Enhancement of methane–water volumetric mass transfer coefficient by inhibiting bubble coalescence with electrolyte

Kwangmin Kim [a], Jaewon Lee [a], Kyeongjun Seo [a], Myung-Gil Kim [b], Kyoung-Su Ha [a], Choongik Kim [a,*]

[a] Department of Chemical and Biomolecular Engineering, Sogang University, 1 Shinsoo-dong, Mapo-gu, Seoul 121-742, South Korea
[b] Department of Chemistry, ChungAng University, 221 Heukseok-dong, Dongjak-gu, Seoul 156-756, South Korea

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ABSTRACT

The effect of electrolyte on methane–water volumetric mass transfer coefficient ($k_L a$) was investigated in this study. Various electrolytes including $MgSO_4$, K_2SO_4, Na_2SO_4, $MgCl_2$, KCl, NaCl, $MgBr_2$, NaBr, KBr, $Mg(NO_3)_2$, KNO_3, and $NaNO_3$ were employed and enhancement of $k_L a$ from $103\ h^{-1}$ (in pure water) to $711\ h^{-1}$ was observed, depending on electrolyte type and concentration. This is the highest methane–water $k_L a$ value measured at ambient condition. For all electrolytes, ions with large charge density (charge valency per ionic volume) exhibited larger enhancement in methane–water $k_L a$ values. Furthermore, anions exhibited larger influence than cations on the enhancement of $k_L a$. Enhancement of methane–water $k_L a$ by electrolytes was due to the inhibition of methane bubble coalescence.

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Introduction

Shale gas, natural gas found within shale formations, has recently sparked an energy revolution as an alternative energy resource around the world [1,2]. Although use of shale gas as cheap fuel is of significant economic value, its use as feedstock to produce high-value chemicals such as alcohols, olefins, and organic acids would possibly reshape chemical industries [3,4]. Especially, biological conversion of methane, main component of shale gas, by microorganisms or enzymes has recently gained much interest [5,6]. For shale gas fermentation, dissolved methane in aqueous solution is major carbon source for the microorganisms to produce the desired products [7,8]. In this regard, low methane solubility in culture medium (~21.7 mg/L at STP) limits biological conversion of methane, leading to low methane conversion yield [9]. High mass transfer rate of methane in aqueous solution could possibly overcome this hurdle, leading to efficient methane conversion.

Many researchers have attempted to enhance gas–water volumetric mass transfer coefficient ($k_L a$), an indicator for the mass transfer rate of gas in water, via various ways such as appropriate design of reactor or addition of chemicals [10,11]. To increase $k_L a$ values, we can either increase 'k_L (gas-water mass transfer coefficient)' or 'a (interfacial area between gas bubbles and water)', or both. To increase k_L value, a few different approaches have been reported including optimization of reactor design and addition of (nano)particles to increase the residence time of gas bubbles via enhanced gas-(nano)particle interaction [10,12]. For instance, Bai et al. investigated the influence of impeller type in a stirred tank bioreactor on oxygen–water mass transfer rate [10]. Impeller with more pitch blades has been demonstrated to exhibit larger $k_L a$ values. Furthermore, addition of particles was effective in enhancing gas–water mass transfer rate. Zhu et al. reported that addition of mesoporous MCM-41 particles in aqueous solution has enhanced the $k_L a$ value of carbon monoxide up to 190%, compared to that in pure water [12].

On the other hand, introduction of electrolyte has been an effective way to increase 'a' via inhibition of bubble coalescence, hence enhancing $k_L a$ values [13]. For instance, Zhu et al. enhanced CO–water volumetric mass transfer coefficient by employing various electrolytes; however, the mechanism of bubble coalescence inhibition via electrolytes is not clearly understood [13,14]. Furthermore, influence of electrolytes on methane in aqueous solution, especially on methane–water volumetric mass transfer coefficient, has never been reported, to the best of our knowledge.

* Corresponding author.
  E-mail address: choongik@sogang.ac.kr (C. Kim).

In this paper, we determined methane–water volumetric mass transfer coefficient in various single-salt electrolyte solutions with various concentrations. Various electrolytes containing cations/anions with different charge valency and ionic radius were employed. Electrolytes with higher charge density afforded smaller bubble sizes and larger k_La values, as high as 711 h^{-1}.

Experimental

Reactor setup

Sparged stirred tank reactor was employed to measure methane concentration and determine k_La values in aqueous solution [11]. Impeller was used to make the solution homogeneous during the experiment. The reactor temperature was maintained at 30 °C by the water jacket and water circulator (Wisecircu, Wisd Laboratory Instruments Co.) surrounding the reactor [15]. Methane gas was injected into the reactor near the impeller by alumina bubbler (pore size = 10–40 μm). Flow rate of methane gas was controlled by mass flow controller (TSD-D220, MFC Korea Co.).

Measurement of methane concentration in aqueous solution

The x wt% electrolyte solution (x = 1, 3 and 5) was prepared by dissolving appropriate salt in distilled water. While methane gas is flowed at 3 L/min, the electrolyte solution containing the dissolved methane gas was taken via reactor septum at different times during 5 min period by syringes. The collected electrolyte samples were heated at 95 °C for 1 h in the heating block (DMB-2, Misung Instrument Co.). During heating, methane dissolved in electrolyte solution was considered to evaporate completely since methane concentration in aqueous solution at 95 °C is very low [16]. Then, gas from the head space was taken by gas-tight syringe from the vials, and was measured by gas chromatography (ACME 6100, Young Lin Instruments Co.) with flame ionization detector.

Determination of methane–water volumetric mass transfer coefficients

The methane–water volumetric mass transfer coefficient was estimated by dynamic gassing-out method [17]. In the system, gas transfer process can be described by:

$$R = \frac{dC_L}{dt} = k_La\left(C* - C_L\right) \qquad (1)$$

where k_La is the volumetric mass transfer coefficient based on liquid-phase resistance to the mass transfer, C^* is the saturated methane concentration in the solution, and C_L is the dissolved methane concentration in the solution. The mass transfer rate decreases during the period of aeration as C_L approaches C^* because of the tendency to decline in (C^*-C_L). Then, Eq. (1) can be integrated as:

$$\ln\left(1 - \frac{C_L}{C*}\right) = -(k_La)t \qquad (2)$$

Since Eq. (2) is a linear form, k_La could easily be obtained by calculating the slope of the line, where t is the time (sec) [15].

Results and discussion

Fig. 1(a) shows the dissolved methane concentration with various concentrations of magnesium sulfate (MgSO$_4$) as a function of time. As shown, methane concentration increases over time and saturates. In pure water, saturation occurs at ~150 s, while in MgSO$_4$ solution, saturation starts earlier (at ~20–40 s)
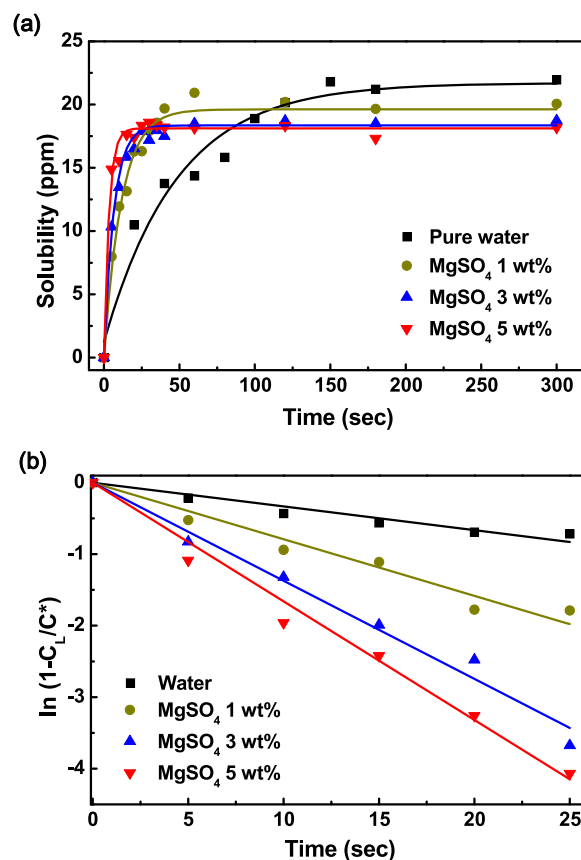

Fig. 1. (a) Methane concentration in pure water and MgSO$_4$ solutions with different concentrations as a function of time. (b) Calibration lines for the determination of methane–water volumetric mass transfer coefficient.

than in pure water, indicating higher methane–water mass transfer rate in electrolyte solution. Furthermore, maximum solubility of methane decreases in electrolyte solutions due to salting-out effect [18–20]. Fig. 1(b) shows calibration line for the determination of methane–water volumetric mass transfer coefficient. As shown, k_La value increases as the electrolyte concentration increases. In pure water, k_La value of 103 h^{-1} was measured. On the other hand, MgSO$_4$ solutions exhibited larger k_La value of 293 h^{-1} (1 wt% concentration), 513 h^{-1} (3 wt% concentration), and 711 h^{-1} (5 wt% concentration), respectively.

Other electrolytes showed similar trend, exhibiting enhanced k_La values at higher concentrations (Table 1). At 1 wt% concentration, k_La value was in the range of 107–293 h^{-1}, while k_La value was enhanced to 121–513 h^{-1} (3 wt% concentration) and 141–711 h^{-1} (5 wt% concentration) at higher concentration. Comparing the effect of cations and anions separately, anions showed a stronger influence than cations on the enhancement in k_La values (Fig. 2). For electrolytes with the same cations, different anions (sulfates, chlorides, bromides, and nitrates) showed different tendency in k_La enhancement. The sulfate-containing electrolyte showed the highest enhancement with k_La value of 613–711 h^{-1}. On the other hand, electrolytes containing other anions showed relatively lower k_La values of 381–488 h^{-1} (chlorides), 141–290 h^{-1} (bromides), and 233–266 h^{-1} (nitrates). For electrolytes with the same anions, magnesium-containing electrolytes exhibited larger k_La values than sodium- and potassium-containing electrolytes. In Fig. 2, we arranged the k_La values of various electrolytes, which clearly shows the effect of different ions. The magnesium sulfate showed the largest enhancement in k_La as high as 711 h^{-1}, at a concentration of 5 wt%. This is the highest methane–water k_La value at ambient condition reported in the literature. Note that