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Surfactant behaviour of metallacarboranes. A study based on the electrolysis of water

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[3,3'-Co(1,2-$C_2B_9H_{11}$)$_2$]⁻, **[1]**⁻, and its chloroderivatives, have been described as displaying surfactant/aggregation properties. We have studied their behaviour as electrolytes in the water electrolysis process. The electrolysis experiments support the surfactant behaviour of these compounds. These conclusions have been drawn on the grounds of the intensity/voltage (I/V) curves of water splitting into H_2 and O_2, of aqueous solutions in which the electrolytes have been tested at the same concentration. The I/V curves have permitted to map and group the different electrolytes studied in this work. Three differentiated zones have been observed: one for true electrolytes, NO_3^- and ClO_4^-; a second one for intermediate electrolytes, BF_4^- and *p*-toluenesulfonate (PTS); and a third having the surfactant dodecylbenzenesulfonate (DBS), **[1]**⁻, and its chloroderivatives. The incorporation in the study of the chloroderivatives of **[1]**⁻ has allowed to correlate molecular structure features with aqueous performance. The studied chloroderivatives perform better as electrolytes in accordance with the descending order of available B-H groups. This comes from the higher capacity to generate B-H···H-C_c dihydrogen bonds in the non- or less-halogenated molecules, considered one of the main reasons for the generation of the aggregates. In order to generate B-H···H-C_c dihydrogen bonds it is needed the H-C_c from the carborane cluster. [$B_{12}H_{12}$]²⁻ was chosen to prove the hypothesis as it has B-H units but lacks H-C_c units. Consequently, it should not produce self-assembling motifs, as it is the case. [$B_{12}H_{12}$]²⁻ has an aqueous behaviour similar to SO_4^{2-}.

Introduction

Weakly Coordinating Anions (WCAs) are anionic ligands that have an extremely low tendency to bind to metal centers. They easily migrate from the metal center to yield an empty site to be occupied by a substrate, what makes them ideal for catalysis.[1] Recognized examples of WCAs are carboranes, boranes and metallacarboranes. These are deltahedra in which most or all of their vertexes are boron atoms.[1b,c] Very stable examples are the ones outlined in Fig. 1: [$CB_{11}H_{12}$]⁻, [$B_{12}H_{12}$]²⁻ and [3,3'-Co(1,2-$C_2B_9H_{11}$)$_2$]⁻, **[1]**⁻. Their weak coordination tendency arises from their low charge density,[2] bulky size and sufficient charge delocalization.[3] However, over the past few years, several researchers have shown that some of the metallacarboranes are not as WCAs as it was thought and that did behave similarly to a surfactant in aqueous solutions. Wipff[4] and co. interpreted by molecular dynamics methods that [Co($C_2B_9H_{11}$)$_2$]⁻ anions, although lacking the amphiphilic topology, behave as anionic surfactants.[4] Later on, Matějíček and co. et al. studied this anion in aqueous solution by a combination of static and dynamic light scattering and microscopy methods. They observed that the compound organizes in spherical aggregates with a radii of around 100 nm in a fairly monodisperse way.[5] More recently, Bauduin et al.[6] demonstrated by small- and wide-angle X-ray and neutron scattering that H⁺[Co($C_2B_9H_{11}$)$_2$]⁻, H**[1]**, forms monolayer vesicles at low concentrations in water. Increase in concentration leads to a phase transition from vesicles to small micelles and results in the coexistence of both aggregation states at higher concentrations. Finally, it has been proven that minor changes in the molecular structure of [Co($C_2B_9H_{11}$)$_2$]⁻ induce major modifications in the solution behaviour. The substitution of two B-H by two B-I in the structure of [Co($C_2B_9H_{11}$)$_2$]⁻ leads to a lamellae lyotropic phase in the high concentration regime.[7] This minor molecular alteration induces large self-organizing consequences that correlate very well with the concept of molecular materials. To progress in the understanding of the solution behaviour of the metallacarboranes, we decided to test their performance in an experiment requiring higher concentration than the one required for vesicles formation.
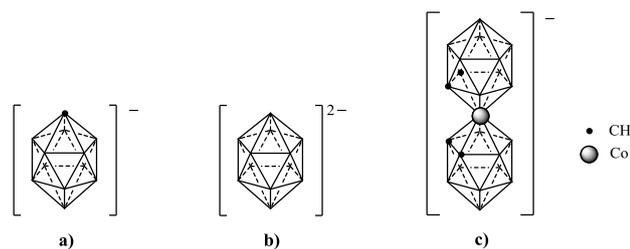
Fig 1. Schematic structure of some weakly coordinating anions (WCAs) based on boron clusters: a) $[CB_{11}H_{12}]^-$, b) $[B_{12}H_{12}]^{2-}$ and c) $[3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]^-$, **[1]**$^-$.

Water splitting is actively researched because demand for cheap hydrogen is expected to rise with the forthcoming hydrogen economy.[8] The electrical energy needed for the electrolysis of water is not fully converted into chemical energy of hydrogen, thus lowering the efficiency of the process to 50–70%.[8a] There are several facts affecting the performance of an electrolysis process, leading to a high overpotential to drive the reaction.[9] Among others, the nature of the electrolyte is paramount to produce hydrogen and oxygen and is the object of this study.

Based on the state of the art about aqueous solutions of $[Co(C_2B_9H_{11})_2]^-$, we hypothesized that $[Co(C_2B_9H_{11})_2]^-$ may participate in the water electrolysis either as a discrete entity or, in the basis of the investigations described above, as a self-organized aggregate. For a fixed concentration of the anion, the behaviour of an electrolyte would be more efficient if the anion performed as a discrete entity; whereas if it was self-organized in agglomerates, the efficiency would be much lower and more similar to the performance of a surfactant.

We shall see that even at 0.1 M, the behaviour of $[Co(C_2B_9H_{11})_2]^-$ is this of a species that self-organizes forming aggregates in solution. In addition, a relationship between fine molecular structure modification and their performance as surfactants in aqueous solutions will be observed

Results and discussion

As carborane anions have a low charge density, it was expected that if they behaved as a discrete entity, and if they performed as WCAs, their residence time on the electrode would be short or, in other words, they would be easily removed from the electrode surface by the electroactive species. Experiments were done with graphite electrodes and, initially, HNO_3, $HClO_4$ and HBF_4 were studied for comparison purposes. Their performance as electrolytes was studied in the same water electrolysis set-up and at the same concentrations as H**[1]** and its chlorinated derivatives. The chlorinated derivatives of **[1]**$^-$ were first studied because they have long term stability and second because they could make a substantial contribution to the understanding of the aqueous solution behaviour of $[3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]^-$ as a result of minor molecular changes in the way described earlier.[7]

Throughout the text, it will be shown that electrolysis experiments will reinforce previous studies on the behaviour of **[1]**$^-$ and its derivatives on their tendency to aggregate. Comparison with other mono- and dianions, either in their protonated form or as Na^+ salts, was necessary to understand the results obtained with the metallacarboranes. Moreover, *p*-toluenesulfonate (PTS), dodecylbenzenesulfonate (DBS), SO_4^{2-} and $[B_{12}H_{12}]^{2-}$ anions were also studied.

Albeit chlorinated derivatives of **[1]**$^-$ are known to have superior stability than **[1]**$^-$ itself, no synthetic protocols exist to produce them in pure form and in fair amount. Thus, mixtures of H[Cl_x**-1**] were utilized. The MALDI-TOF technique allowed to determine the composition of three mixtures of H[Cl_x**-1**], named here as mixtures **I**, **II** and **III**. Because of the existence of two isotopes for boron, ^{10}B (20%) and ^{11}B (80%), all metallacarboranes exhibit an envelope of signals centred at the molecular signal in their mass spectra. The high stability of these anions enable to run MALDI-TOF-MS experiments avoiding the use of a matrix, and this is most probably the reason for the direct relationship between the peak intensity and the molar fraction.[10] As clusters have the same number of boron atoms (18), the molecular peaks roughly show a similar envelope shape, just modulated by the number of chlorine substituents that are influenced by two isotopes: ^{35}Cl (76%) and ^{37}Cl (24%). Thus, the integral of the area under the multiplets is used to estimate the composition of each mixture directly from the spectra (see Table 1 and Fig. 2).[10]

Table 1. Composition of some mixtures of H[Cl_x**-1**] obtained by the experimental method detailed in the Experimental Methods section; x refers to the number of chlorine atoms in the molecule. The composition of each sample has been determined by the analysis of the corresponding MALDI-TOF mass spectrum.

	H[Cl_x**-1**] / %							
Mixture	2	3	4	5	6	7	8	9
I	12.3	49.8	35.1	2.8	-	-	-	-
II	0.9	27.9	35.3	17.8	17.1	1.0	-	-
III	-	-	2.8	12.4	16.7	32.5	33.8	1.8

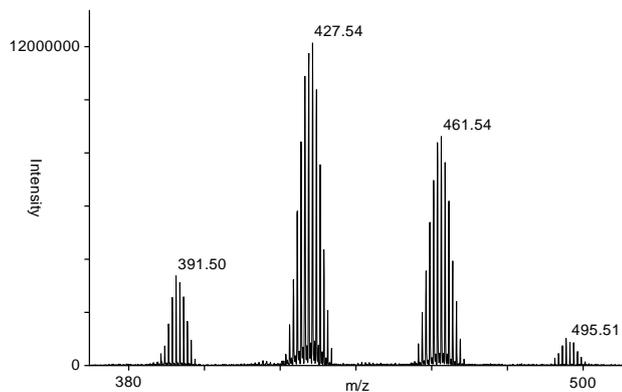**Fig 2.** MALDI-TOF mass spectrum of mixture **I** containing **[Cl$_x$-1]** with x = 2-5.

Electrolysis performance of H[Cl$_x$-1] mixtures with regard to monoprotic acids: HNO$_3$, HClO$_4$ and HBF$_4$

Experiments have been carried out with a variable DC power supply, recording the intensity *vs.* the applied voltage. All experiments were conducted with graphite electrodes. The plots of intensity *vs.* voltage (I/V) of H[**1**] and mixtures **I**, **II** and **III** are shown in Fig. 3 as plots **a** – **d**. If an intensity of 40 mA is used as threshold to compare between the different compounds, it is seen that all metallacarboranes are found within the same region. Similar experiments have been carried out with HNO$_3$, HClO$_4$ and HBF$_4$ and their I/V plots have been represented as **e**, **f** and **g** in Fig. 3.
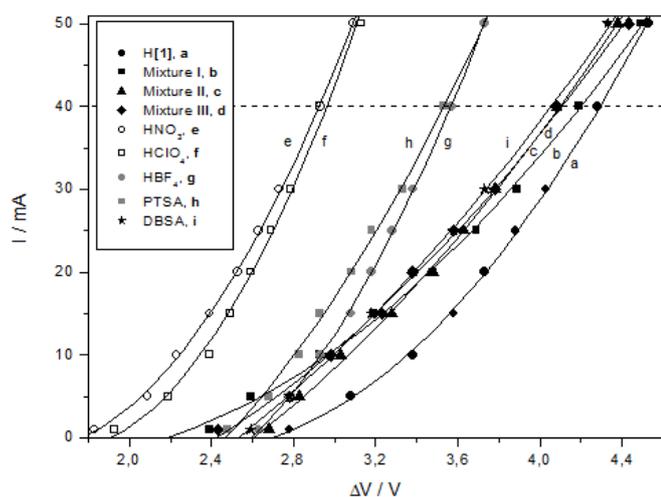

Fig 3. I/V curves of 0.1 M aqueous solutions of H[**1**], mixtures **I – III**, HNO$_3$, HClO$_4$, HBF$_4$, PTSA and DBSA.

Figure 3 show that H[**1**] and the mixtures **I**, **II** and **III** are, among all electrolytes studied in this work, these that behave more poorly since the voltage required to reach 40 mA is in the range 4 – 4.3 V, whereas for electrolytes HNO$_3$ and HClO$_4$ it is required around 2.9 V and for HBF$_4$ it is needed 3.5 V. The results are in disagreement with the supposed WCA behaviour of the metallacarboranes and also of them performing as separate entities. These results should then be interpreted as if the effective concentration of electrolyte in H[**1**] or the metallacarborane mixtures **I – III** was lower than would be expected on the basis of the nominal concentration, 0.1 M. A visual inspection on the electrolysis experiments is shown in Figure 4. It can be clearly seen that foam is produced during the generation of H$_2$(g) and O$_2$(g) in all experiments in which metallacarboranes were the electrolytes (see Fig. 4 left). By contrast, no foam is observed when conventional electrolytes are used. As foaming is commonly attributed to surface active agents, and in the electrolysis experiments we observed low efficiency for H[**1**] and mixtures **I – III**, we thought that their behaviour was that of surfactants, which would reduce the free (un-aggregated) concentration of the electrolyte. These results could be considered as an experimental demonstration of the surface active property of metallacarboranes, extended also to its chlorinated derivatives.
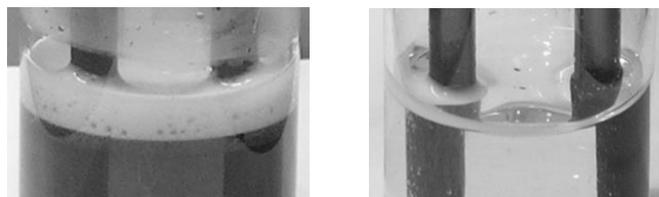

Fig 4. Formation of a foam during the electrolysis of water in the presence of H[**1**] or the mixtures **I – III** (left) and absence of this foam when Na$_2$[B$_{12}$H$_{12}$] is used as the electrolyte (right).

Electrolysis performance of H[Cl$_x$-1] mixtures with regard to CH$_3$C$_6$H$_4$SO$_3^-$ (*p*-toluenesulfonate, PTS) and C$_{12}$H$_{25}$C$_6$H$_4$SO$_3^-$ (dodecylbenzenesulfonate, DBS)

PTS and DBS have the same chemical structure, R-Ar-SO$_3^-$, only differing in the R group (methyl for PTS and dodecyl for DBS), which also implies a difference in their surfactant properties. DBS, unlike PTS, is a well-known anionic surfactant, commonly used in the production of commercial washing powders.[11] Since it forms micelles in aqueous solutions,[12] its mobility is expected to be reduced in water, therefore becoming a bad electrolyte for the electrolysis of water. This would turn DBS into a good reference to ascertain the behaviour of H[**1**] and the H[Cl$_x$-**1**] mixtures.

The I/V curves for the electrolysis performance of PTS and DBS have also been represented in Fig. 3 as plots **h** and **i**. Note that three regions appear in the plot, denoting three different

behaviours between the studied electrolytes. The most efficient electrolytes are HNO_3 and $HClO_4$, followed by HBF_4 and PTSA. The latter belongs to a class of molecules generally called hydrotropes, that are defined as small amphiphilic molecules that do not form well defined micelles in water.[13] The least efficient electrolytes are the metallacarboranes and DBSA, which appear at the same region in the I/V plot through the whole range of applied voltages. Although the molecular structure of [1]⁻ does not display the conventional structure of a surfactant, in this work we provide the results of a macroscopic experiment proving the surfactant behaviour in aqueous solutions of [1]⁻ and that this is due to the formation of aggregates.

Nature of the aggregates

Surfactants are amphiphilic compounds meaning that they contain hydrophobic tails and hydrophilic heads. Metalla-carboranes lack the amphiphilic topology characteristic of surfactants. However, metallacarboranes at low and high aqueous concentrations display many characteristics of surfactants. Despite both having a similar behaviour, the type of forces that generate the aggregates are expected to be very different in the two cases. For the metallacarboranes used in this work, a good deal of structural interactions information can be retrieved from the Cambridge Structural Database, CSD.[14] In this way, [1]⁻ has been found featuring a chain in which the metallacarborane clusters are bound one to the other through simple and double dihydrogen bonds $B-H\cdots H-C_c$,[15] as outlined in Fig. 5. Dihydrogen bonds are also found in other structures,[16] some of them involving boron clusters.[17] Hence, the presence of both B-H and $H-C_c$ bonds in the structure is likely to be responsible for the formation of aggregates of [1]⁻ in water.[12,18]
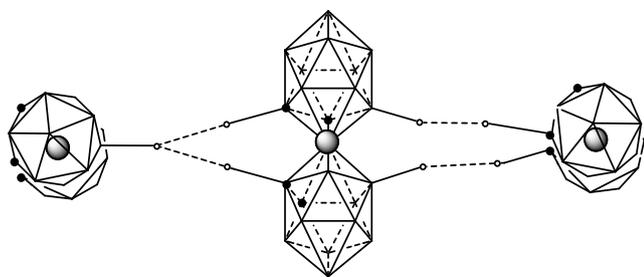

Fig 5. Molecular chain of [1]⁻ stabilized by simple and double intermolecular dihydrogen bonds, shown here as dashed lines.

The studies reported in this work support this theory. A thorough visual inspection of Fig. 3 at the region of the metallacarboranes shows that H[1]⁻ is the worst eletrolyte for water splitting, followed by mixture **I**, mixture **II** and **III** being the best among them. This is in accordance with the descending order of available B-H groups for $B-H\cdots H-C_c$ dihydrogen bonds. The lesser availability of B-H entities occurs as a result of an increasing substitution of B-H by B-Cl. Mixture **III** has a higher number of B-Cl substitutions than **II**, and the latter higher than **I** and [1]⁻, in this order. This correlation fully supports the relevance of $B-H\cdots H-C_c$ dihydrogen bonds to generate the aggregates.

All metallacaboranes studied, either [1]⁻ or mixtures **I-III**, have in their structures C-H and B-H units. To generate the $B-H\cdots H-C_c$ non-bonding contacts it is required to have in the same cluster C-H and B-H units. Thus, a further experiment has been carried out in which the metallacarboranes have been compared with non containing C_c-H groups boron cluster, such as dodecaborane $[B_{12}H_{12}]^{2-}$. This anion is divalent and it cannot be directly compared to the monoanionic metallacarboranes. Therefore, we added to the study the divalent SO_4^{2-} anion, which is one of the most typically used anions in water electrolysis due to its high oxidation potential.

As shown in Fig. 6, $[B_{12}H_{12}]^{2-}$ exhibits the same behaviour as the non-surfactant anion SO_4^{2-}. Comparison with a $NaNO_3$ solution with the same ionic strength corroborates that the dodecaborane does not behave as a surfactant. The absence of foam during the electrolysis experiment, as shown in Fig. 4 right, supports the hypothesis that $B-H\cdots H-C_c$ bonds are responsible for the formation of metallacarborane aggregates in water.

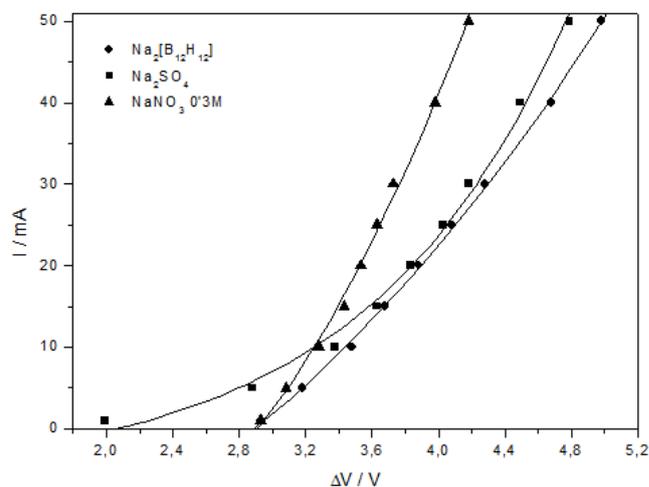**Fig 6.** I/V curves of aqueous solutions of $Na_2[B_{12}H_{12}]$, Na_2SO_4 and $NaNO_3$; concentrations are 0.1 M but for $NaNO_3$ that is 0.3M.

To further study these electrolytes in solution, electrolysis experiments have been carried out in which an organic solvent, acetonitrile, has been added to water in different ratios to observe the effect on the response of the metallacarboranes and the borane cluster. In Fig. 7 are represented the results of these experiments for H[1] and the non-surfactant electrolyte $HClO_4$.

As seen in Fig. 7, HClO$_4$ becomes less and less efficient when increasing the ratio of acetonitrile, since more potential is needed to achieve the same intensity. On the contrary, H[1] improves its performance when increasing the ratio of water/acetonitrile to 50:50. This may be taken as an indication of the destruction of aggregates of H[1] when adding a more compatible solvent with the metallacarborane. As a result, more free ions are available for electrolysis and the conductivity of the solution is increased. However, when shifting from 50:50 to 30:70 the response gets worse again, most probably due to the overall decrease of the dielectric constant (ε_{water} = 78.4, $\varepsilon_{acetonitrile}$ = 36.2), that determines the degree of dissociation of the ions. The initial improvement on the response of H[1] in contrast to HClO$_4$ demonstrates that they behave oppositely.

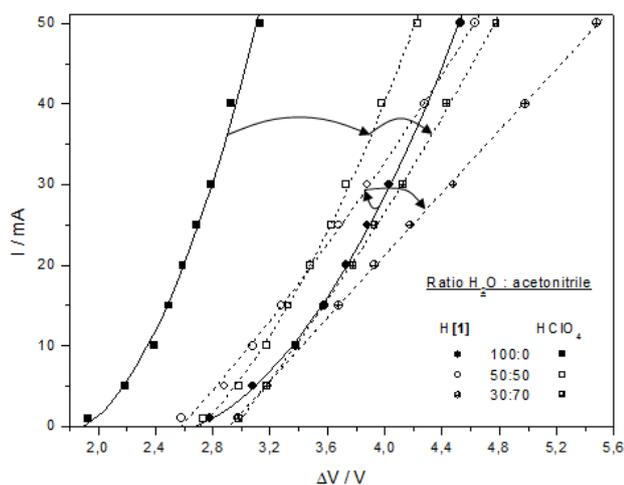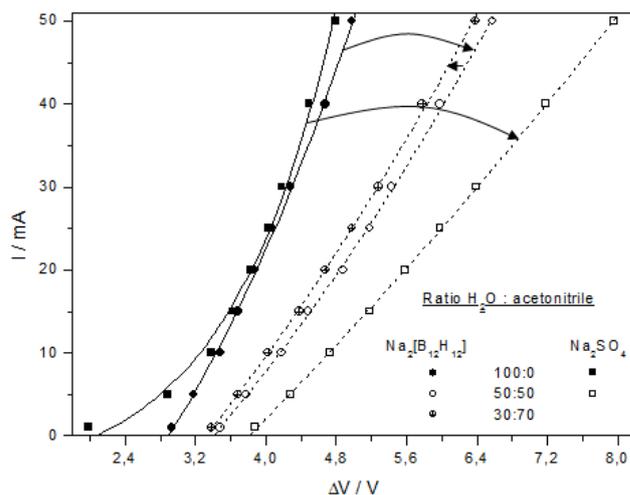**Fig 8.** I/V curves of 0.1 M solutions of Na$_2$[B$_{12}$H$_{12}$] and Na$_2$SO$_4$ in different ratios of water/acetonitrile; the arrows indicate the movement of the curves when increasing the proportion of acetonitrile.

Fig 7. I/V curves of 0.1 M solutions of H[1] and HClO$_4$ in different ratios of water/acetonitrile; the arrows indicate the movement of the curves when increasing the proportion of acetonitrile.

The same experiment has been carried out with Na$_2$[B$_{12}$H$_{12}$] and Na$_2$SO$_4$ as electrolytes (see Fig. 8) and, as expected for their non-surfactant properties, they behave in a similar manner to HClO$_4$: their performance is reduced when adding acetonitrile because they do not form aggregates in water and, therefore, no effect related to the destruction of aggregates (or variation of the electrolyte concentration) is observed. However, the response of Na$_2$[B$_{12}$H$_{12}$] is better than Na$_2$SO$_4$ upon addition of acetonitrile, indicating more compatibility with organic solvents. This may be also the reason for the slight improvement observed in Na$_2$[B$_{12}$H$_{12}$] when increasing the ratio of solvents to 30:70, despite the decrease in the dielectric constant. No experiment at 30:70 could be done with Na$_2$SO$_4$ due to its insolubility.

In conclusion, the use of mixed solvents evidences that [B$_{12}$H$_{12}$]$^{2-}$ does not behave as a surfactant, in opposition to [1]$^-$, and this reinforces the well-established hypothesis that B-H···H-C$_c$ bonds are necessary to form aggregates in water.[14]

NMR evidences of the formation of [1]$^-$ aggregates

Further evidence of the distinct behaviour of [1]$^-$ and [B$_{12}$H$_{12}$]$^{2-}$ can be encountered in the ^{11}B-NMR and ^{11}B{^{1}H}-NMR in aqueous solution. NMR measurements give information on the molecules in the bulk of the solution, therefore providing information on their aggregation in one particular solvent.
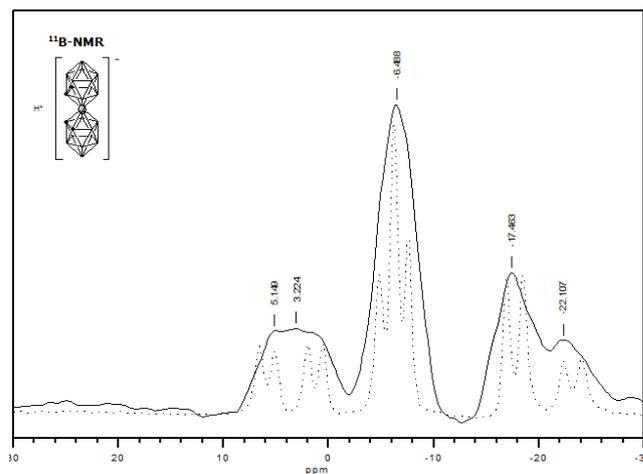

Fig 9. ^{11}B-NMR spectrum a 0.1 M solution of H[1] in water (—) and in diethyl ether (···).

As previously commented, the cluster C$_c$-H units in [1]$^-$ are ready to generate B-H···H-C$_c$ dihydrogen bonds. When this moiety is surrounded by water molecules, it rearranges its internal conformation to avoid the direct contact with water

molecules. Therefore, in an aqueous medium, **[1]⁻** tend to aggregate in supramolecular entities, and similarly to the surfactants, its periphery must face the water molecules. These interactions and the dimension of the aggregates prevents a facile rotation of the aggregate, thus of the guests **[1]⁻** molecules within the H_2O frame; the consequence is a widening of the ¹H-NMR resonances (Fig. 9). For $[B_{12}H_{12}]^{2-}$, the lack of C_c-H vertex prevents the self-assembly of the molecules, easing a free rotation, and producing narrow NMR signals, observed in Fig. 10. The ¹¹B-NMR of H**[1]** exhibits much wider signals in water than $Na_2[B_{12}H_{12}]$. Moreover, an organic solvent would cause the destruction of the aggregates and, consequently, the existence of free monomers. Therefore, narrower signals would appear in the spectrum as is the case for a diethyl ether solution of **[1]⁻** (see Fig. 9 (···)).
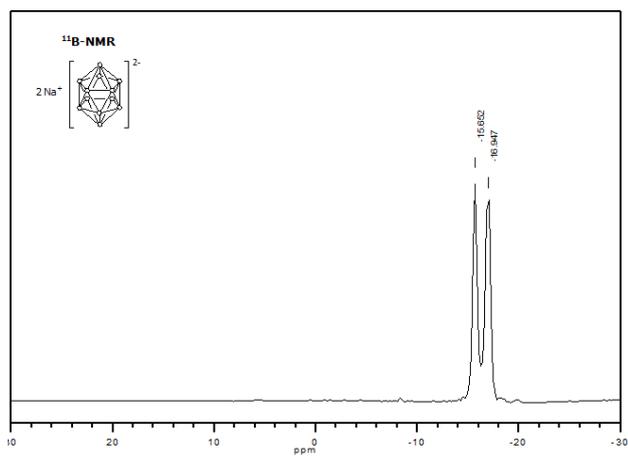

Fig 10. ¹¹B-NMR spectrum a 0.1 M solution of $Na_2[B_{12}H_{12}]$ in water.

Experimental methods

Reagents and materials

The cesium salts of some chlorinated derivatives of **[1]⁻**, Cs**[Cl_x-1]**, were synthesized as mixtures in our laboratory from compound Cs**[1]** (KatChem, Prague, Czech Rep.), using N-chlorosuccinimide as the chlorinating agent. Near 0.1 mmol of Cs**[1]** and the corresponding molar quantity of N-chlorosuccinimide, NCS, for the main target anion in the expected resulting mixture were crushed together in a glove box until a homogeneous powder was obtained.[10] As an example, if **[Cl₁₀-1]⁻** was aimed as one of the dominant anions in the mixture, a 1:10 ratio of Cs**[1]** and NCS would be mixed. A thick-walled Pyrex tube (20 cm long, 5 mm id and 8 mm od) was charged with the powder. The lower part of the tube was then cooled with liquid N_2, evacuated and sealed under vacuum with an energetic flame. Afterwards, the tube was placed inside a protective iron cylinder and put inside a preheated tubular

furnace. The temperature of the furnace was maintained for 2 hours at 194 ± 6 ºC. The protective cylinder containing the tube was then carefully removed and the whole cooled down to room temperature. The tube was then opened. Cs**[1]** and the resulting synthesized mixtures were subjected to a cation exchange to obtain their corresponding acidic forms. Liquid-liquid extraction of an ether solution with HCl 1M was employed as the exchange method; the ether phases were separated, dried with $MgSO_4$ and evaporated to dryness, obtaining H**[1]** and mixtures **I – III** (see Table 1).

$Na_2[B_{12}H_{12}]$ was synthesized from $NaBH_4$ (ABCR GmbH & Co. KG) and $Et_3N\cdot BH_3$ (Sigma-Aldrich) according to literature procedures.[17]

Graphite rods, 3mm diameter, were supplied by Sigma-Aldrich.

Set-up for the electrolysis of water

A 40V/5A DC supply was used as the electron source for the electrolysis experiments. The graphite electrodes were connected to this device separated 1.5 cm from each other and submerged 1.5 cm in the electrolyte solution (10mL).

Characterization

All synthesized compounds and mixtures were characterized by ¹¹B-NMR and ¹¹B{¹H}-NMR. Mixtures were also analysed by MALDI-TOF mass spectroscopy.

¹¹B-NMR and ¹¹B{¹H}-NMR (96.29 MHz) spectra were recorded with a Bruker ARX 300 instrument. Chemical shift values for ¹¹B-NMR and ¹¹B{¹H}-NMR are referenced to external $BF_3\cdot OEt_2$ and reported in units of parts per million.

Mass spectra were recorded in the negative ion mode using Bruker Biflex MALDI-TOF-MS [N_2 laser; λ_{exc} 337nm (0.5ns pulses); voltage ion source 20.00kV].

Conclusions

The sandwich metallacarborane **[1]⁻** and its chloroderivatives, have been recently claimed, on the basis of computational studies, static and dynamic light scattering and neutron diffraction methods to display surfactant/aggregation properties in water. In this work we have used the performance as electrolytes of **[1]⁻** and its chloroderivatives in the water electrolysis process, to ascertain if under such conditions these compounds also manifest the surfactant properties. The experiments carried out fully support the sentence "although lacking the amphiphilic topology, metallacarboranes behave as anionic surfactants". These conclusions have been drawn on the grounds of I/V curves of water splitting into H_2 and O_2, in which the electrolytes have been tested at the same concentration. These curves have permitted to map and group the different electrolytes studied. Three clearly differentiated zones have been observed: one for true electrolytes, NO_3^- and

ClO$_4^-$; a second one for intermediate electrolytes, BF$_4^-$ and *p*-toluenesulfonate (PTS); and a third one having the surfactant dodecylbenzenesulfonate (DBS), **[1]**$^-$ and its chloroderivatives, **[Cl$_x$-1]**$^-$. The incorporation in the study of the chloroderivatives of **[1]**$^-$ has enabled to correlate molecular structure with aqueous performance. The three mixtures of chloroderivatives studied differentiate from each other in the number of B-Cl functions in the framework molecule. These compounds perform better as electrolytes in accordance with the descending order of available B-H groups. The worst performing as electrolyte is **[1]**$^-$, which has the highest number of B-H bonds in the molecule. The explanation for this is the higher capacity to generate B-H$\cdots$H-C$_c$ dihydrogen bonds in the non- or less-halogenated molecules. The formation of these dihydrogen bonds is the reason, or one of the main reasons, for the self-assembling ordering observed in these compounds that have led to the unusual aqueous behaviour. To generate B-H$\cdots$H-C$_c$ dihydrogen bonds, it is needed the presence of H-C$_c$ vertices at the carborane cluster. If this assumption was correct, the absence of such unit would prevent the formation of the aggregates. Thus, [B$_{12}$H$_{12}$]$^{2-}$ was also studied: it has B-H units but lacks H-C$_c$ units. Consequently, it should not produce self-assembling motifs, as it is the case. In fact, [B$_{12}$H$_{12}$]$^{2-}$ has a behaviour in aqueous media similar to SO$_4^{2-}$. We expect that this surfactant behaviour of metallacarboranes can have relevance both for molecular materials and medical applications.

Acknowledgements

Notes and references

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