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Measurement of Effective Interfacial Area In A Packed-Column Absorber By Sulphite Oxidation Method: Influence Of Liquid Viscosity

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ABSTRACT

The effective interfacial area of glass Raschig rings (8.0 x 8.0 x 1.0 mm), for gas absorption with chemical reaction, was measured in the range 0.1–0.6 cm/s of superficial liquid velocity and for kinematic viscosities of 1.18 – 1.87 cm²/s by using the well-known Co^{+2} catalysed sulphite oxidation method. The aim was to study experimentally the effect of liquid viscosity on the effective interfacial area by adding different amounts of sugar to sodium sulphite solutions.

The increase in the effective interfacial area (a) was maximum 7 % only at high liquid flow rates. At low liquid flow rates, the gas-liquid interfacial area (a) was not affected noticeably by the viscosity of solution. It was found that the regression analysis of measured (a) values, as function of liquid flow rate and kinematic viscosity, followed the following equation:

$$a = 3.76\ \nu^{0.104}\ L^{0.256}$$

INTRODUCTION

Design of gas absorbers for physical absorption requires knowledge only of volumetric mass transfer coefficients (k_Ga and k_La). However, the majority of industrial chemical processes involves gas absorption with chemical reaction. Design of an equipment (in this case a packed column) for gas absorption with chemical reaction necessitates to know the values of liquid-side mass transfer coefficient (k_L) and gas-liquid interfacial area (a) separately in order to evaluate the effect of chemical reaction on the absorption rate, that is the enhancement factor E. It is now well known that when a gas-liquid reaction occurs in a packed column, the interfacial area depends not only on the hydrodynamic conditions, but also on the reacting system.

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Many models have been proposed to explain the relative influence of these two factors. The well-known one-parameter "surface renewal" model was introduced by Danckwerts (1,2). Using this model, Joosten and Danckwerts (3) carried out experiments to explain the influence of the chemical reaction on the interfacial area. They compared the results of physical, chemical and instantaneous reaction absorption regimes and, in order to obtain dynamical similarity, matched both the viscosity and the density of the absorbing solutions. The influence of the chemical reaction was described by defining a parameter γ, the ratio between the amplifying factor of the capacity of the absorbent to the amplifying factor of the absorption rate. Schwartz and Roberts (4) developed the "cross flow" valid only for first order reactions in the liquid phase, which uses two parameters defining the hydrodynamic behaviour: the static hold-up and the rate of interchange between the static and the dynamic hold-ups. Puranik and Vogelpohl (5), performing a regression analysis on the data of various authors, proposed a generalized correlation for the prediction of the effective interfacial area. Their equation correlates the ratio of the effective interfacial area to the total dry area with the the Reynolds, Weber and Froude numbers and with a factor which depends on the chemical kinetics in the liquid phase. Their correlation agrees with the experimental data to within ± 20 %. Baldi and Sicardi (6) developed a three-parameter model in which the column was simulated by a series of equal stages. In each of them, the liquid flows in the form of a set of separate small plug flow streams which is perfectly mixed at the end of each stage. In the same paper (6), they correlate the data of Joosten and Danckwerts (3). In a following paper, Sicardi and Baldi (7) successfully apply the same model to the data of Shulman et. al. (8,9). Finally ,Patwardhan (10–12) presented a theoretical development of the "crossflow" model in which the total interfacial area is divided into parts, proportional to the static and dynamic hold-ups, respectively. The concept of the effectiveness of the static hold-up on the interfacial area is also introduced. The data of Joosten and Danckwerts (3), Richards et. al. (13) and Shulman et. al. (9) are well described by this "extended crossflow" model.

What appears to be lacking in most of the previously reported papers is that the influence of the physical properties of the liquid, such as viscosity, is not studied explicitly, except the recent work of Rizzuti et. al. (14), who found a very strong dependence of the effective interfacial area on the liquid viscosity for sugar solutions ($\nu = 0.9.10^{-2} - 1.55.10^{-2}$ cm^2/s). They proposed:

$$a = 39\ \nu^{0.70}\ L^{0.326} \tag{1}$$

One disadvantage of their experiments was that the ratio of column diameter to that of packing was unfortunately less than 4 so that the effect of wall flow might well be very significant. Therefore it was considered useful to work further in this area.

In this paper, an experimental study of the influence of the liquid viscosity on the effective interfacial area is reported. The well known and commonly used (air + SO_3^{-2} + Co^{+2}) chemical system (2,15,16,17) was used for the measurement of interfacial area.

PRINCIPLE OF THE METHOD

1. Kinetic data

The principle of "chemical methods" consists in resorting to a very fast reaction between two species, one of which, A, is initially in the gaseous phase, the other one, B, being dissolved in the liquid phase.

Oxidation by atmospheric oxygen of a sodium sulphite solution, according to the scheme:

$$SO_3^{-2} + \frac{1}{2}\ O_2 \xrightarrow[k_c]{CoSO_4} SO_4^{-2} \tag{2}$$

is widely used by several researchers (15, 20).

A review of the kinetic data for this reaction has been made by

$$r = k_c\ C_A^m\ C_B^n\ C_c^p = k_c\ C_{O_2}^m\ C^n_{Na_2SO_3}\ C^p_{CoSO_4} \tag{3}$$

The experimental conditions suitable for determining interfacial area in gas-liquid reactors are as follows:

$0.2 \leq P_{Oxygen} \leq 0.8 - 1$ atm $0.4 < C_{Na_2SO_3} \leq 0.8$ mol/l

$10^{-4} \leq C_{CoSO_4} \leq 1 - 2 \times 10^{-3}$ mol/l

$$C_{Na_2SO_3} + C_{Na_2SO_4} = \text{Constant} \tag{4}$$

$20 \leq t \leq 50$ °C, $7{,}5 \leq pH \leq 8.5$

At these conditions, reaction orders are respectively two with respect to oxygen, zero with respect to sulphite and one with respect to catalyst. It is noteworthy that the reaction rate also depends -in some cases, significantly- on the presence of impurities. Hence impurities such as traces of oil in the air, or from contact of the solution with metal should be avoided.

2. Computation of the degree of oxygen absorption

Mass transfer due to oxygen absorption followed by a very fast and irreversible chemical reaction will be interpreted by the film model, which assumes that transfer takes place in the steady state by molecular diffusion inside a liquid film of a constant thickness δ. Here, it can be assumed that (a) oxygen concentration in the liquid bulk is zero and (b) resistance to the transfer is entirely localized in the liquid film; therefore, oxygen concentration at the interface C_A^* is in equilibrium with its concentration in the gas bulk, that is:

$$C^*_A = p/He \tag{5}$$

For the fast reaction in the diffusion film (fast pseudo-mthorder reaction regime):

$$3 < \sqrt{M} << E_i \tag{6}$$

$$E = \sqrt{M} \tag{7}$$

then gas absorption rate per unit gas /liquid interfacial area is given by

$$R = Ek_L C_A^* = \sqrt{M}\, k_L C_A^* \tag{8}$$

where

$$\sqrt{M} = \frac{1}{k_L} \left(\frac{2}{m+1} D_A k_{mn} C_A^{*m-1} C_{Bo}^{\,n} \right)^{1/2} \tag{9}$$

Thus for catalytic oxidation of sulphite solutions, we obtain:

$$R = C_A^{*3/2} \left(\frac{2}{3} k_2 D_A \right)^{1/2} \tag{10}$$

or

$$R = K\, P^{3/2}\, y^{3/2} \tag{11}$$

where

$$K = \left(\frac{2\, k_2\, D_A}{3\, (He)^3} \right)^{1/2} \qquad (12)$$

Here K is a function of sulphite and cobalt concentrations, temperature, ionic strength and pH but does not depend on oxygen partial pressure (15,21).

The rate of absorption per unit area of interface is independent of the conditions of agitation, as represented by k_L; the conditions to be fulfilled are:

$$3 < \sqrt{D_A\, k_2\, C_A^*}/k_L \leqslant 1 + \left(\frac{D_B}{D_A} \right) \left(\frac{C_B}{2C_A^*} \right) \qquad (13)$$

Under these conditions, the interfacial area in a given reactor (in this case, a packed column) can be found by measuring the rate of absorption of 0_2 with the same partial pressure of 0_2, the same absorbent and the same temperature and pH, in laboratory equipment such as a falling film, laminar jet, or stirred vessel in which the interfacial area A_m is known. It is emphasized that exactly the same reactants must be used in both types of equipments, so that the influence of the catalyst and of trace impurities will be the same.

Eqn. (11) becomes inaccurate at 0_2 pressures above about 0.8 atm, because the reaction shifts from second-order to first-order as the pressure increases above this value. Alper (21) has observed first-order dependence on 0_2 pressure in the range from near 1 to 7 atm. Therefore, the air at atmospheric pressure was used.

A differential mass balance in a packed column gives:

$$d\,(Gy) = -\, Ra\, dh \qquad (14)$$

where G is given by the following mass balance on inerts:

$$G\,(1 - y) = G_i\,(1 - y_i) \qquad (15)$$

From equations (11), (14) and (15), one obtains:

$$aH = \frac{G_i\,(1-y_i)}{K\, P^{3/2}}\,(F\,(y_o) - F\,(y_i)) \qquad (16)$$

where

$$F(y) = \frac{2 - 3y}{(1-y)\sqrt{y}} - 1{,}5 \ln \left(\frac{1 + \sqrt{y}}{1 - \sqrt{y}}\right) \qquad (17)$$

Therefore a plot of $\frac{K\,P^{3/2}\,H}{G_i}$ against $F(y_o) - F(y_i)$ should yield the value of a. Here K was obtained each time by measuring the absorption rate and oxygen partial pressure in a stirred cell with known interfacial area using a sample from the inflowing solution, that is $K = R/p^{3/2}$.

3. Experimental set-up

Figure 1 shows the experimental set-up schematically. The packed column, used in this work (Q.V.F Ltd., England) is a 7.62 cm (3 in) inside diameter glass tube packed by glass Raschig rings (8.0x8.0x1.0 mm) to a height of 143 cm. Table 1 shows physical characteristics of Raschig rings used.

Table 1. Physical characteristic of Raschig rings.

Material	Size	Geometric surface area	Void fraction	Packing density	Packing factor
glass	mm	cm^2/cm^3	cm^3/cm^3	number/cm^3	cm^{-1}
	8x8x1.0	4.61	0.760	1.31	10.50

Figure 2 shows the stirred cell set-up which was similar to that described by Alper elsewhere (21). The ratio of column diameter to packing size was 9.5; therefore, it was thought that it would not be necessary to to use a distributor at the top of packing. Liquid and gas flowed countercurrently through the packing, the temperature of both fluids being close to 25 °C. The liquid was circulated in a closed loop by means of centrifugal pump. Before the liquid flow rate was measured by a rotameter, its temperature was controlled by a heat exchanger in which water from a thermostat at around 26 C° flowed and kept the reacting liquid temperature at 25 °C during the experiments. The liquid inlet and outlet temperatures were measured to keep the average temperature at 25 °C. The liquid level was adjusted by an overflow device so as to be immediately below the gas inlet. Air was blown into the bottom by means of a compressor. After its pressure was regulated to the atmospheric pressure, it was passed on an active coal filter and its flow rate

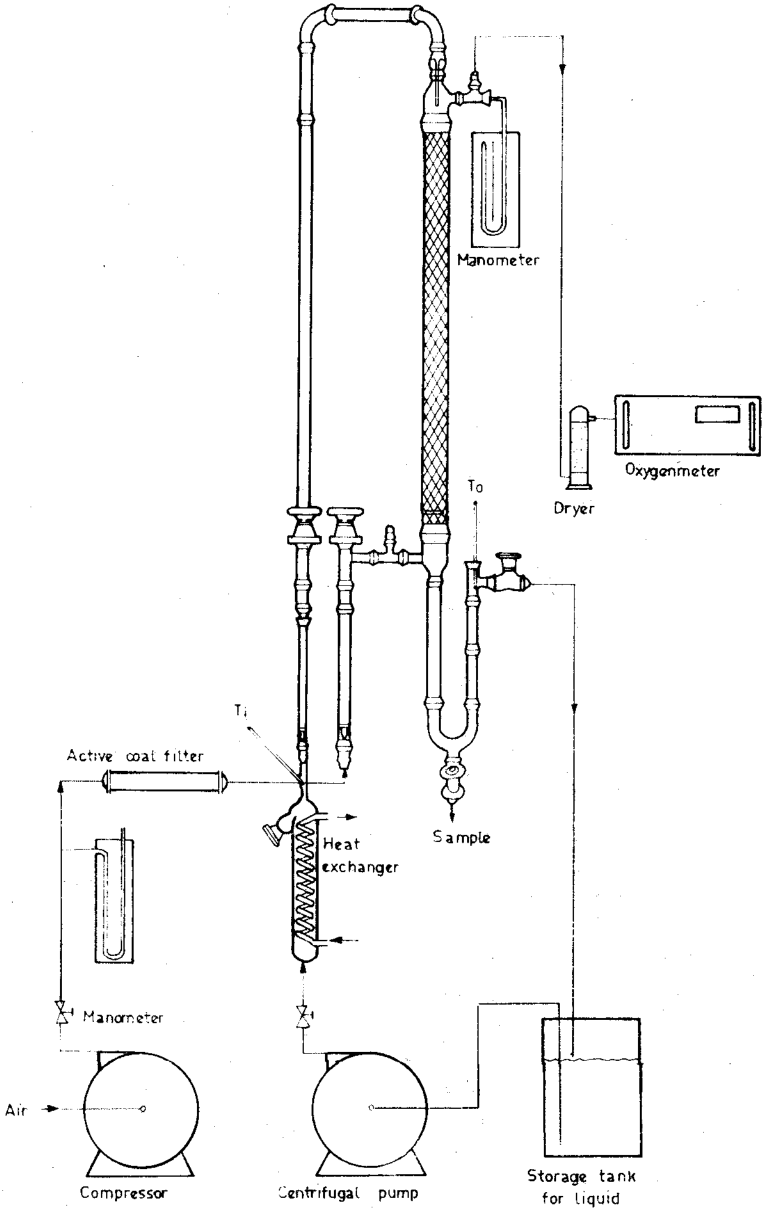

Fig. 1.: Experimental set-up

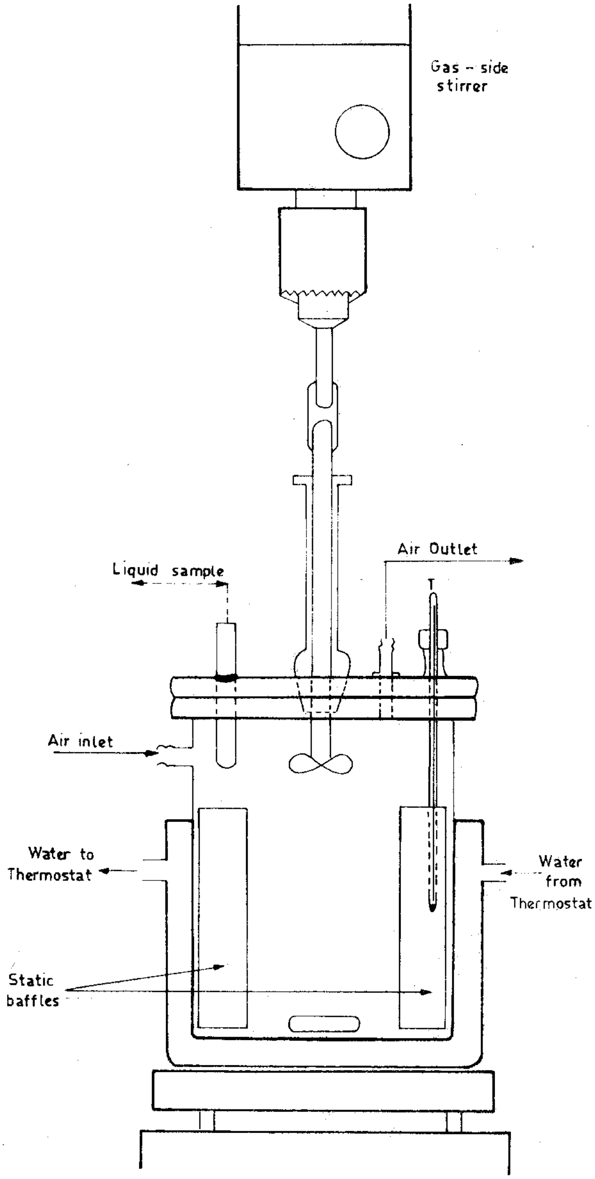

Fig. 2: Stirred cell set-up

was adjusted to the chosen value by means of a valve. The air and liquid flowrates were measured by rotameters and the concentration of oxygen was measured very conveniently by a paramagnetic oxygen meter (P.K. Morgan Ltd, England). Owing to the already mentioned influence of some metallic impurities on the reaction kinetics (20, 21), all parts in contact with the liquid were made of "Pyrex" glass, or of Teflon, or of plastic.

4. Experimental conditions

The absorbent was made up by using technical sodium sulphite and initial concentrations were 0.8 M $Na_2\ S0_3$ and 4×10^{-4} M $CoS0_4$. Any cobalt with a concentration higher than 10^{-3} M, formed a solid precipitate with the sulphite hence the concentration of $CoS0_4$ was kept well below this value. Total volume V_L of the liquid circulating in the loop was equal to about 15 l. Four series of runs were performed at different liquid kinematic viscosities and the value of the effective interfacial area at several values of the liquid flow rate (in the range of 0.2 – 0.6 cm/s) was obtained. The viscosity of the absorbing solutions was increased by adding different amounts of sugar which does not affect the chemical kinetics of the system (3). The viscosity of the absorbing solution was measured by an Ostwald viscosimeter. In the first set of data, the solutions used were 0.8 M Na_2S0_3 and 4×10^{-4} M $CoS0_4$. The kinematic viscosity of these solutions, at the temperature of the experiments was $\nu = 1.18 \times 10^{-2}$ cm^2/s. For the last three sets of experiments, different amounts of sugar were added to solutions prepared as above. The corresponding kinematic viscosities had the values of 1.56×10^{-2}, 1.83×10^{-2} and 1.87×10^{-2} cm^2/s.

EXPERIMENTAL RESULTS AND INTERPRETATION

Figure 3 and 4 show some typical experimental results which were plotted according to Eqn. (16).

Figure 5 which summarises the whole experimental data, shows that, the gas-liquid interfacial area "a" in packed columns is not strongly influenced by the liquid viscosity. As expected, interfacial area was found to be a strong function of liquid flow rate. Most effective interfacial area results could be correlated by a relationship of the form:

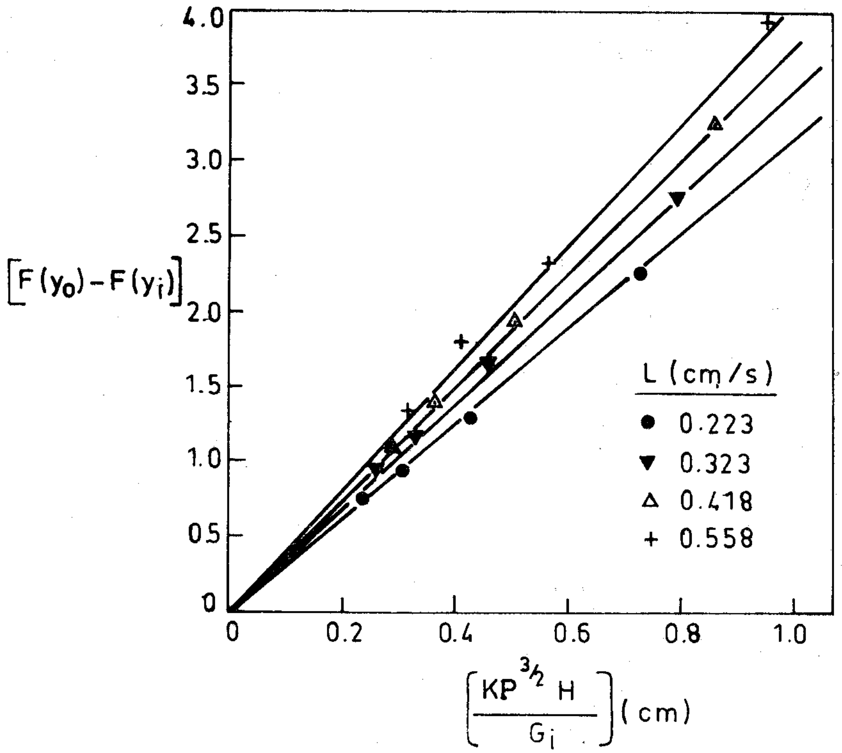

Fig. 3: Some typical experimental results

$$a = C.\ \nu^{x}\ .\ L^{y} \tag{18}$$

where ν is the liquid kinematic viscosity and L, the superficial liquid velocity. Here C, x and y were obtained by a regression analysis of experimental data which resulted:

$$a = 3.76\ \nu^{0.104}\ L^{0.256} \tag{19}$$

Eqn. (19) gives explicitly the dependence of the effective interfacial area on liquid kinematic viscosity and liquid flow rate, for packings employed in this work.

Rizzuti et. al. (14), contrary to this work, found that the liquid viscosity had a significant influence on the effective interfacial area, even larger than that of the liquid flow rate, and correlated their data

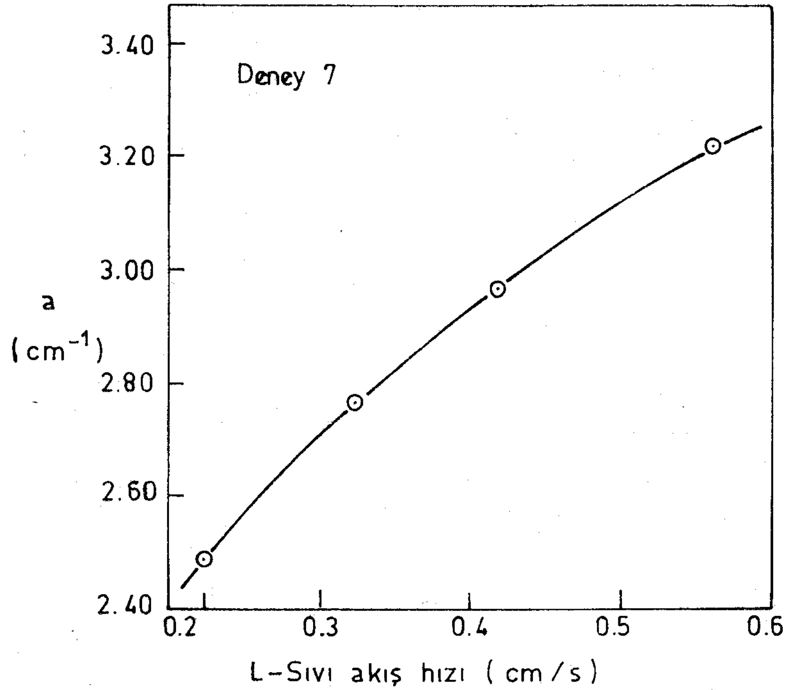

Fig. 4: Effective interfacial area as function of superficial liquid velocity according to Fig. 3.

by Eqn. (1). One important drawback of their experiments was that the ratio of column diameter to that of packing was unfortunately less than 4. This implies that the maldistributed flow pattern was established, that is the proportion of liquid flowing down the wall was excessive. The values of "a" given in literature were generally obtained using ratios of column to particle diameter of 8–10 (2), and our system was in this range. Recently, Alper (22) has measured the interfacial areas by using sulphite oxidation method in the absence and presence of CMC and found that the interfacial area increases considerably by adding CMC, the effect being much less at high liquid flow rates. He believed however, that further work was needed in this area which involves other less complicated viscosity increasers.

In this work, it was observed that the interfacial area increases slightly by adding sugar, the effect being 7 % at maximum at high li-

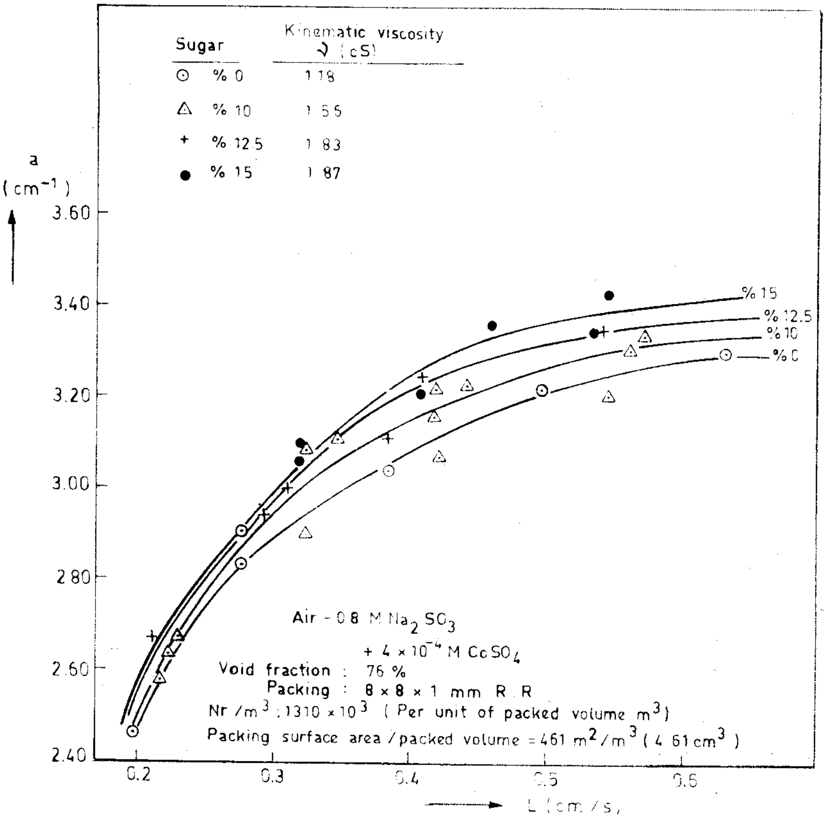

Fig. 5: Effective interfacial area as function of superficial liquid velocity and kinematic viscosity.

quid flowrates. It was considered that this increase at high liquid flow rates could be due to better wettability and the increase of the thickness of the liquid film flowing over the packing.

Experimental results were also interpreted in terms of the most general formulas proposed for correlating interfacial areas in the countercurrent packed colums. This included those of Onda et. al. (23) and Puranik and Vogelpohl (24) which show that the gas-liquid interfacial area is a strong function of liquid surface tension (σ) and critical surface tension, but only a weak function of liquid viscosity and density. Results of this work support the same conclusion; that is, since the surface tension of Na_2S0_3 solution did not change noticeably when sugar was added, its effect remained the same for all solutions.

In the measurement of effective interfacial area, here the determination of K values caused maximum discrepancies. In order to minimise this effect, two sets of experiments were performed for each solution and also an another method was used to evaluate "K" (see, Appendix). This second method was found to be more reliable and formed the basis of evaluation here.

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APPENDIX

K values cause maximum error on the effective interfacial area measurements; hence another methods were also used in order to reach a conclusion. Since the sample which was taken from outflowing stream does not represent the whole column, average sulfite concentration $\left(\frac{C_i + C_o}{2}\right)$ was estimated at the time that sample was taken from the column and plotted versus the time spent in the column.

From mass balance:

$$\frac{L}{2} (C_i - C_o) = G_i y_i - G_o y_o \tag{20}$$

$$C_i - C_o = \frac{2 (G_i y_i - G_o y_o)}{L} \tag{21}$$

mass balance on inerts yields:

$$G_i (1 - y_i) = G_o (1 - y_o) \tag{22}$$

and from eqn. (21):

$$C_i - C_o = \frac{2\,G_i y_i \left(1 - \dfrac{(1-y_i)y_o}{(1-y_o)y_i}\right)}{L} \qquad (23)$$

From eqn. (23), $\left(\frac{C_i + C_o}{2}\right)$ was calculated and plotted against time. Then, K values were plotted versus the final concentration of sodium sulphite in the stirred cell. Since the time in the column for each experiment was known from the graph of $\left(\frac{C_i + C_o}{2}\right)$ versus t, average concentration and K values corresponding to this average sulphite concentration were obtained. This value was used to calculate $KP^{3/2}\,H/G_i$ to be used in the analysis.

ÖZET

8x8x1 mm cam Raschig halkalarıyla doldurulmuş camdan gaz absorpsiyon kolonunda etkin gaz-sıvı arayüzey alanı; kimyasal reaksiyonlu gaz absorpsiyonu deneylerinden, çok kullanılan "Co^{+2} katalizörü içeren Na_2SO_3 çözeltisinin oksidasyon" yöntemiyle; sıvı akış hızının 0.1 – 0.6 cm/s, sıvı kinematik viskozitesinin 1.18 – 1.87 cm^2/s aralığında ölçülmüştür. Amaç Na_2SO_3 çözeltilerine değişik miktarlarda şeker ilavesiyle viskoziteyi artırarak etkin gaz-sıvı arayüzey alanına sıvı viskozitesi etkisini deneysel olarak incelemek olmuştur.

Etkin gaz-sıvı arayüzey alanındaki artış, yüksek sıvı akış hızlarında en fazla % 7 olmuştur. Düşük sıvı akış hızlarında etkin gaz-sıvı arayüzey alanı "a" nın viskozite ile hissedilebilir bir biçimde değişmediği görülmüştür. Sıvı akış hızı ve sıvı viskozitesinin fonksiyonu olarak; ölçülen "a" değerlerinin regresyon analizi ile;

$$a = 3.76\ \nu^{0.104}\ L^{0.256}$$

eşitliğine uyduğu bulunmuştur.

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