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THE DETERMINATION OF THE KINETIC PARAMETERS TO SULFUR DIOXIDE CHEMOSORPTION IN AMMONIA SULFITE

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ABSTRACT. The main experimental results regarding the SO_2 absorption kinetics in ammonia sulfite are shown in this paper. The working conditions in which the mass transfer through the gaseous and liquid phase does not influence the chemical reaction speed have been determinate. The paper describes the temperature and concentration of influence on the reaction rate. The activation energy of the reaction and the reaction order for the ammonia sulfite was determined. The obtained kinetic data can be used for calculation of process acceleration factor taken into consideration in the design calculation of the absorption devices.

1. Introduction

The gas emissions desulphurisations containing sulfur dioxide is of great importance nowadays, given its ecological impact. For the elimination of SO_2 from waste gases were proposed many processes: the Battersa process which uses as absorbent a very diluted alkaline solution, the process of eliminating SO_2 by absorption in xylidine uses as an absorbent a mixture of xylidine and water, etc [1]. These processes allow the SO_2 recovery, but from resulting compounds don't recovery of the absorbents.

In comparison with these processes were developments processes, which allow the recovery of the absorbents, and producing the pure SO2, which is an important source of sulfur by reduction. Thus processes are:

a) the Wellman-Lord (WL) process [2, 3] is currently the leading SO_2 recovery process, where SO_2 is absorbed in an aqueous solution of sodium sulfite, producing sodium bisulfite.

The loaded solution is termally regenerated by evaporation of H_2O+SO_2. After condensing the water vapor, nearly pure gaseous SO_2 is obtained as an overhead product, ready for further processing. Solid Na_2SO_3, which is precipitated in the evaporator, is redissolved in condense/water to the appropriate concentration for a new absorption cycle.

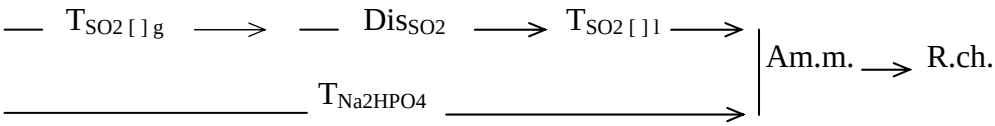
b) the citrate absorption – steam-stripping process is best known as the Flakt-Boliden process. In this process absorption and regeneration take place in packed towers whit small pressure losses, no solids formation and very small oxidation losses. The most serious limitation of this process concerns its application to gases whit very low SO_2 contents, such as are often found in thermal power plants, since the specific steam requirement will then be too high. The citrate absorption process is considered to be very competitive for SO_2 recovery from relatively rich gas [4].

c) the adipate absorption – steam-stripping process offers the same advantages as the citrate process and, in addition, a system specific possibility of reducing the specific steam requirement. The adipate process is therefor suitable for much lower feed gas SO_2-partial pressures than the citrate process. However, both these processes require relatively high the specific steam requirement values for very lean gases, and problems may arise when extremely low emission limits have you be met [4].

Such procedures present a great disadvantage: their economic efficiency is satisfactory only when the concentration of SO_2 in the gases is relatively high. To the same category of processes belongs the separation of SO_2 by absorption into buffer solution of mono- and disodic phosphates. This process is characterized by in the desorption phase the steam consume is very low, a relatively high capacity of absorption and a reduced oxidability of the SO_2 to SO_4^{2-}.The study upon the absorption within the buffer solutions made by Erga [4] reveals the fact that one can obtain relatively easy concentrations of SO_2 in the purified gases at low values of 10 ppm even when the temperature is between 50 – 60 degrees Celsius; this denotes that such a solution is an excellent absorbant which can be used whit weak, diluted gases; consequently this method will have good perspectives in the future. The literature in the field does not come up whit studies referring to the kinetic of the chemosorption process. This paper present a part of the possible kinetic models as well as the experimental data obtained in order to determine the kinetic parameters determination (constant rate of the chemical reaction, the reaction order, and activation energy) of the chemosorption of the SO_2 within phosphate buffer. The paper also draws a comparison between the rate of absorption within the disodic phosphate solutions and that within the buffer phosphate solutions.

2. The possible macrokinetics models

The absorption process of SO_2 into phosphate solution is a gas-liquid process [5, 6, 7], which has the following scheme:



This scheme shows that SO_2 gas is first transferred through gas phase ($T_{SO2\,[\,]\,g}$), until the gas-liquid interface, then SO_2 is dissolved into the liquid phase (Dis_{SO2}), then dissolving SO_2 is transferred through liquid phase ($T_{SO2\,[\,]\,l}$). The Na_2HPO_4 is transferred through into liquid phase ($T_{Na2HPO4}$) too, then chemical reaction (R) between SO_2 and Na_2HPO_4 is taking place in the liquid phase.

The comparing the chemical reaction rate between SO_2 and Na_2HPO_4 (v_r) with transfer process rate (v_{tr}) carries at the following models:

- $v_r << v_{tr}$, when the chemical reaction is very slow and global process rate is equal with chemical reaction rate, and the kinetics equation for this case is given by:

$$-r_{SO_2} = k_1 \cdot C_{SO_2}^n \cdot C_{Na_2HPO_4}^m \tag{1}$$

- $v_r >> v_{tr}$, when the chemical reaction is practically instantaneous and this has been placed at the gas-liquid interface. The SO_2 transfer process is slower than the SO_2 dissolving process, and the kinetics equation is given by:

$$-r_{SO_2} = -\frac{dn_{SO_2}}{S \cdot d\tau} = k_{g,SO_2} \cdot C_{SO_2} \tag{2}$$

- $v_{tr} \approx v_r$, chemical reaction rate is equal with transfer process rate and in this case the global process is described by the equation for diffusion with chemical reaction in the stationary system:

$$D_{SO_2} \frac{\partial^2 C_{SO_2}}{\partial x^2} + k \cdot C_{SO_2}^n = 0 \tag{3}$$

If n=1, for an irreversible reaction, equation (3) can be write:

$$D_{SO_2} \frac{\partial^2 C_{SO_2}}{\partial x^2} + k \cdot C_{SO_2} = 0 \tag{4}$$

The solution of equation (4) is:

$$C_{SO_2}(x) = \beta_1 \cdot e^{A \cdot x} + \beta_2 \cdot e^{-A \cdot x} \tag{5}$$

where $A = \sqrt{k / D_{SO_2}}$

At the gas-liquid interface (x = 0) the rate of gas absorption at any time is given by equation:

$$r = D_{SO_2}\left(\frac{dC_{SO_2}}{dx}\right)_{x=0} = A \cdot D_{SO_2} \frac{ch(A \cdot x_0)}{sh(A \cdot x_0)}\left[C_{SO_2}^* - \frac{C_{SO_2}}{ch(A \cdot x_0)}\right] \tag{6}$$

when is equal to the Hatta number (Ha) and x_0 is equal to D_{SO2}/k_{SO2} and the global process rate is given by equation:

$$r = k_{SO_2} \frac{Ha}{thHa}\left(C^*_{SO_2} - \frac{C_{SO_2}}{chHa}\right) \tag{7}$$

The SO_2 transfer process rate without chemical reaction is given by equation:

$$r_{tr} = k_{l,SO_2}\left(C^*_{SO_2} - C_{SO_2}\right) \tag{8}$$

The enhancement factor, E, is the ratio of the process rate with chemical reaction and without chemical reaction is given by equation:

$$E = \frac{r}{r_{tr}} = \frac{Ha}{tgHa}\left(\frac{1 - \frac{\varphi}{chHa}}{1-\phi}\right) \tag{9}$$

where $\phi = C_{SO_2} / C^*_{SO_2}$. In general ϕ has low value and $C_{SO_2} \to 1$ and the enhancement factor in this case is:

$$E = \frac{Ha}{tgHa} \tag{10}$$

$$r = E \cdot r_{tr} = E \cdot k_{l,SO_2} \cdot \left(C^*_{SO_2} - C_{SO_2}\right) \tag{11}$$

The equation (11) shows that the chemical reaction speeds the absorption process rate and the influence of the chemical reaction about global process rate is given by enhancement factor, which depends, from number of Hatta.

To agreement with these theoretical studies is necessary experimental determination of kinetic parameters as the constant rate of the process, k, activation energy, E_a, and reaction order.

3. Experimental

In order to determine the kinetic parameters that we have discussed above, we must establish if the conditions of the transfer phenomena during the liquid and gaseous phases do not influence the process. To avoid the influence of the transfer during the gaseous phase, pure SO_2 has been used. To eliminate the influence of the transfer during liquid phase, kinetic

studies upon different rotation speeds of the agitator proved necessary. In a previous paper it has been determined that at an agitator speed higher than 80 rotations/minute the speed of the process remains constant - as a consequence, the transfer of the mass through the liquid phase is not o factor of influence. The SO_2 used has the 99% concentration and flow was measured using a flow meter. The SO_2 that was not absorbed at first was transferred in a bubbling container and absorbed in NaOH (sodium hydroxide). The conditions were temperatures = 15^o, 33^o, and 50^oC, and the concentration variation of ammonia sulphite.

The process evolution in time was determined noting the SO_2 concentration from the phosphate solution. The determination of SO_2 concentration was made on iodometric means, titration with $Na_2S_2O_3$ 0.1N the excess of iodine.

4. Results

The first experimental determination draws out the influence of the absorbent nature on the rate and capacity of absorption. In this scope we worked at three different concentration of ammonia sulfit and different temperatures.

The kinetic results were processed for the reaction rate estimation, for which the ln C =f(t) curves were traced, from the straight lines slopes obtained the k constants rate. Fig 1 shows the variation of SO_2 absorption rate at different concentration of ammonia sulfit at rotation speed of stirrer n=70 rot/min. Fig. 2 shows the variations of the absorbed SO_2 concentrations in time and that the absorbed SO_2 ratio increases at temperatures. The activation energy was determined, having as a purpose the drawing of the diagrams lnk = f(1/T) on the basis of the Arhenius equation.

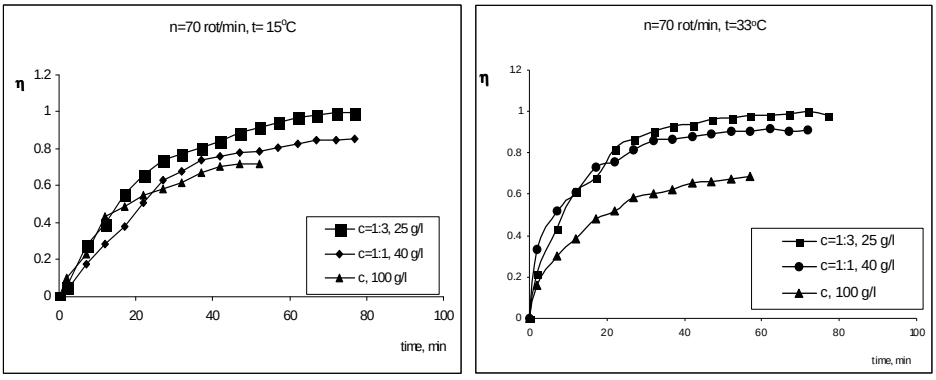


Fig. 1. SO_2 absorption rate versus time at different concentration of ammonia sulphit, at the rotation speeds of the stirrer 70 rot/min

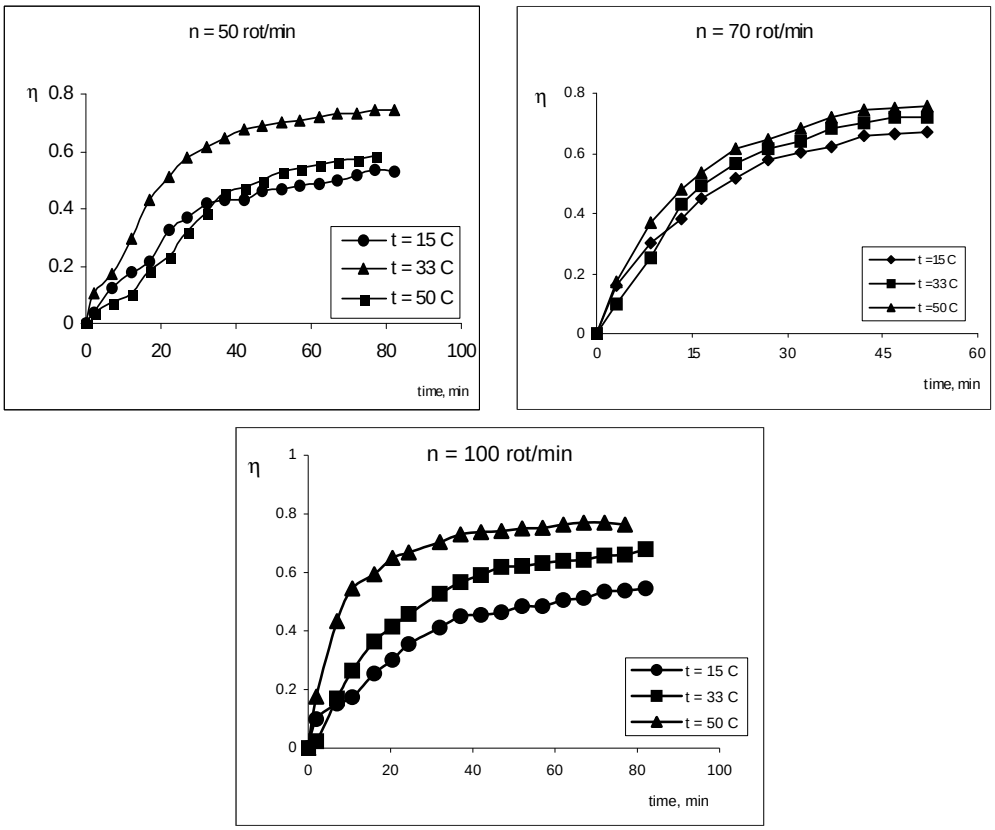


Fig. 2. SO_2 absorption rate versus time at different temperatures and the different rotation speeds of stirrer.

5. Conclusions

1. It was established the constants rate, k, and activation energies, E_a of the SO_2 absorption into ammonia sulfite. The high values of the activation energies show that the chemical reaction is the limitative step of the absorption process in the experimental conditions.

2. It was determined the reaction order of SO_2 absorption into ammonia sulfite, and the obtained results show that the order of the reaction between SO_2 and ammonia sulfite is equal to one.

3. The determined kinetic parameters can be used for determination the enhancement factor of the absorption process from the mathematics model of the SO_2 chemisorption process into ammonia sulfite.

Symbol used

$C^*_{SO_2}$	[mol/l]	SO_2 concentration at gas-liquid interface
C_{SO_2}	[mol/l]	SO_2 concentration into bulk liquid
D_{SO_2}	cm^2/s	diffusivity of SO_2 in liquid
E	-	enhancement factor
E_0	cal/mol.K	activation energy
k_{l,SO_2}	cm/s	liquid-film mass transfer coefficient
k	s^{-1}	constant of reaction rate
r	$mole/m^2min$	absorption process rate
S	cm^2	surface
v_r	$mole/m^2min$	reaction rate
v_{tr}	$mole/m^2min$	SO2 transfer process rate in liquid phase
τ	s	time
η		transformation rate

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