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EVALUATION OF GAS PHASE MASS TRANSFER AT LOW REYNOLDS NUMBERS: A NEW MODEL SYSTEM†

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A new experimental system is presented which is suitable for studying gas side mass transfer coefficients in packed columns at Reynolds numbers even lower than 1.0. The system involves desorption of iodine from aqueous KI solutions. The reversible complex formation between iodine and iodine ions effectively slows down the concentration changes which otherwise would be too rapid for accurate experimentation.

KEYWORDS Mass transfer iodine absorption static hold-up packed column absorption with reaction low Reynolds number

INTRODUCTION

The liquid hold-up in a packed absorption column operated in the trickle flow regime consists of two parts, i.e. the dynamic hold-up and the static hold-up. Both of them have gas-liquid interfacial areas associated with them. There is also a slow exchange of liquid between the volumes of liquid held up in these two regions. These ideas have been used for quantitatively explaining the experimentally observed differences between the effective interfacial areas for different mass transfer operations, with or without chemical reaction [1–4]. Knowledge of several parameters associated with the static regions of liquid is essential for this purpose. The static hold-up for various packings has been reported extensively in literature. The interchange between dynamic and static hold-ups has been studied for some common packings [5–7]. No experimental data have been reported so far, as regards the interfacial area of the static hold-up. In this study we present a new method which has been used for determining the ($k_G a$) values for the static hold-up. This method is based on the desorption of iodine from aqueous solutions of potassium iodide from the static hold-up in a packed column. The ($k_G a$) values thus obtained can be used in conjunction with k_G values (for which standard procedures have been reported, involving methods like sublimation of naphthalene from coated packing pieces [8]) for determining the interfacial area of the static hold-up.

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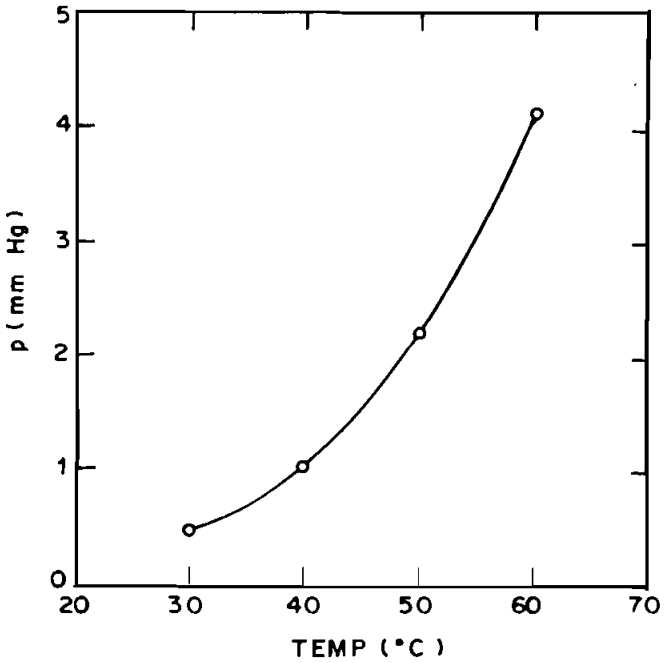

FIGURE 1 Vapour pressure of solid iodine [13].

Dissolution of Iodine in Water and Potassium Iodide Solutions

Solid iodine is known to sublime easily. The vapor pressure of solid iodine is shown in Figure 1. Iodine has only low solubility in water at ordinary temperatures, as seen from Figure 2. On dissolution, iodine hydrolyses according to the following reaction

$$I_2 + H_2O \rightleftharpoons HIO + H^+ + I^- \quad (1)$$

The equilibrium constant for this reaction is 4.6×10^{-3} mole^2/lit^2 at 25°C, which is so low [9] that this reaction can be neglected for the present purpose. The solubility of iodine in water is very significantly enhanced by addition of small amounts of potassium iodide to the solution, as seen from Figure 3. This enhancement is due to the following reaction

$$I_2 + I^- \rightleftharpoons I_3^- \quad (2)$$

The equilibrium constant for this reaction is 1.35×10^{-3} moles/lit at 25°C; potassium iodide thus complexes with I_2 thereby reducing the concentration of free iodine in solution. Figure 4 clearly shows this effect for solutions containing 11.0 gm/liter of KI, which is the concentration used in this study. Iodine solutions exposed to atmosphere quickly lose dissolved iodine through desorption. However, solutions to which KI has been added, retain iodine for a much longer period. The reason for this qualitative observation lies in reaction (2) which reduces the free iodine concentration and results in lower desorption rates.

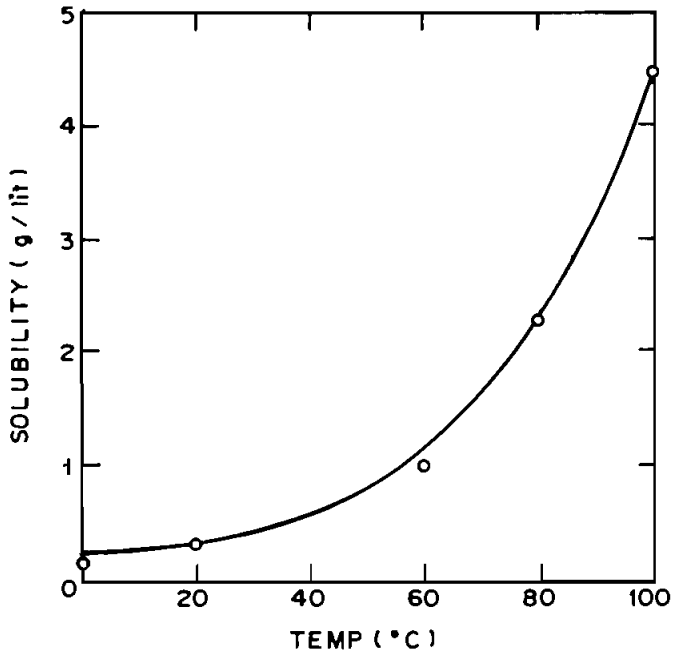

FIGURE 2 Iodine solubility in water [13].

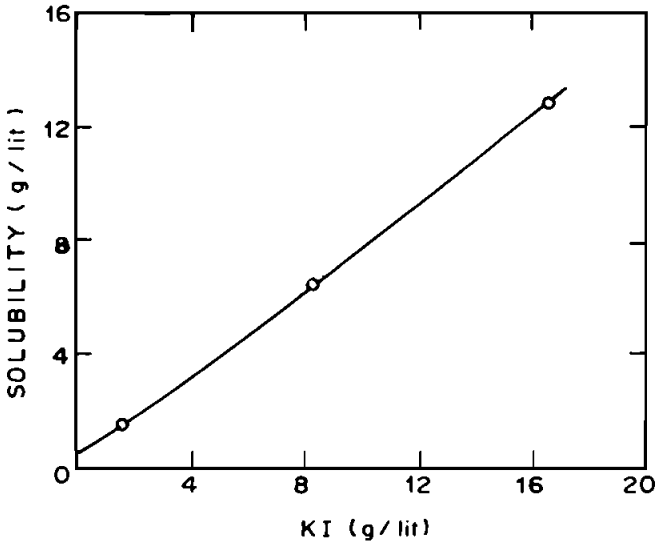

FIGURE 3 Iodine solubility in aqueous KI solutions at 25°C.

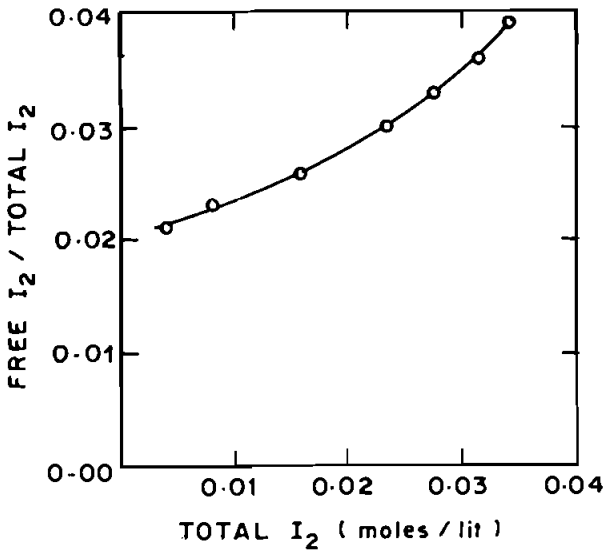

FIGURE 4 Concentration of free iodine in aqueous 11.0 g/liter KI solutions at 25°C.

Experimental The experimental set up consists of a cylindrical glass column, 10.0 cm in diameter and 7.4 cm in height, packed with 1.25 cm ceramic raschig rings. It was filled completely with an aqueous solution containing 11.0 gm/liter of KI and approximately 1.0 gm/liter of total iodine. The column was drained fully and flow of nitrogen saturated with moisture, at the desired rate, was started through the column. The column was not irrigated with liquid during the experiments. The outcoming gases were bubbleed through two consecutive bubblers through spargers. The bubblers were filled with 5.5 percent aqueous formaldehyde solution, whose pH was adjusted to 8.5 with sodium hydroxide. Periodic samples were drawn from each bubbler, and the total iodine absorption was calculated at various times by standard analytical procedures involving ion-selective electrodes [10].

RESULTS AND DISCUSSION

The total iodine desorbed from the column as a function of time was calculated from the analysis of the bubbler contents at regular intervals and is shown for different N_2 gas flow rates in Figure 5.

Controlling mass transfer resistance Since most of the iodine in the liquid phase is present as I_3^-, the chemical reaction given by Eq. (2) plays an important role in the desorption of iodine from such solutions. A local equilibrium can be assumed to exist between I_2, I^- and I_3^- everywhere since the reaction involves ionic species. Mass transfer with a chemical reaction of this kind has been treated by

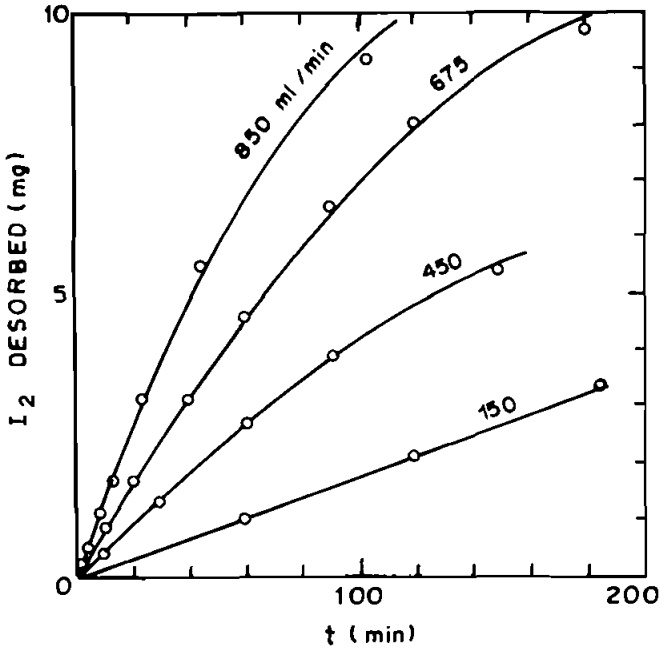

FIGURE 5 Total desorbed iodine as a function of time for different nitrogen flow rates.

Olander [11] whose results give the desorption rate to be

$$\bar{R} = k_L(A_b - A_i)\left[1 + \frac{D_B d_P B_b}{D_A(A_i D_P + K D_B)}\right] \tag{3}$$

where A, B and P refer to I_2, I^- and I_3^- respectively and K is the equilibrium constant given by

$$K = \frac{AB}{P} \tag{4}$$

Consider the run corresponding to a nitrogen flow rate of 850 ml/min. The total iodine concentration at the beginning in the liquid phase was 0.856 g/lit which corresponds to 7.083×10^{-5} moles/lit free iodine. The k_L value is not known. However, taking the very low value of $k_L = 10^{-4}$ cm/s (corresponding to a surface element life of the order of 2 minutes), $\bar{R}_t = 0.12$ mg/min (which is the maximum for this run), $A_b = 7.083 \times 10^{-5}$ moles/lit, $B_b = 6.63 \times 10^{-2}$ moles/lit, $K = 1.35 \times 10^{-3}$ moles/lit, and taking all diffusivities to be equal as a first approximation, Eq. (3) gives $A_i = 6.61 \times 10^{-5}$ moles/lit. This is within 7 percent of A_b. In other words, the driving force exists mainly in the gas phase. Considering the conservative values of $\bar{R}_t$ and k_L used here, the desorption of iodine from potassium iodide solutions reported here can be assumed to be gas-phase controlled. To reduce the liquid phase resistance further, one could use more concentrated KI solutions or use some polymeric additives which complex reversibly and very strongly with I_3^-. This is discussed again later.

TABLE I

Experimental conditions and results

NO.	Nitrogen flow rate (ml/min)	Initial total iodine (g/lit)	k_Ga (moles/cm^3. atm. S)	*Re*
1	850	0.856	9.30×10^{-7}	1.615
2	675	0.927	6.31×10^{-7}	1.283
3	450	0.736	3.38×10^{-7}	0.855
4	150	0.976	9.25×10^{-8}	0.285

Consider a packed column where the liquid phase concentration of I_2 is uniform throughout. Let the iodine content of the gas phase be zero at the inlet. The outlet partial pressure of iodine is then given by the following equation:

$$p_{out} = p^*[1-\exp(-k_GaP_tL/V)] \quad (5)$$

Let us consider the experimental run corresponding to a flow rate of 850 ml/min. The initial desorption rate of iodine was 0.12 mg/min which gives $p_{out} = 9.45 \times 10^{-3}$ mm Hg. Since the solubility of iodine in KI solutions used in this work is 8.7 g/lit at 25°C, the vapour pressure of iodine over such a saturated solution would be equal to the vapour pressure of solid iodine at 25°C, i.e. 0.31 mm Hg. The concentration of free iodine in such saturated solutions is 1.33×10^{-3} moles/lit. The starting concentration of total iodine for this run was 3.37×10^{-3} moles/lit which gives a free iodine concentration of 7.08×10^{-5} moles/lit. Thus $p^* = 0.31 \times 7.08 \times 10^{-5}/1.33 \times 10^{-3} = 1.65 \times 10^{-2}$ mm Hg. Equation (5) then gives $k_Ga = 9.30 \times 10^{-7}$ moles/(cm^3.atm. S). The same procedure was applied to different runs listed in Table I. The k_Ga values obtained are also listed in the same table.

The k_Ga values obtained are shown in Figure 6 as a function of the Reynolds number. It is seen that k_Ga is proportional to $Re^{1.24}$. The analysis presented by Nelson and Galloway [12] for mass transfer in packed columns at low Reynolds numbers leads to a power of unity on the Reynolds number. However, previous experimental data as reported by the same authors show the power on Reynolds number to be as high as 1.4. The interfacial area of the liquid in the static hold-up has been estimated previously [2] as 0.6 cm^2/cm^3 for the 1.27 cm ceramic raschig rings used in this study. Using this value of a, k_G can be estimated from the K_Ga values listed in Table I.

Characteristics of the I_2 desorption system The contribution of the static hold-up for gas–liquid mass transfer has been recognised in several earlier studies [1–3]. The difference in effective interfacial area under different experimental operating conditions has been reported earlier [3,4]. It has also been shown that this difference can be attributed to the different roles played by the static hold-up in different operations. A direct determination of k_Ga for the static hold-up, however, has not been reported so far. Shulman *et al.* [3] studied the start-up

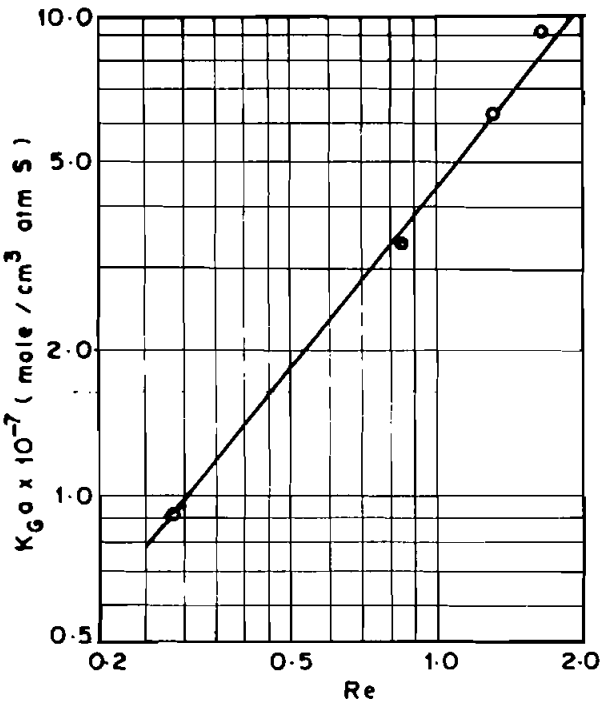

FIGURE 6 $k_G a$ vs *Re*.

absorption of ammonia in packed columns. They found that the overall value of $k_G a$ decreased from a high initial value to the steady state value within a minute or so. This duration is too short for achieving a high experimental accuracy. The present method overcomes this difficulty through the complex formation between iodine and iodide ions. The net effect of the addition of KI is to reduce the vapour pressure of iodine, and thus the desorption rate, without affecting the total iodine available for desorption (since the complex formation is a reversible reaction). Therefore the desorption experiment can be conducted over a longer time period. Accurate analytical methods are available for determining the total iodine desorbed, including very convenient methods involving ion-selective electrodes. Larger reduction in desorption rates can be achieved by using higher concentration of KI. Alternatively, the same effect can be achieved by addition of small amounts (around 1 percent or so) of polymers like polyvinyl alcohol which forms a complex with I_3^- ions. Under appropriate conditions, a constant desorption rate of iodine can be maintained for long durations [14]. Figure 6 shows that the 11 g/lit of KI used in this study can give a constant desorption rate of iodine for well over three hours for low flow rate. Such a constancy implies that there is not much depletion of total dissolved iodine over the duration of the experiment.

CONCLUSION

It has been shown that the desorption of iodine from aqueous KI solutions can be used for determing k_G for the static hold-up in packed columns. The complex formation between iodine and iodine ions can be effectively utilised to slow down concentration changes which otherwise would be too rapid for accurate experimentation.

NOMENCLATURE

a	interfacial area of static hold-up
A	concentration of free iodine
B	concentration of I^-
d	packing size
D	diffusivity
k_G	gas phase mass transfer coefficient
K_L	liquid phase mass transfer coefficient
K	equilibrium constant defined by Eq. (4)
L	column height
p	vapour pressure
P_t	total pressure
p^*	vapour pressure of dissolved iodine
$\tilde{R}$	desorption rate p.u. interfacial area
Re	$vd\rho/\mu$
Sh	$k_G d/D_A$
Sc	$\mu/(\rho d)$
v	superficial gas velocity
V	molar gas flowrate p.u. cross section

Greek letters

μ	viscosity of nitrogen
ρ	density of nitrogen

Subscripts

A	free iodine
b	bulk
B	iodide ion
i	at the interface
P	tri-iodide ion

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