

TWO-COMPONENT DESORPTION OF AMMONIA AND CARBON DIOXIDE FROM AQUEOUS SOLUTIONS WITH POTASSIUM

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Received June 2nd, 1971

Using the experimental data obtained on a glass desorption column, the problem of desorption of ammonia and carbon dioxide from solutions $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ and $\text{NH}_3\text{-CO}_2\text{-K}_2\text{O-H}_2\text{O}$ is compared. The effect of potassium ions present in the solution can be characterized by a change of the specific steam consumption or by a change of the slope of a pseudoequilibrium line determined by the stripping factor method. On the basis of a small number of results from the experimental column, the desorption process can be described in a simplified manner without a knowledge of equilibrium data. The method suggested here can be used in the design of a column for other systems where vapour-liquid equilibrium data are not available.

The task to design an absorption or desorption column for multicomponent systems is often met in industrial practice. With respect to the fact that vapour-liquid equilibrium data are not often known for a system of interest, the problem arises how to design a column on the basis of a limited number of experiments performed on a model apparatus. In a previous paper¹ the method of the absorption (desorption) factor was suggested for this purpose. An application of the modified method of the stripping factor is extended in this paper at a study of desorption of NH_3 and CO_2 from the solution $\text{NH}_3\text{-CO}_2\text{-K}_2\text{O-H}_2\text{O}$ that is of considerable industrial importance.

The vapour-liquid equilibrium data for this, basically four-component, system have not been found in the literature. A considerable amount of vapour-liquid equilibrium data had been published for the system without potassium, *i.e.* $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$, but the problem of their correlation has not yet been solved satisfactorily². The main difficulty is that the system cannot be treated as a three-component system, but it is necessary to consider besides bicarbonate NH_4HCO_3 and carbonate $(\text{NH}_4)_2\text{CO}_3$ also carbamate $\text{NH}_4\text{CO}_2\text{NH}_2$ in the solution. Equilibrium rectangular diagrams made for different total pressures are usually used for rapid estimations^{3,4}.

Using simplifying assumptions of constant gas and liquid flow rates in the desorption column and a linear vapour-liquid equilibrium relation, Kremser⁵ and Souders and Brown⁶ developed the equation

$$\frac{X_2 - X_1}{X_2 - Y_1/m} = \frac{(1/A)^{N+1} - (1/A)}{(1/A)^{N+1} - 1} \quad (1)$$

The equation (1) has been developed using simple relations of material balance between different trays and the total balance of the column. Goring⁷ started with a component balance of the n -th tray that solved as a linear difference equation with constant coefficients. Inlet concentrations of gas and liquid phases at the top and bottom of the column were used as boundary conditions. Tiller⁸ and Goring called attention to a certain inconsistency of Eq. (1) that may occur in the limiting case when the number of trays increases infinitely ($N \rightarrow \infty$). Eq. (1) can be used even if the stripping factor, $1/A \equiv mG/L$, varies moderately along the column. In these cases, the geometric average of values of the stripping factor at the top and the bottom of the column is used⁹. Edmister¹⁰⁻¹² suggested to use the so-called "effective factor" defined by the equation (2)

$$(1/A)_{ef} = \{(1/A)_2 [(1/A)_1 + 1] + 0.25\}^{0.50} - 0.50, \quad (2)$$

where the indexes 1 and 2 are related to the bottom and top trays in the desorption column. If the equilibrium relation and efficiency of the column are known, the number of actual trays can be determined by Eq. (1) for the required fractional desorption at different reflux ratios. In turn, the fractional desorption for a fixed number of trays can be computed. Using live steam for desorption in an experimental column, we can write

$$Y_1 = 0 \quad (3)$$

and the quantities X_1 , X_2 , G and L in Eq. (1) can be determined experimentally. With respect to Eq. (3), we can rewrite Eq. (1) as

$$(1/A)^{N+1} - (X_2/X_1) \cdot (1/A) + (X_2/X_1) - 1 = 0. \quad (4)$$

If the number of theoretical trays in Eq. (4) is substituted by the number of actual trays in the experimental column, a value of the stripping factor $1/A$ can be determined. From this value and from the gas and liquid rates, we can determine the remaining quantity m . This procedure is an approximation of the real equilibrium line by a pseudo-equilibrium straight line within the concentrational interval (X_1 , X_2). The slope, obtained in this way, includes also the efficiency of plates in the column. Eq. (4) is a polynomial of the $(N + 1)$ order that is mostly solved numerically. The approximate root of this equation can be also found by the aid of graphical solutions⁹ for the selected values of variables.

On the basis of a small number of results obtained on the experimental column, the procedure described above allows to determine the degree of difficulty of gas removal from solutions without a knowledge of the vapour-liquid equilibrium data. Therefore, this approach is especially useful in the case of multicomponent systems, when the laboratory determination of equilibrium data is often laborious and time consuming. In search of the most economical conditions of desorption, the dependence of the number of trays on the reflux ratio for a fixed degree of desorption can be easily obtained from the slope of a pseudoequilibrium line, determined by experiments, and using Eq. (1).

As the higher degree of desorption found in experiments and, therefore, the higher efficiency of the column results in a higher value of the slope m , this quantity may be also used as an efficiency factor of trays or packing in the experimental column¹. As mentioned above, this method assumes a value of the desorption factor constant along the column. The condition of constant gas and liquid flow rates is often met,

at least approximately. But the cases when a linear relation between liquid and gas equilibrium concentrations can be assumed are rare. Therefore, it is desirable to keep concentrations of the inlet and exit liquid at the experimental column close to the concentrations at the designed desorption unit.

It is obvious that the method discussed here can be applied to other stage processes where the mass transfer between two phases is accomplished in a countercurrent contact.

EXPERIMENTAL

Apparatus. The glass column employed in this study had an internal diameter of 80 mm. The number of plates could be changed from 8 through 12. The stainless sieve trays with the free area 3%, hole size 1.5 mm and height of weir 50 mm were used. The flow rates of steam and feed, the temperature at the top of the column, the pressure drop and the concentration of the liquid leaving the column were measured. The apparatus has been described in detail elsewhere¹ and the flowsheet is shown in Fig. 1. The live steam from the distribution system was used in these measurements. The flow rate of the steam was measured by the calibrated orifice plate. The flow rate of the feed was measured by the calibrated rotameter. The accuracy of these measurements was about $\pm 2\%$.

The Feed. The solution $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ was made introducing intermittently NH_3 and CO_2 from cylinders into distilled water. The cylindrical absorption vessel was manufactured from

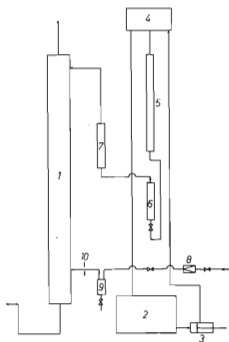


FIG. 1

Schematic Diagram of Apparatus

1 Column, 2 tank, 3 piston pump, 4 constant head tank, 5 tube exchanger, 6 rotameter, 7 electrical preheater, 8 reduction valve, 9 separator of drops, 10 orifice plate.

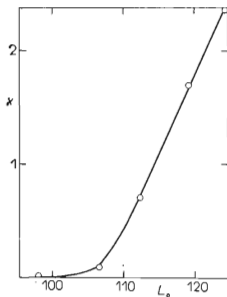


FIG. 2

Dependence of Effluent Concentrations of NH_3 (%) on Flow Rate of Feed L_0 (g/min)
 G_p 40.0 gm/min, x_0 12.5%, u_0 16.0%, N 8.

a stainless sheet and equipped with a stainless cooling spiral. The concentrations of gases were adjusted after preliminary analyses so that the final solution could contain about 12.5% NH_3 (by weight) and 15.5% CO_2 (by weight). The solution $\text{NH}_3\text{-CO}_2\text{-K}_2\text{O-H}_2\text{O}$ was prepared in a similar way. Pure potassium hydroxide was added before the final introducing of carbon dioxide. The final solution contained about 6.5% KOH (by weight). The concentration of both dissolved gases was about the same as that in the solutions without potassium.

The time required for attainment of steady state conditions was about 1 h and samples were withdrawn after this period of time. The samples were taken from the feed and the liquid leaving the column. The concentrations of NH_3 and CO_2 were determined in the samples. Ammonia was determined by oxidimetric titration with sodium hypochlorite in the presence of sodium bromide. CO_2 was determined as a volume of gas released by hydrochloric acid. The accuracy of analyses was about ± 1 and $\pm 2\%$ (rel.) respectively.

RESULTS

In preliminary experiments strong foaming of the solutions in the column was found that caused rapid flooding of the column. The silicone antifoaming agent "Anti-foam B" was added to the feed in the ratio 1 : 10^5 (by weight) to suppress the foaming. Using the antifoaming agent, a layer of the dense foam formed on the plates the height of which was limited by the height of a downcomer tube. The behaviour and the structure of the foamed liquid layer were the same on all the plates in the column.

The experiments with solutions without potassium *i.e.* with the system $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$, were performed to compare the difficulty of desorption of both dissolved gases

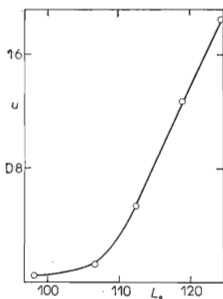


FIG. 3

Dependence of Effluent Concentrations of CO_2 (%) on Flow Rate of Feed L_0 (g/min)
 G_p 40.0 gm/min, x_0 12.5%, u_0 16.0%
 N 8.

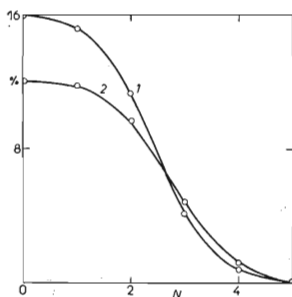


FIG. 4

Computed Concentration Profile of Liquid in Desorption Column
 $L/G \approx 2.7$, 1 CO_2 , 2 NH_3 .

from the respective solutions. The dependence of the concentrations of NH_3 and CO_2 in the liquid leaving the column, with eight plates, on the reflux ratio is shown in Fig. 2 and 3. During the experiments the gas rate was held constant and the liquid rate was varied, so that the concentration of ammonia in the liquid leaving the column could fall within the interval 0.0–0.5% NH_3 . It can be seen from the course of curves in Fig. 2 and 3 that the amount of NH_3 and CO_2 in the product increases linearly with the reflux ratio, when the concentrations are higher than 0.3%. At the same reflux ratios, the concentrations of ammonia are higher than those of carbon dioxide in this concentration region. The corresponding concentrations of both components lower than 0.3% are approximately equal.

The highest reflux ratio, at which both dissolved gases were completely removed from the solution, was about $L_0/G_p = 2.4$ (by weight). This value was practically the same as that obtained on the column with fifteen plates. Using the equilibrium diagram from Ginzburg⁴, the concentration profil of liquid in the column was estimated by stage-to-stage calculations assuming the reflux ratio $L/G \approx 2.7$ and the feed composition 12% NH_3 and 16% CO_2 . The results are shown in Fig. 4. It is obvious from the figure that, under the conditions in consideration, 5–6 theoretical stages are required for practically complete removal of both gases dissolved. Almost the same results on the columns with 8 and 15 plates are not then surprising. It can be seen further that the desorption rate of carbon dioxide is on the top plates substantially higher than that of ammonia.

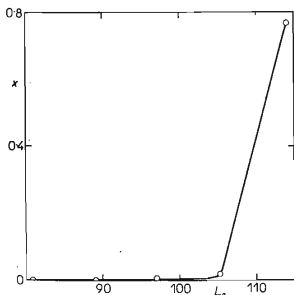


FIG. 5

Dependence of Effluent Concentrations of NH_3 (%) on Flow Rate of Feed with Potassium L_0 (g/min)

G_p 40.0 gm/min, x_0 13.7%, u_0 17.9%,
 v_0 6.4%, N 8.

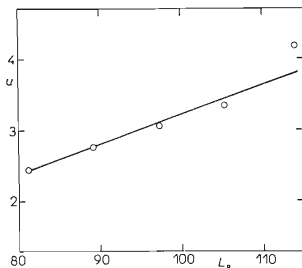


FIG. 6

Dependence of Effluent Concentrations of CO_2 (%) on Flow Rate of Feed with Potassium L_0 (g/min)

G_p 40.0 gm/min, x_0 13.7%, u_0 17.9%,
 v_0 6.4%, N 8.

It is seen on comparing Figs 2,3 and Figs 5,6 that the presence of potassium ions in the solution has a strong influence on the relation between the concentrations of ammonia and carbon dioxide in the liquid leaving the column. In the system $\text{NH}_3\text{-CO}_2\text{-K}_2\text{O-H}_2\text{O}$, the concentration carbon dioxide in the liquid is substantially higher than that of ammonia over the whole concentration region. The maximum reflux ratio, at which all ammonia was desorbed, was about $L_0/G_P = 2.6$. This value is slightly higher than that in the system without potassium.

The potassium ions present in the solution reduced strongly the partial pressure of CO_2 above the solution. The lowest concentration of CO_2 , reached at the reflux ratio $L_0/G_P = 2.02$, was 2.45% by weight. The molar ratio of potassium hydroxide and CO_2 was close to two in this solution. It may be assumed that further decreasing the reflux ratio can not reduce the exit concentration of carbon dioxide significantly. The effect of potassium ions on the relative volatility of CO_2 is also obvious in Fig. 7. The specific consumption of steam for desorption of CO_2 , determined as a ratio of the quantity of steam introduced to the column and the amount of carbon dioxide desorbed, was substantially higher in the system with potassium. The exponential shape of the curve suggests that the difficulty of CO_2 removal is rapidly increasing toward its lower concentrations. The obvious cause is the increasing alkalinity of these solutions.

The specific consumption of steam in the system $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$, related to the amount of NH_3 desorbed, was about 3.2 kg steam/kg NH_3 . This value corresponds

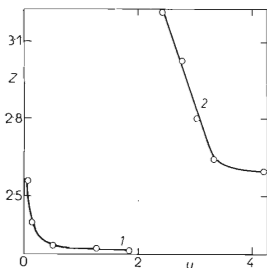


FIG. 7

Dependence of Specific Consumption of Steam Z (kg steam/kg CO_2) on Effluent Concentration of CO_2 u (%)

1 $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$, 2 $\text{NH}_3\text{-CO}_2\text{-K}_2\text{O-H}_2\text{O}$

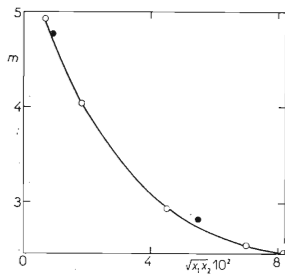


FIG. 8

Dependence of Slope of Pseudoequilibrium Line for NH_3 on Its Concentration in Liquid

○ $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$, ● $\text{NH}_3\text{-CO}_2\text{-K}_2\text{O-H}_2\text{O}$.

to the reflux ratio $L_0/G_p = 2.4$. The specific consumption of steam did not change significantly with the concentration of ammonia in the product. The maximum reflux ratio, when ammonia was completely desorbed from the solution $\text{NH}_3\text{-CO}_2\text{-K}_2\text{O-H}_2\text{O}$, was about $L_0/G_p = 2.6$. The specific consumption of steam corresponding to this value was about 2.9 kg steam/kg NH_3 . A significant effect of the concentration of NH_3 in the product on the specific consumption of steam was not found either at this system. In the system $\text{NH}_3\text{-CO}_2\text{-K}_2\text{O-H}_2\text{O}$, practically the same results on the columns with eight and fifteen plates were also found.

From the experimental data shown in Figs 2, 3, 5, 6, values of the slope of the pseudoequilibrium lines for NH_3 and CO_2 were computed by Eq. (4) for both systems. The slope depends on the inlet and outlet concentrations of liquid and the parameter $(X_1X_2)^{1/2}$ was chosen as convenient. The dependence of the slope m on this concentration parameter is shown for ammonia in Fig. 8 and for carbon dioxide is in Fig. 9. It is interesting to note that the slopes of the pseudoequilibrium lines for NH_3 and CO_2 in the system $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ decrease with increasing concentration. The presence of the potassium ions in the solutions resulted in somewhat higher values of the slope and, therefore, in the lower solubility of ammonia. Compared with the system without potassium, the lower specific consumption of steam in the system $\text{NH}_3\text{-CO}_2\text{-K}_2\text{O-H}_2\text{O}$ corresponds thus to the higher slopes of the pseudoequilibrium lines. The moderate effect of the potassium ions on the relative volatility of ammonia is rather surprising. This can be explained by the fact that a portion of potassium hydroxide is neutralized in the solution to a certain degree by dissolved carbon dioxide.

It is natural that the presence of such a strong hydroxide as potassium hydroxide greatly reduces the partial pressure of CO_2 above its aqueous solutions. Although the experiments with solutions $\text{NH}_3\text{-CO}_2\text{-K}_2\text{O-H}_2\text{O}$ were done at the lower reflux ratios ($L_0/G_p = 2.0\text{--}2.8$) than in the system $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$ ($L_0/G_p = 2.4\text{--}3.1$),

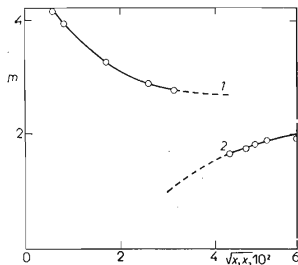


FIG. 9

Dependence of Slope of Pseudoequilibrium Line for CO_2 on Its Concentration in Liquid

1 $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$, 2 $\text{NH}_3\text{-CO}_2\text{-K}_2\text{O-H}_2\text{O}$.

the end concentrations of CO_2 were substantially higher at the first system. Consequently, the direct comparison of the slopes cannot be made. But from the course of the curves in Fig. 9, greatly reduced values of the slope can be expected in the system with potassium. Different signs of derivatives of the curves in Fig. 9 suggest qualitative differences in behaviour of the systems with respect to carbon dioxide. Comparing Figs 7 and 9, it is obvious that the considerable differences in the slopes of the equilibrium lines correspond to the largely different specific consumptions of steam. In the case of ammonia, the slightly larger slopes of the pseudoequilibrium line for the solutions with potassium, shown in Fig. 8, correspond to the specific steam consumptions slightly lower than those at the solutions without ammonia. These relations indicate that the slopes of the pseudoequilibrium lines, found by the procedure discussed above, are physically well-founded.

CONCLUSION

Potassium hydroxide present in the system $\text{NH}_3\text{-CO}_2\text{-K}_2\text{O-H}_2\text{O}$ makes desorption of carbon dioxide from this solution difficult. The specific consumption of steam for this desorption increases very rapidly toward lower concentrations of CO_2 in the solution and is substantially larger than that in the system $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$. The consumption of steam related to the amount of NH_3 desorbed from the solution $\text{NH}_3\text{-CO}_2\text{-K}_2\text{O-H}_2\text{O}$ is slightly lower than the corresponding quantity at the system $\text{NH}_3\text{-CO}_2\text{-H}_2\text{O}$. The desorption process does not require a large number of trays in the column. The degree of desorption of NH_3 and CO_2 in both systems was on the columns with eight and fifteen plates practically the same. The method of the desorption factor, used in this study of two-component desorption, proved convenient. The slopes of the pseudoequilibrium lines obtained here can be used to assess the degree of difficulty in removal of ammonia and carbon dioxide from the solutions in the desorption column. The change of the relative volatility of NH_3 and CO_2 due to the potassium ions present in the solution is indicated by the change of the specific consumption of steam and by the change of a slope of the pseudoequilibrium line as well.

LIST OF SYMBOLS

- $1/A \equiv mG/L$ desorption (stripping) factor (1)
 $(1/A)_{\text{ef}}$ effective desorption factor (1)
 G molar flow rate of vapour (gas) phase (mol/min)
 G_p amount of steam introduced into column (g/min)
 L molar flow rate of liquid phase (mol/min)
 L_0 amount of feed introduced into column (g/min)
 m slope of equilibrium (pseudoequilibrium) line (1)
 N number of theoretical (actual) trays (1)
 u conc. of CO_2 in liquid leaving column (% by weight)

| | |
|-------|---|
| u_0 | conc. of CO_2 in feed (% by weight) |
| v_0 | conc. of KOH in feed (% by weight) |
| x | conc. of NH_3 in liquid leaving column (% by weight) |
| x_0 | conc. of NH_3 in feed (% by weight) |
| X_1 | conc. of volatile constituent in liquid leaving column (mol/mol($\text{H}_2\text{O} + \text{KOH}$)) |
| X_2 | conc. of volatile constituent in feed (mol/mol($\text{H}_2\text{O} + \text{KOH}$)) |
| Y_1 | conc. of volatile constituent in gas introduced into column (mol/mol H_2O) |

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Translated by the author (M.H.).