CarboSchools

pH-Regulation of Seawater: The Role of Carbonate (CO_3) and Bicarbonate (HCO_3)

Introduction:

The major carbon reservoir in the ocean is in the **dissolved** inorganic carbon (DIC), which is the total of aqueous CO_2, bicarbonate (HCO_3) and carbonate (CO_3) ions. The pH of seawater is dependent on which of these species is the most predominant. The normal present day pH of seawater is more on the basic side between 7,9 – 9,0. At this pH the HCO_3 ions predominate. Carbonate ion concentrations increase with increasing pH and when more CO_2 dissolves in seawater it becomes more acidic. This can be better understood by looking at Fig. 1.

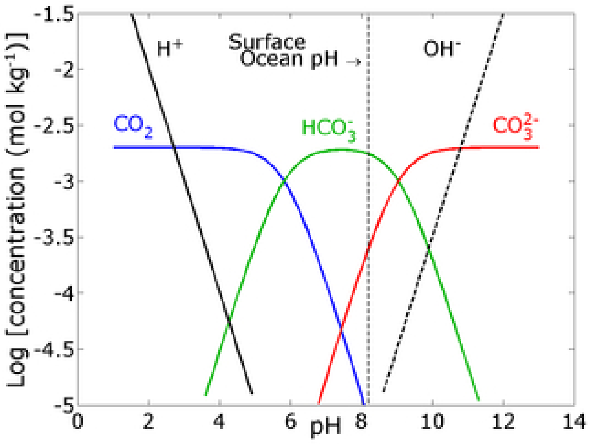

Fig. 1

When CO_2 from the atmosphere reacts with seawater, it immediately forms carbonic acid (H_2CO3), which in itself is unstable. This further dissociates to form bicarbonate and carbonate ions. The bicarbonate and carbonate ions are responsible for the buffering capacity of seawater, i.e. seawater can resist drastic pH changes even after the addition of weak bases and acids. The carbonate ion can react with calcium ions (Ca), which are in excess in seawater, to form calcium carbonate ($CaCO_3$), the material out of which the shells of mussels, the skeleton of corals and the exoskeleton of some microalgae is made of.

Aim:

The following experiment aims to show how bicarbonate and carbonate regulates the pH of seawater in a simple activity to enable pupils to visualise the buffering capacity of seawater.

Preparation time:	5 minutes
Activity time:	30 minutes
Type of activity:	Hands-on experiment
This activity had been tested on students aged:	10-16 yrs.
Application:	Physics, Chemistry, After-school activity
Time for data analysis and discussion:	20 minutes
Prior knowledge required:	acid-base interaction, concept of “indicators”
Cost:	Indicator (12€/250 ml)
Degree of difficulty:	Medium

Materials:
3 to 6 150 or 250 ml bottles with lids
distilled water and seawater
drinking straw6
sodium carbonate ($Na_2\mathbf{CO_3}$)
sodium bicarbonate (baking soda) ($Na\mathbf{HCO_3}$)
Mc Crumb Indicator Solution* with colour chart
pulverised eggshells (optional)

Fig. 2 Materials

*The McCrumb indicator solution has a pH range of 1-12. It turns from green to purple in basic solutions and from yellow to red in acidic solution.

Procedure:

1. Fill three bottles with 200 ml seawater and the other 3 with 200 ml distilled water. Add a small pinch of $Na_2\mathbf{CO_3}$ into one of the bottles containing seawater and in another containing distilled water. Do the same for the $Na\mathbf{HCO_3}$.

2. Compare the colours of the water inside the bottles. Do you see any differences?

3. Add 20 drops of the McCrumb indicator solution in each bottle. Using the colour chart, determine the pH of the water in each bottle. Can you see any differences now?

4. Insert drinking straws through the openings of the bottles making sure that they are immersed in the water.

5. Blow air through the drinking straw to introduce CO_2 into the bottles, first for 20 seconds. Try to blow uniformly. Replace the lids of the bottles and determine the pH. Record the pH in the table below.

6. Do the same for 40 seconds and 60 seconds. Be sure that the lids are in place and no air is entering into or escaping from the bottles. Do you notice any differences?

Results:
Using the colour chart for the Indicator solution record the pH of the different solutions in the table next page:

	Estimated pH (see colour chart)				
Water Samples	Initial colour	After addition of Indicator solution	After blowing for 20 seconds	After blowing for 40 seconds	After blowing for 60 seconds
Seawater					
Seawater with NaHCO3					
Seawater with Na2CO3					
Distilled water					
Distilled water with **$NaHCO_3$**					
Distilled water with **Na2CO_3**					

Discussion:

1. Do you notice any differences in the appearance of the water in the different bottles before the addition of the indicator solution?

2. After addition of the indicator solution, how do the pH of the water differ in the different bottles? How did the addition of $NaCO_3$ or $NaHCO_3$ to seawater and distilled water prior to bubbling with CO_2 affect the pH?

3. What happens to the pH of the water in the bottles after blowing in CO_2 into them? Does addition of $NaHCO_3$ and Na_2CO_3 to seawater and to distilled water make any difference with regard to pH changes?

4. What is the effect of the addition of Na**HCO_3** and Na**CO_3** on the pH of distilled water and seawater?

5. Eggshells are made of Ca**CO_3**. Add pulverised eggshells to the acidic seawater and distilled water. Do you notice any changes in the pH? Why? What is the difference between the CO_3 in the powdered eggshell and in Na_2CO_3?

6. Can you now make a conclusion about the roles of **HCO_3** and **CO_3** in the buffering capacity of seawater?

Notes:

1. No differences in appearance can be seen between the different water samples. This will enable especially younger pupils to appreciate that the properties of water cannot be seen per se but can be made visible by a little chemistry. Fig. 3

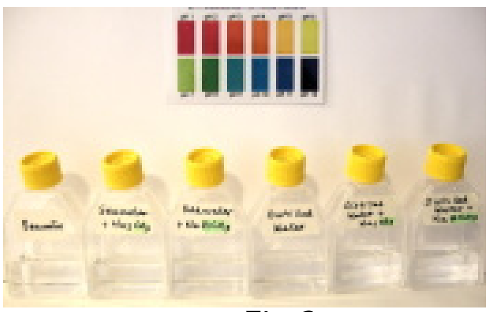

Fig. 3

2. However, since a small pinch of Na_2CO_3 can already cause a supersaturation (definition: the given volume of solvent, in this case seawater, already contains more of the dissolved material, here Na_2CO_3, than it can normally dissolve) of seawater with CO_3 the pupils may get a cloudy solution when Na_2CO_3 is added to seawater (Fig. 4a). This will not be observed for distilled water (Fig. 4b). Comparing the appearance of seawater and distilled water after the addition of a pinch of Na_2CO_3, the solutions may look as in Fig. 4c.

(a) **(b)** **(c)**

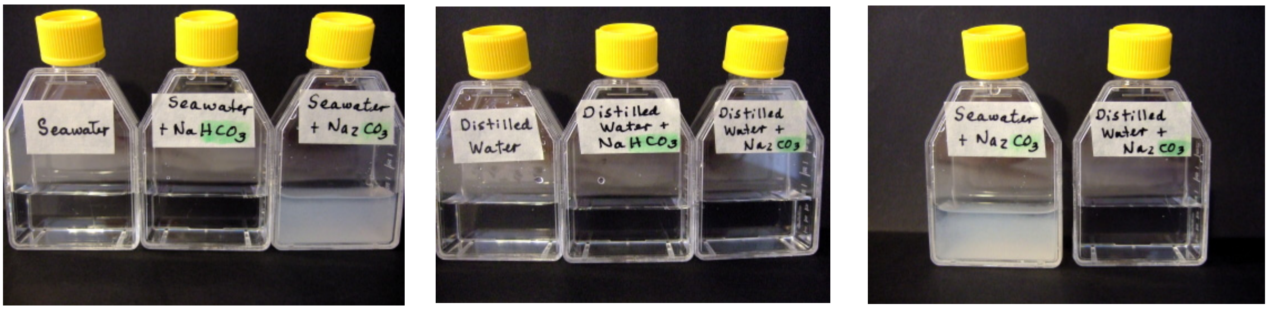

Fig. 4

3. Upon addition of the indicator solution, the pupils will now see differences in what seemed to be similar looking water samples (Fig. 5).

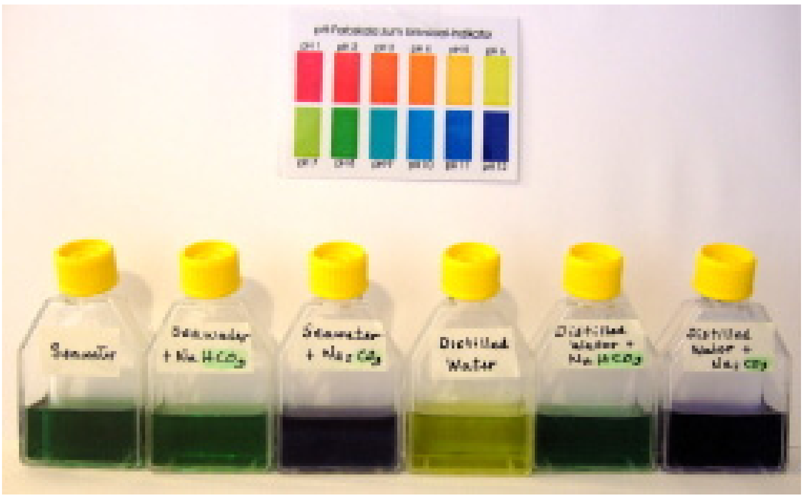

Fig. 5

4 The table below shows the estimated pH of the different water samples after addition of different amounts of CO_2 (varied by different durations of blowing into the sample). If the teacher has a way of giving exact doses of CO_2 to the samples, for example from a CO_2 cylinder, then it is advised to do this, especially for older pupils. It is also recommended to test the pH of the seawater and the distilled water, which will be used for the experiment beforehand. The seawater should have a pH of about 8 and distilled water a pH of 7. If this is not the case, transfer the water samples in containers with big openings or bowls and let the samples stand overnight, or aerate the samples. This way, the gases in the samples will equilibrate with that in the air.

	Estimated pH (see colour chart)				
Water Samples	Initial colour	After addition of Indicator solution	After blowing for 20 seconds	After blowing for 40 seconds	After blowing for 60 seconds
Seawater	clear	8	7	7	6-7
Seawater with NaHCO3	clear	8	8	8	8
Seawater with Na2CO3	clear/may be cloudy	12	12	12	12
Distilled water	clear	7	5	4	3-4
Distilled water with **$NaHCO_3$**	clear	8	18	8	8
Distilled water with **$Na2CO_3$**	clear	12	12	12	12

From the table above, it can be observed that the pH of distilled water changes quite rapidly after the first addition of CO_2. The change of pH of seawater was not as great as in the distilled water. However, further addition of CO_2 may also lower the pH of seawater to the acidic range. In both seawater and distilled water, no pH changes can be observed when $NaHCO_3$ or Na_2CO_3 is added. The appearance of the water samples in the bottles after blowing CO_2 into them for 60 seconds can be seen in Fig. 6.

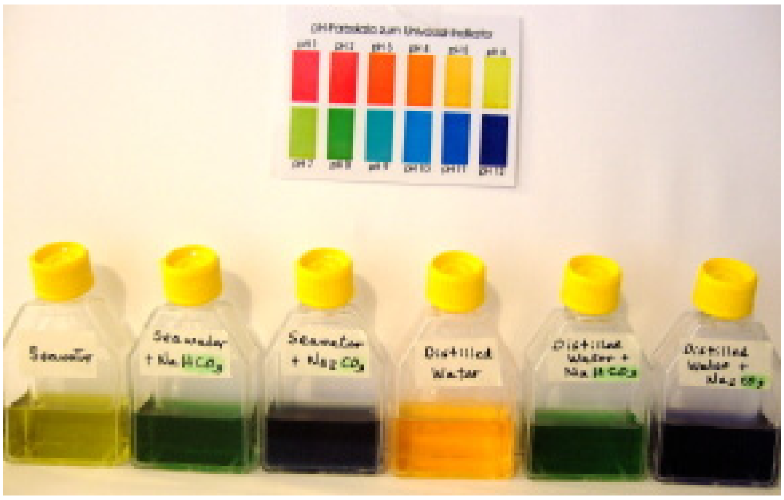

Fig. 6

5 The addition of eggshells to the acidic seawater and distilled water will not cause any pH changes in the water sample even if then eggshells are made of $CaCO_3$ because the CO_3 in the eggshell is not in its dissolved form. Remind the pupils that the pH of seawater is determined by the **dissolved** inorganic carbon species in seawater.

Additional experiments:

1. Let the pupils determine pH changes in distilled water samples with increasing concentrations of Na_2CO_3. If you have a good balance in school, weigh different amounts of Na_2CO_3 and ad this to distilled water. Blow CO_2 into the samples as described above. The pupils will observe that the less Na_2CO_3 they add, the more the pH of the sample will change with addition of CO_2. Explain to them that seawater also has a limited amount of CO_3 and that the capacity of the ocean to take up CO_2 is not an unlimited.

2. Let pupils do their own experiments with the water samples. Let them find out what happens to the pH of a water sample with $NaHCO_3$, if you add Na_2CO_3. Let them find out what happens if they do it the other way round. This will show them that the pH of the water is dependent on which form of the dissolved inorganic carbon ion is predominant. This exercise can also lead them to understand that addition of HCO_3 to supersaturation will not make the water more basic and it can even make the water less basic (not more acidic) if added in excess to a basic solution containing Na_2CO_3. This is best seen in the graph at the start of this activity.

Additional reading:

Zeebee, Richard. 2006. Marine Carbonate Chemistry. The Encyclopedia of the Earth. http://www.eoearth.org/article/Marine_carbonate_chemistry

Solution chemistry of carbon dioxide in seawater. http://cdiac.ornl.gov/ftp/cdiac74/chapter2.pdf

The basics of ocean chemistry. http://oceancolor.gsfc.nasa.gov/SeaWiFS/TEACHERS/CHEMISTRY/

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