

충전된 가스흡수탑 내의 유효물질 전달면적과 물질 전달 계수

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Effective Mass Transfer Area and Mass Transfer Coefficient in a Packed Gas-Absorber

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요 약

충전된 가스흡수 탑내에서의 유효 경제면적과 액측 물질전달 계수를 결정하기 위해서 비가역 일차 반응을 일으키는 흡수 계에 대해서 관찰하였다. 흡수탑에는 여러가지 다른 모양과 크기의 충전물을 충전시키고, 또 액체의 종류와 성질을 여러가지로 바꿔서 실험을 하여 이들의 변수가 유효경제 면적과 액측 물질전달계수에 미치는 영향을 고찰하였다. 이들 시험결과를 분석하여 무차원군 사이의 상관식을 얻었으며, 그 상관식은 다른 연구 결과에도 잘 적용됨을 알았다.

ABSTRACT

Chemical absorption with irreversible first order reaction was used to determine the effective interfacial area and the liquid-side mass transfer coefficient in a packed gas-absorber. Experiments were undertaken for packings of different shapes and sizes and for several kinds of liquid with various properties so that their effects on the effective interfacial area and the liquid-side mass transfer coefficient are observed. Correlations were obtained in terms of dimensionless groups through the regression analysis

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of the experimental results. The results of this work were compared with the other results, and a good agreement was observed.

I. Introduction

Solid packing is the most important part in gas absorption using a packed column, because its dry surface area and geometry have close relation to effective absorption area and mass transfer coefficient. Usually the packing provides a large effective absorption area and increases mass transfer coefficient. Also it is known that the properties of liquid flowing in the column affect effective absorption area and mass transfer coefficient.

There are two methods measuring the effective interfacial area in a packed column, and they are physical and chemical method. In the physical method, as an indirect method, the effective interfacial area is calculated from volumetric mass transfer coefficient by using the mass transfer coefficient which is calculated from the known correlation or measured in test column filled with the same solid packings.

Sharma and Danckwerts¹²⁾ summarized the chemical methods to measure the effective interfacial area and the mass transfer coefficient in packed columns. Sahay and Sharma¹¹⁾ measured the effective interfacial areas of various packings by the different chemical methods and found that highest values are offered by stainless steel Pall rings. Puranik and Vogelpohl⁹⁾ gathered experimental results on the effective interfacial area and obtained the correlation pre-

dicting the effective interfacial area from liquid properties and packing size. Chemical method using Danckwerts plot is frequently used to measure mass transfer coefficient in packed columns.

The countercurrent flow system where CO₂ gas diluted in air was absorbed by water flowing downwardly in a packed column, was used in this study. The effective interfacial areas and the liquid-side mass transfer coefficient were correlated with a variety of factors influencing them by using regression analysis. From the analysis the specific dimensionless groups which characterize the effect of the type, size, and material of packing and liquid properties were made. Secondary regression analysis between dimensionless effective interfacial area or liquid-side mass transfer coefficient and the above dimensionless groups led to the dimensionless correlations which could be used to design the packed columns, to enhance the performance of them, and to develop the new packing material.

II. Theoretical Background

Provided that the reaction between the gas absorbed in the liquid film flowing on solid packing and the reactant in liquid bulk is an irreversible first order reaction, the diffusion equation is

$$\frac{\partial a}{\partial t} = D_A \frac{\partial^2 a}{\partial x^2} + k_1 a \quad (1)$$

and its initial and boundary conditions are

$$a = 0, \quad x > 0, \quad t = 0$$

$$a = A^*, \quad x = 0, \quad t > 0 \quad (2)$$

$$a = 0, \quad x = \infty, \quad t > 0$$

The solution obtained by using Laplace transformation is

$$\bar{a} = A^* \exp \left[- \left(\sqrt{\frac{(s + k_1)}{D_A}} \right) x \right] \quad (3)$$

The average rate of absorption per unit absorption area in Danckwerts model is

$$\begin{aligned} \bar{R} &= s \int_0^\infty R e^{-s\theta} d\theta \\ &= -D_A \left(\frac{d\bar{a}}{dx} \right)_{x=0} \end{aligned} \quad (4)$$

Average absorption rate, \bar{R} is derived from Eq. (3) and the relation between mass transfer coefficient and fractional rate of surface renewal, s in physical absorption.⁴⁾

$$\bar{R} = A^* \sqrt{(k_L^2 + D_A k_1)} \quad (5)$$

Multiplying the effective interfacial area per

unit volume, a_e , we obtain

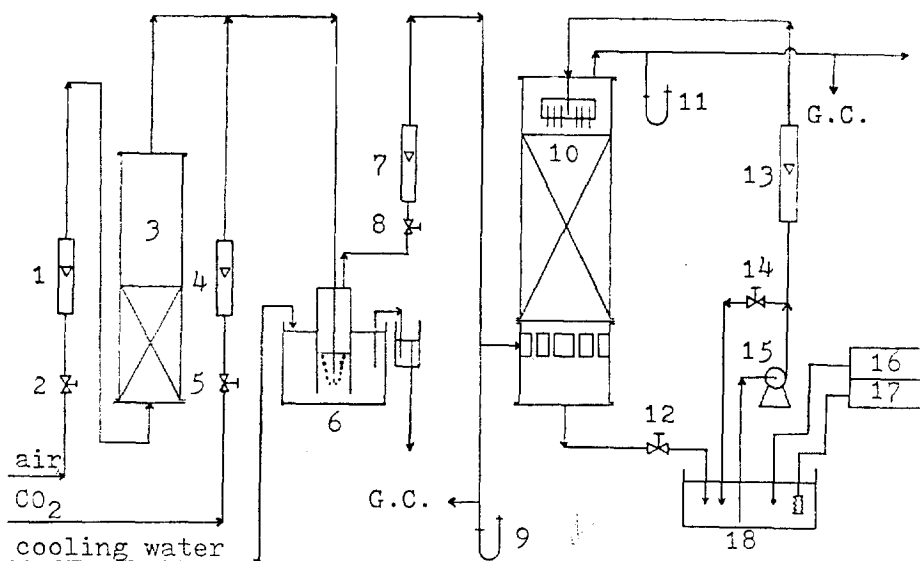
$$\left(\frac{\bar{R} a_e}{A^* \sqrt{D_A}} \right)^2 = a_e^2 k_1 + \frac{a_e^2 k_L^2}{D_A} \quad (6)$$

By plotting the first order reaction rate constant, k_1 , vs. $\left(\frac{\bar{R} a_e}{A^* \sqrt{D_A}} \right)^2$, which is Danckwerts plot, the effective interfacial area and liquid-side mass transfer coefficient were found from the slope and intercept of the plot, respectively.

Pohorecki³⁾ obtained the rate equation of the reaction with absorbed carbon dioxide occurring in the liquid bulk of carbonate-bicarbonate buffer solution.

$$r = k_1 [\text{CO}_2] = k_{\text{OC1}} - [\text{OC1}^-] [\text{CO}_2] \quad (7)$$

where the catalytic reaction rate constant, k_{OC1} depends only on buffer ratio in isothermal system.



1. air flow meter
2. air valve
3. air scrubber
4. CO₂ flowmeter
5. CO₂ valve
6. inlet gas temperature control & water saturator
7. inlet gas flowmeter
8. inlet gas valve
9. inlet gas manometer

10. packed column
11. outlet gas manometer
12. outlet liquid valve
13. inlet liquid flowmeter
14. liquid bypass valve
15. liquid pump
16. liquid temperature controller
17. liquid cooler
18. liquid reservoir

Fig. 1. Experimental Apparatus

$$k_{OC1} = 1518 + 1381 \frac{[\text{CO}_3^{--}]}{[\text{HCO}_3^-]} \quad (8)$$

III. Experiment

(1) Experimental Apparatus

The experimental set-up is shown in *Fig. 1*. The transparent column of methyl methacrylate was used in the experiment because it was durable in corrosive liquid and it was easy to observe the inside liquid flow and to measure packing height. The nominal size of column was 5-in. diameter and its actual inside diameter was about 12 cm. Thus the wall effect in the column could be avoided because the column diameter was more than 8 times of packing size.¹³⁾ The height of packed bed was 50 cm. to refer Danckwerts and Gillham's result.³⁾ The immersion type of P.V.C. pump was used to deliver liquid into the top of the column, and stainless immersion cooler and a heater with controller were used to control the liquid temperature.

Two manometers filled with water installed each at the top and bottom of the column, and the pressure drop through the column was measured to monitor the operating condition of the column.

(2) Experimental Procedure

Solid packings used in the experiment were 8 different kinds; 3/8-in. and 1/2-in. in nominal size; sphere and center-holed cube in shape; ceramic and polypropylene in material. A pneumatic control valve and a surge tank were equipped at the inlet of air stream, and the roughly controlled air pressure was again smoothened by a line pressure regulator. Referred to *Fig. 1*, the flow rate of air was controlled and measured with the air valve [2] and the flowmeter [1], respectively.

Table 1. Operating conditions

[K ₂ CO ₃]	0.60~0.45 g-mol/l
[KHCO ₃]	0.25~0.55 g-mol/l
[KCl]	1.95±0.05 g-mol/l
[NaOCl]	0.02~0.14 g-mol/l
Packed height	50 cm
Liquid viscosity	1.4~3.8 c.p.
Liquid density	1.18~1.19 g/cm ³
Liquid surface tension	34.7~58.4 dyne/cm
volumetric gas velocity	390 cm ³ /sec
Superficial liquid velocity	0.3~0.7 cm/sec
Gas temperature	22.0±1.0 °C
Liquid temperature	21.0±0.5 °C
Inlet gas pressure	1.00 atm
CO ₂ partial pressure(inlet)	0.05 atm.

ively. In the air scrubber [3] dust and the minor components, which could dissolve in liquid solution, contained in air were withdrawn by dissolving in 0.5 N-sodium hydroxide solution. Another gas, carbon dioxide, was provided from a liquefied carbon dioxide cylinder, and controlled in flow rate with flowmeter [4] and valve [5]. Air mixed with carbon dioxide in 5 volume percent was saturated with water and was maintained at 21°C in the water saturator [6]. Before gas went into the bottom of the column, the carbon dioxide content in gas stream was checked with a gas chromatograph and an Orsat gas analyzer. The carbon dioxide content of exhausted gas from the top of the column was also measured, so the average absorption rate per unit volume of the column was calculated from the difference between the contents of carbon dioxide at the bottom and top of the column.

The reservoir [18] contained 7 liters of liquid solution, and liquid temperature was controlled at 21°C in advance with the temperature controller [16] and the immersion cooler [17]. A required portion of the liquid

pumped by the circulation pump [15] was delivered to the top of the column, and the rest was recycled to the reservoir. From the top of the column liquid dispersed on the solid packing through a liquid distributor. The liquid collected at the bottom was discharged, and the liquid was maintained at constant level so that it could prevent gas from escaping with liquid.

Carboxy methyl cellulose sodium salt was used to obtain the liquid of different viscosity, and surfactant Triton X-100 was used for the different surface tension of liquid solution.

The operating conditions for the experiments were listed in Table 1.

IV. Results and Discussion

Effective interfacial area and liquid-side mass transfer coefficient were obtained by plotting the average absorption rate with

different reaction rate constant as predicted from Eq. (6). The Danckwerts plots were obtained for various shapes and sizes of the packing materials(8 different kinds) from the experimental data. Fig. 2 and Fig. 3 are the examples of these plots.

Nominal size, dry surface area per unit volume of the column, and void fraction of each packing were related to the geometrical shape of solid packing. The critical surface tension of packing material was used to characterize the effect of material on the performance of the packed column. And the physical properties of liquid, i.e., viscosity and surface tension, were used as variables. The superficial liquid flow rate was also included as a variable.

The effects of these variables on effective interfacial area and liquid-side mass transfer coefficient were found from the regression analysis using matrix composed of experimental results. In case of effective interfacial

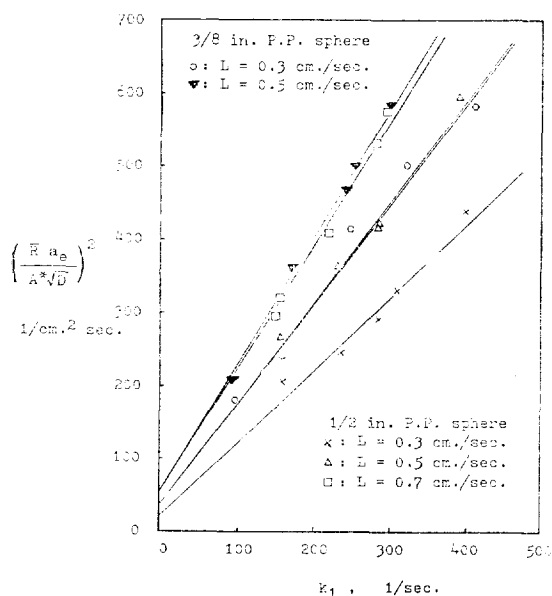


Fig. 2. Danckwerts plots for polypropylene sphere at various liquid flow rates

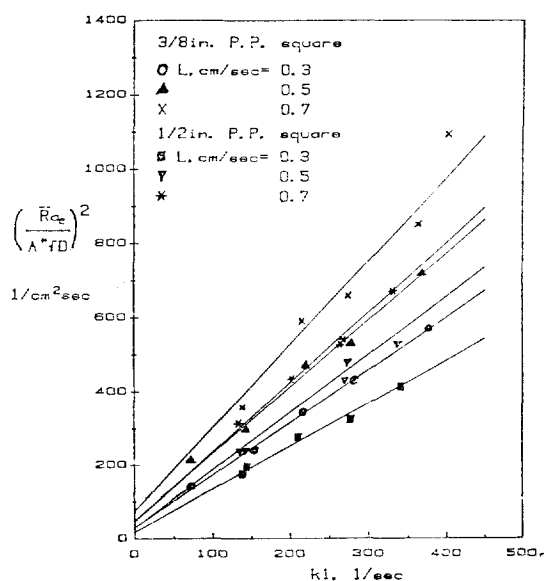


Fig. 3. Danckwerts plots for polypropylene square at various liquid flow rates.

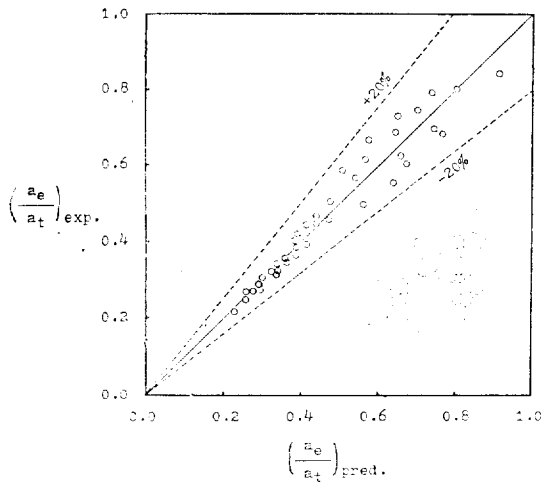


Fig. 4. Comparison of predicted values vs. experimental data of effective interfacial area.

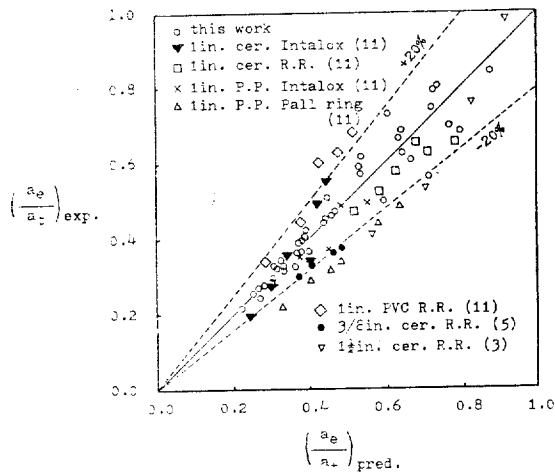


Fig. 5. Comparison of values predicted with dimensionless groups vs. experimental data of effective interfacial area.

area, it was found that

$$\frac{a_e}{a_t} = 0.826 L^{0.25} (1 - \epsilon)^{-0.43} a_t^{-1.38} D_p^{-1.03} \sigma_c^{1.04} \mu^{0.38} \sigma^{-0.28} \quad (9)$$

Considering the property and exponent of each variable and using the critical surface tension of glass as a reference critical surface tension, three dimensionless groups were formed. The effect of each group was obta-

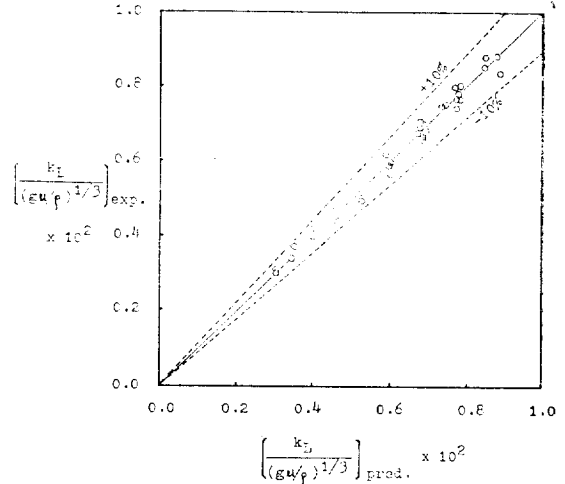


Fig. 6. Comparison of predicted values vs. experimental data of liquid-side mass transfer coefficient.

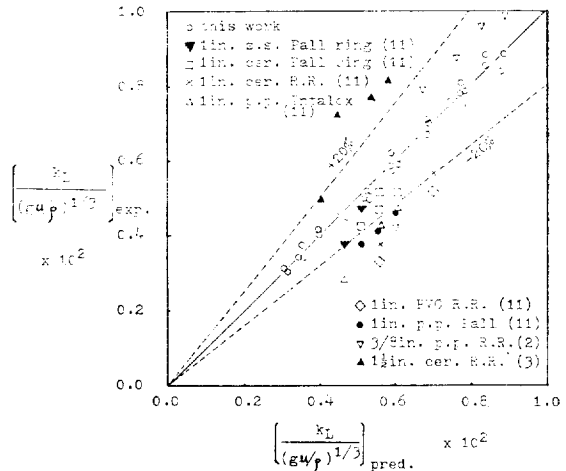


Fig. 7. Comparison of values predicted with dimensionless groups vs. experimental data of liquid-side mass transfer coefficient.

ined by regression analysis in the following form.

$$\frac{a_e}{a_t} = 1.69 \times 10^2 \left(\frac{L\mu}{\sigma} \right)^{0.35} \left(\frac{\sigma_c}{\sigma_{cr}} \right)^{1.03} [a_t D_p (1 - \epsilon)^{1/3}]^{-1.88} \quad (10)$$

Similarly, the relation between dimensionless liquid-side mass transfer coefficient and each variable was obtained.

$$\frac{k_L}{(g\mu/\rho)^{1/3}} = 7.77 \times 10^{-4} L^{0.25} (1-\epsilon)^{0.09} a_t^{-0.29} D_p^{-0.78} \sigma_c^{-0.03} \mu^{-0.73} \sigma^{0.01} \quad (11)$$

This relation shows that the effects of critical surface tension and liquid surface tension on liquid-side mass transfer coefficient are negligible. In the secondary regression the dependence of liquid-side mass transfer coefficient upon the dimensionless groups, which were composed by omitting above two variables, and considering the characteristics and exponent of each variable, was obtained.

$$\frac{k_L}{(g\mu/\rho)^{1/3}} = 9.17 \times 10^{-4} \left(\frac{L\rho}{a_t\mu} \right)^{0.24} \left(\frac{\sigma_{cr}}{\rho g^2 \mu^2 D_p^3} \right)^{0.24} [a_t D_p / (1-\epsilon)^2]^{-0.05} \quad (12)$$

The effective interfacial area calculated from Eq. (9) and the experimental values were compared in Fig. 4. And the effective interfacial area predicted from Eq. (10) and experimental values in this study, Sahay and Sharma,¹¹⁾ Jhaveri and Sharma,⁵⁾ and Danckwerts and Gillham³⁾ in different packings and liquid properties, were plotted in Fig. 5 to check the validity of Eq. (10).

In the same manner, the liquid-side mass transfer coefficient predicted from Eq. (11) and the experimental data of this work were compared in Fig. 6, and the value predicted from Eq. (12) and the experimental data of this work, Sahay and Sharma,¹¹⁾ Chang,²⁾ and Danckwerts and Gillham³⁾ were also compared in Fig. 7.

Puranik and Vogelpohl⁹⁾'s correlation, which is often used to predict the effective interfacial area of packed columns, specifies only the dry surface area of solid packing per unit volume as the factor to describe the geometrical shape of packings, but, as shown in Eq. (9), the effects of the nominal size and void fraction of packings are not

negligible. Therefore, it is rational that all of them are treated as the geometrical shape factor.

While the effective interfacial area in chemical absorption has approximately same value with wetted area, they are quite different from the effective interfacial area in physical absorption. The reason for the difference is that the fraction of semi-stagnant liquid pool and thin liquid film in total liquid hold-up is considerable, and the liquid surface in these regions is very quickly saturated with gas and loses the ability to absorb gas when gas is absorbed physically.^{6),9)} On the other hand, saturation is not obtained in most of chemical absorption.

The effective interfacial area in physical and chemical absorption and wetted area are plotted at various liquid flow rates in Fig. 8, and they are compared one another. In the figure, the effective interfacial area in physical absorption was Yoshida and Koyanaki¹⁴⁾'s experimental result, that in chemical absorption was calculated from Eq. (10), and wetted area was calculated from the correlation of Onda et al.⁷⁾ The fact that effective interfacial area increases with liquid viscosity increases as shown in Eq. (9), supports the above explanation.

The area in semi-stagnant pool and thin liquid film is effective to absorb gas when absorption capacity increases by chemical reaction. When absorption rate, however, increases, these regions are soon saturated and are no longer effective. Joosten and Danckwerts⁵⁾ proved it with the experimental result of the chemical absorption having instantaneous reaction, and defined Danckwerts parameter, ξ , as the ratio of absorption capacity to absorption rate. They claimed that, if Danckwerts parameter is much hi-

gher than unity, the area in semi-stagnant pool and thin liquid film is effective in gas absorption.

Puranik and Vogelpohl⁹⁾ defined a kinesic factor to calculate the gas absorption effectiveness of the area of semi-stagnant pool and thin liquid film in the intermediate case having moderately high Danckwerts parameter. Baldi and Sicardi¹⁾ found that the effective interfacial area of their experiment was different from that of Richards et al.¹⁰⁾ and Joosten and Danckwerts,⁶⁾ even though they used the same packing and similar absorbent, and they said that it was impossible to explain the difference only with the kinetic factor.

In this study Danckwerts parameter was more than 63, and it was reasonable that there was the difference between the effective interfacial areas in physical and chemical absorption as shown in Fig. 8.

Because liquid-side mass transfer coefficient is effected only by the hydrodynamic condition of liquid stream, the geometry of packings and liquid flow rate have strong influence on it as Eq. (11) represents.

V. Conclusions

The information on effective interfacial area and mass transfer coefficient is very important in packed columns, owing to its usefulness in the design and the performance prediction, but the determination or estimation of them is difficult.

The chemical method based on the Danckwert's surface renewal model was used to measure effective interfacial area and liquid-side mass transfer coefficient with varying major variables affected on them. The de-

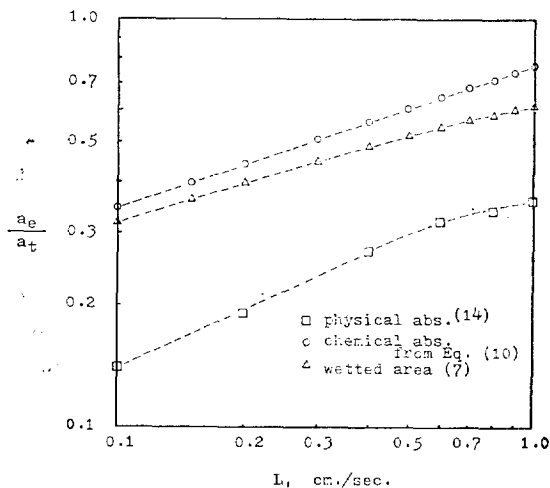


Fig. 8. Effective interfacial area changes in physical and chemical absorption and wetted area by superficial liquid velocity

pendences of them upon each variable were calculated by using regression analysis, and the dimensionless groups were composed by considering the property and exponent of each variable.

The correlation on the normalized effective interfacial area and dimensionless groups was obtained by regression analysis, and it was

$$\frac{a_e}{a_t} = 1.69 \times 10^2 \left(\frac{L_t \mu}{\sigma} \right)^{0.35} \left(\frac{\sigma_c}{\sigma_{cr}} \right)^{1.03} [a_t D_p (1 - \epsilon)^{1/3}]^{-1.88}$$

The first group of the right hand side of above correlation represents operation condition of the column and liquid properties; the second group represents the material of solid packing; the third group represents the geometrical shape of packing.

As for liquid-side mass transfer coefficient, it was obtained

$$\frac{k_L}{(g\mu/\rho)^{1/3}} = 9.17 \times 10^{-4} \left(\frac{L_t \rho}{a_t \mu} \right)^{0.24} \left(\frac{\sigma_{cr}^3}{g^2 \mu^2 D_p^3} \right)^{0.24} [a_t D_p / (1 - \epsilon)^2]^{-0.05}$$

The first group of the right hand side represents the operating condition and the second and third groups represent liquid property and the geometrical shape of packing, respectively.

Nomenclature

- a concentration of dissolved gas A, g-mol/cm³
 \bar{a} Laplace transformation of a
 a_e effective interfacial area per unit packed volume, cm⁻¹
 a_t dry surface area per unit volume, cm⁻¹
 A^* concentration of dissolved gas A at interface, in equilibrium with gas at interface, g-mol/cm³
 D_A diffusivity of dissolved gas A, cm²/sec.
 D_p nominal size of the packing, cm
 ϵ void fraction of the packing
 g gravitational acceleration, cm/sec.²
 k_1 first order reaction rate constant, sec.⁻¹
 k_L liquid-side mass transfer coefficient, cm/sec.
 k_{oc1} catalytic rate constant, 1/g-mol. sec.
 L superficial velocity of liquid, cm/sec.
 R rate of absorption per unit area of surface after contact time, g-mol/cm². sec.
 r reaction rate, g-mol/l. sec.
 \bar{R} average rate of absorption over contact time, g-mol/cm². sec.
 s fractional rate of surface renewal, sec.⁻¹
 t time, sec.
 x distance beneath liquid surface, cm

Greek Symbols

- θ time of exposure of liquid to gas, sec.
 μ viscosity of liquid, g/cm. sec.

- ξ Danckwerts parameter
 ρ density of liquid, g/cm³
 σ surface tension of liquid, dyne/cm
 σ_c critical surface tension of the packing material, dyne/cm
 σ_{cr} reference critical surface tension, critical surface tension of glass, dyne/cm

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