

Theoretical Study on Sulfur Dioxide Absorption with Citrate Solution

XUE Juan-qin(薛娟琴), HONG Tao(洪涛), WANG Zhao-qi(王召启), LI Lin-bo(李林波)

(School of Metallurgy Engineering, Xi'an University of Architecture and Technology, Xi'an, Shaanxi 710055, China)

Abstract: The citrate absorption of SO₂ is currently one of the most successful and economic methods to harness sulfur dioxide pollution. In order to theoretically elucidate the mechanism of SO₂ absorption by citrate solution and provide theoretical instruction for experiments and industrial process, the theory of multi-buffer solution, combined with computer numerical calculation methods, was applied to study the distribution parameters of the components of the citrate solution in the process of SO₂ absorption and the following results were obtained: (1) H₂Ci²⁻ and H₃Ci⁻ in the citrate solution played the dominant role in the absorption and desorption processes; (2) Through the calculation for the buffer capacity of citrate solution, it was found that the pH of the absorption and desorption solution should be in the range of 2~8, while at pH=4.5 the buffer capacity reached its maximum. Some valuable parameters were obtained, which are instructive to the ensuing experiments and industrial design.

Key words: citrate solution; absorption; sulfur dioxide; theoretical analysis

CLC No.: O645.11; O646.1

Document Code: A

Article ID: 1009-606X(2006)03-0388-04

1 INTRODUCTION

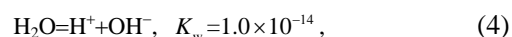
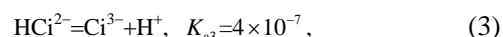
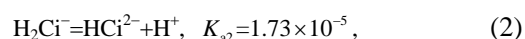
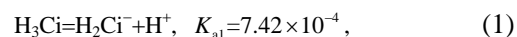
Currently, the absorption and desorption of sulfur dioxide by using citrate solution is one of the efficient methods to curb sulfur dioxide pollution^[1-7]. The fundamental principle of this method is that when the SO₂-containing gas flows through the citrate solution, SO₂ reacts with water to produce H₂SO₃, in which the released H⁺ combines with citric radical to form citric acid. Due to its good buffer capability, the citrate solution can continually catch H⁺ produced when SO₂ dissolves into water, thus significantly enhancing the SO₂ solubility in the citrate solution. Afterwards, the SO₂ desorption from the solution makes SO₂ flow out to form pure SO₂ gas which can be recycled.

So far the existing analyses about such a process are mainly focused on the determination of the concentration and pH of the absorption solution from the study of existing state of SO₂ in the solution as well as its dependence on the concentration and pH of the solution^[8-11]. In order to theoretically elucidate the mechanism of the SO₂ absorption by citrate solution, by applying the theory of buffer solution and the computer numerical method to such a system, theoretical calculations and analyses for the process of absorption and desorption of SO₂ in citrate solution are carried out in this work. Some valuable parameters are obtained, which are instructive to the ensuing experiments and industrial design.

2 ANALYSES OF BUFFER CAPABILITY OF CITRATE SOLUTION SYSTEM

2.1 Determination of the Initial pH of Citrate Solution at Different Concentrations

Citrate solution has buffer capability because citric acid is a kind of ternary weak acid. The chemical equilibrium and decomposition constants^[12,13] are given by:



where Ci stands for the citrate radical and

$$K_{a1} = [H^+][H_2Ci^-]/[H_3Ci], \quad (5)$$

$$K_{a2} = [H^+][HCi^{2-}]/[H_2Ci^-], \quad (6)$$

$$K_{a3} = [H^+][Ci^{3-}]/[HCi^{2-}], \quad (7)$$

$$K_w = [H^+][OH^-]. \quad (8)$$

Then the relations among the concentration of hydrogen ion [H⁺], general concentration of citric acid radical [Ci³⁻]_t and the concentrations of other ions are

Received date: 2005-06-09, **Accepted date:** 2005-08-08

Foundation item: Supported by the National Natural Science Foundation of China (No.50244012); the National Science Foundation of Shaanxi Education Department (No.02JC37)

Biography: XUE Juan-qin(1966-), female, native of Fufeng City, Shaanxi Province, Ph.D., associate professor, main research fields are chemical engineering, metallurgy, environmental protection and synthesized utilization of resources, E-mail: xuejq0305@sohu.com.

obtained:

$$[H^+] = [OH^-] + [H_2Ci^-] + 2[HCi^{2-}] + 3[Ci^{3-}], \quad (9)$$

$$[Ci^{3-}]_t = [H_3Ci] + [H_2Ci^-] + [HCi^{2-}] + [Ci^{3-}]. \quad (10)$$

From the above equations, the relation between $[H^+]$ and $[Ci^{3-}]_t$ is obtained:

$$[H] = \frac{K_w}{[H]} + [Ci]_t \frac{3K_{a1}K_{a2}K_{a3} + 2K_{a1}K_{a2}[H] + K_{a1}[H]^2}{K_{a1}K_{a2}K_{a3} + K_{a1}K_{a2}[H] + K_{a1}[H]^2 + [H]^3}. \quad (11)$$

Through the iteration calculation by using C codes^[14], pH values of citrate solution at different concentrations are obtained, as shown in Fig.1. Figure 1 shows that pH decreases with the increase of the citrate concentration. When the concentration varies in the range of 0.05~1.00 mol/L, pH changes drastically. But when the concentration is higher than 1.00 mol/L, pH is no longer sensitive to the concentration and remains at about 1.57.

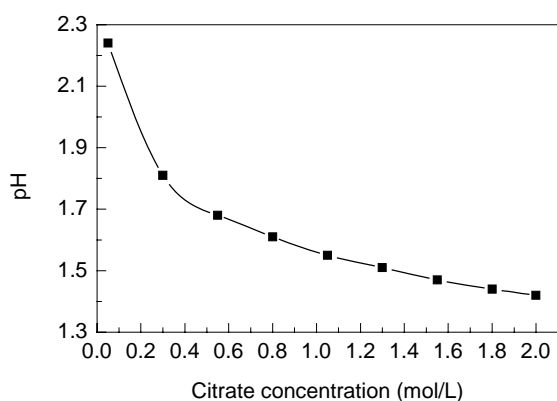


Fig.1 The dependence of pH of citrate solution on the citrate concentration

2.2 Distribution Parameters of Citric Radical Components in Absorption Solution

The distribution parameter of a component is defined as the percentage of the concentration of the component in the total concentration in the equilibrium system. Citric acid is a kind of mononuclear complex. When citric acid reaches equilibrium in the solution, the equilibrium components are H^+ , Ci^{3-} , HCi^{2-} , H_2Ci^- , H_3Ci . The contents of these components in the equilibrium system are equal to the equilibrium concentrations. Its distribution parameters can be expressed as

$$\delta_{H_3Ci} = [H_3Ci]/[H_3Ci]_t = \beta_i^H [H^+]^i / \left(1 + \sum_{i=1}^3 \beta_i^H [H^+]^i \right), \quad (12)$$

where β_i^H is the protonization constant of citric acid.

The distribution parameters of citric radicals can be calculated in the following steps:

(1) Derivation of pK of citric acid in each step dissociation

$$pK_{a1} = \lg(-K_{a1}) = -\lg(7.4 \times 10^{-4}) = 3.13,$$

$$pK_{a2} = \lg(-K_{a2}) = -\lg(1.73 \times 10^{-5}) = 4.76,$$

$$pK_{a3} = \lg(-K_{a3}) = -\lg(4 \times 10^{-7}) = 6.40.$$

(2) Derivation of the protonization constant β_i^H

$$\text{From } \lg\beta_3 = pK_{a1} + pK_{a2} + pK_{a3} = 14.29,$$

$$\lg\beta_2 = pK_{a2} + pK_{a3} = 11.16,$$

$$\lg\beta_1 = pK_{a3} = 6.40,$$

$\beta_3 = 1.95 \times 10^{14}$, $\beta_2 = 1.45 \times 10^{11}$ and $\beta_1 = 2.51 \times 10^6$ are obtained.

(3) Determination of the distribution parameters

Putting β_1 , β_2 and β_3 into Eq.(12) and assuming pH to be x, the following formulae are obtained:

$$\delta_{H_3Ci} = \frac{\beta_3 (10^{-x})^3}{1 + \beta_1 10^{-x} + \beta_2 (10^{-x})^2 + \beta_3 (10^{-x})^3}, \quad (13)$$

$$\delta_{H_2Ci^-} = \frac{\beta_2 (10^{-x})^2}{1 + \beta_1 10^{-x} + \beta_2 (10^{-x})^2 + \beta_3 (10^{-x})^3}, \quad (14)$$

$$\delta_{HCi^{2-}} = \frac{\beta_1 10^{-x}}{1 + \beta_1 10^{-x} + \beta_2 (10^{-x})^2 + \beta_3 (10^{-x})^3}, \quad (15)$$

$$\delta_{Ci^{3-}} = \frac{1}{1 + \beta_1 10^{-x} + \beta_2 (10^{-x})^2 + \beta_3 (10^{-x})^3}. \quad (16)$$

Then inputting the values of β_1 , β_2 , β_3 and pH, and programming in VB^[15], the relation of pH with the distribution parameters of various citric acid radical ions can be obtained, as shown in Fig.2.

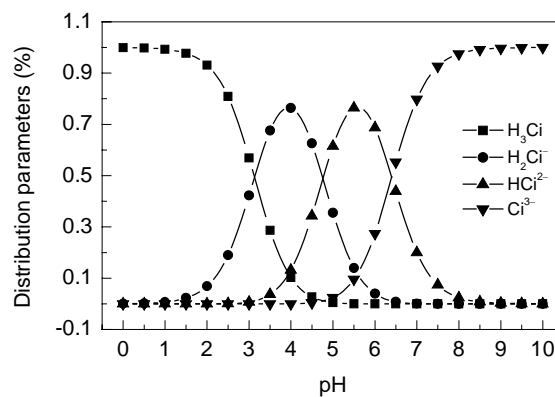


Fig.2 The dependence of the distribution parameters of various citric acid radicals on the pH of citrate solution

Figure 2 shows that due to the configuration of citric acid radicals varies with the change of the acidity, in the absorption solution with fixed acidity there mainly exists only one or several configuration citric acid radical ions. H_3Ci is dominant when pH is below 3, Ci^{3-} is dominant when pH is above 7, and H_2Ci^- and HCi^{2-} are dominant (with a total percentage of about 85%) when pH is in the range of 3~7.

2.3 Differential Buffer Capacity of Citrate Solution

The differential buffer capacity of citrate solution

includes that of water and that of conjugated acid-base. Assuming pH of buffer solution is x , the differential buffer capacity of citrate solution in the following steps can be derived:

(1) Derivation the differential buffer capacity of water $\beta_{H_2O}^D$

$$\beta_{H_2O}^D = 2.303([H] + [OH]) = 2.303(10^{x-14} + 10^{-x}). \quad (17)$$

The relation between $\beta_{H_2O}^D$ and pH is shown in Table 1.

Table 1 The relation between the buffer capacity and the pH of water

pH	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
$\beta_{H_2O}^D$	2.303	0.2303	0.02303	0.0023	0.0002	0	0	0	0	0	0.0002	0.0023	0.0230	0.2303	2.303

Table 1 shows that $\beta_{H_2O}^D$ contributes to the differential buffer capacity of buffer solution mainly in the range of high acidity and high alkalinity, such contribution is almost zero when pH lies in the range of 4.5~9.5. This is the reason why water cannot absorb sulfur dioxide efficiently.

(2) Derivation of the differential buffer capacity of conjugated acid-base

$$\beta_{H_3Ci}^D = -2.303C \sum_{j=0}^3 \sum_{i=0}^3 (j-i)(n-j) \delta_{H_3Ci} \delta_{H_3Ci},$$

which can be further simplified as

$$\beta_{H_3Ci}^D = 2.303C \left[\delta_{Ci} \delta_{H_3Ci} + 4\delta_{Ci} \delta_{H_2Ci^+} + \delta_{H_3Ci} (9\delta_{Ci} + 4\delta_{H_3Ci} + \delta_{H_2Ci}) \right]. \quad (18)$$

Inputting C value and the distribution parameters of various citric acid radical ions, $\beta_{H_3Ci}^D$ can be obtained. Furthermore, inputting $\beta_{H_2O}^D$ for different pH values, the differential buffer capacity of citric acid β^D is obtained. The results are shown in Fig.3.

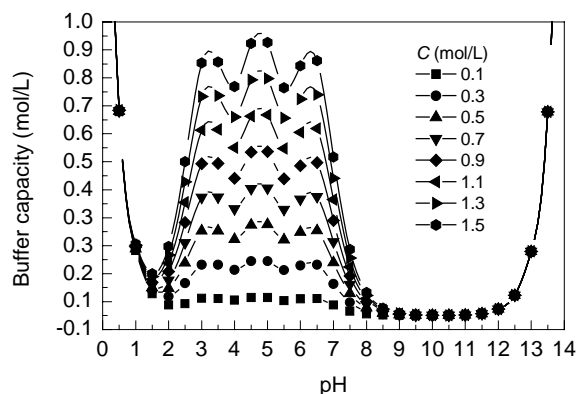
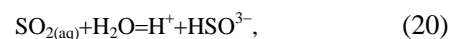


Fig.3 The dependence of the buffer capacity of H_3Ci on the pH of citrate solution for different concentrations of citrate solution

From Eq.(18) we know that the differential buffer capacity of citrate solution increases with the increase of the concentration. From Fig.3 it can be seen that the buffer capability of citrate solution shows up mainly in the range of 2~8 of pH. In such a range of pH the absorption and desorption are simultaneously realized, thus the initial pH should take a value in the range of 2~8. From Fig.3 it can be seen that the differential buffer capacity of citrate solution reaches its maximum when pH is around 4.50.

3 EXPERIMENTS OF SO_2 ABSORPTION

SO_2 absorption process in the citrate solution is determined by the following chemical reactions:



The absorption efficiency of SO_2 is defined as follows:

$$\eta = [(C_1 - C_2)/C_1] \times 100\%, \quad (24)$$

where C_1 and C_2 are the SO_2 concentrations before and after absorption, respectively. Experiments of SO_2 absorption were performed under the following conditions: air flow rate is at 700 L/h, pressure of incoming gas is at 0.136 MPa, SO_2 concentration in the gas is at $0.48\% \pm 5\%$, the liquid flow rate is at 16.80 L/h, the total amount of circulating liquid is about 3.0 L. The experimental results are shown in Fig.4.

From the results shown in Fig.4 it can be seen that

the absorption efficiency goes up with the increasing of pH. However, we should note that the increase of the citric acid pH will make the later desorption process more difficult and reduces the recycle rate of desorption. The balance of these aspects indicates a reasonable pH being at 4.5 for the citric acid solution. The reason can be seen from Fig.2 and Eq.(19) to Eq.(23). From that we know that the increase of the citric acid pH enhances the absorption gradient of the liquid and in turn strengthens the impetus of mass-transfer. From Fig.2 it can be seen that H_3Ci is dominant when pH is below 3, Ci^{3-} is dominant when pH is above 7, H_2Ci^- and HCi^{2-} are dominant (with a total percentage of about 85%) when pH is in the range of 3~7. It is clear that H_2Ci^- and HCi^{2-} play the dominant role in the absorption and desorption process, thus pH of the solution should also lie in such a range. The changing order of the components is expressed as $Ci^{3-} \rightarrow HCi^{2-} \rightarrow H_2Ci^- \rightarrow H_3Ci$ for the absorption process and $H_3Ci \rightarrow H_2Ci^- \rightarrow HCi^{2-} \rightarrow Ci^{3-}$ for the desorption process. Therefore, a reasonable pH should be at 4.5 for the citrate solution and the conclusion is consistent with the result of Fig.3.

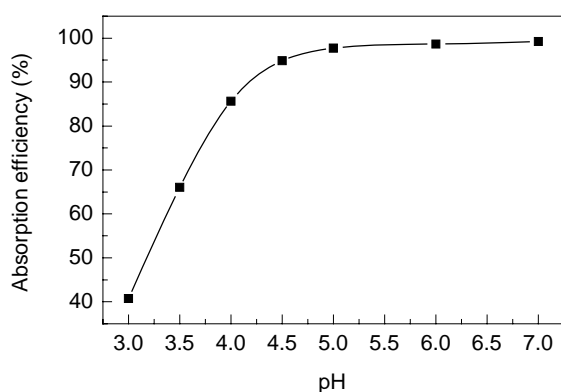


Fig.4 Dependence of absorption efficiency of SO_2 on the pH of citrate solution

4 CONCLUSIONS

The theory of multi-buffer solution, combined with computer numerical calculation methods, was applied to study the distribution parameters of the components of the citrate solution in the process of SO_2 absorption. Some conclusions are drawn as follows:

(1) pH value of the citrate solution decreases with the increase of the citrate concentration; pH value is sensitive to the change of the concentration in the range of 0.05~1.00 mol/L.

(2) The distribution parameters of the components of the citrate solution are different under different pH values. When pH lies in the range of 3~7, the total

distribution parameter of H_2Ci^- and HCi^{2-} is about 85%, which indicates that in the absorption and desorption process H_2Ci^- and HCi^{2-} play the dominant role.

(3) The buffer capacity of citrate solution increases with the increase of the concentration. The buffer capability presents mainly in the pH range of 2~8, thus the initial pH should take a value in the range of 2~8. The buffer capacity of citrate solution reaches its maximum when pH is around 4.50.

NOTATIONS:

C	Concentration (mol/L)	Ci	Citrate radical
K	Decomposition constant	x	Unkown variable pH
β	Protonization constant	δ	Distribution parameter
η	Absorption efficiency		

Subscripts and superscripts

aq	Liquid phase	g	Gas phase
t	Total	w	Water

REFERENCES:

- [1] Louis K B, Peter S J. Flue Gas Desulfurization Process [P]. US Pat.: 4366134, 1982-12-28.
- [2] Lien R H, Martin D A, Nissen W I. Description and Economic Evaluation of Flue Gas Desulfurization by the Modified Citrate Process [J]. Bur. Mines, 1982, 38(6): 30-34.
- [3] Xue J Q, Li W D, Li L B. Absorption of Sulfur Dioxide Using Liquid Membrane [J]. J. Xi'an Univ. Arch. & Tech. (Natural Edition), 2005, 37(2): 229-233 (in Chinese).
- [4] Hong T, Li L B. Characteristics of SO_2 Absorption in Flue Gas by Citrate Solution in Packing Columns [J]. Chem. Eng., 2004, 32(4): 49-52 (in Chinese).
- [5] Li W C. Study on Harmless of Low SO_2 Concentration by Sodium Citric Acid [J]. Nonferrous Metals (Extractive Metallurgy), 2002, (6): 20-22 (in Chinese).
- [6] Xiong D L, Deng X, Dai G C. Flue Gas Desulfurization by Contained Liquid Membrane [J]. J. Chem. Eng. Chin. Univ., 1998, 12(1): 33-38 (in Chinese).
- [7] Laura W L, William J F, Brack G H. Gas Permeability of Hollow Fiber Membranes in Gas-Liquid System [J]. Membr. Sci., 1996, (117): 207-219.
- [8] Zhang J S. Production of SO_2 Liquid by Sodium Citric Acid [J]. Sulphuric Acid Industry, 1998, (3): 3-6 (in Chinese).
- [9] Farrington J, Bengtsson S. Absorption of SO_2 in Citric Acid-sodium Solution [J]. Chem. Eng., 1980, 16(2): 88-90.
- [10] Shi G D. Operation Mode of Hollow Fiber Membrane Reactor [J]. Chem. Eng. J., 1993, 44(2): 151-156 (in Chinese).
- [11] Nissen W, Crocker L. Citrate Process for Flue Gas Desulfurization [J]. Bull. US Bur. Mines, 1985, 68(6): 75-82.
- [12] Zhou X R, Ren J G. Ionic Equilibrium in Analytical Chemistry [M]. Beijing: Science Press, 1998. 213-235 (in Chinese).
- [13] Sukti M P, Senthil K A, Pandit B. Effect of Liquid-phase Properties on Ultrasound Intensity and Cavitation Activity [J]. Ultrason. Sonochem., 1998, 5: 113-118.
- [14] Tan H Q, Zhang J W, Tang Y Y. The Study Course of C Language Design Program [M]. Beijing: Higher Education Press, 1998. 150-158 (in Chinese).
- [15] Pan Y. The Example and Skill of Visual Basic 6.0 Program [M]. Wuhan: Huazhong University of Technology Press, 2000. 169-176 (in Chinese).