Experiment 6. Potentiometric Sensor

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Abstract. Ion-selective electrodes respond directly to activity. Thus, concentration of an unknown substance can be determined using an ion-selective electrode. Our objective was to develop a Ag/AgCl ion-selective electrode and to quantitatively determine chloride ion concentration. Construction of a calibration curve was possible through a linear fit with correlation factor $R^2 = 0.88$ and was used to find the concentration of chloride ions $[Cl^-]$ in Gatorade which was found to be 0.000532 M.

I. INTRODUCTION

The development of potentiometric ion sensors or ion-selective electrodes has great relevance due to their low cost and portability. Over the past twenty years deep theoretical understanding and new sensing concepts have resulted in a new wave of ion-selective electrodes. [5]

Ion-selective electrodes respond directly to activity and not to concentration. Nevertheless, the activity of an ion can be written as the product of an appropriate activity coefficient and its concentration. So with appropriate calibration procedures, the later can be determined using an ion-selective electrode. [4]

The correlation between activity and potential is described by the Nernst equation:

$$E = E^o - \frac{RT}{nF}ln(\frac{a_{red}}{a_{oxd}}) \qquad (1)$$

where R represent the ideal gas constant (8.314 $Jmol^{-1}K^{-1}$), T is temperature in K, F is the Faraday constant (96,487 $Cmol^{-1}$) and n is the number of transferred electrons. [4]

In direct potentiometry ion-selective electrodes are designed in order to produce a specific response to a determined ion. For the chloride ion, it is used a silver electrode covered with silver chloride. The reaction considered is:

$$AgCl + e^- \rightarrow Ag + Cl^- \qquad (2)$$
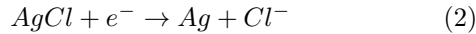
where the concentration of Cl^- is indicative of activity. Nernst equation can be expressed then as

$$E = E^o - 0.0257ln(a_{cl-}) \qquad (3)$$

To measure the potential of a solution between two electrodes a reference electrode and an indicator electrode are used. The first has constant potential, while in the other potential changes with the composition of the sample.

Analysis of commercially available sport drinks by ion chromatography for chloride (Cl^-) was made in Drossman 2007 [3].

Our objective is to develop a Ag/AgCl ion-selective electrode for quantitative determination of chloride ion concentration. Construction of a calibration curve and determination of concentration of an unknown sample are expected.

II. EXPERIMENTAL PROCEDURE

Reference electrodes were developed inside the lab using commercial wire with soldered silver edges. Reference electrodes were constructed using wire sealed in a glass tube using thermo-contractile plastic tube. Silver wire was cleaned using concentrated ammonium hydroxide, acetic acid and water. Anodization for the electrodes was done in a 0.1 M HCL solution for 30 seconds using constant current. Then, reduction was done for 15 minutes.

Dilutions for 0.5, 0.3 and 0.1 M KCl were created in 1:10, 1:100, 1:1000. 100 ml of 1M of NaNO$_3$. Finally, potential difference measurements were done for 3 minutes for each of the dilutions. At the end, a last measurement was done on a sample of the Gatorade sport drink. All results were logged using the LoggerPro software.

III. RESULTS

A. Making a calibration curve

Using the software LoggerPro it was possible to create a spreadsheet with the potential difference measured with the ion-selective electrode as a function of time for each one of the solutions prepared.

Figures 1, 2 and 3 show the evolution of the electrochemical potential for the different concentrations of KCl in each solution. It can be appreciated how after some time the potential value stabilized. The last value of each series was used to construct the calibration curve.
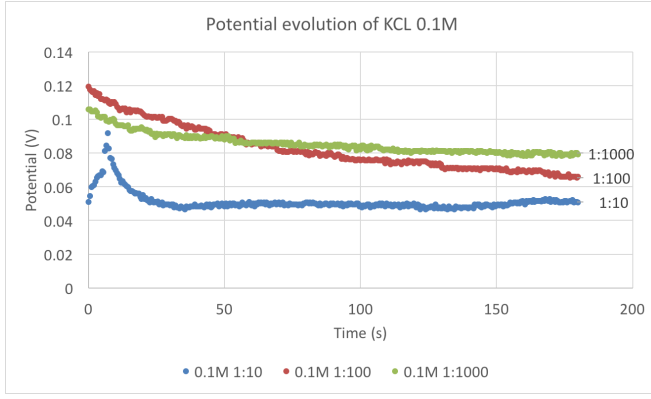
FIG. 1: Electrochemical potential vs Time curves obtained using a lab-made chloride ion-selective electrode in dilutions of KCL 0.1M in ratios 1:10, 1:100, and 1:1000
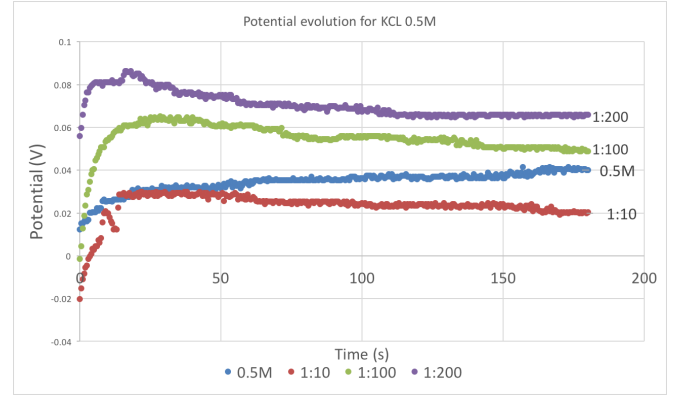

FIG. 3: Electrochemical potential vs Time curves obtained using a lab-made chloride ion-selective electrode in dilutions of KCL 0.5M in ratios 1:1, 1:10, 1:100, and 1:1000

TABLE I: Stabilized and corrected potential value after three minutes of measurement per solution.

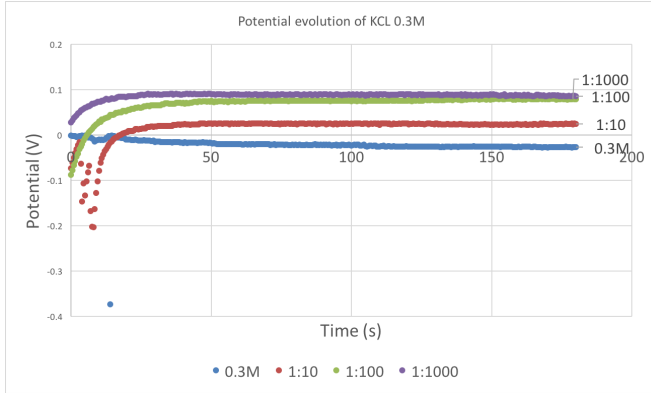| Solution	[KCl] [M]	E [V]
0.5 M	0.5	0.03628
0.5 M 1:10	0.05	0.09671
0.5 M 1:100	0.005	0.12509
0.5 M 1:200	0.0025	0.14218
0.3 M	0.3	0.0494
0.3 M 1:10	0.03	0.10098
0.3 M 1:100	0.003	0.15561
0.3 M 1:1000	0.0003	0.16201
0.1 M	0.1	——-
0.1 M 1:10	0.01	0.12692
0.1 M 1:100	0.001	0.14218
0.1 M 1:1000	0.0001	0.15561

FIG. 2: Electrochemical potential vs Time curves obtained using a lab-made chloride ion-selective electrode in dilutions of KCL 0.3M in ratios 1:1, 1:10, 1:100, and 1:1000
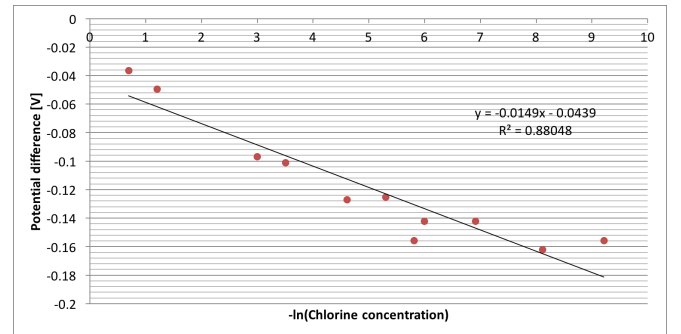

FIG. 4: Nernst equation for KCL

Table 1 shows these values for each of the solutions.

With these data it was possible to build the calibration curve. Figure 4 shows all the data of Table 1 as scatter plot with the potentials and natural logarithms of the KCl concentrations. Changing to this logarithmic arrangement allowed for a linear fit to be used.

B. Determination of unknown sample's concentration

For the Gatorade sample a potential of E = 0.15622 V was determined. Using the linear correlation obtained in

the last section this would entail a [Cl⁻] of 0.000532 M.

IV.   DISCUSSION OF RESULTS

Quality of measurements is heavily influenced by the construction of the reference electrodes, specifically soldering and sealing inside the glass tube. Anodization and reduction processes directly influence electrochemical potentials as well. Figures 1 to 3 show a similar behavior related to the potential stabilization and relative value differences between each of the dilation (In average, a bigger dilution tends to give a higher value for potential values).

The values of Figure 4 show the scatter plot of the natural logarithm of the concentration values versus the value of its potential. Although not exactly similar to the slope of Nernst eq., the values for the logarithm of concentrations do show a convincing linear behavior. The linear trendline shows a decent fitting with a correlation factor $R^2 = 0.88$. Equation 3 describes an slope with value -0.0257 whereas our trendline predicted a value of -0.0149, which although different is still in the same order.

As for the Gatorade test, Drossman 2007 mentions [Cl⁻] (KCl concentrations are equivalent to Cl⁻ ones) of about 425 mg/L with the reported label value of 380 mg/L. This is equal to aprox. 0.0119 M and 0.01072 M respectively [3], while our predicted value was 0.000532 M ($> 5\%$). The team believes the main reason for this may have to do with precisely the quality of the measurements. It's is believed that while the general behavior of the results is consistent with theory, some of them may have a questionable quality. These disturb the resulting slope in Figure 4 and thus the unlikely prediction.

The team is positive that further repetition of the experiment will resolve this.

V.   CONCLUSION

In this paper we report in-lab electrochemical measurements using self made Ag electrodes. Measurements were made for various concentrations of KCL (fig 1 to 4) and a calibration curve was fit with slope values of -0.0149 and E_o values of 0.0439. Determination of unknown concentrations were done using this curve with a value of E=0.15622 V for gatorade. Measurements may have deviated from literature based on construction quality for the electrodes and accuracy on dilution for each of the KCL solutions. Potentiometry is still relevant for the industry and research is still beinng done after more than 100 years of the invention of this technique (specifically in the development of new materials to create ion-selective electrodes). Other potentiometric applications include high accuracy titration, which is used in various industries (most notably clinical applications). Other more recent applications include trace-metal analysis within drinking water and potentiometric biosensing.[6]

VI.   REFERENCES

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