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# The Central Role of Bicarbonate Anions in Charging Water/Hydrophobic Interfaces

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Boisson-Da Cruz,<sup>a</sup> Julien Bernard,<sup>a</sup> François Ganachaud<sup>\*a,b</sup>*

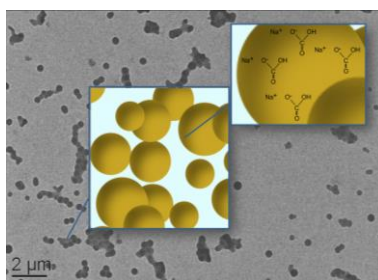
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**ABSTRACT:** Aqueous interfaces are ubiquitous in Nature and play a fundamental role in environmental, biological processes, or modern nanotechnologies. These interfaces are negatively charged and despite several decades of research, the rationale behind this phenomenon is still under debate. Two main controversial schools of thought argue on this issue; the first relies on the adsorption of hydroxide anions on hydrophobic surfaces, whereas the second one supports a self-rearrangement of water molecules at the interface bearing hydronium ions. Here, we report on two series of independent experimental studies (nanoprecipitation and interfacial tension measurements) that demonstrate that in the pH 5-10 range, the negative interfacial charge of the colloids mostly stems from bicarbonate ions; whereas, at lower and higher pH, protons and hydroxide ions contribute, with bicarbonate ions, to the interfacial charging. This new interpretation complies with previous studies and opens new prospective to this striking physical chemical issue.

## Table of Contents Graphic



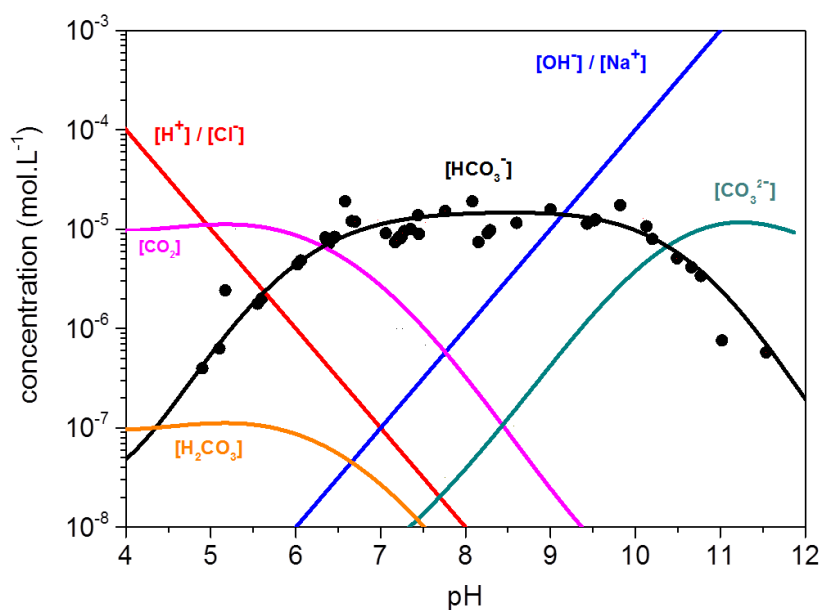
The origin of the negative charge arising on surfaces in contact with water is a relevant question that did not get a definitive answer so far (For two very recent, complete reviews on the field, see<sup>1-2</sup>). For about 100 years, it has been established that air bubbles<sup>3</sup> and oil or polymers dispersions<sup>4</sup> display a negative potential in water. Initially evidenced by (micro)electrophoresis, this phenomenon was further investigated by acid-base titration experiments on oil/water interfaces over a large pH range (from 3-4 to 11-12).<sup>5</sup> More recently, Colussi *et al.* nebulized acid or basic vapors at water/air surface to promote the reaction of the generated ions with interfacial ones and probe the pH of water at the interface with air. The authors detected an isoelectric point around 4, the surface becoming negatively charged above this pH value.<sup>6-7</sup> Hence, there is currently a general consensus on the fact that the surface of neutral water is negatively charged.<sup>8</sup> On the other hand, in spite of the high level of interest expressed by the scientific community in solving this open question, there is currently no clear understanding of the nature and the extent of ions present at hydrophobic interfaces. A first explanation put forward for such a behavior is that hydroxide ions preferentially adsorb at the interface.<sup>9</sup> Some theoretical models proposed by Gray-Weale and Beattie<sup>10-11</sup> and others,<sup>12-13</sup> suggest the autolysis of water molecules close to the interface, releasing excess hydroxide ions keen to reach the interface. This natural splitting of water molecules close to interfaces would occur under a large pH range, independently of the natural content of hydroxides in solution. The concurrent school of thought relies on molecular simulation,<sup>14-16</sup> sum frequency spectroscopy analyses,<sup>17-18</sup> and surface tension of concentrated salt solutions,<sup>19-20</sup> to infer that water/air surfaces and hydrophobic/water interfaces are primarily covered by protons. In their views, water molecules then self-arrange to accommodate these physisorbed hydronium ions at the interface, which then displays a virtual negative charge. Consistent with this assumption, it was recently shown by

electrophoresis that water droplets floating in different oils (silicone, paraffin) bear a positive charge, whatever the original pH of the drops.<sup>21</sup>

Both schools thus propose convincing arguments to support their view and debate vigorously on potential inconsistencies between experimental and simulation data for each proposed model.<sup>22</sup> As a consequence, it is at present difficult to side with one movement of thought. Besides, it is worth noting that direct observation, identification and quantification of adsorbed ions is hardly feasible (for instance by SFG<sup>23-24</sup>), owing to the very low content of ions to be found at the interface (*vide infra*). It remains nevertheless that these two proposed approaches seem somehow oversimplified in the fact that they consider exclusively one type of ions at the time to account for the interfacial charge. Quite originally, the team of Ruckenstein proposed to reconcile observed surface tensions with zeta potentials at air/water interfaces by taking into account ‘all ions’ introduced in water for measurement: namely,  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  (the pH is generally adjusted by using HCl or NaOH solutions).<sup>25-27</sup> Doing so, and using up to 5 adjusting parameters, adsorption of  $\text{OH}^-$  at the interface was validated, but in far less quantity than what zeta potential measurements suggest, which is not satisfactory.

Another important fact when dealing with aqueous dispersions is the carbonation of water.<sup>28</sup> Indeed, even under inert conditions, it is impossible to avoid the uptake of carbon dioxide by water (into its  $\text{H}_2\text{CO}_3$  form), and its transformation into bicarbonate ( $\text{HCO}_3^-$ ) anions, and at high pH into carbonate ones ( $\text{CO}_3^{2-}$ ) (basically  $>10$ ).<sup>29</sup> All these species, in addition to the ions quoted above, should theoretically be considered as potential participants to the overall charge of the hydrophobic interface. Theories about a potential role of such ions on the negative charge of hydrophobic surfaces are not new *per se*: bicarbonate adsorption was suggested back in 1991 by Medrzycka, but the author stated “*that further experiments are necessary for explaining the*

observed phenomena [negative zeta potential of hexadecane droplets in water]”.<sup>30</sup> Recently, Jungwirth and Vacha also put some hints on the presence of carbonic acid in water,<sup>14-16</sup> but did not take it into account in their simulation parameters. Authors defending the OH<sup>-</sup> adsorption theory<sup>9</sup> have also evoked water carbonation and discarded this hypothesis on the basis of non-conclusive experiments.<sup>31</sup> Other authors proposed to boil water before use to remove CO<sub>2</sub>,<sup>32</sup> a protocol that does not avoid instantaneous re-carbonation of water through fast reaction with aqueous OH<sup>-</sup>.<sup>33</sup>



**Figure 1. Carbonation of water at different pHs and other present ions:** water completed either by HCl or NaOH solutions and considered in a closed system. The content of Na<sup>+</sup> and Cl<sup>-</sup> are, as a first (but relevant) approximation, based on OH<sup>-</sup> and H<sup>+</sup> concentrations, respectively. The data are those recalculated from pH and conductimetry for the solutions we used in IFT and Ouzo measurements, showing the rather fair reproducibility of the technique (see Section S5 for calculation details).

From this basis, we revisit here the open question about the origin of hydrophobic surface charging and propose a unified theory that points out the key role of bicarbonate anions, and

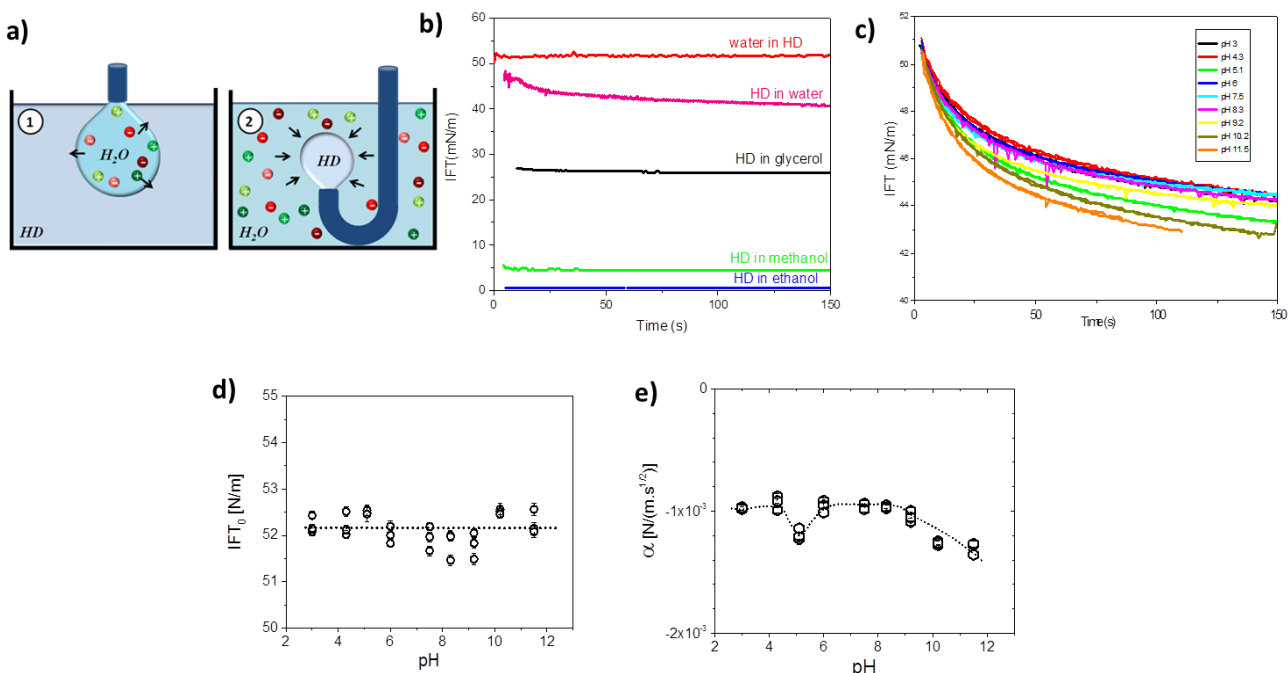
their preferential interfacial adsorption, on a large range of pH. In the following, after a thorough evaluation of the content and properties of the ions in presence in water as a function of pH, two series of experiments are displayed to unravel the respective influence of these different ions. The first one deals with interfacial tension (IFT) measurements of hexadecane (HD) in (pH-varied) water, so as to track the kinetics of adsorption of (any) ions at the oil interface. The other set of studies deals with the nanoprecipitation of HD or standard polymers at different pHs, where the size of the resulting colloids is directly related to the rapid adsorption of species at their interface during the nanoparticles growth. Then, by processing these data, and comparing them with available literature, we propose a general interpretation relying on the respective quantities of the different ions and, most importantly, on the conditions of measurements (see e.g. direct and reverse interfacial tension measurements). Note that all products used here have been characterized in details and when needed, purified accordingly, to remove any impurity that would lead to the misinterpretation of our results.<sup>34</sup>

Figure 1 shows the content of all species present in a pH-stabilized aqueous dispersion in a closed system.<sup>35</sup> Several major facts can be said from this carbonation textbook figure. First, there is a constant equilibrium between all species, i.e. dissolved  $\text{CO}_2$  gas,  $\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$ , according to the pH. In a close system, pKas given for  $\text{CO}_2/\text{HCO}_3^-$  and  $\text{HCO}_3^-/\text{H}_2\text{CO}_3$  ions pairs are 6.3 and 10.3, respectively.  $\text{H}^+$  and  $\text{CO}_2$  curves cross each other at 5, a value that corresponds to the pH of distilled water. The intersection between  $\text{H}_2\text{CO}_3$  and  $\text{HCO}_3^-$  curves is found at  $\text{pKa}=3.5$ ,<sup>36</sup> according to the ratio between gaseous  $\text{CO}_2$  soluble in water, and liquid  $\text{H}_2\text{CO}_3$ , of around 100. pH-neutral counter-ions, i.e.  $\text{Na}^+$  and  $\text{Cl}^-$ , are present approximatively at similar concentrations as  $\text{OH}^-$  and  $\text{H}_3\text{O}^+$ , respectively, whereas bicarbonate anions are found in much larger quantities in a large pH window. In the study that follows, we have prepared



aqueous solutions using either HCl or NaOH and measured their pH and conductance prior to use. Knowing the CO<sub>2</sub> concentration at targeted pH, we can recalculate HCO<sub>3</sub><sup>-</sup> content using the Henderson–Hasselbalch (see section S1 for details). Figure 1 shows the numerous solutions that we prepared in this study.

Another important parameter to take into account deals with ions' propensity to adsorb at apolar interfaces, which principally depends on their polarizability and hydrophilicity. Some coefficients obtained from viscosity measurements (Jones and Dole B coefficient) or NMR analyses (called B' coefficient) are good indicators of ions behavior towards surfaces:<sup>37</sup> positive values are characteristic of fully hydrated kosmotropic (hard) ions, whereas negative values are the signature of chaotropic (soft) ions, keen to interact with hydrophobic planes.<sup>38</sup> Typical values for the ions we have listed are given in Table S1. Both OH<sup>-</sup> and carbonate anions are kosmotropes (average values of B and B' coefficients ~0.15 and 0.27 M<sup>-1</sup>, respectively), for two different reasons: OH<sup>-</sup> is a small anion, with little polarizability, whereas carbonate is a big but doubly charged anion, thus entailing a very large hydrophilicity. H<sup>+</sup> and Na<sup>+</sup> are slightly marked kosmotropes, with B values around 0.07 M<sup>-1</sup>. The B/B' values for bicarbonate anions are, as Cl<sup>-</sup>,<sup>39</sup> close to zero, reflecting intermediate behavior in contrast with the other cited ions. The ions affinity towards hydrophobic interfaces can also be evaluated by measuring the surface tension of highly concentrated corresponding water solutions. Typically, H<sup>+</sup> prefers interfaces more than OH<sup>-</sup> does.<sup>14</sup> Studies on flotation of bicarbonate and carbonate concentrated brine solutions showed that bicarbonate ions specifically adsorb at the air/water interface, whereas carbonate ions hardly do;<sup>40-41</sup> such result was confirmed by sum frequency spectroscopy.<sup>42</sup> These results clearly underline that bicarbonate anions, which are excessively present in a fair pH range (6-10), are among the best candidates for interacting with surfaces.



**Figure 2. Interfacial tension measurements: kinetics of ion adsorption.** a) Scheme showing the mode of measurement of interfacial tensions. When measuring a water droplet in hexadecane, the content of ions to be driven towards the interface is very low, whereas it is the other way around for direct measurements; b) experimental curve as a function of time. Only HD drops in water show a neat decrease of IFT with time c) same curves as in a) but at different pHs; d) and e) extracted values from a diffusion model in the short time limit: IFT<sub>0</sub> and α, respectively, as a function of pH (see text for details).

Whereas the surface tension between air and water has been extensively studied,<sup>43</sup> there is very little information on (direct or reverse) interfacial experiments between oil and water.<sup>19-20</sup> Commercial oil HD 99% (used in this study) typically contains variable amounts of heptadecane and fatty acids (section S2 and Figure S2-1), making interfacial tension measurements of a HD drop in deionized water poorly reproducible (section S3 and Figure S3-1a). Purification of HD on alumina columns (X5) allows for quantitatively removing the traces of fatty acids (as confirmed by titration, see section S2, Figure S2-1) while heptadecane remains in HD after

treatment. This simple purification step is however sufficient to obtain highly reproducible IFT data (Figure S3-1b). The standard direct pendant drop measurement (Fig. 2a (1)) of a distilled water drop in HD is given in Fig. 2b. Similar to the report of Goebel and Lunkenheimer in 1997,<sup>44</sup> the IFT does not change for an alkane in which a drop of water is formed. The other IFT measurements shown in Fig. 2b were performed with HD drops in different solvents including water using a reverse pendant drop methodology, (Fig 2a (2), i.e. oil drop in a given medium). In contrast with the direct pendant drop methodology, interfacial tension between HD drop and water progressively decreases whereas, the IFT remains constant for the other oil drop/solvents systems (methanol, ethanol, glycerol). These divergent IFT behaviors (instantaneous IFT stabilization for water drop/HD or HD/solvents vs progressive decrease of IFT for HD drop in water) are consistent with the disparate content of ions present in the two scenarios (Figure 2a, vide infra).

Complementary experiments were then done at different pHs by adding HCl or NaOH into water prior to measurements. IFT curves are reported in Figure 2c. Basically, there is no clear difference of behavior as a function of pH, except for high pHs and around pH 5. The IFT declines in two steps, a steep decrease in the first minute and then a slow decrease with time. The curves (IFT as a function of time, IFT(t)) can be fitted with a diffusion model in the short time limit. In the first stages of adsorption, IFT(t) depends on the bulk concentration  $c$  and the diffusion coefficient  $D$  of the adsorbing species (values reported in Table S1) :

$$IFT(t)_{t \rightarrow 0} = IFT_0 - 2RTc\sqrt{Dt/\pi} \quad (1)$$

where  $IFT_0$  is the bare interfacial tension. IFT data were also plotted as a function of  $\sqrt{t}$  and fitted simply by:

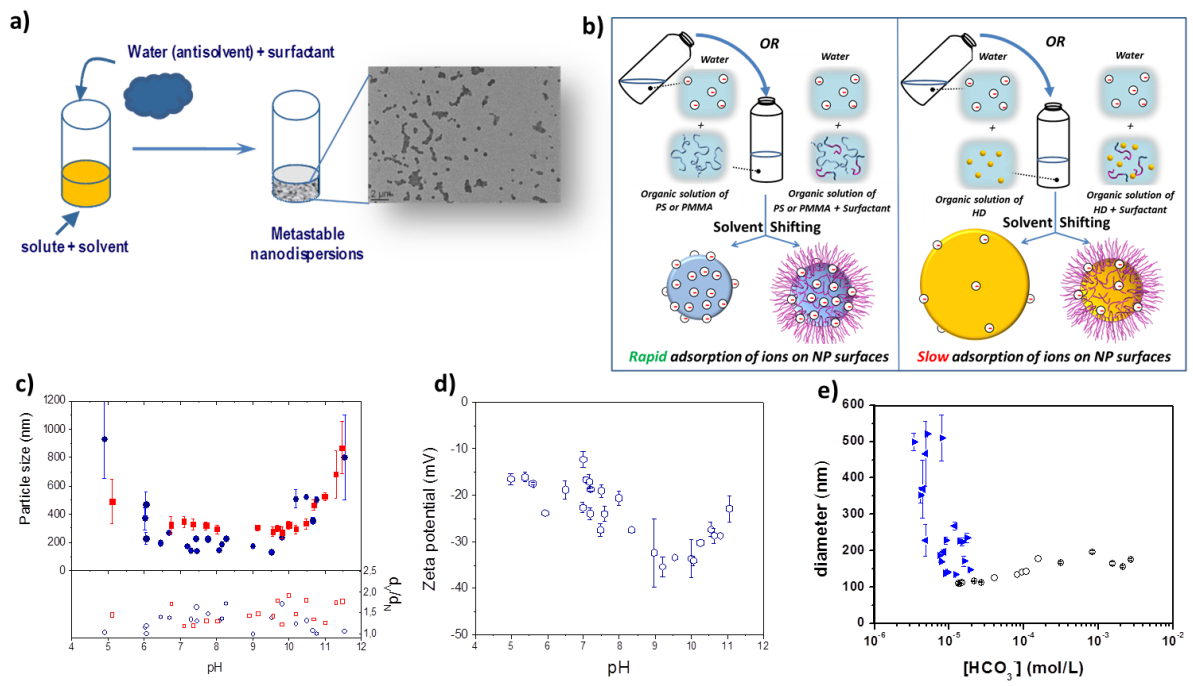
$$IFT(t)_{t \rightarrow 0} = IFT_0 + \alpha\sqrt{t} \quad (2)$$

$$\alpha = -2RTc\sqrt{D/\pi} \quad (3)$$

Results are compiled in Figures 2d and 2e. Since  $t_0 = 0$  is very difficult to assign for these experiments,  $IFT_0$  varies slightly, with an average value of 52 mN/m that agrees with literature values for the HD/water system.<sup>44</sup> On the other hand, the slope ( $\alpha$ ) is not dependent on this initial value and shows a clear trend as a function of pH. The slope is constant from pH 3 to about 8, and starts to decrease slightly above that. We further extrapolated the IFT curves at infinite time (Figure S3-2) to obtain an equilibrium interfacial tension value of about 38 mN/m, independent of the starting pH. Note that the latter interfacial tension is surprisingly low when compared to the values typically observed at the aqueous-air interfaces. In section S3 of the supporting information, we discuss this strong decrease of IFT observed at the alkane-water interface. One can conclude here that in a large range of pH (5 to 10), there is a strong adsorption of ions at the HD/water interface, first in a fast motion and then slowly with time.  $\text{OH}^-$  and  $\text{H}^+$  ions represent a small minority, albeit between 6 and 8, which cannot explain the strong adsorption observed through these indirect interfacial tension measurements. We anticipate that the surface is first progressively covered with bicarbonate anions originally present in water, and then slowly gets saturated with excess bicarbonates generated from the atmospheric  $\text{CO}_2$  (we can consider here an open system on long range of time).<sup>45</sup>

Another way to qualitatively and quantitatively investigate ion adsorption on interfacial surfaces as a function of pH relies on the nanoprecipitation technique (see reviews in <sup>46-48</sup>). This solvent shifting process indeed implies the very quick generation of particles or droplets by supersaturation of a solute (polymer or oil, respectively) initially added in a solvent (typically acetone), when the latter migrates towards the antisolvent (water) (Figure 3a). The process generates submicronic colloids in a given frame of the phase diagram, generally in a diluted

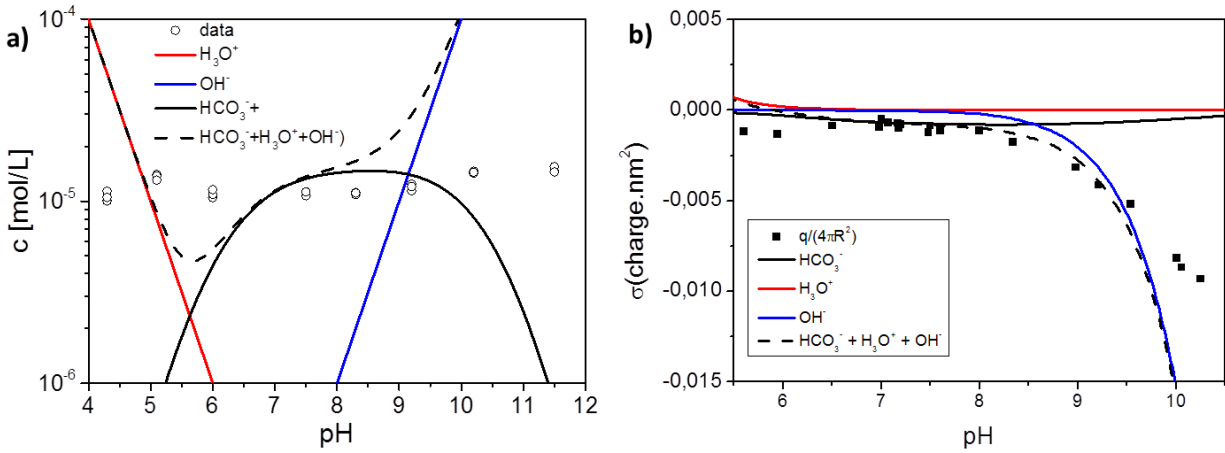
region.<sup>49</sup> In this spontaneous emulsification technique, oil emulsions and polymer dispersions are grown by nucleation/aggregation events at a very fast rate of encounters.<sup>50</sup> The aggregation phenomenon stops when surfaces repulse each other. Most authors have shown that, even in absence of surfactants, polymer particles having a negative surface charge are generated, as confirmed by zeta potential measurements.<sup>4</sup> The idea admitted so far was that OH<sup>-</sup> anions adsorb at interfaces thus stopping coalescence at some point.<sup>51</sup> In this context, we have undertaken a series of experiments with different solutes, i.e. HD oil,<sup>52</sup> and polymers, PMMA and PS.<sup>53</sup> For the former, we have compared data on an as received hexadecane oil and a purified one. For the latter, polymer polar end-groups clearly influence the nanoprecipitation process;<sup>54</sup> we have then used polymer standards prepared by anionic polymerization, for which neutral chain ends, clearly identified by NMR, do not play any role in colloids stabilization (see full NMR characterization in supporting information, section S2). Note that to ensure mid-term colloidal stability required for size characterization by QELS, a slight amount of non-ionic surfactant (here brij 56) was added in the organic phase prior to solvent shifting (see section S4 for experimental conditions). It is worth noting that polymer nanoprecipitation gives particles whose dimensions are independent of the surfactant content and phase location;<sup>46</sup> whereas, for molecular solutes including oils, adding a surfactant in the organic phase gives much lower droplet sizes than when introduced in water.<sup>50</sup> We assign this behavior to the fact that, for polymers, the size of the resulting nanoparticles is driven solely by the (very fast) adsorption of ions (compared to surfactant's one) at particles' interface whereas, for HD, the rate of surfactant adsorption at the droplet's surface, directly arising from acetone, is significantly larger than ions' one (Figure 3b). Results for HD, given in supporting information, nevertheless illustrate the general character of the conclusions drawn from polymer nanoprecipitation experiments (Section S4).



**Figure 3. Spontaneous emulsification via Ouzo effect: ion adsorption vs pH.** a) Principle of Ouzo effect emulsification with a TEM photo showing PMMA particles obtained by this method; b) influence of the presence of surfactant on the final size of polymer particles and droplets, respectively; fast ion adsorption occurs for polymers, and not for oil (see text for references on the subject); c) dispersion size variations (plain symbols) and polydispersities ( $d_V/d_N$ , open symbols), as a function of pH, for polymer nanoparticles prepared by Ouzo effect (PMMA ● and PS ■). The size of the symbols was chosen so as to see the small error bars; d) zeta potential of PMMA particles vs pH after solvent evaporation; measurements at pH below 7 were carried out rapidly after acetone evaporation to ensure a sufficient colloidal stability on the course of the data collection; e) PMMA dispersion size variations as a function of bicarbonate contents: (◀, ▶) from pH variation experiments, at acidic and basic pH, respectively; (○) using bicarbonate solutions of increasing concentration

Figure 3c shows the variation of particle diameters for the two polymer systems as a function of the pH of the water phase before solvent shifting. One clearly sees a range of lower dispersion size, typically between 6 and about 9.5. Below pH 4.5, and above pH 12, unstable dispersions were obtained so that sizes could not be measured by the Nanosizer. Note that this lack of stability is not due to a too large ionic strength as, at pH 10, the ionic strength has been evaluated at  $5 \times 10^{-2}$  M (according to the content of  $\text{OH}^-$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$  in the medium), conditions that our dispersion perfectly stands in presence of the non-ionic surfactant. It is also important to point out the rather constant and small values of  $d_V/d_N$  (where  $d_V$  is the volume-average particle size and  $d_N$  is the number-average particle size) for both polymers, independent of particle sizes (Figure 3c). This feature of the resulting polymer dispersions clearly demonstrates that the observed variations of colloid dimensions are not the consequence of undesired particles aggregation. A similar trend is noticed for HD droplets, either starting from the pristine HD 99% or the purified one, albeit in a narrower size range due to surfactant competitive adsorption (Figure S4). We further plotted the zeta potential of PMMA dispersions (after evaporation of acetone) versus the pH at which the nanoprecipitation was done (Figure 3d). As particle size has a significant impact on zeta potential measurements, data processing is limited here to the pH range (6-10) where colloidal dimensions are constant (see next section). Basically, the zeta potential follows a marked decrease on a large range of pH, and an increase above pH 9. Figure 3e depicts the evolution of PMMA NP diameter vs the content of bicarbonate ions in aqueous dispersions of various pHs. Regardless of the error naturally occurring in these experiments, the plot highlights that the size of PMMA dispersions is minimal with a bicarbonate concentration as low as  $10^{-5}$  M, irrespective of the pH. This concentration is so small that it is likely that colloidal stability is not achieved in these systems without the presence of brij surfactant. Interestingly,

addition of extra sodium bicarbonate salt in the aqueous solution (prior to solvent shifting) does not promote further decrease of the particle size because of increasing ionic strength (while not drastically changing the pH, see Figure S5). In brief, the range of pH where the size is best controlled by nanoprecipitation is when the bicarbonate concentration is at its maximum (in agreement with the diagram of carbonate species distribution vs pH given in Figure 1), and both  $H^+$  and  $OH^-$  are in large depression.



**Figure 4: Modeling of interfacial adsorption.** a) Calculated content of different ionic species from interfacial tension measurements on purified HD; b) calculated content of ionic species on PMMA particles as a function of pH, fitted on zeta measurements.

Taking advantage of the two sets of experiments presented above, we subsequently aimed at determining average overall ion contents on HD droplet interfaces or on polymer particles. The slope  $\alpha$  of the interfacial tension evolution is expressed using the following equation  $\alpha = -2RTc(D/\pi)^{1/2}$ . In a first approximation, assuming an average diffusion coefficient of  $10^{-9} \text{ m}^2/\text{s}$  for every ion (Table S1), we calculated the overall concentration  $c = -\alpha/[2RT(D/\pi)^{1/2}]$  of ions adsorbing onto the interface. Figure 4a shows these  $c$  values as a function of pH. The concentration of each species  $HCO_3^-$ ,  $H_3O^+$ ,  $OH^-$  at different pHs was determined from carbonation equilibria data from Figure 1.<sup>55</sup> Comparing the concentrations of carbonation



equilibria with  $c = -\alpha/[2RT(D/\pi)^{1/2}]$  (IFT data), we find a good agreement for a narrow pH range of 6 to 9. At acidic or basic pH, data do not fit with the model of full coverage of any ion, suggesting that  $H^+$  or  $OH^-$  ions hardly adsorb at these pHs, respectively.

We also analyzed the zeta potential data for the PMMA particles using the Debye-Hückel theory in the pH range where particle sizes are constant (*i.e.* between 6 and 10). The electric potential  $\Phi$  as a function of the distance  $r$  from the center of the drop/particle is:

$$\Phi(r) = \frac{q}{4\pi\epsilon_r\epsilon_0} \frac{\exp(-\kappa r)}{r} - \frac{\exp(\kappa R)}{R} \quad (4)$$

where  $q$  is the charge,  $\kappa$  is the inverse of the Debye length and  $R$  is the particle radius. The zeta potential describes the potential at the shear plane of the particle. Here, their diameter is about  $\sim 130$  nm and the shear plane of the particle is about 1 nm far. We neglected this ca. 1 nm difference given the dispersion of the data and the shape of the potential at this  $r$  range. From eq. 4 we can calculate the charge  $q$  or the charge density  $\sigma$  (in charge/nm<sup>2</sup>):

$$\sigma = q/(4\pi R^2) \quad (5)$$

as a function of the pH, see Fig. 4b. We then compared the surface charge density measured for polymer particles in water in terms of the adsorption of the three molecular species  $HCO_3^-$ ,  $H_3O^+$ ,  $OH^-$  at the water-polymer drop interface. In order to make this comparison, one should estimate the characteristic time of the drop formation. The calculated surface concentration is:

$$\Gamma \left( \frac{\text{molecules}}{\text{nm}^2} \right) = 2c \sqrt{\frac{Dt^*}{\pi}} \quad (6)$$

assuming that 1 molecule of  $HCO_3^-$  ( $OH^-$ ) corresponds to 1 negative charge and 1 molecule of  $H_3O^+$  to a positive charge. The best fit was obtained for a characteristic adsorption time  $t^* = 10^{-5}$  s, in agreement with the very fast emulsification rate found in Ouzo effect. Note that in this time interval, a Brownian particle travels a distance of about  $(2Dt^*)^{1/2} = 141$  nm, which agrees

with typical distances of adsorption processes. Again, the best agreement is seen for the intermediate range of pH, typically between 6 and 9. Here, we could not state on the adsorption of ions at lower pH than 6, where the size of the particles increase. On the other hand, at basic pH, the zeta potential reaches values that are below those expected for full surface ionization with hydroxide anions.

Both fits show clear trends. For  $\text{pH} < 6$ , the number of interfacial charges is low, and for  $\text{pH} > 9$ , only a small fraction of anionic species available in solution are found at the surface of the particles. Between these two pHs, bicarbonates, the most prominent ions in those conditions, adsorb at interfaces to generate a negative charge. From the literature, we know that an isoelectric point is observed at around pH 3-4. This critical pH value corresponds to the pKa of the  $\text{H}_2\text{CO}_3/\text{HCO}_3^-$  pair, *i.e.* where carbonate starts to be naturally formed. Colussi *et al*, who evaluated the content of charges at air/water interfaces, confirmed this value of pKa. They also reported a second transition at around pH 9.5, which matches with the pKa of the  $\text{HCO}_3^-/\text{CO}_3^{2-}$  pair.<sup>6-7</sup> These data are in line with the trends observed in our study. If we consider acidic pHs, *i.e.* below pH 4, the surface in average becomes positive. Even if the hydronium ion adsorbs, chloride, a chaotropic ion, can also adsorb and neutralize to some extent the surface charge. It is however not clear whether it is  $\text{CO}_2$  in its neutral form ( $\text{H}_2\text{CO}_3$ ) that is more likely to adsorb or the hydroxonium ion ( $\text{H}_3\text{O}^+$ ). At high pH,  $\text{OH}^-$  and  $\text{Na}^+$  adsorptions compete, whereas bicarbonate anions can definitively be set aside. It can also be anticipated that, due to fast conversion of  $\text{CO}_2$  into bicarbonate by reaction with  $\text{OH}^-$  at basic pH, an excess of the latter could form and adsorb onto the interface, thus increasing the overall charge density. Note that the presence of impurities, and also the substantial ionic strength brought by saline solutions, have definitively a role in the stabilization/ionization of hydrophobic surfaces, even if the extent

of these are only qualitatively shown here. These assumptions are just open propositions for further works.

Finally, the fact that studies report neutral, negative or positive interfacial charges at water/hydrophobic interfaces from one study to another, depends principally on how measurements are done. For instance, the surface tension of water droplets in air does not change with pH.<sup>43</sup> This is explained by the fact that the very few ions present in the small volume of the droplet (typically 60  $\mu\text{L}$  in our experiment) do not change drastically the IFT. On the other hand, air bubbles in water show negative zeta potentials and low interfacial tensions, because excess ions in water can easily reach the interface. We have found similar differences here when measuring direct or reverse IFT of HD/water systems. A droplet of water shows a constant IFT with time, whereas a reverse one sees its interfacial tension drop with time. As stated at the beginning of this article, water drops in oils have positive zeta values, independent of the pH. The presence of  $\text{CO}_2$ , as slightly soluble in oils as in water,<sup>56</sup> can protrude to the interface and affect the surface charge, like bicarbonate ions do in the reverse system. Protons in excess cover the few ions present in water, and thus promote a positive charge. Similarly, bubbles of  $\text{CO}_2$  in water give stable interfaces below pH 4 and basically dissolve above that value. On the other hand, in a study devoted to the natural electrostatic stabilization of water droplets in supercritical  $\text{CO}_2$  emulsions, the authors showed that the natural ionization of interfaces was due to the bicarbonate adsorption.<sup>57</sup>

In conclusion, we have shown that the carbonation of water is an important parameter to take into account when exploring hydrophobic/water interfaces. Bicarbonate ions, naturally present in water, or generated from atmospheric  $\text{CO}_2$ , has a large propensity to adsorb at hydrophobic interfaces, particularly on polymers, on a quantitative level. Whereas these ions do not suffer

competition at pHs around neutrality (6-9 range), all other ions present in the aqueous solutions can also adsorb, albeit in part, at lower or larger pHs. The content of interfacial ions is generally too low to ensure efficient colloidal stability, and to be tracked by the different techniques quoted above. We hope that in the future, the several teams cited here will confirm the presence of bicarbonate ions at hydrophobic interfaces from their experimental expertise. For instance, FTIR spectroscopy of the OH band in carbonated aqueous solutions shows signatures not seen for other ions,<sup>58</sup> whereas Raman spectroscopy shows two separated, specific peaks in the carbonyl region for bicarbonate and carbonate ions.<sup>59</sup> Hopefully, Raman coupled to SFS studies could shed some light on interfacial carbonation. It could also be worth to carry out experiments in a glovebox so as to discard any trace of CO<sub>2</sub> from water (and oils) and show its impact on interface charging.

## ASSOCIATED CONTENT

### **Supporting Information.**

Methods and materials, experimental procedures, NMR spectra, interfacial measurement and ouzo experiment are included in supporting information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. ‡These authors contributed equally.

## Notes

The authors declare no competing financial interests.

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## DEDICATION

This article is dedicated to the memory of Vincent Judais.

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