Investigation and prediction of the salting-out effect of methane in various aqueous electrolyte solutions

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ABSTRACT

The maximum solubility of methane was determined in aqueous solution of $Al_2(SO_4)_3$, $MgSO_4$, K_2SO_4, Na_2SO_4, $AlCl_3$, $MgCl_2$, KCl, NaCl, $MgBr_2$, KBr, and NaBr with various concentration (1, 3 and 5 wt%) at ambient pressure. Salting-out effect was observed in all electrolyte solutions, exhibiting lower solubility of methane compared to that in pure water. In general, electrolyte solutions comprising cations/anions with high charge valency and small ionic radius exhibited stronger salting-out effect due to large charge density of the corresponding ions. Furthermore, anions exhibited larger influence on the degree of salting-out compared to cations. Scaled particle theory was employed to corroborate the trend of the experimental solubility of methane in electrolyte solutions.

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Introduction

Gas solubility in liquid is one of the very important issues in various engineering fields, such as petroleum refinery, coal gasification, gas crystallization with anti-solvent, natural gas exploitation, and gas hydrate formation [1]. Among various gases, methane solubility in liquid has been of great interest since methane is byproduct of thermal cracking or organic matter [2]. Especially, as main component of shale gas, methane has shaded new light as feedstock for high-value chemicals via bio-conversion [3,4].

Since Hofmeister series was reported [5], using electrolytes (salts) as additives became a common occurrence to increase or decrease solubility of solute (non-electrolyte) in solution [6]. When electrolytes are added to solution, salting-out or salting-in can occur. The salting-out effect is the phenomenon in which solute becomes less soluble at high salt concentration, while salting-in effect is reverse. Although proteins are commonly employed as solutes to test salting-out or salting-in effects, gases as solutes show similar behavior upon addition of electrolytes [6,7]. For instance, Carvalho et al. investigated salting-out of carbon dioxide gas in various electrolyte solutions [6d]. For

methane gas, although a few studies have been reported in the literatures [7], these studies were limited to methane solubility in the mixture of seawater and water [7b] or under high pressure (e.g. 800 psia) [7c]. Investigation on methane solubility in various electrolyte solutions at ambient condition has never been reported, to the best of our knowledge.

To determine the salting-out effect quantitatively, Setschenow (salting-out) constant can be deduced based on the equation [7c]:

$$\log_{10}\frac{S_0}{S} = K_s C \tag{1}$$

where S_0 is the solubility of the solute in pure water, S is the solubility of the solute in the presence of electrolyte, K_s is the Setschenow constant, and C is the electrolyte concentration. As represented in the equation, the larger K_s, the stronger salting-out effect at a given electrolyte concentration. Various factors such as charge density of ions, concentration of electrolyte solutions, temperature, pressure, and dielectric constant of solution have been known to affect Setschenow constant [6b,8].

Furthermore, there has been much effort to understand the solvation of gases in fluid media theoretically, which led to the development of scaled particle theory (SPT). SPT explains thermodynamic behavior of dissolved gas in fluid media using molecular parameters and intermolecular interactions [9]. Pierotti et al. first developed SPT to predict the solubility of gases in water [9,10]. Masterton et al. calculated Setschenow constant for several

nonpolar gases with different electrolyte solutions using SPT. However, their study was limited to electrolyte solutions with very low concentration (∼0.1 wt%) [11a]. Kiepe at al. used experimental data of methane solubility at temperature range of 313–373 K and pressures up to 10 MPa in monovalent electrolyte solutions (KCl, KBr, LiCl and LiBr) to fit gas-ion parameters for extended predictive Soave–Redlich–Kwong model. They successfully predicted salting-out of methane in the electrolyte system, however, they used only alkali halides and fitted parameters for the comparison between experimental and theoretical data [11b].

In this report, we measured the maximum solubility of methane in various single-salt electrolyte solutions and investigated salting-out effect as a function of electrolyte concentrations. Various electrolytes with different charge valency and ion sizes including $Al_2(SO_4)_3$, $MgSO_4$, K_2SO_4, Na_2SO_4, $AlCl_3$, $MgCl_2$, KCl, NaCl, $MgBr_2$, KBr, and NaBr were employed. Setschenow constants were determined to quantify salting-out effect with respect to the kinds of electrolytes. Furthermore, theoretical calculation was employed to compare the trend in the calculated and experimental solubility of methane in electrolyte solutions.

Experiment

Reactor setup

The reactor used in this paper is a bubble column reactor (Fig. 1). To measure methane solubility in aqueous solution, 4-pitched blade impeller was used to make the solution homogeneous during the experiment. Septums were located at the side of the reactor for harvesting solutions with disposable syringes [12]. The temperature of the solution was maintained at 30 °C during experiment by the outer water-jacket and water-circulator (Wisecircu, Wisd Laboratory Instruments Co.) [13]. Methane gas was flowed continuously into the reactor near the impeller (300 rpm) by glass bubbler. Flow rate of methane was fixed at 3 L/min by gas flow controller (TSD-D220, MFC Korea Co.).

Determination of methane solubility and Setschenow constant

The aqueous solutions of x wt% electrolyte (x = 1, 3 and 5) were prepared by dissolving salts in distilled water. While methane gas (3 L/min) was flowed into the reactor (methane was introduced into the reactor under atmospheric pressure), the electrolyte solutions were harvested from the reactor at different times of 5, 10, 15, 20, 25, 30, 35, 40, 60, 120, 180, and 300 s by disposable syringes. The harvested electrolyte samples were injected into

Fig. 1. Schematic view of the experimental apparatus: (1) 4-pitched blade impeller; (2) syringe; (3) water jacket and water bath; (4) glass bubbler; (5) gas flow controller; (6) methane gas storage tank; (7) gas chromatography.

vials with sealed cap and were heated and maintained at 95 °C for 1 h in a heater (DMB-2, Misung Instrument Co.). During heating, dissolved methane in electrolyte was thought to evaporate completely because methane solubility in electrolyte solution at 95 °C is very low (<1 ppm). Then, 0.04 mL of head space gas 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 [13]. From this scheme, we measured S_0 (solubility of the methane in pure water) and S (solubility of the methane in electrolyte with various concentrations), and then calculated Setschenow constant using these values by Eq. (1) [7]. Each experimental measurement was performed at least three times.

Theoretical calculation of methane solubility in electrolyte solutions

Calculation of solvation Gibbs energy

Pierotti [9] suggested that the Gibbs free energy change for solvation as,

$$\Delta G_s = RT \ln K_{px} = \Delta G_c + \Delta G_i + RT\left(\frac{RT}{V_{m,1}}\right) \qquad (2)$$

where K_{px} is the Henry's constant based on mole fraction, ΔG_c is the cavity formation energy, ΔG_i is the molar Gibbs free energy of interaction, R is the gas constant, T is the temperature of system, and $V_{m,1}$ is the molar volume of the solvent. Pierotti suggested SPT formula based on the mole fraction of solubility, but it is preferable to introduce the solvation Gibbs energy on the concentration scale.

According to Ben-Naim [14a], solvation Gibbs energy is represented as:

$$\Delta G_s = -RT \ln \frac{C_L}{C_g} \qquad (3)$$

where C_g and C_L are the molar concentrations of the solute in the gas and liquid phase, respectively, at equilibrium. Combining (2) and (3), solvation Gibbs energy can be represented based on the concentration, dimensionless Henry's constant, ($K_{H,cc} = C_L/C_g$).

$$\Delta G_s = -RT \ln(K_{H,cc}) = \Delta G_c + \Delta G_i$$

Calculation of cavity formation energy (ΔG_c)

When solute is inserted into solvent, change in free energy occurs due to the entropy change via rearrangement of solvent molecules [14b]. This is termed as cavity formation energy,

$$\Delta G_c = RT\left[-\ln(1-\xi_3) + \frac{3\xi_2}{1-\xi_3}\sigma_c + \frac{3\xi_1}{1-\xi_3}\sigma_c^2 + \frac{9\xi_2^2}{2(1-\xi_3)^2}\sigma_c^2\right]$$

where $\xi_i = (\pi/6)\sum \rho_j \sigma_j^i$, in which ρ_j is the number density (number of molecules or ions per Å³) of each species j, σ_j is the corresponding hard sphere diameter for solvent and ions, and σ_c is the diameter for cavity (equal to the hard sphere diameter for solute molecule). We neglected the pressure-volume work for the calculation of ΔG_c because it can be neglected for incompressible liquid at ambient pressure [15,16].

Calculation of Gibbs energy of interaction (ΔG_i)

Gibbs energy of interaction is enthalpy term for solute-solvent attractive potential when a solute molecule introduces into a cavity [17]. Gibbs energy of interaction ΔG_i, originally derived by Pierotti [9], consists of three terms: dispersion energy, dipole–dipole energy, and dipole-induced dipole energy. Graziano assumed that the parametrizatio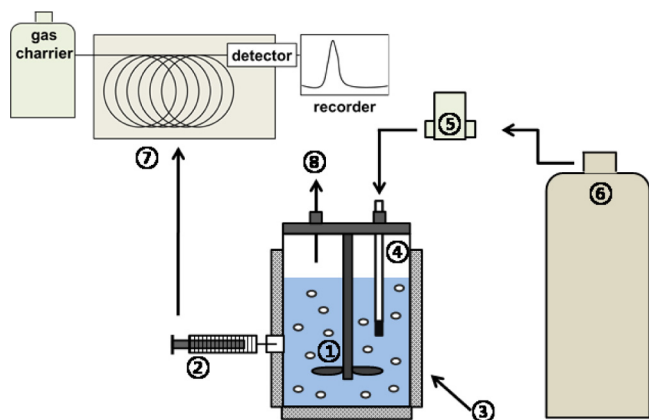n of the dispersion contribution