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Overview of mass transfer enhancement factor determination for acidic and basic compounds absorption in water

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Keywords

Absorption; mass transfer; enhancement factor; acid; base; reversible reaction

Abstract

Absorption or gas-liquid mass transfer is a fundamental unit operation useful in many fields, particularly gas treatment (wet scrubbing). Absorption of basic or acidic compounds, even hydrophobic, in water can be achieved successfully due to the mass transfer enhancement linked to proton transfer reactions in the liquid film. The absorption rate takes this phenomenon into account through the enhancement factor E , which depends on many parameters: nature (irreversible or reversible), kinetics and stoichiometry of the reaction, reagents and products diffusion coefficients and concentrations. This article gives an overview of the enhancement factor determination for acidic and basic compounds transfer in water. Modeling is performed for three compounds of interest, hydrogen sulfide H_2S , methyl mercaptan CH_3SH and ammonia NH_3 , for different scenarios to assess the influence of the pH. The results demonstrate that recombination with HO^- and protonation reactions are respectively the two preponderant reactions for respectively acidic and basic compounds. They enable to reach large values of the enhancement factor at appropriated pH and to reduce the mass transfer resistance in the liquid film. Furthermore, the simulations highlight that, in many cases, knowledge of the reaction kinetics is not necessary since the reaction can be considered as instantaneous compared to mass transfer.

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1 Introduction

Absorption or gas-liquid mass transfer is widely used in environmental engineering for pollutant removal [1-4]. This unit operation involves pollutant transfer from the gas phase to a liquid phase and is performed in a gas-liquid contactor dedicated to provide a large interfacial area [5]. The key factor influencing the operation efficiency is the compound solubility in the liquid phase. For obvious cost issues, water is the main selected liquid phase even if organic solvent could be used for hydrophobic compounds treatment.

For acidic and basic compounds, even when they have a hydrophobic tendency, water could be a suitable scrubbing liquid since the absorption rate can be significantly increased by two mechanisms:

- The first mechanism is the apparent solubility increasing due to the formation of the conjugated base (acid) for acidic (basic) compounds when the pH is close or higher (close or lower) than the pK_A ($=-\log K_A$ with K_A the acid dissociation constant). This mechanism enables to increase the concentration gradient between the interface and the bulk which is the mass transfer driving force.
- The second mechanism is the mass transfer enhancement due to the proton transfer reaction in the liquid film located at the interface vicinity. It increases the absorption rate in the liquid film, *i.e.* decreases the mass transfer resistance. By this way, all the resistance could be located in the gas phase.

Consequently, adding an acid (H_2SO_4 for example) or sodium hydroxide (NaOH) to the scrubbing water to set an appropriated pH, it becomes possible to reach very good removal efficiencies even for hydrophobic compounds. This is typically the case for hydrogen sulfide (H_2S) [6]. The mass transfer enhancement factor, E , must be quantified to determine the absorption rate of the gas phase reactant and to achieve a proper scrubber design [7-11]. Enhancement factor quantification could be easily achieved for the film theory when considering one irreversible bimolecular reaction using an approximated but relevant analytical equation [12,13]. For a reversible reaction which is obviously the case of acid base reactions in water, its quantification is more complex. It depends on several parameters such as forward and reverse reaction kinetics (and the equilibrium constant of the reaction which is the ratio of them) which are often unknown, reaction stoichiometry, products and reagents bulk concentrations and diffusion coefficients. Simple analytical solutions could be obtained for a few special cases only [14]. The problem can be significantly simplified assuming that the reaction kinetics is not the limiting step and that equilibrium prevails everywhere in the liquid film (instantaneous reaction). Several authors developed analytical equations for different reaction

stoichiometries with this assumption [15,16]. Astarita and Savage [17] proposed a method which is applicable to any reversible reaction with the same hypothesis, based on the determination of the extent of reaction by a simple numerical resolution. Since reversible proton transfer reactions are very fast (diffusion controlled specifically) [18], forward and reverse reaction kinetic constants are usually poorly known. They are often considered as “instantaneous” by chemists. However, even if the reaction is very fast, its rate could not be instantaneous compared to the mass transfer rate and drives many authors to erroneous results. Onda et al. (1970) developed an approximated solution for the general case using the linearization method proposed by Hikita and Asai (1964) to simplify the reaction rate [19,20]. Another approach, developed by Kenig and his coworkers, is to solve directly a multicomponent two-zone advection-diffusion-reaction model using a Maxwell-Stefan formulation of the problem [21-25].

In addition to the intrinsic complexity of the mathematical resolution of the problem to determine E, many supplementary difficulties could be highlighted for the case of acidic or basic compounds absorption:

- Several reactions can happen simultaneously in the liquid film. For example, in pure water, two reactions can be observed for an acid: dissociation and/or recombination with HO^- . A basic compound can react with a proton or with H_2O directly. The enhancement factor determination is even more complicated in the case of parallel reactions. A simple solution could be obtained only if the reactions are pseudo-first order or instantaneous compared to the absorption rate and if they are independent [26-28];
- In natural water, “parasite” reactions are possible, especially with the alkaline species (H_2CO_3 , HCO_3^- , CO_3^{2-}) and can improve the enhancement factor;
- Reagents and products diffusion coefficients are required for the enhancement quantification. The experimental determination of the diffusion coefficients in the gas (Winkelman method) and the liquid phases (two cells system) remains the most accurate technique [29,30]. The alternative way is to use semi-empirical correlations (Wilke-Chang, Hayduk-Laudie, Fuller-Schettler-Giddings, etc.) widely commented in the literature [5,29]. However, calculation of diffusion coefficients in a liquid phase can present a relatively large uncertainty [5]. For low solute content, this calculation is done considering an infinite dilution. To simplify the resolution, it is convenient to assume that the diffusion coefficients are constant in the liquid film [15]. For free ions (H^+ or HO^- for example) and electrolytes (NaOH, H_2SO_4 , etc.), diffusion coefficients calculation is related to ions conductivity [31]. However, depending on the conditions (pure water or water containing salt), the ions diffusion coefficients must be calculated considering the free ions or not [15,32]. This aspect is discussed deeper in the section 3.1.

- For electrolyte solutions, the electric potential can have an influence on the ion diffusion. Glasscock and Rochelle implemented the Nernst-Planck equation to take this electric potential into account [33]. They calculated the electric potential using the Henderson equation. Littel et al. also studied the influence of ionic species on the absorption rates [34]. As reported by Van Swaaij et al., they concluded that compared to the absorption models in which electroneutrality was assured by means of equal diffusivities of the ionic species, the deviation was negligible [7].
- Unless the liquid phase is perfectly mixed (which is usually not the case of gas scrubbers), the liquid composition and pH vary from the inlet to the outlet of the gas-liquid contactor and the enhancement factor determination must be achieved for infinitesimal volume elements, which can lead to heavy numerical resolutions. It confirms the need of simple procedure to calculate the enhancement factor.
- The exothermicity of the reactions can be neglected since the transfer of several $\text{g}\cdot\text{m}^{-3}$ of acidic or basic compounds are necessary to increase the water temperature of only 1 K considering a classical liquid-to-gas mass flow rates ratio of 3 and enthalpies of reaction in the order of magnitude of $10^2 \text{ kJ}\cdot\text{mol}^{-1}$.

To our knowledge, a few article in the literature focuses on the mass transfer enhancement factor determination for acid-base reactions in water depending on the pH. Sometimes, the determination is done assuming that the reaction is irreversible and instantaneous which can lead to overestimations of the enhancement factor [35]. The aim of this article is to give an overview of enhancement factor determination for acidic and basic compounds transfer in water trying to give a better understanding of the process. The development is based on the two films theory which has proven for several decades very good numerical calculations of the absorption rate for many cases and which is still used by both engineers and researchers (academicians and industries). Three pollutants of interest will be particularly studied: NH_3 , H_2S and CH_3SH . The article provides guidelines to select the pH of the scrubbing liquid and if necessary to choose the good assumptions for simplifications. A pertinent pH selection is very important since a compromise is required between a large mass transfer enhancement (which naturally will require extreme pH) and the need to limit the operating costs (which will be affected by extreme pH due to reagents consumption and parasite reactions such as carbon dioxide absorption at alkaline pH).

2 Mass transfer enhancement factor determination

2.1 Mass transfer rate

Gas-liquid mass transfer can be described according to various theories. Usually, the steady state two-film theory is applied. At a given location of the reactor, the molar flux per square meter of gas-liquid interface, for a gas phase reactant A transferred into a liquid (dJ in $\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$) in which a reaction takes place, is [5]:

$$dJ = Ek_L(C_A^* - C_A) = K_L(C_A^{\text{Eq}} - C_A) \quad \text{Eq. 1}$$

E is the so-called enhancement factor (dimensionless) which is the ratio of the absorption rate with and without the reaction for the same difference $C_A^* - C_A$. C_A is the pollutant concentration in the bulk ($\text{mol}\cdot\text{m}^{-3}$ or $\text{mol}\cdot\text{L}^{-1}$). C_A^* is the liquid pollutant concentration at the gas-liquid interface. C_A^{Eq} is the liquid pollutant concentration in equilibrium with the gas phase concentration:

$$C_A^{\text{Eq}} = \frac{p_A}{H_A} = \frac{RTC_A^G}{H_A} \quad \text{Eq. 2}$$

p_A is the partial pressure (Pa), C_A^G is the gas phase concentration ($\text{mol}\cdot\text{m}^{-3}$), H_A the Henry's law constant ($\text{Pa}\cdot\text{m}^3\cdot\text{mol}^{-1}$). The Henry's coefficient can be found in the literature, using the compilation of Sander or specific articles [36-41]. When the value cannot be found for a specific compound or in specific conditions, it remains possible to use some thermodynamic models which provide good accuracies [39,42-45]. k_L and K_L are respectively the local and overall liquid film mass transfer coefficient ($\text{m}\cdot\text{s}^{-1}$) linked together by the following relation:

$$\frac{1}{K_L} = \frac{1}{Ek_L} + \frac{RT}{H_A k_G} \quad \text{Eq. 3}$$

k_G is the local gas side mass transfer coefficient. k_L and k_G order of magnitude are respectively $1\text{-}5 \cdot 10^4 \text{ m}\cdot\text{s}^{-1}$ and $1\text{-}5 \cdot 10^{-2} \text{ m}\cdot\text{s}^{-1}$ and can be measured or determined by semi-empirical correlations for different contactors at fixed operating conditions (temperature, viscosities, densities, ionic strength, etc.) [5,29,46]. Eqs. 1 to 3 enable to write:

$$C_A^* = \frac{k_G(RTC_A^G - H_A C_A)}{H_A k_G + RTEk_L} + C_A \quad \text{Eq. 4}$$

This relation shows that C_A^* depends on the local mass transfer coefficients, C_A^G , C_A and the enhancement factor. C_A^* is naturally $\geq C_A$. Two limit behaviors can be observed. For a poorly soluble compound (large value of H_A) and with a low E value, C_A^* tends toward C_A^{Eq} . For a very soluble compound (low value of H_A) and/or if E is high (which enables to reach important removal efficiencies), if C_A can be neglected:

$$C_A^* \approx \frac{k_G C_A^G}{E k_L} \quad \text{Eq. 5}$$

In this case, the absorption rate is maximal and the resistance in the liquid phase is negligible. The condition to respect is :

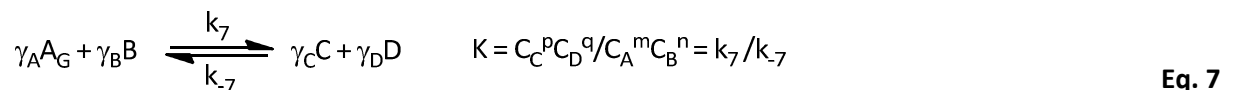
$$RTEk_L \gg H_A k_G \Rightarrow \frac{E}{H_A} \gg \frac{k_G}{RTk_L} \approx 0.04 \text{ assuming } k_L = 10^{-4} \text{ m.s}^{-1} \text{ and } k_G = 10^{-2} \text{ m.s}^{-1} \text{ at } 293 \text{ K} \quad \text{Eq. 6}$$

2.2 Enhancement factor determination for reversible reactions

2.2.1 General case

Depending on the amount of acid or basic salt (H_2SO_4 , HCl , $NaOH$, etc.) added to the scrubbing solution to set the pH, the ionic strength should be taken into account when calculating the absorption rate (Eq. 1). Indeed, the ionic strength has a rather strong influence on the absorbed compound solubility (the solubility decreases when the ionic strength increases due to the salting out effect) and the liquid mass transfer resistance. However, the ionic strength has a limited influence on the enhancement factor calculation for acid and basic compounds and only at very extreme pH ($pH < 3$ or > 12) through the counterions concentrations whose activity coefficients can be different of one. In order to simplify, the ionic strength is neglected in this development.

The following reversible reaction is considered after absorption of the specie A in solution:



Here, C and D are respectively the conjugated acid or base of A and B. k_7 and k_{-7} are the forward and reverse kinetic constants, K (k_7/k_{-7}) is the equilibrium constant and m, n, p, q are the kinetics order of respectively A, B, C and D. Onda et al. (1970) deduced from the material balances and the boundary conditions that [19]:

$$E = \frac{1 - C_A/C_A^* + \frac{\gamma_A D_C}{\gamma_C D_A} \left(\frac{C_C^* - C_C}{C_A^*} \right)}{1 - C_A/C_A^*} = \frac{C_A^* - C_A + \frac{\gamma_A D_C}{\gamma_C D_A} (C_C^* - C_C)}{C_A^* - C_A} \quad \text{Eq. 8}$$

$$C_B^* = C_B - \frac{\gamma_B D_C}{\gamma_C D_B} (C_C^* - C_C) \quad \text{Eq. 9}$$

$$C_D^* = C_D + \frac{\gamma_D D_C}{\gamma_C D_D} (C_C^* - C_C) \quad \text{Eq. 10}$$

D_i and C_i are respectively the molecular diffusion coefficient ($\text{m}^2.\text{s}^{-1}$) and the concentration (mol.L^{-1}) of any compound i . The subscripts * refers to the interface. The concentration should be used in mol.L^{-1} .

For any problem to solve, 4 parameters are unknown (C_B^* , C_C^* , C_D^* and E) for three equations. Therefore, another equation is required. Onda et al. (1970) proposed an approximated solution of E obtained by linearization of the material balance differential equation of the compound A [19]. With the assumption that the equilibrium prevails at the interface; if $m = p = 1$ (case of proton transfer reactions [18]), this approximated solution is:

$$E = \frac{1 + \frac{\gamma_A D_C}{\gamma_C D_A} \frac{KC_B^{*n}}{C_D^{*q}} + \frac{\gamma_A D_C}{\gamma_C D_A} \left(\frac{KC_B^{*n}}{C_D^{*q}} C_A - C_C \right) \frac{1 - 1/\cosh(\sqrt{M_2})}{C_A^* - C_A}}{1 + \frac{\gamma_A D_C}{\gamma_C D_A} \frac{KC_B^{*n}}{C_D^{*q}} \frac{\tanh(\sqrt{M_2})}{\sqrt{M_2}}} \quad \text{Eq. 11}$$

With M_2 a dimensionless number (familiar with the Hatta number):

$$M_2 = \frac{\gamma_A D_A k_7 C_B^{*n}}{k_L^2} \left(1 + \frac{\gamma_C D_A}{\gamma_A D_C} \frac{C_D^{*q}}{KC_B^{*n}} \right) \quad \text{Eq. 12}$$

When γ_c or γ_b are equal to 0 (one reagent or one product), n and q must be respectively replaced by 0 in Eqs. 11 and 12 since proton transfer reactions are elementary reactions. Versteeg et al. (1989) demonstrated that the approximated equation 11 is valid and provide a good estimation of E with a deviation lower than 2%, only if one product is formed ($\gamma_b = 0$) or if $m = p$ (which is considered here) [14].

For acidic or basic compounds, C_A and C_C (C_B and C_D) can be deduced from the total concentrations in solution (noted $C_A^{\text{Total}} = C_A + C_C$ and $C_B^{\text{Total}} = C_B + C_D$) for an infinitesimal volume element (or the whole

reactor for a continuous stirred tank reactor). The pH and the pK_A of each couple (Table 1) are required. Therefore, E can be determined for a given value of C_A^* :

- Knowing C_A^{Total} and C_B^{Total} , the pH, the pK_A , the diffusion coefficients, the reverse or forward kinetics constant, the stoichiometric coefficients and the liquid film coefficient k_L ;
- By using a solver (for example the Solver Excel®) to solve the set of Eqs. 8 to 11 following the procedure presented Fig. 1.

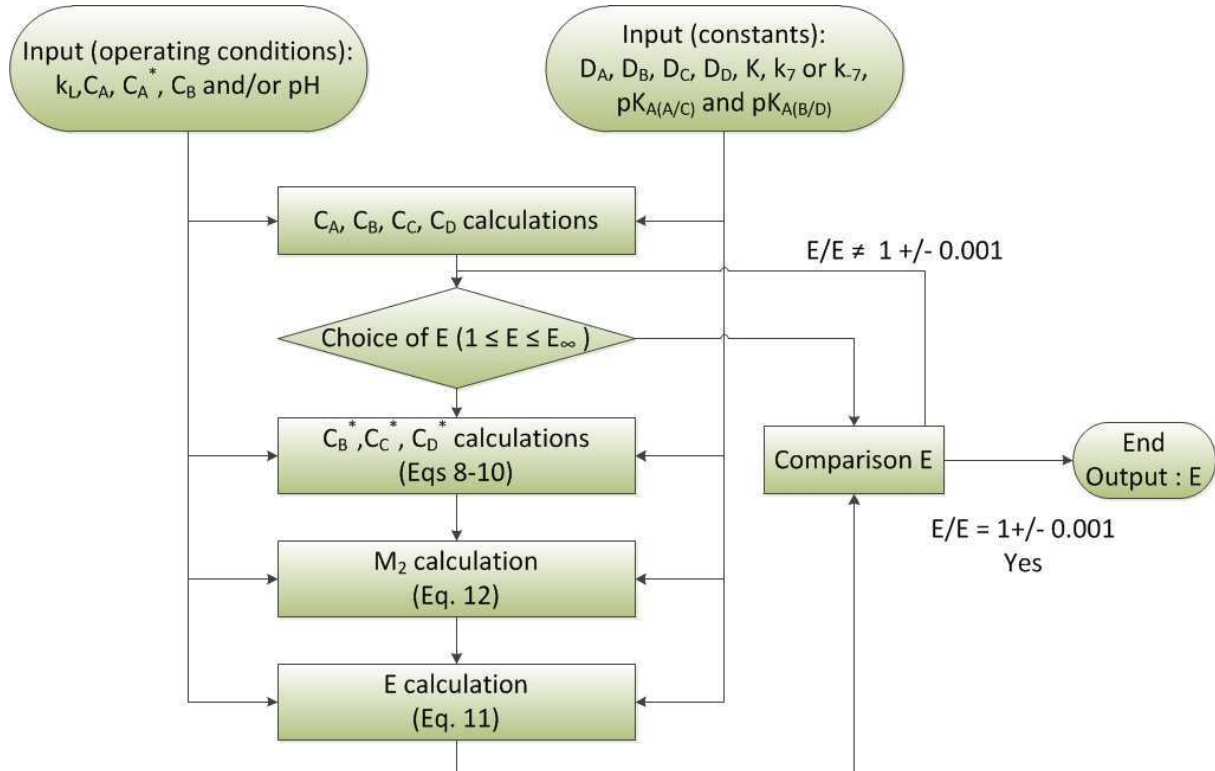


Figure 1 : Numerical resolution procedure.

Astarita et al. (1980) developed an alternative method which can be used for any kind of reversible reactions considered as instantaneous [17]. They assumed that the kinetics of reaction is so fast that the chemical equilibrium must prevail everywhere in the liquid phase. If we note ξ the extent of reaction in the liquid film, they demonstrated for a reaction as presented by Eq. 7 that:

$$\xi = (E_\infty - 1)(C_A^* - C_A) \Rightarrow E_\infty = 1 + \xi / (C_A^* - C_A) \quad \text{Eq. 13}$$

$$\frac{C_A^*}{C_A} = \left(1 - \frac{\gamma_B D_A \xi}{D_B C_B} \right)^{-1} \left(1 + \frac{\gamma_C D_A \xi}{D_C C_C} \right) \left(1 + \frac{\gamma_D D_A \xi}{D_D C_D} \right) \quad \text{Eq. 14}$$

Eq. 14 is a polynomial equation for ξ and could have more than one root. However, only one root will make the ratio $C_A^*/C_A > 1$ (for absorption) and will enable to determine the enhancement factor E_∞

for an instantaneous reaction. A numerical resolution is required to solve Eqs. 13 and 14 in the general case. However, for all the cases considered in this study (γ_B and $\gamma_D = 0$ or 1), an analytical equation can be derived.

2.2.2 Particular case of a acid-base pairs reaction: $\gamma_A = \gamma_B = \gamma_C = \gamma_D = 1$

In this case, Eqs. 11 and 12 can be slightly simplified:

$$E = \frac{1 + \frac{D_C}{D_A} \frac{KC_B^*}{C_D^*} + \frac{D_C}{D_A} \left(\frac{KC_B^*}{C_D^*} C_A - C_C \right) \frac{1 - 1/\cosh(\sqrt{M_2})}{C_A^* - C_A}}{1 + \frac{D_C}{D_A} \frac{KC_B^*}{C_D^*} \frac{\tanh(\sqrt{M_2})}{\sqrt{M_2}}} \quad \text{with } M_2 = \frac{D_A k_7}{k_L^2} \left(C_B^* + \frac{D_A}{D_C} \frac{C_D^*}{K} \right) \quad \text{Eq. 15}$$

For an instantaneous reaction, M_2 is so large that an analytical solution can be deduced to determine E_∞ from Eqs. 8 to 12:

$$E_\infty = 1 + \frac{D_C}{2D_A(C_A^* - C_A)} \left(\sqrt{\left(\frac{D_D}{D_C} C_D + \frac{D_D}{D_B} KC_A^* - C_C \right)^2 + 4KC_A^* \left(\frac{D_D}{D_C} C_B + \frac{D_D}{D_B} C_C \right) - \frac{D_D}{D_C} C_D - \frac{D_D}{D_B} KC_A^* - C_C} \right) \quad \text{Eq. 16}$$

It confirmed the solution previously determined by Olander (1960) with another mathematical development and this equation is also a solution of the method of Astarita and Savage (1980) [16,17]. Indeed, in this case, Eq. 14 is a second degree polynomial equation whose the positive root injected in Eq. 13 leads to Eq. 16. Consequently, whereas the mathematical developments are different between these studies, the analytical solutions are identical.

2.2.3 Particular case of the recombination with HO· or H⁺: $\gamma_A = \gamma_B = \gamma_C = 1$ and $\gamma_D = 0$

Eqs. 8 and 9 lead to Eq. 17 and Eqs. 11 and 17 to Eq. 18:

$$E = \frac{1 - C_A/C_A^* + \frac{D_B}{D_A} \left(\frac{C_B - C_B^*}{C_A^*} \right)}{1 - C_A/C_A^*} = 1 + \frac{D_B}{D_A} \frac{C_B - C_B^*}{C_A^* - C_A} \quad \text{Eq. 17}$$

$$E = \frac{1 + \frac{D_C}{D_A} K \left(C_B^* + C_A \frac{C_B^* - C_B}{C_A^* - C_A} \left(1 - 1/\cosh(\sqrt{M_2}) \right) \right)}{1 + \frac{D_C}{D_A} KC_B^* \frac{\tanh(\sqrt{M_2})}{\sqrt{M_2}}} \quad \text{with } M_2 = \frac{D_A k_7}{k_L^2} \left(C_B^* + \frac{D_A}{KD_C} \right) \quad \text{Eq. 18}$$

Only Eqs. 17-18 are necessary to determine E by a simple numerical resolution (Fig. 1). For an instantaneous reaction, *i.e.* large values of M_2 , Eqs. 17 and 18 leads to Eq. 19:

$$E_{\infty} = 1 + \frac{D_B C_B}{\frac{D_A D_B}{K D_C} + D_A C_A^*} \quad \text{Eq. 19}$$

This equation is identical to the one previously found by Olander (1960) and is also the solution of the system of equations developed by Astarita and Savage [16,17].

2.2.4 Particular case of dissociation and hydrolysis: $\gamma_A = \gamma_C = \gamma_D = 1$ and $\gamma_B = 0$

In this case, Eq. 11 leads to Eq. 20 which still needs to be solved numerically using Eqs. 8 and 10:

$$E = \frac{1 + \frac{D_C K}{D_A C_D^*} + \frac{D_C}{D_A} \left(\frac{K}{C_D^*} C_A - C_C \right) \frac{1 - 1/\cosh(\sqrt{M_2})}{C_A^* - C_A}}{1 + \frac{D_C K}{D_A C_D^*} \tanh(\sqrt{M_2})/\sqrt{M_2}} \quad \text{with } M_2 = \frac{D_A k_7}{k_L^2} \left(1 + \frac{D_A C_D^*}{D_C K} \right) \quad \text{Eq. 20}$$

For an instantaneous reaction, it comes from Astarita and Savage (1980):

$$\frac{C_A^*}{C_A} = \left(1 + \frac{D_A \xi}{D_C C_C} \right) \left(1 + \frac{D_A \xi}{D_D C_D} \right) \quad \text{Eq. 21}$$

This equation is a second degree polynomial equation. Determination of the positive root leads to:

$$E_{\infty} = 1 + \frac{\sqrt{(D_D C_D + D_C C_C)^2 - 4(1 - C_A^*/C_A)(D_D C_D D_C C_C) - (D_D C_D + D_C C_C)}}{2D_A (C_A^* - C_A)} \quad \text{Eq. 22}$$

This equation was also determined by Chang and Rochelle with different assumptions (1982).

Table 1 presents all the reactions investigated in this article with the method of calculation of K, concentrations and E.

Table 1 : Synthesis of the different reactions investigated and of the equilibrium constant, the concentrations and E calculations.

Type of reaction	Chemical equation	Equilibrium constant K	Concentrations	Determination of E
Dissociation	Eq. 23: $A \rightleftharpoons C + D$ Example, Eq. 24 : $H_2S \rightleftharpoons HS^- + H^+$	Eq. 25: $K_A = 10^{-pK_A} = \frac{C_C C_D}{C_A}$	Eq. 26: $C_A = \frac{C_A^{Total}}{1 + 10^{pH - pK_A}}$ $C_B = [HO^-] = 10^{pH - pK_e}$	E: Eqs. 8,9 and 20 (procedure in Fig. 1) E _∞ : Eq. 22
Recombination with HO⁻	Eq. 27: $A + B \rightleftharpoons C + H_2O$ Example, Eq. 28: $H_2S + HO^- \rightleftharpoons HS^- + H_2O$	Eq. 29: $\frac{K_A}{K_e} = 10^{-pK_A + pK_e} = \frac{C_C}{C_A C_B}$	$C_C = \frac{C_A^{Total}}{1 + 10^{pK_A - pH}}$ $C_D = [H^+] = 10^{-pH}$	E: Eqs. 17 and 18 (procedure in Fig. 1) E _∞ : Eq. 19
Recombination with H⁺ (protonation)	Eq. 30: $A + B \rightleftharpoons C$ Example, Eq. 31: $NH_3 + H^+ \rightleftharpoons NH_4^+$	Eq. 32: $\frac{1}{K_A} = 10^{pK_A} = \frac{C_C}{C_A C_B}$	Eq. 33: $C_A = \frac{C_A^{Total}}{1 + 10^{pK_A - pH}}$ $C_B = [H^+] = 10^{-pH}$	E: Eqs. 17 and 18 (procedure in Fig. 1) E _∞ : Eq. 19
Hydrolysis	Eq. 34: $A + H_2O \rightleftharpoons C + D$ Example, Eq. 35: $NH_3 + H_2O \rightleftharpoons NH_4^+ + HO^-$	Eq. 36: $\frac{K_e}{K_A} = 10^{pK_A - pK_e} = \frac{C_C C_D}{C_A}$	$C_C = \frac{C_A^{Total}}{1 + 10^{pH - pK_A}}$ $C_D = [HO^-] = 10^{pH - pK_e}$	E: Eqs. 8,9 and 20 (procedure in Fig. 1) E _∞ : Eq. 22
Acid reaction with a base	Eq. 37: $A + B \rightleftharpoons C + D$ Example, Eq. 38: $H_2S + HCO_3^- \rightleftharpoons HS^- + H_2CO_3$	pK_A : pK _A of A/C pK_A : pK _A of D/B Eq. 39: $\frac{K_A}{K_A'} = 10^{pK_A' - pK_A}$	Eq. 40: $C_A = \frac{C_A^{Total}}{1 + 10^{pH - pK_A}}$ $C_B = \frac{C_B^{Total}}{1 + 10^{pK_A' - pH}}$ $C_C = \frac{C_A^{Total}}{1 + 10^{pK_A - pH}}$ $C_D = \frac{C_B^{Total}}{1 + 10^{pH - pK_A'}}$	E: Eqs. 8,9,10 and 15 (procedure in Fig. 1) E _∞ : Eq. 16
Base reaction with an acid	Eq. 41: $A + B \rightleftharpoons C + D$ Example, Eq. 42: $NH_3 + HCO_3^- \rightleftharpoons NH_4^+ + CO_3^{2-}$	pK_A : pK _A of C/A pK_A : pK _A of B/D Eq. 43: $\frac{K_A'}{K_A} = 10^{pK_A - pK_A'}$	Eq. 44: $C_A = \frac{C_A^{Total}}{1 + 10^{pK_A - pH}}$ $C_B = \frac{C_B^{Total}}{1 + 10^{pH - pK_A'}}$ $C_C = \frac{C_A^{Total}}{1 + 10^{pH - pK_A}}$ $C_D = \frac{C_B^{Total}}{1 + 10^{pK_A' - pH}}$	E: Eqs. 8,9,10 and 15 (procedure in Fig. 1) E _∞ : Eq. 16

3 Results and discussion

3.1 Introduction

Table 2: Presentation of the various scenarii investigated.

Operating conditions						
T = 293.15 K	$k_L = 10^{-4} \text{ m.s}^{-1}$		$k_G = 10^{-2} \text{ m.s}^{-1}$		L/G = 3.5	
H ₂ S and CH ₃ SH studies						
Description	Scenario 1		Scenario 2		Scenario 3	
	High value of C_A^G		Low value of C_A^G			
	Eff = 0.05		Eff = 0.001		Eff = 0.05	
C_A^G (mg.m ⁻³)	100		1			
C_A^* (mol.L ⁻¹)	8.1×10 ⁻⁶ (H ₂ S) / 1.11×10 ⁻⁵ (CH ₃ SH)		8.1×10 ⁻⁷ (H ₂ S) / 1.11×10 ⁻⁷ (CH ₃ SH)			
C_A^{Total} (mg.L ⁻¹)	1.7		0.034		0.017	
C_A^{Total} (mol.L ⁻¹)	5.1×10 ⁻⁵ (H ₂ S) 3.6×10 ⁻⁵ (CH ₃ SH)		1.0×10 ⁻⁶ (H ₂ S) 7.2×10 ⁻⁷ (CH ₃ SH)		5.1×10 ⁻⁷ (H ₂ S) 3.6×10 ⁻⁷ (CH ₃ SH)	
NH₃ study						
Description	Scenario 1	Scenario 2	Scenario 3	Scenario 4	Scenario 5	Scenario 6
	High value of C_A^G		Medium value of C_A^G		Low value of C_A^G	
	Eff = 0.9		Eff = 0.05		Eff = 0.9	
C_A^G (mg.m ⁻³)	100		1		0.01	
C_A^* (mol.L ⁻¹)	5.6×10 ⁻⁴		5.6×10 ⁻⁶		5.6×10 ⁻⁸	
C_A^{Total} (mg.L ⁻¹)	31.0	1.7	0.31	0.017	0.0031	0.00017
C_A^{Total} (mol.L ⁻¹)	1.82×10 ⁻³	1.01×10 ⁻⁴	1.82×10 ⁻⁵	1.01×10 ⁻⁶	1.82×10 ⁻⁷	1.01×10 ⁻⁸

Table 3 : Values of the diffusion coefficients at infinite dilution, pK_A and Henry's law constant in water used for the simulations (293.15 K).

Compound	pK _A	H _i (Pa.m ³ .mol ⁻¹)	10 ⁹ D _i (m ² .s ⁻¹)	Reference or method for D _i
Free HO ⁻	pK _e = 14.15		5.17	Self-diffusivity [15]
Free H ⁺			9.16	Self-diffusivity [15]
NaOH	Strong base		2.09	Nernst-Haskell [27]
H ₂ SO ₄	Strong acid		3.41	Nernst-Haskell [27]
H ₂ S	7.08 [29]	864 [41]	1.75	[47]
Free HS ⁻			1.75	Approximation
CH ₃ SH	10.33	430 [29]	1.26	[29]
Free CH ₃ S ⁻			1.26	Approximation
NH ₃	9.37 [48]	1.36 [48]	1.51	[49]
Free NH ₄ ⁺			1.92	Self-diffusivity [15]
H ₂ CO ₃	6.47/10.38 [29]		1.80	[50]
HCO ₃ ⁻			0.966	[50]
CO ₃ ⁻			0.707	[50]

E determination can be achieved depending on C_A^* (which depends mainly on C_A^G and H_A and more or less on k_L , k_G , E) and C_A^{Total} . Therefore, to assess the influence of C_A^* and C_A on the enhancement factor, simulations are performed for 4 scenarii for H_2S and CH_3SH and 6 scenarii for NH_3 (Table 2). These scenarii corresponds to several cases of figure. For all scenarii, C_A^* is deduced from fixed values of C_A^G using Eq. 4 with $E = 1$ and assuming $C_A \ll C_A^*$. In a volume element of the liquid phase, C_A^{Total} depends on the liquid flow pattern, the configuration (co-current or counter-current), the gas and liquid flow rates and the removal efficiency already reached in this element. C_A^{Total} is deduced from the amount transferred for a given removal efficiency Eff (which ensures that $C_A^* > C_A$ whatever the simulated pH), a given gas phase concentration C_A^G , and a gas-to-liquid mass flow rate ratio L/G of 3.5 (classical value in packed columns):

$$C_A^{Total} = \frac{\rho_G}{\rho_L L/G} Eff \times C_A^G \quad \text{Eq. 45}$$

Simulations are performed for various pH. It requires the values of the diffusion coefficients of each compound (Table 3). These values are considered constant in the liquid film and are determined assuming an infinite dilution [5]. Special considerations arise for the determination of ionic species diffusion coefficients. For ionic species and electrolytes ($NaOH$ or H_2SO_4 added to set the pH), if the coefficients do not exist in the literature, calculations are performed using the Nernst-Haskell equations for electrolytes ($NaOH$, H_2SO_4 , etc.) and the relation cited by Danckwerts for free ions (H^+ or HO^- for example) which require the ions conductivity λ ($S \cdot mol^{-1} \cdot m^2$) [5, 15, 27, 31]:

$$D_{i^+i^-} = \frac{RT}{F^2} \frac{z_{i^+} + z_{i^-}}{z_{i^+} \times z_{i^-}} \frac{\lambda_{i^+} \times \lambda_{i^-}}{\lambda_{i^+} + \lambda_{i^-}} \quad \text{with } F \text{ the faraday constant and } z \text{ the electrical charge of } i^+ \text{ or } i^- \quad \text{Eq. 46}$$

$$D_{i^+} = \frac{RT}{F^2} \frac{\lambda_{i^+}}{z_{i^+}} \quad \text{and} \quad D_{i^-} = \frac{RT}{F^2} \frac{\lambda_{i^-}}{z_{i^-}} \quad \text{Eq. 47}$$

H^+ and HO^- free ions diffuse 2 or 3 times faster than the corresponding electrolytes (Table 3). When H^+ and HO^- are provided by an electrolyte ($NaOH$ and H_2SO_4 for example) in sufficient amounts, Eq. 46 is used to determine effective HO^- and H^+ diffusion coefficients since the condition of electrical neutrality requires that HO^- or H^+ diffuse at the same rate than their counterions (HO^- and H^+ are slowed down whereas the counterions are sped up) [15,32]. When HO^- and H^+ are provided by pure water, free ion diffusion coefficients should be used since the conditions of electrical neutrality is respected. Between this two limit cases (for example natural water or water containing a small amount of acid or base to slightly change the pH), the choice of the diffusion coefficients of the ionic

species is a critical issue. On the contrary, when H^+ or HO^- are released in pure water (for example when $H_2S_g \rightleftharpoons HS^- + H^+$), electrical neutrality requires that counterions (HS^- in this example), H^+ and HO^- diffuse at the same rate [32]. In this case, the H^+/HO^- and counterions diffusion coefficients are calculated using Eq. 46. When an extraneous electrolyte is added to the water (NaCl for example), if sufficient relative excess of any salt is distributed uniform concentration throughout the system, the effective diffusion coefficients of H^+ and HO^- which are released are the free ions diffusion coefficients [15,32]. Assuming in this article that in any case, electrolytes are added to set the pH, in order to simplify the simulation and considering that it will not change with a great extent the conclusions, the free ions diffusion coefficients are chosen for the ions released and the effective conductivity calculated with Eq. 46 are chosen for the reacting ions. We recommend to anyone to adapt to his own conditions (pure water, natural water containing buffers such as carbonates, process water doped with NaOH or H_2SO_4 , etc.).

Unfortunately, for HS^- and CH_3S^- , the molar conductivity and diffusion coefficient has not been found in the literature. Therefore, we considered the free ion diffusion coefficients equal to the molecular diffusion coefficient of H_2S and CH_3SH since the diffusion of small molecule in water do not vary widely as mentioned by Danckwerts [15].

The simulation requires also the knowledge of at least the reverse or the forward kinetics constant. However, the reactions are extremely fast and therefore these values are poorly known. One of the goal of this article is to prove that this ignorance is not always determinant since the assumption of an instantaneous reversible reaction can provide a good estimation of the enhancement factor in many cases.

3.2 Absorption of an acid in pure water doped with sodium hydroxide

When an acid is absorbed in water (in which sodium hydroxide can be added to set an alkaline pH), potentially two reactions are possible: dissociation or recombination with HO^- . For H_2S , these reactions are respectively Eqs. 24 and 28. For dissociation reactions, the forward kinetic constant is usually very high (10^{10} to 10^{11} $L.mol^{-1}.s^{-1}$) [18]. For H_2S , the reverse kinetic constant k_{-24} is equal to 7.5×10^{10} $L.mol^{-1}.s^{-1}$ [18]. Therefore, the forward kinetic constant k_{24} is equal to $10^{-pK_A} \times k_{-24} = 6.24 \times 10^3$ s^{-1} with $pK_A = 7.08$ at 293 K [29]. For reaction 28, both forward and reverse kinetic constants are unknown. However, the order of magnitude of a recombination reaction with HO^- is expected between 10^9 and 10^{11} $L.mol^{-1}.s^{-1}$ [18]. Consequently, for the recombination with HO^- reaction, different simulations will be presented with varying values of k_{28} in this range. We note that the

simulation has been extended to acidic pH (which would require to set the pH with an acid more than with NaOH) since even at such pH, E values larger than 1 are calculated.

3.2.1 Study of the dissociation reaction

Fig. 2 presents the evolution of E due to the dissociation reaction vs. the pH for the 4 scenarii (Table 2). The first and probably the most important conclusion is that the dissociation reaction does not enable to reach large values of E and consequently to increase very significantly the absorption rate. It means that dissociation on the liquid film remains marginal by comparison to the recombination with HO^- except for $\text{pH} < 9$ where both reactions can participate to the process (§ 3.2.2). The enhancement depends predominantly on C_A^* , the pH and the total concentration of H_2S in solution. From a global point of view, E is higher when C_A^* and C_A^{Total} decrease at a given pH. E stays constant for $\text{pH} > \text{pK}_A + 2$. Even at pH lower than the pK_A (7.08), which means that H_2S is predominant over HS^- , a small enhancement exists. Another important conclusion is that E is equal to E_∞ except for extreme pH where the deviation is lower than 3% for scenarii 3 and 4. It means that at low pH, the process is totally controlled by the equilibrium while at high pH, the reaction kinetics can have a small influence.

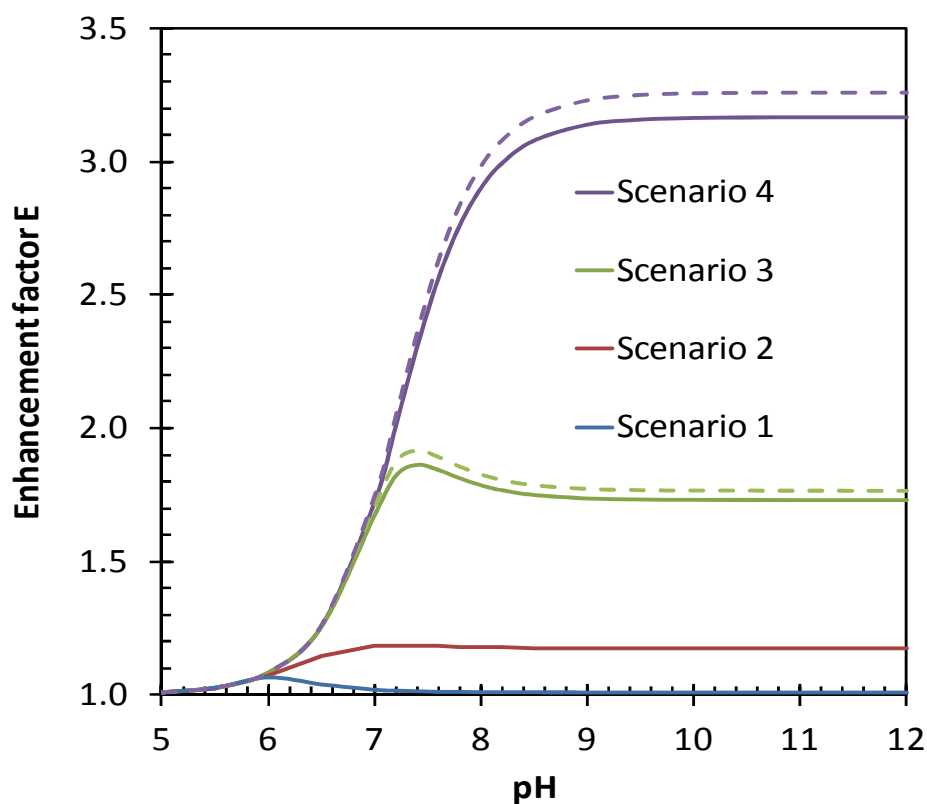


Figure 2 : Evolution of E vs. the pH due to the H_2S dissociation reaction for scenarii 1 to 4 ($K = 8.32 \times 10^{-8} \text{ mol.L}^{-1}$). Dash lines correspond to E_∞ .

For CH_3SH ($K = 1.66 \times 10^{-5} \text{ mol.L}^{-1}$), the maximal values of E_∞ ($E_\infty = 1.05$) are obtained for scenario 4 at pH 9.5-10 showing that this reaction is not significant. It means that dissociation reaction has an influence only for strong acid or acid whose pK_A remains lower than 7-8.

3.2.2 Study of the recombination with HO^- reaction

Fig. 3 presents the evolution of E due to the recombination with HO^- for scenarii 1 and 3 vs. the pH for different values of k_{28} . The results of scenarii 2 and 4 are not presented since they are identical to the results of respectively scenarii 1 and 3 which means that in this case, C_A has no influence. The first important conclusion is that, contrary to the dissociation reaction, recombination with HO^- reaction enables to reach large values of E for alkaline pH. The increasing amount of reactant (HO^-) with the pH improves the influence of this reaction. For scenarii 1 and 2, the ignorance of the kinetic constant is not problematic except for extreme pH since the values found with different values of k_{28} are equal at low pH. Furthermore, for higher pH, the enhancement factor is so high that its calculation is not required anymore. Indeed, according to Eq. 6, as soon as $E > 320$, only 10% of the total resistance for mass transfer is located in the liquid film ($E > 680$ for 5%). Therefore, the absorption rate depends on a limited extent on E for $E > 320$ and can be approximated by neglecting the liquid resistance with a low error. Consequently, designers can determine with a low uncertainty the enhancement factor with the assumption that the reaction is instantaneous when the kinetic constant cannot be found in the literature. For low values of C_A^* (in the top of a scrubber operating at counter-current), this assumption should be considered carefully depending on the true value of k_{28} . A value of k_{28} close to $3.0 \times 10^{10} \text{ L.mol}^{-1}.\text{s}^{-1}$ can be expected in many cases for acid recombination with HO^- and can be used in the computation [51]. To maximize the absorption rate, a pH larger than 10-11 will be required. For $\text{pH} > 10.5$, the absorption rate increasing with the pH is less sensitive since the E values are so large that the liquid resistance is almost negligible. This conclusion is in accordance with the results reported by Chen et al. (2001) [6].

For the CH_3SH recombination with HO^- , the simulation is done with a kinetics constant = $3.0 \times 10^{10} \text{ L.mol}^{-1}.\text{s}^{-1}$. Due to a higher pK_A , it is necessary to increase the pH to at least 11-11.5 (Fig. 4) to reach interesting E values ($E = 5.56$ for $\text{pH} = 11$). The difference between scenarii 1-2 and 3-4 is rather small and the results are close to those obtained considering an instantaneous reaction.

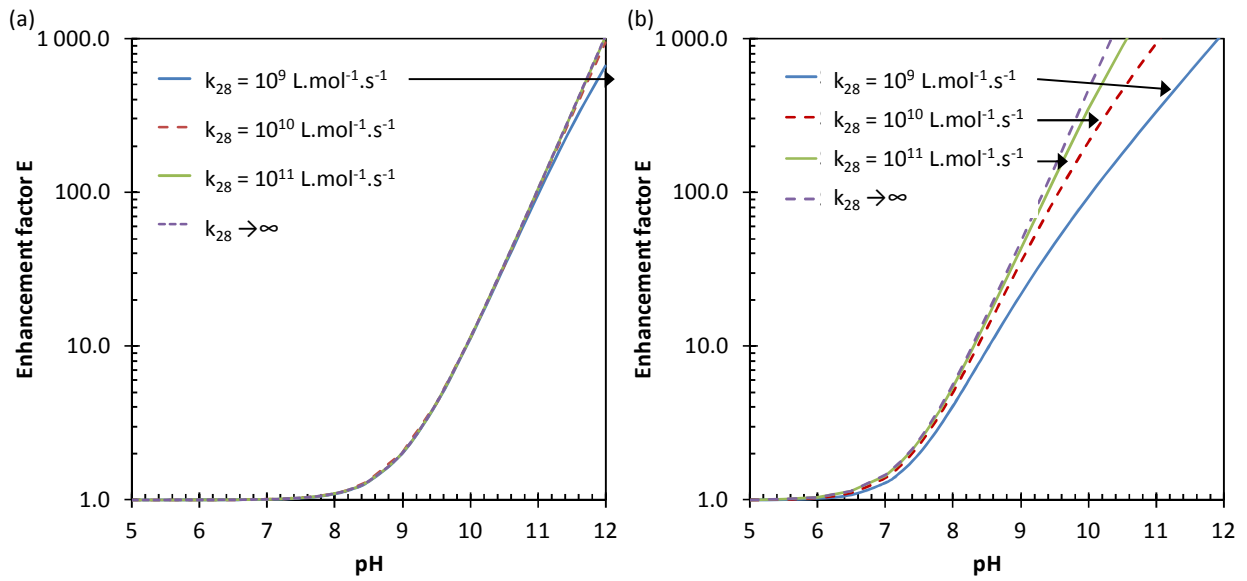


Figure 3 : (a) Evolution of the expected E vs. the pH due to the H_2S recombination reaction for scenarii 1 and 2 for different values of k_{28} . (b) Evolution of the expected E vs. the pH due to the H_2S recombination reaction for scenarii 3 and 4 for different values of k_{28} ($K = 1.18 \times 10^7 \text{ L}\cdot\text{mol}^{-1}$).

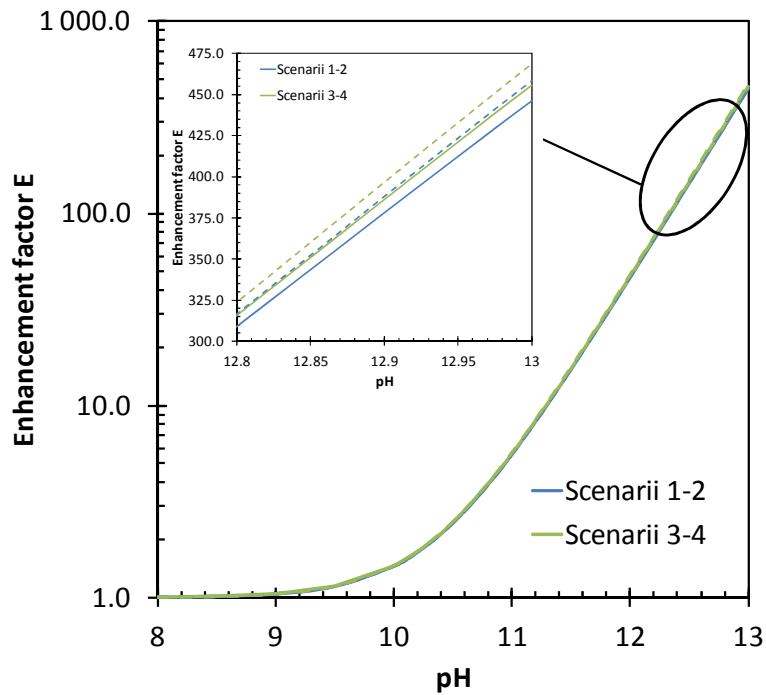


Figure 4 : Evolution of the expected E vs. the pH due to the CH_3SH recombination reaction ($K = 6.64 \times 10^3 \text{ L}\cdot\text{mol}^{-1}$). Dash lines correspond to $E \rightarrow \infty$.

3.2.3 Influence of alkaline species

Previous results (3.2.1 and 3.2.2) were calculated by considering that the scrubbing liquid was composed of pure water and sodium hydroxide. However, process water contains compounds which can interact in the process, especially CO_3^{2-} , HCO_3^- and H_2CO_3 which are the main buffers in the system. The main issue dealing with proton transfer reactions between two different acid-base pairs in water is the ignorance of the kinetic constant. As mentioned by Eigen (1964), there are relationships between the rate constant for proton transfer and pK_A difference (noted ΔpK_A) between the donor (acid) and the acceptor (base) [18]. CO_3^{2-} and HCO_3^- are potentially two acceptors with respective ΔpK_A equal to -3.30 and 0.61 at 293.15K. For many inorganic acid-base pairs, for $\Delta\text{pK}_A = -3.30$ (0.61) the $\log(k_{\text{forward}})$ is in the order of magnitude 9.5-10 (8-8.5) which leads to k_{forward} of at least 1.0×10^8 for the reaction between H_2S and CO_3^{2-} ($3.6 \times 10^9 \text{ L.mol}^{-1}.\text{s}^{-1}$ for the reaction between H_2S and HCO_3^-).

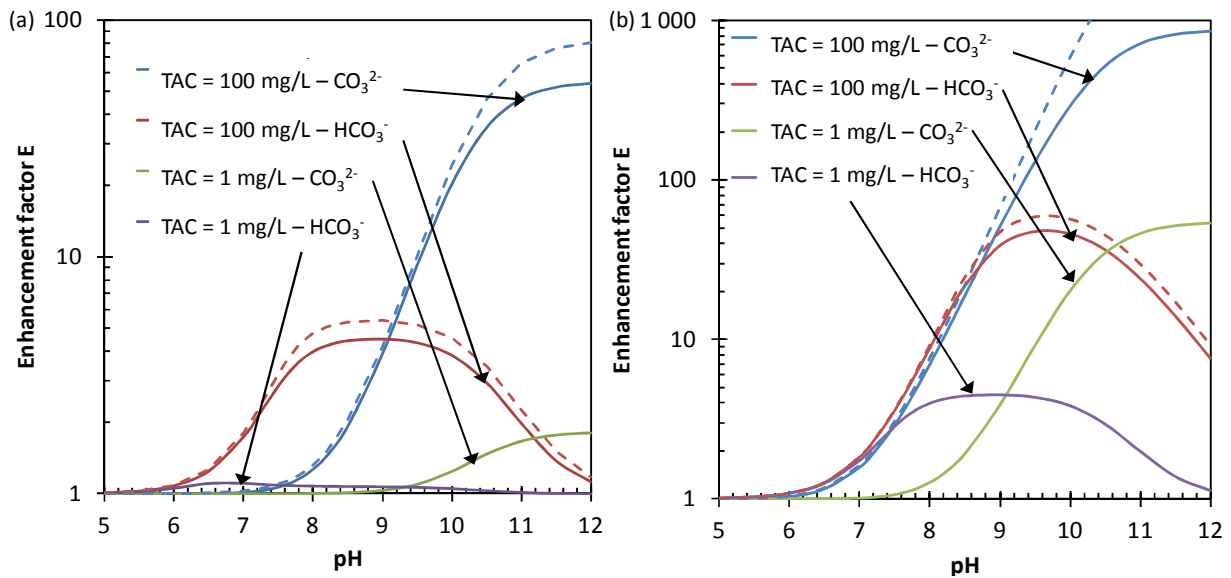


Figure 5 : (a) Evolution of the expected E vs. the pH due to the reaction with CO_3^{2-} and HCO_3^- for scenarii 1 for $\text{TAC} = 100$ and 1 mg/L . (b) Evolution of the expected E vs. the pH due to the reaction with CO_3^{2-} and HCO_3^- for scenarii 3 for $\text{TAC} = 100$ and 1 mg/L . (K with $\text{CO}_3^{2-} = 2.02 \times 10^3$ and K with $\text{HCO}_3^- = 2.43 \times 10^{-1}$). Dash lines correspond to E_∞ .

Simulations are performed for scenarii 1 and 3 for a high value ($\text{TAC} = 100 \text{ mg of CO}_2/\text{L}$) and for a low value ($\text{TAC} = 1 \text{ mg of CO}_2/\text{L}$) of the total alkalinity (Fig. 5). The main conclusion is that parasite reactions with CO_3^{2-} and HCO_3^- can play an evident role in the global enhancement of H_2S transfer. This is obviously the case when the TAC is large. Reaction with HCO_3^- is more significant at circumneutral pH and the reaction with CO_3^{2-} is more significant at high pH in their respective predominance domains. The enhancement due to these parasite reactions is particularly significant for low C_A^* . We note that in many cases, E is close to E_∞ . To really assess the potential of

enhancement of these reactions, a global enhancement factor should be calculated taking into account at the same time these reactions and the reaction with HO^- and the dissociation. This calculation can be solved with a complicated numerical resolution taking into account the differential equations relative to material balances of each species and all the reactions possible between them. To simplify, when all the reaction can be considered as instantaneous, the overall enhancement factor can be deduced from the sum of the individual enhancement factors [7].

3.3 Absorption of a base in pure water doped with sulfuric acid

When a base is absorbed in water (in which an acid such as sulfuric acid can be added to set an acid pH), two reactions are potentially possible: protonation or hydrolysis. For NH_3 , these reactions are Eqs. 31 and 35. For protonation reaction, the forward kinetic constant is very large (10^{10} to 10^{11} $\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ for many bases) and for ammonia $k_{31} = 4.3 \cdot 10^{10}$ $\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ [18]. For the hydrolysis reaction, k_{35} is equal to $3.4 \cdot 10^{10}$ $\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ [18]. Therefore, the forward kinetic constant k_{35} is equal to $10^{-\text{p}K_A} \times k_{35} = 5.65 \cdot 10^5 \text{ s}^{-1}$ with $\text{p}K_A = 9.37$ at 293 K [48]. We note that the simulation has been extended to basic pH (which would require to set the pH with a base more than with an acid) since values of E larger than 1 are calculated.

Fig. 6 demonstrates that the protonation reaction enable to reach larger values of E than the hydrolysis except for pH close to the neutrality where both reactions must be considered. The behavior is close to the one obtained with H_2S . Indeed, in both cases, the enhancement factor increases when C_A^* decreases. For relatively high values of C_A^* (scenarii 1 to 4), E is equal to E_∞ which means that the process is controlled by the equilibrium and not the kinetics (*i.e* the reaction is instantaneous). Consequently, Eq. 17 can be used to determine the enhancement factor very easily. Moreover, while:

$$\frac{D_B}{KD_C} \ll C_A^* \Rightarrow C_A^* \gg \frac{3.41}{1.92 \times 10^{-\text{p}K_A}} = 7.5 \times 10^{-10} \text{ mol/L} \quad \text{Eq. 48}$$

E is equal to:

$$E = 1 + \frac{D_B \cdot C_B}{D_A \cdot C_A^*} \quad \text{Eq. 49}$$

This equation is the same than for an instantaneous irreversible bimolecular reaction [29]. It means than in this case, the reverse reaction is negligible compared to the forward reaction, contrary to the case of H_2S reaction with HO^- . Consequently, the assumption of an irreversible instantaneous reaction must be avoided. For low values of C_A^* (scenarii 5 and 6), there is a deviation between E and

E_{∞} which varies from 1% at pH 9 to 98% at pH 2. Ammonia is highly soluble in water with a low Henry's constant (Table 3). When $E = 1$, only 5% of the mass transfer resistance is located in the liquid phase (1% when $E = 6$). Therefore, for ammonia, a low enhancement is required to maximize the absorption rate.

For the hydrolysis reaction, the enhancement factor is constant except near the pK_A (Fig. 5 b). E increases as expected when C_A^* decreases but is almost independent of C_A^{Total} for low values of C_A^* (scenarii 5-6).

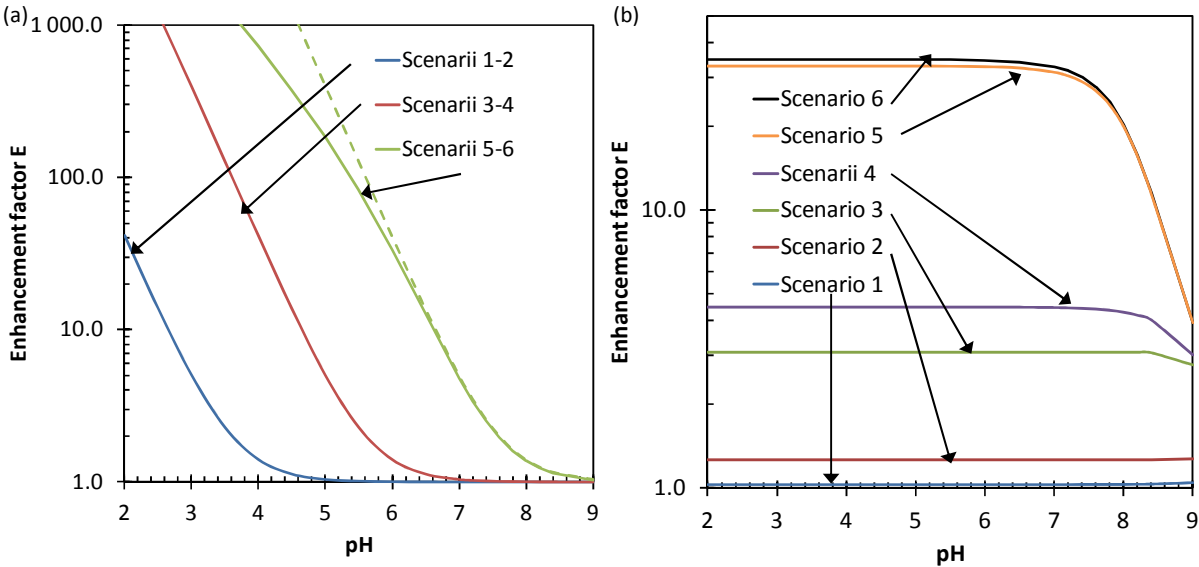


Figure 6: (a) Evolution of E vs. the pH due to the NH_3 protonation reaction for scenarii 1 to 6 ($K = 2.36 \times 10^9 \text{ L.mol}^{-1}$). (b) Evolution of E vs. the pH due to the NH_3 hydrolysis reaction for scenarii 1 to 6 ($K = 1.66 \times 10^{-5} \text{ mol.L}^{-1}$). The dashed lines correspond to E_{∞} .

4 Conclusions

This article gives an overview of mass transfer enhancement factor determination for acidic and basic compounds transfer in water. This enhancement results from reversible acid-base reactions in the liquid film (dissociation, protonation, hydrolysis and recombination with HO^-). The main conclusions are:

- Usually, E increases when C_A^* decreases.
- Influence of these reactions increases when the pK_A decreases (increases) for an acid (a base).
- The enhancement factor due to monomolecular reactions (dissociation, hydrolysis) has an asymptotic behavior. It is significant only for acidic (basic) compounds with a pK_A close or lower (larger) than 7. Since the reactions involved are really fast, in some cases, they can be assumed instantaneous. In this case, analytical equations are usable, making the enhancement factor determination easier. However, they must not be considered as irreversible assuming that the reverse reactions is negligible.
- When the reaction is not instantaneous compared to mass transfer rate, the reaction kinetics must be considered. In this case, a simple numerical resolution is required to solve the set of Eqs. 8-11 following the procedure reported in Fig. 1. A solver such as the Excel® solver can be used without restriction.
- Even if the reaction is not instantaneous, this approximation can leads to rather low deviations especially when the pH is close to the pK_A . Usually, the deviations increased for pH far from the pK_A which large enhancement factor. In this case, the liquid resistance could be low. It means that in this case the absorption rate depends poorly on E , *i.e.* a rather large deviation of E have a small influence on the gas-liquid contactor design.
- The assumption of an instantaneous reaction can be necessary to avoid a numerical resolution and/or if the kinetic constant is unknown. In this case, one should confirm that this assumption does not lead to a large uncertainty by trying to compare E_∞ and E obtained with a low but realistic value of the kinetics constant (Fig. 3b).
- For acidic (basic) compounds, at alkaline (acidic) pH, the enhancement is mainly due to the recombination with HO^- (protonation) reaction. In these cases, E is significantly influenced by the pH and C_A^* .
- Usually, one reaction can be neglected comparing to the other one for a large pH range. This conclusion is not completely true at circumneutral pH. However, in many cases, both reversible reactions can be considered as instantaneous and it becomes possible to calculate the total enhancement factor with the sum of the individual ones [7]. If natural water is used, alkalinity

(CO_3^{2-} , HCO_3^- and H_2CO_3) must be considered. Nevertheless, in industrial processes, it would be interesting to demineralize the process water to limit the buffer power and decrease the consumption of acid and soda necessary to set the pH.

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