

ANALYSIS of URANYL CARBONATE COMPLEXES IN  
an OPEN AND CLOSE  
ENVIRONMENTAL SYSTEM by ANALYTICAL CHIMISTRY

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ABSTRAK

KOMPLEKS URANIL KARBONAT DI DALAM SISTEM LINGKUNGAN

TERBUKA DAN TERTUTUP DITINJAU DARI SUDUT KIMIA ANALITIK..

Diterangkan perubahan konsentrasi ion  $C^{2-}$  di dalam air alam pada lingkungan terbuka dan tertutup berasal dari gas  $CO_2$  yang terdapat di udara terhadap pH larutan. Reaksi antara kation  $UO_2^{2+}$  dengan anion  $CO_3^{2-}$  juga diterangkan dengan menggunakan perhitungan, perbandingan antara masing-masing species kompleks uranyl karbonat terhadap nilai totalnya. Perangkat lunak Lotus 123 release 2.4 digunakan untuk menghitung masing-masing molfraksi dari masing-masing species kompleks uranyl karbonat terhadap pH larutan. Didapatkan bahwa species kompleks uranyl karbonat di dalam air alam pada lingkungan terbuka pada kondisi asam lebih sederhana dibandingkan dengan di dalam air alam pada lingkungan tertutup. Sebaliknya kompleks uranyl karbonat di dalam air pada lingkungan terbuka dan dalam suasana basa kandungannya lebih sederhana daripada di dalam air alam pada lingkungan tertutup.

ABSTRACT

URANYL CARBONATE COMPLEXES IN OPEN AND CLOSED ENVIRONMENTAL SYSTEM FROM ANALYTICAL CHEMISTRY VIEWPOINT. Variation of  $CO_3^{2-}$  ion concentration from  $CO_2$  gas originated from atmosphere, in natural water in an open and close system versus pH of the solution is described. Reaction between  $UO_2^{2+}$  cation with  $CO_3^{2-}$  anion is also described by using calculation, comparison of each species of uranyl carbonate complexes to its total values. Each mol fraction of uranyl carbonate complex versus pH of the solution is calculated using Lotus 123 release 2.4. It is found that uranyl carbonate complexes species in natural water which is slightly acid in an open system is simpler than that in a close system. On the other hand, uranyl carbonate complexes species in natural water which is slightly base is simpler in an open system than that in a close system.

INTRODUCTION

Carbon dioxide is an important element for various processes, such as biological process of respiration, biosynthesis and other. Recently  $CO_2$  gas is rising rapidly in

atmosphere because chemical and transportation industry are burning fossil fuel in large amount. The huge amount of  $CO_2$  in atmosphere can be understood from the green house effect and corrosion of

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steels which can become serious problems, especially in oil and petrochemical industries.

Compared with other gasses, CO<sub>2</sub> gas is quite soluble in water. Some of soluble CO<sub>2</sub> gas in water will react with water to form carbonic acid. Concentration of carbon dioxide in carbonic acid solution depends on the partial pressure of carbon dioxide gas in atmosphere. A higher partial pressure of carbon dioxide gas in atmosphere will produce higher concentration of C<sup>-</sup> in solution. So the chemical equilibrium of the carbonate system plays an important role in environments, for it will react with other cation in natural water, such as Ca<sup>2+</sup>, UO<sub>2</sub><sup>2+</sup>, Ba<sup>2+</sup>, Fe<sup>2+</sup> etc.

Carbonic acid in water will dissociate into its anions and cations, in two steps. The amount of carbonate ion in solution strongly depends on the pH of the solution. H<sub>2</sub>CO<sub>3</sub>, HCO<sub>3</sub><sup>-</sup> and C<sup>-</sup> are not found in solution of the same pH. The amount of [C<sup>-</sup>] in solution is not determined only by pH of the solution, but it is also determined by properties of the system. In an open system, the concentration of [C<sup>-</sup>] is higher than that in a close system, because CO<sub>2</sub> gas is always supplied by the atmosphere. On the other hand CO<sub>2</sub> gas in a close system is limited.

Uranium, is an element which has many oxidation states (+3,+4,+5 and +6), in which +3 and +5 states are unstable, +4 is less stable in the air, and +6 state is stable. Uranyl ion, UO<sub>2</sub><sup>2+</sup> with oxidation state +6, is always found in uranium minerals, such as in carnotite K<sub>2</sub>(UO<sub>2</sub>)<sub>2</sub>(VO<sub>4</sub>)<sub>3</sub>·3H<sub>2</sub>O, rutherfordina UO<sub>2</sub>CO<sub>3</sub> etc. Rutherfordina, UO<sub>2</sub>CO<sub>3</sub> mineral is slightly soluble in water.

Sea and ground water always contain uranyl ion or uranyl carbonate complex. These are caused by uranyl ion which has a strong tendency to form carbonate complexes in carbonate media, uranyl carbonate complexes such as UO<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub><sup>-</sup>, UO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub><sup>4-</sup>.

The relatively strong complexes of uranyl ion with carbonate can be seen from the values of log

-log K<sub>1</sub> ~2 and log K<sub>2</sub> ~3 of UO<sub>2</sub>CO<sub>3</sub>, UO<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub><sup>-</sup>, UO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub><sup>4-</sup>. The concentration of uranyl ion or metal and complex ion in water is governed by pH of the solution.

This paper will discuss of uranyl carbonate and its complexes in an open and close system in varying pH value by use of Lotus 123 as a tool for the calculation which is based on -log K<sub>1</sub> ~2 and -log K<sub>2</sub> ~3 values.

### THEORY

Most commonly used equilibrium between carbonate species and hydrogen is Henry's constant, which is written as follows



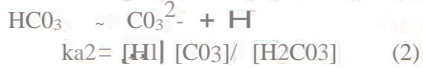
Where k<sub>h</sub> is Henry's constant



Figure 1 shows the effect pH variation on mole fraction of each carbonate ions. It can be seen that H<sub>2</sub>CO<sub>3</sub> predominantly exists in a solution with pH less than 6. For pH under 4, the amount of [HCO<sub>3</sub><sup>-</sup>] and [C<sup>-</sup>] in solution are very low and they can not be seen in mole fraction as seen figure 1 above. [HCO<sub>3</sub><sup>-</sup>] exists predominantly in a range of 6 to 8.5. In this range, H<sub>2</sub>CO<sub>3</sub> is decreasing drastically. In a range of 10 to 14, [C<sup>-</sup>] is predominant, while [HCO<sub>3</sub><sup>-</sup>] is decreasing and H<sub>2</sub>CO<sub>3</sub> is almost nothing.

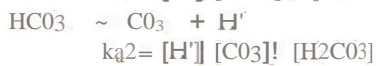
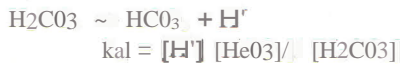
The amount of [C<sup>-</sup>] is necessary to know because it will affect the results of reaction of uranyl and carbonate ion. For calculating [C<sup>-</sup>] concentration in open and close systems, the value of normal atmosphere is used. In normal atmosphere, the air contains 10<sup>-3.5</sup> atm C<sup>-</sup>, while its equilibrium with CO<sub>2</sub> (sol) can be obtained from Henry's constant above, [H<sub>2</sub>CO<sub>3</sub>] = [CO<sub>2</sub> (sol)] = k<sub>h</sub>P<sub>CO<sub>2</sub></sub> = 10<sup>-1.5</sup> x 10<sup>-5</sup> M.

As mentioned above that the amount of  $[CO_3]^{2-}$  in solution is not determined only by pH of the solution, but also by properties of the system. Figure 2 shows that in an open system, carbonate species in solution are always in equilibrium with  $CO_2$  gas, so it is reasonable to take the concentration of  $H_2CO_3^*$  to be  $10^{-5}$  M. For others species, such as  $CO_3^{2-}$  and  $HCO_3^-$ , they can be calculated as follows.



Since in an open system, the concentration of  $H_2CO_3^*$  is always constant at  $10^{-5}$  M, then the concentration of  $[HCO_3^-]$  will be  $10^{-5} \times K_{a1} / [H^+]$  and  $\log [HCO_3^-] = -5 - pK_{a1} + pH = pH - 11.3$ . This equation produces a straight line for  $[HCO_3^-]$  versus pH as shown in figure 2. Similarly, for  $[CO_3^{2-}]$  concentration which can be calculated from eq 2 gives  $\log [CO_3^{2-}] = -5 - pK_{a1} - pK_{a2} + 2pH = 2pH - 21.6$ . This equation also produces a straight line for  $\log [CO_3^{2-}]$  versus pH as shown in figure 2.

In a close system, carbonate system follows the normal acid which dissociates into 2 species,  $HCO_3^-$  and  $CO_3^{2-}$  respectively.



If the total concentration of carbonates is  $10^{-5}$  M, the amount of  $[CO_3^{2-}]$ ,  $[HCO_3^-]$  and  $H_2CO_3^*$  then can be calculated. Based on the mass balance, the total  $[CO_3] = C_{TCO_3} = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}] = 10^{-5}$ .

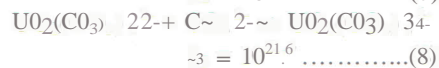
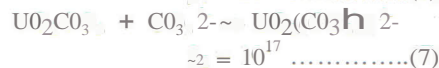
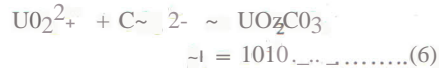
The lines for each of the  $CO_3^{2-}$  species can be drawn by using the following expression.

$$[H_2CO_3^*] = C_{TCO_3} \left( \frac{1}{1 + K_{a1}[H^+] + K_{a1}K_{a2}[H^+]^2} \right) \dots \dots \dots (3)$$

$$[HCO_3^-] = C_{TCO_3} \left( \frac{[H^+]}{K_{a1} + 1 + K_{a2}[H^+]} \right) \dots \dots \dots (4)$$

$$[CO_3^{2-}] = C_{TCO_3} \left( \frac{[H^+]^2}{K_{a1}K_{a2} + [H^+] + K_{a2}[H^+]^2} \right) \dots \dots \dots (5)$$

From Figure 2, it can be known as following. The amount of  $[CO_3^{2-}]$  in an open system increases linearly and rapidly for the range of pH 1-11, while for pH > 11 it remains constant. If there are some uranyl ion in an open and close system, uranyl carbonates and its complexes would be produced, for uranyl and carbonates ions will react to form uranyl carbonate first. Since uranyl carbonates will also react with other carbonate ion to form uranyl complexes, the result of those reactions are not simple. As mentioned above, the form and the concentration or mole fraction of carbonate ion depend on the pH of the solution, the reaction between uranyl and carbonate ions depends on pH of the solution too. For forming complex reaction between uranyl and carbonates ions, it has to have enough uranyl and carbonates ions in the same solution. The amount of each complex can be calculated and it is based on the chemical equilibrium of the reaction below. Chemical reaction between uranyl and carbonate ions can be written as follows.



where  $\sim$  = Summed Formation Constant  
K = Stepwise Formation Constant,

and

$$\sim_1 = K_1$$

$$\sim_2 = K_1 \times K_2$$

$$\sim_3 = K_1 \times K_2 \times K_3$$

**RESULT AND DISCUSSION**

The effect of pH on the  $H_2CO_3^*$  and its ions:

Natural water containing carbonates and uranyl ions will react to form uranyl

carbonate, through a simple reaction. Uranyl carbonate forms a complex with another carbonate ions, but through complex reactions, because the result is the substance which is not simple and has a negative charge. If carbonate ion is more than enough in the solution containing uranyl carbonate complex, it will produce another uranyl carbonate complexes. That result is a substance which has 3 ion carbonates and one uranyl ion and has negative charge. As is seen in the eqs (6,7,8) the uranyl carbonate and its complexes strongly depend on the amount of  $(CO_3)^{2-}$  in open or close system.

Based on the atmosphere normal condition the amount of species  $(RCO_3)^-$  and  $(CO_3)^{2-}$  are found from very low concentration to high concentration. The comparison between them can be seen in figure 2, the same amount of  $H_2CO_3$  in close and open system as a source of  $(CO_3)^{2-}$  does not produce the same amount of  $(CO_3)^{2-}$ . Concentration of  $(CO_3)^{2-}$  does not depend on the pH of the solution, but also is dependent on the kind of the system. Concentration of  $(CO_3)^{2-}$  in close system is higher than in open system for pH 1 - 6, but the opposite is happened for pH 7-14. From Figure 2, it can be seen the  $(CO_3)^{2-}$  produced at pH = 8 in open system is about  $10^{-6}$  and in close system is about  $10^{-7}$ , meanwhile at pH = 11, the  $(CO_3)^{2-}$  in open system has a concentration close to 1, while, the  $(CO_3)^{2-}$  in close system has a concentration  $10^{-6}$ . The difference in concentration of  $(CO_3)^{2-}$  which is significantly high, will affect the result of the reaction between uranyl cation and carbonates to form uranyl carbonate and its complexes, because the amount of uranyl complex in natural water depends strongly on the concentration of  $(CO_3)^{2-}$ . Since the amount carbonate ion in natural water depends on the acidity or pH of the solution, so the result of the reaction between uranyl and carbonates ion depends on the pH of the solution.

In an open system, for example, at pH < 4 uranyl carbonates has not formed yet, because the concentration of  $CO_3^{2-}$  is less than  $10^{-10}$  as can be seen from Figure 2, carbonic acid

$H_2CO_3$  and the uranyl ion predominant in the solution. In a solution of the pH less than 4, there is no reaction between  $H_2CO_3$  and uranyl ion. Uranyl ion reacts with carbonate ion, if there is enough  $(CO_3)^{2-}$  in the solution. In addition, if the  $(CO_3)^{2-}$  concentration is very low, the concentration of  $(UO_2)^{2+}$  will be governed by the solubility of  $UO_2CO_3$ . However, at higher  $(CO_3)^{2-}$  concentration, reaction of eq (6,7,8) above are driven to the right and the total concentration of dissolved  $(UO_2)^{2+}$  is considerably greater than of  $(UO_2)^{2+}$  alone, then more complexes of uranyl carbonate will be produced. The concentration of uranyl decreases rapidly as pH increases because there is reaction between uranyl and carbonate ions to form simple uranyl carbonate and complex uranyl carbonate. In a solution of pH > 4 uranyl carbonate is formed, the maximum mole fraction is reached at pH close to 7. Complex  $UO_2(CO_3)_2^{2-}$  is formed in the range pH 2 and 10, because the  $(CO_3)^{2-}$  concentration is rising rapidly from  $10^{-12.5}$  to  $10^{-2}$ . The amount of  $UO_2CO_3$  decreases for neutral condition, exactly at pH > 6.6 and at pH = 9, the solution practically is run out of  $UO_2CO_3$ . On the other hand complex  $UO_2(CO_3)_2^{2-}$  starts to form and it has achieved to maximum mole fraction at pH 8. The utmost complex of  $UO_2(CO_3)_4^{4-}$  starts to form at pH 6.5 and it has achieved to maximum at pH 10 as can be seen at Figure 3 below.

Uranyl ion has completely reacted with carbonates at pH 7.4 as can be seen in Figure 3. In the range of pH 4 and 10 there are 4 species of uranyl-carbonates, meanwhile in the range of pH > 10 almost all uranyl and carbonates is in the form of  $UO_2(CO_3)_4^{4-}$ . A solution containing uranyl and carbonate ions will produce complex of uranyl carbonate, its complex can be determined in simple uranyl carbonate, simple uranyl carbonate complex or really uranyl carbonate complexes.

Effect of closed system for the form of uranyl carbonate complex,

Since the amount of carbonates in close and open systems are different, it causes different in the distribution of uranyl carbonate complex. Both the chemical reaction calculations between uranyl and carbonate ions in close and open system are the same but the result are different; because the amount of carbonate ions in open and close system has the same pH is different. If the amount of carbonates ion in open and closed system are the same, it will be produced the same amount of uranyl carbonate complex. Since the calculation method and the  $\beta_1$ ,  $\beta_2$  and  $\beta_3$  values are the same, so the result should be same.

All the calculations are based on the mass balance and total analytical concentration. The mass balance equation of  $UO_2$  in the  $UO_2$  containing substances is :

$$\{UO_2\} + [UO_2CO_3] + [U(CO_3)_2] + [U(CO_3)_3] = C_{total} \text{ of } UO_2$$

Each of the species of uranyl complex is then compared to the total concentration of uranyl complex. The result of that comparison is called mole fraction of each species, that is  $[UO_2] / C_{total} \text{ of } UO_2$ , mole fraction of  $[UO_2CO_3]$  is  $[UO_2CO_3] / C_{total} \text{ of } U$ . Reaction between uranyl and carbonate with the known equilibrium above, for example, which is sum of the total concentration uranyl, uranyl complex. It can be written as  $(1 + 10^{10}x [CO_3] + 10^{17}x [CO_3]^2 + 10^{21.6}x [CO_3]^3)$ . Each mole fraction of the uranyl complex can be seen in Figure 4.

The distribution of uranyl carbonate complex in Figure 4 is not similar to that in Figure 3 even the amount  $H_2CO_3$  is the same. That means the distribution of uranyl carbonate complexes  $U(CO_3)_2$  in both systems are not the same. In addition, the range of formation of uranyl carbonate species is wider in Figure 4 than in Figure 3. Simple Uranyl Carbonate has been formed at  $pH < 2$ , meanwhile in the opened system uranyl carbonate is formed at  $pH < 4$ . Species

of uranyl carbonate complexes  $U(CO_3)_2$  is formed at  $pH = 4.6$  until  $pH = 14$  and uranyl carbonate complexes  $U(CO_3)_3$  is formed at  $pH 7.2$  until  $pH = 14$ . Uranyl carbonate complexes  $UO_2(CO_3)_2$  become maximum at  $pH = 10$  and it decreases slowly as  $pH$  increases, meanwhile uranyl carbonate complexes  $U(CO_3)_2$  increases slowly until  $pH = 12$ , then remains stable. In comparison, in open system at  $pH = 8$  there are 3 uranyl carbonate complexes, while in close system there are only two uranyl carbonate complexes. In contrast, for  $pH$  more than 11, in open system there is only one uranyl carbonate complexes as  $U(CO_3)_2$ , while in close system there are two uranyl carbonate complexes. In neutral solution open system is more complicated than close system, but in base solution, close system becomes more complicated than in open system. However, in acid solution, in open system is simpler than in close system.

#### CONCLUSIONS

1. Based on the composition of uranyl carbonate complexes, the source of uranyl complex can be predicted.
2. The description of the above diagrams are simple, since there are only two components used. For actual open and close environmental systems which usually have more than two components, such as  $Cl^-$ ,  $NO_3^-$ ,  $SO_4^{2-}$  etc, the diagrams therefore will be more complicated.
3. If other cations in environmental is also considered as in forming uranyl carbonate complexes, they would have produced very complicated diagrams.
4. In a slightly acid solution, in open system the composition of uranyl and uranyl carbonate are not mixed, but it is mixed in close system. In a slightly base solution, on the contrary, the composition of uranyl complexes are more complicated in closed than in opened system due to concentration of  $[CO_3]^{2-}$

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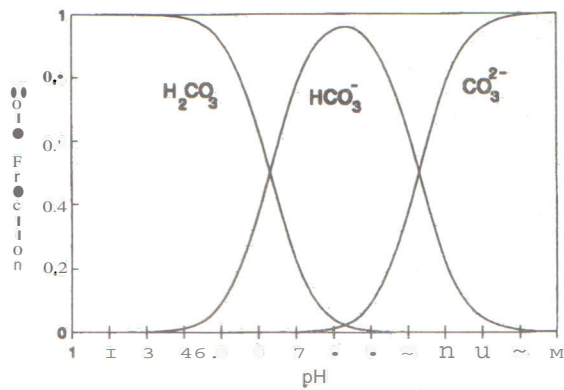


Figure 1. mole fraction of carbonate ions as a function of pH

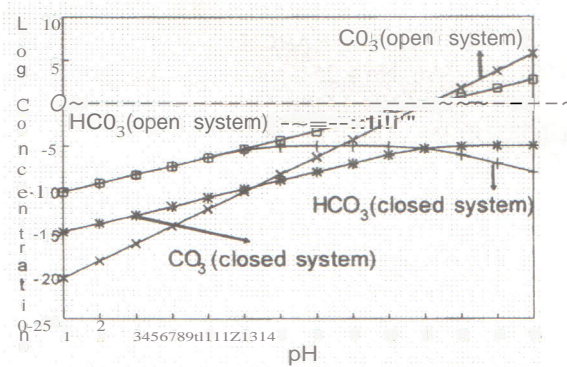


Figure 3 : Distribution of complex uranyl carbonates vs pH in opened system.

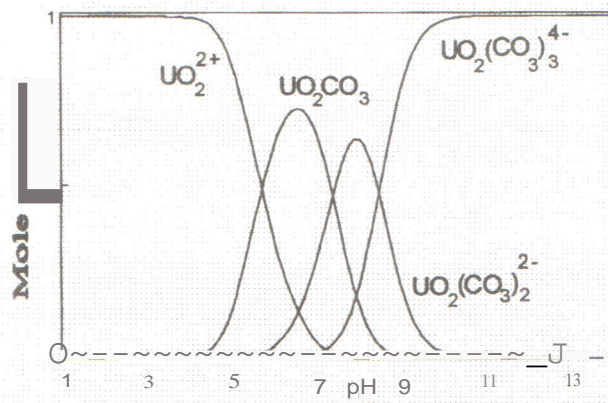


Figure 2. Logarithm of species  $HCO_3^-$  and  $CO_3^{2-}$  versus pH in open and close system

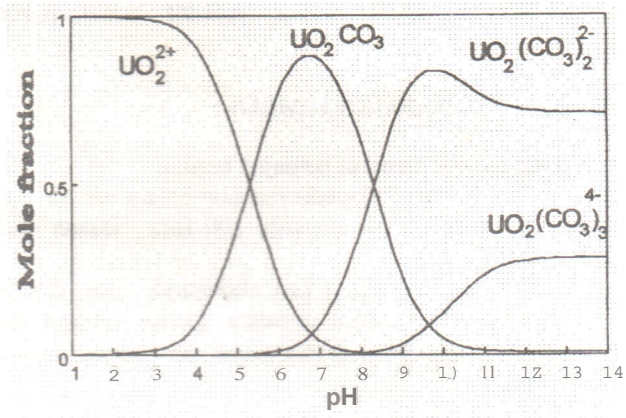


Figure 4 :Distribution of complex uranyl carbonates vs pH in close system