

THE EFFECT OF pH ON EQUILIBRIUM DISTRIBUTION OF AMMONIA IN AIR AND RIVER WATER

Wahyudi Budi Sediawan*, Maharani Dewi Solikhah*, Diana Rosita*

ABSTRACT

Ammonia is an important component in chemical industries. Very often, the water effluent of chemical plants contains ammonia, which may cause environmental problems. The equilibrium distribution of ammonia in air and water is hence of importance, especially in predicting the fate of this component in the environment, as well as in the design of equipment needed for the treatment of this effluent. In that system, two equilibria are involved, which are ionic and phase equilibria. In water phase, ammonia is present in two forms, free ammonia and ammonium ion. The two forms are in ionic equilibrium, in which the ionic equilibrium is affected by pH. Meanwhile, free ammonia in water is also in equilibrium with the ammonia in air (phase equilibrium). As a result, the equilibrium between ammonia in air and total ammonia in water is influenced by pH. Since effluent and natural water have a wide range of pH values, the effect of pH on that equilibrium needs to be studied. Experimental and theoretical studies have been conducted, and the results, which are represented in the form of mathematical model, can be applied to quantitatively predict the equilibrium distribution of ammonia at various value of pH, for the natural water studied.

INTRODUCTION

Ammonia is widely used in chemical industry. For example, in the synthesis of organic nitrogen compounds, ammonia is commonly used as the reactant. Conversion of nitrogen gas in air into organic nitrogen is usually conducted via ammonia synthesis. Ammonia is also used in fertilizer industries. As a result, the water effluent of such industries may contain small amount of ammonia. Hence, treatment of wastewater containing ammonia is of importance, so are studies on the fate of ammonia in the environment.

Mass transfer of ammonia from water into air or vice versa is an important step in the treatment of ammonia effluent, and in the fate of ammonia in the environment. In the study of mass transfer, equilibrium is very important, since the driving force of mass transfer is the deviation of existing condition from the equilibrium condition. For example, the rate of liquid-gas mass transfer can be mathematically represented as

$$N_A = K_y (y_A^* - y_A) \quad (1)$$

in which y_A^* is the mole fraction of A in gas that is in equilibrium with the liquid phase.

Lots of studies on equilibrium distribution of ammonia in air and water have been conducted (Adams, 1974, Alaerts, 1987, Clark, 1988, Ponce, 1991, Reed, 1988, Smith, 1988, Thibodeaux, 1996). But the data and information available are commonly obtained from laboratory experiments using relatively pure water. Whether or not those data and theories can be applied for natural water, which commonly contains wide variety of other chemicals, is an important question. This study generated equilibrium data of ammonia in river water and air, as well as conducted theoretical analysis on the data obtained, based on fundamental theories of physics and chemistry. Even though the study was conducted on typical natural water, it is expected that the basic ideas of the approach can be applied for other types of natural water. Further studies using more variety of natural water need to be conducted.

THEORETICAL DEVELOPMENT

In water, ammonia presents in two forms, which are free ammonia (NH_3) and ammonium ion (NH_4^+). Those two are in ionic equilibrium, and its ionic reaction can be written as (Adams, 1974):



The equilibrium condition can be mathematically represented by:

$$K = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3][\text{H}_2\text{O}]} \quad (3)$$

Since the concentration of H_2O is relatively constant (dilute solution), equation 3 can be simplified into the following form:

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} \quad (4)$$

Equation 4 is commonly used in analyzing ionic equilibrium of ammonia.

Another ionic equilibrium exists in water is:



in which the equilibrium condition is usually written as:

$$K_w = [\text{H}^+][\text{OH}^-] \quad (6)$$

Combination of equation 4 and 6 gives:

$$\frac{K_b}{K_w} = \frac{[\text{NH}_4^+]}{[\text{NH}_3][\text{H}^+]} \quad (7)$$

The total concentration of ammonia calculated as ammonia, $[\text{NH}_3]_t$, is the summation of free ammonia and ammonium ion concentration, so that :

$$[\text{NH}_3]_t = [\text{NH}_4^+] + [\text{NH}_3] \quad (8)$$

Substitution of equation 8 into equation 7 gives:

$$\frac{K_b}{K_w} = \frac{[\text{NH}_3]_t - [\text{NH}_3]}{[\text{NH}_3][\text{H}^+]} \quad (9)$$

Rearrangement of equation 9 results in:

$$\frac{[\text{NH}_3]}{[\text{NH}_3]_t} = \frac{1}{1 + \frac{K_b}{K_w}[\text{H}^+]} \quad (10)$$

Equation 10 shows that the fraction of free ammonia depends on the value of $[\text{H}^+]$. Since the value of $[\text{H}^+]$ is usually represented by pH , with the relation:

$$\text{pH} = -\log [\text{H}^+], \quad (11)$$

the fraction of free ammonia is influenced by pH . The free ammonia in water phase is also in equilibrium with the ammonia in air (phase equilibrium). For dilute solution, the equilibrium follows the Henry's law (Thibodeaux, 1996),

$$P_{\text{NH}_3} = H' [\text{NH}_3] \quad (12)$$

Equation 12 gives a correlation between concentration of free ammonia in water and partial pressure of ammonia in air. The more important correlation is the one between total ammonia in water and ammonia in air. That correlation can be obtained by combining equation 10 and 12. The result is:

$$\frac{P_{\text{NH}_3}}{[\text{NH}_3]_t} = \frac{H'}{1 + \frac{K_b}{K_w}[\text{H}^+]} \quad (13)$$

For dilute solution, in which the concentrations are represented by ppm, equation 13 becomes:

$$\frac{P_{\text{NH}_3}}{(C_A)_t} = \frac{H}{1 + \frac{K_b}{K_w}[\text{H}^+]} \quad (14)$$

Equation 14 can be written as:

where H^* is the apparent Henry's constant, which can be expressed by:

$$H^* = \frac{H}{1 + \frac{K_b}{K_w} [H^+]} \quad (16)$$

EXPERIMENTAL PROCEDURES

The materials used for this study were water from Code River, Yogyakarta, Indonesia, ammonia and air, while the equipment set up for this experiment is schematically shown in Figure 1.

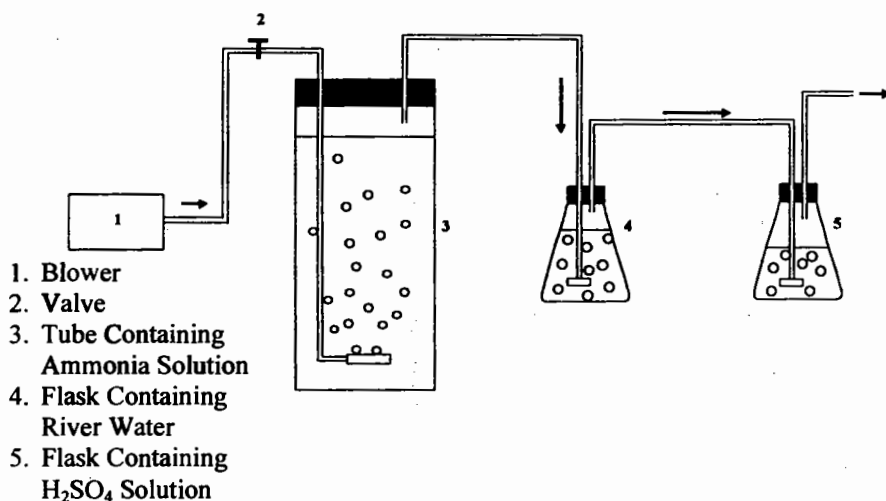


Figure 1. Gas-Liquid Equilibrium Apparatus

Air was blown by blower 1, and bubbled through ammonia solution in tube 3. Tube 3 was long enough (16.1 cm), so that the air leaving the ammonia solution is expected to be in equilibrium with the ammonia solution. Then, the air went through river water in flask 4, and finally left the apparatus after the ammonia was removed by acid solution in flask 5. The pH of the river water in flask 4 was controlled by addition of sodium hydroxide solution or buffer solution (potassium and sodium phosphate). The volume of ammonia solution in tube 3 was very large compared to the volume of river water in flask 4, so that until the river water in flask 4 reached equilibrium concentration with the air, the ammonia concentration in tube 3 was practically constant. The experiment was conducted until the total ammonia concentration of the liquid in flask 4 was practically constant. The data collected were the concentrations of ammonia in the liquid in the tube 3 and the one in the liquid in flask 4.

The experiments were conducted at various values of ammonia concentration in

and 1 atm respectively. The samples of the solution were treated by Nessler's reagent, and then their total ammonia concentrations were measured by spectrophotometer (Christian, 1986). The ammonia content of the air leaving tube 3 was estimated using equilibrium data in Perry, 1997, based on the ammonia content in the ammonia solution in tube 3. After the liquid in the tube 4 was in equilibrium with the air, the ammonia content in the air entering and leaving tube 4 would be the same. The equilibrium correlation was shown by the ammonia partial pressure of the air and the total ammonia content in the liquid in tube 4.

RESULT AND DISCUSSION

The experimental data obtained are shown in the Table I, and Figure 2.

Table I. Equilibrium Data at Various pH (T=27°C)

pH	PNH ₃ 10 ⁶ , atm	(CA) _t , ppm
6.29	2.98	30.0
	7.45	62.1
	14.9	466
7.33	44.7	944
	2.98	20.5
	7.45	57.1
8	14.9	134
	44.7	352
	2.98	32
8.33	7.45	60
	14.9	126
	44.7	358
9.3	2.98	23.8
	7.45	59.5
	14.9	119
11	44.7	357
	2.98	7
	7.45	14
	14.9	27
	44.7	85
	2.98	2
	7.45	7
	14.9	14
	44.7	41

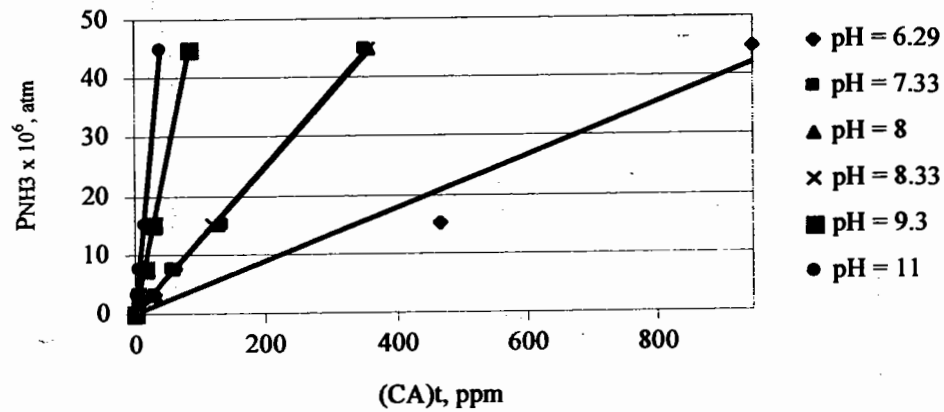


Figure 2. Equilibrium Data at Various pH

Figure 2 shows that the equilibrium relation can be represented by straight line with intercept of zero, so Henry's law holds. The apparent Henry's constant was estimated by least-squares method and the results are shown in Table II.

Table II. Apparent Henry's Constant (T=27°C)

pH	H x 10 ⁷
6.29	0.446
7.33	1.25
8	1.24
8.33	1.25
9.3	5.28
11	10.9

The value of K_b and K_w in pure water are approximately 1.8×10^{-5} and 10^{-14} respectively (Lide, 1992), so that the value of K_b/K_w is 1.8×10^9 . That number and equation 16 show that at pH=11, in which $[H^+] = 10^{-11}$, the value of H^* is very close to H. Furthermore, equation 16 suggests the value of H is approximately 1.12×10^{-6} . The value of K_b/K_w for river water is then evaluated by visual inspection, based on linear equation obtained by rearrangement of equation 16, as the following:

$$-\log\left(\frac{H}{H^*} - 1\right) = -\log\left(\frac{K_b}{K_w}\right) + pH \quad (17)$$

It turns out that the value of K_b/K_w is 1.4×10^9 . If the value of K_w is taken to be 10^{-14} , the

Henry's constants using equation 16 and the experimental values is shown in Table II, Table III and Figure 3.

Table III. Apparent Henry's Constant Predicted by Equation 16

pH	H* x 10 ⁷
6.29	0.016
7.33	0.169
8.00	0.747
8.33	1.48
9.30	6.59
11.00	11.05

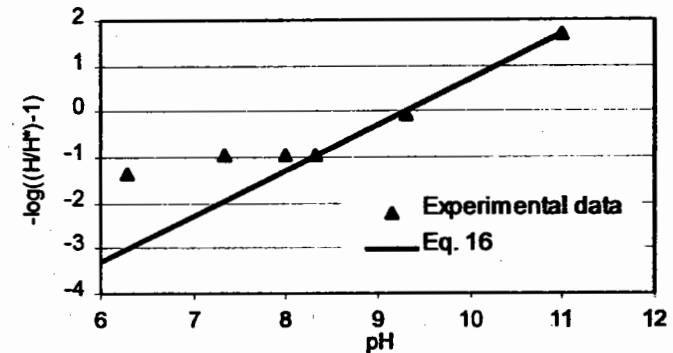


Figure 3. $-\log\{(H/H^*)-1\}$ versus pH

Figure 3 shows that for the high values of pH (pH > 8.2), the model is in good agreement with the experimental data. But for low values of pH, significant deviation is observed.

It is concluded that for high values of pH, the model that was developed based on ionic equilibrium theory can be applied to predict the effect of pH on ammonia equilibrium for river water used. However, based on figure 3, the value of K_b needs to be slightly adjusted to be 1.4×10^{-5} . The value of K_b obtained is in good agreement with the values obtained from transient desorption by Ummi Kalsum (Kalsum, 1997), which were between 1.78×10^{-6} and 1.87×10^{-5} .

In order to quantitatively describe the effect of pH at low value of pH, the second model is proposed. It is assumed that because of the effect of organic substances in the river water, the NH_4^+ ions that affect the ionic equilibrium in equation 2 are present in two forms, which are the real NH_4^+ ion and a modified form (organic form). The organic form is undetected by spectrophotometer. The two forms are in equilibrium:

The equilibrium equation is assumed to be :

$$K_o = \frac{[NH_4^+]_{org}}{[NH_4^+]} \quad (19)$$

The total concentrations of NH_4^+ ion is:

$$[NH_4^+]_t = [NH_4^+] + [NH_4^+]_{org} \quad (20)$$

$$[NH_4^+]_t = [NH_4^+] + K_o \cdot [NH_4^+] \quad (21)$$

$$[NH_4^+]_t = (1 + K_o) [NH_4^+] \quad (22)$$

Because of this effect, equation 7 needs to be modified. Ammonium ion (NH_4^+) ion in equation 7 is replaced by total NH_4^+ , so it is obtained that:

$$\frac{K_b}{K_w} = \frac{[1 + K_o][NH_4^+]}{[NH_3][H^+]} \quad (23)$$

The observed total ammonia concentration is:

$$[NH_3]_t = [NH_3] + [NH_4^+] \quad (8)$$

Combination of equation 8 and 23 gives:

$$\frac{[NH_3]}{[NH_3]_t} = \frac{1}{1 + \frac{K_b}{K_w(1+K_o)}[H^+]} \quad (24)$$

Rearrangement analogues to previous model (model I) gives:

$$\frac{P_{NH_3}}{(C_A)_t} = \frac{H}{1 + \frac{K_b}{(1+K_o)K_w}[H^+]} \quad (25)$$

and

$$H^* = \frac{H}{1 + \frac{K_b}{(1+K_o)K_w}[H^+]} \quad (26)$$

By substituting:

$$\beta = 1 + K_o \quad (27)$$

it is obtained that:

$$H^* = \frac{H}{1 + \frac{K_b}{\beta K_w}[H^+]} \quad (28)$$

or

$$-\log\left(\frac{H}{H^*} - 1\right) = pH - \log\left(\frac{K_b}{K_w}\right) + \log\beta \quad (29)$$

Figure 3 suggests that $\log\beta$ is a linear function of pH,

$$\log\beta = a + b(pH) \quad (30)$$

Combination of equation 29 and 30 results in :

$$-\log\left(\frac{H}{H^*} - 1\right) = \left(a - \log\frac{K_b}{K_w}\right) + (b+1)(pH) \quad (31)$$

The plot of $-\log\left(\frac{H}{H^*} - 1\right)$ versus pH at low values of pH is shown in figure 4. The line turns out to be approximately linear, hence the model proposed (model II) is adequate.

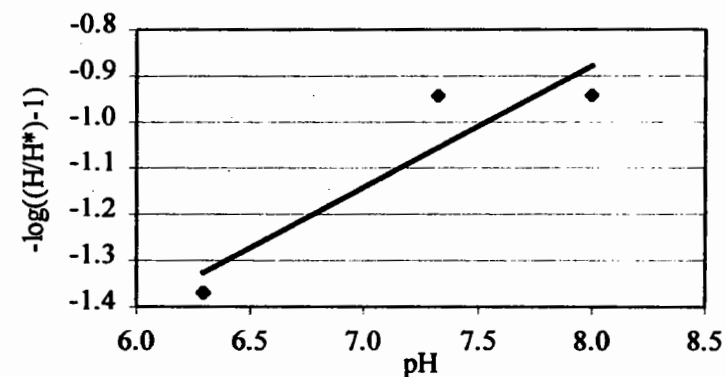


Figure 4. Plot of $-\log\left(\frac{H}{H^*} - 1\right)$ versus pH at low values of pH

A linear regression in the form of equation 31 gives $a = 6.162$ and $b = -0.7366$. As a result, it is obtained that:

$$\log\beta = 6.162 - 0.7366(pH) \quad (32)$$

The comparison of the calculated results using the two models (model I for high values of pH and model II for low values of pH) and the experimented data is presented in figure 5.

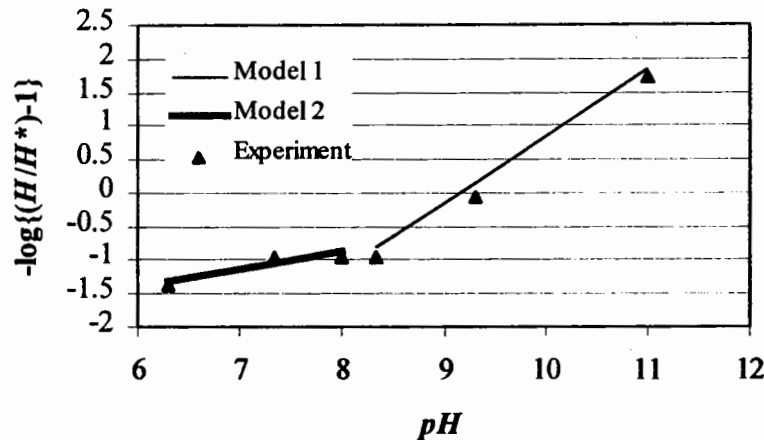


Figure 5. Comparison of Calculated Results and Experimental Data

Figure 5 shows that the models proposed can be used to predict the ammonia equilibrium at various values of pH for the river water studied. To generate the more general approach, further studies using more types of natural water are needed. It is expected that for other types of natural water, the basic ideas of the approach can be still applied, even though the values of the parameters may need to be adjusted accordingly.

CONCLUSIONS

Based on this study, it can be concluded that:

1. At high values of pH ($\text{pH} > 8.2$), the effect of pH on equilibrium distribution of ammonia in air and the river water studied can be approximated by the combination of Henry's law and the ionic equilibrium theory (Model I).
2. The value of H is 1.12×10^{-6} atm/ppm and the value of K_b needs to be adjusted to be 1.4×10^{-5} .
3. At low values of pH ($\text{pH} < 8.2$), model II, a modification of model I, assuming that NH_4^+ ions are present in two forms, gives a good approximation.

NOMENCLATURE

$(C_A)_l$ = total ammonia concentration in water, ppm
 P_{NH_3} = partial pressure of ammonia in air, atm
 $(C_A)_g$ = total ammonia concentration in water, mol/L

$[\text{NH}_4^+]_l$ = concentration of total NH_4^+ ion in water, mol/L
 a = constant in equation 30
 b = constant in equation 30
 H = Henry's constant defined in equation 14
 H^* = Henry's constant defined by equation 15 and 16
 H' = Henry's constant defined by equation 12
 K = equilibrium constant defined by equation 3
 K_b = equilibrium constant defined by equation 4
 K_o = equilibrium constant defined in equation 19
 K_w = equilibrium constant defined by equation 6
 K_y = overall mass transfer coefficient
 N_A = flux of gas-liquid mass transfer
 y_A = mole fraction of A in gas
 y_A^* = mole fraction of A in gas that is in equilibrium with the liquid phase
 β = ratio of total NH_4^+ ion to the real NH_4^+ ion

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