Kinetics of Ammonia Removal from Waste Water by Air Flow

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Received May 28, 2010, Accepted August 12, 2010

Recently, Yoon, *et al*. investigated kinetics of the ammonia removal process in which ammonia molecules in waste water or in solution are evaporated into the gas phase and then swept away by an externally supplied flow of air.[1] Figure 1 shows a schematic diagram of the ammonia removal system considered in ref 1. One of the two key assumptions assumed in ref 1 is that the ratio of concentration C_g of ammonia vapor to concentration C_L^V of volatile ammonia molecules in solution phase is given by the following modified Henry's law:

$$\frac{C_g}{C_L^V} = \beta H \tag{1}$$

where β is a time-independent constant, called the saturation degree. Saturation factor β deviates from one unless the ammonia molecules in vapor phase are in thermal and chemical equilibrium with those in solution phase. In eq 1, H denotes Henry's law constant of volatile ammonia.[2]

By comparing their result and the experimental data, the authors of ref 1 find that β decreases with the total air flow rate but is independent of other control parameters such as pH of the solution, temperature, and the submerged airflow rate. However, the authors didn't provide any explanation about the dependence of saturation factor β on the total air flow rate. The other assumption in ref 1 is that the aqueous ammonia molecules $NH_3\,(aq)$ are in chemical equilibrium with the ammonium ions $NH_4^+\,(aq)$ in the solution throughout the ammonia removal process. With use of these assumptions, the authors could derive a simple approximate solution that could provide a quantitative description of the experimental data reported in ref 1.
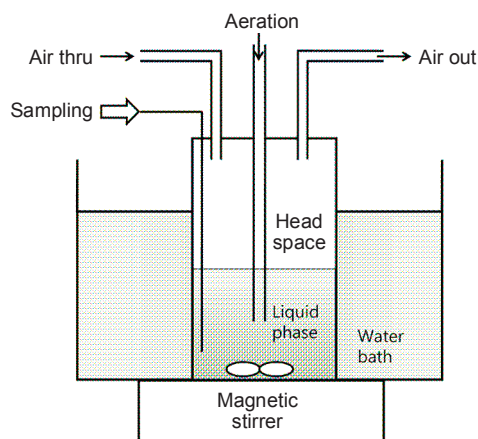
In this note, we present the standard mass action law describing the kinetics of the ammonia removal process and find the exact solution of the kinetic equations without making the two assumptions assumed in ref 1. In addition, we show that the approximation invoked in eq 1 is, in fact, equivalent to the steady-state approximation often used in the conventional chemical kinetics.[3-5] Furthermore, we establish the quantitative relationship between β and the rate of total air flow, which provides the clear explanation about the previously unexplained dependence of β on the total air flow rate shown in Figure 7 of ref 1. From the comparison to the exact solution, we define the application range of the assumptions assumed in ref 1.

In the solution of the experimental chamber shown in Figure 1, volatile ammonia molecules, $NH_3\,(aq)$, can associate with the aqueous proton, $H^+\,(aq)$, to form nonvolatile ammonium ions $NH_4^+\,(aq)$:

$$NH_3(aq) + H^+(aq) \underset{k_r}{\overset{k_f}{\rightleftarrows}} NH_4^+(aq) \tag{2}$$

Here, k_f and k_r denote the rate constants of the forward and the backward reactions, respectively. The volatile ammonia in aqueous phase can evaporate into the gas phase in the head space in Figure 1:

$$NH_3(aq) \underset{k_{GL}}{\overset{k_{LG}}{\rightleftarrows}} NH_3(g, in) \tag{3}$$
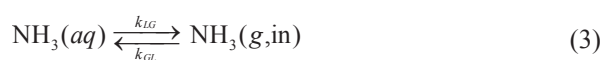
k_{LG} and k_{GL} the rate of the evaporation of the aqueous ammonia and the rate of the ammonia transfer from the gaseous head space to the solution phase. Both k_{LG} and k_{GL} are proportional to the area of the interface between the solution and the gas phase in the head space. Finally, the external air flow carries the ammonia vapor, $NH_3\,(g,\,in)$, in the head space out of the experimental chamber:

$$NH_3(g, in) \xrightarrow{k_E} NH_3(g, out) \tag{4}$$

Here, $NH_3\,(g,\,out)$ denotes the ammonia vapor swept out of the experimental chamber by externally supplied air flow. The mass action law describing reactions (2)-(4) are given by

$$\frac{d}{dt} m_L^{NV} = k_f [H^+] m_L^V - k_r m_L^{NV} \tag{5a}$$

$$\frac{d}{dt} m_L^V = -k_f [H^+] m_L^V + k_r m_L^{NV} - k_{LG} m_L^V + k_{GL} m_g^i \tag{5b}$$

Figure 1. Schematic diagram of the ammonia removal system.

$$\frac{d}{dt} m_g^i = k_{LG} m_L^V - k_{GL} m_g^i - k_E m_g^i \tag{5c}$$

$$\frac{d}{dt} m_g^o = k_E m_g^i \tag{5d}$$

Here m_L^{NV}, m_L^V, m_g^i, and m_g^o respectively denote the mass of NH_4^+ (aq), NH_3 (aq), NH_3 (g, in), and NH_3 (g, out). When pH of the solution is fixed, the exact solution of eq 5 can be obtained, which is presented in Supporting Information.

Next, we discuss the connection of the conventional mass action law given in eq 5 to the kinetic description presented in ref 1. In ref 1, it is assumed that the relaxation of the reaction in eq 2 occurs faster than any other process in the experimental system so that the reaction is always in equilibrium, i.e.

$$\frac{m_L^{NV}}{m_L^V [H^+(aq)]} \cong K_{eq} \left(= k_f / k_r \right) \tag{6}$$

In eq 6, K_{eq} denotes the equilibrium constant of the reversible reaction in eq 2. The mass, m_L^V, of volatile ammonia molecules is related to the total concentration m_L^T ($\equiv m_L^{NV} + m_L^V$) of ammonia in solution by

$$\frac{m_L^V}{m_L^T} \cong \left(1 + K_{eq} [H^+(aq)] \right)^{-1} \equiv \alpha. \tag{7}$$

Substituting eq 7 into eqs 5(a)-5(c), one obtains

$$\frac{d}{dt} m_L^T = -k_{LG} \alpha m_L^T + k_{GL} m_g^i \tag{8a}$$

$$\frac{d}{dt} m_g^i = k_{LG} \alpha m_L^T - k_{GL} m_g^i - k_E m_g^i \tag{8b}$$

Now we are ready to show that the assumption in eq 1 is equivalent to the steady-state assumption. For this purpose, let us first establish the relationship between the Henry's law constant and the rate constants, k_{LG} and k_{GL}. In the absence of the carrier air flow, k_E vanishes, and the ammonia vapor in the head space will be in equilibrium with the aqueous ammonia at long times. Henry's law constant H is defined by $H = \dfrac{C_{g,eq}^i}{C_{L,eq}^V}$, with $C_{g,eq}^i$ and $C_{L,eq}^V$ being the concentration of NH_3 (g, in) and NH_3 (aq) at equilibrium. By applying the equilibrium condition, $\dfrac{d}{dt} m_L^T = \dfrac{d}{dt} m_g^i = 0$, to eq 8 with k_E being equal to zero, we obtain the following expression for Henry's law constant H

$$H = \frac{k_{LG}}{k_{GL}} \frac{V_L}{V_G} \tag{9}$$

where V_L and V_G denote the volume of the solution and that of the head space in Figure 1. In the presence of the carrier air flow, k_E is finite, but m_g^i can still be approximated by a time-

independent constant, i.e. $\dfrac{dm_g^i}{dt} \cong 0$, in the non-equilibrium steady state. By applying the steady state approximation to eq 8b, the ratio of concentration C_g^i of NH_3 (g, in) to concentration C_L^V of NH_3 (aq) in the steady-state can be obtained as follows:

$$\frac{C_g^i}{C_L^V} \cong \frac{V_L}{V_g} \frac{k_{LG}}{k_{GL} + k_E} = H \frac{1}{1 + k_E / k_{GL}} \tag{10}$$

By making comparison between eq 1 and eq 10, we obtain the following expression for saturation degree β:

$$\beta = \left[1 + \left(k_E / k_{GL} \right) \right]^{-1} \tag{11}$$

Equation 11 tells us that saturation degree β can be approximately one if k_E / k_{GL} is small enough; otherwise, β decreases with k_E / k_{GL}. Noting that k_E is proportional to the total air flow rate, eq 11 is consistent with the experimental data shown in Figure 7 in ref 1. With use of the steady-state approximation, one can easily obtain the solution of eq 8 as

$$m_L^T(t) = m_L^T(0) \exp \left(-\alpha \frac{k_E k_{LG}}{k_{GL} + k_E} t \right). \tag{12}$$

Equation 12 is the same as the main result, eq 13, of ref 1.

Now we discuss the application range of the approximate solution given in eq 12. Remember that eq 12 is obtained by assuming the persistent chemical equilibrium between ammonia and the ammonium in solution phase throughout the ammonia removal process, eq 6, and the validity of the steady state approximation.

The latter assumptions are true when the evaporation rate k_{LG} is much smaller than the relaxation rate, $k_f[H^+] + k_r (\equiv \lambda)$, of reaction (2) and when the fraction of the intermediate, NH_3 (g, in) in this case, is negligible,[3] as demonstrated in Figure 2.

$k_{LG} = 1$
$k_{GL} = 0.1$
$k_r = 1$
$k_E = 10$

$k_f[H^+] = 1000$

— Exact result (eq A13)
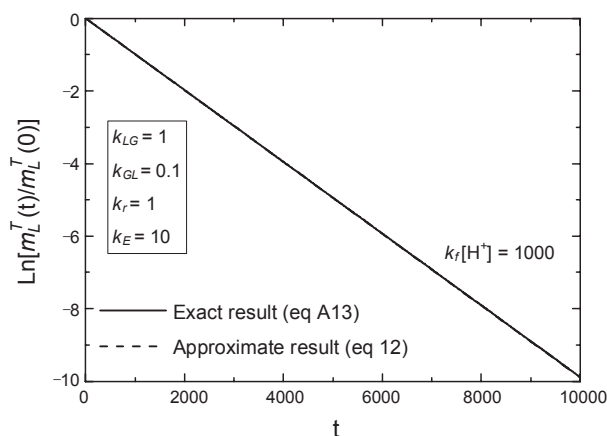- - - Approximate result (eq 12)

Figure 2. Comparison between the exact result, eq A13, and the approximate result, eq 12 when the evaporation rate k_{LG} of aqueous ammonia is much smaller than the relaxation rate, $k_f[H^+] + k_r$, of reaction (2) and the rate k_E of ammonia escape process given in reaction (4).
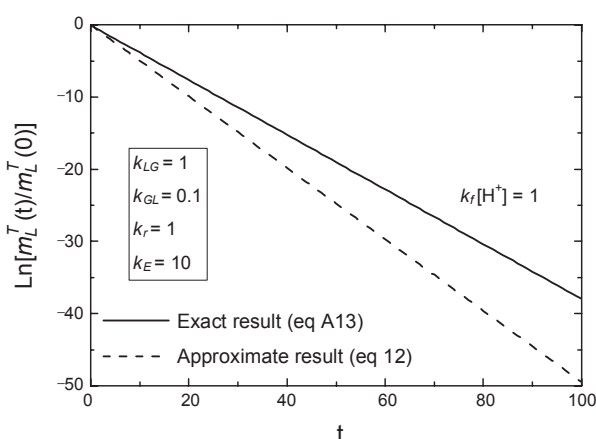
Figure 3. Comparison between the exact result, eq A13,[6] and the approximate result, eq 12 when the evaporation rate k_{LG} of aqueous ammonia is greater than the relaxation rate, k_f [H$^+$] + k_r, of reaction (2). In this case, the approximation given in eq 6 does no longer hold, and the approximate result, eq 12, shows a significant deviation from the exact result, eq A13.

Figure 4. Comparison between the exact result, eq A13,[6] and the approximate result, eq 12 when escape rate k_E of gaseous ammonia is much smaller or greater than the evaporation rate k_{LG} of aqueous ammonia. The steady state approximation, $dm_g^i/dt \cong 0$, works well when the value of k_E is much greater than that of k_{LG}.

For the experimental data reported in ref 1, it turns out the assumptions hold so well that eq 12 in this work or eq 13 in ref 1 provides a good quantitative description of the experimental data.

However, as k_{LG} is directly proportional to the area of the liquid-gas interfaces, the magnitude of k_{LG} can be far greater than that of the relaxation rate, λ, of reaction (2) whenever the liquid-gas interface is large enough. In the latter case, the equilibrium assumption, given in eq 6, does not hold any more and the resulting approximate solution, eq 12, shows a significant deviation from the exact solution, A11. This is shown in Figure 3.

When the total air flow is large enough, k_E is much greater than k_{LG}, and the ammonia molecules evaporated from the liquid solution would be swiftly swept out of the head space before they can accumulate. It is known that the steady-state approximation, $dm_g^i/dt \cong 0$, works well in the latter case.[5] However, whenever the air flow rate is not large enough, or when k_E is not much greater than k_{LG}, the accumulation of the evaporated ammonia will be significant, and the stead-state approximation and the resulting approximate solution, eq 12, are no longer accurate as shown in Figure 4.

Finally, we present a quantitative analysis for the experimentally measured saturation degree β, reported in Figure 7 of ref 1. The experimental data indicate that the saturation degree decreases with the headspace aeration rate, which is consistent with the prediction of eq 11, because the headspace aeration rate, R_E^H, would be proportional to the rate k_E of the ammonia escape out of the headspace. Being not so effective as the headspace aeration, the air flow submerged into the ammonia solution would also enhance the ammonia escape from the headspace. That is to say, the ammonia escape rate k_E is a function of the headspace aeration rate k_E^H and the submerged air flow rate R_E^S, i.e. $k_E = f(R_E^H, R_E^S)$. With use of Taylor expansion up to the linear order, we get
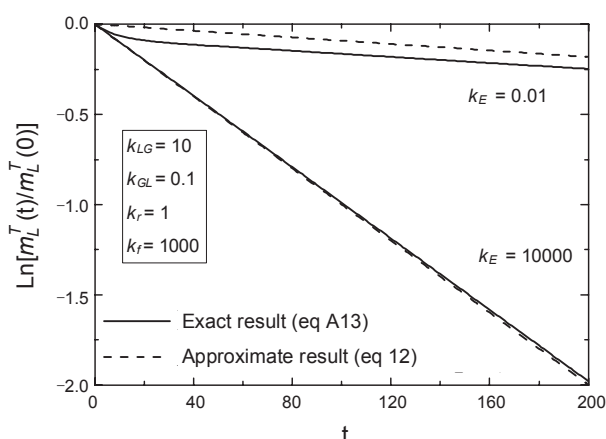
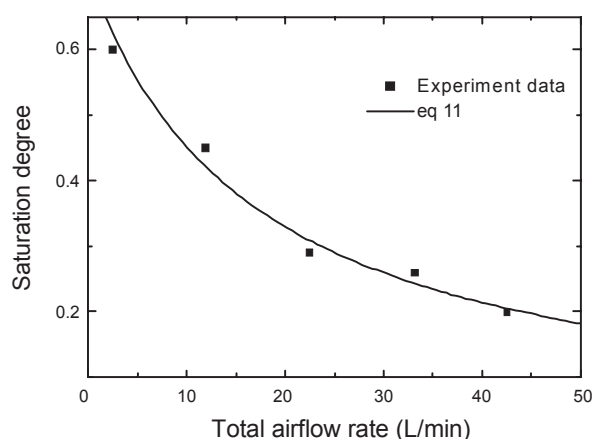$$k_E = c_H R_E^H + c_S R_E^S \qquad (13)$$

Figure 5. Comparison between experimentally measured saturation degree data and eq 11 of the present work. The experimental data are read off from figure 7 of ref 1. The ammonia escape rate k_E in eq 11 is assumed to be linearly related to the headspace aeration rate R_E^H and the submerged air flow rate R_E^S as given in eq 13.

where x and y denote the constants given by $c_H =$

$$\left[\frac{\partial f(R_E^H, R_E^S)}{\partial R_E^H} \right]_{R_E^S} \bigg|_{(R_E^H = 0, R_E^S = 0)} \quad \text{and} \quad c_S = \left[\frac{\partial f(R_E^H, R_E^S)}{\partial R_E^S} \right]_{R_E^H} \bigg|_{(R_E^H = 0, R_E^S = 0)}.$$

As shown in Figure 5, eq 11 with k_E being given by eq 13 provides an excellent quantitative description of the experimental data for the saturation degree β. In the experiment, the submerged air flow rate R_E^S is fixed as 2.5 L/min, and the head space air flow rate R_E^H is varied from 0 to 40 L/min. The total airflow rate in the x axis of Figure 5 stands for the sum of R_E^H and R_E^S. The optimized values for c_H and c_S in eq 13 are found to be $c_H/k_{GL} = 2.4 \times 10^{-1}$ min/L and $c_H/k_{GL} = 8.2 \times 10^{-2}$ min/L.

In the present work, we present the kinetic equation for the ammonia mass transfer in the ammonia removal process from waste water on the basis of the standard mass action law and find the exact solution to the kinetic equations. If the liquid-gas

interface is so small that the evaporation rate k_{LG} of aqueous ammonia is much smaller compared to both the relaxation rate $\lambda(= k_f[\text{H}^+] + k_r)$ of reaction (2) and the rate k_E of ammonia escape out of the head space, the steady state approximation, $dm_g^i/dt \cong 0$, as well as the assumptions that reaction (2) is in chemical equilibrium throughout the ammonia removal process work well and consequently the results of the simple approximate solution given in eq 12 are nearly indistinguishable from those of the exact solution given in eq A13. However, the approximate solution, eq 12, shows a significant deviation from the exact solution when the evaporation rate k_{LG} of aqueous ammonia is not smaller than either of the relaxation rate λ of reaction (2) and the rate k_E of the ammonia escape process given in reaction (4).

References

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