CHAPTER 6

MATHEMATICAL MODELLING OF INTERFACIAL AREAS AND MASS TRANSFER COEFFICIENTS

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6.1.0 INTERRELATIONSHIPS BETWEEN STATIC AREA AND INTERFACIAL AREAS :

6.1.1 Liquid distribution in packed columns :

The diffusion model for the distribution of liquid trickling through a randomly packed bed which was first proposed by Cihla and Schmidt (70) and further extended by investigators such as Porter and Jones (71), Dutkai and Ruchkenstien (72) and Onda et al. (73) assumes that the liquid spreads over the packings as a film with equal probability for a liquid element to go towards the wall or to the centre of the column. This implies that the liquid flows as a film on the packings and the liquid load is practically uniform in all regions of the packed bed.

However, experimental observations by LeGoff and Lespinasse (74) and Porter (180) suggest that liquid load distribution over the packings is not uniform and the liquid flows through the packings in "preferred paths". Porter (180) termed the preferred paths, as rivulets and has demonstrated that there is no significant difference between the preferred paths model and the diffusion model of liquid distribution. Groenhof (181) has also observed that the liquid flows through preferred path and this liquid flow pattern is stable with respect to time.

Therefore, it appears that liquid prefers to flow from those paths which have been wetted previously by other liquid elements. Such flow pattern arises due to the non uniform structure of the packings and the combined influence of gravity and surface tension of the liquid. .However, since the liquid distribution is random, it is easy to visualise that some liquid elements move into regions of the bed wherein such preferred paths/rivulets are not developed. Hence the journey of these elements in the form of films is rather slow one, due to lack of liquid load in these regions. Further the liquid flowing in the bed also gets trapped in packing interstices. Such elements would get renewed more rapidly only if present in the viscinity of a preferred path/rivulet. Therefore, the liquid flowing through a randomly packed bed is likely to have different flow histories. There will be fast moving liquid layers coexisting with slow moving layers and semistagnant liquid pockets.

6.1.2 Concept of static and dynamic holdup :

The volume of liquid present in the form of the fast moving rivulets, the slow moving films as well as the stagnant liquid held in slowly renewable pockets of the bed, when expresseed per unit packing volume is termed as total liquid hold up. Extensive work has been done by Shulman and coworkers (85,86), Buchanan (89), and Gelbe (92) etc. with respect to liquid holdup in a packed column. It is a well established fact that total holdup equals the sum of the dynamic or operating holdup and the static holdup, wherein the dynamic holdup is a measure of the rapidly moving liquid layers in the bed and the static holdup quantifies the slow moving /semistagnant liquid held in the bed.

6.1.3 Concept of static and dynamic area.

The values of interfacial area available for mass transfer are very closely connected with the liquid holdup in a column. By analogy, one may then assume that the dynamic holdup correlates with the dynamic area (a_{dy}) and the static holdup correlates with the static area (a_{st}) as suggested by Puranik and Vogelpohl (106). Then the maximum effective area for mass transfer $a_{e\ (max)}$ should be equal to the sum of these two areas, which in turn could be given by the following equation :-

$$a_{e(max)} = a_{st} + a_{dy} \qquad (6.1)$$

Since liquid gets distributed over packings in the form of films /rivulets, the wetted surface area of the packings (a_w) will be obviously equal to the maximum effective interfacial area available for mass transfer. Hence, equation (6.1) takes the form as under:

$$a_w = a_{e(max)} = a_{st} + a_{dy} \qquad (6.2)$$

6.1.4 Effective interfacial area during physical absorption :

In the case of physical absorption in a packed column, semistagnant pockets as well as the slow moving films over the packings tends to become very rapidly saturated with the solute gas. However, the fast moving film/rivulets, where the liquid load is more hence renewal is rapid, retain their capacity to absorb the gas. Hence, in this case it is apparent that the static area is ineffective for gas absorption and the area contributing to mass transfer i.e the effective interfacial area for physical absorption (a_p) is the dynamic area only. Hence for the case of physical absorption one can write as under :-

$$a_p = a_{dy} \tag{6.3}$$

Therefore, the values of a_{st} can be estimated conveniently by equation (6.4), provided the values of a_w and a_p are available under otherwise identical conditions.

$$a_{st} = a_w - a_p \tag{6.4}$$

6.1.5 Effective interfacial area during chemical absorption :

When gas absorption is accompanied by a chemical reaction, the presence of reactive species in the liquid/absorption media enhances its capacity to absorb the gas. Therefore, when gas absorption is accompanied by a chemical reaction, under certain conditions the semistagnant film/pockets/regions could be equally effective as moving liquid.

Consider the case of a fast pseudo first order reaction between the solute gas and the reactive species present in the liquid. Since the reactive species would not be totally depleted by the reaction in the semistagnant pockets/slow moving regions, these regions would continue to be effective for gas absorption. Therefore, in such cases, the effective interfacial area for absorption with chemical reaction (a_c) will be given by equation (6.5).

$$a_c = a_{st} + a_{dy} \tag{6.5}$$

Under these conditions, the values of a_{st} can be estimated by use of equation (6.6) provided the values of a_c and a_p are available under otherwise identical conditions.

$$a_{st} = a_c - a_{dy} = a_c - a_p \tag{6.6}$$

However, when the concentration of the reactive species in the liquid is very low, then again the semistagnant pockets would get saturated in a very short span and would lose their effectivity to contribute towards mass transfer. Hence, under these conditions, the values of effective interfacial area for mass transfer during chemical absorption and physical absorption would be identical. Therefore, the interrelation between a_c, a_{dy} and a_p is as under :-

$$a_c = a_{dy} = a_p \tag{6.7}$$

Further, when an instantaneous reacion occurs between the solute gas and reacting species present in the absorption media, the semistagnant pockets are again likely to become completely depleted in a very short time, and thus lose their effectiveness for mass transfer. Under these conditions also, the values of effective interfacial area for mass transfer during chemical absorption and physical absorption would be identical and would also be given by equation (6.7)

Therefore, it is observed that for the case of gas absorption with chemical reaction, depending on the concentration of reactive species and also type of reaction, the effectiveness of static area could vary from fully effective to a value tending to zero. Hence, under certain conditions, the quantification of static area as $(a_{st}) = (a_c - a_p)$ as done by Puranik and Vogelphol (106) appears to be inappropriate. Hence, it is more appropriate to use equation (6.4) instead of equation (6.6) for estimating the values of static area düring gas absorption in a packed column.

6.2.0 PARAMETERS AFFECTING STATIC AREA.

In order to investigate the nature of static area and the factors affecting its value, one has to take into cognizance of the fact that the concept of static holdup (from which the concept of static area is derived) has been reintereted / reanalysed in recent years. Earlier investigators - namely, Shulman and coworkers (86) have considered the adherent holdup as static holdup. It has been shown by Gelbe (92), Bennet and Goodridge. (93) and also by the recent investigations of Schubert et al. (94) and Kushalkar and Pangarkar (95) that the magnitude of static holdup existing under actual conditions is expected to be substantially lower than the adherent holdup. The values of static holdup get affected by the liquid flow rate (L), packing size and its wettability and the physical properties of the liquid / absorption media like density viscosity, surface tension etc. It is expected that these parameters affecting the static holdup are also likely to have effect on the values of static area.

6.2.1 **Effect of liquid flow rate:**

Liquid holdup in packed columns has been analysed in detail by Gelbe (92). His analysis indicated that the values of static holdup show a definite increase with an increase in the values of L. Kushalkar and Pangarkar (95) have also confirmed these observations. Hence, it is expected that the values of static area (a_{st}) are also likely to increase with an increase in the values of L . With an increase in the liquid flow rate more and more packing surface is covered by the increased radial spread of the liquid. As a result, the liquid elements distribute out into the regions of bed without established rivulets and it is likely that a part of such liquid elements could also get trapped in packing interstices etc., thereby increasing the static holdup and by correspondence, also increasing the static area.

However, when the bed is very well irrigated, the values of static area are unlikely to show any further increase as rivulets could get established in all the regions of the bed. Moreover, when a bed is well irrigated with high liquid turn over rates, the values of static area would become insignificantly small as all the liquid pockets are likely to get rapidly renewed.

6.2.2 Effect of packing size :

In a randomly packed bed liquid gets held up in shallow pools at the packing intersections. These are the locations of the static holdup, and hence also for the static area. Thus a packed bed with large number of packing intersections will generate more static holdup and hence also more static area. Therefore, the packing size is likely to have profound effect on the values of static area. When the packing size is increased there is a sharp reduction in packing density. Thus, for example, when the size of ceramic Raschig rings is increased from 0.013 m to 0.025m, the packing density decreases substantially from 378,000 (N/m^3) to 47,700 (N/m^3). Therefore, the number of packing intersections will be more in a column packed with 0.013 m size Raschig rings than that packed with 0.025m size Raschig rings. Therefore, under otherwise identical conditions, the values of static area for smaller size of packings are expected to be more than those for larger size of packings.

An evidence in tnis regard could be also provided by Residence Time Distribution (RTD) studies of Hoogendoorn and Lips (182) and DeWaal(183). Hoogendoorn and Lips (182) observed highly skewed RTD curves showing pronounced tailing in a column packed with 0.013m Raschig rings and indicating the existence of the stagnant regions in the liquid phase. However, DeWaal (183) observed symmetrical distribution curves in a column packed with 0.025m Raschig rings indicating negligible amount of stagnant liquid regions in the fluid phase.

Thus, it can be concluded that as the packing size increases, the values of static area are likely to decrease considerably.

6.2.3 Influence of wettability of packing material :

The influence of the wettability of packing material and its surface texture on the values of hold up was investigated by

Shulman and coworkers (86).The values of adherent holdup obtained for carbon Raschig rings were higher than that obtained for unglazed porcelain rings. VanSwaaij et al. (184) made an extensive RTD study using wettable and non wettable packings. Their observations can be summarised as under:

(i) A wettable packing gives strongly asymmetric curves for low and moderate liquid flow rates. Such tailing indicates the presence of the stagnant pockets in the bed. While using a non wettable packing, tailing is not at all significant indicating the absence of the stagnant pockets in the bed.

(ii) When the flow rates are very high, the RTD curves become practically indentical for the wettable and non wettable packings.

Therefore, it can be concluded that the existence of the stagnant/semistagnant liquid in a packed bed is more pronounced when the packing is wettable. Under those conditions, the values of static area are expected to be large. However, for the non wettable packings, the stagnant/semistagnant liquid does not appear to exist in large quantity. Hence, under otherwise identical conditions, the values of static area for the non wettable packings are expected to be lower than the wettable packings. The critical surface tension of the packing material (σ_C) thus happens to be a very important governing parameter.

6.2.4 Effect of physical properties of absorption media :

The values of static area are likely to be influenced by the change in density, viscosity and surface tension of the liquid/absorption media.

With an increase in the values of density and viscosity, the values of static area are likely to decrease. A dense liquid due to the combined effect of inertial and gravitational forces would have a rapid turn over, thereby decreasing the value of a_{st}. Further, the spread over of a highly viscous liquid in the bed is likely to be relatively of a lesser magnitude than that of a less viscous liquid. Therefore, under otherwise identical conditions the values of a_{st} are likely to decrease. A reduction in the value of surface tension is also likely to increase the tendency of the liquid to spread over packings in the bed and, therefore, it is more likely to get trapped in packing interstices. Thus, under otherwise identical conditions, the values of a_{st} are likely to increase.

6.3.0 MATHEMATICAL MODELLING OF STATIC AREA (a_{st}) :

As has been already mentioned, the values of a_{st} can be estimated conveniently by the use of equation (6.4) provided the values of a_w and a_p are available under otherwise identical conditions. In order to correlate the data for a_{st} in terms of model parameters - system parameters and hydrodynamic parameters, one can propose the following equation :

$$a_{st} = f\,(L,\ a_t,\ \rho_L^{-1},\ \mu_L^{-1},\ \sigma^{-1},\ \sigma_c) \qquad (6.8)$$

With the help of dimensional analysis, these model parameters can be grouped in terms of following dimensionless numbers ; Reynold's (Re), Froude number (Fr), Weber number (We) and (σ / σ_c).

Therefore, equation (6.8) for predicting the values of a_{st} takes the following form :

$$a_{st}/a_t = C\,(Re)^{\alpha}\,(Fr/We)^{\beta}\,(\sigma/\sigma_c)^{\delta} \qquad (6.9)$$

The correlation of Puranik & Vogelpohl (106) mentioned in Chapter (2): Literature Survey [Equation - (2.11)] does not take into account the effect of (Re) and (σ / σ_c) on the values of a_{st}. As has been already discussed under the heading - "Parameters affecting static area", these two dimensionless groups are likely to affect the values of a_{st}. Hence, it will be worthwhile to include these two groups also as model parameters along with other model parameters. Accordingly, equation (6.9) has been proposed in this investigation for performing the mathematical modelling of a_{st} data with the help of a software developed in this investigation based on the DSC-Powell combination algorithm.

6.4.0 INTERRELATIONSHIPS BETWEEN MASS TRANSFER COEFFICIENTS WITH CHEMICAL REACTION AND WITHOUT CHEMICAL REACTION :

A review of various mechanisms that could result in for the different cases when mass transfer during gas absorption is accompanied by a chemical reaction, has been presented by Danckwerts and Sharma (3). This information could be used conveniently while proposing a mathematical model for predicting the values of the liquid side mass transfer coefficient during chemical absorption $(k_L^{'}a)$. No study has been reported in the literature which establishes a relationship between $(k_La)_{phy}$ and $(k_L^{'}a)_{chem}$ values.

6.4.1 Enhancement factors ' β ' and ' α ' during chemical absorption :

When mass transfer during gas absorption is accompanied by a chemical reaction, liquid side mass transfer coefficient $(k_L^{'}a)$ as well as effective interfacial area available for mass transfer (a_c) get enhanced. This enhancement is characterised by a reaction factor - β (also known as enhancement factor) which is the ratio of the liquid side mass transfer coefficient with chemical reaction to that without chemical reaction i.e. $\beta = k_L^{'}/k_L$. Based on the static area model proposed in the previous section, an enhancement in the value of interfacial areas i.e. effective interfacial area during chemical absorption (a_c) and effective interfacial area during physical absorption (a_p), could be given by the following equation :

$$\alpha = (a_c/a_p) = (a_{st} + a_{dy}) / (a_{dy}) \qquad (6.10)$$

As has been already discussed during chemical absorption, when the concentration of reactive species is very very low and when the regime of reaction under consideration happens to be an instantaneous reaction regime, the values of α will approach to one. Otherwise, for all the other regimes of reaction, the values of will be greater than one.

6.4.2 Different reaction regimes during chemical absorption and $(k_L^{'}a)_{chem}$:

CASE I : Consider a reaction between the solute (A) and the reactive species [B] in the liquid/absorption media when the concentration of reactive species [B] is very low and also the reaction is a slow/very slow reaction. The condition to be satisfied in terms of difusivity of the solute gas in liquid (D_L) second order reaction velocity constant (k_2), concentration of the reactive species in the bulk of the liquid [B] and the liquid side mass transfer coefficient (k_L) is given by the following equation :

$$\sqrt{D_L \; k_2 \; [B]}/(k_L) \;\; << \;\; 1 \qquad (6.11)$$

Under these conditions, the interrelationship between volumetric liquid side mass transfer coefficient during chemical absorption $(k_L^{'}a)$ and that during physical absorption (k_La) could be expressed by the following equations :

$$(k_L^{'}a)_{chem} \;=\; k_L^{'}a_c \;=\; k_L^{'}\, a_{dy} \qquad (6.12)$$

$$(k_L^{'}a)_{chem} \;=\; k_La_{dy} \;=\; k_La_p \;=\; (k_La)_{phy} \qquad (6.13)$$

It has already been discussed that when the concentration of the reactive species in the liquid is very low, the slow moving parts/films/semistagnant pockets of the interface would get completely saturated in a very short time and would loose their effectivity to contribute towards mass transfer. Hence, under these conditions, the values of effective interfacial area for mass transfer during chemical absorption and that during physical absorption will be identical. Accordingly, the above mentioned interrealtionships - equations (6.12) and (6.13) could thus be established.

CASE II : When an instantaneous reaction occurs between the solute gas and the reactive species present in absorption media/liquid, the specefic rate of absorption (R') is given by equation (6.14).

$$R' = (R)\ (a_c) = k_L\ (a_c)\ [A^*] \left[1 + \frac{[B]\ D_B}{Z\ [A^*]\ D_L} \right] \qquad (6.14)$$

where R is the rate of absorption per unit effective interfacial area of the packing, $[A^*]$ is the concentration of solute gas at the interface, D_L and D_B are the diffusivities of the gas and reactive species in the absorption media, Z is stoichiometric coefficient and a_c is effective interfacial area during chemical absorption. Further, if $[B]\ D_B/Z[A^*]D_L \gg 1$, then equation (6.14) reduces to equation (6.15).

$$R' = (R)\ (a_c) = k_L(a_c)\ [B]\ \ D_B\ /\ [Z\ \ D_L] \qquad (6.15)$$

The condition to be satisfied is :

$$\frac{\sqrt{D_L\ k_2[B]}}{k_L} \gg \frac{[B]\ D_B}{Z\ [A^*]\ D_L} \qquad (6.16)$$

Thus by utilising the chemical technique method, one can obtain the values of $(k_La)_{chem}$. When gas absorption is accompanied by an instantaneous reaction, the rate of absorption is completely controlled by the diffusion of the solute gas and reactant through the liquid film to the reaction zone. The reaction is so rapid that it leads to depletion of the reactant in the film. Thus, the rate of absorption at the moving part of the interface is so high that absorption at the semistagnant part/slow moving part of the interface becomes insignificant in comparison to that of the moving part. Therefore, the volumetric liquid side mass transfer coefficient $(k_L.a_c)$ can be interrelated to the other k_La values as under :

$$(k_La)_{chem} = k_L.a_c = k_L.a_{dy} = k_L.a_p = (k_La)_{phy} \qquad (6.17)$$

CASE III : When absorption is accompanied by a fast reaction, under certain conditions, the concentration of the reactive species at the interface can be practically the same as that in the bulk of the phase. The reaction becomes pseudo first order and Danckwerts model predicts that the specific rate of absorption is given by the following equation :-

$$R' = (R)\ (a_c) = (a_c)\ [A^*]\ \sqrt{D_L\ k_2\ [B] + k_L^2} \qquad (6.18)$$

The conditions to be satisfed is :

$$\frac{\sqrt{D_Lk_2\ [B]}}{k_L} \ll 1 + \frac{[B]}{Z\ [A^*]} \qquad (6.19)$$

Here, a part of the reaction occurs in the film and a part in the bulk phase B. Equation (6.18) indicates that a plot of

$[R.a_c/A^*]^2$ against $k_2[B]$ will be a straight line and the intercept will give the value of $(k_L.a_c)$ and slope will give the value of a_c provided the physico chemical properties and hydrodynamic conditions of phase B remain constant. Such a plot is commonly referred to as a Danckwerts plot and it thus gives the value of $\bar{k}_L$ and a_c separately.

Further, when absorption is accompanied by a very fast pseudo first order reaction so that all [A] is consumed in the film and none goes unreacted in the bulk. The necessary condition is given by:

$$\frac{D_L k_2\ [B]}{k_L^2} > 10 \qquad (6.20)$$

From equations (6.19) and (6.20), it is obvious that R' will be given by the following equation :-

$$R' = (R)\ (a_c) = (a_c)\ [A^*]\ \sqrt{D_L\ k_2\ [B]} \qquad (6.21)$$

Equation (6.21) indicates that the rate of absorption becomes independent of hydrodynamic factors. Under these conditions, the interrelationship between a_c, a_{dy} and a_{st} is given by the equation (6.22).

$$a_c = a_{dy} + a_{st} \qquad (6.22)$$

This aspect has been already discussed in the static area model.

It is interesting to observe that the Danckwerts plot, using the chemical technique methodology, gives the value of true liquid side mass transfer coefficient for physical absorption. Further, for this case under consideration, the values of effective interfacial area are expected to be equal to the sum of a_{dy} and a_{st}. Therefore, interrelationships between volumetric liquid side mass transfer coefficients for chemical and physical absorption could be given by the following equations :-

$$(k_L a)_{chem} = k_L (a_{st} + a_{dy}) = k_L a_{dy} + k_L a_{st} \tag{6.23}$$

$$= k_L a_p + k_L a_{st} \tag{6.24}$$

$$= (k_L a)_{phy} + k_L a_{st} \tag{6.25}$$

CASE IV : When absorption is accompanied by a chemical reaction and the reaction regimes are neither a slow/very slow reaction (Case I) nor an instantaneous reaction (Case II), the following analysis is likely to be helpful for obtaining the interrelationships between mass transfer coefficients with chemical reaction $(k_L' a)$ and with out chemical reaction $(k_L a)$.

If one assumes that the interface consists of two parts, that is the moving part and the semistagnant part, the volumetric mass transfer coefficient for chemical absorption can also be splitted in two parts as under :-

$$(k_L' a)_{Chem} = (k_L' a)_{dy} + (k_L' a)_{st} \tag{6.26}$$

The reaction factor for a fast/very fast pseudo first order reaction is given by Hatta (185) as under :-

$$\beta = \frac{\gamma}{\tanh \gamma} \qquad (6.27)$$

and $$\gamma = (\sqrt{D_L k_2 [B]})/k_L = k_L' / k_L \qquad (6.28)$$

Therefore, introducing the values of β and k_L' in equation (6.26) gives the following equation :-

$$(k_L' a)_{chem} = \beta . (k_L a)_{dy} + \sqrt{D_L k_2 [B]}\ (a_{st}) \qquad (6.29)$$

$$= \beta . (k_L a)_{phy} + \sqrt{D_L k_2 [B]}\ (a_{st}) \qquad (6.30)$$

It has to be realised that due to different hydrodynamic conditions prevailing in the moving part of the interface and the semistagnant part of the interface, the values of γ in the moving part of the interface will be substantially different from the semistagnant part of the interface.

Thus, when the values of k_2 and/or [B] are expected to be relatively low, under these conditions even when the values of γ in the moving part are expected to be less than 5 ; in the semistagnant parts where k_L value is relatively very small, $\gamma < 5$ does not hold good. Therefore, in the semistagnant part of the interface the value of γ is expected to be substantially greater than 5 and these regions/pockets are expected to be fully effective during chemical absorption. Therefore, the above mentioned equation (6.30) could be utilised to predict the values of $(k_L' a)$.

6.5.0 PREDICTION OF $k_L'a$ BY MATHEMATICAL MODELLING :

The correlation proposed in this Chapter (6) i.e. equation (6.30) could be utilised to predict the values of volumetric liquid side mass transfer coefficient during chemical absorption ($k_L'a$). This equation (6.30) requires the knowledge of model parameters : β, $\sqrt{D_L k_2 [B]}$, $(k_L a)_{phy}$ and a_{st}.

A generalised correlation could be developed for predicting the values of $(k_L a)_{phy}$ based on the data bank available in literature for volumetric liquid side mass transfer coefficients during physical absorption. The generalised correlation could also be developed for predicting the values of a_{st} based on static area model proposed in this chapter. Knowing the values of $(k_L a)_{phy}$ and a_{st} coupled with the values of β and $\sqrt{D_L k_2 [B]}$, the values of $k_L'a$ can thus be predicted by using equation (6.30).

Data banks on $K_G a$ - Overall mass transfer coefficients during chemical absorption, could be utilised to obtain the observed values of $k_L'a$ under otherwise identical conditions. These observed values of $k_L'a$ could be obtained by using the relevant equations mentioned in Chapter - (4) : General Considerations. It is expected to be interesting to compare these observed values of $k_L'a$ with the predicted values of $k_L'a$ by use of a "mass transfer coefficient model" proposed in this chapter.

Under the conditions (i) concentration of reactive species is very very low and (ii) the reaction happens to be an instantaneous reaction, the values of a_{st} are likely to be practically ineffective. Therefore, equation (6.27) reduces to equation (6.31).

$$(k_L^{'}a)_{chem} = \beta \; (k_La)_{phy} \qquad (6.31)$$

Data Banks on K_Ga or $k_L^{'}a$ during chemical absorption falling under the above mentioned two regimes could be utilised to test the validity of equation (6.31).