

A New Teaching Laboratory Experiment to Address the Effect of pH on Solubility

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Abstract: This paper presents a teaching experience involving an experiment based on the potentiostatic and electrochemical titration of a silver acetate solution with sodium hydroxide, a chemical system where at least three chemical equilibria are involved. It is known that natural samples are inherently complex, and several different chemical equilibria are simultaneously present. That is why we believe the understanding of complex systems is essential for carrying out chemical analysis. Solubility of many compounds is highly dependent on pH and many of the exercises in the inorganic chemistry classroom are focused on calculating the solubility of different species at different pHs, most of the times using speciation coefficients. However, the dependence of solubility on pH is usually analyzed in a point by point basis. This experiment, which only requires equipment usually available in any general chemistry teaching laboratory, allows students to analyze both a complex system and the dynamic nature of solubility when pH changes continuously in time. It gives them the possibility to reach a broader understanding of simultaneous chemical equilibria. Thus, we consider it to be an excellent complement to typical chemistry exercises.

Combined equilibria is usually a topic in the inorganic or analytical chemistry syllabus. However, we consider that there are not enough quantitative laboratory experiments to assess these complex processes and there are few references in Journals in the last years describing combined equilibria activities for the classroom or the laboratory [1–7].

Natural samples are inherently complex, and several different chemical equilibria are simultaneously present. Therefore, the understanding of complex systems is essential for carrying out chemical analysis. Solubility of many compounds is highly dependent on pH and many of the exercises in the inorganic chemistry classroom are focused on calculating the solubility of different species at different pHs, most of the times using speciation coefficients. However, the dependence of solubility on pH is usually analysed in a point by point basis. This particular experiment that we present allows students to analyse both a complex system -where at least three chemical equilibria are involved- and the dynamic nature of solubility when pH changes continuously in time. Thus, this work opens the possibility to a broader understanding of simultaneous chemical equilibria.

This experiment is based on the potentiostatic and electrochemical titration of a silver acetate solution with sodium hydroxide, which was suggested by a student in a Chemistry for Physicists' course (a course similar to General Chemistry). The laboratory section of the course was composed of standardized experiments for the first part of the semester. For the second part, the students could choose

between: (a) doing another set of standard experiments and taking a written exam, or (b) creating a whole new laboratory experience for the course or coming up with an original way to renew an existing one and writing a final report about it. Most students chose the latter and showed engagement in the production of the new proposals, trying to find ways to adapt their ideas to the availability of instruments and discussing them with the Teaching Assistants and Professors of the course. One particular group of students was engaged in proposing a teaching experience, which could be completed in one four-hour class. This activity involved the quantitative analysis of a system where solubility and acid-base equilibria act simultaneously -in a relatively simple system- by measuring two variables (pH and electric potential difference) with equipment usually available in every general chemistry teaching laboratory (pH-meter, multimeter and silver and silver chloride electrodes). Even though this experiment measures only two variables corresponding to two different chemical equilibria, the students must perform a previous and thorough analysis of the system in order to choose which of the chemical equilibria are essential to characterize the system and which ones can be disregarded due to the species involved being present in negligible concentrations or not reaching saturation point. This complexity transforms the classroom into a rich environment for discussion of the concepts involved (free energy, chemical equilibria, Le Chatellier's principle, distribution coefficients, stoichiometry) and promotes the students to progressively refine their grasp of these abstract constructions.

Here we present the theoretical background of this experiment and the measurements and analysis of the data collected throughout the course.

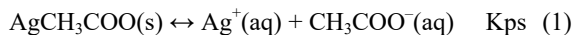
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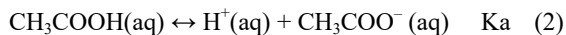
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Theoretical Background

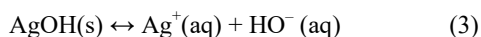
Solid silver acetate beneath an aqueous solution is in equilibrium with its solvated ions:



Acetate ions also participate in an acid-base equilibrium with water:



We should also consider the solubility equilibrium of silver hydroxide:



If we work at hydroxide and silver ions concentrations that do not exceed the solubility product, we can disregard the precipitation of silver hydroxide. By writing down a mass balance in solution, we can calculate the silver acetate solubility as:

$$s = [\text{Ag}^+] = [\text{CH}_3\text{COO}^-] + [\text{CH}_3\text{COOH}] \quad (4)$$

Replacing eq 4 onto eq 2 we obtain:

$$[\text{CH}_3\text{COO}^-] = \frac{s}{1 + \frac{[\text{H}^+]}{K_a}} \quad (5)$$

Replacing equations 5 and 4 into equation 1, we get:

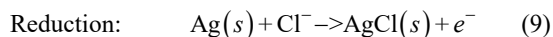
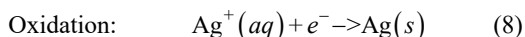
$$K_{ps} = \frac{s^2}{1 + \frac{[\text{H}^+]}{K_a}} \quad (6)$$

Rearranging equation 6, we get this result:

$$s^2 = \frac{K_{ps}}{K_a} \cdot [\text{H}^+] + K_{ps} \quad (7)$$

This equation is the functional form of the solubility dependence on the concentration of protons.

Silver ions concentration is calculated by measuring the potential difference of a silver electrode in the silver acetate solution against a silver/silver chloride electrode (which has a porous glass on one wall to allow contact with the solution). The hemireactions for the electrochemical cell are:



Then, using the Nerst equation, we end up with:

$$\Delta E = \Delta E^\circ - 0,059 \cdot \log \frac{1}{[\text{Ag}^+]} \quad (10)$$

Experimental Procedure

The experiment that we present here was part of a special practice carried out in the General Chemistry Laboratory of the Bsc/Msc Physics degree at the Universidad de Buenos Aires. The topic was selected by the students and several tutoring encounters were held in order to develop an experimental procedure for the student's laboratory.

A silver/chloride electrode connected to a voltmeter and a silver electrode is placed in a beaker containing a 0.01 M standard silver nitrate solution, in order to calculate the standard electrochemical potential difference. Solid silver acetate is placed in another beaker and a 10^{-4} M perchloric acid solution is poured over the solid. This beaker is sealed and left to rest for two days.

After the 48 hour period, a pHmeter and a silver/silver chloride electrode connected to a voltmeter that is connected to a silver electrode are placed in the beaker containing the solid silver acetate. The solution is titrated with 0.5 M sodium hydroxide under constant agitation. The pH and the electrochemical potential difference of the solution are registered every 0.2 ml.

The students proceed to calculate hidronium ions and silver ions concentrations, then producing the graph of $[\text{Ag}^+]^2$ versus $[\text{H}^+]$ and the linear regression from where the $K_{ps}[\text{AgCH}_3\text{COO}]$ and the $K_a[\text{CH}_3\text{COOH}]$ are calculated.

Hazards. Handle strong acid and basic solutions with special caution. Silver ion solutions are hazardous in case of skin/eye contact or ingestion. In case of contact with the solution, immediately flush with abundant water for at least 10 minutes. If ingested, drink plenty of water.

Results

The raw data obtained in this experiment is presented in Table 1 and a linealization of the data is shown in Figure 1. The practice consisted in calculating both $K_{ps}[\text{AgCH}_3\text{COO}]$ and $K_a[\text{CH}_3\text{COOH}]$ and the students are asked to present a report discussing the dependence of the AgCH_3COO solubility with pH. The values of the constants calculated and the tabulated ones are presented in Table 2.

Students analysed the results based on the Le Chatellier's principle, stating how proton's concentration pushes the acid-base equilibrium of acetic acid one way or the other, thus sequestering acetate or not and affecting the solubility equilibrium. When proton concentration increases, part of the acetate is protonated and the solubility equilibrium displaces towards silver ions in solution, increasing solubility. Performing this experiment allowed the students to quantitatively address this topic and to compare their previous qualitative predictions with their analysis of the data measured.

This experiment also involved the students to do a qualitative analysis to assess how silver acetate and silver hydroxide precipitate differently, and how there is almost no dependence of solubility of silver acetate two pH units above pK_a , but that silver hydroxide solubility equilibrium depends on pH on the whole pH range, as protons are directly involved in the solubility equilibrium. Constructing graphs superimposing the distribution coefficient of acetate and

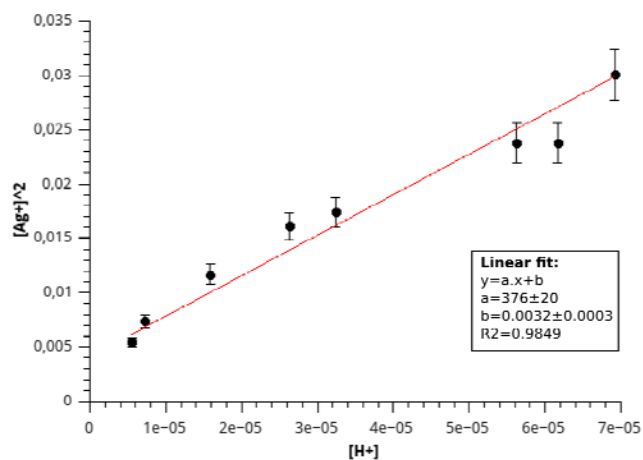
Table 1. Experimental Results

Volume of NaOH Solution/mL	pH	$\Delta E/V$
0.0±0	4.16±0.01	-0.489±0.001
0.20±0.05	4.21±0.01	-0.486±0.001
0.40±0.05	4.25±0.01	-0.486±0.001
0.60±0.05	4.32±0.01	-0.477±0.001
1.00±0.05	4.49±0.01	-0.482±0.001
1.30±0.05	4.58±0.01	-0.481±0.001
1.50±0.05	4.80±0.01	-0.477±0.001
1.75±0.05	5.00±0.01	-0.468±0.001
1.95±0.05	5.14±0.01	-0.471±0.001
2.10±0.05	5.26±0.01	-0.467±0.001

Table 2. Calculated and Tabulated pKps and pKa values

	Calculated	Tabulated*
pKps	2.48±0.11	2.357
pKa	5.05±0.15	4.75

*Values obtained from: <http://www.uia.mx/campus/publicaciones/quimanal/pdf/tablasconstantes.pdf>

**Figure 1.** Ag^+ ions concentration versus hydronium ions concentration.

solubility of silver acetate versus pH functions greatly improved the student's understanding of this topic. Students proved theoretically and checked experimentally that silver hydroxide does not precipitate at silver ions and hydroxide ions concentrations present in the experiment. They discussed how this solubility equilibrium can be neglected from analysis by characterizing the system at these conditions, despite the presence of both silver and hydroxide ions in the system.

Students were also able to observe how precipitation of silver acetate is slow while precipitation of silver hydroxide is more sudden when saturation point is reached. They conclude that this is related to silver acetate precipitation equilibrium being indirectly affected by pH due to the acid-base behavior of acetate ions, while silver hydroxide is directly affected by pH, as hydroxide ions concentration is a direct function of pH.

Conclusion

As a whole, this procedure allowed students to: (i) fit mathematical functions to experimental data, (ii) calculate chemical constants out of the parameters of the fit and address the validity of the model used, (iii) search in literature for the thermodynamical constants and compare them to the ones calculated by them, (iv) establish which chemical equilibria are fundamental for a given state of the system so as to properly characterize this state and calculate properties out of experimental data. This complex analysis of the system is hardly achieved through a problem based class, using only paper work, that is why we believe that this experiment is an excellent complement to typical chemistry exercises.

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Supporting Materials. One PDF file for the laboratory procedure is available.

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