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Reaction rate of sulfite oxidation catalyzed by cuprous ions

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ABSTRACT

Wet limestone scrubbing is one of the most widely used flue gas desulfurization processes for control of sulfur dioxide emissions from combustion of fossil fuels. A key step in the process is forced oxidation in the scrubber loop, which substantially improves the dewatering properties of the sludge, leading to the formation of gypsum ($CaSO_4{\cdot}2H_2O$). This paper deals with the experimental study of calcium bisulfite oxidation in the presence of catalysts (ferrous and cuprous ions) added to the reaction vessel. A laboratory-scale apparatus was used; the experiments were performed at a fixed oxygen partial pressure (21.3 kPa) and at a temperature of 45 °C. In particular, the effect of the simultaneous addition of both catalysts has been studied. The analysis of the experimental results, carried out by using the theory of mass transfer with a chemical reaction, indicates that the slow reaction regime has been explored, and the transition from the kinetic to the diffusional sub-regime has been reached. Experimental results have been compared with those obtained in the presence of the single catalytic species (Cu^+ alone and Fe^{2+} alone), showing that copper is less effective than iron as a catalyst; no synergy between the two catalysts added simultaneously has been observed.

1. Introduction

Among all the various Flue Gas Desulfurization processes (FGD) to control sulfur dioxide emissions from fossil fuels combustion, wet limestone-gypsum is one of the most widely used, since it gives excellent results for SO_2 removal and limestone utilization; the oxidation of calcium bisulfite is a key step in this process because forced oxidation in the scrubber loop improves the dewatering properties of the sludge, leading to the formation of gypsum ($CaSO_4{\cdot}2H_2O$), a byproduct with a lower adverse impact on the environment than the solid mixture of $CaSO_3{\cdot}1/2H_2O$ and $CaSO_4$ usually produced [1].

Several researchers have focused on the calcium bisulfite oxidation reaction, which has been extensively studied, both in the absence [2,3] and in the presence [4–6] of catalysts. Understanding the oxidation reaction path [4,7], in particular when the occurrence of a chemical reaction is accompanied by the diffusion of oxygen in the liquid phase, is made complex by some interactions that are difficult to interpret [8]. This happens when the oxidation reaction takes place in the so-called heterogeneous conditions, when a sulfurous solution is in contact with the oxygen containing gas phase that is the operating condition in FGD processes, while homogeneous conditions are obtained when a sulfite solution is in contact with an oxygen saturated solution. As to sulfite oxidation in homogeneous conditions, relatively consistent results have been reached: in a previous work Lancia et al. [1] show how the following equation appears to be the most appropriate to describe the kinetics of the oxidation reaction for a pH range of 7.5–9 in homogeneous conditions:

$$r = kc_{M}^{1/2}c_{S(IV)}^{3/2} \tag{1}$$

where r is the reaction rate expressed as moles of $SO_4{}^{2-}$ produced per unit time and volume, k is the kinetic constant, c_M the catalyst concentration and $c_{S(IV)}$ the total sulfite concentration. Literature results seem to agree only on the value of kinetic constant at 25 °C, which ranges between 2×10^6 and 36×10^6 m^3/mol, while the activation energy ranges from 50 to 150 kJ/mol. Eq. (1) can be interpreted by assuming that the reaction takes place via a free radical mechanism, with a chain initiated by the catalyst auto-oxidation or by the action of UV light [9,10]. On the other hand, both in homogeneous and heterogeneous oxidation, the reaction is highly sensitive to operative conditions, such as the liquid phase composition (sulfite concentration, dissolved oxygen, pH).

The previous experimental study [1] of uncatalyzed bisulfite oxidation reaction in heterogeneous conditions has identified the

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Nomenclature

a	specific interfacial area (m^{-1})
a_I	activity of the I species (mol/m^3)
c_I	concentration of the I species (mol/m^3)
$c^i_{O_2}$	oxygen interfacial concentration (mol/m^3)
FI	ionic strength (mol/m^3)
k	kinetic constant ($m^3/mol\,s$)
k_c	kinetic constant for the "catalyzed" reaction (s^{-1})
k_u	kinetic constant for the "uncatalyzed" reaction (s^{-1})
k^0_L	liquid side mass transfer coefficient (m/s)
K	equilibrium constant
M^{2+}	catalytic species (Cu^+, Fe^{2+})
p	pressure (Pa)
r	reaction rate ($mol/m^3\,s$)
R	overall oxidation rate ($mol/m^3\,s$)
T	temperature (°C)
z_I	electric charge, dimensionless
Greek letters	
α_I	stoichiometric coefficient of the I species, dimensionless
γ_I	activity coefficient of the I species, dimensionless
τ	liquid residence time (s)

following kinetic equation for calcium bisulfite which is of zero-order in oxygen and three halves in $HSO_3{}^-$ ions:

$$r = k_u c^{3/2}_{HSO_3{}^-} \tag{2}$$

where k_u is the uncatalyzed kinetic constant and $c_{HSO_3{}^-}$ the bisulfite ion concentration, with $k_u = 1.19 \times 10^{-4}\ m^{3/2}/mol^{1/2}s$ at $T = 45\,°C$.

The reaction has then been carried out in the presence of different catalysts, and namely ferrous ions and manganese ions, added both separately and together in solution, in a laboratory-scale well-mixed reactor [11,8,12,13]. The kinetic equation has been devised by considering a parallel reaction mechanism in which the total reaction rate is the sum of the uncatalyzed reaction rate and of the two reaction rates catalyzed by manganese and by ferrous ions. The overall kinetic equation is [13]:

$$r = r_u + r_{c_1} + r_{c_2} = k_u c^{3/2}_{HSO_3{}^-} + k_{c_1} c_{Mn^{2+}} + k_{c_2} c_{Fe^{2+}} \tag{3}$$

where k_u is the kinetic constant of Eq. (2), $c_{Mn^{2+}}$ the manganese ion concentration, k_{c1} is the manganese catalyzed kinetic constant with $k_{c1} = 0.193\ s^{-1}$ at $T = 45\,°C$ [8], $c_{Fe^{2+}}$ the ferrous ion concentration and k_{c2} is the iron catalyzed kinetic constant, with $k_{c2} = 0.548\ s^{-1}$ at $T = 45\,°C$ [12].

The purpose of the present paper is to study the oxidation reaction in the presence of a different catalyst, namely the cuprous ion, and in the simultaneous presence of both catalysts (Fe^{2+} and Cu^+), in order to check for any interfering effect. As a matter of fact desulfurization of flue gas from power plants produces a heavy metal-containing sludge (*e.g.*, Mn, Fe, Co, Ni, Pb, Zn, Cu [14,15]), in which the typical total iron and total copper contents are in the range 116:6400 ppm and 0.3–66 ppm, respectively [16]. For this reason the study of sulfite oxidation in the presence of catalytic species that are already present in FGD liquor such as Fe and Cu ions is particularly interesting [17].

2. Materials and methods

A sketch of the laboratory-scale apparatus is reported in Fig. 1. The apparatus consists of a thermo-stated stirred reactor with lines for continuous feeding and discharging of both gas and liquid phase. The reactor is a Pyrex 0.088 m i.d. cylinder with a hemispherical bottom, with two vertical baffles and a liquid overflow, allowing a liquid head of about pH 100 mm. A two-flat blade axial stirrer, located about 70 mm below the liquid overflow, was used to provide thorough mixing in the liquid phase, with stirrer speed variable in the range 0–13.3 s^{-1}. The vessel is jacketed, and the temperature was set at 45 °C in all the experiments. The gas phase was a mixture of oxygen and nitrogen with oxygen concentrations of 21%; the mix it was taken out from cylinders and bubbled in the reactor through a glass tube submerged at about 80 mm below the liquid free surface. The volumetric flow rate of the gas fed to the reactor, measured by a rotameter (ASA), was kept constant at $1.39 \times 10^{-4}\ m^3/s$. This gas flow rate, in conjunction with the stirrer speed of 6.7 s^{-1}, gave a liquid holdup of $4.2 \times 10^{-4}\ m^3$. As to the liquid solution, a particular attention was paid to its preparation, having the care of setting up two distinct feed solutions, in order to avoid the reaction initiation by catalyst in the tank itself. Thus one tank was filled with a clear solution prepared by dissolving analytical grade calcium hydroxide into analytical grade sulfur dioxide in solution and by diluting with bi-distilled water. A second tank was instead filled with a solution of the catalyst (CuCl) in bi-distilled water or with a mixture of the two catalysts (CuCl and $FeSO_4{\cdot}7H_2O$). It is to point out that in wet limestone processes Ca is supplied in the form of calcium carbonate and not as calcium hydroxide; however carbonic acid, as well as sulfurous acid, does not have any effect on the oxidation reaction, but only on solution chemistry. To this purpose, rigorous calculations demonstrated that the presence of $Ca(OH)_2$ or $CaCO_3$ as to equilibria in solution does not alter the speciation. As to the concentrations in the reactor volume, the Ca^{2+} concentration ranged from 0.5 to 30 mol/m^3, while the total S(IV) concentration ranged from 0.6 to 64 mol/m^3, with a pH in the range of 2.0–4.0. As for pH, even if the oxidation reaction is usually carried out by bubbling air into a solution saturated with respect to calcium sulfite at pH 3.5–5, always remaining below the maximum value pH 5.5, nevertheless this reaction has been widely studied in very different pH ranges, from 1 to 6 [1], therefore the pH levels chosen for the experimentation appear to be fully adequate. The concentration of $FeSO_4{\cdot}7H_2O$ was varied in the range 1×10^{-3} to $1 \times 10^{-1}\ mol/m^3$, while the concentration of CuCl was varied in the range 3.3×10^{-3} to $1.6 \times 10^{-2}\ mol/m^3$. The total liquid flow rate was kept constant at the value $9.53 \times 10^{-7}\ m^3/s$, corresponding to a mean residence time into the reactor τ of about 440 s.

At the beginning of each experiment, as soon as the liquid in the reactor reached the overflow, agitation was started and the gas stream was introduced. It was assumed that steady state was reached after a time longer than 6τ had elapsed. The oxidation rate at steady state was evaluated by measuring total sulfate concentration in the inlet and in the outlet liquid streams; total sulfate concentration was measured by means of a turbidimeter (Hach DR/2010) at 450 nm wavelengths. Furthermore, in both streams the concentration of total sulfite and Ca^{2+} ion were measured. Total sulfite concentration was measured by iodometric titration using starch as an indicator, while the Ca^{2+} ion concentration was measured by EDTA titration using murexide as an indicator.

3. Results and discussion

To determine the effect of some process parameters on the oxidation reaction, particularly of catalyst concentration, three sets

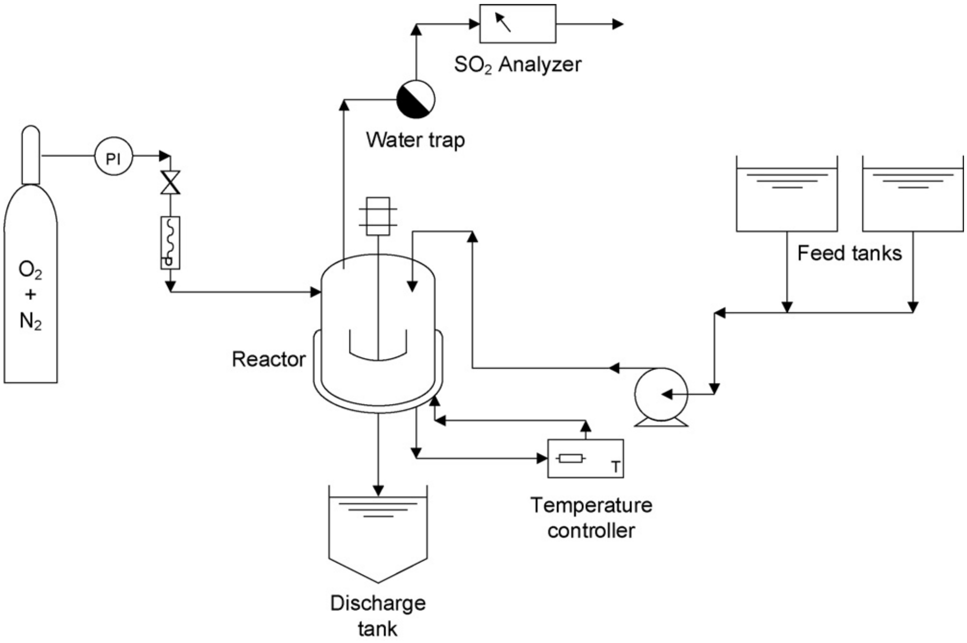

Fig. 1. Experimental apparatus.

of experiments have been performed, with a fixed p_{O_2} equal to 21.3 kPa, since a previous experimentation by using manganese as a catalyst has shown that p_{O_2} variations have no influence [8] and preliminary tests have shown that even in the presence of copper ions this zero-order dependence still exists. The first set includes experimental runs carried out by varying bisulfite concentration in the range $1 \times 10^{-1} < c_{HSO_3^-} < 3 \times 10^1$ mol/m^3, at fixed Cu$^+$ level, and namely $c_{Cu^+} = 0.0326$ mol/m^3; the second experimental set concerns runs carried out for various Cu$^+$ concentrations in the range 4×10^{-4} to 7×10^{-1} mol/m^3, and with $c_{HSO_3^-}$ in the range 0.6–3.5 mol/m^3. The third set includes two series of experiments carried out at fixed bisulfite concentration in the feed solution, with varying Cu$^+$ and Fe^{2+} concentrations in order to get two fixed Cu$^+$/Fe^{2+} concentration ratios equal to 16 and 5, respectively. The bisulfite concentration levels have been chosen since experiments carried out without any catalyst [1], have indeed shown that at low $c_{HSO_3^-}$ the slow kinetic sub-regime occurs, in which the rate of uncatalyzed sulfite oxidation is controlled by the kinetics of the reaction itself, rather than by diffusional processes; therefore experiments in that regime may be useful to individuate a kinetic equation. Moreover, experiments carried out in the presence of different catalytic species (Mn^{2+} [12]; Fe^{2+} [13]) have shown that in the kinetic sub-regime the uncatalyzed contribution is negligible in comparison with the overall rate, therefore the catalytic oxidation rate is independent of the bisulfite ion concentration. Consequently, experiments obtained with HSO$_3^-$ concentration low enough to have a negligible uncatalyzed rate, may be used to find a catalytic kinetic equation.

First of all, the composition of the liquid phase out-flowing from the reactor has to be speciated in order to identify a kinetic equation on the basis of the experimental measurements. With this aim the equilibrium equations for the following reactions were used (see Appendix A):

$$SO_{2(aq)} + H_2O = H^+ + HSO_3^- \quad (4)$$

$$HSO_3^- = H^+ + SO_3^{2-} \quad (5)$$

$$HSO_4^- = H^+ + SO_4^{2-} \quad (6)$$

$$H_2O = H^+ + OH^- \quad (7)$$

for which the values of the thermodynamic equilibrium constants were calculated using data reported by Goldberg and Parker [18] (reactions (4) and (5)) and by Brewer [19] (reactions (6) and (7)). Together with the equilibrium equations relative to reactions (4)–(7), the stoichiometric equations for total sulfite and sulfate concentrations, and the electro-neutrality equation were considered:

$$c_{SO_{2(aq)}} + c_{HSO_3^-} + c_{SO_3^{2-}} = c_{S(IV)} \quad (8)$$

$$c_{HSO_4^-} + c_{SO_4^{2-}} = c_{S(VI)} \quad (9)$$

$$\sum_I z_I c_I = 0 \quad (10)$$

where z_I is the electric charge of the I species, with I = Ca^{2+}, H$^+$, HSO$_3^-$, SO$_3^{2-}$, HSO$_4^-$, SO$_4^{2-}$, OH$^-$, M^{2+} (where M^{2+} stands for the bivalent catalytic species used).

In Fig. 2, the behavior of oxidation rate *vs.* the bisulfite ion concentration is reported, for the low fixed Cu$^+$ concentration level (*i.e.*, $c_{Cu^+} = 0.0326$ mol/m^3); oxidation rate increases in the presence even in traces of the catalyst with respect to the uncatalyzed reaction. Moreover the oxidation rate is constant for low bisulfite concentration and grows as $c_{HSO_3^-}$ does until it reaches a plateau, where r becomes almost independent of it. For comparison's sake, the kinetic equation previously found in uncatalyzed conditions (Eq. (2)) has been reported in the plot as a continuous line. The catalytic effect of Cu$^+$ ions is particularly evident at low bisulfite concentrations; precisely, when $c_{HSO_3^-} \cong 1$ mol/m^3, the difference between catalyzed and uncatalyzed oxidation rates is more than one order of magnitude, while for higher $c_{HSO_3^-}$ the difference between the catalyzed and the uncatalyzed reaction rate becomes less marked. Eventually, as bisulfite concentration continues to grow, the oxidation rate coincides with the uncatalyzed reaction rate, reaching the plateau identified by the diffusional sub-regime, the value of such a limit depending on the oxygen partial pressure in the gas phase.

Fig. 3 reports the behavior of oxidation rate *vs.* the cuprous ion concentration. It can be noted that the oxidation rate increases with increasing c_{Cu^+}, until the upper limit of the diffusional limit is reached. The diffusional ceiling was not experimentally reached in the case of copper catalyst, due to the low solubility of cuprous chloride that prevents from attaining higher dissolved Cu concentrations. However, the trend of reaction rate *vs.* catalyst concentration was drawn out, through a linear regression analysis of experimental data. Moreover, it can be observed that in the slow reaction regime, the slope of this regression line is lower than those obtained in the presence of Fe^{2+} and Mn^{2+} ions.

These results have been analyzed following the approach of Astarita and coworkers [20,21]. Actually, as far as cuprous ion catalyzed oxidation reaction (see Fig. 2) is concerned, the absorption rate for low bisulfite concentration, that is the same of the reaction rate in the slow kinetic reaction regime, is almost constant; then it grows until it reaches the transition towards the slow diffusional reaction regime, where it becomes almost constant again. For the left part of the plot (see Fig. 3), the reaction rate is very sensitive to the catalyst concentration and can be expressed by a parallel reaction mechanism as it was the case with the manganese and ferrous catalysis.

Considering the uncatalyzed contribution (Eq. (2)), together with a cuprous catalyzed contribution, the overall kinetic equation for cuprous catalyzed bisulfite oxidation is:

$$r = r_u + r_c = k_u c_{HSO_3^-}^{3/2} + k_{c3} c_{Cu^+}^{0.3} \tag{11}$$

where k_{c3} is the constant of the catalyzed reaction, equal to 0.0034 $mol^{0.7}/m^{2.1}$ s. The constant k_{c3} and the power of cuprous ion concentration have been estimated by a non-linear regression analysis. The proposed reaction mechanism derives from testing various kinetic models, among which this parallel model gives the best fit of experimental data. The reaction rate dependence on oxygen concentration was considered of zero-order, as reported in a previous work [8]. Eq. (11) is reported as a continuous line in Figs. 2 and 3, showing that there is a good agreement with the experimental data in the kinetic sub-regime.

Fig. 4 shows the behavior of oxidation rate as a function of bisulfite concentration for two fixed Cu^+/Fe^{2+} ratios, equal to 5 and 16, respectively. The highest oxidation rate is reached at the lowest ratio adopted between the two catalysts, and the experimental results in the presence of both catalysts are comprised between the two curves obtained for the individual catalysts.

As for experimental results obtained in the presence of both catalysts, it is important to specify that catalyst concentration levels have been chosen in order to work in the slow kinetic sub-regime. Once again, the kinetic equation has been devised by considering a parallel reaction mechanism in which the total reaction rate is the sum of the uncatalyzed reaction rate and of the two catalyzed reaction rates, by ferrous and cuprous ions. The overall kinetic equation is thus:

$$r = r_u + r_{c_2} + r_{c_3} = k_u c_{HSO_3^-}^{3/2} + k_{c_2} c_{Fe^{2+}} + k_{c_3} c_{Cu^+}^{0.3} \tag{12}$$

where k_u is the kinetic constant of Eq. (2), k_{c2} is the rate constant of Eq. (3) and k_{c3} is the kinetic constant of Eq. (11), respectively. Eq. (12) has been reported as a continuous line in Fig. 4, which interpolates quite well experimental data. Since the actual rate of bisulfite oxidation catalyzed by a mixture of Cu^+ and Fe^2 is equal to the rate obtained by summing the rates of the individual catalysts as in Eq. (12), a synergistic effect of the catalysts added simultaneously can be excluded.

A different approach shall be used to interpret the data in diffusional sub-regime; as suggested by Danckwerts [22], in this sub-regime the overall rate does not depend on liquid phase composition, and it is only controlled by the rate of diffusive oxygen absorption. Therefore, the overall rate of the process (R), relative to the diffusional sub-regime in Fig. 2 can be described by means of

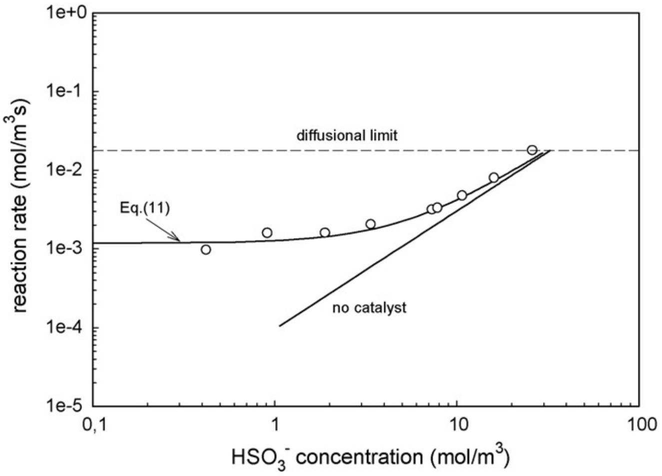

Fig. 2. Reaction rate as a function of $c_{HSO_3^-}$. (○) $c_{Cu^+} = 0.0326\ mol/m^3$.

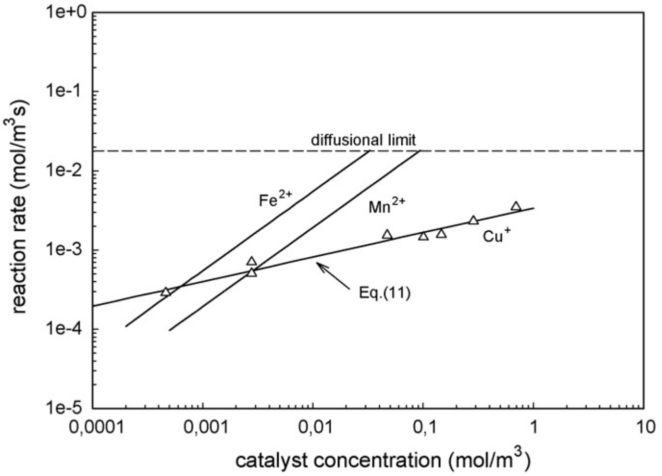

Fig. 3. Reaction rate as a function of catalytic species concentration; (△) present results.

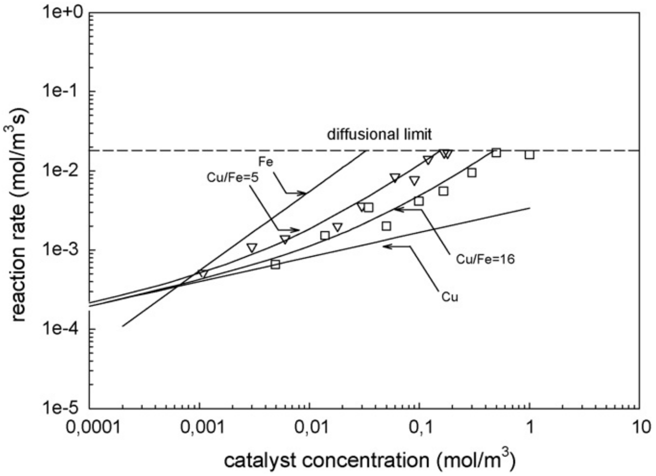

Fig. 4. Reaction rate as a function of $c_{HSO_3^-}$ for different ratios $c_{Cu^+}/c_{Fe^{2+}}$; (▽) $c_{Cu^+}/c_{Fe^{2+}} = 5$; (□) $c_{Cu^+}/c_{Fe^{2+}} = 16$; (—) Eq. (12).

the following equation [21]:

$$R = 2k_L^0 a c_{O_2}^i \tag{13}$$

where $k_L^0 a$ is the product between the liquid side mass transfer coefficient and the specific gas–liquid contact area, and $c_{O_2}^i$ is the interfacial oxygen concentration, which can be evaluated by means of the Henry's Law. Using the data in the right side of Fig. 2 and the value of 1.02×10^5 m^3 Pa/mol for the Henry's constant for O_2 at 45 °C [23], it is possible to estimate the value of $k_L^0 a$ that is equal to 4.63×10^{-2} s^{-1}. With this value of $k_L^0 a$, the straight horizontal lines reported in Figs. 2–4 have been achieved.

4. Conclusions

The oxidation reaction of bisulfite in the presence of catalysts, *i.e.*, cuprous ions and a mixture of ferrous and cuprous ions, has been experimentally studied. The reaction takes place in the slow kinetic regime, and the transition from slow kinetic to slow diffusional sub-regime has been described, with the identification of the diffusional plateau. A kinetic equation has been devised, with a parallel reaction mechanism, for which the overall reaction rate is the sum of the catalyzed and the uncatalyzed reaction rates. The comparison between present experimental data and those previously obtained by using manganese ions as a catalytic species has shown that Fe^{2+} is more effective than Cu^+ as a catalyst and that Fe^{2+} and Cu^+ added simultaneously do not produce any synergistic effect, *i.e.*, that the actual rate of bisulfite oxidation catalyzed by the catalytic mixture is comparable with that obtained by summing the rates for single catalysts. The kinetic equation devised in this work may be useful in designing the oxidation process during wet desulfurization in the presence of copper as a catalyst.

Appendix A

The chemical reactions taken into account can be written in the following general form:

$$\sum_I \alpha_I I = 0 \tag{A1}$$

where α_I is the stoichiometric coefficient of the *I* species and is assumed positive for the reactants and negative for the products. The equilibrium condition for reaction (A1) is:

$$K = \prod_I a_I^{-\alpha_I} \tag{A2}$$

where a_I is the activity of the *I* species.

The activity a_I is related to the molar concentration by:

$$a_I = c_I \gamma_I \tag{A3}$$

where γ_I is the activity coefficient.

Values of the activity coefficients for cations and anions can be calculated by means of the extension of the Debye–Hückel equation, proposed by Davies [24]:

$$\log \gamma_I = -0.509 z_I^2 \left(\frac{\sqrt{\mathrm{FI}}}{1 + a\sqrt{\mathrm{FI}}} - 0.2\mathrm{FI} \right) \tag{A4}$$

where FI is the ionic strength, which can be evaluated by means of the following equation:

$$\mathrm{FI} = \frac{1}{2} \sum_{I=1}^{N} c_I z_I^2 \tag{A5}$$

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