INTERFACIAL AREA, MASS TRANSFER COEFFICIENT AND POROSITY IN AQUEOUS SOLUTIONS OF AMMONIA REACTING WITH CARBON DIOXIDE

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Absorption of carbon dioxide into aqueous solution of ammonia is studied. This reaction proves to be suitable for determination of interfacial area in bubbled beds. At the same time the high mass transfer coefficients indicate an existing interfacial turbulence in this system which is confirmed by the made photographs.

Behaviour of the bubbled bed in the system of aqueous solution of ammonia reacting with carbon dioxide was studied. This system was expected to be interesting for measurement of interfacial area and for studies on interfacial turbulence which appearance was anticipated. Kinetics of this reaction is relatively well known in relation to industrial applications of absorption of acid gases into aqueous solution of alcaline amines and information are available concerning the chemical equilibria of the partially carbonised ammonia solutions.

THEORETICAL

Absorption of pure carbon dioxide (A) into aqueous solution of ammonia (B) in the bubbled bed satisfies, in a wide range of experimental conditions, the condition of the pseudo-first order reaction and the absorption rate is given by the relation

$$R_{\rm A} = H_{\rm A} \, p_{\rm G} (k_{\rm L}^2 + D k c_{\rm B})^{1/2} \,. \tag{1}$$

From the kinetic point of view, the controlling reaction is the formation of the activated complex from carbon dioxide and ammonia. For the equilibrium pressure CO_2 on the interfacial boundary we substitute

$$p_{\rm G} = \bar{p} - (p_{\rm A} + p_{\rm B} + p_{\rm C}), \qquad (2)$$

where the index C denotes water and where the equilibrium pressures p_A and p_B can be calculated on basis of the existing equilibrium balances (e.g. by Van Krevelen).

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From the material balance of ammonia results in the steady state

$$R_{\rm B}S = c_{\rm B}^{0}x_{\rm s}CV_{\rm L} \,. \tag{3}$$

Under the assumption that z moles of ammonia react with 1 mol CO₂ we define the carbonisation degree and conversion

$$R_{\rm B} = z R_{\rm A} , \qquad (4)$$

$$C = c_{\rm A}/c_{\rm B}^0, \qquad (5)$$

$$x_s = zC. (6)$$

Relations (1) to (6) are modified with regard to the original Danckwerts method¹ to the form

$$q_1 = z_2 + z_1 m_1 \tag{7}$$

where

$$q_{1} = (c_{B}^{0}CV_{L})^{2}/H_{A}^{2}p_{G}^{2}D,$$

$$m_{1} = k \cdot c_{B},$$

$$z_{1} = S^{2},$$

$$z_{2} = 4S^{2}/\pi t_{D}.$$
(8)

The mass transfer coefficient in liquid was expressed by use of the contact time in agreement with the classical approach according to Highbie (the arrangement is made with an aim to avoid the implicite temperature dependence of $k_{\rm L}$).

At the assumption that z_1 and z_2 (*i.e.* the over-all interfacial area and the bubble size) are not in the range of considered temperature interval $(20-40^{\circ}\text{C} \text{ in practical cases})$ too dependent on temperature the procedure can also be applied to non-isothermal conditions. Eq. (7) is then equation of a straight line and the constants z_1 and z_2 can be easily evaluated statistically from the set of experimental non-isothermal data.

The dependence of interfacial area on temperature was studied by Mashelkar and Sharma². For absorption of CO₂ into the aqueous solution of sodium hydroxide they determined a change in the interfacial area at the temperature rise from 20 to 40°C only by 6%. This result was confirmed by our experimental dependences of the nonisothermal pairs $q_1 - m_1$ for the system CO₂—H₂O—NH₃ (Fig. 1).

EXPERIMENTAL

Relations for Determination of Physico-Chemical Parameters of the System

Diffusion coefficient. On basis of the published data³⁻⁸ for diffusion coefficient of CO_2 in water the optimum values were statistically selected for the range of temperatures from 20-40°C. For the given temperature the linear interpolation was used. The results are given in Table I. For aqueous solution of electrolytes a correction⁹ has been made according to the relation

$$D = D_{\rm C}(\mu_{\rm L}/\mu_{\rm C})^{-0.637}.$$
(9)

Rate constant. The value was calculated according to the published¹⁰ relation

$$\log k = 11.13 - 2530/T [1/\text{mol s}], \quad T = 273 - 313 \text{ K}.$$
 (10)

The same authors have studied the dependence of the rate constant on ionic strength in the

TABLE I Diffusion Coefficients of CO₂ in Water

<i>t</i> , °C	20	21	22	23	24	25	26	27	28	29	30
<i>D</i> . 10 ⁵ , cm ² /s	1·71	1·75	1·8	1·84	1·88	1·92	1·97	2·02	2·16	2·11	2·17
$t D \cdot 10^5$	31 2·22	32 2·27	33 2·32	34 2·47	35 2·43	36 2·48	37 2·55	38 2·60	39 2·66	40 2·73	



FIG. 1

range I = 0-4 mol/l, their results were presented in a graphical way. We have expressed their results analytically by a simple equation

$$\begin{aligned} \gamma &= 1 + 0.033I, \qquad (11)\\ \gamma &= \log k_{\rm I} / \log k_0, \end{aligned}$$

which holds in the given interval I at 20°C. Due to lack of additional data the same form of this dependence was assumed to be valid also beyond the given temperature.

Rate constants in dependence on temperature and ionic strength. The temperature dependences were interpolated on basis of the tabelled data of individual equilibrium constants for 20 and 40°C as published by Van Krevelen and others¹¹ in the form

$$\log K_i = A/T + B . \tag{12}$$

Equilibrium constants given in Table II are defined

$$K_1 = [NH_4^+][HCO_3^-]/[NH_3] p_A; \quad (p_A \text{ in Torr})$$

$$K_2 = [NH_2COO^-]/[NH_3][HCO_3^-];$$

$$K_3 = [NH_4^+][CO_3^{2^-}]/[NH_3][HCO_3^-].$$

The equilibrium data must be supplemented by the total ammonia and carbon dioxide balances (analytically determined), ionic balances and the Henrys' law. The procedure of calculation of the total free ammonia which is substituted into relation (1) $([NH_3] \equiv c_B)$ is obvious and is given in literature¹¹.* The constant K_1 is strongly dependent on ionic strength of the solution¹¹. Thus we have defined the correction factor

$$\varkappa = K_1^1 / K_1^0 . \tag{13}$$

TABLE II Equilibrium Constants Calculated on Basis of Published Data Constants			TABLE III Dependence of K_1 in Ionic Strength in the Range of Temperatures $20-60^{\circ}$ C			
Constants	А	В	<i>I</i> , mol/l	×		
K ₁ ^a	2 979.0	-11.4627	0 -0.3	1 + 6.2I		
K_{2}	867.84	- 2.4288	0.3-0.9	2.15 + 2I		
<i>K</i> ₃	113-95	- 1·2710	0.9-2.2	1.1 + 3.15I		
			2.2-3.0	4.9 + 5.89I		
^{<i>a</i>} For $I = 0$.						

In original literature there is a printing error in the relation for [NH⁺₄].

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The dependence of this factor on ionic strength, calculated on basis of published data can be advantageously approximated by straight lines (Table III).

Henry constant for CO_2 and NH_3 . On basis of the published data¹² the temperature dependence for the range of temperatures from 20 to 60°C has been expressed by the relation

$$\log H_{\rm A} = -7.727 + 973.47/(273.16 + t) \,. \tag{14}$$

Correction for solution of electrolytes^{13,14} has the form

$$-\log\left[H_{electrolyte}/H_{C}\right] = hI, \qquad (15)$$

where h is the sum of contributions of individual ions and of the dissolved gas $h = h_+ + h_- + h_G$ For these purpose the simplification¹⁵ has been made by introducing the assumption that the resulting solution is ammonium carbonate. For individual contributions h are data available in literature¹⁶ (0.028 l (mol H⁺)⁻¹ 0.021 l (mol H⁻)⁻¹ and -0.019 l/mol. On basis of empirical data the relation has been derived

$$\log H_{\rm B} = -7.2525 + 1.831.7/(273.16 + t), \quad [\rm{gmol/l\,Torr}], \quad (16)$$

where H_{B^-} is affected contrary to H_{A^-} by the ammonia concentration. The corrected value of the Henry constant¹⁷ has the form

$$H'_{\rm B} = \omega H_{\rm B}; \quad \log \omega = -0.0237 (c_{\rm B}/\varrho_{\rm B}) \tag{17}$$

where $\rho_{\rm B}$ is density of the ammonia solution with the conc. of free ammonia $c_{\rm B}$.

Vapour pressure. On basis of tabelled data¹⁸ the dependence has been evaluated

$$\log p_{\rm C} = 2291.025/T - 6.571$$
, [Torr] (18)

Ionic strength. The ionic strength of solution has been in agreement with literature¹⁵, calculated at the simplified assumption that the aqueous solution is ammonium hydrogen carbonate according to the general relation

$$I = 1/2 \sum c_i z_i^2 , (19)$$

where z_i is the charge of the *i*-th ion.

Stoichiometric constant. According to Van Krevelen¹⁹ the stoichiometric constant z expressing the number of moles of NH₃ reacting with one mol of CO₂ depends on the concentration of free ammonia in the reaction mixture. For the range from 0 to 4 g mol/l NH₃, the published data have been corrected by the relation

$$\log z = 0.1982 - 0.0257c_{\rm B}^0. \tag{20}$$

Densities of aqueous solution of ammonia. The dependence of aqueous solution of ammonia on concentration^{20,21} has been in the range of conc. from 0 to 4 gmol/l and temperatures from 20 to 25°C approximated by the straight line

$$\varrho_{\rm B} = 0.9981 - 0.0073c_{\rm B}^{\rm o} \,, \quad (g/{\rm cm}^3) \tag{21}$$

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Viscosity of ammonia solutions. Empirical data^{21,22} were correlated for the range from 0 to 4 gmol/l NH₃ and 25°C by the Eq. (22)

$$\mu_{\rm B} = 0.997 + 2.15 \cdot 10^{-2} c_{\rm B}^0, \quad [\rm cP]$$
⁽²²⁾

Measurements

Apparatus. The measurements were performed in the cylindrical column with the perforated plate with circular holes as a distributor, ID of the column was 152 mm, $\varphi = 3\%$, $d_0 = 1.6$ mm, clear liquid height ~0.5 m, flow arrangement of both phases cocurrent. The geometrical plate parameters were chosen so as not to affect the hydrodynamic character of the bubbled bed and the results obtained could be used for other geometrical arrangements of the experiments as well. The superficial gas velocities were from 2.2 to 18.2 cm/s, superficial liquid velocity was 6.6 . $.10^{-3}$ m/s. Below the distributing plate was situated in the distance 0.1 m a perforated plate with the free plate area 0.5% needed for uniform distribution of the gas in the gas chamber below the distributing plate. In the wall of the column were equidistantly situated 11 manometric taps for measurement of porosity of the bed. All metal parts were covered by a layer of baked silicone varnish Lukosil 200 X, packings were made of polyvinyl chloride and polyethylene. The gas was supplied from a pressure flask through a system of reduction valves and rota-meters.

Residence time distribution. We have used the method of impulse and response to the impulse of the tracer compound (methylene blue), the dimensionless *E*-function was expressed for linear gas velocities 0.027, 0.05, 0.21 m/s and liquid $6.6 \cdot 10^{-3}$ m/s.

Measurement of the course of secondary hydrolysis. Into the 0.96M-NH₃ solution free of CO₂ was introduced pure CO₂ through the sintered glass. Simultaneously with closing of the gas inlet was registered the decrease in pH in time for solutions carbonised to a different degree C = 0.0619 - 0.2919.

State of the interface. Behaviour of the interface during the mass transfer was observed visually by the strioscope Zeiss-Jena, type 80, for the light source served Hg lamp HBO 500. A bubble of the observed gas was introduced through the polyethylene hose with ID 5 mm into the studied liquid poured into the cell and shots were taken of individual time phases of the gas dissolving. The systems studied were: aqueous solution of ammonia 1 to 4 mol/l reacting with gaseous CO₂. for comparison the solution of buffer K₂CO₃ and NaHCO₃ 0·6 : 0·2 mol/l catalysed by 0·4M NaClO--CO₂ and the aqueous solution of Na₂SO₃ 0·4 mol/l catalysed by the 10⁻⁴M CoSO₄--O₂ were also studied.

Determination of total CO₂ and NH₃ concentrations. CO₂ evolved by the diluted sulphuric acid (1:1) was led by the carrier gas N₂ through the reflux condenser and drying flask (filled with H₂SO₄ and U-tube with Mg(ClO₄)₂ into the absorption U-tube filled with the mixture of soda lime and Mg(ClO₄)₂. The total CO₂ was calculated from the weight gain. Total NH₃ was determined by titration by standard acid to methylorange.

Porosity was measured by determination of static pressure along the bed height. From experimental pressures y_i , read on manometers connected to taps situated at the distance x_i from the plate were determined: mean porosity $e_p = (y_k - y_0)/(x_k - x_0)$, where k-th tap is the last one in the upper surface of clear liquid still filled with liquid, x_0 is the tap in the plate level. Mean porosity e_s is the value in the central part of the heterogeneous bed which is constant with the bed height. Its numerical value equals to the slope of the central straight part of the graph in co

ordinates $\Delta y_i - x_i$ where $\Delta y_i = y_i - y_0$. The slope was calculated numerically by the least square method. Porosity e_N was calculated from the height of the bubbled bed N, estimated visually and the clear liquid height determined manometrically.

RESULTS

Liquid mixing in the column. From comparison of E-curves (Fig. 2) for different gas velocities with the theoretical E-curve for the perfectly stirred liquid is obvious that at the chosen hydrodynamic conditions and geometrical arrangement the liquid can be considered perfectly mixed in all cases from the point of view of residence time distributions. By additional measurements of temperature distribution and concentrations of dissolved CO₂ is this conclusion confirmed. The temperatures were taken at two points situated 0.05 and 0.4 m apart from the plate, their readings differed by 0.1°C at max (at the maximum difference of liquid temperatures at the inlet and outlet into and from the column by 20°C). In additional measurements of conc. of dissolved CO₂ performed at distances 0.05, 0.25 and 0.6 m from the plate, the maximum difference accounted to 2% rel.

Condition for validity of calculation relations. Danckwerts¹ gives the criterion of the pseudo-first order for the reaction of CO₂ with amines. The Danckwerts criteria were calculated for mass transfer coefficients $k_{\rm L} = 0.047 - 0.15$ cm/s the equilibrium concentrations of all components according to the Van Krevelen model¹¹ of equilibrium, initial concentrations of ammonia $c_{\rm B}^{\rm B} = 1 - 5$ gmol/l and the carbonisation degree C = 0 - 0.95 (corresponding values of $M^{1/2} = 0.3 - 3.5$). In all cases was confirmed the pseudo-first order reaction with its rate close to that of physical absorption and suitable for measurement of interfacial area.



Comparison of equilibrium models. Equilibrium in the system CO₂-NH₃-H₂O in the liquid phase is described in literature basically by two models^{11,15} which are giving different values at the calculation of the over-all absorption rate with chemical reaction or of interfacial area. The model by Danckwerts is based on the assumption (which we consider to be valid more for amines than for ammonia itself) that the secondary hydrolysis of carbamide is so slow when compared with the primary reaction that it does not take place at all within the residence time in the reactor. On basis of these considerations is obvious that for the conditions of the uncarbonised initial solution at maximum holds $C_{max} = 0.5$. As we have frequently exceeded this ratio for 1M solution in our measurements we have made an attempt to express the rate of secondary hydrolysis by measurements of pH in time after the absorption was completed. The results have not indicated any decrease in pH even after 18 h. But it seems that it is possible to assume that hydrolysis is so fast that it takes place practically simultaneously with the primary reaction and that for solutions of ammonia it is more realistic to apply the model by Van Krevelen. This model was verified by experimental data by Pexton and Badger²³ and by data of Gibson and Cribbs²⁴ on the numerical computer. The agreement of theoretical values according to the Van Krevelen model with the experimental data for partially carbonised solution was very good, the mean deviation of the whole set of data was 9.2%. Thus for our calculations this model was preferred.

Interfacial area. Interfacial area in the studied range of operating conditions was evaluated by use of relations given in the first part of this paper. The results are plotted in Fig. 3. For comparison the available results of other $authors^{25-29}$ were also drawn on this figure. Though it is very difficult to compare conclusions made by various authors with respect to different methods used (chemical, physical), different systems and sizes of devices, it is obvious that our results of specific interfacial areas by the ammonia method basically correspond with the results obtained by use of specific instruments (physical methods) or by use of less suitable systems with regard to the discussion made in the introduction.

An attempt for universal correlations of a general character enabling calculation of absolute values of interfacial areas for an arbitrary system has – in our opinion – no chance for success as it is nearly impossible to express at present all parameters which can affect the structure of the bubbled bed and consequently of the interfacial area. But it would be very advantageous from the practical point of view to know how the interfacial area will change in the bubbled bed of the given system with the changing conditions *i.e.* especially with the flow rate of both phases and dimensions of the column. From this point of view are interesting the theoretical conclusions on the interfacial area based on the concept of mutual relation of interfacial area with the dissipated energy. This approach has been applied by Kolář^{30,31}, Calderbank³² and Nagel³³ as well as in our earlier studies^{34,35}. In general, for bubbled J. PATA, F. KAŠTÁNEK, J. KRATOCHVÍL and M. RYLEK:

Interfacial Area, Mass Transfer Coefficient and Porosity in Aqueous Solutions of Ammonia Reacting with Carbon Dioxide



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Optical Observation of Interfacial Area

a Absorption with chemical reaction O_2 -S O_3^{2-} (C O^{2+}), b absorption with chemical reaction, C O_2 into soln. of NH₄OH.

beds our last theoretical study leads to the relation

$$a \sim v_{\rm g}^{0.4} e \,. \tag{23}$$

Our data together with data of other authors^{25,27,28,36} who measured simultaneously with interfacial area also the porosity of the bed are plotted, according to this correlation in Fig. 4. Diameters of columns on the basis of which were these results obtained are within the range 0.14 to 0.41 m. On basis of these data can be stated that the data are situated in the coordinates on straight lines passing through the origin except of data by Reith and Beek²⁸ which are shifted. As porosity is not profoundly dependent on the diameter of the bubled bed^{37–39} it is possible to estimate, on basis of one known value of interfacial area in the model equipment at one gas velocity, the magnitude of *a* also in another geometrical arrangement and at different gas velocity. Somewhat surprising seems the straight line obtained in Fig. 5 for the dependence of *a* on porosity (*e_s*). With exception of data by Deckwer, which are different from all results available at present the data of four authors for different systems and diameters of columns can be approx. correlated by the dependence *a*-*e* so that at least approximate conclusions can be made on the absolute values of interfacial areas if either the porosity of the bed is known or if it can be estimated





Specific Interfacial Area in Dependence in Superficial Gas Velocity

 \odot Absorption CO₂⁻²M-NaOH²⁹, \oplus water-photographically²⁵, \ominus water-photographically²⁶, \ominus our measurements, this study, Θ O₂-1·6n-Na₂SO₃, CO²⁺²⁷, Φ O₂-0·4N--Na₂SO₃, CO^{2+28,37}.



Dependence $a \sim v^{0.4} e$ \circ References²⁷, \bullet (ref.^{28,37}), \otimes (ref.²⁵),

 \oplus (ref.³⁶), \odot this study.

(it is always better to estimate a than to take it directly from the dependence $a - v_g$, see Fig. 3). But correlation must be accepted with caution as only an approximation and any generalization should not be made since its general acceptance would lead to acceptance of the assumption that various systems with differing geometry have the same average diameter of the bubble (with the approximation of spherical bubbles), which is not true from experience. From Fig. 5 results the diameter of the mean spherical bubble ($a = (3/r_B) e$) $d_b = 5.7 \text{ mm}$ (for e = 0.1).

Liquid side mass transfer coefficient and the volumetric coefficient k_1a . The experimental mass transfer coefficients obtained by the described method (Fig. 6) differ considerably from the published data The estimate according to the Calderbank's correlation gives the value $k_L = 4.3 \cdot 10^{-4}$ m/s, according to the classical relation by Highbie (for $d_b = 5.7$ mm and the corresponding time of floating of isolated bubbles⁴⁰, $t = 30^{\circ}$ C gives the value $3.3 \cdot 10^{-4}$ while our experimental data give the value k_L (calculated from k_La) in average $k_L = 1.1 \cdot 10^{-3}$ which slightly decreases with increasing gas velocity (*i.e.* with increasing carbonisation





Dependence of Interfacial Area on Mean Porosity of the Bed

○ References²⁷, ④ (ref.^{28,37}), \otimes (ref.²⁵), \oplus (ref.³⁶), \oplus this study.





Volumetric Mass Transfer Coefficient k_L in Dependence on Gas Velocity

 $\begin{array}{l} \bullet \mbox{ Desorption } O_2-NaCl, \ Na_2SO_4 \ (ref.^{36}), \\ \bullet \ \ air-Na_2SO_3 \ \ (ref.^{39}), \ ID = 0.3 \ m, \ \ \otimes \\ desorption \ \ CO_2 \ \ (ref.^{25}), \ \ \bullet \ \ air-Na_2SO_3, \\ (ref.^{39}), \ ID = 0.15 \ m, \ \ \oslash \ \ O_2-Na_2SO_3(ref.^{27}), \\ \circ \ \ \ CO_2-CO_3^2 \ \ /HCO_3- \ \ (ref.^{29}), \ \ \bullet \ \ O_2- \\ -Na_2SO_3, \ \ e \ this \ study. \end{array}$

of the solution) to values of about $90 \cdot 10^{-4}$ m/s at the maximum used v_g . We are explaining this disagreement for absorption of CO₂ into aqueous solution of ammonia by a considerable exothermic reaction (we have determined $\Delta H = -28.1$ kcal/mol CO₂) resulting in interfacial turbulence which is positively affecting the mass transfer coefficient. An increase in the mass transfer coefficient due to interfacial turbulence was recently described for absorption of CO₂ into aqueous solution of alkali amines and so it should not be surprising in the case of reaction with ammonia. The optical observations of concentration inhomogeneities confirm this conclusion (Fig. 7*). Other methods used at present for determination of interfacial turbulence considerably contributes to the increase in the mass transfer coefficient but that the active interfacial area does not change.

Porosity of aqueous solution of ammonia at bubbling by CO₂. Porosities e_p , e_s and e_N slightly differ^{35,38}. The most reliable and most suitable characteristics of porosity is considered the quantity e_s where the effect of an experimental error is less profound. The least reliable is the quantity e_N in view of difficulties with the estimate of the height N for the moving surface of the bed.

The dependence of the mean porosity e_s on gas velocity for ammonia concentrations from 0 to 4 gmol/l is plotted in Fig. 8. On basis of our experiments we have proposed an empirical correlation which gives values of e_s at bubbling by CO₂ into aqueous solution of ammonia

$$e_{\rm s} = 1.2v_{\rm g} + 0.08/(0.2 + c_{\rm B}^{0.2}), \quad (v_{\rm g} \,{\rm m} \,{\rm s}^{-1}, c_{\rm B}^{0} \,{\rm gmol/l}).$$
 (24)



FIG.8

Porosity of the Bed in Dependence on Ammonia Concentration in Solution

 $v_{\rm G}$ (m/s): $\bigcirc 0.02$, $\bigcirc 0.04$, $\bigcirc 0.06$, $\bigcirc 0.08$, $\ominus 0.10$, $\bigcirc 0.12$, $\oslash 0.14$, $\bigcirc 0.16$, $\odot 0.18$.

See insert facing page 2658.

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The agreement of experimental and calculated data is very good and with the exception of the limiting dilution at the smallest linear velocities, this error does not exceed 20%.

The measured porosities were correlated by the relation according to ${\rm Reith}^{37}$ in the form

$$e = v_{\rm g}/(2v_{\rm g} + K_{\rm R}), \qquad (25)$$

by the relation of Akita and Yoshida39

$$e/(1 - e)^4 = K_Y v_g \tag{26}$$

and by the relation we described earlier⁴¹.

The corresponding values of constants and relative deviations are given in Table IV. It is possible to see that the constants recommended by the mentioned authors do differ considerably from the optimum values calculated from Eqs (25) and (26) and that on basis of correlations available at present the porosity of solution cannot be estimated. Our relation gives the smallest relative error in the given range of concentrations (about 10%) which is the most suitable for expression of the porosity behaviour. The surprisingly small porosity is due to the considerable mass transfer and removal of the gas in the bed.

TABLE IV

Actual Constants of Porosity Correlations According to Reith³⁷ K_R , Akita and Yoshida³⁹ K_Y and our⁴¹ K_K for the Partially Carbonised Aqueous Solutions of Ammonia

Concentration gmol/l	K _R	K _Y	K	Relative error ^a , %			
				K _R	K _Y	K _K	
3.6	0.559	2.45	463	- 4.8	— 8·7	- 5.5	
3.5	0.521	2.19	395	3.5	— 9·8	- 7.0	
2.8	0.667	1.95	323	-23.6	-27.0	-20.4	
2.0	0.478	2.94	534	27.5	-31.0	- 22.4	
1.7	0.603	2.25	402	- 6.8	-11.1	6.0	
1.2	0.377	3.88	735	-15.3	-18.7	- 9.3	
1.0	0.281	5.36	1 000	-20.2	20.8	- 9.2	

^a At $v_G = 0.1$ m/s.

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LIST OF SYMBOLS
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specific interfacial area, m<sup>-1</sup>
а
       concentration, mol m<sup>-3</sup>
с
c^0
       initial concentration, mol m<sup>-3</sup>
C
       carbonisation degree, Eq. (5)
d
       diameter, m
D
       diffusion coefficient, m<sup>2</sup> s<sup>-1</sup>
       porosity
ρ
       contribution of ions defined by Eq. (15), m<sup>3</sup> mol<sup>-1</sup>
h
       Henry law constant, mol m<sup>-3</sup> Pa<sup>-1</sup>
Η
       Henry law constant corrected to the effect of ammonia ions, mol m<sup>-3</sup> Pa<sup>-1</sup>
H'
\Delta H
      heat of absorption, J \mod^{-1}
       ionic strength, mol m<sup>-3</sup>
Ι
       rate constant, m<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>
k
       rate constant in solution with ionic strength I = 1, m^3 \mod^{-1} s^{-1}
k_0
       rate constant in solution with ionic strength I, m^3 mol^{-1} s^{-1}
k_{I}
       mass transfer coefficient in liquid. ms<sup>-1</sup>
k_{\rm I}
Κ
       equilibrium constant,
       equilibrium constant, mol m<sup>-3</sup> Torr<sup>-1</sup>
K<sub>1</sub>
       equilibrium constant. m3 mol-1
K_{2}
       equilibrium constant
K_3
       constant (Kaštánek and coworkers41)
Kκ
       constant from Eq. (25), ms<sup>-1</sup>
K_{\rm R}
       constant from Eq. (26), s m^{-1}
Ky
m_1
       parameter in Eq. (8)
M = DKc/k_{\rm L}^2 parameter
Ν
       height of bubbled bed, m
       pressure, Pa
p
       equilibrium pressure on interfacial area, Pa
PG
       parameter in Eq. (8)
q_1
r
       radius, m
       absorption rate, mol m<sup>-2</sup> s<sup>-1</sup>
R
       over-all interfacial area. m2
S
t
       temperature, grad C
       contact time, s
t_{\rm D}
T
       temperature, grad K
       liquid velocity, ms<sup>-1</sup>
u<sub>L</sub>
       gas velocity, ms<sup>-1</sup>
VG
       volumetric flow rate, m3 s-1
\nu
       distance of tape from the plate, m
х
       degree of conversion,
x_{s}
       height of liquid in manometer, m
v
       stoichiometric constant,
Ζ
       valency of the i-th ion
z_i
       parameter in Eq. (8)
z_1
       parameter in Eq. (8)
z_2
       correction factor in Eq. (11)
Y
       correction factor in Eq. (13)
×
       density, kg m<sup>-3</sup>
O
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μ	dynamic viscosity,	kg m ⁻¹ s ⁻¹
ω	correction factor in	Eq. (17)

Subscripts

- A carbon dioxide
- b bubble
- B ammonia
- C water
- i *i*-th value
- k final value
- L liquid
- o initial value
- s mean value

REFERENCES

- 1. Danckwerts P. V.: Gas-Liquid Reactions. McGraw Hill, New York 1970.
- 2. Mashelkar R. A., Sharma M. M.: Trans. Inst. Chem. Eng. 48, T 162 (1970).
- 3. Cullen E. J., Davidson J. P.: Trans. Faraday Soc. 53, 113 (1957).
- 4. Nijsing R. A., Hendrikz R. H.: Chem. Eng. Sci. 10, 88 (1959).
- 5. Stefan S. B.: Akad. Wiss. Wien, Math. Naturwiss. Kl. Abt. 1878, 77, 371.
- 6. Tamman G., Jessen V.: Z. Anorg. Allg. Chem. 179, 125 (1925).
- 7. Thomas W. J., Adams M. J.: Trans. Faraday Soc. 61, 668 (1965).
- 8. Hufner G.: Ann. Phys. Chem. 60, 134 (1897).
- 9. Ratcliff G. A., Holdcroft J. G.: Trans. Inst. Chem. Eng. 41, 315 (1963).
- 10. Pinset B. R. W., Pearson L., Ronghton J. W.: Trans. Faraday Soc. 52, 1594 (1956).
- van Krevelen D. W., Hoftijzer P. J., Huntjens F. J.: Rec. Trav. Chim. Pays-Bas 68, 191 (1949).
- 12. Andrew S. P. S.: Chem. Eng. Sci. 3, 279 (1954).
- 13. Setchenov M.: Ann. Chim. Phys. 25, 1391 (1892).
- van Krevelen D. W., Hoftijzer P. J.: Chimie et Industrie. Numero Special du XXIe Congres International de Chimie Industrielle, p. 168. Bruxelles 1948.
- 15. Danckwerts P. V., Sharma M. M.: The Chem. Eng. (New York) 1966, CE 244.
- 16. Barret P. V. L .: Thesis. University of Cambridge, Cambridge 1966.
- 17. Šír Z.: Unpublished results.
- Perry R. H., Chilton C. H.: Chemical Engineers Handbook, 5th Ed., p. 3. McGraw Hill, New York 1973.
- 19. van Krevelen D. W., van Hooren C. J.: Rec. Trav. Chim. Pays Bas 67, 587 (1948).
- 20. International Critical Tables, Band 3. McGraw Hill, New York 1929.
- Timmermans H.: The Physico-chemical Constants of Binary Systems. Interscience, London 1960.
- 22. D'Ans-Lax Taschenbuch für Chemiker und Physiker. Springer, Berlin 1967.
- 23. Pexton S., Badger E. H. M.: J. Soc. Chem. Ind. 57, 106 (1938).
- 24. Gibson G. H., Gribb G. S.: Trans. Inst. Chem. Eng. 42, T 140 (1964).
- Towell G. D., Strand C. P., Ackerman G. H.: AICHE Chem. Eng. Symposium Series No 10, 10: 97, London 1965.
- 26. Voyer R. D., Miller A. I.: Can. J. Chem. Eng. 46, 335 (1968).
- 27. Carleton A. J., Flain R. J.: Report RL 59 (CE), Warren Spring Lab. 1967.

- Reith T., Beek W. J.: Proceedings of the 4-th Europ. Symposium on Chem. React. Eng., 191, Bruxelles 1968.
- Sharma M. M., Mashelkar R. A.: Symposium on Mass Transfer with Chemical Reactions (Symp. Ser. No 28, 10) Montreal 1968.
- 30. Kolář V.: This Journal 26, 335 (1961).
- 31. Kolář V.: This Journal 35, 3678 (1970).
- 32. Calderbank P. H., Moo-Young M. B.: Chem. Eng. Sci. 16, 39 (1961).
- 33. Nagel O., Kürten H., Sinn R.: Chem.-Ing.-Tech. 44, 899 (1972).
- 34. Kaštánek F., Nývlt V.: This Journal 39, 3068 (1974).
- 35. Pata J.: Thesis. Czechoslovak Academy of Sciences, Prague 1975.
- 36. Deckwer W. D., Burckhart R., Zoll G.: Chem. Eng. Sci. 29, 2177 (1974).
- 37. Reith T.: Thesis. Technische Hogeschool, Delft 1968.
- 38. Nývlt V.: Thesis. Czechoslovak Academy of Sciences, Prague 1973.
- 39. Akita K., Yoshida F.: Ind. Eng. Chem., Process Des. Develop. 12, 76 (1973).
- 40. Miller D. N.: AIChE J. 20, 445 (1974).
- 41. Kaštánek F., Nývlt V., Rylek M.: This Journal 39, 528 (1974).

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