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Stripping of Carbon Dioxide from Monoethanolamine Solutions in a Packed Column

A procedure using only fundamental physico-chemical data is developed for the design and analysis of packed columns used for solvent recovery in gas purification processes involving chemical reaction. The results of 173 experiments on the mass transfer performance of a pilot-scale regenerator stripping CO_2 from loaded monoethanolamine solutions are reported and compared with model predictions. Anomolous responses of the overall mass transfer coefficient to changes in process conditions are observed and explained by the process model which is found to predict correctly both the magnitude of the coefficient and its response.

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SCOPE

The literature on gas absorption into chemically-reactive solution is vast and the fundamentals of the process are well understood. Most gas purification plants, however, require the solvent to be regenerated, yet the stripping operation has been studied hardly at all despite the fact that it is the major cost component in impurity removal processes. Recently, Astarita and Savage (1980a) have shown that the theory of absorption can be applied to desorption with only mild restrictions. Desorption is considerably more complicated, however, because in stripping one must account always for the reversibility of the chemical reactions so that chemical thermodynamics invariably enters into the calculations.

Sufficient appears to be known to permit the design of packed *absorbers* from first principles. Here we examine the design of packed strippers using fundamental physico-chemical data as our primary basis, and a detailed procedure for the design of new columns and the analysis of existing ones emerges. Then we present an extensive set of measurements of mass transfer coefficients obtained in a pilot-scale regenerator using the carbon dioxide—aqueous monoethanolamine system. These results are compared with theoretical predictions. The effect of several operating variables on stripping column performance are evaluated and the sometimes counterintuitive results are explained through a detailed analysis of the way in which a change to one variable can simultaneously affect several others.

CONCLUSIONS AND SIGNIFICANCE

The two-film model of Whitman (1923) forms the basis of a procedure for the design of packed regeneration columns used

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in the solvent recovery section of gas purification plants. The analysis employs only fundamental data such as individual-film mass transfer coefficients specific to the packing type and size, and thermodynamic relations for the chemical system.

When model predictions are compared with experimental measurements of the performance of a packed solvent-regeneration column of semicommercial scale, it is found that the 173 measured mass transfer coefficients are predictable on average to within ±25%. The results reported here represent the first comprehensive investigation of the influence of plant operating variables on the stripping of CO_2 from carbonated monoethanolamine solutions.

Stripping appears to be controlled entirely by neither the gas nor liquid film resistances; rather, each is found to be important, with the dominance of one over the other varying with vertical position in the column. Thus, at the top of a typical stripper the liquid-film resistance controls, but by the time the bottom of the column is reached, control has been transferred to the vapor phase. Under some circumstances increased liquid or vapor rates are found to *reduce* the overall mass transfer coefficient $K_{OL}a$. When vapor rates are low $K_{OL}a$ is found to be extremely sensitive to solvent loading, and high amine concentrations are shown to result in greatly reduced mass transfer coefficients. Values of H_{OL} as high as 3 m were found. Under all combinations of operating conditions studied, $K_{OL}a$ was observed to exhibit a minimum as a function of operating pressure.

To within the accuracy of the data, the process model was found capable of correctly predicting the magnitude and trend of $K_{OL}a$ with changing operating conditions. This gives some degree of confidence that stripping column performance can be predicted from first principles, and these columns can be designed in a real sense, and that stripping plants can be optimized.

INTRODUCTION

There is a vast literature on the subject of gas absorption into chemically reactive solutions and it can now be claimed that the theory is very well understood (cf. Astarita, 1967; Danckwerts, 1970). By contrast, very little has appeared that deals with the reverse process of solvent regeneration and the stripping of dissolved gases from reactive liquids. This is despite the fact that, economically, stripping is the most relevant part of the process. For example, Butwell et al. (1979) have recently reported that for a 1000 short ton per day ammonia plant using the so-called Amine Guard III system, 88% of the total annual utility cost of $3,199,000 represents steam needed for solvent recovery. Design methods for stripping plant appear to be lacking and new processes require costly large-scale pilot plants.

Shah and Sharma (1976) have reviewed the theory of gas desorption which results from the formation of a volatile species by reaction with the solvent of *another* species that is simultaneously being absorbed. The much more prevalent case in which an already absorbed gas is stripped from the solvent purely by the action of heat has been addressed recently by Astarita and Savage (1980a) using the film model. The key result of their analysis is the delineation of the conditions under which chemical absorption theory can be applied to desorption. The conditions are: (i) mass transfer must lie within or between the diffusional and fast reaction regimes; (ii) there is only a single overall reaction; (iii) the total capacity of the liquid for dissolved gas greatly exceeds its purely physical (e.g., Henry's law) capacity; and (iv) the gas phase composition is linearly related to the concentration of dissolved but unreacted gas. In a subsequent paper, Astarita and Savage (1980b) gave a more detailed analysis of the instantaneous reaction case. They obtained a complete analytical solution for the film model and asymptotic solutions of the penetration theory equations. Promoted mass transfer (e.g., homogenous catalysis) has also been examined (Astarita et al., 1981) although experimental measurements were not reported.

Our present interest is in the *a priori* prediction of packed stripping column performance based solely on physico-chemical parameters and equilibrium data. For this purpose the ability to apply chemical absorption theory, although important, is only one component of the overall analysis. Unlike absorption, in chemical desorption the reversibility of the chemical reactions is critical. As pointed out by Astarita and Savage (1980a) this necessarily introduces thermodynamic relations as an integral part of the theory. Furthermore, heat effects cannot be ignored because a substantial amount of heat is required to cause decomposition of the solvent-gas compound and to liberate the freed gas from solution. The implication is that stripping steam condenses to provide the heat of desorption so that gas and liquid rates vary significantly throughout the column. (The column itself, however, operates substantially isothermally). Enhancement factors which result from chemical reaction and which modify liquid-film coefficients are composition dependent as is the physical solubility of the gas; compositions vary widely within the column. To compound the difficulty in predicting stripper performance, one finds that much of the necessary physico-chemical data, even if they are fairly accurate (and often they are not), are available only at the moderate conditions of room temperature and pressure. Thus extrapolation to stripping conditions of elevated pressure and temperature is unavoidable, albeit undesirable.

Previous literature dealing experimentally with solvent recovery in gas purification includes the early work of Reed and Wood (1941) and Benson et al. (1954, 1956). Reed and Wood presented a small amount of equilibrium data for the CO_2-MEA system at stripping conditions and found that the reactivation of carbonated solutions was much more complete at higher regenerator pressures. However, they were unable to respond to a question of the late Professor T. K. Sherwood enquiring about plate efficiencies and mass transfer coefficients, a situation we attempt to remedy for the first time in this paper.

Ellis et al. (1963) have reported results on the rate of desorption of CO_2 from MEA solutions obtained by continuously recirculating hot amine solutions through a so-called flash tank. Although it is not clear from their work, presumably the contents of this tank were boiled by external heating so the system was equivalent to a stirred pot or CSTR. High retention times were found necessary for "good" desorption of CO_2 and from this they implied that maximum submergence should be used in tray towers. They commented that tray efficiencies were low (as is common in highly reactive systems) although no quantitative data were given.

Regeneration of CO_2-MEA solutions has also been briefly considered by Gridin et al. (1976) from the point of view of steam consumption rates and the maximum degree of stripping. No useful mass transfer data were given.

The only other system which has received attention of any significance seems to be the hot carbonate process for CO_2 removal. The use of carbonate as an absorbent for CO_2 was first reported by Benson et al. (1954, 1956). They presented data on overall absorption coefficients in a packed scrubber, but only the steam consumption rates for solvent regeneration were determined. Recently, Savage et al. (1980) reported absorption and desorption rate data for this system using a single-sphere mass transfer device. Data were interpreted from film theory.

The steam stripping of CO_2 from soda-lye solutions in a wetted-wall column was studied at 100°C by Young and David (1957) who concluded that neither the vapor nor the liquid rate had any effect on the overall mass transfer coefficient. They found this to be about 1.3×10^{-7} kgmol/s-m^2-kPa and concluded that the major mass transfer resistance was associated with the decomposition rate of bicarbonate in the liquid phase. A similar conclusion that bicarbonate decomposition is rate controlling was reached by Langley and Haselden (1968) who experimented with a stirred cell using potassium carbonate solutions. However, the decomposition rate of bicarbonate is most unlikely to be rate controlling at temperatures prevalent in stripping and, indeed, Savage et al. (1981) have commented on the fact that Langley and Haselden misinterpreted their data.

Experimental results on the desorption of CO_2 from aqueous potassium carbonate in a bubble-cap column have been reported by McLachlan and Danckwerts (1972). They found good agreement between experiment and a theory based on pseudo-first-order reaction in the absence of arsenite ion (a catalyst). In that case the process was equivalent to simply physical desorption, the contribution of the chemical reaction to the desorption rate being negligible since the reaction was apparently quite slow. When the reaction was catalyzed, however, their predicted desorption rates greatly exceeded the experimental measurements unless it was assumed that catalyzed hydration of carbon dioxide was a third-order reaction involving carbonate ion as well as arsenite and CO_2.

Based on a favorable report by Dorfman and Lupanov (1960) on the carbon dioxide-ethylenediamine system, Trass and Weiland (1971) studied absorption and solvent regeneration for this system in a pilot-scale packed column. Mass transfer coefficients for stripping, predicted on the basis of a physical mass transfer model, were in disagreement with experiment and the experimental results themselves showed tremendous scatter. Nevertheless, it was found that unlike absorption which was controlled almost entirely by liquid-phase resistance, in stripping, resistances in the gas and liquid phases were of roughly equal importance.

It can be concluded only that reliable mass transfer data on chemical stripping, particularly in packed columns, have yet to be reported in the literature. In this paper, we shall begin by presenting a method based on the film model for predicting desorption rates and for designing these columns from fundamental principles. Then we shall present an extensive set of measurements of mass transfer coefficients obtained in a pilot-size packed regenerator using the carbon dioxide—monethanolamine system. The experimental results will be found to be predictable using the process model to within ±25% on average. The model qualitatively predicts the effects on the overall mass transfer coefficient of varying gas and liquid rates, operating pressure, MEA concentration and solution loading.

PROCESS MODEL

We begin by decomposing the packed column into a number of sections of height Δz and unit cross-sectional area; the j-th section is shown in Figure 1. Our analysis of the stripping process will be based on the film model of Whitman (1923). Although it is generally agreed that this model is not very realistic, it is a matter of experience that predictions based on it are usually very similar to those based on the physically more satisfying penetration theories, and indeed, are identical when all diffusivities are equal. Commonly one accounts for the effect of liquid-phase chemical reaction through an enhancement factor ϕ. This is the ratio of absorption rates with and without chemical reaction when resistance to mass transfer resides solely in the liquid phase.

Then, for the average conditions prevailing in the section, mass transfer rates in the liquid and vapor phases are, respectively

$$\bar{N}_j = \phi\, \bar{k}_L^o a\, (\bar{A}_j - \bar{A}_j^*)\, \Delta z \tag{1}$$

$$\bar{N}_j = \bar{k}_G a (\bar{p}_j^* - \bar{p}_j) \Delta z \tag{2}$$

in which the asterisk refers to the interface and the liquid and vapor compositions are connected through the *physical* solubility relation

$$p^* = HA^* \tag{3}$$

with Henry's law constant H. In general, H would depend on the concentrations of *all* species in solution through salting-out and possibly salting-in effects. Note that $\bar{A}$ refers to the average bulk concentration of dissolved but *unreacted* gas.

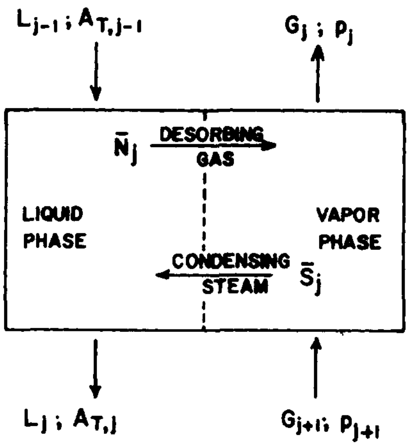

Figure 1. Schematic of the j-th section in the column.

The first step in the model calculations would be to solve Eqs. 1 to 3 for $\bar{A}_j^*$ or $\bar{p}_j^*$; hence, $\bar{N}_j$ and then realizing that stripping is highly endothermic, use the estimated stripping rate for the section to calculate the vapor condensation rate from an enthalpy balance:

$$\lambda_s \bar{S}_j = \Delta H_R[(A_T L/\rho_L)_{j-1} - (A_T L/\rho_L)_j] + \Delta H_2 \bar{N}_j \tag{4}$$

Here, λ_s, ΔH_R, and ΔH_s are the heats of condensation of steam, decomposition of the compound formed by the gas with the solvent, and dissolution of the gas, respectively, and $\bar{S}_j$ is the steam condensation rate.

Overall mass balances on the liquid and vapor phases lead to the following equations for liquid and vapor flows at the bottom of the section

$$L_j = L_{j-1} + \bar{S}_j - \bar{N}_j \tag{5}$$

$$G_{j+1} = G_j + \bar{S}_j - \bar{N}_j \tag{6}$$

Balances on the transferring component $\mathcal{A}$ give

$$(A_T L/\rho_L)_j = (A_T L/\rho_L)_{j-1} - \bar{N}_j \tag{7}$$

$$(pG/P\mathcal{M})_{j+1} = (pG/P\mathcal{M})_j - \bar{N}_j \tag{8}$$

where A_T is the concentration of dissolved gas in *all* forms, P is total pressure, and $\mathcal{M}$ is the molecular weight of the vapor, while a

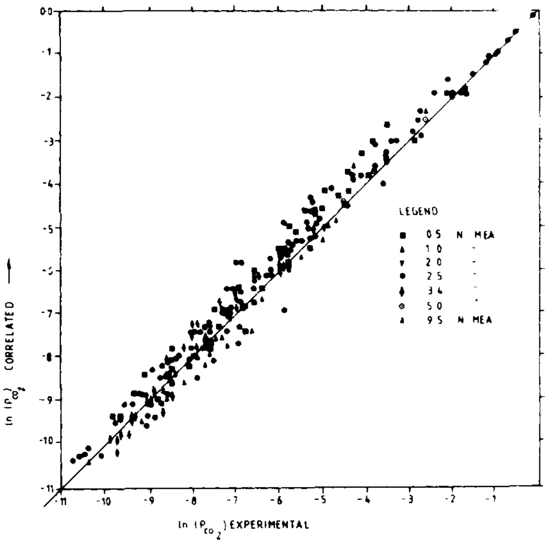

Figure A-1. Comparison of equilibrium data with correlation (Eq. A3) for p_{CO_2} above carbonated MEA solutions.

balance on the reactive component, B, of the solvent gives

$$(BL/\rho_L)_j = (BL/\rho_L)_{j-1} \tag{9}$$

A first estimate of desorption rate could be obtained by assuming all flows and compositions to be constant within a section and equal to their values at the top. Then the solution of Eqs. 1 to 3 is used in Eq. 4 to find $\bar{S}_j$ and the result used sequentially in the rest of the equations to obtain first estimates of section bottom conditions. Further iterations would be based on average flows and compositions and calculations would proceed from section to section until conditions at the bottom of the column were reached. Finally we note that if more than one gas is being desorbed we would have separate equations like Eqs. 1 to 3 for each component, and the rate $\bar{N}_j$ in the other equations would be replaced by the sum of the individual rates. Thus, provided sufficient fundamental physicochemical data are available, we are in a position to predict *a priori* the height of a packed column required to give a specified separation.

One of the key parameters in such a model is the enhancement factor ϕ which accounts for the chemical reaction. In the present case of desorption, the reversibility of the chemical reactions plays an essential role in determining transfer rates. In general, insufficient kinetic data exist to allow one to establish whether stripping takes place in the fast or instantaneous reaction regimes—see Savage et al. (1980) for a discussion related to the hot carbonate process—and this makes considerable difference to the calculation of enhancement factors. For stripping, we will consider only the case of reversible instantaneous chemical reaction. The high temperatures common in stripping seem likely to result in sufficiently high reaction rate constants for this approximation not to be wildly in error; on the other hand, to consider finite rates of chemical reaction would result in a considerably more complex analysis, possibly so complex as to make the interpretation of experimental data almost impossible.

Recently, Astarita and Savage (1980b) have presented a complete mathematical analysis of the reversible instantaneous chemical reaction case in the context of the film model for mass transfer and they have provided an asymptotic analysis of certain special cases for the penetration theory. For a liquid-phase chemical reaction with the stoichiometry

$$\mathcal{A} + \nu_i \mathcal{B}_i = 0 \tag{10}$$

they found that the enhancement factor ϕ is the solution to

$$\frac{A^*}{A} = \prod_i \left(1 - \frac{\nu_i \xi}{r_i B_i}\right)^{-\nu_i} \tag{11}$$

where the quantity ξ is defined by

$$\xi = (\phi - 1)(A^* - A) \tag{12}$$

They commented that ϕ depends only on bulk-liquid compositions $\{A, B_i\}$ and the interface concentration A^*, but it is independent of the thermodynamic equilibrium constant for the reaction of Eq. 10; of course, the bulk-liquid phase concentrations are related through the thermodynamic constant and this could be used to replace one of them. Use of Eqs. 11 and 12 is possible only if A^* is known. Although it cannot be measured experimentally, it is certainly calculable from Eqs. 1 to 3.

The influence of packing size and type, and the liquid and vapor fluxes through the column is exerted largely by way of the individual film coefficients for mass transfer, $k_L^\circ a$ and $k_G a$. For many packings, these quantities have been correlated with liquid and vapor fluxes for specific systems, usually at room temperature, and they can be translated to other systems at other conditions through diffusion coefficients, phase viscosities, and so on. Unfortunately, these correlations are not always of high accuracy, nevertheless, they do provide the designer with guidance and they permit the ready scaleup of pilot-plant data obtained using relatively small packing to full-size columns using large packings.

A task alternative to design is the analysis of existing equipment. In that case, *the column height and feed rate and composition are* known. If we assume that the vapor rate leaving the top of the column is also available, then for a given pressure the procedure would be to iterate around its composition. A first guess at this composition allows the determination of the lean liquid composition at the column bottom through a mass balance, and comparison of *predicted height with known physical height gives* a fresh estimate of the top vapor composition. The ability to make such performance predictions would make faulty or substandard performance much easier to diagnose.

Finally, the foregoing procedure allows one to report results in terms of overall mass transfer coefficients. For example, using mole fractions x the overall liquid-based coefficient is

$$K_{OL}a = \frac{1}{h}\int_{x_T}^{x_B} \frac{L_m dx}{\rho_m (1 - x)(x - x_e^*)} \tag{13}$$

where x_e^* is the mole fraction CO_2 in the liquid which would be in equilibrium with the bulk vapor. Because liquid and vapor flows vary within the column, both operating and equilibrium lines are curved, requiring numerical integration. However, once the height for a given duty, or duty for a given height has been established, it is quite simple to partition into increments of concentration difference Δx and make step by step calculations taking due account of the steam condensation rate which provides the heat of reaction in each increment. Here x refers to CO_2 in all forms.

In summary, the model is the traditional one; it uses the classical two-film theory of interphase mass transfer coupled with an enhancement factor to account for the liquid-phase chemical reaction. Two of the primary requirements for its application to industrial columns are that equilibrium and physical property data for the chemical system be available, and that individual film coefficients for mass transfer relevant to the particular packing be known. This latter requirement can be met through the use of standard correlations, as given, for example, by Danckwerts (1970), although a review of the literature on such data leads one to question their accuracy and reproducibility.

If the task is column design, then for specified boilup and rich liquor flows, solvent amine concentration, rich liquor loading, targetted lean liquor loading, and stripper pressure, the column height can be predicted by the following procedure:

(i) Calculate the bottom vapor composition, assuming the reboiler to be an equilibrium stage.

(ii) From overall mass and energy balances calculate the top vapor composition.

(iii) For a chosen incremental packing height and, as a first estimate taking flows and compositions as constant within this increment, determine ϕ for the top section of the packing from the simultaneous solution of Eqs. 1, 2, 3, 11, 12 along with the chemical equilibrium relation for the system. As part of the solution the flux $\bar{N}_1$ and the interfacial compositions $\bar{A}_1^*$, $\bar{b}_1^*$ will be found as well.

(iv) Equation 4 is now used to estimate the vapor condensation rate for this first section; following this, Eqs. 5 to 9 yield estimates of section bottom flows and compositions.

(v) After averaging section top and bottom quantities the entire procedure is repeated from step (iii) to convergence. If the incremental packing height chosen is not too large, the flows and compositions at the section bottom will closely approximate reality. These section bottom quantities provide initial data for the next section.

(vi) Section to section calculations are continued until conditions corresponding to the column bottom (design separation) are reached. The sum of incremental heights gives the required packing height for the column.

For the analysis of an existing column, one approach is to predict the separation that *should* be achieved, for comparison with operating data. Thus, the column height is known but the lean liquor composition is not. The analysis procedure is iterative; we select a bottom liquid composition and go through steps (i) to (vi) above except that calculations are stopped when the known packed height has been traversed. This will produce a lean liquor composition for comparison with our initial guess. The entire procedure is repeated until the estimated bottom composition agrees with the calculated value. The calculated separation can now be used as the basis for diagnosing faulty column performance.

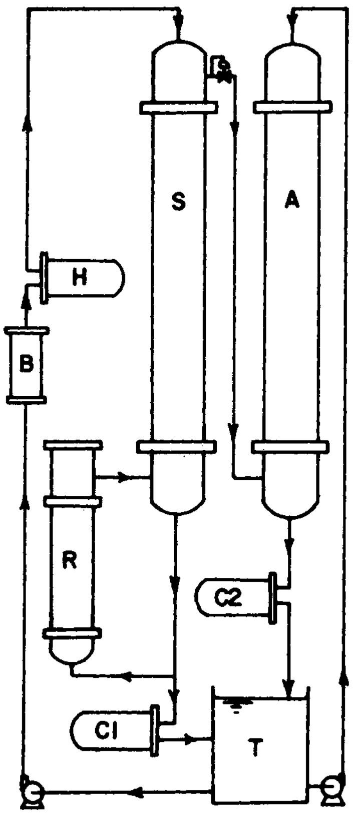

Figure 2. Schematic of pilot plant showing stripper (*S*), reabsorber (*A*), feed preheater (*H*), coolers (*C1,C2*), reboiler (*R*), and common storage (*T*).

EXPERIMENTAL

The layout of the pilot plant is shown in simplified schematic form in Figure 2. Only major equipment items and process streams are indicated; valving arrangements, instruments for the measurement of flow rate, temperature and pressure, cooling water lines and steam lines have been omitted.

An important feature of the plant is that it was a totally closed system. Steam and carbon dioxide stripped from the CO_2-rich solution were completely recovered by direct-contact condensation and reabsorption in the packed column *A* and returned to the storage tank *T*. Any small amounts of impurities formed by the thermal decomposition or oxidation of MEA which might have produced foaming problems were removed by passing the solution through a short bed of activated carbon in the thick-walled glass vessel *B*. All parts of the equipment in contact with the process fluids were of type-316 stainless steel, or on occasion, glass.

The stripper was 152 mm (6 in.) in diameter packed to a height of 1.64 m with 12.7-mm (nominal ½-in.) unglazed ceramic Raschig rings of wall thickness approximately 3 mm. Thus, the column to packing diameter ratio was 12. Liquid distribution was by means of a five-legged spider arrangement.

Temperatures at various points in the process were monitored using iron-constantin thermocouples in stainless steel sheaths. The feed temperature leaving the preheater *H* was controlled through shell-side steam pressure to be as close as possible to the stripper top temperature so that feed entered substantially at its boiling point. Liquid and vapor samples were taken at the packing support and holddown plates (4-mesh light wire screens). Liquid samples were cooled during removal from the column and were analyzed for CO_2 and MEA content using a method proposed by Weiland and Trass (1969); at least three separate samples of each stream were always analyzed. Vapor samples were slowly withdrawn and passed directly to the high temperature sampling valve of a gas chromatograph; analyses were in quadruplicate.

Steady state was assumed to have been reached when, over a ½-hour period, consecutive samples of the vapor at the stripper top showed no consistent variation in composition. The approach to steady state took about two hours.

Computations and Error Analysis

Sufficient data were collected to enable the closure of a mass balance within the stripper to be checked. Although the liquid and vapor rates at the base of the column could not be measured directly, they could be inferred from the measured flow rates at the top of the column, the changes in composition across the column and the known heat of decomposition and dissolution of CO_2. Allowing for errors of 1% in liquid flow rates, 3% in vapor analysis and ½% in liquid analysis it is estimated that on average the boilup rate is known to no better than ±17% and a mass balance can be expected to close to within ±22%, both on a 95% confidence interval. Of 173 experiments performed, a mass balance failed to close to within these limits in only nine cases.

TABLE 1. SENSITIVITY OF $K_{OL}a$ to 1% POSITIVE ERRORS IN EACH PRIMARY MEASUREMENT

Variable	% Change in $K_{OL}a$
L	+2.1
G	−1.2
$T^{\dagger}$	−9.6
M	+1.2
α_T	+1.4
α_B	−5.5
Y_T	+1.5
Y_B	−1.5

† A 1% change in temperature is 4 K. and corresponds approximately to a pressure change of 0.15 atm.

Liquid flow rates and compositions could be measured with greatest precision; hence, mass transfer coefficients were calculated based on the liquid phase. Furthermore, this is the phase of most interest in solvent regeneration. The integral in Eq. 13 was evaluated numerically by the summation

$$K_{OL}a = \frac{1}{h}\sum_{j=1}^{N}\frac{\bar{L}_{m,j}\Delta x_j}{\bar{\rho}_{m,j}(1-\bar{x}_j)(\bar{x}_j-\bar{x}^*_{e,j})} \tag{14}$$

Computations were started at the top of the column and terminated when the calculated liquid-phase concentration reached that measured experimentally at the bottom of the column. The calculation procedure was precisely as outlined earlier. Finally, to ensure that accuracy was not sacrificed by too coarse partitioning, the number of partitions was increased and the entire procedure repeated. Vapor condensation caused by thermal losses from the column (1–2% of total flow) was taken into account.

The likely errors in the calculated mass transfer coefficients are related to errors in primary measurements in a highly nonlinear way. The sensitivity of $K_{OL}a$ to errors in each measured quantity was determined for a typical set of experimental conditions by increasing the value of each quantity (taken one at a time) by 1% and repeating the calculation of $K_{OL}a$ outlined above. The change in $K_{OL}a$ which resulted is listed in Table 1. Taking liquid rates accurate to ±1%, vapor rates to ±17%, solvent concentration, *M*, and solution loading α, to ±½%, vapor-phase concentrations to ±3% and temperatures to ±1°C, the probable error in $K_{OL}a$ is ±24%. It must be noted that this error estimate does not include errors in the equilibrium data themselves. However, the data were collected from a large number of sources and correlated; the same correlation has been used throughout for both experimental results and theoretical predictions so any error in the equilibrium relation would cause consistent error in both of these without much affecting the comparison between the two. The procedure adopted for correlating these data, and the resulting correlation are given in Appendix 1.

Model Predictions

Essentially, the model predicts the separation that *should* be achieved in the experimental column, along with the theoretical composition profiles, then uses Eq. 14 to determine a predicted value for the overall coefficient $K_{OL}a$.

A number of parameters are needed for use in the model; of these, the liquid-side coefficient k_L^o for physical mass transfer and the interfacial area a were measured independently using CO_2 absorption into water and into sodium hydroxide solutions (under pseudo-first-order conditions), respectively. Experimental data on the liquid-film coefficient $k_L^o a$ for physical mass transfer were correlated in SI units by the expression

$$k_L^o a/D_L = A(L/\mu_L)^{1-n}(\mu_L/\rho_L D_L)^{0.5} \tag{15}$$

suggested by Sherwood and Holloway (1940). The values of A and *n* were found to be 144.8 ± 4.3 and 0.114 ± 0.073, respectively. Measured interfacial areas followed the correlation of Onda et al. (1968) but were 10% lower. As suggested by Danckwerts (1970), the correlation of Dwyer and Dodge (1941) was used for the gas-film coefficient. For ammonia absorption from air into water this is

$$k_G a = 0.145 G^{0.90} L^{0.39} \qquad (16)$$

which can be used for CO_2 transfer into water vapor by correcting for the Schmidt number and accounting for the fact that $k_G a$ varies inversely with the partial pressure of inerts. The Henry's law solubility of CO_2 in solution is strongly influenced by the presence of dissolved ionic species and indeed, by MEA itself. This was accounted for as follows: the ionic species $RNHCOO^-$ and RNH_3^+ cause a salting-out effect (Danckwerts, 1970; Hikita et al., 1979) given in terms of Henry's law constant, H, by

$$\log_{10}(H/H^\circ) = hI \qquad (17)$$

where $h = h_+ + h_- + h_G$ and $I = \frac{1}{2} c_i Z_i^2$ is the ionic strength. Here Z_i is the valency of the i-th species and c_i its concentration. We assume that RNH_3^+ and $RNHCOO^-$ are equivalent to NH_4^+ and HCO_3^-, respectively since values of h_+ and h_- are available for these ions (van Krevelen and Hoftijzer, 1948; Hikita et al., 1974). There is some controversy concerning the effects of dissolved MEA on the solubility of CO_2. Hikita et al. (1979) found a salting-in effect correlated by

$$\log_{10}(H/H^\circ) = hI - 0.3B/(1 + \kappa B) \qquad (18)$$

where B is the MEA concentration; whereas, Laddha et al. (1981) found a salting-out effect, based on measurements of the solubility of the analogous gas N_2O. The dispute seems unresolved and we have chosen the approach of Hikita et al., (1979) who lists four values of κ in the range 15 to 45°C. For temperatures much above this, κ appears to have an asymptotic value of about 0.75 although there could be considerable error in this extrapolation. Whatever the true situation is, the large errors inherent in other physicochemical data used in the model would very likely mask this uncertainty.

The diffusion coefficient of MEA in aqueous solution is known to be concentration sensitive and the data of Ibrahim and Kuloor (1962) and Thomas and Furzer (1962) were used to account for this. The diffusivity of CO_2 in MEA was assumed to be affected by amine concentration in the same way as amine diffusivity, while temperature effects were described by the correlation of Barrett (1958). Finally, the viscosity of MEA solutions as a function of temperature was found to follow the correlation

$$ln(\mu/\mu_{25}) = -7.00 + 2.1 \times 10^3/T \qquad (19)$$

and the Wilke-Chang (1955) correlation was used to estimate the effect of viscosity variations on the diffusivity of MEA in aqueous solution.

RESULTS AND DISCUSSION

All experimental results are presented in terms of the overall mass transfer coefficient, $K_{OL}a$, based on the liquid phase and are always compared with model predictions (solid lines on the figures). Gas and liquid rates and compositions vary significantly throughout the column and the parameter values indicated on the figures correspond to conditions at the *top* of the column. The effect of each operating variable will be discussed separately but it must be realized that changes to one condition almost invariably affect others so that the segregation cannot always be made cleanly. Finally, in the interests of space, only some of the data can be presented here; a complete set of data in both graphical and tabular form is available on request from the corresponding author.

Liquid Feed Rate

The variation of overall mass transfer coefficient with liquid feed rate is shown in Figure 3 for three solution loadings, α. Except at low α, it can be seen that $K_{OL}a$ is an increasing function of liquid rate. This is as expected because both the liquid-film coefficient, k_L^o, and the interfacial area increase with liquid rate. The results for low α, however, are quite surprising especially for low vapor rates in that increasing liquid rates can actually *reduce* the overall transfer coefficient.

As part of the explanation for this behavior we need to establish the conditions under which one or the other of the gas and liquid phases offers a major resistance to mass transfer. This can be done by considering the enhancement factor ϕ which is a direct consequence of the chemical reaction. It is easy to show from either Eqs. 11 and 12, or directly from the governing diffusion equations and boundary conditions, that the enhancement factor for instantaneous equilibrium chemical reaction between CO_2 and MEA is

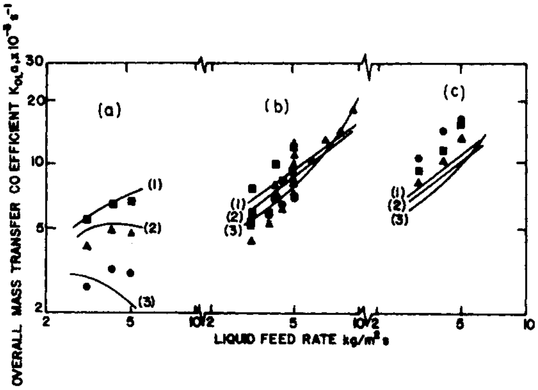

Figure 3. $K_{OL}a$ as a function of liquid rate for 2.5 kmol/m^3 amine at 2.36 atm. Plots (a), (b), (c) are for α_T = 0.163, 0.322 and 0.42, respectively; curves (1), (2), (3) are for G_T = 0.441 (■), 0.309 (▲) and 0.177 (●) kg/m^2·s.

$$\phi = 1 + \frac{D_P}{D_A}\sqrt{KB}\Big/\Big[\Big(1 + 2\frac{D_P}{D_B}\sqrt{KA^*}\Big)\Big(\sqrt{A} + \sqrt{A^*}\Big)\Big] \qquad (20)$$

in which A, B and P refer to free CO_2, free amine and carbamate, respectively. The overall reaction is

$$CO_2 + 2\,RNH_2 = RNHCOO^- + RNH_3^+ \qquad (21)$$

where R is the alkanol group, so that the equilibrium constant, K, is

$$K = \frac{1}{[CO_2]_e}\left(\frac{\alpha}{1-2\alpha}\right)^2 \qquad (22)$$

It is important to note here that $[CO_2]_e$ is the bulk liquid-phase equilibrium concentration of dissolved but free *unreacted* CO_2.

At low solvent loadings both A^* and A are relatively small while B is high; therefore ϕ is large and the resistance offered by the liquid phase is lowered. If the gas velocity G is also low then the gas-phase resistance may be significant at low α. Neither one, however, is necessarily dominant. For example, it can be seen from Figure 3(a) that at a high gas rate, increasing liquid has a relatively strong positive effect on $K_{OL}a$ but this weakens and begins to exhibit a mildly negative influence as the gas rate is lowered. This suggests that both the gas and liquid-side resistances may be important and need to be considered together. At the other extreme, when α is very large the enhancement factor will be quite small and it is the liquid-film resistance which probably dominates.

One usually thinks of the effect of increasing liquid rates in terms of the resulting increases to the interfacial area a and the more modest increases to the physical liquid-film coefficient k_L^o. (We note, however, that interfacial area is known to be a nonlinear function of liquid rate, the former tending to rise but level off as the latter increases.) When a fast equilibrium chemical reaction is involved, quite contrary behavior may be found.

Consider the curve corresponding to the lowest gas rate in Figure 3(a), which itself is for a low solution loading. When L is also low we expect the liquid film to contribute significantly to the overall resistance to mass transfer. The *mean* solvent loading within the column will be somewhat below its value in the feed, i.e., a modest amount of stripping takes place. However, as L increases, the mean value of α will rise toward its value in the feed. A change in α implies an opposite change in the enhancement factor ϕ because B, A, A^* and especially the equilibrium constant K are affected. The equilibrium partial pressure of CO_2 in the vapor phase is extremely sensitive to solution loading. Thus, $[CO_2]_e$ in the liquid phase (found using Henry's law) is equally responsive and, refering to Eq. 22, this sensitivity is transmitted to the equilibrium constant. Thus, the increase in the mean value of α which results from a higher liquid rate causes ϕ to drop and in the present case this reduction is greater than the simultaneous increase to $k_L^o a$. The net result is an overall mass transfer coefficient which is a *reducing* function of liquid rate.

Contrast this with the curve for the highest vapor rate in Figure

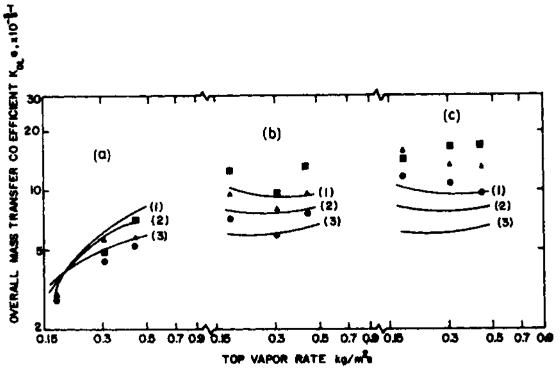

Figure 4. Effect of vapor rate on $K_{OL}a$ for 2.5 kmol/m^3 amine at 1.68 atm. Plots (a), (b), (c) correspond to feed solution loadings of 0.163, 0.322 nd 0.24; curves (1), (2), (3) correspond to L_T = 4.98 (■), 4.07 (▲), and 3.11 (●) kg/m^2·s.

3(a). Now, when L is low the mean value of α will be very low indeed, compared to its feed value. Thus the mean enhancement factor is very high and the gas film resistance becomes more dominant. (That a higher gas rate can lead to a *greater* proportion of the overall resistance residing in the vapor phase seems curious—the effect is an indirect, albeit important, one acting through the reversible kinetics of the liquid-phase chemical reactions.) As the liquid rate rises of course, the mean value of α increases and ϕ drops but now the effect on the overall process is weak because the liquid-film resistance is relatively insignificant. Rather the interfacial area goes up and its influence is unimpaired by other effects. Furthermore, the rate of mass transfer, hence, the condensation rate of steam (the heat source for the endothermic reaction) and the average vapor rate go up. The result is an increase in both k_G and a with increasing liquid rate and a positive effect on the overall coefficient $K_{OL}a$.

The (b) and (c) plots in Figure 3 all correspond to sufficiently high solution loadings that ϕ is quite low (but never less than unity) and the liquid-film resistance controls. Changes to the mean solution loading which result from increased liquid rates now have virtually no effect on ϕ and the changes to the physical film coefficient $k_L^\circ a$ are the ones directly responsible for the increases to $K_{OL}a$ with increasing L.

The common experience that high liquid rates lead to better mass transfer coefficients can be misleading in some chemically reactive systems. If equilibrium and thermodynamic considerations play a role, these can have quite a strong *negative* effect, brought into play indirectly by a seemingly harmless variable such as the liquid rate. These factors interact in a rather complicated way, which however, can be successfully modelled, as a comparison between theory and experiment shows. Although the fit between model (solid lines) and observation is far from perfect, the model does reflect the magnitude of the coefficients and the general trends observed.

Stripping Steam Rate

The effect of steam rate on the mass transfer coefficient is shown in Figure 4 for three solution loadings and an operating pressure of 1.68 atm (absolute). From previous experience with the absorption of sparingly soluble gases into highly reactive solution, one might again anticipate that the bulk of the resistance to mass transfer resides in the liquid phase. The effect of vapor rate in the (b) and (c) portions of Figure 4 is weak, perhaps tending to support this contention, although an interesting observation is that when α is high and G is low, an increase in gas rate can mildly *reduce* the overall mass transfer coefficient. Of at least equal significance, however, the plots for low α show a strong effect of vapor rate, perhaps indicating a significant gas-film resistance.

When solution loading is high the driving force and mass transfer rate are both relatively large. However, the curves themselves amply demonstrate that the process is not gas-side controlled so the explanation for the sometimes negative effect of vapor rate on $K_{OL}a$ cannot be found there; rather, it is the dominant liquid-side resistance which is being indirectly influenced. It must be kept in mind that the vapor rates quoted on the figures are those *leaving* the column and that substantial heat effects are involved in the stripping process. (Undoubtedly it would be more pleasing to see results reported on the basis of the boilup rate at the bottom of the column; however, experimentally it was the top vapor rates that were measured.) Thus, as vapor rates increase from low values, the increased mass transfer rates require proportionately higher rates of heat supply for carbamate decomposition and CO_2 evolution. This heat is provided by the latent heat of condensation of stripping steam within the column; hence, as it flows over the packing, the liquid phase becomes progressively diluted. At high α the free amine concentration B in Eq. 20 is already low; further dilution lowers it even more and it would seem that it is the resulting slightly-reduced enhancement factor which is responsible for the decrease in mass transfer coefficient. On the other hand, when the vapor rate is already high, the average solution loading in the column is much reduced so that A_i and A_L are lower and this leads to a slightly higher enhancement factor, hence, transfer coefficient. The balance is a delicate one and weakly affects the mass transfer coefficient in a subtle way.

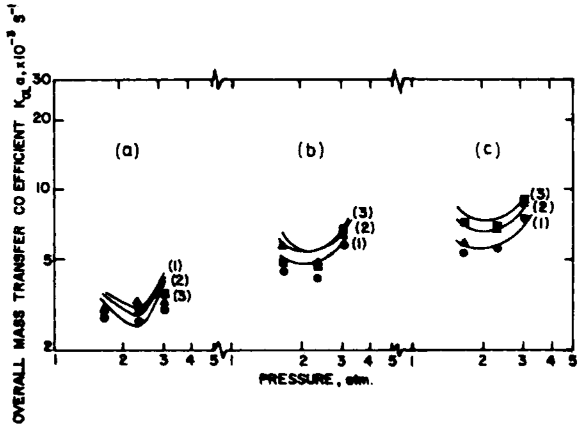

Figure 5. Effect of operating pressure on $K_{OL}a$ for 2.5 kmol/m^3 MEA feed solution loaded to 0.163. Plots (a), (b), (c) are for G_T = 0.177, 0.309 and 0.440, respectively. Curves (1), (2), (3) correspond to L_T = 4.98 (■), 4.07 (▲), 3.11 (●) kg/m^2·s.

Turning to corresponding results for low solution loadings, we find what appears to be significant gas-side resistance. When α is low the free CO_2 concentration is low while the concentration of free amine, B, is high. Thus ϕ is large, the effective liquid film coefficient is high and, as a result, much of the resistance is transferred to the gas phase. Then, increases in k_G with gas rate are significant and in addition the interfacial concentration of CO_2, A^*, drops so that ϕ increases still more. The effect is synergistic and we find a *very* strong influence of G on $K_{OL}a$ at low solution loadings.

An interesting conclusion can be drawn about the operation of commercial strippers in which solvent loadings typically vary from very high near the top of the column to very low near the bottom. It is quite probable that the controlling resistance shifts from being liquid-side at the top to gas-side at the bottom. Thus, an increase in boilup rate, for example, will improve column performance near the base but have little or no positive influence on stripping in the rest of the column so that the net effect of increased vapor rates can be disappointing in view of the additional costs involved.

Stripper Operating Pressure

The overall mass transfer coefficient exhibits an unusual dependence on the operating pressure of the stripper as can be seen from Figure 5. Vapor rate varies between the three plots. In nearly every case $K_{OL}a$ appears to pass through a minimum in the vicinity

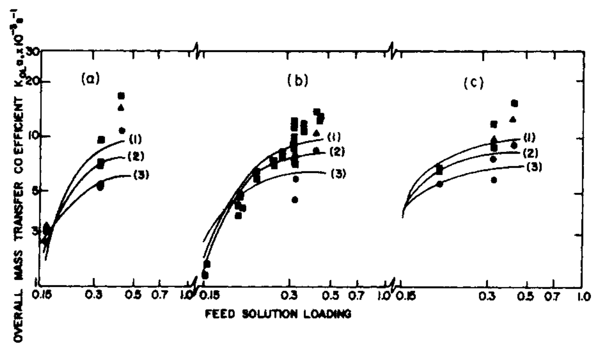

Figure 6. Dependence of $K_{OL}a$ on solution loading for 2.5 kmol/m^3 amine and a column pressure of 2.36 atm. Plots (a), (b), (c) are for vapor rates of 0.177, 0.309 and 0.440 kg/m^2·s, respectively; curves (1), (2), (3) correspond to L_T = 4.98 (■), 4.07 (▲) and 3.11 (●) kg/m^2·s, respectively.

of an operating pressure of two atmospheres absolute, although the sharpness of the minimum weakens to some extent as the vapor rate goes up. (Although not shown here, the minimum becomes less sharp also as the solution loading increases.) The most likely explanation for a minimum is the action of competing effects.

Because we are dealing with a boiling system, a change in pressure results in a concomitant change in temperature. A pressure change directly affects the gas-side coefficient k_G through gas viscosity and diffusion coefficients but, of far greater importance, it profoundly affects the thermodynamics of the liquid-phase chemical reactions. For example, the equilibrium constant K given in Eq. 22 is extremely sensitive to temperature. Equilibrium partial pressures of CO_2 depend exponentially on temperature and, in the range of interest in stripping, they may increase by factors of 5 to 8 for a 10°C temperature rise. Thus K is a strongly decreasing function of temperature. Temperature changes also affect the liquid-side coefficient $k_L^\circ a$ through the solution viscosity and diffusion coefficients of the various species. (The effect of temperature on interfacial area seems never to have been successfully studied.)

At low absolute pressures the dominant resistant is in the gas phase and, since $k_G \propto 1/P'$, we expect $K_{OL}a$ to decrease with rising pressure; however, the simultaneous rise in temperature drastically *reduces* the equilibrium constant K and causes an equally drastic rise in the free dissolved CO_2 concentrations A^* and A. Thus, the enhancement factor ϕ, which is greatest at lowest temperature, falls dramatically with rising temperature and *the dominant resistance swings to the liquid phase*. Of course, the asymptotic value of ϕ is unity and as this value is approached the process becomes essentially a physical one, but also one in which the thermodynamics of the chemical equilibrium is still important in determining driving forces. Since $k_L^\circ a$ is an increasing function of temperature (to which diffusion coefficients are especially sensitive) it is, therefore, understandable that $K_{OL}a$ then begins to rise.

Depending on other operating conditions, an increase in stripper pressure can provide large, modest and sometimes negative benefits in terms of mass transfer coefficients.

Solution Loading

The sole purpose of the solvent recovery section of a gas purification plant is to reduce the loading of the recirculating solution from very high to acceptably low levels. Thus, it is the solution loading which experiences the greatest variation within the stripping column.

The effect of solution loading on $K_{OL}a$ is shown in Figure 6 with vapor rate varying between the plots. At first glance, the positive effect of increasing α seems contradictory to what one might expect on the basis of Eq. 20. There, increasing α reduces the free amine concentration B and increases both A^* and A leading to an expected reduction in the enhancement factor. However, the influence of α is rather indirect and care is needed in interpreting the data. At low solution loadings and the low vapor rates typified by Figure 6(a) the controlling resistance is mainly in the vapor phase; even though ϕ drops with increasing α, the *overall* coefficient remains relatively unaffected.

The vapor rates quoted on these plots are those leaving the top of the column. A large proportion of the vapor phase condenses within the column to provide the heat of reaction and, as α increases, the mass transfer rate, hence, the vapor condensation rate goes up even though the leaving vapor flow remains constant. Thus, as α goes up, the *mean* vapor rate in the column also rises very significantly. This results in an increased gas-side coefficient which is responsible for the improvement to the overall coefficient $K_{OL}a$.

The sensitivity is greatest at the *lowest* solution loadings and vapor rates since then gas-phase resistance is most important. As α climbs, the effect weakens because the controlling resistance is gradually transferred to the liquid phase. This is a result, not only of k_G increasing, but also of ϕ decreasing and gradually approaching unity, i.e., no direct enhancement at all. Thus, one must anticipate that as α becomes very large, the overall mass transfer coefficient will level off and may even decrease slightly because of the higher viscosity and reduced diffusion coefficients within heavily loaded solutions.

When vapor rates are high, a good part of the resistance to mass transfer has already shifted into the liquid phase for moderately high α and above. The foregoing arguments still apply but the effects we see are necessarily weakened so that by the stage at which the liquid-phase resistance is the controlling one, ϕ is unity and $K_{OL}a$ is unresponsive to further increases in solution loading.

In industrial practice, solution loadings well in excess of one-half are often encountered. We refrain from speculating on what the mass transfer coefficients for very large α might be, however, because in that range the chemical kinetics itself is totally different and the whole complexion of the problem probably changes. Nevertheless, the current results show quantitatively what undoubtedly has been common experience for a long time—the bulk of the dissolved gas can be stripped easily; it is low solution loadings that are hard to reach.

Amine Concentration

The final variable that needs to be considered is the total concentration, M, of ethanolamine in solution. Figure 7 shows the effect on $K_{OL}a$ of varying the amine concentration M over a tenfold range from 0.5 to 5.0 kmol/m^3. It may be noted that the conditions under which these experiments were conducted correspond to control essentially by the liquid-phase resistance.

It is apparent that the best mass transfer coefficients are obtained when M is lowest, in seeming contradiction to the effect on the enhancement factor indicated by Eq. 20. However, ϕ depends linearly on the *free* amine concentration B_L while the equilibrium constant K is not affected. This is relatively weak so that the expected positive effect of increasing M would be modest at best. Rather, the effect we are seeing is a result of solution viscosity being a strong function of amine concentration, particularly at the concentrated end. For example, the viscosity of MEA solutions at 25°C rises by nearly a factor of 2.5 from infinite dilution to 5 kmol/m^3 (Thomas and Furzer, 1962; Union Carbide, 1969). These viscosity increases simultaneously cause a reduction in the diffusion coefficients of the dissolved species and both effects combine to force large decreases in k_L°. Counteracting this of course we still have an increase in ϕ which delays *serious* reductions in the overall coefficient $K_{OL}a$ until M exceeds about 2.5 kmol/m^3.

This is indeed a fortunate circumstance. Solutions low in amine have a very much reduced capacity for dissolving the gas and high circulation rates would be needed for a given plant load. The high steam costs associated with heating and boiling the extra solution could be disasterous. However, solutions as high as 2.5 kmol/m^3 can be used with little penalty in terms of mass transfer rates; beyond that one must weigh the benefits of reduced circulation rates and heat loads against the costs of a higher column.

Although we have not collected data on the effect of amine

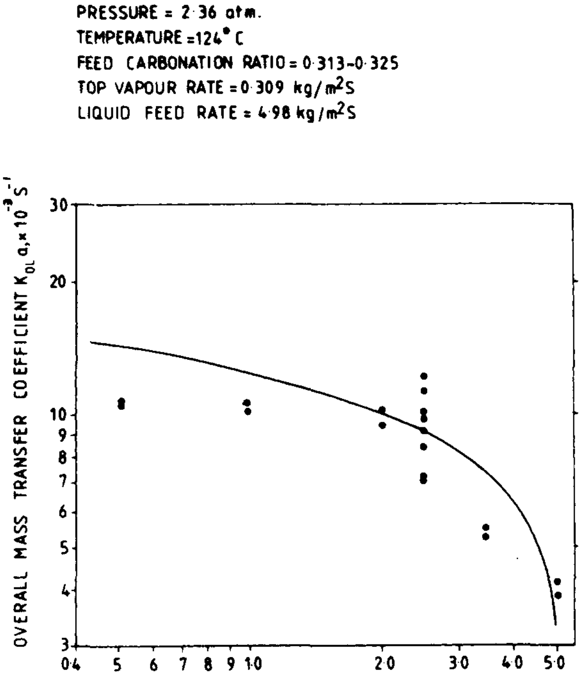

Figure 7. Effect of MEA concentration on $K_{OL}a$ for solution loadings between 0.313 and 0.325 and a column pressure of 2.36 atm; L_T = 4.98 kg/m²·s and G_T = 0.309 kg/m²·s.

concentration at low solution loadings and gas rates (for which both the gas and liquid phase resistances would be important) it is safe to surmise from the foregoing that M would have only a small effect on the overall mass transfer coefficient in these cases.

CONCLUDING REMARKS

The experimental mass transfer coefficients $K_{OL}a$ we have determined ranged from 1.7×10^{-3} s^{-1} to 18.0×10^{-3} s^{-1} when liquid and gas rates were varied from 3.1 to 10 kg/m²·s and 0.15 to 0.55 kg/m²·s, respectively. The pressure (temperature) range covered was 1.3 atm (108°C) to 4.4 atm (148°C) absolute and feed solution loading varied between 0.103 and 0.44, although values as low as 0.090 were found at the bottom of the column. It is interesting to note that overall height of a transfer unit based on the liquid phase was found to vary from 0.26 m to as high as 2.9 m. This latter figure corresponds to middle-of-the-range gas and liquid rates and pressure with a very *low* feed liquor loading of 0.104. In general, light solution loadings lead to very large transfer unit heights regardless of other conditions, while for α much above 0.2 a safe value of H_{OL} for design purposes seems to be 0.6 to 0.7 m (i.e., about 2 ft). Bearing in mind, however, that very low loadings are achieved at the base of most commercial towers, a column design based on 0.6 m would be grossly inadequate.

A summary comparison between all of our experimental data and predictions from first principles made as outlined earlier is shown in Figure 8. Predicted values of $K_{OL}a$ seem to be fairly evenly scattered about the line of perfect agreement, with a root mean square deviation of about ±25%. Considering large uncertainties in many of the basic parameters used in the model the agreement between theory and experiment must be considered somewhat better than one might anticipate. Thus, the model gives every indication of being a potentially good representation of this type of process.

Our present concern has been with the applicability of currently-available fundamental knowledge to the more pragmatic problem of design and analysis of industrial-scale equipment. The analysis presented here has involved absolutely no parameter estimation or curve fitting; predictions have been strictly *a priori*. Nevertheless, the model does a creditable job of predicting stripping column performance given the facts that certain parameters have had to be obtained by independent experiments, others have been taken from conflicting sources, and still others could be found only by extensive extrapolation. Of course, this must not be construed as proof that the model accurately portrays fundamental truth; packed columns are not the type of equipment best-suited to testing the efficacy of basic models of mass transfer. Rather, it gives some hope that stripping column performance can be predicted from first principles, that these columns can be designed in a real sense, and that stripping plants can be optimized in terms, for example, of energy costs.

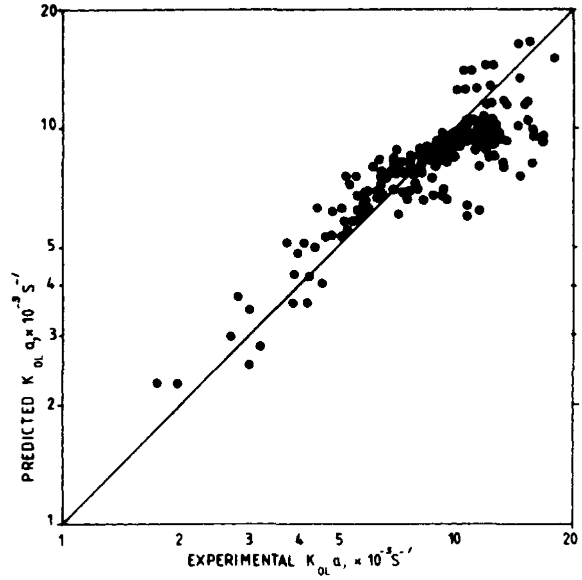

Figure 8. Summary comparison between predicted and experimentally measured overall mass transfer coefficients.

ACKNOWLEDGMENT

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NOTATION

a = interfacial area (m^{-1})
A = concentration of free CO_2 in liquid (kmol/m³) or parameter in Eq. A2
$\mathcal{A}$ = transferring component (acid gas)
B = concentration of free MEA in liquid (kmol/m³) or parameter in Eq. A2
c_i = ionic concentration of species i (kg-ion/m³)
$[CO_2]_e$ = concentration of dissolved free CO_2 in equilibrium with gas phase (kmol/m³)
D = diffusion coefficient (m²/s)
G = vapor rate (kg/m²·s)
h = salting out parameter (m³/kg-ion) or packed height of column (m)
h_G, h_+, h_- = contributions of solute gas, positive ions and negative ions to salting-out parameter (m³/kg-ion)
H = Henry's law constant for solutions (atm·m³/kmol)
H^o = Henry's law constant for water (atm·m³/kmol)
H_{OL} = overall height of transfer unit based on liquid phase (m)
I = ionic strength of aqueous electrolytes (kg-ion/m³)
k_G = gas-film coefficient (kmol/m²·atm·s)
k_L^o = liquid-film coefficient without reaction (m/s)
K = equilibrium constant (m³/kmol)

$K_{OL}a$ = overall coefficient based on liquid phase (s^{-1})
L = liquid rate ($kg/m^2 \cdot s$)
L_m = molar liquid rate ($kmol/m^2 \cdot s$)
M = concentration of MEA ($kmol/m^3$)
$\mathcal{M}$ = molecular weight of vapor phase (kg/kmol)
N = mass transfer rate ($kmol/m^2 \cdot s$)
p = partial pressure (atm absolute)
P = stripper pressure (atm absolute)
P' = partial pressure of inerts (atm)
r_i = ratio of diffusivities, $= D_i/D_A$
R = universal gas constant
S = steam condensation rate ($kmol/m^2 \cdot s$)
T = temperature (K)
x = mole fraction of CO_2 in all forms in the liquid phase
x_e^* = mole fraction CO_2 in liquid phase which would be in equilibrium with the bulk vapor
Z = parameter in Eq. A1

Greek Letters

α = solution loading (kmol CO_2/kmol amine)
ΔH = total heat of desorption (MJ/kmol)
ΔH_R = heat of reaction (MJ/kmol)
ΔH_s = heat of dissolution (MJ/kmol)
λ_s = latent heat of condensation of steam (MJ/kmol)
μ = shear viscosity ($kg/m \cdot s$)
ν_i = stoichiometric coefficient
ξ = defined by Eq. 12
ρ = density (kg/m^3)
ρ_m = molar density of liquid ($kmol/m^3$)
ϕ = enhancement factor

Subscripts

B = bottom of column
G = gas phase
i = component number
j = section number in column
L = liquid phase
m = molar
T = top of column

Superscripts

$*$ = at equilibrium at the interface
$-$ = (overbar) average

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APPENDIX I: EQUILIBRIUM RELATION

Calculation of the enhancement factor ϕ requires a correlation of the equilibrium solubility of CO_2 in aqueous MEA solutions. Of the wealth of data available, almost all are in the form of plots of the equilibrium partial pressure of CO_2 as a function of solution loading with temperature as parameter; this format is quite unsuitable for correlation. When Henry's law is combined with Eq. 20 and the usual exponential dependence on temperature is assumed, the expression

$$p_{CO_2} = Z\left(\frac{\alpha}{1-2\alpha}\right)^2 \exp(-\Delta H/RT) \qquad (A1)$$

would be most suitable for correlation. Here the parameter Z and the total enthalpy of solution (including reaction) H may depend on concentration and solution loading. The procedure adopted was to fit each set of data in the form $\ln P_{CO_2}$ vs. α at fixed temperature and MEA concentration with a polynomial of up to third degree in α. This allowed the smoothed data to be converted into the form $\ln P_{CO_2}$ vs. $1/T$ for fixed α and MEA concentration. Straight lines of the form

$$\ln p_{CO_2} = A + B\,(10^3/T - 3.0) \qquad (A2)$$

were fitted through each smoothed data set to obtain the least squares values and standard deviations of A and B. (Data were found to be centered at a temperature of about 60°C; hence, the factor 3.0 appears in Eq. A2 to maintain roughly equal weighting of all data.) Finally, A and B, weighted according to their respective standard deviations, were correlated with solution loading α. For $\alpha < 0.45$ no dependence on MEA concentration was found. The final correlation in the form of Eq. A1 was

$$\ln p_{CO_2} = -3.70 - 4.83\,\alpha + 2\ln[\alpha/(1-2\alpha)] + (-9.71 - 8.18\,\alpha + 25.2\,\alpha^2)(10^3/T - 3.0) \qquad (A3)$$

The actual experimental data of Jones et al. (1959), Lawson and Garst (1976), Lee et al. (1974), Lyudkovskaya and Liebush (1949), Mason and Dodge (1936), Mulbauer and Monaghan (1957), Murzin et al. (1969), and Nasir and Mather (1977) are compared with the correlation in Figure A-1. The experimental measurements cover a temperature range from 0°C to 140°C for MEA concentrations between 0.5 N and 9.5 N and solution loadings less than 0.45, and include some 250 points.

The equilibrium data of various workers typically differ from each other by about 50% although differences of a factor of two or three are not uncommon. This is reflected in the considerable scatter which is apparent in Figure A-1. Because of the necessity to go through a preliminary fitting procedure to convert the data into usable form, it cannot be claimed that Eq. A3 is statistically the best fit. However, the procedure adopted does guarantee that the correlation is not unduly biased.

By comparing Eqs. A1 and A3 it can be seen that the total heat of solution is

$$\Delta H = 80.8 + 67.8\,\alpha - 209.0\alpha^2 \qquad (A4)$$

in MJ/kgmol and that this depends on solvent loading. Danckwerts (1970) reports the heat of solution of CO_2 in water to be about 19.9 MJ/kgmol while Hikita et al. (1977) have found that the heat of reaction of uncarbonated MEA is 75.8 MJ/kgmol at 35°C, and to be temperature dependent. The sum of these two is 95.7 which is about 15% higher than the value 83.7 obtained from Eq. A4 at $\alpha = 0.05$, the smallest value of α in the range correlated.

To calculate the equilibrium constant K all one need do is use Eq. A3 to find p_{CO_2} and relate this to the liquid-phase concentration $[CO_2]_e$ through Henry's law, appropriately modified to account for the presence of all the species in solution.

Laminar Tube Flow with a Thermosetting Polymerization

Two models describing the laminar flow of a polymerizing liquid through a tube have been developed and tested experimentally. One model is a full finite difference solution of the balance equations. The other is an approximate analytical solution which assumes that flow ceases after viscosity increases about tenfold. The models are compared to two experimental cases: 1) the pressure rise needed to keep the flow rate through the tube constant and 2) the flow rate decrease when pressure at the tube entrance is held constant. The finite difference model is more accurate in the early stages of polymerization while the approximate analytical model is more accurate at long times. The models have application to runner flow in reaction injection molding, to nozzles in thermoset molding, to thermoset dispensing equipment and to continuous reactive polymer processes in general.

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SCOPE

The introduction of Reaction Injection Molding (RIM), (Prepelka and Wharton, 1975; Lee, 1980) has resulted in considerable interest in molding thermosetting polyurethanes. Whereas high pressures are needed to inject mold conventional, high viscosity thermoplastic materials, the low viscosities of the polyurethane reactants allow a mold to be filled using much lower pressures. RIM is thus particularly advantageous in molding large surface area parts and is being used, among

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