Summary

We have used the potentiometric titration technique to study the poly(acrylic acid), also known as PAA. The experimental values obtained for the interaction parameter and for the dissociation of the polymer are close to the theoretical ones and to the value calculated from the Debye Hückel theory. The differences have been discussed and so the relation between these results and the structure of the polymer.

We have also used the same technique to analyze the commercial waters: Vichy, Evian and Swiss Alpina in order to get the concentrations of the main carbonates species. The results and the differences with the values featured in the bottles labels have been discussed.

Introduction

This experiment is divided in two parts:
In the first part we determine the charge of the polymer PAA as a function of the pH. Our purpose is to get the degree of ionization of PAA as a function of the pH (at two different ionic strengths) and use these results to obtain the interaction parameter ($\Lambda$) and the dissociation constant ($pK_0$) of the polymer. We will compare these values with the theoretical ones, and discuss the differences.

In the second part our objective is to determine the concentrations of carbonic acid and bicarbonate anion in different water samples. First of all we do one manual titration and after that we do the automatic titration for all the samples. We will compare the results with the values indicated in the labels of each water sample and discuss the differences.
Methodology

Titration of PAA

The first thing to do before starting the analysis of the polymer is to calibrate the pH electrode with two buffer solutions of pH 4 and 7. After that, we have to make a fine calibration with a blank titration. In the first place we prepare everything for the analysis: we wash the large titration vessel, adjust the gas stream (1 bubble per second approx.), restart the burettes and verify that there is no bubbles in the tubes. We set up the pH range for the analyze between 3 and 9; and set the ionic strength at 0.1 and at 0.01 M. Then we start the titration.

Now we can make the titration of the PAA. We take 50 mL of a PAA solution (diluted 10 times from the stock solution) and put them into the vessel; we keep the same parameters from the previous titration and we start the analysis.

Determination of carbonates concentrations in water samples

First of all, we do a manual titration of a sample of Vichy water: in a beaker, we put 10 mL of KOH 0.1 M solution, 10 mL of Vichy water and around 15 mL of Millipore water, and we add some drops of phenolphthalein indicator, then we titrate with a HCl 0.1 M solution. After observing the change of color (from purple red to colorless) indicating the first point of equivalence, we add some drops of bromocresol green indicator and we continue the titration until we observe the second turning of color (from blue-green to yellow) that indicate the second point of equivalence.

Now we start the automatic titration of the water samples. First of all, we calibrate the pH meter like in we did in the first part of the experiment; secondly we measure the pH of the Vichy water sample. After that, we start with the titrations of the samples. We put inside the titration vessel 10 mL of KOH 0.1 M solution, 10 mL of Vichy water and around 15 mL of Millipore water, and we start the titration. For the other samples the procedure is the same except for the volume to analyze: for Swiss Alpina sample we use 50 mL and for Evian water we use 100 mL. We do this in order to have an optimal amount of anion bicarbonate inside the titration vessel (around 0.8 mmol) and so the points of equivalence will be easier to determine.
Results

Equilibrium titration of a macromolecule

Fig. 1 – The charge of PAA (in moles) is plotted as a function of the pH. The charge values have been set to 0 by adding the value of the lowest point to all points.

\[
\begin{align*}
\text{pK}_{\text{eff}} &= \text{pH} - \log \frac{\alpha}{1 - \alpha} \\
&= \text{pK}_0 + \Lambda \alpha
\end{align*}
\] (1)
(2)

Fig. 2 – To get the ionization constant \( \alpha \) (here \( 1-\alpha \) because we began at pH high) the charge of PAA is divided by the total concentration (in moles).

Fig. 3 – The degree of ionization (\( \alpha \)) is plotted as a function of pH.

Fig. 4 – \( \text{pK}_{\text{eff}} \) is calculated with equation 1. The fitting gives the values in equation 2.

\[
\begin{array}{ccc}
I=0.01 \text{ M} & \text{pK}_0 & \Lambda \\
& 4.56 & 2.5 \\
I=0.1 \text{ M} & 4.30 & 2.1
\end{array}
\]

Tab. 1 – The \( \text{pK}_0 \) and \( \Lambda \) of the PAA at ionic strength 0.01 and 0.1 M.

The total concentration value we used to calculate was the value on the bottle (total carbon concentration 3.27 g/l). This value is divided by the number of carbon in the
monomer (3) the molar mass of carbon and the dilution factor, finally it’s multiplied by
the volume.
\[
n_{\text{total PAA}} = \frac{3.27 \times 50}{10 \times 3 \times 12 \times 1000} = 4.54 \times 10^{-4} \text{ mol}
\]
This value was chosen and it’s close to charge difference at low and high pH \( n_{\text{total}} = 4.20 \times 10^{-4} \) which is not very precise.

The interaction parameter can by estimated with the following equation :

\[
\Lambda = \frac{L_B}{\ln 10 b} f(\kappa a)
\]

Where \( L_B \) is the Bjerrum length and is equal to \( e^2/(4\pi\varepsilon_0\kappa T) \approx 0.72 \text{ nm} \), \( \kappa \) is the inverse Debye length and the function can be approximated by the planar geometry as \( f(x) = 2/x \). The constant "a" is the radius from PAA and "b" is the distance between the carboxylic groups (visualize PAA in linear conformation as a cylinder).

Those two constant where evaluated with a 3D visualization program and the found values are : 2.70 Å for "a" and 6.78 Å for "b". Debye length \( (\kappa^{-1}) \) is for a salt concentration of 0.1 M is 0.96 nm. With those parameters \( \Lambda \) is equal to 3.27 according to DH theory.

**Carbonate analysis in drinking water**

**Manual titration**

\[
\begin{align*}
n_{\text{H}_2\text{CO}_3} & = n_{\text{KOH}} - n_{\text{H}_2\text{Cl}}^1 \quad (3) \\
n_{\text{HCO}_3^-} & = n_{\text{H}_2\text{Cl}}^2 - n_{\text{KOH}} \quad (4)
\end{align*}
\]

The equations 3 and 4 will be derived with the titration curve (figure 5, 6 or 7).

Before the beginning of the titration, there is an equilibrium between the \( \text{H}_2\text{CO}_3 \) and the \( \text{HCO}_3^- \) (pH 7) but we don’t know their concentration. To titrate the \( \text{H}_2\text{CO}_3 \) in solution, we have to add a known amount of base to move the equilibrium where all the \( \text{H}_2\text{CO}_3 \) has been deprotonated (pH base). To know the excess of KOH we put, we titrate the solution with HCl until the equivalence point is reached.

In the end, we have \( n_{\text{KOH}} = n_{\text{H}_2\text{CO}_3} + n_{\text{KOH excess}} \) or \( n_{\text{KOH excess}} = n_{\text{H}_2\text{Cl}}^1 \) where \( n_{\text{H}_2\text{Cl}}^1 \) is the amount of HCl needed to reach the first point of equivalence so \( n_{\text{KOH}} = n_{\text{H}_2\text{CO}_3} + n_{\text{H}_2\text{Cl}}^1 \). If you continue the titration with HCl until the second point of equivalence, you titrate the \( \text{HCO}_3^- \) that was initially present in the solution.

\[
n_{\text{H}_2\text{Cl}}^2 - n_{\text{H}_2\text{Cl}}^1 = n_{\text{HCO}_3^-} + n_{\text{H}_2\text{CO}_3} \]

where \( n_{\text{H}_2\text{Cl}}^2 \) is the amount of HCl needed to reach the second point of equivalence so \( n_{\text{H}_2\text{Cl}}^2 - (n_{\text{KOH}} - n_{\text{H}_2\text{CO}_3}) = n_{\text{HCO}_3^-} + n_{\text{H}_2\text{CO}_3} \leftrightarrow n_{\text{H}_2\text{Cl}}^2 - n_{\text{KOH}} = n_{\text{HCO}_3^-} \)
| \( n_{\text{KOH}} \) | \( 10^{-3} \pm 2.0 \times 10^{-6} \) mol |
| \( C_{\text{HCl}} \) | \( 0.1 \pm 2.2 \times 10^{-4} \) mol/l |
| \( V_{(1)}^{\text{HCl}} \) | \( 7.5 \pm 7.5 \times 10^{-2} \) ml |
| \( V_{(2)}^{\text{HCl}} \) | \( 15.1 \pm 7.5 \times 10^{-2} \) ml |
| \( n_{(1)}^{\text{HCl}} \) | \( 7.50 \times 10^{-4} \pm 7.7 \times 10^{-6} \) mol |
| \( n_{(2)}^{\text{HCl}} \) | \( 1.51 \times 10^{-3} \pm 8.2 \times 10^{-6} \) mol |
| \( n_{\text{H}_{2}\text{CO}_{3}} \) | \( 2.50 \times 10^{-4} \pm 7.9 \times 10^{-6} \) mol |
| \( n_{\text{HCO}_{3}^{-}} \) | \( 5.10 \times 10^{-4} \pm 8.5 \times 10^{-6} \) mol |
| \( V_{\text{eau}} \) | \( 1.00 \times 10^{-2} \pm 2.0 \times 10^{-5} \) l |
| \( C_{\text{H}_{2}\text{CO}_{3}} \) | \( 2.50 \times 10^{-2} \pm 8.0 \times 10^{-4} \) mol/l |
| \( C_{\text{HCO}_{3}^{-}} \) | \( 5.10 \times 10^{-2} \pm 1.0 \times 10^{-3} \) mol/l |
| \( C_{\text{H}_{2}\text{CO}_{3}} \) | \( 1550 \pm 51.64 \) mg/l |
| \( C_{\text{HCO}_{3}^{-}} \) | \( 3111 \pm 60.30 \) mg/l |

Tab. 2 – Manual titration data analysis of carbonate species in Vichy water

Automatic titration

Fig. 5 – Titration curve of Vichy water with HCl 0.1 M and differential curve with two lorentzian fit.

Fig. 6 – Titration curve of Evian water with HCl 0.1 M and differential curve with two lorentzian fit.
FIG. 7 – Titration curve of Swiss Alpina water with HCl 0.1 M and differential curve with two lorentzian fit

<table>
<thead>
<tr>
<th></th>
<th>Vichy</th>
<th>Evian</th>
<th>Swiss Alpina</th>
</tr>
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<tbody>
<tr>
<td>$n_{\text{HCl}}$</td>
<td>$9.01 \times 10^{-4}$ $\pm 6.6 \times 10^{-7}$</td>
<td>$7.83 \times 10^{-4}$ $\pm 1.8 \times 10^{-6}$</td>
<td>$6.43 \times 10^{-4}$ $\pm 2.3 \times 10^{-6}$</td>
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<tr>
<td>$n_{\text{H}^2\text{Cl}}$</td>
<td>$1.50 \times 10^{-3}$ $\pm 2.6 \times 10^{-7}$</td>
<td>$1.38 \times 10^{-3}$ $\pm 6.9 \times 10^{-7}$</td>
<td>$1.64 \times 10^{-3}$ $\pm 9.0 \times 10^{-7}$</td>
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<tr>
<td>$n_{\text{KOH}}$</td>
<td>$1 \times 10^{-3}$ $\pm 2.0 \times 10^{-6}$</td>
<td>$1.00 \times 10^{-3}$ $\pm 2.0 \times 10^{-6}$</td>
<td>$1.00 \times 10^{-3}$ $\pm 2.0 \times 10^{-6}$</td>
</tr>
<tr>
<td>$n_{\text{H}_2\text{CO}_3}$</td>
<td>$9.93 \times 10^{-3}$ $\pm 2.1 \times 10^{-6}$</td>
<td>$2.17 \times 10^{-3}$ $\pm 2.7 \times 10^{-6}$</td>
<td>$3.57 \times 10^{-3}$ $\pm 3.1 \times 10^{-6}$</td>
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<tr>
<td>$n_{\text{HCO}_3^-}$</td>
<td>$4.98 \times 10^{-4}$ $\pm 2.0 \times 10^{-6}$</td>
<td>$3.77 \times 10^{-4}$ $\pm 2.1 \times 10^{-6}$</td>
<td>$6.43 \times 10^{-4}$ $\pm 2.2 \times 10^{-6}$</td>
</tr>
<tr>
<td>$V_{\text{water}}$</td>
<td>$0.01 \times 10^{-4}$</td>
<td>$0.1 \times 2.0 \times 10^{-5}$</td>
<td>$0.05 \times 2.0 \times 10^{-5}$</td>
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<tr>
<td>$C_{\text{H}_2\text{CO}_3}$</td>
<td>$615.78 \pm 14.5$</td>
<td>$134.65 \pm 13.2$</td>
<td>$442.88 \pm 13.2$</td>
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<td>$C_{\text{HCO}_3^-}$</td>
<td>$3034.75 \pm 32.8$</td>
<td>$230.09 \pm 1.3$</td>
<td>$784.46 \pm 3.1$</td>
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<tr>
<td>$C_{\text{carbonate tot}}$</td>
<td>$5.97 \times 10^{-2}$ $\pm 5.9 \times 10^{-4}$</td>
<td>$5.94 \times 10^{-3}$ $\pm 2.1 \times 10^{-4}$</td>
<td>$2.00 \times 10^{-2}$ $\pm 2.2 \times 10^{-4}$</td>
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<tr>
<td>$C_{\text{carbon inorg}}$</td>
<td>$3650.5 \pm 35.8$</td>
<td>$364.7 \pm 13.3$</td>
<td>$1227.3 \pm 13.5$</td>
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<td>$C_{\text{bottle}}$</td>
<td>$2989$</td>
<td>$360$</td>
<td>$770$</td>
</tr>
</tbody>
</table>

Tab. 3 – Automatic titration data analysis of carbonate species in drinking water

Discussion

The found values for the pK₀ were 4.30 (for ionic strength 0.1 M) and 4.56 (ionic strength 0.01 M) whereas the literature value for pKa of the acrylic acid (one monomer of PAA) is 4.25[4]. The results of this experiment are good because the pK₀ of the polymer should be equal to the pKa of the monomer. The interaction parameter that was found is a normal value for a weak electrolyte like PAA. The estimated value of $\Lambda$ (3.27) is close to the experimental one for the salt concentration of 0.1 M but with the 0.01 M ($\kappa^{-1}$=3.03 nm) the value rise to 10.35. This means that the planar geometry approximation is not very accurate and the exact formula for the cylinder geometry should be used.

The interaction parameter diminish with the increasing ionic strength (see figure 8) for the reason that there is a less space for the carboxylic charges to interact with each other because there are more ions in solution.

The ionic strength decrease the interaction parameter like seen in figure 4 where the slope
The interaction parameter $\Lambda$ is plotted as a function of ionic strength for planar surface only.

$$\kappa = \sqrt{8 \pi L_B N_A I}$$

With the ionic strength in mol/m$^3$.

For industrial application, "PAA can be used as scale inhibitor and dispersant in circulating cool water systems in power plants, iron & steel factories, chemical fertilizer plants, refineries and air conditioning systems."[3]

For the carbonate titration it is observe that the equivalence points that were found with the manual titration are different from the automatic method. The discrepancies comes from the fact that indicators were used to find the values. Indicators « react » by changing color in a range of pH so the precision is average and there is also the « burette » that is less precise (seen in the error) and the eye isn’t extremely good to differentiate colors after a small addition.

The found values for bicarbonate ion (table 3) are acceptable for Vichy and Swiss Alpina.
but for Evian there seems to be a problem because the value is less than 2/3 of the bottle indication. The origin of this difference can’t be from a bicarbonate ion gas loss because we had a new bottle. Other possibilities can be that the values on the bottle are old but we don’t think that there would be such a big variation. An error in manipulation isn’t impossible but unlikely.

The literature values for the ionization constants for carbonate are: 6.37 and 10.25. The pH of the Vichy water that was measured to be 6.72 (bottle value was 6.8) with the following formula the pKa can be calculated: $pK_a = pH - \log \left( \frac{[\text{base}]}{[\text{acid}]} \right)$ and were found to be 6.02 and 9.90. Those values are not very good but if the bottle pH is taken they rise to 6.10 and 9.98.

\[ \text{pH} = 6.72 \]

\[ pK_a = 6.02 \] and \[ pK_a = 9.90 \]

\[ \text{pH} = 6.10 \] and \[ pK_a = 9.98 \]

\[ \text{CO}_2^- = 1.47 \times 10^{-5} \text{ M} \] or 0.88 mg/l at measures pH 6.72 for Vichy water.

**Conclusion**

In this experiment we observed that potentiometric titration is a very strong method of analysis to measure the interaction parameter of a polyelectrolyte (PAA) in solution and also to determine the ionization constant.

The manual titration is even though not very precise a good method to get quick idea of the amount of carbonic acid and bicarbonate ion in a solution. On the other side the automatic method which is a potentiometric titration takes more time but give better results.

1 This value is a mean. The pH was rising linearly from 6.6 and after 10 minutes a mean was taken because the pH meter was unable to stabilize.
Annexe

\[ pK_\text{eff} = pK_0 + \Lambda \alpha \]
\[ pK_0 + \frac{e}{kT \ln 10} \psi_0 = pK_0 + \Lambda \alpha \]
\[ \frac{e}{kT \ln 10} \psi_0 = \Lambda \alpha \]
\[ \psi_0 = \frac{\sigma}{C_s} = \frac{e \Gamma_0 \alpha}{\epsilon \epsilon_0 \kappa} = \frac{e \alpha}{2 \pi a \beta \epsilon \epsilon_0 \kappa} \]
\[ \frac{2e^2}{4\pi ab \epsilon \epsilon_0 \kappa kT \ln 10} = \Lambda \]
\[ \frac{e^2}{4\pi \epsilon \epsilon_0 \kappa kT} = \frac{2L_B}{\ln 10 ba \kappa} = \Lambda \]

Where \( L_B \) is the Bjerrum length it represents the distance at which the electrostatic interaction and thermal energy are equal for two monovalent ion. The Debye length \((\kappa^{-1})\) is the distance at which electrostatic forces are present in solution. \( \psi \) is the surface potential, \( C_s \) is the specific capacitance and \( \Gamma \) is the surface concentration.

Références