Thermodynamic and Kinetic Effect of a Dual-Function Inhibitor on Gas Hydrate Formation

Dongwook Lim\textsuperscript{1}, Seongmin Park\textsuperscript{1}, Hyeryon Ro\textsuperscript{1}, Jong-Won Lee\textsuperscript{2}, Hyery Kang\textsuperscript{1}, Minchul Kwon\textsuperscript{1}, Huen Lee\textsuperscript{1,*}

1. Department of Chemical and Biomolecular Engineering, KAIST, Daejeon, Korea
2. Department of Environmental Engineering, Kongju National University, Cheonan, Chungnam, Korea

ABSTRACT

The unexpected formation of gas hydrates during production and transportation processes in petroleum industries has caused serious problems, blocking oil and gas pipelines with safety hazards. To cope with this trouble, the gas hydrate community has searched for hydrate inhibitors that have great performance and cost effectiveness. Recently, the ionic liquids (ILs) have been suggested as novel hydrate inhibitors that are able to act in both thermodynamic and kinetic ways which are designated as dual-function inhibitors. In this study, we suggest a non-ionic liquid compound, morpholine as a dual-function inhibitor. We observed that this inhibitor shifts the hydrate phase equilibrium curve and reduces the hydrate formation rate as well. The formation kinetics of gas hydrates in the presence of morpholine was found to be better than two comparators of 1-ethyl-3-methylimidazolium tetrafluoroborate and polyvinylpyrrolidone. In addition, a series of microscopic analyses (powder X-ray diffraction, solid-state $^{13}$C NMR and Raman spectroscopy) were adopted to identify their crystal structure and molecular behavior during hydrate formation. Such inhibition effects of morpholine are thought to be mainly attributed to the nucleophilicity of the ring compound forming hydrogen bonds between surrounding water molecules. Moreover, it can be speculated that the more energy is required to form the structure II hydrate in the presence of morpholine instead of the structure I CH$_4$ hydrate with milder formation conditions.

KEY WORDS: Morpholine; Gas Hydrate; Dual-Function inhibitor; Flow assurance; Phase Equilibrium; Induction time.

INTRODUCTION

Clathrate hydrates, or gas hydrates are non-stoichiometric crystalline compounds formed by physically stable interactions between host water and guest molecules (Sloan and Koh, 2008). Connected water molecules can form polyhedral cage-like hydrogen-bonded frameworks to accommodate gaseous guest species with small molecular size (Atwood, Davis and MacNicol, 1984). Three common structures, structure I, II and H, are known to exist for gas hydrates mainly depending on the molecular size of guest molecules. Over the past few years, growing attention has been paid to gas hydrates regarding their potential application in the resourcing of natural gas(Ji, Ahmadi and Smith, 2001), CO$_2$ sequestration in deep ocean(Teng, Yamasaki, Chun and Lee, 1997), and recovery/separation of greenhouse gases from flue gas(Kang and Lee, 2000) because it can hold a large amount of gas in a unit volume of solid hydrate phase.

Although there has been growing interest regarding some applications recently, the unexpected formation of gas hydrate during production and transportation processes in petroleum industries is known as a severe problem(Kelland, 2006). Hydrate formation may block oil and gas pipelines(Ostergaard, Masoudi, Tohidi, Danesh and Todd, 2005), resulting in safety hazards. To deal with this problem, the oil and gas industry has been searching for hydrate inhibitors that have great performance and cost effectiveness. In general, hydrate inhibitors can be categorized into three types; thermodynamic and kinetic hydrate inhibitors and anti-agglomerants (Sloan and Koh, 2008). Thermodynamic hydrate inhibitors (THIs) shift the thermodynamic equilibrium curves of gas hydrates into the inhibition region, (that is, higher pressures or lower temperatures are required to form gas hydrates at a given temperature or pressure, respectively) so that operational conditions can reside outside the hydrate forming region. Methanol and monoethylene glycol (MEG) are the most well-known thermodynamic hydrate inhibitors which are normally used at the concentration of around 20.0-40.0 wt% (Koh, 2002). During the last two decades new groups of chemical inhibitors have been developed that act in a different way. Kinetic hydrate inhibitors (KHI) are water-soluble polymers that delay nucleation time (induction time), which is one of the most critical factors for field operations, without modifying the thermodynamic behaviors of hydrate systems. Anti-agglomerants (AAs) prevent hydrates from agglomerating and thereby accumulating into large masses also without affecting the thermodynamic hydrate-phase equilibrium. AAs make the gas hydrate form as transportable non-sticky slurry of hydrate particles dispersed in the liquid hydrocarbon phase. The effective concentrations of KHIs and AAs are much lower than those required for thermodynamic inhibitors; therefore, they are...