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Computer simulation of precipitation titration for some cations using pH glass electrode

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Abstract

The analytical methods of qualitative and quantitative determination of ions in solutions are very flexible to automation. In this research by using a computer simulation a potentiometric titration of bromide and chloride ions by nitrate solution of some monovalent cations with pH glass electrode has been done. A proper reagent called mediator is added to the medium that in end point of the reaction will develop an intense change in pH. So, pH electrode indirectly becomes sensitive to the changes of cations concentration (titrant). The results show that, the added reagent to the medium should be a weak acid so that its conjugate base creates a less soluble precipitate with titrant cation by approaching to the end point of the reaction.

Keywords: Precipitation titration, computer simulation, mathematical modeling pH, electrode.

INTRODUCTION

The process of titration is a recurrent process that can be watched by permanent measurement of a simple property such as mass, current intensity, tension, volume [1-5] or a complex property such as adsorption, heat of reaction [6-7], which need a complex evaluation. Most of the biological tests include the determination of glucose, urea, proteins, sodium, calcium, HCO_3^- / H_2CO_3 , uric acid and pH that can measure with titration [8-10].

The first step in design of an analytical process is to establish the objective to follow. Only by clear identification of proposed scope it can imagined logic way that lead to correct solving of the problem [11,12]. A big responsibility for the analyst is to choose an analytical

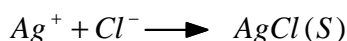
method that is leading to best solving of followed scope. If more than one similarly probe exists, such as quality control, the automation becomes possible [13].

One of the ways to make an analytical method for quantitative determinations is precipitation. In order to recognize the final point of a precipitation titration, Volhard, Mohr and Fajans methods are common. In such methods, the end point is distinguished, when the titrate finished and the reagent reacts with titrant and a colored complex make up, so the chemist can see the colorless solution becomes colorful.

In the present work, a weak acid named mediator was added to the medium so that just as titrate finished, the titrant reacts with mediator (conjugate base of weak acid) releases a great number of H^+ ions, that can be easily detected by pH meter, which is a more precise method.

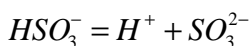
Reaction Modeling

In this section, the titration of sodium chloride with silver nitrate was considered as a model in the presence of sodium bisulphate as a mediator (Eqs. 1-4). Silver ion participates in (1) and (4) and develops $AgCl(s)$ and $Ag_2SO_3(s)$ less soluble salts, respectively. Considering ion hydrolysis of HSO_3^- based as well as water ionization we will have Eqs. 3 and 5, respectively:

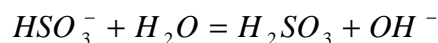
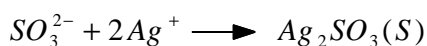


$$K_{sp} = [Ag^+][Cl^-] \quad (1)$$

$$K_2 = \frac{[H^+][SO_3^{2-}]}{[HSO_3^-]} \quad (2)$$

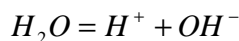


$$K_b = \frac{[H_2SO_3][OH^-]}{[HSO_3^-]} \quad (3)$$



$$K'_{sp} = [Ag^+]^2[SO_3^{2-}] \quad (4)$$

$$K_w = [H^+][OH^-] \quad (5)$$



Here K'_{sp} is the solubility product of less soluble salt, Ag_2SO_3 and in $K_b = \frac{K_w}{K_1}$, K_1 is dissociation constant of first step of H_2SO_3 in the first phase of acid sulfur.

Charge balance

We can consider the charge balance Eq. as following:

$$[Na^+] + [Ag^+] + [H^+] = [Cl^-] + [NO_3^-] + [HSO_3^-] + [OH^-] + 2[SO_3^{2-}] \quad (6)$$

Proton balance

The proton balance Eq. is as follow: (7)

$$[H^+] = C_{NaHSO_3} - [HSO_3^-] - [H_2SO_3] + \left(\frac{K_w}{[H^+]} - [H_2SO_3]\right)$$

Using Eqs 1-7 and rearrangement of them (8) and (9) give.

$$K_2[Ag^+]^3 - (K_2[Ag^+]^2)(C_{AgNO_3} - [Na^+] + \frac{K_w}{[H^+]} - [H^+]) - K_2K_{sp}[Ag^+] - K'_{sp}(2K_2 + [H^+]) = 0 \quad (8)$$

and :

$$-2K'_{sp}[H^+]^3 - K_1[H^+]^2(K'_{sp} + K_2[Ag^+]^2) + K_1K_2[Ag^+]^2[H^+]C_{NaHSO_3} + K_1K_2K_w[Ag^+]^2 = 0 \quad (9)$$

By solving (8) and (9) through numerical method Bisection in terms of two variables $[Ag^+]$ and $[H^+]$ could be obtain at equilibrium state.

Program Projecting and Implementation

Once you have an operating system installed, the next step is to choose a proper programming language for software developing.

The home made SEPEHR could be run under MATLAB software. MATLAB program is a applicable and powerful software in mathematics, engineering and statistics. Over the course of time much more capabilities have been added to this software so that at the present time MATLAB has been become a powerful tool for drawing of data, programming and doing engineering computations and research. This program has been written in three basic parts:

- ✓ *Main1*: it draws the curve of dpH/dv in titrant milliliter.
- ✓ *Main2*: it shows the curve of pH in titrant milliliter on the screen.
- ✓ *Main3*: it can draw the curve of dpH based on reagent's concentration in mmol.

In Fig. 1, the main window of Main1 program is observed.

```

Editor - C:\Documents and Settings\Administrator\Desktop\Project1\main.m
File Edit Text Go Cell Tools Debug Desktop Window Help
1 - Cn=1.0e-5; _____ A
2 - C=0.1; _____ B
3 - Na=0.1; _____ C
4 - ksp=5.2e-13; _____ D
5 - kpsp=8.2e-12; _____ E
6 - kw=1.0e-14; _____ F
7 - k1=4.6e-7; _____ G
8 - k2=4.4e-11; _____ H
9 - V=10; _____ I
10 - step=0.01; _____ J
11 - [v,S,SS,B,d] = find3(Cn,C,Na,ksp,kpsp,kw,k1,k2,V,step)
12 - [v',B',S',SS']
13 - d
14 - hold on
script Ln 14 Col 8
  
```

Figure1. Main window of Main 1.

The data A to J are variables that the user could run the program easily according to his selected titration by entering of the values. These variables are:

- A. Reagent concentration
- B. Titrant concentration
- C. Titrate concentration
- D. The solubility product constant for precipitate titrant and titrate (K_{sp})
- E. The solubility product constant for titrant and the reagent (K'_{sp}).
- F. Water dissociation constant
- G. The first step constant of reagent
- H. The second step constant of reagent
- I. Starting volume of titrate
- J. Steps of titrant increase

View Data

SEPEHR titration program designed to show Figs. from point to point calculations for the review, during on the each step of titrant increasing.

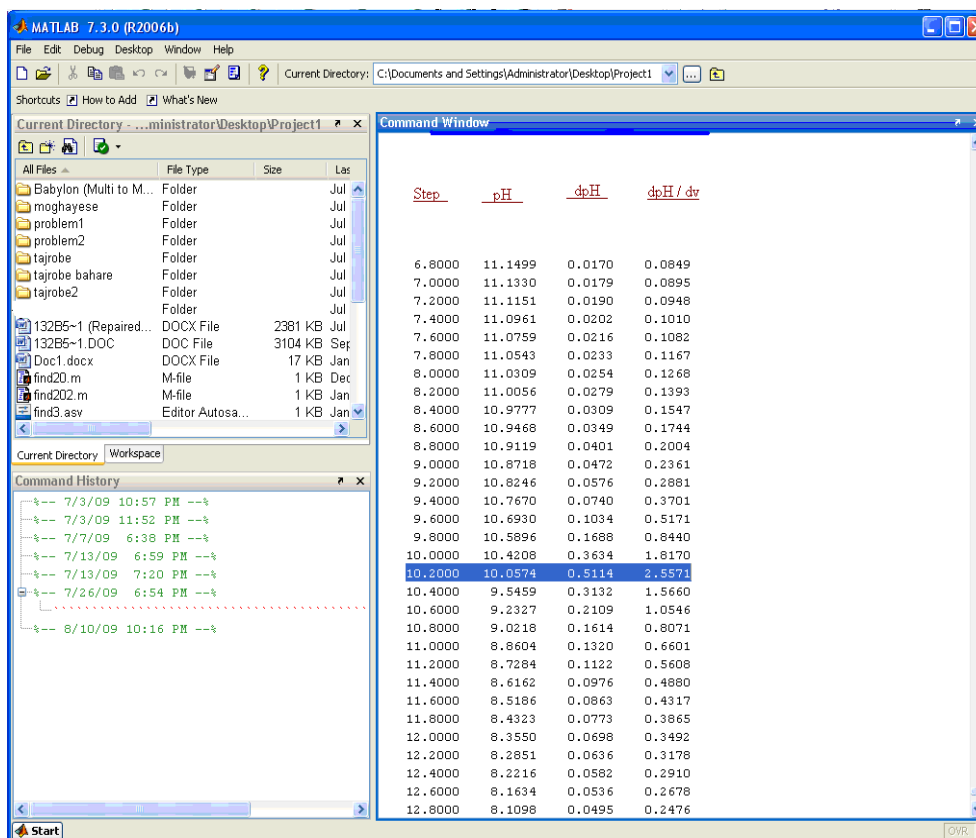


Figure 2. The view data and calculations have derived from SEPEHR software.

As Fig. 2 shows, the user can see the result in each step of increasing the titrant. The results of Figs. 3 and 4 show that, the user can easily assess conditions and review results after precipitation.

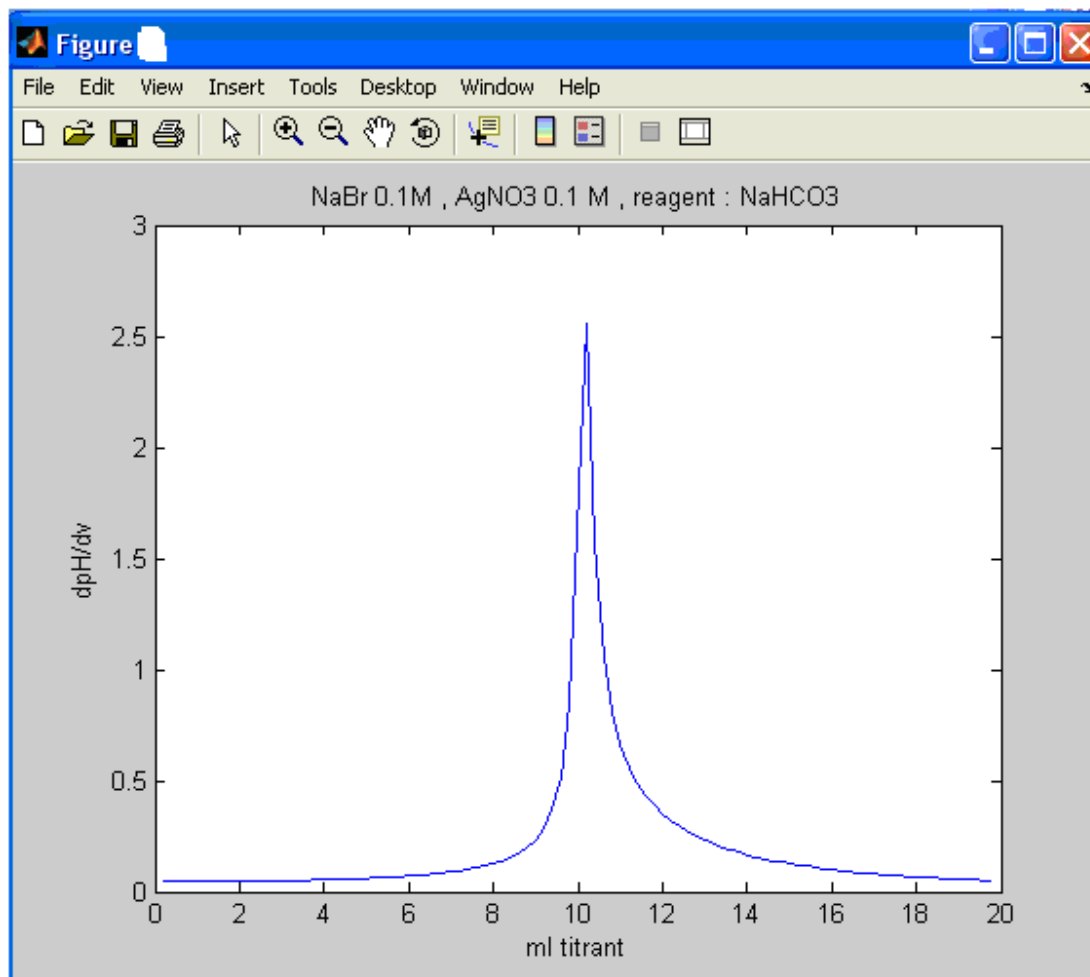


Figure 3. Simulation of 10ml of 0.1M NaBr titration with AgNO₃ in the presence of NaHCO₃ as mediator

RESULTS AND DISCUSSION

In this section by using SEPEHR titration program the optimal values of the reagent (mediator) are reached that the most changes of pH is seen in it. Figs. 4 and 5 show optimal values of sodium hydrogen sulphite and sodium hydrogen carbonate reagent, respectively in titration of 10 ml sodium bromide 0.1M with silver nitrate as titrant. Also, by entering the data this program can draw the curve of dpH/dv in ml of titrant as well as pH in ml of titrant.

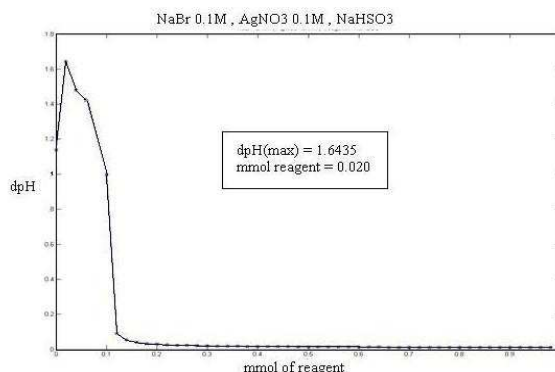


Figure 4. The optimal value of NaHSO_3 in precipitation titration of 10ml NaBr 0.1M with AgNO_3 0.1M.

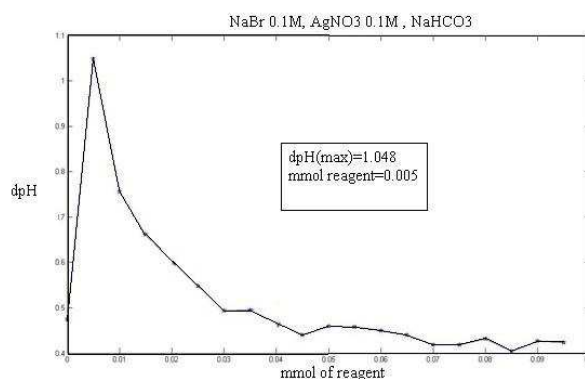


Figure 5. The optimal value of NaHCO_3 in precipitation titration of 10ml NaBr 0.1M with AgNO_3 0.1M.

As it is seen in Figs. 3 and 4, the optimal value of the reagent in this titration NaHSO_3 is equal to 0.02 mmol and for weak acid NaHCO_3 is equal to 0.005 mmol. By comparing of dpH/dv these two curves it is concluded that the reagent of sodium bisulphite has a better sensitivity to bicarbonate sodium. The selected reagent should have the appropriate conditions. So that regarding the related equations for NaHSO_3 and NaHCO_3 produce the salts $\text{Ag}_2\text{SO}_3(\text{s})$ or $\text{Ag}_2\text{CO}_3(\text{s})$ that their solubility is a little more than $\text{AgBr}(\text{s})$. If the solubility of silver salts with the reagents would be much more than $\text{AgBr}(\text{s})$ in this case the identification of equivalent point would delay and in measuring of bromide ion it will develop a positive error. If solubility of the mentioned cases is less than solubility of $\text{AgBr}(\text{s})$ the final point would be reached sooner and we will have a negative error.

With regard to what mentioned above, apparently NaHCO_3 is in better conditions to NaHSO_3 respecting the solubility, but from acidic power perspective NaHSO_3 is in better conditions to NaHCO_3 . Being low of acid dissociation constant will cause the reduction of acid resolution

and the changes of H^+ would not be significant in final point of the action. Being high of acid constant will have reversal result and the curve's gradient will be more.

Effect of Concentration

Figs. 6 and 7 show the titration of NaBr with $AgNO_3$ (both titrate and titrant at two different 0.1 and .05M concentrations) using $NaHCO_3$, $NaHSO_3$, $NaHC_2O_4$ and $NaHCrO_4$ as reagents. As, it was expected from the K values of the weak acids and solubility products of them with Ag^+ ion $NaHSO_3$ reagent has the biggest dpH/dv value in the present conditions.

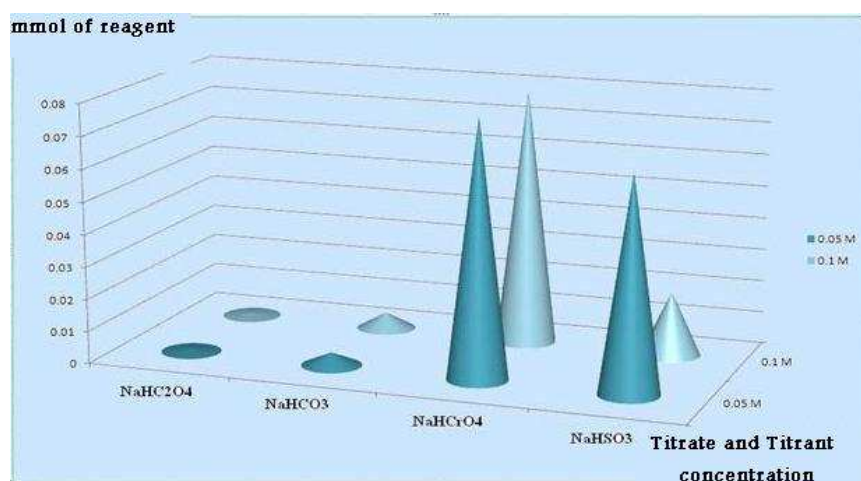


Figure 6. Comparison of four mediator mmoles ($NaHCO_3$, $NaHSO_3$, $NaHC_2O_4$ and $NaHCrO_4$) in the titration of NaBr with silver nitrate for both 0.05 and 0.1M of titrate and titrant.

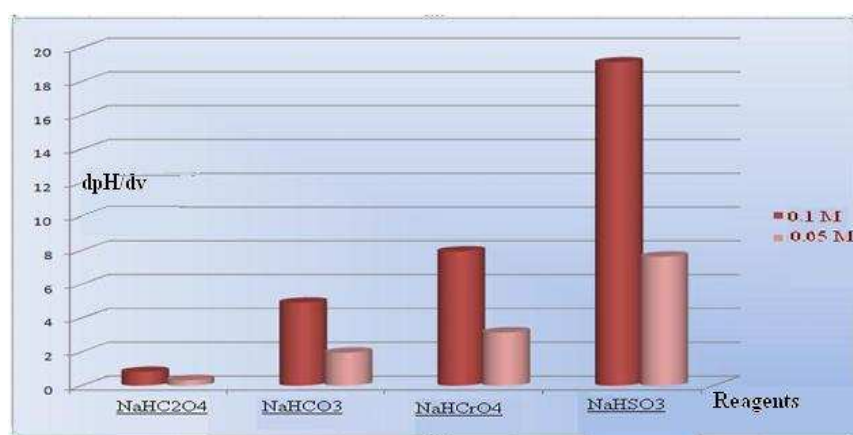


Figure 7. Comparison of dpH/dv values of using four ($NaHCO_3$, $NaHSO_3$, $NaHC_2O_4$ and $NaHCrO_4$) mediators at optimal conditions in the titration of NaBr with silver nitrate for both 0.05 and 0.1M concentrations.

Figs. 8 and 9 show, the results of precipitation titration using different titrant (AgNO_3 and CuNO_3) for the measuring of NaBr solution. As it is seen in Fig. 8 and 9, clear different variation in concentration of H^+ ion in the end point will found. Here, the amount of NaHCO_3 as mediator for the both simulation was the same. This differences for the dpH/dv values, depends to the K_{sp} , K'_{sp} , K_1 and K_2 value of the salts and mediators.

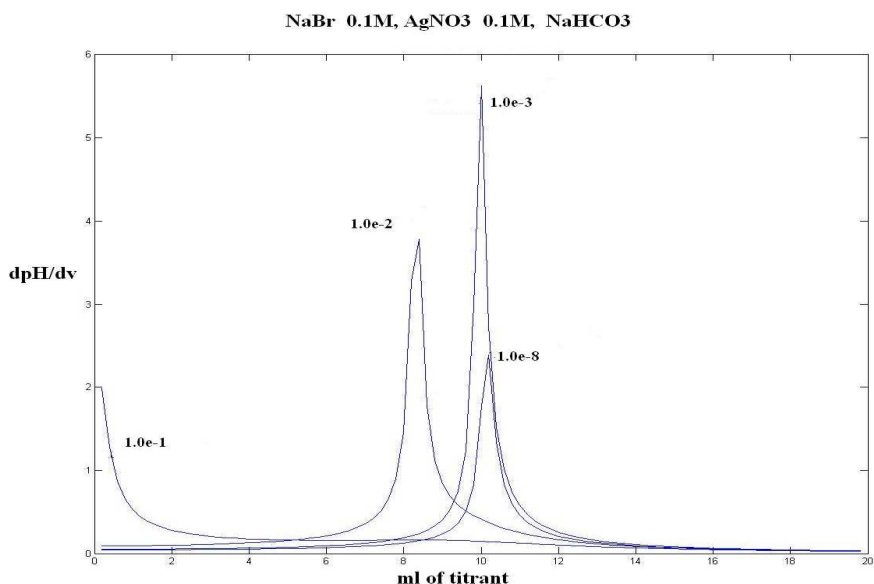


Figure 8. Comparison of different amounts of sodium hydrogen carbonate reagent in NaBr titration with AgNO_3 , 0.1M

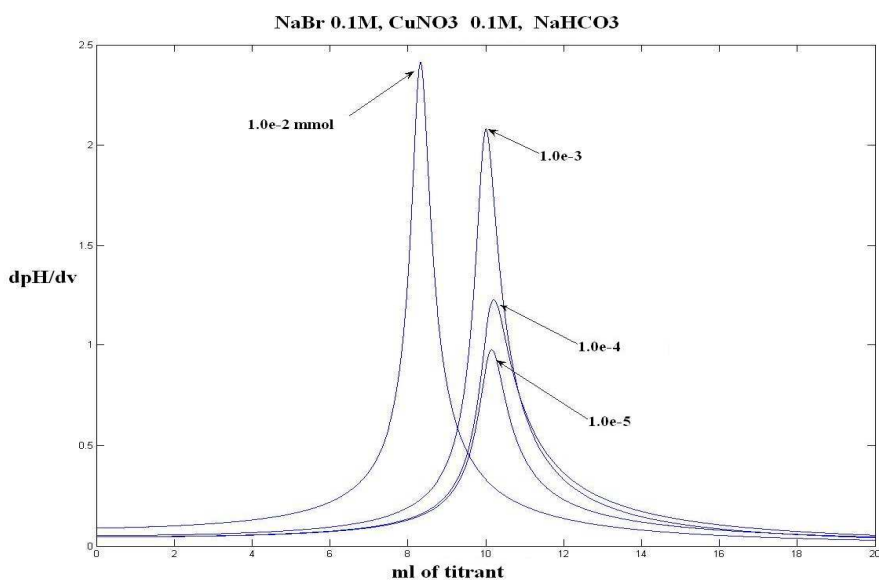


Figure 9. Comparison of different amounts of sodium hydrogen carbonate reagent NaBr titration with CuNO_3 , 0.1M

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