	0.93	3.5×10^{-4}	9.2	59.4
6.8×10^{-4}	128.4			4.0×10^{-4}	9.2	59.4
7.4×10^{-4}	170			5.0×10^{-4}	9.2	59.4

Tmix$_2$: a mix of different EDS, prepared starting from different initial solutes or dilution degrees (CH). $\chi^i = 50$ µS cm^{-1}; $M^+_{Na} = 1.7 \times 10^{-4}$ mol L^{-1} m_{DS}/mol kg$^{-1} \equiv M_{DS}$/mol L$^{-1} = 3.0 \times 10^{-4}$

used, chosen on the basis of the concentration range of sodium, was 589.6 nm. Sodium is partially ionized in the air–acetylene flame. In order to suppress the ionization, some potassium chloride solution was added, to produce a final concentration of 2000 μg/mL in every solution, including the blank.

Results and discussion

In the tables, we report the results of the conductometric and calorimetric titrations of four different extremely diluted solutions (EDS) using, as titrants, HCl (calorimetric and conductometric titration) and NaOH solutions (calorimetric titrations).

Tables 1, 2, 3, and 4 contain: the analytic concentration of HCl or NaOH in the final solution, after conductometric titration (M_{HCl}^f/mol L^{-1}) and calorimetric titration (m_{HCl}^f/mol kg^{-1} or m_{NaOH}^f/mol kg^{-1}); the corrected conductivity, χ_r/μS cm^{-1}, namely, the experimental one minus the initial one, multiplied by the ratio of the initial volume of the solution to the sum of the initial volume, V_i, and the volume of the added solutions, V_{add}, to take into account the dilution process of the whole solution with the added probe solutions; ΔH^E (see the Calorimetry section) in J kg^{-1} of water in the final solution, during the mixing of the EDS with the probe. The last columns of the tables report the excess enthalpy using NaOH as titrant, $\Delta H^E/m_{DS}$ in kJ mol^{-1}, divided by the concentration of the DS obtained via conductometric titration. This value is obtained from the experimentally determined "break point", $M_{b.p.}$/mol L^{-1}, subtracting the contribution of the analytically determined concentration of sodium bicarbonate in the EDS, M_{Na+}/mol L^{-1}. According to the the hypothesis that the solution density is one, it follows that m_{DS}/mol kg^{-1} $\equiv$ M_{DS}/mol L^{-1}. The bottom of Tables 1, 2, 3, and 4 report the nature of the studied EDS; their initial conductivity, χ_i/μS cm^{-1}; the analytic concentrations of sodium bicarbonate M_{Na+}/mol L^{-1}, determined through atomic absorption (see the Analytic determination of impurities section), and the concentration of dissipative structures.

Table 5 contain the thermodynamic parameters of association between OH⁻ probe ions and dissipative structures in the EDS.

For the two EDS studied (T_{mix2} and Mix_{122}), two Figures are reported: the first, divided in two sections, shows the curves for the conductometric and calorimetric titrations with HCl and NaOH; the second Figure shows the calorimetric titration with NaOH, and expresses the ΔH^E as kJ per mole of dissipative structure (Figs. 1, 2).

The conductometric titrations show a much higher "break point" than the one due to the equivalent point for the presence of sodium bicarbonate. On the other hand, the conductometric curves are not different in shape from what it must be expected for the neutralization of the weak base, but with a "break point" that is very different to the equivalent point due to sodium bicarbonate.

The calorimetric titrations reveal that, in both the HCl and NaOH mixing, the EDS exhibit a trend characterized by a plateau. The trend, resembling a rectangular

Table 3 Corrected conductivity, χ_r; analytic concentration of HCl or NaOH in the final volume, ΔH^E of mixing the EDS with NaOH or HCl

M_{HCl}^f/mol L^{-1}	χ_r/μS cm^{-1}	m_{HCl}^f/mol kg^{-1}	$-\Delta H^E$/J kg^{-1}	m_{NaOH}^f/mol kg^{-1}	$-\Delta H^E$/J kg^{-1}	$-\Delta H^E/m_{DS}$ kJ mol^{-1}
0	0.0	0	0	0	0	0
6.6×10^{-5}	0.5	2.5×10^{-5}	0.12	2.0×10^{-4}	3.9	45.8
1.3×10^{-4}	1.9	3.7×10^{-5}	0.22	4.0×10^{-4}	7.6	89.4
2.0×10^{-4}	4.4	5.0×10^{-5}	0.26	1.2×10^{-3}	11.6	136.4
2.6×10^{-4}	6.8	1.0×10^{-4}	0.3	2.0×10^{-3}	12.8	150.6
3.2×10^{-4}	8.3	1.5×10^{-4}	0.31	3.0×10^{-3}	13	154
3.8×10^{-4}	10.7	2.5×10^{-4}	0.32	3.5×10^{-3}	13.1	154.2
4.4×10^{-4}	12.1	5.0×10^{-4}	0.32	4.0×10^{-3}	13.1	154.2
5.1×10^{-4}	19.5	2.0×10^{-3}	0.32	4.5×10^{-3}	13.1	154.2
5.7×10^{-4}	25.0	3.0×10^{-3}	0.32	5.0×10^{-3}	13.1	154.2
6.2×10^{-4}	40.4					
6.8×10^{-4}	53.8					
7.4×10^{-4}	71.2					
8.0×10^{-4}	85.6					
8.5×10^{-4}	103.0					
9.1×10^{-4}	123.4					

Mix_3: a mix of different EDS, prepared starting from different initial solutes or dilution degrees (CH). $\chi^i = 70$ μS cm^{-1}; $M_{Na}^+ = 3.6 \times 10^{-4}$ mol L^{-1}; m_{DS}/mol kg^{-1} $\equiv$ M_{DS}/mol L^{-1}=1.8 $\times 10^{-4}$

Table 4 Corrected conductivity, χ_r; analytic concentration of HCl or NaOH in the final volume, ΔH^E of mixing the EDS with NaOH or HCl

| M^f_{HCl}/mol L^{-1}	χ_r/µS cm^{-1}	m^f_{HCl}/mol kg^{-1}	$-\Delta H^E$ J kg^{-1}	m^f_{NaOH}/mol kg^{-1}	$-\Delta H^E$/J kg^{-1}	$-\Delta H^E$/m_{DS}/kJ mol^{-1}
0	0.0	0	0	0	0	0
5.0×10^{-5}	6.6	1.2×10^{-5}	0.569	1.0×10^{-4}	5.3	28.8
9.9×10^{-5}	9.1	2.5×10^{-5}	0.769	2.0×10^{-4}	7.4	36.5
1.5×10^{-4}	10.7	3.7×10^{-5}	0.89	3.5×10^{-4}	9.3	48.8
2.0×10^{-4}	13.3	5.0×10^{-5}	0.89	6.0×10^{-4}	9.6	55
2.4×10^{-4}	14.8	1.0×10^{-4}	0.89	1.0×10^{-3}	9.6	64.1
2.9×10^{-4}	16.3	2.5×10^{-4}	0.89	1.5×10^{-3}	9.6	66.2
3.4×10^{-4}	17.9	5.0×10^{-4}	0.89	2.0×10^{-3}	9.6	66.2
3.8×10^{-4}	19.4	1.0×10^{-3}	0.89	3.0×10^{-3}	9.6	66.2
4.3×10^{-4}	23.0			4.0×10^{-3}	9.6	66.2
4.8×10^{-4}	24.5			5.0×10^{-3}	9.6	66.2
5.2×10^{-4}	26.0					
5.7×10^{-4}	27.5					
6.1×10^{-4}	30.0					
6.5×10^{-4}	32.5					
7.0×10^{-4}	35.0					
7.4×10^{-4}	37.5					
7.8×10^{-4}	39.0					
8.3×10^{-4}	42.5					
8.7×10^{-4}	45.0					
9.1×10^{-4}	48.5					
9.5×10^{-4}	51.9					
9.9×10^{-4}	56.4					
1.0×10^{-3}	59.9					
1.1×10^{-3}	63.3					
1.1×10^{-3}	69.8					
1.15×10^{-4}	74.2					
1.19×10^{-4}	80.7					
1.23×10^{-3}	89.1					
1.27×10^{-3}	97.6					
1.30×10^{-3}	109.0					
1.34×10^{-3}	125.4					
1.38×10^{-3}	139.9					
1.42×10^{-3}	147.3					

Mix$_{122}$: a mix of different EDS, prepared starting from different initial solutes or dilution degrees (CH). χ^i = 115 µS cm^{-1}; M^+_{Na} = 7.1×10^{-4} mol L^{-1}. m_{DS}/mol kg^{-1} $\equiv$ M_{DS}/mol L^{-1} = 2.9×10^{-4}

**Table 5** Thermodynamic parameters for the association between EDS and OH$^-$ ions, at 298 K

System	K'_a/Kg mol^{-1}	$-\Delta H°_a$/kJ mol^{-1}	$-\Delta G^{°\prime}_a$/kJ mol^{-1}	$T\Delta S^{°\prime}_a$/kJ mol^{-1}
Tmix$_1$	2612 ± 1170	188 ± 32	19 ± 1	−168 ± 33
Tmix$_2$	1876 ± 615	80 ± 18	18.8 ± 0.8	−61 ± 19
Mix$_3$	1986 ± 519	184 ± 25	18.8 ± 0.7	−165 ± 26
Mix$_{122}$	8977 ± 877	70 ± 2	22.6 ± 0.2	−47 ± 2

hyperbola, is characterized by the formation of an association complex. What differentiates the titration with acids from that with bases, in every studied case, is the value of titrant concentration at which the plateau is reached, and its value. For titrations with HCl, the plateau is reached at very low concentrations of titrant, with a rather high slope and a
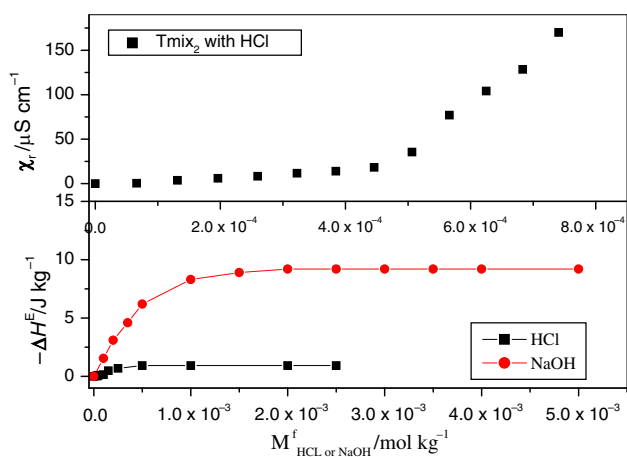
Fig. 1 The conductometric and calorimetric titrations with HCl and NaOH; The titration curves show the corrected conductivity, χ_r, and the excess enthalpy, ΔH^E/J kg⁻¹ as a function of the titrant concentration in the final solution
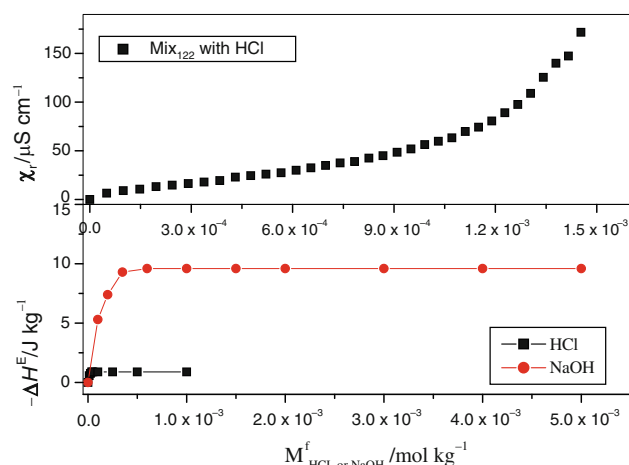
Fig. 3 The conductometric and calorimetric titrations with HCl and NaOH; The titration curves show the corrected conductivity, χ_r, and the excess enthalpy, ΔH^E/J kg⁻¹ as a function of the titrant concentration in the final solution
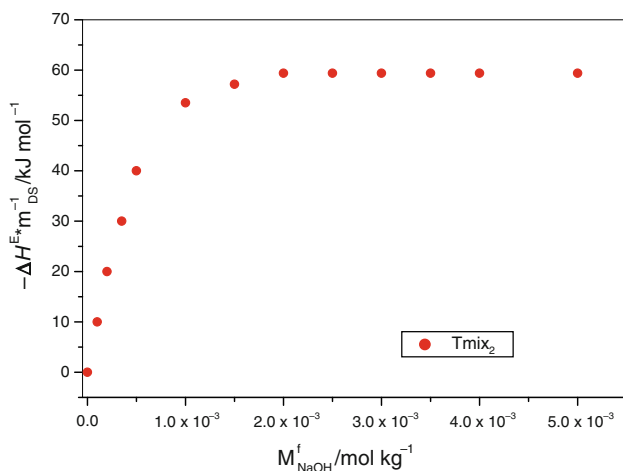
Fig. 2 The Figure shows the calorimetric titration, and expresses the $\Delta H^E/m_{DS}$, as a function of the NaOH concentration in the final solution, m_{NaOH}^f
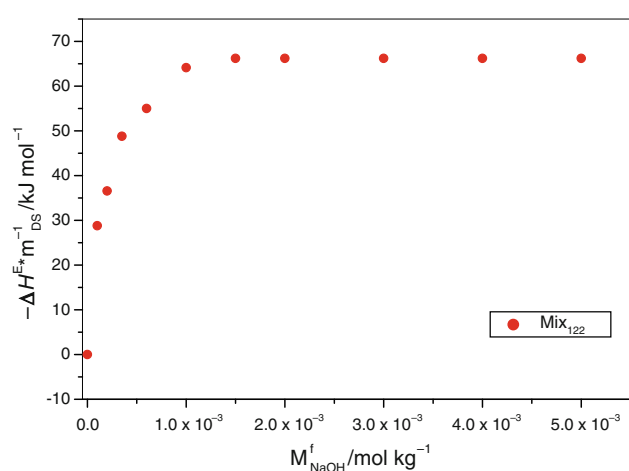
Fig. 4 The Figure shows the calorimetric titration, and expresses the $\Delta H^E/m_{DS}$, as a function of the NaOH concentration in the final solution, m_{NaOH}^f

value for the horizontal part of the trend that is always lower than characterizing the NaOH titration of the same EDS (see Figures). A behavior that can be explained with the formation of association complexes between the H_3O^+ ions and the dissipative structures, characterized by a very high association constant, compared to that determined through calorimetric titrations with NaOH, featuring an exothermic ΔH°_a, but quite smaller, which leads us to hypothesize that the driving force of the association process, in the H_3O^+ ions case, is essentially of entropic nature. The HCl titrations' features do not enable us to calorimetrically derive the association process constant. It is in fact known that threshold values exist for the association constant, above which it is not possible to derive its value [23] (Figs. 3, 4)

The titrations with NaOH are instead easily dealt with to determine the process thermodynamics. Table 5 reports the thermodynamic parameters related to the association of the studied EDS. It can be seen that, for NaOH titrations, the standard molar enthalpy of association is high and negative, like the standard molar entropy, and is thus strongly unfavorable to the complex formation. The ΔH°_a values as well as the entropic ones change from sample to sample, but the $\Delta G_a^{\circ\prime}$ values are all very close. This hypothesis can be explained on the basis of the enthalpy–entropy compensation, a very common phenomenon in association processes in water. Samples with lower concentration of dissipative structures present the more negative values of standard molar enthalpy and entropy of association. It has to be remembered that numerous factors

contribute to the thermodynamic parameters during the complexes formation: what are called interaction forces, the formation and disruption of hydrogen bonds, as well as the variation of hydration sphere of the interacting species. It is not yet possible to perform a factorization of thermodynamic parameters on the basis of the gathered data, even though it appears evident that the titration probe nature prominently affects the process through what seems an entropic driving force for H_3O^+ ions and, conversely, an enthalpic one for OH^- ions. This thermodynamic characterization of the binding phenomena of H_3O^+ and OH^- ions with the dissipative structures leads to the possibility of explaining the higher values of pH measured for the EDS compared to those expected from their chemical composition. In fact, the binding constant value for the H_3O^+ ions is higher than that of OH^- and that could produce a lower concentration of H_3O^+ than OH^-. An alternative hypothesis could be a variation of the dissociation constant for water, K_w, since the activity of the proton is lower than that of the OH^- ions, while the activity of water remains substantially invariant. Referring to the thermodynamic data of Table 5, it must be noted that the $Tmix_2$ and Mix_3 systems are characterized by very similar values of the dissipative structures concentration, m_{DS}, and very similar values of the association constant, but by very different values of binding enthalpy and, consequently, of entropy. On the other hand, the conductometric titration curve of $Tmix_2$ is characterized by a very simple curve, consisting of two linear trends crossing at the "break point." The titration curve relative to Mix_{122} shows three different linear trends. Probably the titration procedure measurements are so rich of information because they reflect the extraordinary complexity of these systems. Further study is in progress to confirm the existence of this extraordinary binding process involving dissipative structures.

References

1. Cacace CM, Elia L, Elia V, Napoli E, Niccoli M. Conductometric and pHmetric titrations of extremely diluted solutions using HCl solutions as titrant. A molecular model. J Mol Liq. 2009;146: 122–6.
2. Elia V, Napoli E, Niccoli M. A molecular model of interaction between extremely diluted solutions and NaOH solutions used as titrant. Conductometric and pHmetric titrations. J Mol Liq. 2009;148:45–50.
3. Elia V, Napoli E, Niccoli M, Nonatelli L, Ramaglia A, Ventimiglia E. New physico-chemical properties of extremely diluted aqueous solutions. A calorimetric and conductivity study at 25 °C. J Therm Anal Calorim. 2004;78:331–42.
4. Elia V, Marchese M, Montanino M, Napoli E, Niccoli M, Nonatelli L, et al. Hydrohysteretic phenomenon of "extremely diluted solutions" induced by mechanical treatments. A calorimetric and conductometric study at 25 °C. J Solut Chem. 2005;34:947–60.
5. Elia V, Elia L, Cacace P, Napoli E, Niccoli M, Savarese F. "Extremely Diluted Solutions" as multi-variables systems: a study of calorimetric and conductometric behaviour as a function of the time parameter. J Therm Anal Calorim. 2006;84:317–23.
6. Elia V, Elia L, Napoli E, Niccoli M. Conductometric and calorimetric studies of serially diluted and agitated solutions: the dependence of intensive parameters on volume. Intern J Ecodyn. 2006;1:1–12.
7. Elia V, Elia L, Montanino M, Napoli E, Niccoli M, Nonatelli L. Conductometric studies of the serially diluted and agitated solutions on an anomalous effect that depends on the dilution process. J Mol Liq. 2007;135:158–65.
8. Elia V, Napoli E, Niccoli M, Marchettini N, Tiezzi E. New physico chemical properties of extremely diluted solutions. A conductivity study at 25 °C in relation to ageing. J Solut Chem. 2008;37:85–91.
9. Belon P, Elia V, Elia L, Montanino M, Napoli E, Niccoli M. Conductometric and calorimetric studies of the serially diluted and agitated solutions. On the combined anomalous effect of time and volume parameters. J Therm Anal Calorim. 2008;93:459–69.
10. Elia V, Elia L, Napoli E, Niccoli M. On the stability of extremely diluted aqueous solutions at high ionic strength. A calorimetric study at 298 K. J Therm Anal Calorim. 2008;92:643–8.
11. Ciavatta L, Elia V, Napoli E, Niccoli M. New physico-chemical properties of extremely diluted solutions. Electromotive force measurements of Galvanic cells sensible to the activity of NaCl at 25 °C. J Solut Chem. 2008;37:1037–49.
12. Elia V, Elia L, Marchettini N, Napoli E, Niccoli M, Tiezzi E. Physico-chemical properties of aqueous extremely diluted solutions in relation to ageing. J Therm Anal Calorim. 2008;93:1003–11.
13. Nicolis G. Physics of far-equilibrium systems and self-organization. In: Davies P, editor. The new physics. New York: Cambridge University Press; 1989.
14. Prigogine I. Time, structure and fluctuations. Nobel Lecture; 1977.
15. Magnani A, Marchettini N, Ristori S, Rossi C, Rossi F, Rustici M, et al. Chemical waves and pattern formation in the 1,2-dipalmitoyl-sn-glycero-3-phosphocholine/water lamellar system. J Am Chem Soc. 2004;126:11406–7.
16. Montagnier L, Aissa J, Ferris S, Montagnier JL, Lavallèe C. Electromagnetic signals are produced by aqueous nanostructures derived from bacterial DNA sequences. Interdiscip Sci Comput Life Sci. 2009;1:81–90.
17. Elia V, Niccoli M. Thermodynamics of extremely diluted aqueous solutions. Ann N Y Acad Sci. 1999;879:241–8.
18. Elia V, Niccoli M. New physico-chemical properties of water induced by mechanical treatments. J Therm Anal Calorim. 2000;61:527–37.
19. Elia V, Niccoli M. New phisico-chemical properties of extremely diluted solutions. J Therm Anal Calorim. 2004;75:815–36.
20. Elia V, Elia L, Marchese M, Montanino M, Napoli E, Niccoli M, et al. Interaction of "extremely diluted solutions" with aqueous solutions of hydrochloric acid and sodium hydroxide. A calorimetric study at 298 K. J Mol Liq. 2007;130:15–20.
21. Hahnemann CFS. Organon. 6th ed. RED; 1985.
22. Wyman J, Gill SJ. Binding and linkage. Mill Valley: University Science Books; 1990.
23. Wadso I. Trends in isothermal microcalorimetry. Chem Soc Rev. 1997;26:79–86.