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## A Thermodynamic Characterization of Aqueous Nanostructures of Water Molecules Formed by Prolonged Contact with the Hydrophilic Polymer Nafion.

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<b>Abstract:</b>	<p>This work investigates the physicochemical alterations of water perturbed by prolonged contact with the hydrophilic polymer Nafion, referred to as Iteratively Nafionized Water (INW). The parameters measured are: electrical conductivity <math>\chi</math> (<math>\mu\text{S cm}^{-1}</math>), heat of mixing with basic sodium hydroxide (NaOH) solutions <math>\Delta Q_{\text{mixNaOH}}</math> (<math>\text{J Kg}^{-1}</math>) and pH. The results indicate supramolecular aggregates of water molecules form after prolonged contact with a Nafion surface. Conductometric, pH-metric and calorimetric titrations of INW were performed by the addition of NaOH solutions to determine the following: i) Concentration of the aqueous nanostructures, via conductometric and pH-metric titration with NaOH solutions; ii) Thermodynamic parameters, via calorimetry titration, for the process of formation of complexes between the nanostructures and the base used.</p>
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## A Thermodynamic Characterization of Aqueous Nanostructures of Water Molecules Formed by Prolonged Contact with the Hydrophilic Polymer Nafion.

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This work investigates the physicochemical alterations of water perturbed by prolonged contact with the hydrophilic polymer Nafion, referred to as Iteratively Nafionized Water (INW). The parameters measured are: electrical conductivity,  $\chi / \mu\text{S cm}^{-1}$ , heat of mixing with basic sodium hydroxide (NaOH) solutions,  $\Delta Q_{\text{NaOH}}^{\text{mix}} / \text{J Kg}^{-1}$  and pH. The results indicate supramolecular aggregates of water molecules form after prolonged contact with a Nafion surface. Analytical determination by Ion Chromatography allows us to exclude the role of contaminants. This suggests that water may possess an exceptional self-organisation capability triggered by the contact with a hydrophilic surface. Conductometric, pH-metric and calorimetric titrations of INW were performed by the addition of NaOH solutions to determine the concentration of the aqueous nanostructures, via conductometric and pH-metric titration with NaOH solutions. Thermodynamic parameters were determined via calorimetry titration, for the process of formation of complexes between the nanostructures and the base used.

**Keywords:** Nafion, INW, calorimetric titration, conductometric titration, complex systems, dissipative structures, aqueous nanostructures.

### Introduction

In previous studies [1-2], we investigated the physicochemical and spectroscopic properties of Iteratively Nafionized Water (INW), i.e., water perturbed by continued contact with Nafion hydrophilic surfaces [3-4]. These works were prompted by the important findings of J. Pollack [5-8], who analysed the interaction between water and hydrophilic polymers. He showed that a zone of highly ordered water forms at the liquid-solid interface with the various studied hydrophilic polymers, among which Nafion stood out due to its peculiarities. The observed width of this ordered zone was in the order of hundreds of molecules (i.e., hundreds of microns), hence much wider than classical theory would predict, and it acted as an exclusion zone (EZ) for chemicals (e.g. dyes) and/or acid-base indicators, as well as macroscopic particles.

The hypothesis of the formation of molecular aggregates of water molecules appears to be supported in our articles [1-2] both by the thermodynamic parameters and by structural observations in the liquid phase. IR Spectroscopy and Atomic Force Microscopy confirm also the possibility that such molecular aggregates survive in the solid phase [2].

The aim of the present work is to further confirm the hypothesized presence, in INW, of molecular aggregates of water molecules. The investigated system consists of Milli-Q (ultrapure) water subjected to perturbation by prolonged contact with a sheet of Nafion, which is removed prior to determining the following physicochemical parameters of the water: pH, specific conductivity  $\chi / \mu\text{S cm}^{-1}$  and heat of mixing with a basic solution  $\Delta Q_{\text{NaOH}}^{\text{mix}} / \text{J Kg}^{-1}$ .

In particular, in this study we applied to INW the same experimental protocol previously used to characterize EDS (extremely diluted solutions) [9-10] and IFW [11] (iteratively filtered water), two other aqueous systems obtained with different preparation protocols [12-15]. Through a procedure of conductometric and pH-metric titration [12-14] it is possible to determine the concentration of dissipative structures, formed by water molecule aggregates (aqueous nanostructures). Using

1 calorimetric titration [15], we determined the thermodynamic parameters that characterize the  
2 formation of complexes between molecular aggregates of water molecules (aqueous nanostructures)  
3 and OH<sup>-</sup> probe ions. Our previous works indicate that EDS and IFW can be regarded as complex  
4 systems that, under the action of various types of perturbations, can take on a structural organization  
5 characterized by variations in local order, through the formation of dissipative structures [16-17],  
6 i.e. nanostructures of water molecules in complex systems [18-20]. We interpret these results as  
7 arising from favourable interactions between the OH<sup>-</sup> ions and the nanostructures, probably due to  
8 favourable steric hindrance and chemical affinity with the aggregates. These previous findings lead  
9 us to believe that the same hypothesis can be extended to INW.  
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## 11 12 13 **Experimental**

### 14 *Preparation*

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18 Samples of water perturbed by the contact with Nafion [3-4], hereinafter referred to as Iteratively  
19 Nafionized Water (INW), were prepared through the following steps:  
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- 21  
22 1. Initially, the pristine membrane was washed 5 times using 20 ml of “ultrapure” (Milli-Q)  
23 water.
- 24  
25 2. Nafion membranes with a surface area of 60-120 cm<sup>2</sup> and a thickness of 50-180 μm, were  
26 placed in a Petri capsule (made either of Pyrex glass or plastic) in contact with 10-20 ml of  
27 Milli-Q water ( $\chi = 1-2 \mu\text{S cm}^{-1}$ ). The containers were manually agitated repeatedly, causing  
28 the liquid to lap against the membrane. We then followed the evolution of  $\chi$  which was  
29 found to systematically increase. The procedure was repeated after turning the membrane  
30 over. All this was iterated some tens of times, with each iteration invariably producing an  
31 increase in conductivity.
- 32  
33 3. After attaining the required conductivity increase, the INF was subjected to physicochemical  
34 characterization. The Nafion membrane was then reused for new procedures. No significant  
35 differences were noted between the results obtained with pristine or previously-used Nafion  
36 membranes.  
37  
38

39 To obtain a sufficiently high conductivity, i.e. 50-200 μS cm<sup>-1</sup>, approximately 10-20 iterations of  
40 the final two steps were needed. Even though successive iterations invariably produce an increase in  
41 electrical conductivity, it has not yet been possible to quantitatively correlate the number of  
42 iterations with the increase in  $\chi$ .  
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44

### 45 *Methods*

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48 The Nafion samples were studied using the following experimental techniques: mixing-flow  
49 microcalorimetry, pH-metry and electrical conductivity.  
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### 51 *Calorimetry*

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54 The heats of dilution and mixing were measured using a Thermal Activity Monitor (TAM) model  
55 2227 (Thermometric, Sweden), equipped with a flow mixing vessel. A P3 peristaltic pump  
56 (Pharmacia) conveyed the solutions into the calorimeter through Teflon tubes.  
57 The values of the experimental heats (of dilution or mixing) can be obtained from the equation:  
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$$59 \Delta H = (dQ/dt)/P_w \quad (1)$$

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1 where  $dQ/dt / \text{Watt}$  is the heat flux,  $P_w / \text{kg s}^{-1}$  is the total mass flow-rate of the solvent through the  
2 calorimeter and  $\Delta H$  is given in  $\text{J kg}^{-1}$  of solvent in the final solution. We determined the heats of  
3 dilution and mixing of probe solutions with the solvent and the INW respectively. Aqueous  
4 solutions of NaOH at different concentrations were used as probe solutions.  
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### 8 *Conductivity measurements*

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10 Systematic measurements of specific conductivity were performed on the INW, using a Radiometer  
11 CDM 210 conductometer, having a conductivity cell constant of  $0.1 \text{ cm}^{-1}$ . Before measuring the  
12 conductivity of a sample, the cell was calibrated by determining the cell constant  $K (\text{cm}^{-1})$ . The  
13 conductometric titrations were performed in a thermostatic room ( $25 \pm 1 \text{ }^\circ\text{C}$ ) using samples that had  
14 been temperature conditioned in a measuring cell by a thermostat-cryostat (Grant LTD6) to within  
15  $\pm 0.1 \text{ }^\circ\text{C}$ .  
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### 19 *pH measurements*

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21 The temperature was controlled within  $\pm 0.1 \text{ }^\circ\text{C}$  with a thermostat-cryostat (Grant LTD6), and the  
22 pH measurements were carried out with a potentiometer-pHmeter (Crison GLP 21-22), having a  
23 resolution of  $\pm 0.01 \text{ pH units}$ .  
24  
25  
26

### 27 *Analytical determination of impurities*

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29 Nafion is a sulfonated tetrafluoroethylene copolymer [3-4]. It must be stressed that the chemical  
30 composition of the Nafion membrane enables it to release only  $\text{F}^-$  and  $\text{HSO}_4^-$  ions over a prolonged  
31 period, while the concentration of soluble impurities is reduced to zero after several cycles of  
32 washing. The concentration of the two ions, analytically determined by ion chromatography, was in  
33 the order of  $10^{-6} \text{ mol L}^{-1}$ :  $[\text{F}^-] = 2.8 \times 10^{-6}$ ,  $[\text{HSO}_4^-] = 2.5 \times 10^{-6} \text{ mol L}^{-1}$  for a high conductivity sample  
34 ( $305 \mu\text{S cm}^{-1}$ ). These quantities are not correlated with the very high conductivity of the examined  
35 sample.  
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### 40 *Theoretical Section*

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42 To determine the thermodynamic parameters for the formation of complexes between the  
43 nanostructures and the base used, the following three kinds of experiments were performed:  
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45

- 46 i) Determination of the heat of dilution  $\Delta H_{\text{dil}} (m_x^i \rightarrow m_x^f)$  from the initial molality  $m^i$  to the final  
47 molality  $m^f$  of binary aqueous solutions of NaOH, at the different concentrations employed.  
48
- 49 ii) Determination of the heat of dilution  $\Delta H_{\text{dil}} (m_y^i \rightarrow m_y^f)$  from the initial molality  $m^i$  to the final  
50 molality  $m^f$  of INW.  
51
- 52 iii) Determination of the heat of mixing  $\Delta H_{\text{mix}} [(m_x^i)(m_y^i) \rightarrow m_x^f, m_y^f]$  of INW with binary  
53 aqueous solutions as probes.  
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57 The enthalpies of mixing two solutions are given by the following equations [21]:  
58

$$59 \Delta H_{\text{mix}} [(m_x^i)(m_y^i) \rightarrow m_x^f, m_y^f] = \Delta H^* + \Delta H_{\text{dil}} (m_x^i \rightarrow m_x^f) + \Delta H_{\text{dil}} (m_y^i \rightarrow m_y^f) \quad (2)$$

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

$$\Delta H^* = \Delta H^E \quad (3)$$

where  $\Delta H^E$  represents the excess enthalpy of mixing of the INW and probe. The latter term is the contribution attributed to the presence of nanostructures. The hypothesis is that some strong favourable interactions take place between the OH<sup>-</sup> ions and the posited nanostructures (NS). The existence of a strong interaction between water molecule aggregates and one of the two ions deriving from the dissociation of water could lead to the formation of a complex.

Assuming that a 1:1 complex is formed when mixing an INW with NaOH solutions, the association process can be represented by the following chemical equation:



Where L = OH<sup>-</sup> and NS denotes the molecular aggregate, i.e. the dissipative structure.

$\Delta H^E$ , normalized to the total molality of the NS,  $m_{\text{NS}}$  nanostructures, is a linear function of the actual molality of the titrant,  $m_L^f$ , of the standard molar enthalpy of association,  $\Delta H_a^\circ$ , and of the apparent association constant,  $K_a'$ , as follows:

$$m_{\text{NS}} / \Delta H^E = 1 / \Delta H_a^\circ + 1 / (\Delta H_a^\circ K_a' m_L^f) \quad (5)$$

For each value of  $\Delta H^E$ , the actual concentration of the probe is given by:

$$m_L^f = m_L - (\Delta H^E / \Delta H_{\text{sat}}^E) m_{\text{NS}} \quad (6)$$

where  $m_L$  is the total stoichiometric molality of the probe. The standard enthalpy and the constant are obtained from equations (4) and (5) by iterative least-squares fitting. The iterations are continued until two successive values of  $\Delta H_a^\circ$  differ by less than 2%. The values of the free energy and entropy are computed from the usual thermodynamic relations. The absence of information about the activity coefficients leads to evaluations of the association parameters that are not precisely defined thermodynamically. We can only determine an apparent constant,  $K_a'$ , and consequently the standard free energy and entropy,  $\Delta G_a^{\circ'}$  and  $\Delta S_a^{\circ'}$ , suffer from the same limitations.

## Results and Discussion

Reported below are the results of conductometric, pH-metric and calorimetric titrations for five different INWs, using NaOH solutions as titrants. The results show that the INW samples exhibit a large variations in these parameters compared to unperturbed water. Confirming the findings of our previous study [1], the experimental data demonstrate that  $\chi$  increases by up to two orders of magnitude, while  $\Delta Q_{\text{NaOH}}^{\text{mix}}$  is exothermic and increases with electrical conductivity, following a

roughly linear trend, by up to one order of magnitude.

The tables show the experimental data for conductometric, pH-metric and calorimetric titrations, using, as titrants, NaOH solutions at different concentrations. The pH-metric and conductometric titrations are carried out by adding known volumes of titrant solution (at known concentration) to a known volume of INW sample. The calorimetric titrations were performed by mixing to the INW sample, solutions of NaOH at a known concentration. Tables 1-5 contain: the analytical concentration of NaOH in the final solution after conductometric and pH-metric titration,  $M_{\text{NaOH}}^f / \text{mol L}^{-1}$ , and after calorimetric titration,  $m_{\text{NaOH}}^f / \text{mol kg}^{-1}$ ; the final conductivity,  $\chi^f / \mu\text{S cm}^{-1}$ , i.e., the experimental specific conductivity after addition of the probe solution; the final pH,  $\text{pH}^f$ , i.e., the experimental pH after addition of the probe solution; the heat of mixing  $\Delta H^E$  (see the Calorimetry section) in  $\text{J kg}^{-1}$  of water in the final solution, during the mixing of the INW with the probe. The last column in each table reports the excess enthalpy using NaOH as a titrant divided by the concentration of the NS obtained via conductometric titration,  $\Delta H^E / m_{\text{NS}} / \text{kJ mol}^{-1}$ . This value is computed from the experimentally determined equivalent point,  $M_{\text{e.p.}} / \text{mol L}^{-1}$ , obtained from the conductometric titration [12-14]. Proceeding from the hypothesis that the solution density is one and taking into account the mass flow-rate in calorimetric titrations, it follows that  $m_{\text{NS}} / \text{mol kg}^{-1} = \frac{1}{2} M_{\text{e.q.}} / \text{mol L}^{-1}$ .

For the interaction with the basic solution an exothermic heat was found, increasing with increasing  $\chi$ . The increase was about one order of magnitude. In the case of HCl as reactant the  $\Delta Q_{\text{mix}}^{\text{HCl}}$  was almost null. In Fig. 1 we show the experimental heats of mixing of the Nafionized samples with basic solutions, as a function of conductivity. A linear correlation was found, indicating a single cause for the phenomena.

The conductometric titrations show curves that do not differ from the expected trend for neutralization of a strong acid with a strong base (Fig. 2-3). As the titration progresses, the protons are neutralized to form water by the addition of NaOH. For each amount of NaOH added, the  $\text{H}^+$  cation is replaced by the slower  $\text{Na}^+$  ion, and the conductivity of the titrated solution decreases. This continues until the equivalence point is reached. When more base is added, the specific conductivity increases. Consequently, in the titration of a strong acid with a strong base, the conductivity has a minimum at the equivalence point. At the bottom of Tables 1-5 we report: the nature of the studied INWs, their initial conductivity  $\chi^i / \mu\text{S cm}^{-1}$  and  $\text{pH}^i$ , and the  $m_{\text{NS}} / \text{mol kg}^{-1}$ .

The calorimetric titrations reveal that, in mixing with NaOH, the INWs follow a trend characterized by a plateau (Fig. 3-4). This curve, resembling a rectangular hyperbola, is a characteristic marker of the formation of an association complex [21]. The experimental results were interpreted as reflecting the interactions that can occur between the  $\text{OH}^-$  and the posited molecular aggregates of water molecules, i.e., nanostructures of water molecules [14]. Table 6 reports the thermodynamic parameters of association between the  $\text{OH}^-$  probe ions and the nanostructures in the INW.

We employed the techniques of conductometric and pH-metric titration to determine the experimental concentrations of the aqueous nanostructures. The same methods had yielded interesting results in our previous work on perturbed water produced by the EDS and IFW preparation protocols [12-14]. It must be underlined that determining the concentration of aggregates of water molecules requires the use of either acid or basic titrants, depending on the nature of the perturbed water. In particular, for EDS and IFW solutions, which exhibit a slightly alkaline pH, the titrant must be a strong acid (HCl). The shape of the titration curve resembles a typical titration between a strong acid and a weak base. The concentration values of the posited nanostructures are reflected by the value of the conductivity of the system and, in general, the higher the conductivity the greater the concentration. In the case of INW, the systems have an acidic pH and the titrant must be a strong base. The shape of the titration curve is typical of a strong acid with a strong base. The concentrations determined by this method are in the order of  $10^{-4} \text{ mol L}^{-1}$  for all three kinds of perturbed water.

In previous studies [12-14], we explained the slightly alkaline values of EDS and IFW by hypothesizing the presence of aqueous nanostructures. The data relating to the calorimetric



1 titrations for these systems are consistent with the same working hypothesis. In fact, the binding  
2 constant value for the  $\text{H}_3\text{O}^+$  ions is higher than that of  $\text{OH}^-$ , which could result in a lower  
3 concentration of  $\text{H}_3\text{O}^+$  than  $\text{OH}^-$ . Extending the same procedure to INW, we obtained a good  
4 confirmation of the hypothesis. In this case, it was necessary to explain the low pH value. For the  
5 INW systems, the heat of mixing with an acid (HCl),  $\Delta Q_{\text{HCl}}^{\text{mix}} / \text{J Kg}^{-1}$  is found to be null. The data  
6 relating to the titration with a base (NaOH), on the contrary, show a strong affinity between NaOH  
7 solutions and nanostructures, as indicated by the high values of binding constants. The binding of a  
8 basic titrant to INW nanostructures reduces the concentration of free  $\text{OH}^-$  ions, thus resulting in an  
9 excess of free  $\text{H}_3\text{O}^+$  ions. Of course the numeric values cannot be easily determined with precision,  
10 due to the as yet unspecified nature of the nanostructures, however the thermodynamic framework  
11 is in good qualitative agreement with this hypothesis. The experimental results were interpreted as  
12 indicating a favourable interaction between the  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  ions and the posited nanostructures,  
13 probably due to favourable steric hindrance and chemical affinity with the aggregates. It can be seen  
14 that, for NaOH titrations, the standard molar enthalpy of association is high and negative, as is the  
15 standard molar entropy, thus making it strongly favourable to complex formation. The values of  
16  $\Delta H_a^\circ$  as well as of entropy vary from sample to sample, however the  $\Delta G_a^\circ$  values are all very close.  
17 This can be explained by enthalpy-entropy compensation. The plot of  $\Delta H_a^\circ$  vs.  $\Delta S_a^\circ$  yields a line  
18 with a positive slope Tc: the compensation temperature (Fig. 5). The value of Tc is  $295 \pm 33$  K, and  
19 falls within the interval reported in the literature for such processes [22-24]. The temperature at  
20 which the experiments were carried out is only slightly higher than the value found, which shows  
21 that the variations in  $\Delta H_a^\circ$  are compensated for by variations in  $\Delta S_a^\circ$  [22-24]. This compensation  
22 effect has been frequently observed in water, and is attributed to the changes undergone by water in  
23 the hydration spheres of the interacting species [24]. The increase in electrical conductivity, a  
24 phenomenon common to all three preparation protocols, is ascribed to an enhanced hopping  
25 mechanism of  $\text{H}_3\text{O}^+$  or  $\text{OH}^-$  ions due to the presence of the nanostructures [25-26].  
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## 31 Conclusion

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34 The very different protocols used for preparing three types of perturbed water produce very large  
35 alterations in the thermodynamic parameters of the systems. All these differences can be accounted  
36 for by a single working hypothesis: the presence of aqueous nanostructures of water molecules in  
37 the liquid phase. These differences can be explained using the binding parameters of the acid or  
38 alkaline reactants, determined by calorimetric titration, which are in good qualitative agreement  
39 with the pH values. The experimental results were interpreted by considering the interactions that  
40 can take place between  $\text{OH}^-$  or  $\text{H}_3\text{O}^+$  ions and the hypothesized molecular aggregates of water  
41 molecules. A comparison can be drawn concerning the nature of the driving force that leads to the  
42 formation of the complexes between the two ions deriving from probes and the molecular  
43 aggregates of water molecules.  
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**Table 1:** Final conductivity,  $\chi^f / \mu\text{S cm}^{-1}$ , final pH,  $\text{pH}^f$ , and analytical concentration of NaOH in the conductometric and pH-metric titration of INW with NaOH solutions.

$M_{\text{NaOH}}^f / \text{mol L}^{-1}$	$\chi^{f,a} / \mu\text{S cm}^{-1}$	$M_{\text{NaOH}}^f / \text{mol L}^{-1}$	$\text{pH}^{f,a}$	$M_{\text{NaOH}}^b / \text{mol L}^{-1}$	$\chi^{f,b} / \mu\text{S cm}^{-1}$	$M_{\text{NaOH}}^b / \text{mol L}^{-1}$	$\text{pH}^{f,b}$
0	169.0	0	3.4	0	146.0	0	3.6
$2.3 \cdot 10^{-4}$	115.2	$1.0 \cdot 10^{-4}$	3.5	$9.9 \cdot 10^{-5}$	118.8	$1.1 \cdot 10^{-4}$	3.8
$4.6 \cdot 10^{-4}$	61.7	$2.0 \cdot 10^{-4}$	3.7	$2.0 \cdot 10^{-4}$	90.4	$2.2 \cdot 10^{-4}$	4.3
$6.8 \cdot 10^{-4}$	74.8	$2.9 \cdot 10^{-4}$	4.0	$2.9 \cdot 10^{-4}$	74.6	$3.2 \cdot 10^{-4}$	5.9
$8.9 \cdot 10^{-4}$	106.1	$3.8 \cdot 10^{-4}$	4.9	$3.8 \cdot 10^{-4}$	77.9	$4.3 \cdot 10^{-4}$	9.0
$1.1 \cdot 10^{-3}$	140.9	$4.8 \cdot 10^{-4}$	8.9	$4.8 \cdot 10^{-4}$	81.3	$5.3 \cdot 10^{-4}$	9.5
$1.3 \cdot 10^{-3}$	175.0	$5.7 \cdot 10^{-4}$	9.7	$5.7 \cdot 10^{-4}$	88.6	$6.3 \cdot 10^{-4}$	9.9
$1.5 \cdot 10^{-3}$	210.5	$6.6 \cdot 10^{-4}$	10.2	$7.4 \cdot 10^{-4}$	114.7	$7.3 \cdot 10^{-4}$	10.2
$1.7 \cdot 10^{-3}$	243.0	$7.5 \cdot 10^{-4}$	10.4	$9.1 \cdot 10^{-4}$	149.2	$8.2 \cdot 10^{-4}$	10.4
$1.8 \cdot 10^{-3}$	274.0	$8.3 \cdot 10^{-4}$	10.6	$1.1 \cdot 10^{-3}$	184.1	$9.1 \cdot 10^{-4}$	10.6
$2.0 \cdot 10^{-3}$	303.7	$9.2 \cdot 10^{-4}$	10.7	$1.2 \cdot 10^{-3}$	218.2	$1.0 \cdot 10^{-3}$	10.7
$2.2 \cdot 10^{-3}$	332.0			$1.4 \cdot 10^{-3}$	251.1		
$2.5 \cdot 10^{-3}$	390.0			$1.7 \cdot 10^{-3}$	314.1		
$2.8 \cdot 10^{-3}$	443.0						
$3.0 \cdot 10^{-3}$	492.7						

a) Nafion Mix 1:  $\chi^i = 169 \mu\text{S cm}^{-1}$ ;  $\text{pH}^i = 3.4$ ;  $m_{\text{NS}} / \text{mol kg}^{-1} = 1/2 M_{\text{e.q.}} / \text{mol L}^{-1} = 2.6 \cdot 10^{-4}$

b) Nafion Mix 2:  $\chi^i = 146 \mu\text{S cm}^{-1}$ ;  $\text{pH}^i = 3.6$ ;  $m_{\text{NS}} / \text{mol kg}^{-1} = 1/2 M_{\text{e.q.}} / \text{mol L}^{-1} = 1.8 \cdot 10^{-4}$

**Table 2:** Final conductivity,  $\chi^f / \mu\text{S cm}^{-1}$ , analytical concentration of NaOH in the conductometric and calorimetric titration,  $\Delta H^E / \text{J kg}^{-1}$  of mixing of the INW with NaOH.

$M_{\text{NaOH}}^f / \text{mol L}^{-1}$	$\chi^{f,a} / \mu\text{S cm}^{-1}$	$m_{\text{NaOH}}^f / \text{mol kg}^{-1}$	$-\Delta H^{E,a} / \text{J kg}^{-1}$	$-\Delta H^E / m_{\text{NS}}^a / \text{kJ mol}^{-1}$
0	178.0	0	0	0
$9.9 \cdot 10^{-5}$	150.1	$1.0 \cdot 10^{-4}$	2.8	11.4
$2.0 \cdot 10^{-4}$	123.9	$1.8 \cdot 10^{-4}$	5.1	20.7
$2.9 \cdot 10^{-4}$	98.2	$3.0 \cdot 10^{-4}$	7.2	29.4
$3.8 \cdot 10^{-4}$	73.1	$5.0 \cdot 10^{-4}$	8.0	32.9
$4.8 \cdot 10^{-4}$	66.5	$1.0 \cdot 10^{-3}$	9.0	36.8
$5.7 \cdot 10^{-4}$	71.8	$2.0 \cdot 10^{-3}$	9.9	40.4
$6.5 \cdot 10^{-4}$	84.0	$2.5 \cdot 10^{-3}$	10.2	41.6
$7.4 \cdot 10^{-4}$	99.1	$5.0 \cdot 10^{-3}$	10.3	42.0
$9.1 \cdot 10^{-4}$	134.4	$1.0 \cdot 10^{-2}$	10.3	42.0
$1.1 \cdot 10^{-3}$	166.3	$1.5 \cdot 10^{-2}$	10.3	42.0
$1.2 \cdot 10^{-3}$	199.1	$2.0 \cdot 10^{-2}$	10.3	42.0
		$2.5 \cdot 10^{-2}$	10.3	42.0

a) Nafion Mix 3:  $\chi^i = 178 \mu\text{S cm}^{-1}$ ;  $\text{pH}^i = 3.4$ ;  $m_{\text{NS}} / \text{mol kg}^{-1} = 1/2 M_{\text{e.q.}} / \text{mol L}^{-1} = 2.45 \cdot 10^{-4}$

**Table 3:** Final conductivity,  $\chi^f / \mu\text{S cm}^{-1}$ , analytical concentration of NaOH in the conductometric and calorimetric titration,  $\Delta H^E / \text{J kg}^{-1}$  of mixing of the INW with NaOH.

$M_{\text{NaOH}}^f / \text{mol L}^{-1}$	$\chi^{f,a} / \mu\text{S cm}^{-1}$	$m_{\text{NaOH}}^f / \text{mol kg}^{-1}$	$-\Delta H^{E,a} / \text{J kg}^{-1}$	$-\Delta H^E / m_{\text{NS}}^a / \text{kJ mol}^{-1}$
0	98.1	$7.5 \cdot 10^{-5}$	3.8	20.0
$1.5 \cdot 10^{-4}$	70.0	$1.3 \cdot 10^{-4}$	6.5	34.2
$2.9 \cdot 10^{-4}$	46.5	$2.0 \cdot 10^{-4}$	8.0	42.1
$4.3 \cdot 10^{-4}$	43.5	$3.0 \cdot 10^{-4}$	8.8	46.3
$5.7 \cdot 10^{-4}$	52.0	$3.8 \cdot 10^{-4}$	9.1	47.9
$7.0 \cdot 10^{-4}$	58.2	$5.0 \cdot 10^{-4}$	10.2	51.6
$8.4 \cdot 10^{-4}$	71.3	$7.0 \cdot 10^{-4}$	10.6	54.2
$9.7 \cdot 10^{-4}$	83.3	$1.0 \cdot 10^{-3}$	10.9	55.8
$1.1 \cdot 10^{-3}$	102.5	$1.5 \cdot 10^{-3}$	10.9	56.8
$1.2 \cdot 10^{-3}$	121.0	$1.8 \cdot 10^{-3}$	10.9	57.4
$1.3 \cdot 10^{-3}$	136.0	$3.0 \cdot 10^{-3}$	10.9	57.4
		$5.0 \cdot 10^{-3}$	10.9	57.4
		$1.0 \cdot 10^{-2}$	10.9	57.4
		$1.5 \cdot 10^{-2}$	10.9	57.4
		$2.0 \cdot 10^{-2}$	10.9	57.4
		$2.5 \cdot 10^{-2}$	10.9	57.4

a) Nafion Mix 4  $\chi^i = 98.1 \mu\text{S cm}^{-1}$ ;  $\text{pH}^i = 3.7$ ;  $m_{\text{NS}} / \text{mol kg}^{-1} = 1/2 M_{\text{e.q.}} / \text{mol L}^{-1} = 1.9 \cdot 10^{-4}$

**Table 4:** Final conductivity,  $\chi^f / \mu\text{S cm}^{-1}$ , analytical concentration of NaOH in the final volume,  $\Delta H^E / \text{J kg}^{-1}$  of mixing of the INW with NaOH.

$M_{\text{NaOH}}^f / \text{mol L}^{-1}$	$\chi^{f,a} / \mu\text{S cm}^{-1}$	$m_{\text{NaOH}}^f / \text{mol kg}^{-1}$	$-\Delta H^{E,a} / \text{J kg}^{-1}$	$-\Delta H^E / m_{\text{NS}}^a / \text{kJ mol}^{-1}$
0	158.0	$1.2 \cdot 10^{-4}$	2.2	6.8
$2.0 \cdot 10^{-4}$	124.2	$2.5 \cdot 10^{-4}$	6.4	19.7
$3.9 \cdot 10^{-4}$	89.5	$5.0 \cdot 10^{-4}$	9.9	30.5
$5.8 \cdot 10^{-4}$	62.0	$1.0 \cdot 10^{-3}$	16.0	49.2
$7.7 \cdot 10^{-4}$	71.5	$1.8 \cdot 10^{-3}$	19.9	61.2
$9.5 \cdot 10^{-4}$	86.0	$2.9 \cdot 10^{-3}$	20.9	64.3
$1.1 \cdot 10^{-3}$	106.1	$4.0 \cdot 10^{-3}$	21.2	65.2
$1.3 \cdot 10^{-3}$	129.6	$4.5 \cdot 10^{-3}$	21.2	65.2
$1.5 \cdot 10^{-3}$	153.4	$6.5 \cdot 10^{-3}$	21.2	65.2
$1.6 \cdot 10^{-3}$	177.4	$8.0 \cdot 10^{-3}$	21.2	65.2
$1.8 \cdot 10^{-3}$	201.4	$9.9 \cdot 10^{-3}$	21.2	65.2
$2.0 \cdot 10^{-3}$	222.4	$1.6 \cdot 10^{-2}$	21.2	65.2
		$2.8 \cdot 10^{-2}$	21.2	65.2

a) Nafion Mix 5:  $\chi^i = 182 \mu\text{S cm}^{-1}$ ;  $\text{pH}^i = 3.3$ ;  $m_{\text{NS}} / \text{mol kg}^{-1} = 1/2 M_{\text{e.q.}} / \text{mol L}^{-1} = 3.2 \cdot 10^{-4}$

**Table 5:** Final conductivity,  $\chi^f / \mu\text{S cm}^{-1}$ , analytical concentration of NaOH in the conductometric and calorimetric titration,  $\Delta H^E / \text{J kg}^{-1}$  of mixing of the INW with NaOH.

$M_{\text{NaOH}}^f / \text{mol L}^{-1}$	$\chi^{f,a} / \mu\text{S cm}^{-1}$	$m_{\text{NaOH}}^f / \text{mol kg}^{-1}$	$-\Delta H^{E,a} / \text{J kg}^{-1}$	$-\Delta H^E / m_{\text{NS}}^a / \text{kJ mol}^{-1}$
0	190.0	$6.0 \cdot 10^{-5}$	3.8	16.1
$1.0 \cdot 10^{-4}$	158.1	$2.1 \cdot 10^{-4}$	8.6	36.6
$2.1 \cdot 10^{-4}$	129.3	$4.9 \cdot 10^{-4}$	13.4	57.0
$3.1 \cdot 10^{-4}$	100.2	$1.2 \cdot 10^{-3}$	13.8	58.7
$4.1 \cdot 10^{-4}$	73.6	$2.3 \cdot 10^{-3}$	14.2	60.4
$5.0 \cdot 10^{-4}$	68.8	$4.3 \cdot 10^{-3}$	14.3	60.9
$6.0 \cdot 10^{-4}$	77.7	$7.5 \cdot 10^{-3}$	14.3	60.9
$6.9 \cdot 10^{-4}$	90.7	$1.5 \cdot 10^{-2}$	14.3	60.9
$7.8 \cdot 10^{-4}$	109.3	$2.5 \cdot 10^{-2}$	14.3	60.9
$8.7 \cdot 10^{-4}$	127.2	$4.0 \cdot 10^{-2}$	14.3	60.9
$9.6 \cdot 10^{-4}$	144.9	$4.9 \cdot 10^{-2}$	14.3	60.9
$1.0 \cdot 10^{-3}$	163.1			
$1.1 \cdot 10^{-3}$	180.0			
$1.2 \cdot 10^{-3}$	198.5			
$1.3 \cdot 10^{-3}$	216.5			

a) Nafion Mix 6:  $\chi^i = 190 \mu\text{S cm}^{-1}$ ;  $\text{pH}^i = 3.1$ ;  $m_{\text{NS}} / \text{mol kg}^{-1} = 1/2 M_{\text{e.q.}} / \text{mol L}^{-1} = 2.3 \cdot 10^{-4}$

**Table 6:** Thermodynamic parameters for the association between INW and  $\text{OH}^-$  ions, at 298 K.

System	$\chi / \mu\text{S cm}^{-1}$	$K'_a / \text{kg mol}^{-1}$ (a)	$\Delta H^\circ_a / \text{kJ mol}^{-1}$ (a)	$-\Delta G^\circ_a / \text{kJ mol}^{-1}$ (b)	$T\Delta S^\circ_a / \text{kJ mol}^{-1}$ (c)
Nafion Mix 3	170	$17081 \pm 3583$	$42 \pm 1$	$24.1 \pm 0.5$	$-18 \pm 2$
Nafion Mix 4	98.1	$24765 \pm 2399$	$58 \pm 0.5$	$25.0 \pm 0.2$	$-32.9 \pm 0.7$
Nafion Mix 5	182	$9840 \pm 3984$	$66.1 \pm 0.8$	$20.5 \pm 0.7$	$-43 \pm 2$
Nafion Mix 6	190	$51140 \pm 11279$	$60.9 \pm 0.3$	$26.9 \pm 0.6$	$-34.0 \pm 0.9$

a) The reported errors are the standard deviations as obtained by fitting the data to Eq. 5. b) Errors are half the range of  $\Delta G^\circ_a$  calculated from the upper and lower error in  $K'_a$ . c) Errors are the sum of the errors on free energy and enthalpy.

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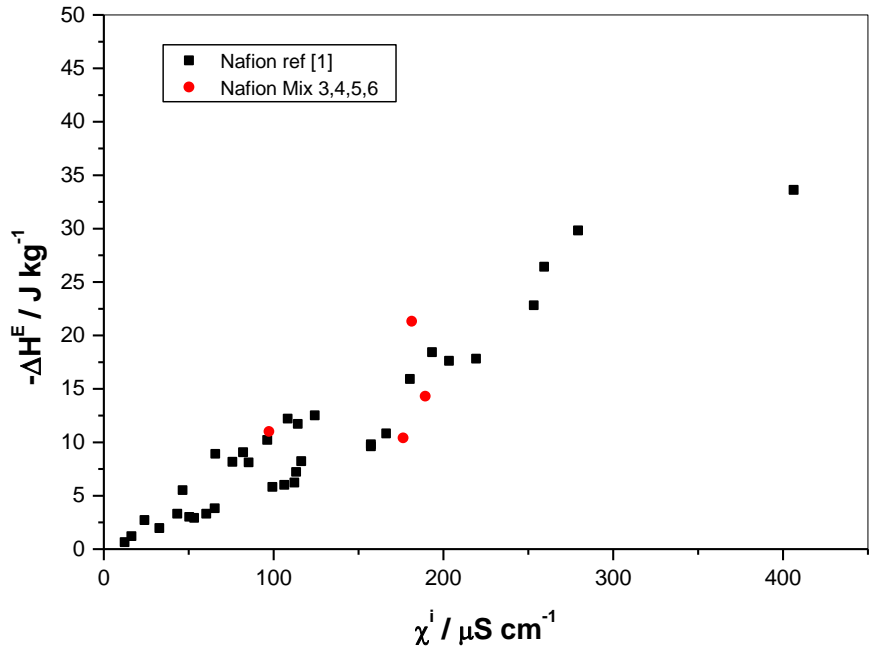


Fig.1-

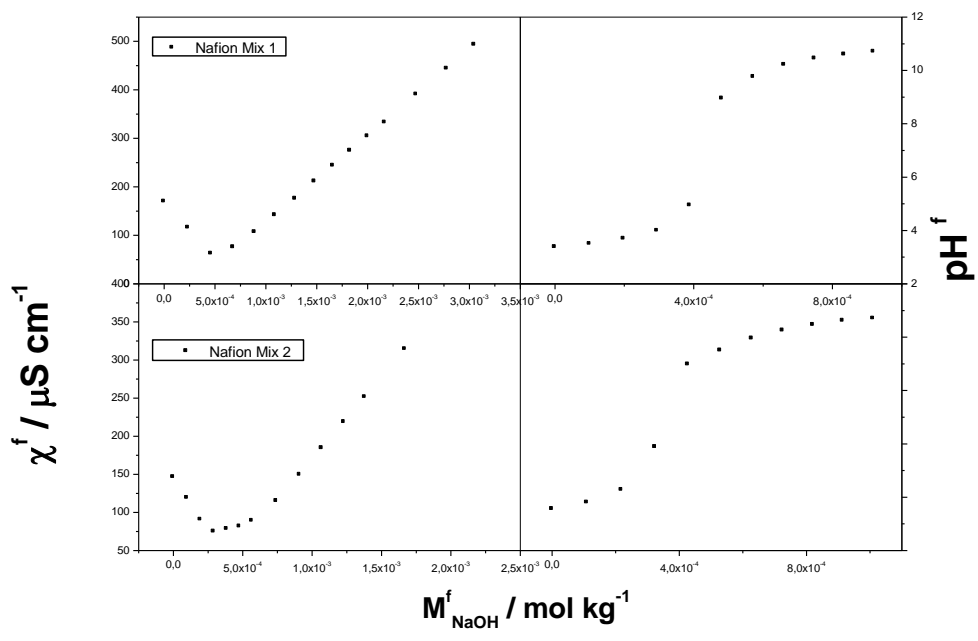


Fig. 2-

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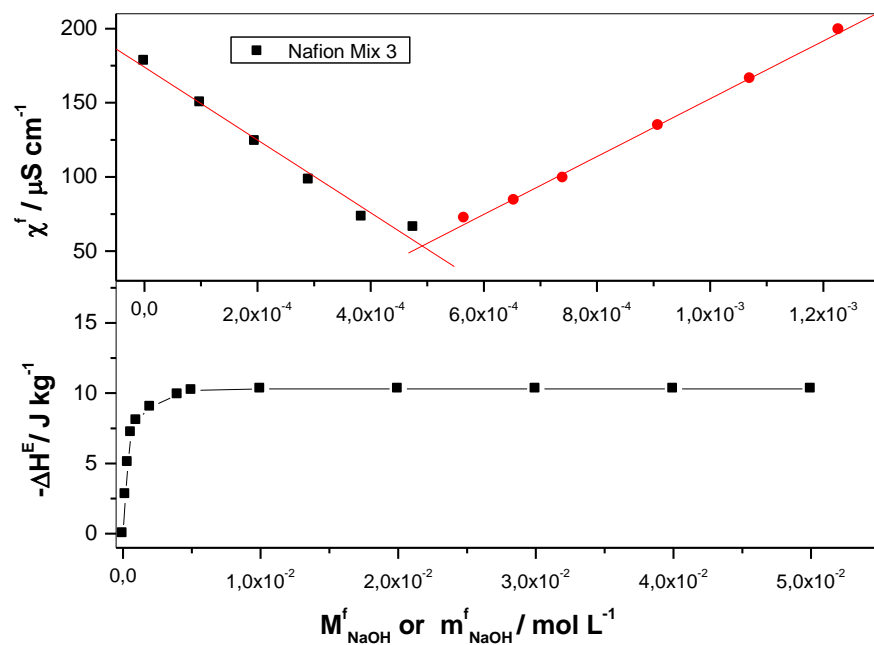


Fig.3-

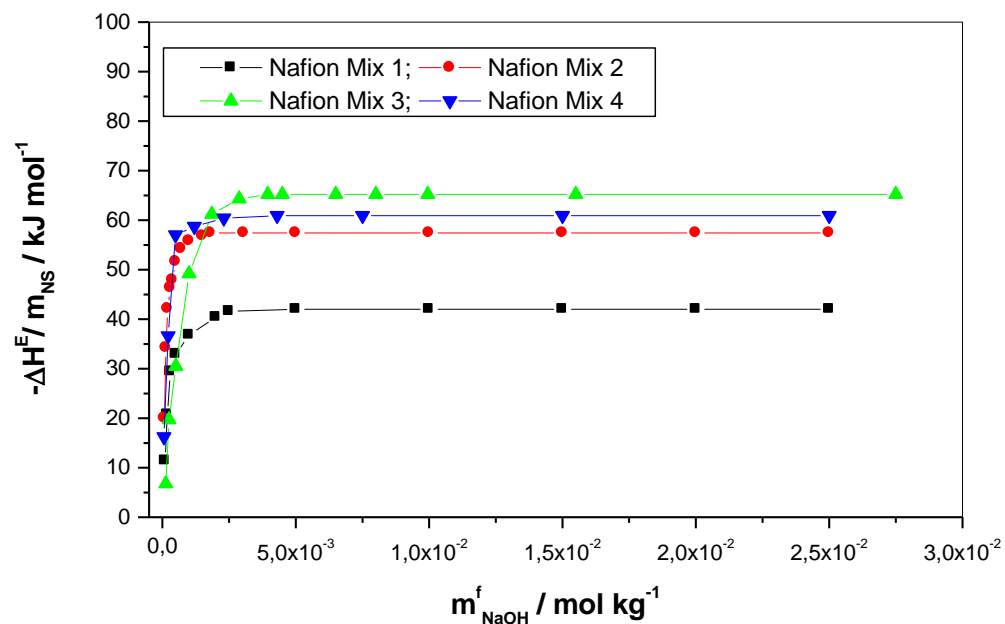


Fig.4-



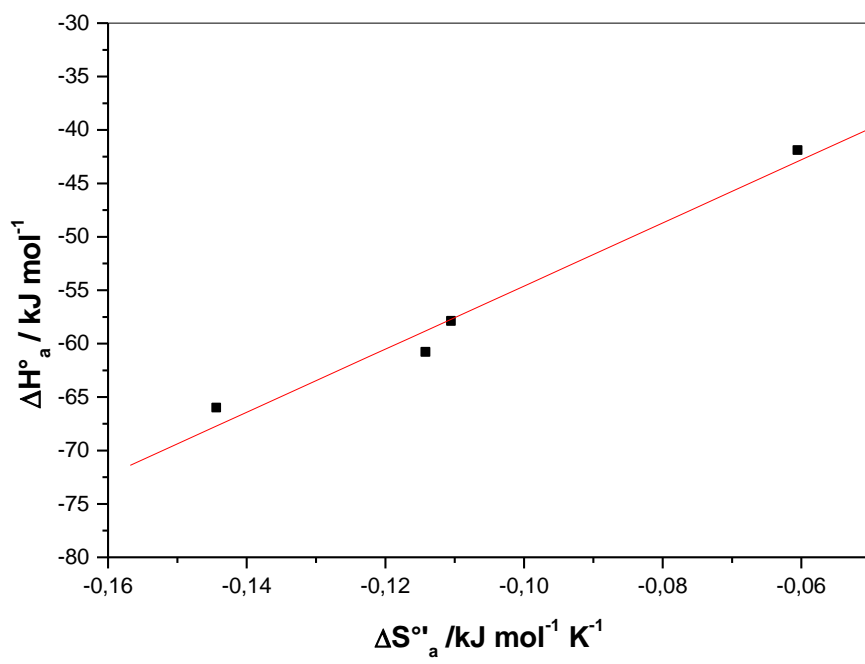


Fig.5-

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Captions to Figures:

Fig. 1

Excess heat of mixing,  $\Delta H^E / \text{J kg}^{-1}$ , vs. initial conductivity,  $\chi^i / \mu\text{S cm}^{-1}$ .

Fig. 2

The conductometric and pH-metric titrations with NaOH of two INW samples. The titration curves show the final conductivity,  $\chi^f$ , and  $\text{pH}^f$  as a function of the titrant concentration in the final solution.

Fig. 3

The conductometric and calorimetric titrations with NaOH; The titration curves show the final conductivity,  $\chi^f$ , and the excess enthalpy,  $\Delta H^E / \text{J kg}^{-1}$  as a function of the titrant concentration in the final solution.

Fig. 4

The Figure shows the calorimetric titration, and expresses the  $\Delta H^E / m_{\text{WNS}}$ , as a function of the NaOH concentration in the final solution,  $m_{\text{NaOH}}$ .

Fig. 5

Standard molar enthalpy of association - the standard molar entropy apparent compensation plot for the formation of complexes.