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Control effects of pε and pH on the generation and stability of chlorine dioxide

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Abstract: A new method, without assistance of activity ratio diagram, was applied to construct the pε-pH diagrams for chlorine system. The optimal pH range for generation of ClO_2 by contacting $Cl_2(g)$ directly with ClO_2^- solution is within pH 1.35—1.94, particularly within pH 1.35—4.00 only if minimizing the formation of Cl_3^-. It is unachievable to synthesize pure ClO_2 from the reaction of Cl_2 and ClO_2^-. Conversely, ClO_2 may be present a variation of stability in different waters owing to the changed pε and pH. ClO_2 could be relatively stable if not disproportionate into ClO_3^-, coexisting with ClO_2^- (pε 17.63 and pH > 9.68), Cl_2 (pH ≤ 0.92) or Cl^- (pH 0.92—9.68). When chlorine system has already reached the ultimate equilibria, ClO_2 is a stable species in strongly acid media. As the acidity decreases, ClO_2 disproportionates into ClO_3^- and Cl_2. Aqueous ClO_2 is unstable within the normal pH range. This work initially, theoretically elucidates the generation and stability of ClO_2 by way of the pε-pH diagrams.

Keywords: chlorine dioxide; generation; stability; pε-pH diagram

Introduction

Due to the formation of some potentially hazardous by-products from chlorine disinfection in drinking water, chlorine dioxide (ClO_2), as an alternative disinfectant and an effective oxidant, formed fewer halogenated DBPs than chlorine (Richardson, 1994; 2000; Bryant, 1992). Investigations of the generation and stability of ClO_2 have already promoted its application. However, previous studies pay no attention to the factor of electron activity (pε) that actually affects the generation and stability of ClO_2. The ignorance of pε appearance, particularly the combined effects of pε and pH, has restricted the application of ClO_2 to a certain degree. This paper discusses the generation and stability of ClO_2 by way of pε-pH diagrams, which enrich the chemistry of ClO_2, as well as particularly enhance the knowledge of chemist to characteristics of ClO_2 and improve the application of ClO_2 in water treatment.

A great number of methods for synthesis of ClO_2 are valid from ClO_2^- and ClO_3^-. ClO_2 may be produced in large quantities by acidifying and reducing ClO_3^- while many generation techniques is mainly focus on the reaction of Cl_2 and ClO_2^-. Moreover, ClO_2 is normally stored in aqueous solution with pH 2—3, protection against light (Richardson, 1994; 2000). A stabilized ClO_2 solution might be obtained at pH 6—8 by passing gaseous ClO_2 into an aqueous solution containing 12% sodium carbonate and hydrogen peroxide, yet ClO_2 is practically completely transited to ClO_2^- in this method, thus the reduction of ClO_2 to ClO_2^- may be partly interpreted as the storage technique for ClO_2 (Richardson, 1994; 2000).

The literature contains controversy as to whether or not ClO_2 is stable in aqueous solution. On one hand, aqueous solutions of ClO_2 were quite stable if kept cool, well sealed, and protected from light. ClO_2 was less sensitive to change in pH, and the stability of ClO_2 is between that of Cl_2 and ozone (Richardson, 1994). Some observations are on the other hand quite the reverse. ClO_3^- may be present as a disproportionate reaction product in measurable quantities in chlorinated drinking water, depending on the applied ClO_2 dosage (Richardson, 1994). Because ClO_2 reacts primarily by a one-electron oxidative pathway, so the principal inorganic by-product is almost invariably ClO_2^-. ClO_2 also decomposes into Cl_2

Foundation item: Partially by The Knowledge Innovation Key Project of the Chinese Academy of Sciences (No. KZCX2-409) and The State Key Project (No. 2002BA806B04-01B); * Corresponding author and O_2 once the temperature has reached 15℃ (Richardson, 2000). OCl^- has been known to cause ClO_2 losses in moderately basic media (Richardson, 2000). Aqueous solution of ClO_2 certainly contains Cl^- (Yin, 1998; Ni, 1997). Different scientists recognized the stability of ClO_2 from their specific experiments, thus the recognitions is diversified. No united theoretical explanation is so far satisfactorily accepted.

1 Method

The traditional method for constructing a pε-pH diagram usually needs to construct an activity ratio diagram either at a given pε or at a given pH, which may clarify the stability relations if any doubt should arise about which species predominates thermodynamically (Richardson, 2000). Excessive work is apparently taken when adopting the traditional method. We suggest a new method constructing the pε-pH diagrams based on the equilibria of tri-oxychlorine species. The method excludes the construction of activity ratio diagram and simplifies the construction of pε-pH diagram.

Consider oxychlorine species A, B and C, the oxidization states decrease sequentially. For any tri-oxychlorine species, only four kinds of equilibria among species A, B and C are summarized in Fig. 1. For instance, ClO_3^-, ClO_2 and Cl_2 satisfy the diagram in Fig. 1a; ClO_2, ClO_2^- and Cl^- fit within the diagram in Fig. 1b; $HClO_2$, HOCl and Cl_2 match the diagram in Fig. 1c; and compared with ClO_2 and Cl_2, no predominance area for $HClO_2$ can exist, which satisfy the diagram in Fig. 1d.

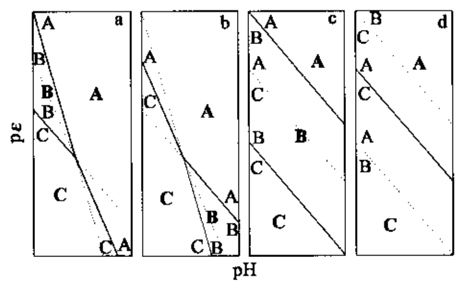

Fig. 1 pε-pH diagrams of tri-species equilibria

Derived from the basic diagrams above, the pε-pH diagrams for chlorine system with multi-oxychlorine species may be established gradually. The pε-pH diagram for chlorine system with HOCl, OCl^-, Cl_2 and Cl^- may be found in the literature (Richardson, 1994; 2000; Aieta, 1986a). This work has further established three pε-pH diagrams for chlorine system with six, seven and eight oxychlorine species based on the equilibria of tri-oxychlorine species, respectively. In the diagrams, unit concentration ratios for oxidants and reductants are considered on the boundaries. The new method has overcome the shortcoming of the traditional method, thus it is simpler and more convenient than the traditional method.

2 Results and discussion

Three pε-pH diagrams, in which the highest oxidation states are III ($HClO_2$), IV (ClO_2) and V (ClO_3^-), have been established to analyze the generation and stability of ClO_2.

Fig. 2 shows the pε-pH diagram for chlorine system with $HClO_2$, ClO_2^-, HOCl, OCl^-, Cl_2 and Cl^- (298 K, 1.013×10^5 Pa). The total dissolved chlorine ($C_{T,Cl}$) is 0.03 mol/L. No predominance area for OCl^- is found in the diagram, which illustrates that OCl^- was unstable and transited to other oxychlorine species before the equilibria have been reached. In the diagram, seven pε-pH equations (Table 1) contribute to as many boundaries. The redox stability of water is in the area between two dot lines whose pε-pH equations are listed in Table 1.

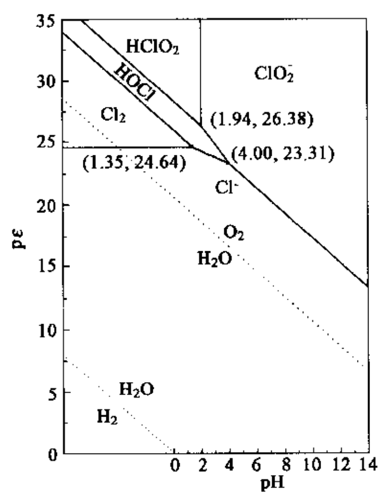

Fig. 2 pε-pH diagram for the chlorine system with $HClO_2$, ClO_2^-, HOCl, OCl^-, Cl_2(aq) and Cl^- (298K, 1.013×10^5 Pa, $C_{T,Cl}$ = 0.03 mol/L.)

The pε-pH diagram for chlorine system with ClO_2, $HClO_2$, ClO_2^-, HOCl, OCl^-, Cl_2 and Cl^- (298 K, 1.013×10^5 Pa, $C_{T,Cl} = 0.03$ mol/L) is shown in Fig. 3. In the diagram, $HClO_2$, HOCl and OCl^- are unstable. Five pε-pH equations (Table 1) are corresponding to the boundaries. Fig. 4 shows the pε-pH diagram for chlorine system with ClO_3^-, ClO_2, $HClO_2$, ClO_2^-, HOCl, OCl^-, Cl_2 and Cl^- (298 K, 1.013×10^5 Pa, $C_{T,Cl} = 0.03$ mol/L). In the diagram $HClO_2$, ClO_2^-, HOCl, and OCl^- had almost been transited to ClO_3^-, ClO_2, Cl_2 and Cl^- before the equilibria were reached. Because the formation of ClO_2^- is always observed in waters, chlorine system is in fact far from the ultimate equilibria. Five pε-pH equations (Table 1) contribute to the boundaries in the diagram.

2.1 Generation of chlorine dioxide

In Fig. 2, no coexisting boundary is presented between Cl_2 and ClO_2^-, thus Cl_2 reacts with ClO_2^- if they contact. On site, it is common to generate ClO_2 from the reaction of Cl_2 and $NaClO_2$. According to the diagram, by-products are certainly produced in the generation process because Cl_2 may disproportionate into HOCl, further into ClO_2^- and Cl^-, which agrees

Table 1 The pε-pH equations reflected to the boundaries in Fig.2, Fig.3 and Fig.4 (298 K, 1.013×10^5 Pa, $C_{T,Cl} = 0.03$ mol/L)

No.	pε-pH equations	Standard electron activity, pε°	Boundaries
1	pε = 24.64[a]	23.64	Cl_2-Cl^-
2	pε = 27.31 − pH	27.31	ClO_2^--Cl^-
3	pε = 28.32 − pH	28.32	$HClO_2$-HOCl
4	pε = 25.99 − pH[a]	26.99	HOCl-Cl_2
5	pH = 1.94		$HClO_2$-ClO_2^-
6	pε = 29.31 − 1.5pH	29.31	ClO_2-HOCl
7	pε = 25.31 − 0.5pH	25.31	HOCl-Cl^-
8	pε = 25.56 − pH[a]	25.81	ClO_2-Cl_2
9	pε = 25.39 − 0.8pH	25.39	ClO_2-Cl^-
10	pε = 17.63	17.63	ClO_2-ClO_2^-
11	pε = 20.39 − 2pH	20.39	ClO_3^--ClO_2
12	pε = 24.53 − 1.2pH[a]	24.73	ClO_3^--Cl_2
13	pε = 24.55 − pH	24.55	ClO_3^--Cl^-
14	pε = 20.6 − pH	20.6	O_2-H_2O
15	pε = − pH	0	H_2O-H_2

Notes: [a] The first coefficient in the equation is different from the standard electron activity (pε°) because the coefficient is related to the concentrations of oxychlorine species (Yen, 1999)). The boundaries in Fig. 2 are drawn by Equations (1)—(7). The boundaries in Fig. 3 are drawn by Equations (1), (2), (8)—(10). The boundaries in Fig. 4 are drawn by Equations (1), (8), (11)—(13). Equations (14) and (15) describe the boundaries of O_2 − H_2O and H_2O − H_2, respectively.

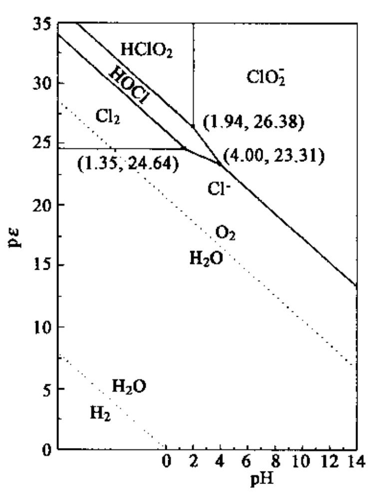

Fig. 3 pε-pH diagram for the chlorine system with ClO_2, $HClO_2$, ClO_2^-, HOCl, OCl^-, Cl_2(aq) and Cl^- (298K, 1.013×10^5 Pa, $C_{T,Cl}$ = 0.03 mol/L)

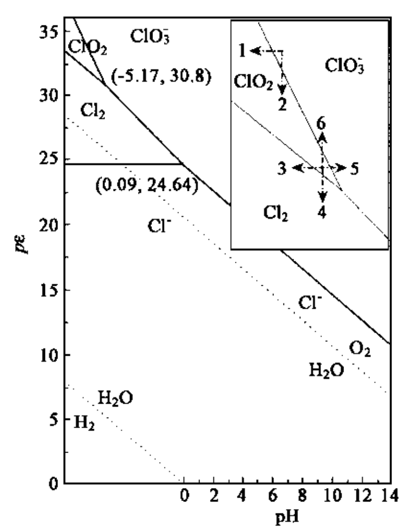

Fig. 4 pε-pH diagram for the chlorine system with ClO_3^-, ClO_2, $HClO_2$, ClO_2^-, HOCl, OCl^-, Cl_2(aq) and Cl^- (298K, 1.013×10^5 Pa, $C_{T,Cl}$ = 0.03 mol/L) to the experimental observation(Richardson, 2000). If adopting the reaction of contacting $Cl_2(g)$ directly with ClO_2^- solution to generate ClO_2, the more optimal pH range is within pH 1.35—1.94. Only for minimizing the formation of Cl_2, without consideration of ClO_2^-, the pH range may enlarge to pH 1.35—4.00. In practice, if the pε is suitably controlled, highly pure ClO_2 can be produced within pH 2—3 (Aieta, 1986b) and pH 3—4(Lauer, 1986). However, it is indeed unachievable to generate pure ClO_2.

Similar to even clearer than Fig. 2, Fig. 3 shows that, Cl_2 and ClO_2^- are stable under different pH and pε ranges. The redox reaction of Cl_2 and ClO_2^- produces ClO_2 and releases Cl^-. Upon introduction of acid into a ClO_2^- solution, the equilibrium shifts toward left along the half dash-dot line 1 (L_1, "L" represents the half dash-dot line, and the subscription "1" represents the serial number), thus ClO_2 and Cl^- may be produced from ClO_2^-. Then Cl^- is however more predominant than ClO_2. The acidification of ClO_2^- solution might have been a way of the generation of ClO_2, yet this method cannot produce ClO_2 well because of the presence of rather excessive Cl^-. Likewise, if pH is held as a constant and pε grows along L_2, ClO_2^- will be oxidized to ClO_2. Electrolytic route may produce ClO_2 from ClO_2^- solution. Actually, generation of ClO_2 from ClO_2^- involves the combined process of acidification and oxidization. As shown in Fig. 4, it is also feasible to synthesize ClO_2 from ClO_3^-. The processes of acidifying (L_1) and reducing (L_2) ClO_3^- may produce ClO_2, which two processes function together in practice.

Generation of ClO_2 through the processes of acidification, oxidization and reduction embodies as the change of pε and pH in the diagrams. As a result, the generation of ClO_2 is in fact to shift the equilibria of chlorine system into the predominance area of ClO_2.

2.2 Stability of chlorine dioxide

As indicated in Fig.3, the oxidizing power of ClO_2 is stronger than that of O_2, thus ClO_2 may oxidize H_2O, releasing O_2. ClO_2 exists above the stable areas of Cl_2, Cl^- and ClO_2^-, thus ClO_2 can steadily coexist with them on the boundaries. When pH is less than 0.92, ClO_2 can coexist with Cl_2, which maybe explain the phenomenon of $Cl_2(g)$ releasing from ClO_2 solution(Griese, 1992). As ClO_2 concentration decreased, ClO_2^- concentration generally increased(Richardson, 2000). According to the diagram, ClO_2 has the same concentrations with ClO_2^- at pε 17.63 when pH is higher than 9.68. ClO_2 also coexists with Cl^- within pH 0.92—9.68, which approves that aqueous solution of ClO_2 certainly contains Cl^- (Yin, 1998; Ni, 1997).

Fig. 3 shows that ClO_2 may decrease its stability and transit to Cl^- (L_3, L_4, L_8 or L_9), Cl_2(L_7 or L_8) and ClO_2^- (L_9) by the variation of pε and pH. ClO_2 may tend to be much stable when the number of protons or electrons decreases (L_5 or L_6). Apparently, the experimental observation does not satisfy the conclusion of which ClO_2 favors alkaline solution. Further discussions are addressed next.

In Fig. 3, the disproportionation of ClO_2 has been not considered. The ultimate equilibria of chlorine system including the disproportionation of ClO_2 are shown in Fig. 4, which reflects the stability of ClO_2 absolutely. ClO_2 may transit to Cl_2(L_3 or L_4), Cl^- (L_4) and ClO_3^- (L_5 or L_6) by the variation of pε and pH. In Fig. 4, ClO_2 is only a stable species in strongly acid media, and disproportionates into ClO_3^- and Cl_2 when the acidity decreases. Thus ClO_2 cannot steadily exist within the normal pH range. In addition, the lower boundary of the predominance area of ClO_2 parallels to the upper boundary of that of H_2O in Fig. 4 (also Fig. 3), no coexisting area both for ClO_2 and H_2O, thus aqueous ClO_2 cannot steadily exist even in strongly acid media.

As described above (see Introduction), there appears controversy as to whether or not ClO_2 is stable in aqueous solution. The actual stability of ClO_2 should be essentially between the descriptions of the diagrams in Fig. 3 and Fig. 4. The pε and pH may control the disproportionation of ClO_2 and equilibria of chlorine system. ClO_2 consequently expresses itself completely dissimilar stabilities under different conditions in waters. Therefore, the pε and pH should be the principal factors when evaluating the stability of ClO_2.

3 Conclusions

Generation, storage, and use of ClO_2 have a strong relationship with the stability of aqueous ClO_2. It is unachievable to synthesize pure ClO_2 from the reaction of Cl_2 and ClO_2^-. ClO_2 may be present a variation of stability in different waters owing to the changed pε and pH. ClO_2 could be relatively stable if not disproportionate into ClO_3^-. When the ultimate equilibria of chlorine system have been achieved, ClO_2 is a stable species in strongly acid media. Aqueous ClO_2 is unstable within the normal pH range.

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