Novel Liquid-Like Nanoscale Hybrid Materials with Tunable Chemical
and Physical Properties as Dual-Purpose Reactive Media for Combined
Carbon Capture and Conversion

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ABSTRACT

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In order to address the global challenges of climate change caused by the increasing concentration of carbon dioxide (CO₂), Carbon Capture, Utilization and Storage (CCUS) has been proposed as a promising strategy in carbon management. In parallel with the target of zero emission in fossil-fired power plants, negative emission has also drawn a great deal of attention in other chemical sectors, including cement making and steel production industries. Thanks to the recent reduction in the cost of renewable energy sources, such as wind and solar, a paradigm shifting concept has emerged to directly convert the captured carbon into chemicals and fuels. In this way, decarbonization in various chemical sectors can be achieved with a reduced carbon footprint.

A variety of carbon dioxide conversion pathways have been investigated, including thermochemical, biological, photochemical, electrochemical and inorganic carbonation methods. Electrochemical conversion of carbon dioxide has been thoroughly investigated with great progress in electrocatalysts and reaction mechanisms. However, fewer studies
have been taken to tackle the constraint of the low solubility of CO$_2$ in conventional aqueous electrolytes.

In an effort to improve the solubility of CO$_2$, various novel electrolytes have been designed with a higher uptake of CO$_2$ and a compatibility with electrochemical conversion, including Nanoparticle Organic Hybrid Materials (NOHMs)-based fluids. NOHMs are a unique liquid-like nanoscale hybrid material, comprising of polymers grafted onto nanoparticles (e.g., silica). NOHMs have demonstrated an excellent thermal stability and a high chemical tunability. Two types of NOHMs with ionic bonding (I) between the polymers and nanoparticles were selected in this study: NOHM-I-PEI incorporating polyethylenimine polymer (PEI) and NOHM-I-HPE consisting of polyetheramine polymer (HPE), illustrative of two modes of carbon capture (e.g., chemisorption and physisorption). The NOHMs-based fluids were synthesized with different secondary fluids and salt to tune the viscosity and conductivity.

As the first liquid hybrid solvent system for combined carbon capture and conversion, the physical, chemical and electrochemical properties of NOHMs-based fluids were systematically investigated. It was found that NOHMs-based aqueous fluids have exhibited a lower specific heat capacity than that of the 30 wt.% monoethanolamine (MEA) solvents. In addition, upon CO$_2$ loading, the increase in specific heat capacity and the reduction of the viscosity of the NOHM-I-PEI based aqueous fluids can be attributed to the formation of intra-molecular hydrogen bonds.

The different chemistries of the two NOHMs can be reflected by the viscosity-based
mixing behavior. The smaller critical concentration and the higher intrinsic viscosity of NOHM-I-HPE based aqueous fluids implied a more significant contribution of viscosity to the system by the addition of NOHM-I-HPE. The viscosity of NOHM-I-HPE (30 wt.%) in water was measured to be 395 cP, an order of magnitude higher than that of NOHM-I-PEI (30 wt.%) in water, which was determined to be 22.6 cP. It was also discovered that the addition of N-methyl-2-pyrrolidone (NMP) has resulted in a dramatic increase of the viscosity of NOHM-I-PEI based aqueous fluids, hypothesized to be due to a possible formation of a complex between NMP and NOHM-I-PEI. On the other hand, the presence of 0.1 M potassium bicarbonate (KHCO₃) salt greatly reduced the viscosity of NOHM-I-HPE based aqueous fluids.

The electrochemical properties of NOHMs-based fluids were also characterized and an excellent electrochemical stability has been demonstrated. The conductivities of NOHMs-based fluids witnessed an unexpected enhancement from the corresponding untethered polymer-based solutions. At 50 wt.% loading, the conductivity was 15 mS/cm for NOHM-I-PEI based aqueous fluids doped by 1 M bis(trifluoromethylsulfonyl)amine lithium salt (LiTFSI), while it was 0.91 mS/cm for PEI based aqueous solutions. Even after the viscosities of the two solutions were converted to the same value, there was still a large gap between the conductivities of the NOHMs-based fluids and polymer-based fluids. The relative tortuosity of ion transport in NOHMs-based fluids compared to untethered polymer-based solutions was less than 1. This result was indicative of a shorter pathway of ion transport in NOHMs-based fluids than in polymer-based fluids. Thus, it is suggested
that in addition to a viscosity effect, unique multi-scale structures were also formed, enabling an enhanced ion transport in the NOHMs-based fluids.

With this hypothesis, ultra-small-angle X-ray scattering (USAXS) technique was utilized to construct the structures of NOHMs morphology in secondary fluids, from agglomerates at large scale to aggregates at mid-scale, and to the interparticle distance at small scale. The sizes of the aggregates and the interparticle distance were highly tunable by varying the concentrations of NOHMs, and the types of NOHMs and secondary fluids. For example, the aggregate size was $(32.30 \pm 0.3)\text{ nm}$ and $(153.9 \pm 1.5)\text{ nm}$ for 50 wt.% loading of NOHM-I-PEI and NOHM-I-HPE in mPEG, respectively. This hierarchical structure was hypothesized to give ions unique channels and pathways to migrate, resulting in the surprising conductivity enhancement. Cryogenic electron microscopy (CryoEM) was also employed to image such multi-scale fractal structures.

The diffusion behavior under this hierarchical structure was studied subsequently. To our surprise, in certain NOHMs-based fluids, such as 10 wt.% NOHM-I-HPE in water at $25^\circ\text{C}$, the diffusion coefficient of water was $3.43 \times 10^{-9} \text{ m}^2/\text{s}$, higher than that of deionized water, $2.99 \times 10^{-9} \text{ m}^2/\text{s}$. This is evident of the channels created by NOHMs in the secondary fluids to allow faster local diffusion of water and ions. Meanwhile, the diffusion coefficient of NOHM-I-HPE was higher with the presence of 0.1 M KHCO$_3$ salt compared to the salt-free case in water. Though counter-intuitive, this was because salt would interact with the ionic bonding sites of NOHMs, facilitating the dynamic hopping of polymers on the nanoparticle surface, and thus improving the fluidity of the NOHM-I-HPE based
aqueous fluids.

This investigation of multi-scale structures and diffusion behavior of NOHMs-based fluids was insightful in understanding how the ions move in the system, and in explaining the enhanced conductivity of NOHMs-based fluids compared to the corresponding untethered polymer-based solutions. It is believed that ions move in two regions of the NOHMs-based fluids, the NOHMs-rich region and secondary fluids-rich region, in the mechanisms of translational movement, and coupled and decoupled ion migration with structural relaxation of NOHMs and secondary fluids.

With the understanding of the fundamental properties and the construction of hierarchical structures, the carbon capture performance was evaluated for NOHMs-based fluids. The carbon capture behavior can be tuned by the concentration of NOHMs, and the presence of salt and physical solvents. The carbon capture kinetics was determined by both the amount of the capture material and the viscosity of the fluids. It was determined that 30 wt.% NOHM-I-PEI based aqueous fluids exhibited an optimal balance between capture capacity and sorption kinetics. As the concentration of NOHMs further increased, the elevated viscosity of the system limited the mass transfer of carbon capture. It was also found that salt induced a minimal impact on carbon capture in the initial 100 min for 5 wt.% NOHMs loading, but would negatively impact the capture capacity and kinetics at higher NOHMs loadings. Meanwhile, the addition of physical solvent (NMP) reduced carbon capture capacity and kinetics.

Various existing forms of CO₂ have been identified in NOHMs-based fluids, including
carbamate, bicarbonate, and physisorbed CO\textsubscript{2}. Carbamate came from the reaction between CO\textsubscript{2} and the amine functional groups on NOHM-I-PEI. Physisorbed CO\textsubscript{2} was identified as the electroactive species for electrochemical conversion of CO\textsubscript{2}. In the combined carbon capture and conversion experiments using 5 wt.% NOHM-I-HPE based aqueous electrolyte, carbon monoxide (CO) production was enhanced on polycrystalline silver by 60%, and selectivity was changed on a pyridinic-N doped carbon-based electrode, in comparison with conventional 0.1 M KHCO\textsubscript{3} electrolyte.

The roles of NOHMs in carbon capture and conversion were also explored. The addition of NOHMs was able to improve the solubility of CO\textsubscript{2} with a tunable pH change. It is hypothesized that NOHMs can complex with the electrochemical reaction species, CO\textsubscript{2} (CO\textsubscript{2}\textsuperscript{-}), and this complex formation can be tunable by the concentration and types of NOHMs.

In the end, an alternative approach of utilizing NOHMs-based fluids has also been proposed through encapsulation. The encapsulation of NOHMs-based fluids has enabled a higher specific surface area for CO\textsubscript{2} uptake, and an enhancement in capture kinetics has been observed compared to the non-encapsulated NOHMs-based fluids.

In summary, a novel nanoscale hybrid solvent system has been developed for combined carbon capture and conversion. The insight into the chemistry of this hybrid solvent system is not beneficial to the advancement in carbon capture and conversion, but it is also enlightening for the interdisciplinary development of various areas involving nanoscale hybrid materials.
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Chapter 1

Introduction

The continuously increasing concentration of carbon dioxide has caused urgent global challenges of climate change (Pacala and Socolow, 2004). In an effort to achieve efficient carbon management, Carbon Capture, Utilization and Storage (CCUS) has been proposed (IPCC, 2005). The discussions on CCUS have indicated that we need not only zero emission in fossil-burning power plants, but also negative emission from other chemical sectors, ranging from cement production to steel making industries. Thanks to the cost reduction of renewable energy sources in the past decade, such as solar and wind energy sources (Renewable Energy Agency, 2018), a paradigm shifting concept has emerged to directly convert the captured carbon dioxide into chemicals and fuels. In this scenario, a possible decarbonization with reduced carbon footprint in a variety of chemical industries can be accomplished.

Various carbon conversion pathways have been studied, including thermochemical (Duyar et al., 2015), (photo)electrochemical (Hori, 2008; Lewis, 2007), biological (H. Li and Liao, 2013) and inorganic carbonation (Hariharan et al., 2017). Among them, electrochemical conversion of CO$_2$ has achieved great advances in electrocatalysts and reaction mechanisms. One limiting factor for electrochemical conversion of CO$_2$ is the low solubility of CO$_2$ in conventional water-based electrolytes. In order to tackle this problem, versatile novel electrolytes, incorporating carbon capture solvents, have been developed,
such as Ionic Liquids (ILs) (Rosen et al., 2011) and Nanoparticle Organic Hybrid Materials (NOHMs)-based fluids.

NOHMs are comprised of nanoparticles (e.g., silica) grafted by a wide range of polymers, with an outstanding chemical tunability and high thermal stability (Lin and Park, 2011). While NOHMs have exhibited excellent carbon capture performance (Lin and Park, 2011), the mass transfer is limited due to the intrinsic high viscosity, similar to other anhydrous carbon capture solvents (B. Gurkan et al., 2010; Malhotra et al., 2017). Thus, a secondary fluid needs to be incorporated to lower the viscosity of NOHMs (Petit, Bhatnagar, et al., 2013), for enhanced mass transfer in carbon capture and to meet the electrolyte requirements.

In this study, NOHMs-based fluids with tunable chemical and physical properties are designed and developed, as dual-purpose reactive media for combined carbon capture and conversion. The contents of this dissertation have been presented and organized in the following chapters.

In Chapter 2, the background and motivation of this research are detailed. An overview of carbon capture solvents, especially the conventional amine-based solvents, and the novel anhydrous Ionic Liquids (ILs) and CO₂-binding organic liquids (CO₂BOLs), is presented, followed by a systematic introduction of Nanoparticle Organic Hybrid Materials (NOHMs). The demand for combined carbon capture and conversion is then elaborated. Lastly, the research objectives of this study are delivered.

In Chapter 3, the detailed design and synthesis methods of NOHMs and NOHMs-
based fluids are presented. The selection criteria of the NOHMs used in this study are discussed. The characterization (e.g., FTIR and TGA) of pure NOHMs is also conducted to ensure a consistency with the previously reported NOHMs.

In Chapter 4, carbon capture measurement using NOHMs-based fluids is conducted, and the impacts of CO₂ loading on the fundamental properties, such as specific heat capacity, density and viscosity, are investigated. The viscosity-based mixing behavior of NOHMs-based fluids are characterized, unveiling different chemistries of NOHM-I-PEI and NOHM-I-HPE. In the last section of this chapter, the effects of additives (e.g., physical solvents and salts) on the viscosity of NOHMs-based fluids are studied.

In Chapter 5, the electrochemical properties of NOHMs-based fluids are explored, such as conductivity and electrochemical stability. An unusual conductivity-viscosity relationship is observed, leading to a hypothesized hierarchical structure of NOHMs-based fluids. A cyclic voltammetry measurement of the CO₂-loaded NOHMs-based fluids is also performed, and a potential CO₂ electrochemical reduction reaction is detected in NOHMs-based fluids.

In Chapter 6, the hierarchical structure of NOHMs-based fluids is constructed using small-angle X-ray scattering (USAXS). The transport behaviors of water and NOHMs under such multi-scale structures are also analyzed via pulsed field gradient (PFG) NMR. From the structure information and diffusion behaviors, the proposed pathways for ion migration are illustrated, in an effort to explain the unexpected enhancement of ionic conductivity of NOHMs-based fluids compared to the untethered polymer-based fluids.
In Chapter 7, the tunable carbon capture performance is investigated with respect to the concentration of NOHMs, and the addition of physical solvent and salts. After the existing forms of CO$_2$ have been identified, a specific NOHMs-based fluid is selected for a combined carbon capture and conversion study. Enhancement of CO production on polycrystalline silver and selectivity alteration on a porous carbon-based electrode are observed. The structural integrity of NOHMs-based fluids over multiple cycles of capture and electrochemical conversion is also presented. Possible roles of NOHMs in carbon capture and conversion are hypothesized at the end of this chapter.

In Chapter 8, an alternative approach of utilizing NOHMs and NOHMs-based fluids is proposed to overcome the high viscosity challenge. Encapsulation of NOHMs and NOHMs-based fluids is achieved with an excellent thermal stability. The encapsulated NOHMs-based fluids have shown an enhanced carbon capture kinetics compared to the non-encapsulated NOHMs-based fluids with an outstanding recyclability.

In Chapter 9, conclusions and future work are delivered for NOHMs-based fluids as dual-purpose reactive media for combined carbon capture and conversion.
Chapter 2

Background and Motivation

This chapter is based on the following manuscript to be submitted to Chemical Reviews, American Chemical Society:

“Novel Materials for Carbon Capture and Conversion: Can we combine \( \text{CO}_2 \) capture and conversion into a single process?” (Ming Gao, Steven Ahn, Youngjune Park, Jianpeng Feng, Suojiang Zhang, Tayhas Palmore, and Ah-Hyung Alissa Park)
2.1. Overview of CO$_2$ capture solvents

Multiple schemes for efficient carbon capture have been proposed, including post-combustion, pre-combustion, oxy-fuel carbon capture (IPCC, 2005) and air capture (Keith, 2009). Post-combustion carbon capture is designed to capture carbon dioxide from point sources, such as fossil-burning power plants. The CO$_2$ concentration from power plants ranges from 5 to 15% (v/v) depending on the power source (e.g., coal and natural gas) (Rackley, 2017). Amine scrubbing has been widely studied as an effective carbon capture strategy with a fast sorption kinetics and large capture capacity, but the approach is constrained by the high parasitic energy consumption (Leung et al., 2014; Pfaff and Kather, 2009). On the other hand, pre-combustion is aimed at capturing CO$_2$ before combustion (Thomas, 2015), and this technology can be incorporated into the Integrated Gasification Combined Cycle (IGCC). The oxy-fuel scheme requires air separation so that pure oxygen is used for the combustion. Thus, the concentration of CO$_2$ in the flue stream is higher, creating a larger concentration driving force for gas separation (Buhre et al., 2005).

To fulfill the requirements of each carbon capture scheme, versatile carbon capture materials have been designed and developed, including conventional amine-based solvents (Rochelle, 2009), Ionic Liquids (ILs) (Bates et al., 2002), CO$_2$-binding organic liquids (CO$_2$BOLs) (Heldebrant et al., 2009), Nanoparticle Organic Hybrid Materials (NOHM)s (Lin and Park, 2011), solid aminosilane sorbents (Choi et al., 2011), metal organic frameworks (MOFs) (Flaig et al., 2017), and ion exchange resin (T. Wang et al., 2011).
In this study, the primary focus is on the liquid carbon capture solvents. The research on the solid carbon capture sorbents will not be discussed in detail.

2.1.1. Conventional amine-based solvents

Carbon capture using conventional amine-based solvents employs an absorber column and a stripper column as shown in Figure 2.1 (Goff and Rochelle, 2004). In a typical amine scrubbing process, CO\textsubscript{2} is captured by amine-based solvents in the absorber column at 40\textdegree{}C. The CO\textsubscript{2}-rich amine solvents are then pumped into the stripper column and the pure CO\textsubscript{2} is released under a temperature greater than 120\textdegree{}C (Heldebrant, Koech, Glezakou, et al., 2017). The CO\textsubscript{2}-lean amine solvents will be transferred back to the absorber column for subsequent carbon capture.

One of the most commonly used amine-based solvents is monoethanolamine, MEA, mixed with water at a concentration of 30 wt.% MEA (Leung et al., 2014). Other amines

![Figure 2.1. Process diagram for CO\textsubscript{2} capture using amine-based solvents.](image-url)
have also been extensively examined in their performance of carbon capture, including sterically hindered amine such as 2-amino-2-methyl-1-propanol (AMP), secondary amines such as diethanolamine (DEA), and tertiary amines such as methylidioethanolamine (MDEA) (Blauwhoff et al., 1983; Dubois and Thomas, 2012; Eide-Haugmo et al., 2009, 2011; Kittel et al., 2009; Lepaumier et al., 2009; Nguyen et al., 2010). The chemistry of carbon capture using amine-based solvents and the corresponding products can be briefly summarized by the following reaction formulas (Goepert et al., 2011; Khatri et al., 2006).

When the system is free of water, tertiary amines are not reactive with CO$_2$ due to the lack of free protons, and only primary and secondary amines are able to react with CO$_2$ to form carbamate (Blauwhoff et al., 1983) as shown in Eq. 2.1. This is a 2:1 reaction in that 2 moles of amine can react with 1 mole of CO$_2$. When water is present, primary, secondary and tertiary amines are all capable of reacting with CO$_2$ and bicarbonate can also be formed. This is a 1:1 ratio where one mole of amine can capture 1 mole of CO$_2$.

Carbamate formation:

$$CO_2 + 2R_1R_2NH \rightleftharpoons R_1R_2NCOO^- + R_1R_2NH_2^+ \quad \text{Eq. 2.1}$$

Bicarbonate formation:

$$R_1R_2NCOO^- + H_2O \rightleftharpoons R_1R_2NH + HCO_3^- \quad \text{Eq. 2.2}$$

$$CO_2 + R_1R_2NH + H_2O \rightleftharpoons HCO_3^- + R_1R_2NH_2^+ \quad \text{(overall)} \quad \text{Eq. 2.3}$$

The capture capacity of CO$_2$ in various amine-based solvents has been reported (Chowdhury et al., 2009, 2011, 2013; S. Park et al., 2014; Porcheron, Gibert, Jacquin, et al., 2011; Porcheron, Gibert, Mougin, et al., 2011; Puxty et al., 2009; Singh et al., 2007,
Puxty et al. investigated the CO$_2$ absorption capacity of 76 amines and found out that seven amines demonstrated better CO$_2$ capture performance (Puxty et al., 2009). These seven amines included one primary (2-amino-2-methyl-1,3-propanediol), three secondary (2-piperidinethanol, 2-piperidinemethanol, diisopropanolamine), and three tertiary amines (3-quinuclidinol, N,N-dimethylethanolamine, 3-piperidino-1,2-propanediol). Examples of the studied amines are presented in Figure 2.2. Henni et al. furthered this study and concluded that the structural steric hindrance to amino groups was beneficial to increasing the capture capacity in the order of primary amines < hindered amines < secondary amines < tertiary amines < diamines (Tontiwachwuthikul and Idem, 2013). However, the hindrance was believed to increase the resistance of CO$_2$ mass transfer. Therefore, to balance the capture capacity and sorption kinetics, solvent blends such as tertiary amines with primary amines, were developed, exhibiting a higher equilibrium capacity of tertiary amines and higher reaction kinetics of the primary amines (Dubois and Thomas, 2012; Idem et al., 2006; G. Kumar et al., 2012; D. Zhu et al., 2012).

![Chemical structures of selected primary, secondary and tertiary amines for carbon capture](Puxty et al., 2009).

Figure 2.2. Chemical structures of selected primary, secondary and tertiary amines for carbon capture (Puxty et al., 2009).
Though advantageous in capture capacity and sorption kinetics, the amine-based solvents for carbon capture are limited by a variety of drawbacks. The energy consumption is intensive during the temperature swing regeneration process. For example, MEA is normally mixed with 70 wt.% of water and this large amount of water has induced a demanding energy requirement for the regeneration of solvents in the stripper column. Other limiting factors for amine-based solvents include degradation and corrosion of the infrastructure (Fredriksen and Jens, 2013; Islam et al., 2011; Rochelle, 2012). Both thermal degradation due to the high temperature in the stripper column and oxidative degradation due to the presence of O₂ have been observed for amine-based solvents (Holub et al., 1998; Lepaumier et al., 2009). It has also been reported that some traces of SOₓ and NOₓ can influence the amine degradation (Fostås et al., 2011; Supap et al., 2009). Considering that the flue gas streams often contain mixtures of CO₂, O₂, CO, SOₓ, NOₓ, and fly ash, the degradation process can be more complicated, and therefore further investigation should be conducted to account for environmental impacts (Meisen and Shuai, 1997).

In response to the high energy penalty induced by the water in amine-based solvents, a number of novel water-lean carbon capture solvents (Heldebrant, Koech, Glezakou, et al., 2017) have been developed, such as Ionic Liquids (ILs) (Bates et al., 2002; B. E. Gurkan et al., 2010), phase changing solvents (Perry et al., 2012), CO₂-binding organic liquids (CO₂BOLs) (Heldebrant, Koech, and Yonker, 2010), and Nanoparticle Organic Hybrid Materials (NOHMs) (Lin and Park, 2011), which will be discussed in detail in the following sections.
2.1.2. Ionic Liquids (ILs)

Ionic Liquids (ILs), comprising of cations and anions, are advantageous in negligible vapor pressure and tunable chemical structures. Conventional ILs capture CO\textsubscript{2} through physical interactions between ILs and CO\textsubscript{2} via Van der Waals forces, electrostatic force and hydrogen bonding (Cammarata et al., 2001; Crowhurst et al., 2003; Kazarian et al., 2000; J. Wang et al., 2016). It was found that when the cations remained the same in conventional ILs, CO\textsubscript{2} capture capacity for various anions followed the order of [NO\textsubscript{3}] < [DCA] < [BF\textsubscript{4}] < [PF\textsubscript{6}] < [TfO] < [Tf\textsubscript{2}N] < [Methide]. Additionally, the incorporation of fluorine groups was beneficial to the enhancement of the capture capacity (Aki et al., 2004; Muldoon et al., 2007).

To further improve the carbon capture performance of ILs, task-specific ionic liquids (TSILs) were developed. TSILs were designed with amino functional groups doped into the chemical structures of ILs. Based on the discussion in the previous section, the capture capacity can be enhanced via the chemisorption mechanism between amine functional groups and CO\textsubscript{2}. Bates et al. first synthesized a novel ILs containing an amino group on the imidazolium cation as shown in Figure 2.3, achieving a reaction ratio of one mole of CO\textsubscript{2} per two moles of amine (Bates et al., 2002). Riding on this momentum, a variety of amino-functionalized ILs were synthesized, developed and evaluated with amines attached to either anions or cations of the ILs (Gurau et al., 2011; B. E. Gurkan et al., 2010; Jiang et al., 2008; Jianmin Zhang et al., 2006; Y. Zhang et al., 2009). Efforts were also taken to
tether amine functional groups onto both cations and anions of certain ILs, achieving an equimolar CO$_2$ capture performance (Xue et al., 2011; Y. Zhang et al., 2009).

![Figure 2.3. The chemical structure of a selected task-specific ionic liquid for carbon capture (Bates et al., 2002).](image)

Though great advances have been achieved for ILs, there are still a number of challenges limiting its wide applications. First of all, the gravimetric capacities of ILs are low due to the high molecular weight of ILs. Novel ILs were designed with improved gravimetric capacities. Wang et al. synthesized a superbase-derived ILs, [MTBDH][Im], with a gravimetric capacity of 0.205 g CO$_2$ per gram of ILs at 23°C and 0.1 MPa (C. Wang et al., 2010). Second, it has become a focus for worldwide researchers to tackle the challenge of the high viscosity of ILs and the dramatic viscosity increase after carbon capture (X. Liu et al., 2009). [P$_{66614}$][2-CNpyr] was developed with a viscosity less than 100 cP at 50°C before CO$_2$ loading (B. Gurkan et al., 2010). Luo et al. discovered that the retention and even a reduction of viscosity of ILs upon CO$_2$ capture were realized by the formation of intramolecular hydrogen bonds with the nitrogen or oxygen atoms (as the hydrogen acceptors) in the ILs (Luo et al., 2016). For example, the viscosity of [P$_{66614}$][Ac-Gly] decreased to 964 cP from 1169 cP after CO$_2$ loading (Luo et al., 2016).
2.1.3. CO₂-Binding Organic Liquids (CO₂BOLs)

Another new class of water-lean solvents for carbon capture has been developed as CO₂-binding organic liquids (CO₂BOLs). It was found that the reverse reaction of carbon loading via CO₂BOLs can be readily achieved via exposure to N₂ (Jessop et al., 2005). The capture of CO₂ by CO₂BOLs utilizes the reactions between a non-nucleophilic base and alcohols (Jessop et al., 2012). The fundamental chemistry of CO₂BOLs regarding the capture mechanism, capture capacity, viscosity and other fundamental properties have also been systematically studied (Heldebrant, Koech, and Yonker, 2010; Heldebrant et al., 2008a; Mathias et al., 2013).

The first generation of CO₂BOLs, as illustrated in Figure 2.4, was a mixture of alcohol and various bases, such as Diazabicyclo[5.4.0]-undec-7-ene (DBU), 1,1,3,3-tetramethylguanidine (TMG), 2-tert-butyl-1,1,3,3-tetramethylguanidine (Barton’s base), and N,N-diisopropylethylamine (Hünig’s base). It was demonstrated that DBU:1-hexanol CO₂BOLs reached a capture capacity of 1.3 mol of CO₂ per mol DBU (Heldebrant et al., 2008a). In the first generation of CO₂BOLs, it was reported that the alcohol reacted with CO₂ to form alkylcarboxonic acid, and the proton was then transferred to the base to form a liquid alkylcarbonate (Heldebrant et al., 2008a). Such CO₂ fixation was able to proceed with a Gibbs free energy of -9 to 2 kJ/mol, and therefore the regeneration of CO₂-loaded CO₂BOLs required a smaller energy input than conventional amine-based solvents (Heldebrant et al., 2008a, 2009).
In order to address the challenge of solvent loss caused by the volatile alcohol component in the first generation of CO\textsubscript{2}BOLs (Mathias et al., 2013), the second generation of single component CO\textsubscript{2}BOLs was developed as demonstrated in Figure 2.5 (Heldebrant, Koech, Ang, et al., 2010). Upon CO\textsubscript{2} capture, a zwitterionic liquid can be formed. In order to overcome the limited mass transfer caused by the high viscosity of CO\textsubscript{2}BOLs (Heldebrant et al., 2011), Koech et al. designed and synthesized a series of alkanolguanidines with viscosity less than 10 cP (Koech et al., 2013).

Two interesting discoveries of CO\textsubscript{2}BOLs are the polarity-swing-assisted-regeneration process (Mathias et al., 2013) and the heterogeneity of the CO\textsubscript{2}BOLs morphology upon...
CO₂ fixation (Heldebrant, Koech, Rousseau, et al., 2017). The polarity-swing-assisted-regeneration (PSAR) process was proposed to address the challenge of the high regeneration temperature up to 120°C of CO₂BOLs (Mathias et al., 2013). Mathias et al. utilized the change of polarity of CO₂BOLs before and after CO₂ capture and employed a chemically inert, nonpolar antisolvent such as hexadecane to assist the CO₂ detachment from CO₂BOLs. In this way, the regeneration temperature was lowered to 75°C (Mathias et al., 2013).

Another interesting discovery was that CO₂ loading into CO₂BOLs can result in a morphology heterogeneity in the system (Heldebrant, Koech, Rousseau, et al., 2017). In this heterogeneity, some regions were CO₂-rich with 200% loading, and other regions were CO₂-lean with even no CO₂ detected (Heldebrant, Koech, Rousseau, et al., 2017). This was believed to fundamentally account for various unique properties of CO₂BOLs.

2.2. Nanoparticle Organic Hybrid Materials (NOHMs)

Recently, Nanoparticle Organic Hybrid Materials (NOHMs) have drawn a growing number of attention as an emerging class of nanoscale nanoparticle/polymer hybrid materials (Lin and Park, 2011). These diverse nanoscale hybrid materials have found their applications in the fields of catalysis (Mäsing et al., 2017), pharmaceutical probes (Ling et al., 2014), lithium ion battery electrolytes (Nugent et al., 2010), and CO₂ capture solvents (Lin and Park, 2011).

Originated from Nanoscale Ionic Materials (NIMs), a wide range of NOHMs has been developed in various forms, such as glassy solids and liquid-like fluids (Rodriguez et al.,
2008). NOHMs are renowned in their high chemical tunability near zero vapor pressure, and a higher thermal stability compared to the corresponding untethered polymers (Lin et al., 2014). A wide range of materials can be employed as the core of NOHMs, including metal oxides (Agarwal et al., 2010; A. B. Bourlinos et al., 2005; Athanasios B. Bourlinos et al., 2004; Athanasios B. Bourlinos et al., 2005; Y. Park et al., 2012; Petit, Lin, et al., 2013; Rodriguez et al., 2008), metals (Warren et al., 2006; Zheng et al., 2010), carbon nanotubes (A. B. Bourlinos et al., 2007; R. Yang et al., 2016), fullerene (Fernandes et al., 2010), and proteins (Perriman et al., 2009).

In the field of carbon capture, Lin and Park used silica nanoparticles as the core. A classification of NOHMs was established based on the kinds of the tethered polymers and bonding types (Lin and Park, 2011). Polymers can be tethered onto the silica nanoparticles via either ionic bonding or covalent bonding, and various polymers can also be utilized. For example, NOHM-I-HPE and NOHM-C-HPE stand for the NOHMs consisting of the polyetheramine (HPE) polymers tethered to the nanoparticles via ionic bonding (“I”) and covalent bonding (“C”), respectively. In some cases, a linker is also employed to link the polymer to the core, and a silane or thiol compound is generally chosen as the linker (Lin and Park, 2011).

Park et al. systematically explored the CO₂ capture behavior of NOHMs comprising of various polymers including polyethylene glycol (PEG), polyetheramine (HPE), and polyethylenimine (PEI) (Lin and Park, 2011; Y. Park et al., 2011, 2014). NOHM-I-HPE utilizes physical interactions between CO₂ and the ether groups on HPE polymers. It
exhibited a capture capacity of 0.22 mmol CO$_2$ per gram of NOHMs at 30°C and $P_{CO_2} \approx 3.2$ atm (Lin and Park, 2011). When polymers with abundant amines were employed, such as PEI, a capture capacity of 2.4 mmol per gram of NOHMs was achieved for NOHM-I-PEI under similar conditions (Lin and Park, 2011). This carbon capture performance can be comparable to that of amine-based solvents at atmospheric pressure as discussed in the previous section. For example, a 0.47 mol-CO$_2$/mol-amine capture capacity was achieved in a 30 wt.% MEA solvents at 40°C, which can be translated to around 2.3 mmol-CO$_2$/g-fluids (Kim et al., 2013).

The selectivity of NOHMs during carbon capture was also investigated. The absorption amount of CO$_2$ and N$_2$ by NOHM-C-HPE, as shown in Figure 2.6, was around 0.4 and 0.01 mmol per gram of NOHM-C-HPE at 30°C and under 3.4 atm of CO$_2$ and N$_2$, respectively (Lin and Park, 2011). Considering the presence of SO$_2$ in flue gas stream, the effect of SO$_2$ on carbon capture by NOHMs was subsequently studied. It was discovered that only 0.01 mmol SO$_2$ was captured by a unit gram of NOHMs when the concentration of SO$_2$ was 200 ppm (Lin et al., 2013).

![Chemical structure of NOHM-C-HPE](image-url)
Various regeneration processes can be tailored to different kinds of CO₂-loaded NOHMs. For NOHMs designed for physisorption of CO₂, such as NOHM-I-HPE, a pressure swing was able to desorb all the captured CO₂ with excellent recyclability (Lin and Park, 2011; Y. Park et al., 2011). On the other hand, a temperature-assisted vacuum swing process was preferred for the regeneration of NOHMs with chemisorbed CO₂, combining pressure swing and temperature swing technologies. Similar to amine-based solvents, the high temperature up to 120°C (Heldebrant, Koech, Glezakou, et al., 2017) was needed in detaching the CO₂ from carbamate.

The carbon capture mechanism using this nanoscale hybrid material was also investigated. The CO₂ capture by NOHMs was realized by two major effects: enthalpic and entropic effects (Y. Park et al., 2011). The enthalpic effect was believed to arise from the chemical functionality in that CO₂ can interact with functional groups in NOHMs, such as ether and amine groups. For NOHMs such as NOHM-I-HPE, a weak Lewis acid-base interaction existed between CO₂ and the ether groups (Y. Park et al., 2011, 2012), and for NOHMs such as NOHM-I-PEI, the amine functional groups were able to react with CO₂ to form carbamate (Lin and Park, 2011).

On the other hand, the entropic effect referred to the conformation of the tethered polymer chains in NOHMs since the polymers were inclined to fill the space between silica nanoparticles (Y. Park et al., 2011; Petit et al., 2012). In some cases, an additional capture capacity could be observed if such process allowed the “frustrated” NOHMs to return to a more relaxed state by incorporating CO₂. Nevertheless, the entropic contribution for CO₂
absorption was determined to be small compared to the enthalpic contribution (Y. Park et al., 2015).

Since NOHMs are composed of tethered polymers, Park and coworkers also investigated and compared the carbon capture performance and swelling behavior of NOHMs and their corresponding untethered polymers. Interestingly, NOHMs showed a higher capture capacity than the corresponding untethered polymers at the same degree of swelling (Y. Park et al., 2012). In other words, less swelling of NOHMs was needed to achieve the same amount of capture capacity using corresponding untethered polymers (Y. Park et al., 2012). This phenomena indicated that the tethered polymers in NOHMs exhibited a unique structure compared to untethered polymers, and this unique alignment was thought to be favorable in carbon capture. The degree of swelling among different NOHMs can also be tuned by modifying the types of polymer and core, and the grafting densities of polymers.

However, NOHMs, similar to other anhydrous carbon capture solvents (Heldebrant, Koech, Rousseau, et al., 2017), show a high viscosity up to $10^4$ cP (Petit, Bhatnagar, et al., 2013). To address the high viscosity challenge from the structural perspective, Petit et al. designed a new type of NOHMs with polyhedral oligomeric silsesquioxane (POSS) as the core (Petit, Lin, et al., 2013). POSS had a much smaller size than silica nanoparticles, and the POSS-based NOHMs showed a viscosity of 1500 cP, 10 times smaller than the neat NOHMs based on silica nanoparticles (Petit, Lin, et al., 2013). Mixing NOHMs with another solvent such as water can also significantly reduce the viscosity. It was found that
by adding water from 15 wt.% to 30 wt.% at 30°C, the viscosity of the NOHM-I-HPE/water mixture decreased from ~12000 cP to ~1500 cP, but at the price of a compromised capture capacity (Petit, Bhatnagar, et al., 2013).

2.3. Combined carbon capture and conversion

Novel carbon capture solvents have been discussed in previous sections to realize a zero-emission target of carbon from fossil-burning power plants. Recently, thanks to the cost reduction in renewable energy sources, including solar and wind energies (Renewable Energy Agency, 2018), a paradigm shifting concept has emerged to directly convert the captured carbon dioxide into chemicals and fuels. In this way, a possible decarbonization can be achieved in a wide range of chemical sectors, such as cement making and steel production industries.

In order to reduce the carbon footprint in various industries, a number of CO₂ conversion routes have been investigated to transform CO₂ into versatile products. Electrochemical conversion utilizes different electrocatalysts and overpotentials to tune the conversion products (Hori, 2008). Biological conversion of CO₂ is able to make biofuels using natural hosts, such as algae and bacteria (H. Li and Liao, 2013; Savvas et al., 2017). Photochemical conversion utilizes solar energy (Lewis, 2007), and a wide range of products can be obtained, including CO (B. Kumar et al., 2010; Lewis and Nocera, 2006), formic acid (Arai et al., 2010; Yadav et al., 2012), and methanol (X. Li et al., 2011; Yamashita et al., 1998). Carbonation involves the chemical reaction between CO₂ and natural mineral, with calcium carbonate and magnesium carbonate as the major carbonate
compounds (Dufaud et al., 2009; Hariharan et al., 2017; A. H. A. Park et al., 2003; Prigiobbe et al., 2009). Thermochemical conversion of CO₂ has also been widely used with a versatile selection of catalysts, temperatures, and pressures (Ashley et al., 2009; Duyar et al., 2015; Gassner and Leitner, 1993).

Integrated carbon capture and thermochemical conversion has been attempted in producing a great deal of products. In particular, CaO with Ru catalyst has been utilized to produce methane in a heterogeneous manner. The absorbed CO₂ by CaO transferred to the catalytic sites for subsequent conversion (Duyar et al., 2015). Polyamine with a homogeneous Ru catalyst has been employed to produce methanol from CO₂ captured from air, with a 79% conversion efficiency (Kothandaraman et al., 2016). Formate production was achieved through integrated carbon capture and conversion using an ethoxyl-functionalized amidine with homogeneous Rh catalyst, achieving a 95 – 99% yield (Y.-N. Li et al., 2014). Production of formate was also attempted by a polyethylenimine-tethered iminophosphine iridium system and it was found that the capture and conversion behavior can be tuned by changing the structures of PEI (McNamara and Hicks, 2014). Meanwhile, thermochemical conversion of CO₂ into cyclic carbonate has been accomplished with the CO₂ captured by Mg-MOF-74 (D.-A. Yang et al., 2012), ionic liquids (Z.-Z. Yang et al., 2011), and nitrogen-doped carbon nanofibers (Y. Li et al., 2016).

In this study, combined carbon capture and electrochemical conversion will be investigated. Many advances in electrocatalysts and reaction mechanisms have been achieved in the electrochemical conversion of CO₂, but fewer studies have investigated
how to overcome the challenge of the low solubility of CO$_2$ in conventional aqueous electrolytes. This is primarily due to the fact that carbon capture and electrochemical conversion technologies have been developed independently. It can be seen from Figure 2.7 that in the separate scheme, the captured CO$_2$ needs to be released at high temperature and/or under vacuum. After compression and transportation, the pure CO$_2$ stream would have to be dissolved into the water-based electrolytes again for subsequent electrochemical conversion. In this decoupled manner, multiple energy barriers need to be overcome.

In the combined scheme of carbon capture and electrochemical conversion of CO$_2$, the captured CO$_2$ by the novel electrolytes can be directly converted to chemicals and fuels, and meanwhile the electrolytes are regenerated for further carbon capture. In this scenario as shown in Figure 2.7, the carbon capture can be pulled by the electrochemical conversion of CO$_2$, and the binding energy of the electrolytes to CO$_2$ can be readily tuned. Therefore, a dual-purpose reactive medium is to be developed that can perform carbon capture and host subsequent electrochemical reduction of CO$_2$, to achieve a potential reduction in the overall energy penalty and carbon footprints.
A variety of novel liquid carbon capture materials have shown a potential to be coupled with electrochemical conversion of CO$_2$. Clathrate hydrates were added as an electrolyte additive. This novel electrolyte was able to not only increase the solubility of the dissolved CO$_2$ but also enhance the faradaic efficiency of CO production (Deciccio et al., 2015). Electrochemical conversion of CO$_2$ to CO (Asadi et al., 2014; Oh and Hu, 2015; Sun et al., 2014; Tanner et al., 2016) and formic acid (Hollingsworth et al., 2015; Huan et al., 2017; Q. Zhu et al., 2016) has also been achieved with ionic liquids (ILs) as the co-catalysts.

Nanoparticle Organic Hybrid Materials (NOHMs), as a novel nanoscale hybrid material, have demonstrated excellent carbon capture performance as discussed in the previous section. In order to reduce the intrinsic high viscosity of NOHMs (Petit, Lin, et al., 2013), secondary fluids doped by salts can be added to enhance the mass transfer of carbon capture and meet electrolyte requirements. The mixing of NOHMs with other
solvents, such as polycarbonate (PC) doped by LiTFSI salt, has been investigated by Archer et al. for lithium ion batteries (A. Agrawal et al., 2015; Choudhury et al., 2015). The knowledge of such NOHMs hybrid solvent systems in combined carbon capture and conversion has drawn growing interests.

In this particular study, NOHMs-based fluids have been developed as a novel liquid nanoscale hybrid system for combined carbon capture and conversion. With this innovative NOHMs-based fluid, the captured CO$_2$ by NOHMs can be converted to chemicals and fuels at ambient conditions in a unique activated form. It is believed that the combination of the outstanding carbon capture behavior of NOHMs and their excellent electrochemical properties can provide a new solution to the challenges in combined carbon capture and conversion under the CCUS scheme. The fundamental chemistries of NOHMs-based fluids in carbon capture and conversion are also beneficial to other interdisciplinary areas involving nanoscale hybrid materials.

2.4. Research objectives

The overall objective of this work is to develop a novel NOHMs-based fluid for carbon capture that has an ability to host the subsequent electrochemical conversion of the captured CO$_2$. A key goal is to understand how the fundamental chemistries within NOHMs-based fluids will affect combined carbon capture and conversion. To achieve this goal, key research questions to be answered are as follows:

(1) Can we develop novel nanoscale hybrid material based fluids for combined carbon capture and conversion?
(2) How do nano- and micro-scale structures develop in NOHMs-based fluids and what are their impacts on the physical and chemical properties, and transport phenomena?

(3) Can carbon capture be pulled by the electrochemical conversion of CO$_2$ using NOHMs-based fluids, and can NOHMs tune the reaction rate and transport phenomena?

(4) What would be the favored form of CO$_2$ captured by NOHMs-based fluids for electrochemical reduction (e.g., physisorbed CO$_2$, carbamate, bicarbonate, and etc.)?
Chapter 3

Design and Synthesis of Nanoparticle Organic Hybrid Materials (NOHMs) and NOHMs-Based Fluids

3.1. Synthesis and characterization of NOHMs

3.1.1. Selection of NOHMs

The classification of NOHMs based on the bonding types (e.g., ionic bond and covalent bond) between polymers and nanoparticles, and the kinds of tethered polymers has been demonstrated (Lin and Park, 2011) in the Chapter 2. Among various NOHMs, NOHM-I-PEI and NOHM-I-HPE are selected for this particular study, illustrative of the two fundamental modes for carbon capture (e.g., chemisorption and physisorption).

The chemical structures of the two NOHMs are shown in Figure 3.1. NOHM-I-PEI, incorporating polyethylenimine (PEI), possesses abundant amine groups, and this structural feature makes it a good candidate for chemisorption of CO$_2$ with fast sorption kinetics and large capture capacity based on the amine chemistry described in Chapter 2. However, the regeneration of NOHM-I-PEI, similar to conventional amine-based solvents, requires a temperature greater than 120°C (Heldebrant, Koech, Glezakou, et al., 2017). On the contrary, NOHM-I-HPE is comprised of polyetheramine (HPE) with a large number of ether groups, designed for physisorption of CO$_2$. CO$_2$ is immobilized via physical interactions with oxygen atoms in the ether groups. The only amine group of the HPE polymer is utilized to form the ionic bond between the HPE polymers and the silica
nanoparticle surface. The resultant protonated amine functional group is incapable of conducting the chemical reaction with carbon dioxide. The regeneration of NOHMs can be realized under vacuum at room temperature (Lin and Park, 2011), but the capture capacity will be compromised.

3.1.2. Synthesis methods of NOHMs

Two types of NOHMs (NOHM-I-PEI and NOHM-I-HPE) were synthesized via previously reported methods (Lin and Park, 2011; Lin et al., 2013; Y. Park et al., 2011). To synthesize NOHM-I-PEI, a 3 wt.% of silica nanoparticle suspension was prepared by diluting silica colloidal suspension (LUDOX SM-30, 7 nm, Sigma-Aldrich) in DI water under vigorous stirring. The silica suspension was stabilized by the sodium ions (Na\(^+\)), and the sodium ions were replaced by protons using ion exchange resin (DOWEX marathon Cation-exchange resin, Sigma-Aldrich). After the ion exchange resin column was washed by DI water until only transparent water was seen, the silica suspension ran through the column four times to ensure a complete exchange of ions. The diluted polyethylenimine (PEI, Mn 1800, Polysciences) solution was then prepared to ensure a ~ 4:1 weight ratio of the tethered PEI polymers to the weight of the silica nanoparticles. The diluted PEI solution was then added dropwise into protonated silica nanoparticle suspension under fast stirring. The neat NOHM-I-PEI was obtained after vacuum drying under 50°C overnight.

NOHM-I-HPE was synthesized in a similar manner, but began with grafting linkers onto silica nanoparticles. The linker was 3-(trihydroxysilyl)-1-propanesulfonic acid (SIT, Gelest). A 3 wt.% silica suspension and a diluted SIT solution was mixed under vigorous
stirring. After pH was adjusted to 5 by adding 1 M NaOH solution, the resultant fluid was kept at 70°C under stirring for 24 h to ensure a complete grafting of SIT linkers. The unreacted SIT molecules were removed by dialysis against DI water for 48 h using dialysis tubes (3.5K MWCO, Thermo Scientific). The sulfonate groups at the end of the grafted SIT linkers were then protonated via ion exchange in the same way as described before. In the last step, this solution was titrated by diluted polyetheramine (HPE, Jeffamine 2070, Huntsman) solution to the equilibrium point as indicated by pH value. The equilibrium point was pre-determined with a small quantity of the protonated silica-SIT solution. The equilibrium point was defined as the point that underwent the largest pH change. NOHM-I-HPE was ready to use after vacuum drying under 50°C.

Figure 3.1. Synthesis and structures of (a) NOHM-I-PEI and (b) NOHM-I-HPE.
3.1.3. Characterization of neat NOHMs

The chemical structures of NOHM-I-PEI and NOHM-I-HPE were characterized by Fourier-transform infrared spectroscopy (FTIR) via a Thermo Nicolet 6700 FTIR spectrometer with Golden Gate ATR accessory with a scan range of 4000 cm\(^{-1}\) to 600 cm\(^{-1}\) and a resolution of 2 cm\(^{-1}\). For NOHM-I-PEI as depicted in Figure 3.2, the broad peak around 3291 cm\(^{-1}\) corresponded to the N-H stretching vibration, and the two peaks at 2940 cm\(^{-1}\) and 2830 cm\(^{-1}\) represented the stretching vibration of C-H groups in the tethered PEI polymers. The N-H bending vibration was reflected by the two absorptions peaks at 1651 and 1582 cm\(^{-1}\) in the spectrum. The strong absorption peak at 1107 cm\(^{-1}\) came from the silica nanoparticles.

For NOHM-I-HPE, it is worth noting that the two peaks at 1630 cm\(^{-1}\) and 1530 cm\(^{-1}\) as highlighted in the inset of Figure 3.2(b) represented the asymmetric and symmetric stretching of protonated amine peaks, respectively. No such absorption peaks were detected for pure HPE polymers. The results confirmed the presence of the ionic bonding between the HPE polymers and the silica nanoparticles (Lin and Park, 2011). The other peaks in the FTIR spectrum of NOHM-I-HPE followed the same rule as NOHM-I-PEI. For example, the large peak at 1083 cm\(^{-1}\) originated from silica nanoparticles.
Figure 3.2. FTIR spectrum of (a) neat NOHM-I-PEI and (b) neat NOHM-I-HPE.

The thermal stability, and the mass fractions of the silica nanoparticles and the tethered polymers of NOHM-I-PEI and NOHM-I-HPE were measured by a Setaram Labsys evo TGA analyzer, with a heating profile from 20°C to 600°C at 10 K/min under air as presented in Figure 3.3. The decomposition profile and thermal stability of NOHM-I-PEI were in agreement with the previously reported TGA data of NOHM-I-PEI (Lin and Park, 2011). The tethered PEI polymers in NOHM-I-PEI underwent a gradual multi-step
decomposition under air. On the other hand, NOHM-I-HPE was stable up to 300°C before decomposition, demonstrating an excellent thermal stability.

![TGA profile](image)

Figure 3.3. TGA profile of (a) neat NOHM-I-PEI and (b) neat NOHM-I-HPE.

3.2. Synthesis of NOHMs-based fluids

3.2.1. Selection of secondary fluids and salt

In this study, two types of secondary fluids are selected, aqueous solvents, water, and non-aqueous fluid, poly(ethylene glycol) methyl ether (mPEG, Mn 550, Sigma-Aldrich). Water and mPEG exhibit a low viscosity and a good miscibility with NOHMs. Water also possesses the ability to provide protons for the electrochemical conversion of CO₂.

Meanwhile, two kinds of salts are employed, LiTFSI (Sigma-Aldrich) and KHCO₃
(Sigma-Aldrich). Archer et al. has developed various electrolytes for lithium ion batteries with LiTFSI doped into both neat NOHMs and NOHMs/PC systems (A. Agrawal et al., 2015; Choudhury et al., 2015; Nugent et al., 2010). This LiTFSI salt has shown a high conductivity and compatibility with NOHMs in lithium ion battery electrolyte applications (A. Agrawal et al., 2015; Choudhury et al., 2015; Nugent et al., 2010). Thus, in the section of electrochemical properties of NOHMs-based fluids in Chapter 5, LiTFSI salt is employed.

Another salt, KHCO$_3$, has also been utilized in this work. KHCO$_3$ has been widely used in electrochemical conversion of CO$_2$ thanks to its ability to buffer the solution pH (Hori, 2008). It was also determined that the electroactive CO$_2$ during electrochemical conversion was not from the existing KHCO$_3$ salt in the electrolyte (Hori and Suzuki, 1983). With these considerations, KHCO$_3$ is used for the section of combined carbon capture and conversion in Chapter 7.

3.2.2. Synthesis methods of NOHMs-based fluids

The recipe to make NOHMs-based fluids is illustrated in Figure 3.4. Before making NOHMs-based fluids, NOHMs were dried in vacuum at 50°C for 3 h to remove any attached water and CO$_2$. NOHMs and a secondary fluid were then mixed in an inert environment under stirring before 1 M or 0.1 M of salts was doped into the system. The as-made NOHMs-based fluids were kept in an inert environment.

It has been determined that the tethered polymers will not detach from the silica nanoparticles in the secondary fluids. A thermogravimetric analysis of NOHMs-based fluids...
aqueous fluids was conducted at a fast heating rate from 20°C to 600°C at 20 K/min. After the evaporation of water, the nanoparticles and the polymers in the fluids still exhibited the same high decomposition temperature. The result means that the polymers were still grafted onto the nanoparticle surface. If the polymers have detached from the nanoparticle surface, the polymers would have limited rearrangement time to be bonded back to the nanoparticle surface, and the decomposition profile of untethered polymers would have been observed. A dialysis test of NOHMs-based aqueous fluids was also performed using a dialysis tube (3.5K MWCO, Thermo Scientific) against DI water. It was speculated that polymers could be detected in the water outside the dialysis tube if the polymers were able to detach from the nanoparticle surface. It was found that no polymers were detected in the water outside the dialysis tube. With the TGA and dialysis studies of NOHMs-based fluids, it demonstrates that the polymers are still able to be grafted onto the silica nanoparticles after mixing with secondary fluids.

Figure 3.4. Recipe for the manufacture of NOHMs-based fluids.
Chapter 4

Investigation of the Impacts of CO₂ Loading on the

Fundamental Properties of the Novel Nanoscale Hybrid

Solvent System and Its Viscosity-Based Mixing Behavior

This chapter is based on the following manuscript to be submitted:

“Investigation of the impacts of CO₂ loading on the fundamental properties of the novel nanoscale hybrid solvent system and its viscosity-based mixing behavior” (Ming Gao, and Ah-Hyung Alissa Park)
Abstract

Carbon Capture, Utilization and Storage (CCUS) has been proposed to tackle the urgent climate change challenges caused by the continuously increasing concentration of anthropogenic carbon dioxide in the atmosphere. In order to achieve both zero emission and negative emission in various industries, it is suggested to develop dual-purpose reactive materials for combined carbon capture and conversion, using carbon-free renewable energies. Among various conversion pathways of CO$_2$, many improvements have been accomplished for electrochemical conversion regarding electrocatalysts and reaction mechanisms. To overcome the challenge of the low solubility of CO$_2$ in conventional aqueous electrolytes, a number of novel electrolytes have been designed, including Nanoparticle Organic Hybrid Materials (NOHMs)-based fluids. The NOHMs-based aqueous fluids have demonstrated a lower specific heat capacity compared to MEA solvents at the same mass loading. The capture performance of NOHMs-based fluids has been measured and it has been discovered that the CO$_2$ loading has resulted in an increase in the specific heat capacity and a reduction of the viscosity of NOHM-I-PEI based aqueous fluids, which was hypothesized to be due to the formation of intra-molecular hydrogen bonding. The investigation into the mixing behavior reveals a non-linear relationship between the viscosity and the concentration of NOHMs. NOHM-I-HPE based aqueous fluids exhibit a smaller critical concentration and a higher intrinsic viscosity than NOHM-I-PEI based aqueous fluids, indicating that the addition of NOHM-I-HPE induces a more significant contribution of viscosity to the system. The impacts of additives, such as
physical solvent, NMP, and KHCO$_3$ salt, on the viscosity of the fluids are also investigated. The newly gained knowledge on the effects of CO$_2$ loading on the chemical and physical properties, and the viscosity-based mixing behavior of this novel hybrid solvent system is crucial in a transformative design of the dual-purpose reactive medium for carbon capture and conversion, and is beneficial to multiple fields involving nanoscale inorganic-organic hybrid materials.
4.1. Introduction

Carbon Capture, Utilization and Storage (CCUS) has been proposed as an effective solution to control and further reduce the carbon dioxide emission, in order to address the challenges of climate change (IPCC, 2005; Vitillo et al., 2017). The target of zero emission from power plants has been pursued with a wide range of conventional aqueous carbon capture solvents, and novel anhydrous carbon capture materials as illustrated in Table 4.1.

Table 4.1. Selected hydrous and anhydrous carbon capture solvents.

<table>
<thead>
<tr>
<th>Hydrous solvents</th>
<th>Anhydrous solvents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monoethanolamine (MEA) (Heldebrant, Koech, Glezakou, et al., 2017)</td>
<td>Ionic Liquids (ILs) (Bates et al., 2002)</td>
</tr>
<tr>
<td>Piperazine (PZ) (Heldebrant, Koech, Glezakou, et al., 2017)</td>
<td>CO₂-binding organic liquids (CO₂BOLs) (Heldebrant et al., 2011)</td>
</tr>
<tr>
<td>Methyldiethanolamine (MDEA) (Heldebrant, Koech, Glezakou, et al., 2017)</td>
<td>Nanoparticle Organic Hybrid Materials (NOHMs)</td>
</tr>
<tr>
<td>Triethanolamine (TEA), Diethanolamine (DEA) and etc.</td>
<td>Carbon anhydrase (Jo et al., 2014), phase changing solvents (Perry et al., 2010), and etc.</td>
</tr>
</tbody>
</table>
As a result of the cost reduction in renewable energies (Renewable Energy Agency, 2018), an increasing number of interests have focused on the direct conversion of the captured carbon dioxide into chemicals and fuels to achieve decarbonization in chemical industry sectors, such as cement production and steel making plants as illustrated in Figure 4.1. In this way, the energy intensive steps of regeneration of carbon capture solvents and compression of the released pure CO$_2$ can be bypassed, thus leading to a potential reduction of carbon emissions and carbon footprint of various chemical industries.

Among various CO$_2$ conversion routes, electrochemical conversion has witnessed tremendous advances in electrocatalysis and reaction mechanisms. However, electrochemical conversion is faced with the challenge of a low solubility of CO$_2$ in conventional aqueous electrolytes. Thus, a variety of anhydrous carbon capture materials have shown a potential to make novel electrolytes that can perform carbon capture and host the electrochemical conversion of CO$_2$, such as Ionic Liquids (ILs) and Nanoparticle Organic Hybrid Materials (NOHMs).
Viscosity is a vital parameter to characterize these novel liquid electrolytes, and the magnitude of viscosity can be translated into the energy consumption in the pumping and transportation of the fluids. One critical challenge of the anhydrous carbon capture solvents is their high intrinsic viscosity (Heldebrant, Koech, Glezakou, et al., 2017). As shown in Figure 4.2(a), the pure anhydrous capture solvents can exhibit a viscosity up to $10^4$ cP (Petit, Bhatnagar, et al., 2013), and this high viscosity can be reduced by blending anhydrous capture solvents with secondary fluids, such as water. It shows that, similar to the 20 wt.% MEA solution (Amundsen et al., 2009), the addition of water can reduce the viscosity of various ILs (Mokhtarani et al., 2009) and NOHMs (Petit, Bhatnagar, et al., 2013) by an order of magnitude. One exception is observed for an alkanolguanidines-based
CO₂BOLs. A 10 wt.% water loading has resulted in an increase in the viscosity of the specified CO₂BOLs (Koech et al., 2013).

The viscosity change upon CO₂ loading in these novel fluids will further influence the reactor design parameters and operation conditions. An increase of viscosity has been observed for the MEA-based solvents after CO₂ loading as depicted in Figure 4.2(b) (Amundsen et al., 2009). This viscosity enhancement becomes more significant for anhydrous capture solvents, such as CO₂BOLs (Malhotra et al., 2017) and ILs (Luo et al., 2016). It has been determined that the viscosity enhancement in ILs is mainly attributed to the formation of an inter-molecular hydrogen bonding network in the system (Gutowski and Maginn, 2008). This behavior will lead to an increased energy consumption in fluids transportation after CO₂ loading. In an effort to minimize the viscosity increase and even to reduce the viscosity of the system after CO₂ capture, Luo et al. utilized the formation of intra-molecular hydrogen bonding within certain ILs and realized a reduction of viscosity after CO₂ loading (Luo et al., 2016).
Figure 4.2. (a) Effect of water content and (b) effect of CO₂ loading on the viscosities of various carbon capture solvents, including 20 wt.% MEA (Amundsen et al., 2009), CO₂BOLs, ILs and NOHMs. CO₂BOLs-1 is an alkanolguanidines CO₂BOLs (Koech et al., 2013). CO₂BOLs-2 is 1-IPADM-3-BOL (Malhotra et al., 2017). CO₂BOLs-3 is 1-MEIPADM-2-BOL (Malhotra et al., 2017). ILs-1 is [BuPy][BF₄] (Mokhtarani et al., 2009). ILs-2 is [OcPy][BF₄] (Mokhtarani et al., 2009). ILs-3 is [P₆₆₆₁₄][Me-Gly] (Luo et al., 2016). ILs-4 is [P₆₆₆₁₄][Ac-Gly] (Luo et al., 2016). NOHMs is NOHM-I-HPE (Petit, Bhatnagar, et al., 2013).
NOHMs are comprised of nanoparticles (e.g. silica) grafted by a wide range of polymers, with an excellent thermal stability and a high chemical tunability (Lin and Park, 2011). The carbon capture performance, mechanism and related swelling behavior have been thoroughly investigated (Lin and Park, 2011; Lin et al., 2014, 2013, Y. Park et al., 2011, 2012; Petit, Lin, et al., 2013). The high viscosity of NOHMs, as shown in Figure 4.2(a), can be greatly reduced by the addition of water (Petit, Bhatnagar, et al., 2013) for enhanced mass transfer and electrochemical applications. In the newly emerged field of combined carbon capture and electrochemical conversion, it has become particularly appealing to investigate the impact of CO$_2$ loading on the physical and chemical properties of the nanoscale hybrid materials, and to understand the viscosity-based mixing behavior of the hybrid solvent system.

In this chapter, NOHMs-based aqueous fluids are designed for combined carbon capture and conversion. The fundamental chemical and physical properties, including specific heat capacity, density and viscosity, are investigated, with the goal of answering the following questions: (1) what is the impact of CO$_2$ loading on the physical and chemical properties of the system, (2) what is the viscosity-based mixing behavior of NOHMs-based fluids, and (3) what are the impacts of additives (e.g., physical solvents and salts) on the viscosity of the fluids. It is believed that the fundamental insights into the NOHMs-based fluids in combined carbon capture and conversion can also be beneficial to extended applications of nanoscale hybrid materials in catalysis (Mäsing et al., 2017), pharmaceutical probes (Ling et al., 2014) and battery electrolytes (Nugent et al., 2010).
4.2. Experimental methods

4.2.1. Synthesis of NOHMs and NOHMs-based fluids

Two types of NOHMs were synthesized, NOHM-I-PEI and NOHM-I-HPE, following the procedures reported by Park et al. in Chapter 3 (Lin and Park, 2011; Y. Park et al., 2012; Petit et al., 2012). A diluted silica suspension (LUDOX 30, 7 nm, Sigma-Aldrich) was prepared by DI water and treated by ion exchange resin (DOWEX marathon C cation-exchange resin, Sigma-Aldrich). Subsequently, the protonated silica suspension was titrated by the diluted polyethylenimine solution (PEI, Mn 1800, Polysciences). The neat NOHM-I-PEI was obtained after vacuum drying overnight.

The synthesis of NOHM-I-HPE began with the reaction between the diluted silica suspension and a diluted 3-(trihydroxysilyl)-1-propanesulfonic acid solution (SIT, Gelest). The pH of the well-mixed solution was adjusted to 5 using a 1 M NaOH solution, reacted at 70°C for 24 h. SIT served as the linker on the nanoparticle surface. The unreacted SIT molecules were removed by dialysis tubes (3.5K MWCO, Thermo Scientific) in DI water for 48 h. A proton exchange operation was then applied to this SIT grafted silica suspension, after which a diluted Jeffamine solution (HPE, Mn 2070, Hunstman) was added dropwise to tether the HPE polymers onto silica nanoparticles. The neat NOHM-I-HPE was obtained after drying under vacuum.

NOHMs-based fluids were made by mixing NOHMs and water at various mass concentrations, under vigorous stirring. Before mixing, NOHMs were dried under vacuum for 3 h to remove the attached water and CO₂. The components of NOHMs-based fluids in
this chapter are illustrated in Figure 4.3.

Figure 4.3. Recipe for the synthesis of salt-free NOHMs-based fluids.

4.2.2. Specific heat capacity of NOHMs-based fluids

A differential scanning calorimetry (DSC) spectrometer was used to measure the specific heat capacity of NOHMs-based fluids at room temperature. 20 mg of NOHMs-based fluids was carefully filled into a crucible with a pin-hole. The sample crucible was sealed and placed into the testing cell. An empty pin-holed crucible was used as the reference. The temperature was raised from -20°C up to 60°C at 10 K/min. A plateau was achieved in the room temperature region where no phase change occurred. The heat capacity was then calculated based on the heat flow value in this plateau.

4.2.3. Viscosity of NOHMs-based fluids

Viscosities of various NOHMs-based fluids were measured using an Ostwald viscometer as shown in Figure 4.4. A minimum 0.5 ml of well-mixed NOHMs-based fluids was injected into arm 1, and then sucked to arm 2 (capillary tube) above the upper mark A.
The NOHMs-based fluids then slowly flew down to lower mark B. The time it travelled from mark A to mark B was recorded as \( t \). DI water was measured as the standard solution whose density, \( \rho_0 \), and viscosity, \( \eta_0 \), were known. The time, \( t_0 \), for DI water was also determined in the same manner as NOHMs-based fluids. The viscosity of NOHMs-based fluids was calculated by the following equation.

\[
\frac{\eta}{\eta_0} = \frac{\rho t}{\rho_0 t_0}
\]

Eq. 4.1

Figure 4.4. Viscosity measurement of NOHMs-based fluids using an Ostwald viscometer.

4.3. Results and discussion

4.3.1. CO\(_2\) capture and its impacts on the specific heat capacity, density and viscosity of NOHMs-based fluids

4.3.1.1. CO\(_2\) capture using NOHMs-based fluids at ambient conditions

Neat NOHMs have demonstrated excellent carbon capture performances (Lin and Park, 2011; Lin et al., 2013), and a promising capture performance at ambient conditions was also observed after NOHMs were transformed into NOHMs-based fluids. As seen from
Figure 4.5, a 20 wt.% NOHM-I-PEI based aqueous fluids was able to reach a 0.5 mmol-CO$_2$/g-fluids capture capacity at 100 min.

In contrast, pure water could take up CO$_2$ only at a capacity of 0.034 mmol/g-water at 25°C. This value has been greatly improved by the addition of NOHM-I-PEI. The impacts of CO$_2$ capture on the properties of NOHMs-based fluids will be evaluated in terms of specific heat capacity, density and viscosity.

![Figure 4.5. CO$_2$ capture using 20 wt.% NOHM-I-PEI based aqueous fluids.](image)

4.3.1.2. Effect of CO$_2$ loading on the specific heat capacity of NOHMs-based fluids

Specific heat capacity represents the system’s ability to store energy at a given temperature range without undergoing phase change, which is strongly related to the molecular interactions within the materials. Therefore, specific heat capacity can be used to understand the mixing behavior of different NOHMs in water and the mechanism of
CO₂ capture.

Water has a high specific heat capacity, 4.18 J/(g·K), due to the strong hydrogen bonds formed between water molecules and the large degree of freedom of pure water molecules. The specific heat capacity of both NOHM-I-PEI and NOHM-I-HPE in water at various concentrations was lower than that of water. The 50 wt.% NOHM-I-PEI and NOHM-I-HPE aqueous fluid exhibited a specific heat capacity of 3.17 and 2.78 J/(g·K), respectively. In addition, the reduction of the specific heat capacity by NOHM-I-HPE was more significant than NOHM-I-PEI. The specific heat capacity was measured to be 1.82 J/(g·K) for neat NOHM-I-HPE, and it was 2.98 J/(g·K) for neat NOHM-I-PEI.

The specific heat capacity of NOHMs-based fluids was also compared with 30 wt.% MEA solution, since 30 wt.% MEA solvents have been widely used for post-combustion carbon capture. The 30 wt.% MEA solution possesses a specific heat capacity of around 3.7 J/(g·K) (Kuusela, 2010; Weiland et al., 1997). A high energy consumption during solvent regeneration has challenged the application of the MEA/water system in carbon capture. As speculated from Figure 4.6, when the concentration of NOHM-I-PEI and NOHM-I-HPE was around 17 wt.% and 12 wt.%, the specific heat capacity could be lower than that of the 30 wt.% MEA solvents. This has given NOHMs-based fluids an advantage in terms of energy consumption compared to 30 wt.% MEA solvents regarding the regeneration of the capture materials.

Interestingly, the two NOHMs-based fluids behaved in different manners upon CO₂ loading. For NOHM-I-PEI, the specific heat capacity increased after CO₂ capture, in
contrary to conventional amine-based solvents (Kuusela, 2010; Weiland et al., 1997). The specific heat capacity for 20 wt.% NOHM-I-PEI in water was 3.47 and 3.90 J/(g•K) before and after CO₂ capture, respectively. A 12.4 % increase was observed. The enhancement of the specific heat capacity of NOHM-I-PEI based aqueous fluids was hypothesized to be due to the formation of intra-molecular hydrogen bonds after CO₂ capture in the NOHM-I-PEI/water system, and thus the amount of energy required for a given temperature change was increased.

For NOHM-I-HPE, specific heat capacity further decreased after CO₂ loading. For 20 wt.% NOHM-I-HPE based aqueous fluids, the specific heat capacity was reduced from 3.35 to 3.21 J/(g•K) after CO₂ capture. Similar phenomena were also observed in an ethylaminoethanol system (Gao et al., 2017). The addition of CO₂ into ethylaminoethanol resulted in the reduction of specific heat capacity of the system, since the specific heat capacity of CO₂ was lower than that of the ethylaminoethanol component in the system (Gao et al., 2017). NOHM-I-HPE, unlike NOHM-I-PEI, captures CO₂ via physical interactions, and no significant chemistry change (e.g., intra-molecular hydrogen bonding) is expected upon CO₂ loading.
Figure 4.6. Effect of CO$_2$ loading on the specific heat capacity of (a) NOHM-I-PEI based aqueous fluids and (b) NOHM-I-HPE based aqueous fluids. The NOHMs-based fluids were loaded by CO$_2$ to saturation.

4.3.1.3. Effect of CO$_2$ loading on the density of NOHMs-based fluids

Figure 4.7 shows the change of density for NOHM-I-PEI and NOHM-I-HPE based aqueous fluids at 5, 20 and 50 wt.% of NOHMs loading. It is shown that the density increased as the concentration of either NOHMs increased. Meanwhile, after CO$_2$ capture, the density increased for all cases. Notably, the density increase for NOHM-I-PEI based
aqueous fluids was much more significant than NOHM-I-HPE based aqueous fluids. With similar molecular weights of PEI and HPE polymers, NOHM-I-PEI captures CO$_2$ via chemisorption through the amine groups on the tethered PEI polymers and thus a higher CO$_2$ uptake can be achieved. On the contrary, NOHM-I-HPE utilizes ether groups of the HPE polymers to capture CO$_2$ in a physisorption manner, resulting in a much lower capture capacity at ambient conditions, and thus a smaller density change.

Figure 4.7. Effect of CO$_2$ loading on the density of (a) NOHM-I-PEI based aqueous fluids and (b) NOHM-I-HPE based aqueous fluids. The NOHMs-based fluids were loaded by CO$_2$ to saturation.
4.3.1.4. Effect of CO₂ loading on the viscosity of NOHMs-based fluids

The 5 wt.% and 20 wt.% NOHM-I-PEI based aqueous fluids showed a viscosity of 2.48 and 6.94 cP, respectively. After CO₂ capture, these values reduced to 2.35 and 6.25 cP, respectively. This is contrary to what has been observed for various amine-based aqueous solvents and ILs (Amundsen et al., 2009; Gao et al., 2017; Gutowski and Maginn, 2008; Hartono et al., 2014; Luo et al., 2016; Mazinani et al., 2011). As shown from Figure 4.8(a), the viscosity of 20 wt.% MEA solvents increased from 1.70 cP to 2.20 cP, upon a CO₂ loading of 0.5 mol-CO₂/mol-MEA. For ILs, an inter-molecular hydrogen bonding network has been identified as a primary reason for the viscosity increase after CO₂ capture (G. Yu et al., 2007). It was found that the formation of intra-molecular hydrogen bonds could inhibit the development of inter-molecular hydrogen bonds (Luo et al., 2016; Qian et al., 2017). Thus, the viscosity reduction of NOHMI-I-PEI based aqueous fluids upon CO₂ loading was hypothesized to be attributed to the newly formed intra-molecular hydrogen bonds within NOHMs-based fluids.

The viscosities of the 5 wt.% and 20 wt.% NOHM-I-HPE based aqueous fluids underwent a minimal change upon CO₂ loading as demonstrated in Figure 4.8(b). Physisorption of CO₂ resulted in a less significant chemical and physical change of the NOHM-I-HPE systems. For 5 wt.% NOHM-I-HPE based aqueous fluids, the viscosity before and after CO₂ loading was 1.38 and 1.31 cP, respectively.

The minimum change and even the decrease in viscosity upon CO₂ capture of NOHMs-based aqueous fluids at a NOHMs loading less than 20 wt.% is beneficial in
maintaining a stable fluid physical condition for reactor design and operation protocols.

Figure 4.8. Effect of CO₂ loading on the viscosity of (a) NOHM-I-PEI based aqueous fluids and (b) NOHM-I-HPE based aqueous fluids. The NOHMs-based fluids were loaded by CO₂ to saturation. The viscosity change of the 20 wt.% MEA solvent upon a CO₂ loading of 0.5 mol-CO₂/mol-MEA loading is plotted as shown by the “x” symbols (Amundsen et al., 2009).
4.3.2. Viscosity-based mixing behavior of NOHMs-based aqueous fluids

4.3.2.1. Critical concentration of NOHMs-based fluids

Figure 4.9 illustrates the dependence of the viscosity on the concentration of NOHMs. It is found that as the concentration of NOHMs, either NOHM-I-PEI or NOHM-I-HPE, increased, the viscosity increased in a nonlinear manner. This is contrary to what the Einstein equation (Einstein, 1906) states, as demonstrated in Eq. 4.2, where $\eta$ is the measured viscosity, $\eta_s$ is the viscosity of the pure solvent free of particles and $\phi$ is the volume fraction of the particles in the suspension. This equation states that in a dilute particle suspension without particle interactions (Haines and Mazzucato, 2011; Mendoza and Santamaría-Holek, 2009; Toda and Furuse, 2006), the viscosity increases linearly with the addition of particles in the system. However, this equation assumes the use of rigid spherical particles in dilute systems. For polymer solutions and hybrid systems, this equation fails due to the overlapping and interactions between polymers.

$$\eta = \eta_s(1 + 2.5\phi) \quad \text{Eq. 4.2}$$

It can be seen in Figure 4.9 that at low concentrations, viscosity increased slightly and it underwent a dramatic increase after a certain concentration. For example, the viscosity was 1.87 cP and 2.91 cP for 5 wt.% and 10 wt.% NOHM-I-PEI based aqueous fluids, respectively. The viscosity then jumped to 80.2 cP when the concentration of NOHM-I-PEI was increased to 40 wt.%. Similar behavior was also observed for NOHM-I-HPE, but a more significant increase in viscosity was observed.
Figure 4.9. Effect of the concentration of NOHMs on the viscosity of (a) NOHM-I-PEI based aqueous fluids and (b) NOHM-I-HPE based aqueous fluids.

Such nonlinear dependence of viscosity on the concentration of NOHMs implied interactions between NOHMs within the system. This behavior can be characterized by “critical concentration”, C*, which is defined as the concentration at which (the aggregates of) NOHMs begin to overlap and interact significantly. The critical concentration can be a
useful design principle for NOHMs-based fluids in practical applications. The NOHMs-based fluids need be designed and manufactured below the critical concentration to avoid significant NOHMs aggregations.

In order to resolve the critical concentration, C*, it has been proposed to plot the logarithm of zero shear viscosity against the logarithm of the mass concentration to obtain the intersection of two fitted lines with different slopes (Skelland and Meng, 1996; Vinogradov and Titkova, 1968). From the intersection, the critical concentration, C*, can be determined. Generally, a constant shear viscosity region is observed at low shear rates for polymer solutions (Cox and Merz, 1959; Morris et al., 1981), and thus in the case of NOHMs-based fluids, it was assumed that the measured bulk viscosity, \( \eta \), was approximate to the zero shear viscosity, \( \eta_0 \).

Figure 4.10(a) shows that at low concentrations of NOHM-I-PEI in water, the fitted line exhibited a slope of 1.34 and the slope changed to 3.61 at higher concentrations. Meanwhile, for NOHM-I-HPE based aqueous fluids, the slope of the fitted line increased from 1.41 to 4.59, after passing over the critical concentration. From Figure 4.10, it was speculated that the critical concentration, C*, for NOHM-I-PEI based aqueous fluids was \(~0.2415\ g/ml\) and this value corresponded to \(~23\ wt.%\ NOHM-I-PEI\ loading\). Meanwhile, the critical concentration, C*, of NOHM-I-HPE based aqueous fluids was \(~0.1918\ g/ml\), referring to a turning point of \(~17\ wt.%\ NOHM-I-HPE\ loading\).

The critical concentration of NOHM-I-HPE aqueous fluids was smaller than that of NOHM-I-PEI based aqueous fluids. It can be inferred that the interaction of the aggregates
of NOHM-I-HPE starts to become more significant at a slightly lower concentration than NOHM-I-PEI. In other words, at the same mass loading of NOHMs, the overlapping and interactions between NOHM-I-HPE can be more significant compared to NOHM-I-PEI, leading to a higher viscosity of NOHM-I-HPE based fluids.

The untethered polymer solutions have also been found to exhibit a critical concentration due to polymer-polymer interactions (Skelland and Meng, 1996; Vinogradov and Titkova, 1968). Thus, the quantified comparison between the viscosity behavior of NOHMs-based fluids and untethered polymer-based fluids will be further studied, to differentiate the role of nanoparticles in the viscosity-based mixing behavior.
Figure 4.10. Determination of the critical concentration of (a) NOHM-I-PEI based aqueous fluids and (b) NOHM-I-HPE based aqueous fluids.

4.3.2.2 Intrinsic viscosity of NOHMs-based aqueous fluids

Intrinsic viscosity, $[\eta]$, is a measure of the contribution of the solute to the viscosity of the solution. The unit of intrinsic viscosity can be expressed as ml/g, representing how much volume will be occupied by the solute’s mass. The bigger the volume, the greater the
viscosity contribution of the solute to the system. Intrinsic viscosity is defined by Eq. 4.3,
where $\Phi$ is the fraction of the solute and $\eta_s$ is the viscosity of pure solvent. It is inferred
from Eq. 4.3 that intrinsic viscosity is determined in the dilute region of the solution.

$$[\eta] = \lim_{\Phi \to 0} \frac{\eta - \eta_s}{\eta_s \Phi} \quad \text{Eq. 4.3}$$

To determine the intrinsic viscosity, Huggins (Huggins, 1942; Michael and Colby, 2003) developed a simple equation as shown in Eq. 4.4 from the Tayler series expansion
of Eq. 4.3. In Eq. 4.4, $k_H$ is the Huggins constant, $c$ is the mass concentration of solute and $\eta_{sp}$ is the specific viscosity, defined in Eq. 4.5.

$$\frac{\eta_{sp}}{c} = [\eta] + k_H [\eta]^2 c \quad \text{Eq. 4.4}$$
$$\eta_{sp} = \frac{\eta - \eta_s}{\eta_s} \quad \text{Eq. 4.5}$$

From the Huggins equation, the intrinsic viscosity $[\eta]$ can be determined by the
intercept of the fitted line in the plot of $\frac{\eta_{sp}}{c}$ (reduced viscosity) versus $c$ (mass concentration of NOHMs). As shown in Figure 4.11(a), the intercept and the slope of the fitted line for NOHM-I-PEI based aqueous fluids were 7.42 and 138.87, respectively, and therefore the intrinsic viscosity, $[\eta]$, and Huggins constant, $k_H$, were determined to be 7.65 ml/g and 1.9. In the same manner, the intrinsic viscosity, $[\eta]$, and Huggins constant, $k_H$, for NOHM-I-HPE based aqueous fluids were calculated to be 9.76 ml/g and 4.9. From the values of intrinsic viscosity, it could be concluded that with the addition of NOHMs at the same mass, NOHM-I-HPE would lead to a more significant viscosity change.

Notably, the Huggins constant, $k_H$, was high for both NOHM-I-PEI and NOHM-I-HPE in water. It is accepted that when the Huggins constant is below 0.3, the polymers are
considered to be in a good solvent (Pamies et al., 2008). The large Huggins constant obtained from NOHMs-based fluids suggested that NOHMs did not uniformly dissolve in water. This non-uniform dispersion of NOHMs in water has been confirmed by the multi-scale structure formed in the system by the technique of ultra-small-angle X-ray scattering (USAXS), which will be discussed in Chapter 6. Additionally, this observed Huggins constant might be overestimated due to that the Huggins equation as shown in Eq. 4.4 did not account for the nanoparticles present in the system.
Figure 4.11. Determination of the intrinsic viscosity of (a) NOHM-I-PEI based aqueous fluids and (b) NOHM-I-HPE based aqueous fluids by linear fitting of the reduced viscosity with respect to the NOHM's concentration.
Table 4.2. Critical concentration and intrinsic viscosity of NOHMs-based aqueous fluids.

<table>
<thead>
<tr>
<th></th>
<th>Critical concentration, $C^*$ [g/ml]</th>
<th>Intrinsic viscosity [ml/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOHM-I-PEI based fluids</td>
<td>0.2415</td>
<td>7.65</td>
</tr>
<tr>
<td>NOHM-I-HPE based fluids</td>
<td>0.1918</td>
<td>9.76</td>
</tr>
</tbody>
</table>

To further compare and analyze the experimental results, a calculation using Mark–Houwink–Staudinger–Sakurada (MHSS) relation was performed based on Eq. 4.6 (Houwink, 1940; Michael and Colby, 2003; Zeng et al., 2007), where $K$ and $\alpha$ are the Mark Houwink parameters. It has been determined that for pure PEI polymers (Mn 1800), $K$ and $\alpha$ are 1 ml/g and 0.26 (Von Harpe et al., 2000).

$$[\eta] = KMn^\alpha$$

Eq. 4.6

Under the assumption that the molecular mass of the PEI polymers could approximate that of the NOHMs, the intrinsic viscosity was calculated as 7.02 ml/g for NOHM-I-PEI based aqueous fluids from Eq. 4.6. This was close to the experimentally determined value. The small deviation was believed to come from the following facts: (1) the molecular weight of the PEI polymers was used to estimate the molecular weight of NOHM-I-PEI, (2) the impact of nanoparticle was not accounted in the equation and (3) the Mark Houwink parameters were determined for PEI polymers without nanoparticles.

In agreement with the smaller critical concentration of NOHM-I-HPE in water, the larger intrinsic viscosity of NOHM-I-HPE based aqueous fluids has suggested a greater viscosity change through the incorporation of NOHM-I-HPE compared to NOHM-I-PEI.
Thus, in order to minimize the viscosity change of the system, NOHM-I-HPE needs to be added at a smaller concentration than NOHM-I-PEI.

4.3.3. Effect of additives on the viscosity of NOHMs-based aqueous fluids

4.3.3.1. Effect of physical solvent, NMP

N-Methyl-2-pyrrolidone (NMP) was used as a physical solvent additive to further enhance capture capacity by introducing additional amine groups in the system. Surprisingly, the viscosity increased drastically as shown in Figure 4.12. When the secondary fluids were changed from water to water/NMP (1:1), the viscosity increased from 2.48 cP to 7.84 cP for 5 wt.% NOHM-I-PEI loading, and the value increased from 6.94 cP to $2.31 \times 10^2$ cP for 20 wt.% NOHM-I-PEI loading. Meanwhile, the viscosity of NMP/water mixture (1:1) without NOHMs was measured to be 3.73 cP (Henni et al., 2004), only slightly higher than that of water. This significant increase of viscosity was believed to be due to the formation of a complex between NOHM-I-PEI and NMP via the electron donating oxygen and nitrogen atoms on NMP. With this increased viscosity, a compromised mass transfer in carbon capture is expected when NMP is added into the NOHM-I-PEI/water system, which will be demonstrated in Chapter 7.
Figure 4.12. Effect of NMP on the viscosity of (a) NOHM-I-PEI based aqueous fluids and (b) NOHM-I-HPE based aqueous fluids.

4.3.3.2. Effect of salt on the viscosity of NOHMs-based aqueous fluids

The effect of potassium bicarbonate salt on the viscosity of NOHM-I-HPE based aqueous fluids was also investigated. Figure 4.13 presents the viscosity change with the concentration of NOHM-I-HPE, with and without 0.1 M KHCO₃ salt. The viscosity of NOHM-I-HPE aqueous fluids doped by KHCO₃ salt also followed the nonlinear relationship with respect to the concentration of NOHM-I-HPE. It was found that the addition of salt greatly reduced the viscosity of NOHM-I-HPE/water system, though additional substances were introduced into the fluids. For 30 wt.% NOHM-I-HPE loading, the viscosity was $3.95 \times 10^2$ cP for the salt-free case, and this value reduced to 24.4 cP.
after 0.1 M KHCO₃ was doped into the system.

Since NOHM-I-HPE was comprised of the polymers grafted onto the nanoparticle surface via ionic bonding, the salt ions were believed to interact with the ionic bonding sites, facilitating the dynamic polymer hopping on the nanoparticle surface. This interaction was able to lessen the rigidity of the system and improve the fluidity of the NOHM-I-HPE based aqueous fluids.

Figure 4.13. Effect of KHCO₃ on the viscosity of NOHM-I-HPE based aqueous fluids.

4.4. Conclusions

In this study, the NOHMs-based aqueous fluids have demonstrated a promising carbon capture performance, and the effects of CO₂ loading on specific heat capacity, density and viscosity were studied. The lowered specific heat capacity of NOHMs-based aqueous
fluids has given NOHMs an advantage in energy consumption regarding regeneration compared to the 30 wt.% MEA solvents. The increase in the specific heat capacity and the reduction of the viscosity upon CO$_2$ loading into NOHM-I-PEI based aqueous fluids were attributed to the formation of intramolecular hydrogen bonds in the system. The viscosity-based mixing behavior was further characterized by critical concentration and intrinsic viscosity. The smaller critical concentration and the higher intrinsic viscosity of NOHM-I-HPE based aqueous fluids, compared to NOHM-I-PEI based aqueous fluids, implied a more significant contribution of viscosity by the incorporation of NOHM-I-HPE. The addition of NMP has greatly increased the viscosity of NOHM-I-PEI based aqueous fluids, and meanwhile, the doping of 0.1 M KHCO$_3$ salt could reduce the viscosity of NOHM-I-HPE based aqueous fluids through the interactions with the ionic bonding sites on NOHM-I-HPE. The detailed comparison of the viscosity-based mixing behavior between NOHMs-based fluids and the untethered polymer-based fluids will be further investigated.

The understanding of the viscosity-based mixing behavior of NOHMs-based fluids can be a useful design principle for the dual-purpose reactive medium intended for carbon capture and conversion. The concentration of NOHMs and the presence of different additives (e.g., physical solvents and salts) can be carefully controlled to tune the carbon capture behavior and fluid rheology. Along with the effects of CO$_2$ loading on the fluids properties, the reactor design parameters can also be engineered.
Chapter 5

Unique Electrochemical Properties of a Novel Hybrid Solvent System and Its Potential Application for Combined Carbon Capture and Conversion

This chapter is based on the following manuscript to be submitted:

“Unique electrochemical properties of a novel hybrid solvent system and its potential application for combined carbon capture and conversion” (Ming Gao, and Ah-Hyung Alissa Park)
Abstract

In order to address the daunting climate change challenges associated with the increasing concentration of carbon dioxide in the atmosphere, Carbon Capture, Utilization and Storage (CCUS) has been proposed as an effective carbon management strategy to achieve both zero emission in fossil-burning power plants and negative emission in various chemical sectors. Thanks to the significant cost reduction in renewable energy sources, such as solar and wind power, a game-changing concept has been suggested to directly convert the captured CO$_2$ into chemicals and fuels. Electrochemical conversion is one of the major pathways for CO$_2$ conversion, and has achieved tremendous developments in electrocatalysis. However, the low solubility of CO$_2$ in conventional aqueous electrolytes has limited its application. Thus, a number of novel electrolytes have been studied, including Nanoparticle Organic Hybrid Materials (NOHMs)-based fluids. With a promising carbon capture performance, the electrochemical properties of NOHMs-based fluids have attracted a growing amount of attention in the scientific community. An unexpected enhancement of ionic conductivity in NOHMs-based fluids is observed compared to corresponding untethered polymer-based fluids. The relative tortuosity of ion transport has suggested the formation of a multi-scale structure within NOHMs-based fluids. A tentative cyclic voltammetry measurement reveals a potential electrochemical reduction of the captured CO$_2$ to CO for the first time using this hybrid solvent system. An outstanding electrochemical stability of NOHMs-based fluids has also been reported. These insights into this novel hybrid solvent system are beneficial to the development of a
dual-purpose reactive medium for combined carbon capture and conversion, and the newly acquired knowledge is enlightening to multiple fields involving nanoscale inorganic-organic hybrid materials.
5.1. Introduction

In the context of climate change challenges, Carbon Capture, Utilization and Storage (CCUS) has been proposed (IPCC, 2005; Vitillo et al., 2017) to effectively mitigate the carbon emission. In order to realize not only a zero emission in fossil-fired power plants, but also a negative emission in other chemical sectors, such as steel making and cement production plants, a game-changing concept, as presented in Figure 5.1, has been suggested to perform a direct conversion of the captured CO₂ into chemicals and fuels, using more affordable renewable energy sources, including solar and wind energies.

A number of CO₂ conversion pathways have been studied, including thermochemical (W.-H. Wang et al., 2015), (photo)electrochemical (Hori, 2008; Lewis, 2007), inorganic carbonation (Krevor and Lackner, 2009) and biological routes (H. Li and Liao, 2013). Extensive studies in electrochemical conversion have focused on electrocatalysis and reaction mechanisms (Hori, 2008; Lu et al., 2013; Sen et al., 2014), but fewer studies have attempted to solve the challenge of the low solubility of CO₂ in conventional aqueous electrolytes. Thus, versatile novel electrolytes have been designed that can perform carbon capture and host the subsequent electrochemical conversion of CO₂, including Ionic Liquids (Rosen et al., 2011), clathrate hydrates (Deciccio et al., 2015) and Nanoparticle Organic Hybrid Materials (NOHMs)-based fluids.
Figure 5.1. Scheme for combined carbon capture and electrochemical conversion using NOHMs-based fluids.

NOHMs consist of nanoparticles (e.g. silica) tethered by a wide range of polymers. NOHMs have displayed an excellent carbon capture performance with a high thermal stability and an extraordinary chemical tunability (Lin and Park, 2011; Lin et al., 2014, 2013, Y. Park et al., 2011, 2012; Petit, Lin, et al., 2013). However, pure NOHMs, similar to a variety of anhydrous solvents (Heldebrant, Koech, Glezakou, et al., 2017), exhibit a high viscosity up to $10^4$ cP (Petit, Bhatnagar, et al., 2013) as discussed in Chapter 4. Thus, a NOHMs-based fluid is synthesized by mixing NOHMs with different secondary fluids, to lower the viscosity (Petit, Bhatnagar, et al., 2013) for electrolyte purposes.

The mixture of nanoparticle/polymer hybrid materials with different solvents has exhibited a number of interesting properties in terms of ion transport (Choudhury et al.,
and nanoparticle self-assembly (Akcora et al., 2009). Archer et al. reported promising ionic conductivities for both pure NOHMs and NOHMs/polycarbonate mixtures as the electrolytes for lithium ion batteries (A. Agrawal et al., 2015; Choudhury et al., 2015; Nugent et al., 2010), and the ion transport in these systems could be tuned by the polydispersity of NOHMs (A. Agrawal et al., 2015). In the newly emerged field of combined carbon capture and electrochemical conversion, it has become particularly attractive to understand how the fundamental electrochemical properties can be engineered by different nanoscale hybrid materials so that carbon capture and electrochemical conversion using these nanoscale hybrid materials can be realized.

In this chapter, NOHMs-based fluids are designed for combined carbon capture and conversion. The carbon capture performance and conductivities of different NOHMs-based fluids were measured. A conductivity-viscosity relationship was constructed, leading to a proposed structure of NOHMs-based fluids. In the end, a tentative electrochemical conversion of CO$_2$ was conducted using a selected NOHMs-based fluid. An excellent electrochemical stability was also reported for NOHMs-based fluids.

5.2. Experimental methods

5.2.1. Synthesis of NOHMs and NOHMs-based fluids

Two types of NOHMs were synthesized, NOHM-I-PEI and NOHM-I-HPE, following the procedures reported by Park et al., (Lin and Park, 2011; Y. Park et al., 2012; Petit et al., 2012) as described in Chapter 3. A diluted silica suspension (LUDOX 30, 7 nm, Sigma-Aldrich) was prepared by DI water and was then treated by an ion exchange resin (DOWEX...
marathon C cation-exchange resin, Sigma-Aldrich). Subsequently, the protonated silica suspension was titrated by the diluted polyethylenimine solution (PEI, Mn 1800, Polysciences). The resultant solution was dried under vacuum overnight to obtain the neat NOHM-I-PEI.

The synthesis of NOHM-I-HPE began with the reaction between a diluted silica suspension and a diluted 3-(trihydroxysilyl)-1-propanesulfonic acid solution (SIT, Gelest) at 70°C for 24 h, after pH adjustment to 5 using a 1 M NaOH solution. SIT served as the linkers on the nanoparticle surfaces. The unreacted SIT molecules were removed by the dialysis tubes (3.5K MWCO, Thermo Scientific) in DI water for 48 h. Proton exchange was then applied to this SIT grafted silica suspension, after which a diluted polyetheramine solution (HPE, Mn 2070, Hunstman) was added dropwise to ensure complete tethering. The pure NOHM-I-HPE was obtained after drying under vacuum for 24 h.

Two kinds of secondary fluids, water and poly(ethylene glycol) methyl ether (mPEG, Mn 550, Sigma-Aldrich) were utilized to make NOHMs-based fluids. NOHMs and a selected secondary fluid were mixed under vigorous stirring. The well-mixed solution was doped by 1 M bis(trifluoromethane)sulfonimide lithium salt (LiTFSI, Sigma-Aldrich). The components in NOHMs-based fluids can be seen from Figure 5.2.
Figure 5.2. Recipe for the synthesis of NOHMs-based fluids doped by LiTFSI.

5.2.2. Conductivity of NOHMs-based fluids

Conductivity was determined using a PARSTAT MC potentiostat (Princeton Applied Research) by the electrochemical impedance spectroscopy (EIS) method. Platinum wires were employed as the two electrodes. The electrochemical cell was immersed in a water bath to maintain the temperature at 25°C. A 1 M Na₂SO₄ solution of a known conductivity, was used to determine the cell constant. The resistivity of each NOHMs-based fluid was determined from Nyquist plot, and then conductivity was calculated by taking the reciprocal of the resistivity.

5.2.3. Viscosity of NOHMs-based fluids

Viscosities of the NOHMs-based fluids were determined using a ViscoPro 2000 (PAC) rheometer. The temperature was maintained at 25°C by a water bath. A pre-selected piston was placed into the testing chamber. After the NOHMs-based fluid was injected into the
chamber, measurements were conducted three times while the chamber was well-sealed.

5.2.4. Electrochemical reduction of CO₂

A Cyclic Voltammetry (CV) measurement for a CO₂-saturated NOHMs-based fluid was conducted to investigate the potential electrochemical reduction of CO₂. Silver (Ag) wire was used as the working electrode. The counter electrode was platinum (Pt) wire. The overpotential was set to be from -0.5 V to -2.0 V (vs Ag|AgCl), at a scan rate of 0.1 V/s.

5.2.5. Electrochemical stability of NOHMs-based fluids

A 100-cycle Cyclic Voltammetry (CV) measurement was also performed for various NOHMs-based fluids to determine the structural integrity after electrochemical treatment. The NOHMs-based fluids were swept from 0 V to -2 V (vs Ag|AgCl), with Pt wires as both the working and counter electrodes, at a scan rate of 0.1 V/s.

The resultant fluids were characterized using a Thermo Nicolet 6700 Fourier-transform infrared (FTIR) spectrometer with Golden Gate ATR accessory. The scanning range was set to be from 4000 to 600 cm⁻¹ with a resolution of 2 cm⁻¹. Each spectrum was generated by taking the average of 18 scans for three separate trials.

5.3. Results and discussion

5.3.1. CO₂ capture using NOHMs-based fluids

Neat NOHMs have demonstrated excellent carbon capture performance when the partial pressure of CO₂ is 3.4 bar (Lin and Park, 2011). After NOHMs were blended with secondary fluids, the mixture still exhibited an outstanding capture behavior at 1 bar as shown in Figure 5.3. With only 5 wt.% NOHM-I-PEI loading, both the capture capacity
and sorption kinetics were greatly improved compared to a 0.1 M KHCO₃ solution, which is generally used for electrochemical conversion of CO₂ (Hori, 2008). As shown in Figure 5.3, at 200 min, the capture capacity of 0.1 M KHCO₃ solution was 0.02 mmol/g, while the capture capacity of the NOHM-I-PEI based fluid was 0.46 mmol/g.

![Graph showing carbon capture performance](image)

Figure 5.3. Carbon capture performance of a 5 wt.% NOHM-I-PEI based aqueous fluid and 0.1 M KHCO₃ solution.

5.3.2. Conductivity of NOHMs-based fluids

LiTFSI was used as the salt to study the electrochemical properties of NOHMs-based fluids due to its high conductivity and great compatibility with NOHMs in lithium ion battery electrolyte applications (A. Agrawal et al., 2015; Choudhury et al., 2015; Nugent et al., 2010). The following questions are worth investigating to determine the electrochemical performance of NOHMs-based fluids: (1) How will the ionic conductivity
of NOHMs-based fluids change compared to the corresponding untethered polymer-based fluids? (2) What parameters will be altered in the conductivity governing equation with the addition of NOHMs? (3) Are there any other factors controlling the conductivity in addition to viscosity? (4) Can we resolve the tortuosity of ion migration in the NOHMs-based fluids? (5) Can we decouple ion migration and structural relaxation?

5.3.2.1. Conductivity of NOHMs-based fluids and related governing equations

The conductivity of nanoparticle/polymer hybrid systems was found to be inversely related to the fraction of the nanoparticles and to the viscosity of the system (A. Agrawal et al., 2015; Nugent et al., 2010). Figure 5.4 demonstrates similar conductivity behavior of various NOHMs-based fluids and their corresponding untethered polymer-based fluids. The conductivity, for all cases, decreased as the concentration of NOHMs or polymers increased, primarily due to the increased viscosity of the system. For example, as shown in Figure 5.4(a), the conductivity decreased from 23 mS/cm to 5.9 mS/cm when the concentration of NOHM-I-PEI increased from 40 wt.% to 60 wt.% in water.

It can also be noted that conductivities can be tuned by different NOHMs and secondary fluids. Water-based fluids have exhibited a higher conductivity than mPEG-based fluids for NOHM-I-PEI as presented in Figure 5.4(a) and Figure 5.4(b). The conductivity of the 50 wt.% NOHM-I-PEI based aqueous fluid was 15 mS/cm, and this value decreased to 0.22 mS/cm when mPEG was used as the secondary fluid. The results implied that different mechanisms might dominate ion migrations in different secondary fluids, giving rise to such significant conductivity variations. On the other hand, NOHM-
I-HPE demonstrated a slightly higher conductivity than NOHM-I-PEI in mPEG.

Surprisingly, it was discovered that the conductivity of NOHMs-based fluids was higher than that of the untethered polymer-based fluids. Initially, this was thought to be counter-intuitive since the silica nanoparticles were not thought to be conductive. As shown in Figure 5.4(a), at 50 wt.% NOHMs loading, the conductivity was 15 mS/cm for NOHM-I-PEI in water, while it was 0.91 mS/cm for PEI based aqueous fluids. The trend was similar in Figure 5.4(b) when mPEG was the secondary fluid. At the 50 wt.% loading, the conductivity for NOHM-I-PEI and PEI in mPEG was 0.22 and 0.058 mS/cm, respectively. NOHM-I-HPE exhibited similar behavior in mPEG as illustrated in Figure 5.4(c).
Figure 5.4. Conductivities of (a) NOHM-I-PEI and PEI based aqueous fluids, (b) NOHM-I-PEI and PEI based mPEG fluids, and (c) NOHM-I-HPE and HPE based mPEG fluids. All fluids were doped by 1 M LiTFSI salt.
Conductivity can be described by Eq. 5.1, where $F$ is the Faradaic constant, $z_i$ is valence charge of species $i$, $u_i$ is the ionic mobility, and $c_i$ is the concentration of species $i$. In the NOHMs case, LiTFSI was the species accounting for the ionic conductivity. Ionic mobility is defined by Eq. 5.2, where $D$ is the diffusion coefficient of the species and $R$ is the gas constant. Diffusion coefficient can be formulated by Stokes-Einstein Eq. 5.3, where $k$ is the Boltzmann constant, $\eta$ is the viscosity of the solution, and $r$ is the hydrodynamic radius of the conducting species.

$$\kappa = F^2 \sum z_i^2 u_i c_i$$  \hspace{0.5cm} \text{Eq. 5.1}

$$u = \frac{D}{RT}$$  \hspace{0.5cm} \text{Eq. 5.2}

$$D = \frac{kT}{6\pi \eta r}$$  \hspace{0.5cm} \text{Eq. 5.3}

$$\kappa = F^2 \sum z_i^2 \frac{k}{6\pi \eta r_i R} c_i$$  \hspace{0.5cm} \text{Eq. 5.4}

$$\kappa = F^2 \sum z_i^2 \frac{k}{6\pi \eta r_i R} a_i$$  \hspace{0.5cm} \text{Eq. 5.5}

After Eq. 5.1, Eq. 5.2 and Eq. 5.3 are combined, the conductivity can be expressed in terms of the viscosity of the solution, the concentration and the radius of conducting species, as shown in Eq. 5.4. Furthermore, activity is often used to describe the effective concentration and when activity is substituted into the Eq. 5.4, the expression for conductivity can be obtained in Eq. 5.5. It can be shown that in Eq. 5.5, $F$, $z_i$, $k$ and $R$ were held constant for various NOHMs-based fluids. The hydrodynamic radius of the salt ions, $r_i$, can be considered constant at low and moderate concentrated regions. The change in the amount of solvent molecules that were carried by salt ions needs to be investigated at high concentrations. Though the concentration of LiTFSI salt was held at 1 M, the
activity of LiTFSI might decrease with the addition of NOHMs due to the enhanced interaction between NOHMs and salt ions. NMR analysis has unveiled such interactions between salt ions and the tethered polymers in Chapter 6, indicated by an upfield chemical shift change of salt ions. Meanwhile, as the concentration of NOHMs increased, viscosity $\eta$ increased in a nonlinear manner as investigated in Chapter 4.

The migration of ions in glass forming polymers, such as mPEG, can also be characterized via the Vogel-Fulcher-Tammann (VFT) equation depicted below. With this equation, the temperature dependence of conductivity can be revealed. $E_a$ is the activation energy of ion hopping through polymers. $A$ and $R$ are the pre-factor constant and gas constant, respectively. $T_0$ is the ideal glass transition temperature, which is selected to be 25 - 50 K below the experimentally determined glass transition temperature (A. Agrawal et al., 2015; Choudhury et al., 2015). The characterization of ion transport using VFT equation will not be discussed in detail in this paper.

$$\kappa = A \exp\left[\frac{-E_a}{R(T-T_0)}\right]$$

Eq. 5.6

5.3.2.2. Conductivity and viscosity

As demonstrated from Eq. 5.5, viscosity is a vital factor in influencing ion transport. The viscosities of NOHMs-based fluids and polymer-based fluids were measured as shown in Figure 5.5. Different trends were observed for NOHM-I-PEI and NOHM-I-HPE. As depicted in Figure 5.5(a) and Figure 5.5(b), NOHM-I-PEI based fluids exhibited a lowered viscosity compared to PEI based fluids in both water and mPEG. On the contrary, the viscosity of NOHM-I-HPE in mPEG was higher than that of HPE based fluids.
Figure 5.5. Viscosities of (a) NOHM-I-PEI and PEI based aqueous fluids, (b) NOHM-I-
PEI and PEI based mPEG fluids, and (c) NOHM-I-HPE and HPE based mPEG fluids. All
fluids were doped by 1 M LiTFSI salt.
The conductivity-viscosity relationship led to the determination of the adjusted conductivity of the untethered polymer-based fluids, if their viscosities were converted to the same value as NOHMs-based fluids. In this adjustment, we first plotted the conductivity of the untethered polymer-based fluids against their viscosity, and performed a nonlinear least-squares fit using an allometric model in the form of \( a \cdot b^x \). The selection of this model equation takes into the account that conductivity is inversely related to viscosity, resembling the conductivity governing equation as shown in Eq. 5.5.

However, a large gap still existed between the conductivity of NOHMs-based fluids and the adjusted conductivity (dashed line) of untethered polymer-based fluids, as shown in Figure 5.6. For example, in Figure 5.6(a), the conductivity of 40 wt.% PEI based aqueous fluid was 2.57 mS/cm. After viscosity adjustment, it became 3.71 mS/cm. This value was still smaller than 23.0 mS/cm, the conductivity of NOHM-I-PEI based aqueous fluid at the same mass loading. Similar behavior was also observed for NOHM-I-PEI based mPEG fluids as in Figure 5.6(b). For HPE based fluid as presented in Figure 5.6(c), the conductivity difference became more significant after the conductivity adjustment compared to the NOHM-I-HPE based fluid in mPEG.

In Figure 5.6(a), \( \kappa_1, \kappa_2 \) and \( \kappa_3 \) represented the conductivity of NOHM-I-PEI based fluids, PEI based fluids and adjusted PEI based fluids, respectively. The conductivity increase associated with the viscosity effect was denoted by \( \kappa_3 - \kappa_2 \). The significant difference between \( \kappa_1 \) and \( \kappa_3 \) goes beyond the viscosity effect alone. While a complete elucidation requires theoretical and modeling work that goes beyond the scope of the
current work, we nevertheless surmise that this difference may be associated with a structure-induced ion transport enhancement associated with the NOHMs hierarchical arrangements. One possible mechanism is that the hierarchical structures formed by NOHMs in secondary fluids are able to introduce multi-scale channels and NOHMs crosslinks for ions to move through. This combination can provide a unique ion-hopping tortuosity that enables a faster ion diffusion in secondary fluids compared with untethered polymer-based fluids.
Figure 5.6. Conductivities (solid line) and adjusted conductivities (dashed line) of (a) NOHM-I-PEI and PEI based aqueous fluids, (b) NOHM-I-PEI and PEI based mPEG fluids, and (c) NOHM-I-HPE and HPE based mPEG fluids. All fluids were doped by 1 M LiTFSI salt.
It is also proposed that the microviscosity is the major factor affecting the ions migration (S.-C. Wang and Tsao, 2003). The local concentrations of NOHMs and secondary fluids can be different, leading to a viscosity heterogeneity in the system. This microviscosity is believed to be closely related to the hierarchical structures of NOHMs in the presence of secondary fluids.

5.3.2.3. Relative tortuosity of ion migration in NOHMs-based fluids

The modified conductivity, $\kappa_0$, is the conductivity of NOHMs-based fluids assuming there are no nanoparticles. This modified conductivity can be determined by measuring the conductivity of the conducting phase with respect to the composition (A. Agrawal et al., 2015). In NOHMs based fluids, the conducting phase was assumed to be everything but the silica nanoparticles. For example, in the case of NOHM-I-PEI based mPEG fluids, the modified conductivity was measured for PEI based mPEG fluids against the volume fraction of PEI/(mPEG+PEI). A straight line was fitted and the modified conductivity could be obtained from this fitted line based on the composition of each NOHM-I-PEI based mPEG fluid. The normalized conductivity was calculated by taking the ratio of the actual conductivity, $\kappa$, to the modified conductivity, $\kappa_0$. It can be seen from Table 5.1 that the normalized conductivity was greater than 1, consistent with the observation that NOHMs-based fluids exhibited a higher conductivity than the corresponding untethered polymer based fluids.

Relative tortuosity, $\tau'$, can then be calculated via Eq. 5.7, where $\phi$ is the volume fraction of silica nanoparticles (A. Agrawal et al., 2015; Bouchet et al., 2014). This relative
tortuosity can be regarded as the correction factor between the actual conductivity and the modified conductivity of NOHMs-based fluids. In other words, this relative tortuosity describes the ratio of the distance of ion migration in NOHMs-based fluids to the distance of ion migration in the untethered polymer-based fluids.

\[ \kappa = \frac{\kappa_0 \phi}{\tau'} \]  

Eq. 5.7

Weissberg (Weissberg, 1963) also proposed an empirical equation to calculate the tortuosity as shown in Eq. 5.8, where \( p \) was determined to be 0.49 for spherical particles (Mauret and Renaud, 1997).

\[ \tau = 1 - p \ln \phi \]  

Eq. 5.8

With these two methods, the experimentally calculated relative tortuosity and empirical tortuosity are presented in Table 5.1. Empirically determined tortuosity was greater than 1. This equation developed by Weissberg was applicable to randomly dispersed spherical particles (Bouchet et al., 2014; Weissberg, 1963). In NOHMs-based fluids, a hierarchical structure was believed to have formed due to the interactions between NOHMs. Thus, deviations might exist regarding the actual tortuosity.

In NOHMs-based mPEG fluids, the relative tortuosity was less than 1, indicating that the ions travelled a shorter distance than in the untethered polymer-based mPEG fluids in mPEG. This counter-intuitive phenomenon is believed to be primarily attributed to two reasons. (1) The underlying principle of this method is that the particles are inert, and the conducting phase is everything excluding the particles. However, in NOHMs system, polymers are grafted onto silica nanoparticles via ionic bonding. The silica nanoparticles
are believed to be able to facilitate the polymer dynamic hopping via the surface charge.

(2) The incorporation of silica nanoparticles is also believed to have led to the formation of a unique structure in NOHMs-based fluids, allowing ions to migrate through a pathway that is different from that of the untethered polymer entanglements. This unique pathway in NOHMs-based fluids is hypothesized to give ions multiple channels to diffuse and a shortcut to hop.

Table 5.1. Normalized conductivity ($\kappa/\kappa_0$), tortuosity and relative tortuosity of ion migration in NOHMs-based mPEG fluids.

<table>
<thead>
<tr>
<th>Weight[\textsuperscript{a}] /wt.%</th>
<th>NOHMs</th>
<th>Normalized conductivity $\kappa/\kappa_0$</th>
<th>Relative Tortuosity[\textsuperscript{b}]</th>
<th>Tortuosity[\textsuperscript{c}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>NOHM-I-PEI</td>
<td>3.541</td>
<td>0.230</td>
<td>1.023</td>
</tr>
<tr>
<td></td>
<td>NOHM-I-HPE</td>
<td>1.202</td>
<td>0.773</td>
<td>1.036</td>
</tr>
<tr>
<td>60</td>
<td>NOHM-I-PEI</td>
<td>2.904</td>
<td>0.325</td>
<td>1.028</td>
</tr>
<tr>
<td></td>
<td>NOHM-I-HPE</td>
<td>1.242</td>
<td>0.736</td>
<td>1.044</td>
</tr>
<tr>
<td>70</td>
<td>NOHM-I-PEI</td>
<td>3.012</td>
<td>0.310</td>
<td>1.033</td>
</tr>
<tr>
<td></td>
<td>NOHM-I-HPE</td>
<td>1.121</td>
<td>0.800</td>
<td>1.053</td>
</tr>
</tbody>
</table>

[\textsuperscript{a}] Weight refers to the weight percent of NOHMs in the fluids.

[\textsuperscript{b}] Relative tortuosity refers to the ion migration in NOHMs-based mPEG fluids with respect to that in untethered polymer-based mPEG fluids.

[\textsuperscript{c}] Calculated from Weissberg equation (Weissberg, 1963).
5.3.3. Proposed structures of NOHMs-based fluids

Based on the adjusted conductivity and relative tortuosity of ion migration in NOHMs-based fluids, the structure of NOHMs-based fluids was hypothesized as illustrated in Figure 5.7. A unique assembly of NOHMs can be realized through the interactions between nanoparticles and polymers, giving rise to an ion hopping pathway that differs from the pathway present in untethered polymer-based fluids. Similar self-assembly of nanoparticle/polymer hybrid materials in different solvents has also been detected and simulated (Akcora et al., 2009; Zhao et al., 2016). It was determined that different shapes of the aggregated polymer-coated nanoparticles could be engineered by altering the molecular weights of the tethered polymers, and the ratio of the length of grafted polymers to the length of the polymer matrix (Akcora et al., 2009; Zhao et al., 2016).

In addition, it is proposed that channels can be formed through NOHMs assembly as represented in Figure 5.7. These channels are supposed to give ions a faster local diffusion rate, resulting in a higher conductivity compared to the untethered polymer-based fluids.

Detailed investigation into this hierarchical structure in the NOHMs-based fluids and its relations to the observed ion transport will be conducted using ultra-small-angle X-ray scattering (USAXS) and pulsed field gradient (PFG) NMR in Chapter 6. The quantified difference between this hierarchical structure in NOHMs-based fluids and the structure formed in polymer-based fluids will also be further studied.
5.3.4. Potential electrochemical conversion of CO$_2$

An electrochemical conversion of the captured CO$_2$ using NOHMs-based fluids was attempted by performing a cyclic voltammetry measurement of a selected CO$_2$-loaded NOHM-I-HPE based aqueous fluid. The gaseous products were determined by a micro gas chromatography (microGC). A silver electrode was employed for the electrochemical reduction of CO$_2$ (Hori, 2008), and a blank measurement using a Pt electrode (Hori, 2008) was also conducted to exclude the interference of possible salt reductions. H$_2$ was detected as the major gaseous product when Pt was used as the electrode. Figure 5.8(a) depicts that the hydrogen evolution reaction was a dominant reaction for the CO$_2$-saturated NOHM-I-HPE based aqueous electrolyte. When Ag was employed as the electrocatalyst, a distinct peak, indicative of a potential electrochemical reduction of CO$_2$, appeared for the CO$_2$-saturated NOHM-I-HPE based aqueous electrolyte as presented in Figure 5.8(b). In this scenario, though the current density was much smaller than the Pt-catalyzed reaction, both CO and H$_2$, were detected in the gaseous products. The quantified electrochemical
production of CO and H\textsubscript{2} will be discussed in Chapter 7.

Figure 5.8. Cyclic Voltammetry (CV) of 40 wt.% NOHM-I-HPE based aqueous fluids doped by 1 M LiTFSI, with the cathode of (a) Pt and (b) Ag.
5.3.5. Electrochemical stability

The electrochemical stability of NOHMs-based fluids was evaluated based on the bulk structures before and after electrochemical treatments. Four kinds of NOHMs-based fluids, involving two types of NOHMs and two kinds of secondary fluids, were investigated as illustrated in Figure 5.9. The maintained wavenumbers for the characteristic peaks (e.g., C-H stretching peak at 2860 cm\(^{-1}\) in Figure 5.9(a), N-H bending peak at 1650 cm\(^{-1}\) in Figure 5.9(b), C-H stretching peak at 2880 cm\(^{-1}\) in Figure 5.9(c) and \(NH_3^+\) stretching peak at 1630 and 1530 cm\(^{-1}\) in Figure 5.9(d).) indicated no bulk structural changes in NOHMs-based fluids after electrochemical treatment for 100 cycles. This excellent electrochemical stability has enabled the operation of combined carbon capture and electrochemical conversion without NOHMs degradation.
Figure 5.9. FTIR spectrum of the original and electrochemically treated (a) NOHM-I-PEI in water, (b) NOHM-I-PEI in mPEG, (c) NOHM-I-HPE in water and (d) NOHM-I-HPE in mPEG. All fluids were at 40 wt.% NOHMs loading and doped by 1 M LiTFSI salt.

5.4. Conclusions

In this chapter, the NOHMs-based fluids have been developed for combined carbon capture and conversion. A promising carbon capture performance was observed after NOHMs were transformed into NOHMs-based fluids. An unexpected enhancement of ionic conductivity was observed for NOHMs-based fluids compared to the untethered polymer-based fluids. Such unique ion transport phenomena was found to occur beyond a simple mixing rule between conductivity and viscosity. With the calculations of the relative tortuosity of ion migration in NOHMs-based fluids, a unique structure formed by NOHMs was hypothesized that enabled enhanced ion diffusion and hopping. A cyclic voltammetry measurement was performed, and a potential electrochemical reduction of CO$_2$ was observed. NOHMs-based fluids have also exhibited an excellent electrochemical stability.

NOHMs-based fluids have shown a potential to be utilized as a dual-purpose reactive medium for combined carbon capture and conversion. The unique ion transport behavior can be used to tune the electrochemical performance of NOHMs-based fluids, and such insight is also beneficial to other areas that involve similar nanoscale hybrid materials. A detailed investigation of the unique structures and the transport behavior of NOHMs-based fluids will be discussed in Chapter 6, and a more comprehensive electrochemical reduction of the captured CO$_2$ using NOHMs-based fluids will be presented in Chapter 7.
Chapter 6

The Hierarchical Structure of NOHMs-Based Fluids and Their Transport Behavior

This chapter is based on the following manuscript to be submitted:

“Investigation of unique hierarchical structures of hybrid solvent system developed for combined CO$_2$ capture and conversion via Ultra-small-angle X-ray Scattering (USAXS)” (Ming Gao, Fan Zhang, Andrew J. Allen, Jan Ilavsky, and Ah-Hyung Alissa Park)

This chapter is based on the following manuscript under preparation:

“PFG NMR study on the transport behavior of a novel nanoscale hybrid material developed for combined CO$_2$ capture and conversion” (Ming Gao, Jing Peng, Tony Feric, Thomas Zawodzinski, and Ah-Hyung Alissa Park)
Abstract

Recent climate change discussion has indicated that we now need not only zero emission strategies but also negative emission approaches. Thus, the decarbonization potentials of other industrial sectors beyond power plants are being investigated. Particularly, the rapid reduction in costs of renewable energy sources, such as solar and wind, in various parts of the world has enabled the conversion of the captured CO$_2$ to chemicals and fuels, contributing to the potential reduction of carbon footprints in the chemical industries. Until now, the CO$_2$ capture and conversion technologies have been developed independently from each other. There are different pathways of CO$_2$ conversion, such as thermochemical, (photo)electrochemical, inorganic carbonation and biological conversion. Recently, electrochemical conversion of CO$_2$ has been extensively studied with an emphasis on electrocatalysis. One constraint associated with the electrochemical reduction of CO$_2$ is the low solubility of CO$_2$ in conventional aqueous electrolytes. Thus, a number of novel electrolyte materials with improved CO$_2$ solubility have been proposed, including Nanoparticle Organic Hybrid Material (NOHMs)-based fluids. In this chapter, an ultra-small-angle X-ray scattering (USAXS) study has revealed unique hierarchical structures within NOHMs-based hybrid solvent systems. This multi-scale structure is found to be highly dependent on the concentration of NOHMs, and the types of NOHMs and secondary fluids. Pulsed field gradient (PFG) NMR is also conducted to further investigate the transport behavior of this hybrid solvent system, in an effort to understand the ion transport mechanism. The newly gained insights into the multi-scale structures of such hybrid
solvent systems promote a more comprehensive understanding of the ion transport and carbon capture behaviors within these novel electrolyte systems, and they have opened up new interdisciplinary research topics involving dual-purpose nanoscale hybrid fluids.
6.1. Introduction

An urgent need for efficient carbon management has led to the development of Carbon Capture, Utilization and Storage (CCUS) technologies as the global CO$_2$ concentration in the atmosphere has increased to beyond 400 ppm (IPCC, 2005; Pacala and Socolow, 2004; Vitillo et al., 2017). In parallel with a target for zero emission from fossil-burning power plants, negative emission approaches are proposed for a wide range of chemical industry sectors, such as steel making and cement production plants to further reduce the global anthropogenic CO$_2$ emission. With the recent reduction in renewable energy costs, a paradigm shifting concept has newly emerged to convert the captured CO$_2$ into chemicals and fuels for a more decarbonized chemical industry.

Various CO$_2$ conversion routes have been proposed to transform CO$_2$ into versatile products: biological (Beer et al., 2009; Wong et al., 2014), photochemical (B. Kumar et al., 2010; Lewis, 2007; Lewis and Nocera, 2006), electrochemical (Hori, 2008; Lu et al., 2013; Sen et al., 2014), inorganic carbonation (Hariharan et al., 2017; A. H. A. Park et al., 2003; Prigiofbe et al., 2009), and thermochemical conversion (Duyar et al., 2015; Y.-N. Li et al., 2014; McNamara and Hicks, 2014). While there have been important discoveries and advances in the area of electrocatalysis related to the electrochemical reduction of CO$_2$ in recent years (M. Liu et al., 2016; Lu et al., 2013), fewer studies exist regarding how electrolyte materials can be advanced to overcome the present limitations in the solubility of CO$_2$. This is mainly due to the fact that CO$_2$ capture and electrochemical conversion technologies have developed independently from each other, as illustrated in Figure 6.1. In
decoupled schemes, the captured CO₂ is released at high temperature or under vacuum to produce a pure CO₂ stream (Y. Park et al., 2015; Rochelle, 2009), while the delivered CO₂ feedstock for electrochemical conversion needs to be dissolved in the electrolyte, which is generally water-based with limited CO₂ solubility. Thus, the decoupled pathway of carbon capture and conversion needs to overcome multiple energy barriers as demonstrated in the dashed lines in Figure 6.1.

In order to address the challenge associated with CO₂ solubility, novel electrolytes with a high CO₂ uptake that can also host the subsequent electrochemical conversion of CO₂ have been proposed. A number of unique carbon capture solvents have been studied, such as CO₂BOLs (Heldebrant et al., 2011, 2008b, 2009; Heldebrant, Koech, and Yonker, 2010; Malhotra et al., 2017; Mathias et al., 2013), Ionic Liquids (ILs) (Bates et al., 2002; Gutowski and Maginn, 2008; H. Davis, Jr., 2004; X. Zhang et al., 2017; X. Zhang, Zhang, Dong, Zhao, Zhang, and Huang, 2012), Nanoparticle Organic Hybrid Materials (NOHMs) (Lin and Park, 2011; Lin et al., 2013; Y. Park et al., 2011, 2014, 2012; Petit et al., 2012), and clathrate hydrates (Deciccio et al., 2015; Moon et al., 2017). ILs showed the effect of being a co-catalyst in mediating electrochemical conversion of CO₂ to CO and HCOOH (Asadi et al., 2014; Hollingsworth et al., 2015; Huan et al., 2017; Oh and Hu, 2015; Rosen et al., 2011; Sun et al., 2014; Tanner et al., 2016; Q. Zhu et al., 2016). CO₂ hydrates were also investigated and it was found that both CO₂ concentration and the faradaic efficiency in the electrochemical production of CO from CO₂ were improved when CO₂ hydrate slurry was used as the electrolyte (Deciccio et al., 2015). The integration of carbon capture and
conversion is illustrated as a solid line in Figure 6.1, and this combined scheme is hypothesized to have a potential to reduce the energy requirement as CO₂ capture can be pulled by the subsequent conversion of CO₂ to chemicals and fuels. There would be no need for a separate solvent regeneration step and a CO₂ compression step for transportation. The required binding energy during CO₂ capture/conversion can also be tuned.

Figure 6.1. Illustrative energy diagram of combined carbon capture and conversion.

NOHMs are a new class of nanoscale hybrid materials that are similar to nanoparticle/polymer hybrid systems developed for various applications including carbon capture (Lin and Park, 2011; Y. Park et al., 2012), catalysis (Kainz and Reiser, 2014; Mä sing et al., 2017), pharmaceutical products (F. Li et al., 2017; Ling et al., 2014), and batteries (A. Agrawal et al., 2015; Choudhury et al., 2015). NOHMs are particularly unique because they are liquid-like. They are comprised of polymers tethered onto nanoparticles (e.g., silica), and have great chemical and structural tenability as well as excellent thermal
stability (Lin and Park, 2011; Petit et al., 2012). With a versatile selection of different polymer and nanoparticle combinations, the mode of CO\textsubscript{2} capture (e.g., chemisorption and physisorption), and CO\textsubscript{2} capture kinetics and capacity can be engineered (Lin and Park, 2011; Petit, Lin, et al., 2013). While NOHMs exhibit great CO\textsubscript{2} capture capacity, their capture rate was found to be limited due to their high viscosity similar to most of other anhydrous capture solvents (e.g., ILs). Thus, a secondary fluid needs to be introduced to reduce the NOHM viscosity (Petit, Bhatnagar, et al., 2013).

In Chapter 5, NOHMs-based hybrid solvent systems have exhibited a unique relationship between conductivity and viscosity that was beyond a simple mixing rule. The unexpected ionic conductivity enhancement was hypothesized to be a result from both a viscosity effect and multi-scale structural effects in the NOHMs morphology.

Thus, in this chapter, ultra-small-angle X-ray scattering (USAXS) and pulsed field gradient nuclear magnetic resonance (PFG NMR) measurements were utilized to construct the multi-scale structures of NOHMs-based fluids, in order to investigate the transport behavior of these unique hybrid solvent systems.

### 6.2. Experimental methods

#### 6.2.1. Synthesis of NOHMs and NOHMs-based fluids

NOHM-I-PEI and NOHM-I-HPE were synthesized via the methods reported in Chapter 3 (Lin and Park, 2011; Lin et al., 2013; Y. Park et al., 2011). To synthesize NOHM-I-PEI, a 3 wt.% silica nanoparticle suspension in DI water was prepared from silica colloidal suspension (LUDOX SM-30, 7 nm, Sigma-Aldrich). Ion exchange (DOWEX
marathon C cation-exchange resin, Sigma-Aldrich) was conducted to replace the sodium ions on the silica nanoparticle surface with protons, after which diluted polyethylenimine (PEI, Polysciences) was added dropwise into the protonated silica nanoparticle suspension. NOHM-I-PEI was obtained after vacuum drying under 50°C overnight.

NOHM-I-HPE was synthesized first via linker grafting, and the linker was selected to be 3-(trihydroxysilyl)-1-propanesulfonic acid (SIT, Gelest). A 3 wt.% silica nanoparticle suspension was added into diluted SIT solution under vigorous stirring. The pH was then adjusted to 5 by adding 1 M NaOH solution. Unreacted linkers were removed in a dialysis tube (3.5K MWCO, Thermo Scientific) against DI water for 48 h. Ion exchange was performed for the silica-SIT system to protonate the sulfonate groups of the linkers. Lastly, polyetheramine (HPE, Jeffamine 2070, Huntsman), after dilution, was added into the silica-SIT solution. The pH was carefully monitored with a pH meter (Accumet AB15) until it reached equilibrium point. 10 ml of the silica-SIT solution was used to be pre-titrated by HPE polymer solutions to determine the equilibrium point, which was defined as the point undergoing the largest pH change. NOHM-I-HPE was obtained after vacuum drying under 50°C overnight.

The NOHM-based fluids were prepared by mixing a selected NOHMs with a secondary fluid, water or mPEG. 1 M bis(trifluoromethane)sulfonimide lithium salt (LiTFSI, Sigma-Aldrich) was also doped into the fluids. Vacuum drying of neat NOHMs at 50°C for 3 h was conducted to remove any attached water and CO₂ before making the NOHMs-based fluid. The recipe of NOHMs-based fluids is summarized in Figure 6.2.
6.2.2. Imaging of NOHMs-based fluids

A Philips CM200 transmission electron microscope (TEM) was used for visualizing the NOHMs-based fluid nanoscale morphologies. The NOHMs-based fluids were frozen at -80°C, after which the frozen liquid was cut into slices, and the slices were then kept in a cryo container. The TEM was equipped with a cryo holder where slices of frozen NOHMs-based fluids were mounted for imaging.

6.2.3. Construction of the hierarchical structures of NOHMs-based fluids

Ultra-small angle X-ray scattering (USAXS) experiments were performed using the USAXS instrument at Advanced Photon Source, Argonne National Laboratory as illustrated in Figure 6.3 to construct the hierarchical structures of NOHMs-based fluids (J. Ilavsky et al., 2013; Jan Ilavsky et al., 2009). The measured q range is between $1 \times 10^{-4}$ Å⁻¹ and 0.3 Å⁻¹. Here, $q = \frac{4\pi}{\lambda} \sin(\theta)$, where $\lambda$ is the wavelength and $\theta$ is $1/2$ of the
scattering angle. The X-ray energy was 17.5 keV ($\lambda = 0.7085$ Å). The X-ray photon flux was around $10^{13}$ mm$^{-2}$s$^{-1}$. Samples were placed into polyimide (Kapton) tubes (1.8 mm I.D. and 1.9 mm O.D., Cole-Parmer) with two ends sealed. Data reduction and analysis were performed using IgorPro-based SAS analysis package Irena (Jan Ilavsky and Jemian, 2009).

Figure 6.3. Illustration of the experimental set-up of ultra-small-angle X-ray scattering (USAXS) (J. Ilavsky et al., 2013; Jan Ilavsky et al., 2009).

6.2.4. Diffusion behavior in NOHMs-based fluids

Pulsed field gradient nuclear magnetic resonance (PFG NMR) measurements were performed using a Varian VNMRS 500 MHz spectrometer. A broadband OneNMR probe was employed. The gradient strength was set to be from 0 to 60 G/cm with 16 intervals. The diffusion time, $\Delta$, was set to be from 20 ms to 100 ms for different samples. A 5 mm NMR tube with an inset was used as shown in Figure 6.4. An inert toluene reference solution (Sigma-Aldrich) was injected into the inset of the NMR tube. The temperature was kept at 25°C.
6.3. Results and discussion

6.3.1. Construction of the hierarchical structures of NOHMs-based fluids

To test for an assumed hierarchical structure formation by NOHMs in NOHMs-based fluids, cryogenic electron microscopy (CryoEM) was employed to image a selected NOHMs-based fluid, NOHM-I-PEI in mPEG. For pure NOHMs, a TEM image shows individual NOHMs with a visible albeit mild particle alignment due to NOHMs-NOHMs interactions (Lin and Park, 2011). While not observable by TEM, it is reasonable to assume that the tethered polymers fill in the gaps between adjacent silica nanoparticles in neat NOHMs. After 40 wt.% NOHM-I-PEI was mixed with mPEG, a strip-like aggregation of NOHMs was spotted by CryoEM as shown in the bottom of Figure 6.5(b), demonstrating that the distribution of NOHMs in the secondary fluids was not as homogeneous as found for neat NOHMs. Indeed, an improvement of sample pre-treatment and imaging resolution is clearly required for an expanded range of NOHMs-based fluids to be studied.
Figure 6.5. (a) TEM image of neat NOHMs (Lin and Park, 2011) and (b) CryoEM image of 40 wt.% NOHM-I-PEI based mPEG fluids.

This strip-like assembly of nanoparticles assisted by polymer grafting and solvent dispersion has also been simulated and observed by Akcora et al. and Zhao et al (Akcora et al., 2009; Zhao et al., 2016). By mixing various polystyrene grafted silica nanoparticles in a polystyrene matrix, they discovered that the shapes of the self-assembly can be attributed to the grafting density, and the ratio of grafted chain length to the matrix chain length (Akcora et al., 2009; Zhao et al., 2016). Complementary to considering the chemistry (nanoparticle grafted by polymers in a solvent matrix) and structure scale (to the range of mm) of these systems, the hypothesized multi-level structures of NOHMs-based fluids can be resolved via ultra-small-angle X-ray scattering (USAXS) (Akcora et al., 2009). In combination with pinhole SAXS methods, the statistically-representative morphology of the NOHMs-based fluid can be quantified over a scale range from < 0.1 nm to several μm.

We investigated the morphology of the NOHMs-based fluids using synchrotron-based USAXS, a technique known for its ability to characterize polymeric materials with
hierarchical microstructures (F. Zhang and Ilavsky, 2010). A typical USAXS profile of the NOHMs samples, as well as its modeling fit, is shown in Figure 6.6. The USAXS profiles have a few common features. They exhibit a low-q power-law curve, an intermediate-q hump, and a high-q Guinier region (where the intensity varies as $\exp(-q^2R_g^2)$ and $R_g$ is the average radius of gyration of the particles) and its associated Porod region (where the intensity varies as a constant/$q^4$ and the constant is proportional to the particle surface area). The low-q power-law indicates that scattering inhomogeneities at sizes greater than 1 µm exist. The intermediate-q hump, depending on its exact location, suggests scattering inhomogeneities in the form of aggregates at the tens to hundreds of nm. The high-q Guinier is accompanied with Bessel oscillations, pointing to the size-monodispersity of the individual NOHMs particles. USAXS data of NOHM-I-HPE based mPEG fluids also demonstrate a second intermediate-q hump, suggesting the presence of agglomerate structures in the size range of hundreds of nm.

Based on these common features, a three-level scattering model was used, with each level representing one common feature (four-level model for NOHM-I-HPE in mPEG). This modeling approach is similar to the Unified method (Beaucage, 1995), with the exception that the high-q scattering is modeled with a spherical form factor and a hard-sphere structure factor. In Figure 6.6, to highlight the scattering model, we show the component plots that describe the contributions from the low-q power-law scattering, intermediate-q aggregate scattering, as well as high-q NOHMs scattering, in addition to an overall model fit. The detailed fitting results are tabulated in Table 6.1. The uncertainties
are one-standard deviation evaluated based on a chi-squares uncertainty analysis.

![Graph](image)

**Figure 6.6.** Example illustrating the scattering model used in this study.

Derived from model fitting of the slit-smeared USAXS data (Jan Ilavsky and Jemian, 2009), the sizes for the agglomerates, aggregates, and interparticle distances are summarized in Table 6.1. It is shown that all cases, including pure NOHMs, exhibited large agglomerate sizes. This coarse network reflected a heterogeneity across the entire system, which can be further revealed after carbon capture in viscous liquid systems (Cantu et al., 2016). A different selection of secondary fluid might be necessary if a uniform dispersion is of interest. Other structural parameters, such as aggregate size and interparticle distance, are largely dependent on the fundamental chemistry and mixing rule of this NOHMs-based hybrid solvent system.
Table 6.1. Structural information of various NOHM-based fluids.

<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>N_PEI[c]</td>
<td>100</td>
<td>&gt;2,000.0</td>
<td>60 ± 0.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N_PEI</td>
<td>40</td>
<td>&gt;2,000.0</td>
<td>27.8 ± 0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>/H₂O</td>
<td>50</td>
<td>&gt;2,000.0</td>
<td>34.1 ± 0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>&gt;2,000.0</td>
<td>41.4 ± 0.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N_PEI</td>
<td>50</td>
<td>&gt;2,000.0</td>
<td>32.3 ± 0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>/mPEG</td>
<td>60</td>
<td>&gt;2,000.0</td>
<td>35.4 ± 0.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>&gt;2,000.0</td>
<td>52.5 ± 0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N_HPE[d]</td>
<td>100</td>
<td>&gt;2,000.0</td>
<td>246.0 ± 2.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N_HPE</td>
<td>40</td>
<td>&gt;2,000.0</td>
<td>9.5 ± 1.0</td>
<td>5.5 ± 0.5</td>
<td></td>
</tr>
<tr>
<td>/H₂O</td>
<td>50</td>
<td>&gt;2,000.0</td>
<td>9.5 ± 1.0</td>
<td>4.8 ± 0.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>&gt;2,000.0</td>
<td>9.7 ± 1.0</td>
<td>5.0 ± 0.5</td>
<td></td>
</tr>
<tr>
<td>N_HPE</td>
<td>50</td>
<td>1,338 ± 13</td>
<td>153.9 ± 1.5</td>
<td>10.1 ± 1.0</td>
<td>3.6 ± 0.4</td>
</tr>
<tr>
<td>/mPEG</td>
<td>60</td>
<td>1,534 ± 15</td>
<td>197.1 ± 2.0</td>
<td>10.6 ± 1.1</td>
<td>3.8 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>1,461 ± 15</td>
<td>305.6 ± 3.1</td>
<td>9.8 ± 1.0</td>
<td>3.7 ± 0.4</td>
</tr>
</tbody>
</table>

[a] All samples are doped by 1 M LiTFSI salt.

[b] Weight percent refers to the percent mass of NOHMs in the fluids.

[c] N_PEI stands for NOHM-I-PEI.
[d] N_HPE stands for NOHM-I-HPE.

[e] Agglomerate is the loose association at large scale, which can be broken up by ultrasound under most conditions.

[f] Aggregate involves some adhesions, if not a chemical bond, at a scale smaller than agglomerates.

6.3.1.1. Effect of chemistry on the aggregate sizes

The degree of aggregate formation of polymer-assisted nanoparticles is dependent on the extent of inter-molecular interaction (Shenhar et al., 2005). It has also been determined that the self-assembly of varying shapes and sizes in nanoparticle/polymer hybrid systems is driven by both enthalpic and entropic effects (Balazs et al., 2006). Such driving forces can be manipulated by different selections of NOHMs and secondary fluids. For 50 wt.% NOHMs in NOHM-I-PEI, the size of the aggregates was determined to be $(34.1 \pm 0.3)$ nm in water, and $(32.3 \pm 0.3)$ nm in mPEG. Meanwhile, when 50 wt.% of NOHM-I-HPE was mixed with mPEG, the size of the aggregates drastically increased to $(153.9 \pm 1.5)$ nm, as seen from Figure 6.7.
Figure 6.7. The effect of the types of NOHMs and secondary fluids on the aggregate sizes at 50 wt.% loading of NOHMs. All fluids were mixed with 1 M LiTFSI salt.

6.3.1.2. Effect of the concentration of NOHMs on the aggregate sizes

The aggregate sizes were also found to be dependent on the concentration of NOHMs as illustrated in Figure 6.8. Both NOHM-I-PEI and NOHM-I-HPE exhibited increased aggregate sizes with increasing concentrations of NOHMs. The increase in aggregate sizes was more significant for NOHM-I-HPE. The aggregate size for 50 wt.% NOHM-I-PEI in mPEG was (32.3 ± 0.3) nm, and this value became (52.5 ± 0.5) nm when the concentration of NOHM-I-PEI was increased to 70 wt.%. Meanwhile, the aggregate size of NOHM-I-HPE in mPEG increased from (153.9 ± 1.5) nm to (305.6 ± 3.1) nm when the concentration of NOHM-I-HPE was increased from 50 wt.% to 70 wt..% The dependence of the
aggregate sizes on the NOHMs concentration can be partially inferred from nanoparticle system free of polymers. It was found that an increase in iron oxide nanoparticle concentration resulted in a higher probability of particle collision, leading to a growing aggregate size (Baalousha, 2009). From this perspective, a higher probability of NOHMs collisions is hypothesized to contribute to the enlarged aggregate size with increasing concentrations of NOHMs.

![Graph showing the effect of concentration on aggregate size](image)

Figure 6.8. Effect of the concentration of NOHMs on the aggregate sizes. All fluids were mixed with 1 M LiTFSI salt.

6.3.1.3. Effect of secondary fluids on the interparticle distance of NOHM-I-HPE

Several self-assembly driving forces, such as the Van der Waals forces and hydrogen bonding (Bishop et al., 2009), can be readily tuned by varying the interparticle distances. A number of methods have been undertaken to control the particle-particle distances
(Shenhar et al., 2005). One example, that was similar to the NOHMs with grafted polymers, was the utilization of a poly(amido-amine) dendrimer to space gold nanoparticles (Frankamp et al., 2002). In the case of NOHM-I-HPE based fluids, the interparticle distance was smaller in water (9.5 nm to 9.7 nm) than that in mPEG (9.8 nm to 10.6 nm) for (40 to 70) wt.% NOHM-I-HPE loading as shown in Figure 6.9. This suggests that NOHM-I-HPE is more hydrophobic to water than mPEG, and therefore NOHM-I-HPE packed and aligned more densely in water. This shorter interparticle distance explains the bigger agglomerate size found for NOHM-I-HPE in water compared to the case in mPEG, from a microscopic point of view.

![Diagram](image)

Figure 6.9. Effect of (a) H2O and (b) mPEG on the interparticle distance at (40 to 70) wt.% NOHMs loading. All fluids were mixed with 1 M LiTFSI salt.

6.3.2. Proposed structure of NOHMs-based fluids

Based on the USAXS/SAXS data analysis, a proposed generic structure for NOHMs-based fluids at (40 to 70) wt.% NOHMs loading is presented in Figure 6.10. Agglomerates of size from 1400 nm to over 2000 nm were formed on coarse length-scales in bulk fluids. Within these agglomerates, aggregates with size from 28 nm to more than 200 nm were
identified. Each NOHMs in the aggregates was found to have a coordination number between 3 and 6. The inter-particle (center-to-center) distances were calculated to be between 9 nm and 10 nm. This small inter-particle distance between NOHMs was, itself, strong evidence that, due to NOHMs-NOHMs and NOHMs-secondary fluids interactions, NOHMs assembled into a unique structure that might have a potential to enhance ion diffusion through channel formations and ion hopping through polymer segmental motions.

USAXS technique is also suitable for constructing the structures of untethered polymer entanglements (S. K. Agrawal et al., 2007; Pignon et al., 2004; F. Zhang and Ilavsky, 2010). Thus, the quantified difference in the structures between NOHMs-based fluids and their untethered polymer-based fluids will be further investigated.

![Diagram](image)

**Figure 6.10.** Proposed hierarchical structures of NOHMs-based fluids at different length scales at (40 to 70) wt.% NOHMs loading.
6.3.3. Transport behavior of NOHMs-based fluids

With the unique multi-scale structures of NOHMs-based fluids, the transport behavior was studied using PFG NMR from the perspectives of the diffusion coefficients of secondary fluids and NOHMs, effect of salt on the diffusion behavior, and interactions between salt ions and NOHMs. In order to exclude the complexity of overlapping peaks, NOHM-I-HPE based aqueous fluids were employed for this section.

6.3.3.1. Determination of the diffusion coefficients of water and NOHM-I-HPE

$^1$H PFG NMR was carried out to study the diffusion behavior of water and NOHM-I-HPE in this system. Different gradient strengths were applied to the samples and the corresponding intensity was recorded. The NMR spectrum at each gradient strength was collected and presented in Figure 6.11. Two major peaks were of interest. Peak 1 was at around 4.8 ppm corresponding to water, and peak 2 was at around 3.5 ppm, referring to the CH$_2$ groups on the tethered HPE polymers in NOHM-I-HPE. The diffusion coefficients of the selected species were resolved by fitting the data of the intensity against the gradient field strength based on the Stejskal-Tanner equation (Röding and Nydén, 2015). In the Stejskal-Tanner equation as listed below, $\gamma$ is the proton gyromagnetic ratio, which is $2.6752 \times 10^8$ rad/(T⋅s), $g$ is the gradient strength in unit of G/cm, $\delta$ is the gradient pulse duration and $\Delta$ is the time interval between the leading edge of the two gradient pulses (Röding and Nydén, 2015), which can be regarded as the diffusion time.

$$I = I_0 \exp[-D(\gamma g \delta)^2(\Delta - \frac{\delta}{3})]$$

Eq. 6.1
The diffusion coefficients of water and NOHMs are presented in Figure 6.12, with respect to the concentration of NOHM-I-HPE. It was found that the diffusion coefficients of both species decreased as the concentration of NOHMs increased, regardless of the presence of KHCO$_3$ salts. This was partially due to the increased viscosity in the system with the addition of NOHMs. Additionally, the diffusion coefficients of water were determined to be an order of magnitude higher than that of NOHM-I-HPE.

It was surprising to find that the diffusion coefficients of water were $3.43 \times 10^{-9}$ and $3.31 \times 10^{-9}$ m$^2$/s for the salt-free 10 wt.% and 20 wt.% NOHM-I-HPE based aqueous fluids at 25°C. These values were even higher than the self-diffusion coefficient of pure DI
water, which was determined to be $2.99 \times 10^{-9}$ m$^2$/s as represented by the dotted line in Figure 6.12. Other values have also been reported for the self-diffusion coefficient of pure water at 25°C, such as $2.57 \times 10^{-9}$ m$^2$/s (J. H. Wang, 1965), but still lower than the values measured for water in the specified NOHMs-based fluids. In connection with the hierarchical structures in NOHMs-based fluids, this unexpected diffusion behavior of water provides evidence for the unique channels created by NOHMs, resulting in a higher local diffusion rate of water.

The information on the exact sizes of the unique channels and the length scales of NOHMs aggregates can also be obtained by PFG NMR. The diffusion time term, $\Delta$, as in Eq. 6.1 can be varied, and thus different length scales of the structures can be differentiated and quantified. Basically, a longer diffusion time is favorable to resolve the structures in larger length scales. Future work in PFG NMR, coupled with techniques such as ultra-small-angle X-ray scattering (USAXS), will be conducted in determining the quantified length scales of the nanoscale hybrid materials in different secondary fluids.
Figure 6.12. Diffusion coefficients of (a) water and (b) NOHM-I-HPE in NOHM-I-HPE based aqueous fluids with and without 0.1 M KHCO₃ salt at 25°C.

6.3.3.2. Effect of salts on the diffusion behavior

The effect of salt on the diffusion behavior of water and NOHM-I-HPE was also investigated. Figure 6.12(a) shows that the diffusion coefficient of water was higher in the salt-free case. In contrast, NOHM-I-HPE diffused faster with the addition of KHCO₃ salt. The viscosity of NOHM-I-HPE based aqueous fluids doped by 0.1 M KHCO₃ was much lower than that of the salt-free NOHM-I-HPE based aqueous fluids as presented in Chapter 4. The results implied that salt was able to facilitate the polymer dynamic hopping on the
surface of silica nanoparticles, thus improving the fluidity of the system. This phenomenon was hypothesized to come from the interactions between the salt ions and the ionic bonding sites in NOHMs.

The impact of salt was further quantified by taking the ratio of the diffusion coefficients of NOHM-I-HPE to the diffusion coefficients of water as in Figure 6.13. The ratio was 0.019 and 0.017 for 10 wt.% and 40 wt.% salt-free NOHM-I-HPE based aqueous fluids, respectively. In contrast, these values became 0.064 and 0.022 in the cases with 0.1 M KHCO$_3$ salt. It can be seen that the ratio underwent no significant change with respect to the concentration of NOHM-I-HPE in the salt-free cases. Instead, in the cases doped by 0.1 M KHCO$_3$, this ratio decreased as the concentration of NOHMs increased, and the ratio was still higher than that of the salt-free case. The result further indicates that salts have played a critical role in promoting the diffusion of NOHM-I-HPE in the presence of water.

![Figure 6.13. Ratio of the diffusion coefficients of NOHM-I-HPE to the diffusion coefficients of water in NOHM-I-HPE based aqueous fluids at 25°C.](image)

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6.3.3.3. Interactions between salts and NOHMs

The interactions between KHCO$_3$ salt and NOHM-I-HPE were confirmed by the $^{13}$C chemical shift of HCO$_3^-$ species in the NOHM-I-HPE based aqueous fluids. An upfield shift was observed for the chemical shift of bicarbonate ions as the concentration of NOHM-I-HPE increased as shown in Figure 6.14. When the system was free of NOHM-I-HPE, the chemical shift of bicarbonate ions was 162.2 ppm, and this chemical shift moved to 161.1 ppm when the concentration of NOHM-I-HPE became 20 wt.%. After the concentration of NOHM-I-HPE reached 40 wt.%, the chemical shift was further reduced to 160.8 ppm.

The results indicated that as the concentration of NOHM-I-HPE increased, the strengthened interactions between HCO$_3^-$ and NOHMs would lead to an addition of electron density onto the carbon nucleus in bicarbonate ions. As a result, the shielding effect on the carbon nucleus was enhanced, leading to an upfield chemical shift change. In water-based fluids, the bicarbonate and carbonate equilibrium exists, and the $^{13}$C atom in HCO$_3^-$ is more electron negative than that in CO$_3^{2-}$. Thus, this upfield chemical shift is also indicative of the equilibrium towards HCO$_3^-$ (Mani et al., 2006). However, the interaction between the cation, K$^+$, and NOHMs is still to be determined.
6.3.4. Proposed ion transport in NOHMs-based fluids

Under the hierarchical structures and the unique diffusion behavior of NOHMs-based fluids, an investigation into the ion transport was performed, in an effort to understand the enhanced ionic conductivity as discussed in Chapter 5.

6.3.4.1. Proposed pathways for ion transport

A number of research have been conducted in understanding the ion transport in polymer-based systems, especially in the field of polymer electrolytes (Druger, Nitzan, et al., 1983; Druger, Ratner, et al., 1983; Schreiner et al., 2010; Yangyang Wang et al., 2012, 2014). This development of ion transport theory can also be applied to polymer systems with the incorporation of nanoparticles.

Figure 6.14. $^{13}$C chemical shift of bicarbonate ions with respect to the concentration of NOHM-I-HPE in NOHM-I-HPE based aqueous fluids.
In particular, Archer et al. (Rodriguez R, Herrera R, Archer LA, 2008; H.-Y. Yu et al., 2014) studied different nanoparticle/polymer based electrolytes for lithium ion batteries and discovered that the ionic conductivity was dependent on various factors, such as the molecular weight of the tethered polymers and the sizes of the nanoparticles. For example, neat NOHMs incorporating polyethylene glycol (PEG, Mn 1100) exhibited a conductivity that was an order of magnitude higher than that of NOHMs consisting of PEG (Mn 2000) at 25°C (Nugent et al., 2010). Meanwhile, NOHMs with 8-nm silica nanoparticles have shown an enhanced conductivity compared to NOHMs with 15-nm silica particles (Nugent et al., 2010).

Archer et al. also correlated the ion transport behavior with the structural configurations of a gel-like NOHMs-based solvent system (SiO$_2$-PEG in polycarbonate) doped by lithium salts (A. Agrawal et al., 2015; Choudhury et al., 2016). It was found that when the fraction of coarse particles was equal to that of finer particles, the system demonstrated the largest ionic conductivity and the shortest tortuosity for ion migration (A. Agrawal et al., 2015).

For liquid-like hybrid solvent system such as NOHMs-based fluids, ions can migrate in two regions, ① secondary fluids-rich region where ions move in the bulk secondary fluids and move through the channels created by the assembly of NOHMs, and ② NOHMs-rich region where ions hop through the unique pathways along the tethered polymers as shown in Figure 6.15. Inspired by the free volume theory and dynamic bond percolation for polymer electrolytes (Bouchet et al., 2014; Druger, Nitzan, et al., 1983;
Druger, Ratner, et al., 1983) and protic ionic liquids (Wojnarowska and Paluch, 2015), it is believed that in NOHMs-based fluids, ions can travel by the following three mechanisms: (1) Translational movement of ions carried by larger species, such as water, mPEG and NOHMs. This is considered of minimum impact (Wojnarowska and Paluch, 2015). (2) Coupled ion hopping with the structural relaxation of the carried species, such as the segmental motions of polymers and the solvation by water molecules. (3) Decoupled ion migration. In this case, the time scale of ion movement is shorter than that of the structural relaxation of the polymers, and this decoupling is believed to mainly occur in the NOHMs-rich region, as illustrated in Figure 6.15.

Between the two major ion migration pathways, it is speculated that in water-based fluids, ions mainly diffuse in the water-rich region through the channels constructed by NOHMs. Meanwhile, in polymer-based solutions, the ion migration through NOHMs (e.g., coupled and decoupled) will also make a significant contribution. The exact relative contributions of the two ion migration pathways, and the quantified comparison of ion migration in NOHMs-based fluids and polymer-based fluids are to be further determined.
Decoupling of ion migration from structural relaxation

Many efforts have been taken to understand the decoupling between ion transport and structural relaxation for superionic liquids (Yangyang Wang et al., 2014). A universal method in characterizing the ionicity is through the development of a Walden plot, which can be derived by employing Eq. 6.2 (Walden, 1906). Alternatively, a fractional Walden plot can be constructed using Eq. 6.3 (Schreiner et al., 2010; Wojnarowska and Paluch, 2015), where $\Lambda$ is the molar conductivity and $\eta$ is the measured viscosity. Eq. 6.3 can be rearranged to Eq. 6.4 and the slope $\alpha$ can reflect the extent of the decoupling of ion transport from structural relaxation (Agapov and Sokolov, 2011; Imrie and Ingram, 2001; MacFarlane et al., 2009; Schreiner et al., 2010; Yangyang Wang et al., 2012).

$$\Lambda\eta = \text{constant} \quad \text{Eq. 6.2}$$

$$\Lambda\eta^\alpha = \text{constant} \quad \text{Eq. 6.3}$$
\[ \log(\Lambda) = \alpha \log \left( \frac{1}{\eta} \right) + c = \text{constant} \]  

Eq. 6.4

However, the complexity of NOHMs-based fluids has limited the applicability of the Walden plot in determining the degree of decoupling of ion transport from the structural relaxation of NOHMs. First of all, the molar conductivity is defined as the conductivity divided by the concentration of the electrolyte. However, in the NOHMs system, the effective concentration of salt might change due to the interactions between salt ions and NOHMs. In addition, NOHMs also carried charge. NOHMs were comprised of the polymer grafted onto silica nanoparticle via ionic bonding, and the presence of salt ions was believed to facilitate the dynamic hopping of the charged polymers on the particle surface. Thus, the molar concentration of the conducting species was unclear. Secondly, it was discussed that the micro-viscosity was more fundamentally important for ions to move in the system due to the heterogeneity of the NOHMs system as mentioned in Chapter 5 (S.-C. Wang and Tsao, 2003). This micro-viscosity and viscosity heterogeneity cannot be accurately reflected in the equations used to construct a Walden plot.

More quantitative analysis on the decoupled ion migration from the structural relaxation of NOHMs will be conducted via specific techniques such as broadband dielectric spectroscopy (BDS).

\textbf{6.4. Conclusions}

Nanoparticle Organic Hybrid Materials (NOHMs)-based fluids have been innovatively designed as dual-purpose media for combined carbon capture and conversion. In order to address the hypothesis of a multi-scale structure formed by NOHMs in the presence of
secondary fluids in Chapter 5, USAXS technique was utilized to unveil and construct the hierarchical structures of the nanoscale hybrid solvent systems. It was found that the multi-scale structure was highly tunable by varying the concentration of NOHMs, and the types of NOHMs and secondary fluids. Interesting diffusion behavior were also observed under such unique structure. PFG NMR characterization showed that in certain NOHMs-based fluids, the diffusion coefficient of water was higher than that of pure water. This was attributed to the fact that structural channels were created by NOHMs to allow faster local diffusion of water. It was also found that the diffusion of NOHM-I-HPE in water was enhanced with the addition of 0.1 M KHCO₃, implying that salt was able to facilitate polymer dynamic hopping on the silica nanoparticles. Such unique structures and resulted surprising diffusion behavior have led to the proposed pathways of ion transport in NOHMs-rich region and secondary fluid-rich region in NOHMs-based fluids.

The structures of NOHMs-based fluids are fundamentally important in understanding the unique properties of the nanoscale hybrid materials, and tuning the ion transport and carbon capture performance in the hybrid solvent systems. It is believed that the knowledge on the detailed structures of NOHMs-based fluids is beneficial in developing the next-generation hybrid solvent system for combined carbon capture and conversion with enhanced chemical, physical and electrochemical performances.
Chapter 7

Combined Capture and Electrochemical Conversion of Carbon Dioxide using Novel Nanoscale Hybrid Materials-Based Fluids

This chapter is based on the following manuscript to be submitted:

“Combined Capture and Electrochemical Conversion of Carbon Dioxide using Novel Nanoscale Hybrid Materials-Based Fluids” (Ming Gao, and Ah-Hyung Alissa Park)
Abstract

As discussed in previous chapters, Carbon Capture, Utilization and Storage (CCUS) has been proposed as a promising carbon management strategy not only to achieve zero emission in fossil-fired power plants, but also to accomplish negative emission in various chemical industries. To realize a potential reduction of carbon footprints in chemical sectors, such as cement production and steel making plants, the concept of the direct conversion of the captured carbon dioxide into chemicals and fuels has been proposed and promoted with more affordable renewable energy sources. Among the major CO₂ reaction pathways, electrochemical conversion of CO₂ has been extensively investigated with a primary focus on electrocatalysts. However, the low solubility of CO₂ in conventional aqueous electrolyte has curbed its progress. Thus, a variety of novel carbon capture materials have been tested to incorporate into novel electrolytes to increase the solubility of CO₂, including Nanoparticle Organic Hybrid Materials (NOHMs)-based fluids. The carbon capture behavior of NOHMs-based fluids can be engineered by the concentration of NOHMs, the addition of salts and physical solvents. Dissolved CO₂, among different forms of carbon, is the electroactive species in this novel hybrid solvent system. Electrochemical conversion of the captured CO₂ has displayed an enhancement of CO production on polycrystalline silver, and a selectivity alteration on a carbon-based electrode. An excellent stability of NOHMs-based fluids is also presented over multiple cycles of carbon capture and conversion. Possible roles of NOHMs, such as a NOHMs-CO₂ complex, in mediating carbon capture and conversion are hypothesized. With NOHMs-based fluids,
the binding energy to CO$_2$ and existing forms of CO$_2$ can be readily tuned by different combinations of NOHMs and secondary fluids. In the way, the NOHMs-based fluids have been granted with a high tunability in carbon capture kinetics, transport and conversion rates. This innovative approach in combined carbon capture and conversion using NOHMs-based fluids is believed to have provided a revolutionary solution to carbon management and to prevent a runaway of climate change.
7.1. Introduction

In response to the urgent climate change challenges (Lin and Park, 2011; Pacala and Socolow, 2004; Vitillo et al., 2017), efficient carbon management with Carbon Capture, Utilization and Storage (CCUS) technologies has been proposed as a promising solution to achieve both zero emission in fossil-burning power plants and negative emission in chemical production sectors. In an effort to reduce the carbon footprints in various industrial sectors, it has been proposed to directly convert the captured CO₂ into chemicals and fuels, using renewable energies, such as wind and solar energy. Various CO₂ conversion routes have been investigated to transform CO₂ into versatile products, including biological (Beer et al., 2009; Savvas et al., 2017; Wong et al., 2014), photochemical (Arai et al., 2010; B. Kumar et al., 2010; Lewis, 2007; Lewis and Nocera, 2006; X. Li et al., 2011; Tatsumi et al., 2017; Yadav et al., 2012; Yamashita et al., 1998), electrochemical (Hori, 2008), inorganic carbonation (Dufaud et al., 2009; Hariharan et al., 2017; A. H. A. Park et al., 2003; Prigiobbe et al., 2009) and thermochemical pathways (Duyar et al., 2015). Thermochemical conversion has been explored with a potential to directly convert the CO₂ captured by a variety of carbon capture materials (Y.-N. Li et al., 2014; Y. Li et al., 2016; Talapaneni et al., 2015; Xie et al., 2013; Z.-Z. Yang et al., 2011), ranging from CaO (Duyar et al., 2015), MOFs (D.-A. Yang et al., 2012), to polyamine (Kothandaraman et al., 2016; McNamara and Hicks, 2014) and nitrogen-substituted amino acids (A. H. Liu et al., 2012).

Electrochemical conversion of CO₂ into value-added products has been thoroughly
studied, with tremendous advances on electrocatalysts and reaction mechanisms. However, fewer studies have been carried out to tackle the critical challenge of the low solubility of CO₂ in the conventional aqueous electrolyte. This has been primarily a result of the independent developments of carbon capture and electrochemical conversion technologies. As shown in Figure 7.1, multiple energy barriers associated with solvent regeneration and CO₂ dissolution/activation need to be overcome in the separate scheme of carbon capture and electrochemical conversion. Thus, a need has been established for the development of novel electrolytes that can both perform carbon capture and host the subsequent electrochemical conversion. In this way, the energy-intensive steps for solvent regeneration, CO₂ compression and transportation can be bypassed. The captured CO₂ can be delivered for subsequent electrochemical conversion with a weaker binding energy in the novel electrolyte. Meanwhile, the binding energy to CO₂ of the novel electrolyte can be tuned, so that the capture kinetics and conversion rate can be further modified. Therefore, a more efficient carbon management system with a reduced energy penalty and carbon footprint can be achieved.
Figure 7.1. Illustration of the energy diagram for (a) separate and (b) combined carbon capture and conversion.

Various novel liquid-state carbon capture materials, including clathrate hydrates, Ionic Liquids (ILs) and Nanoparticle Organic Hybrid Materials (NOHMs) have shown a potential to be coupled with electrochemical conversion of CO$_2$. Clathrate hydrates were utilized as an electrolyte additive, promoting both the CO$_2$ concentration in the electrolyte and the faradaic efficiency of CO production (Deciccio et al., 2015). ILs have been found to exhibit a role of co-catalyst in the electrochemical conversion of the captured CO$_2$ to
various products, including CO (Asadi et al., 2014; Oh and Hu, 2015; Sun et al., 2014; Tanner et al., 2016) and formic acid (Hollingsworth et al., 2015; Huan et al., 2017; Q. Zhu et al., 2016), under ambient conditions.

Nanoparticle/polymer hybrid materials have demonstrated versatile applications in different areas, such as carbon capture (Lin and Park, 2011; Y. Park et al., 2012), the pharmaceutical industry (F. Li et al., 2017; Ling et al., 2014), novel catalysts (Kainz and Reiser, 2014; Mäsing et al., 2017), and battery electrolytes (A. Agrawal et al., 2015; Choudhury et al., 2015). One unique liquid-like nanoscale hybrid material is NOHMs. NOHMs are comprised of polymers tethered onto nanoparticles (e.g. silica) with tunable structures and an outstanding thermal stability (Lin and Park, 2011). Neat NOHMs can achieve a carbon capture capacity of 2.4 mmol/g at 3.4 atm (Lin and Park, 2011), and this value is comparable to that of the 30 wt.% MEA solvents at atmospheric pressure (Kim et al., 2013). In order to lower the high viscosity of NOHMs, similar to other anhydrous carbon capture solvents (e.g., ILs) (Luo et al., 2016; Malhotra et al., 2017), a secondary fluid can be introduced (Petit, Bhatnagar, et al., 2013). Archer et al. developed a series of gel-like NOHMs-based electrolytes for lithium ion batteries, demonstrating promising electrochemical properties and excellent mechanical properties (A. Agrawal et al., 2015; Choudhury et al., 2015; Nugent et al., 2010). Until now, the fundamentals still need to be revealed of liquid-state hybrid solvent systems in combined carbon capture and electrochemical conversion of CO₂.

Therefore, to the best of our knowledge, NOHMs-based fluids are developed as the
first of the liquid-kind nanoscale hybrid solvent system for combined carbon capture and conversion. In this chapter, tunable carbon capture performance of NOHMs-based fluids and identification of different existing forms of carbon are investigated. We also report the first electrochemical conversion of the captured CO$_2$ using this novel hybrid solvent system. Possible mechanisms of how NOHMs assist the carbon capture and conversion are presented. In particular, electrochemical production of CO from the captured CO$_2$ is of interest, since the produced CO can be combined with H$_2$ to form syngas, a useful chemical feedstock for the Fischer-Tropsch process in making synthetic fuels.

7.2. Experimental methods

7.2.1. Design and synthesis of NOHMs

Nanoparticle Organic Hybrid Materials (NOHMs) were designed and synthesized via an ion exchange method as described in Chapter 3 (Lin and Park, 2011; Lin et al., 2014, 2013). Two types of NOHMs were selected for investigation, NOHM-I-PEI and NOHM-I-HPE, as demonstrated in Figure 7.2. To synthesize NOHM-I-PEI, a silica nanoparticle suspension (LUDOX-30, 7 nm, Sigma-Aldrich) was protonated after running through an ion exchange resin column (DOWEX marathon C cation-exchange resin, Sigma-Aldrich). Afterwards, the protonated silica nanoparticle suspension was fully reacted with polyethylenimine (PEI, Mn 1800, Polysciences). The neat NOHM-I-PEI was obtained after drying under vacuum for 24 h.

The synthesis of NOHM-I-HPE began with grafting linker onto silica nanoparticles. The silica nanoparticle suspension was thoroughly reacted with 3-(trihydroxysilyl)-1-
propane-sulfonic acid (SIT, Gelest) after pH adjustment to 5 by adding 1 M NaOH solution. Dialysis was performed to completely remove the unreacted SIT linkers using dialysis tubes (3.5K MWCO, Thermo Scientific). After an ion exchange treatment, the solution was further titrated by polyetheramine (HPE, Mn 2070, Huntsman) for complete tethering. The neat NOHM-I-HPE was ready to use after vacuum drying overnight.

Figure 7.2. Chemical structures of NOHM-I-HPE and NOHM-I-PEI.

7.2.2. Design and synthesis of NOHMs-based fluids

NOHMs were treated under vacuum at 50°C for 3 h before mixing with a secondary fluid, such as DI water. 0.1 M potassium bicarbonate (KHCO₃, Sigma-Aldrich) was also added, considering its good conductivity and compatibility with electrochemical conversion of CO₂ (Hori, 2008). The resultant fluid was stored in an inert environment and
thoroughly mixed under stirring for 3 h before use.

7.2.3. CO₂ capture capacity

Carbon capture capacity was determined via a customized reactor as illustrated in Figure 7.3. NOHMs-based fluids were placed into a sample holder of 30 mm in height, and the holder was then fitted into a sample chamber. The reactor was purged by humid CO₂ for 30 min under ambient pressure and temperature, after which the sample chamber was connected to the CO₂ reservoir. The pressure drop was recorded and the carbon capture capacity was calculated based on the ideal gas law. The CO₂ reservoir was designed with a large enough volume that the concentration gradient of CO₂ from the reservoir to fluids surface could be considered constant.

Figure 7.3. Experimental set-up for carbon capture using NOHMs-based fluids.

7.2.4. Structural characterizations of NOHMs-based fluids

7.2.4.1. NMR characterization

A ¹³C nuclear magnetic resonance (NMR) measurement was conducted with a Bruker 400SL NMR spectrometer. NMR tubes of 5 mm O.D. (Wilmad) were used. 3 wt.% of
NOHMs-based fluids were prepared with dilution by D₂O (Sigma-Aldrich).

7.2.4.2. FTIR characterization

A Thermo Nicolet 6700 Fourier-transform infrared (FTIR) spectrometer with Golden Gate ATR accessory was utilized for the characterization of NOHMs-based fluids. A resolution of 2 cm⁻¹ was chosen with a scanning range of 4000 to 600 cm⁻¹. Every measurement was the average of 18 scans for three trials.

7.2.4.3. TGA characterization

Thermogravimetric Analysis (TGA) was performed using a Setaram Labsys evo analyzer. ~50 mg of sample was placed into alumina crucible. The samples were heated from 20°C to 600°C at 10 K/min under air. The air flow was 20 ml/min. A blank measurement was also conducted to exclude the buoyancy effect on weight change.

7.2.5. Electrochemical conversion of the captured CO₂

A combined CO₂ capture with subsequent electrochemical reduction of CO₂ to CO was performed using NOHMs-based fluids as shown in Figure 7.4. Polycrystalline silver (Hori, 2008) (Sigma-Aldrich) and a non-metallic pyridinic-N doped porous carbon electrode, BAX-M-950 (W. Li et al., 2017), were chosen as cathode. A platinum (Pt) wire was used as the anode. An overpotential of -1.4 V was applied with respect to Ag|AgCl reference electrode. The NOHMs-based fluids were purged with humid CO₂ under stirring for 30 min. The cell was tightly sealed and an electrolysis of the CO₂-loaded NOHMs-based fluids was conducted for 20 min. The cell was connected to a microGC (INFICON) to determine the gaseous products, after which the liquid sample was analyzed using NMR spectrometer.
The integrity of NOHMs-based fluids over multiple cycles of electrochemical treatment was also tested. A fresh Ag electrode was used for each cycle to exclude the effect of electrode degradation on the electrochemical performance.

Figure 7.4. Electrochemical cell for combined carbon capture and conversion using NOHMs-based fluids.

7.3. Results and discussion

7.3.1. CO$_2$ capture by NOHMs-based fluids

As discussed in Chapter 3, NOHM-I-HPE absorbs CO$_2$ via physical interactions between CO$_2$ and the ether groups of the tethered HPE polymers. Physisorption of CO$_2$ reaches equilibrium faster, but the uptake of CO$_2$ is limited. On the other hand, NOHM-I-PEI interacts with CO$_2$ via task-specific amine groups. This chemical interaction results in the formation of carbamate in water-lean conditions, and leads to the production of bicarbonate in humid environments. In this chapter, the carbon capture performance will be investigated mainly through NOHM-I-PEI based fluids under ambient pressure and
temperature, from the perspectives of the concentration of NOHM-I-PEI, the addition of salts and the variation of physical solvents.

7.3.1.1. Effect of the concentration of NOHM-I-PEI

As shown in Figure 7.5(a), the 5 wt.% NOHM-I-PEI based aqueous fluid possessed a lower capture capacity, but a shorter time to reach carbon capture equilibrium. The 30 wt.% NOHM-I-PEI based fluid exhibited a capture capacity of 0.9 mmol/g-fluid at 100 min. However, as the concentration of NOHM-I-PEI further increased from 30 wt.% to 40 wt.% and 50 wt.%, carbon capture kinetics started to decrease. The trend was similar for fluids doped by 0.1 M KHCO₃. The optimal concentration of NOHM-I-PEI was around 30 wt.% in terms of the balance between capture capacity and kinetics. In comparison with the conventional 0.1 M KHCO₃ electrolyte as shown in Figure 7.5(b), the addition of NOHM-I-PEI, even at only 5 wt.%, has greatly increased the capture capacity of the fluids.
Figure 7.5. CO₂ capture using NOHM-I-PEI based aqueous fluids (a) without KHCO₃ and (b) with 0.1 M KHCO₃ at different concentrations of NOHM-I-PEI under atmospheric pressure and at room temperature.

The carbon capture kinetics of NOHMs-based fluids is determined by both the amount of the carbon capture material and the viscosity of the fluids. The relationship between the
initial carbon capture rate and the viscosity of the salt-free NOHMs-based fluids was further investigated as illustrated in Figure 7.6. The critical concentration, labeled as $C^*$ in Figure 7.6, is the concentration at which the overlapping and interactions between NOHMs aggregates start to become significant as defined from Chapter 4. The critical concentration, $C^*$, is marked in a region, ± 10% of the experimentally determined $C^*$ from Chapter 4. The slight reduction in the capture kinetics was observed when the NOHMs loading was changed from 5 wt.% to 20 wt.%$. This was because 20 wt.% loading was close to the critical concentration of NOHM-I-PEI based aqueous fluids, resulting in a much different micro-environment (e.g., viscosity behavior) within the fluids compared to the 5 wt.% sample. As the concentration of NOHM-I-PEI increased from 20 wt.% and 30 wt.% in the range that was beyond the critical concentration, the carbon capture kinetics was enhanced thanks to the increased amount of effective carbon capture materials. However, as the concentration of NOHM-I-PEI further increased, the effect of the increased viscosity dominated the effect of the increased amount of capture materials, thus leading to a reduction in carbon capture kinetics.
Figure 7.6. Initial CO\textsubscript{2} capture rate by salt-free NOHM-I-PEI based aqueous fluids with respect to the fluid viscosity at different concentrations of NOHM-I-PEI at \( t = 50 \) min. The viscosity of the 50 wt.% NOHM-I-PEI based aqueous fluid was calculated based on the data fitting in the determination of critical concentration.

The carbon capture capacity was also normalized by the mass of NOHM-I-PEI as presented in Figure 7.7. It was interesting to find that for both salt-free and salt-present cases, the 5 wt.% NOHM-I-PEI based aqueous fluid exhibited the highest capture capacity and the fastest kinetics of unit mass of NOHMs, and 50 wt.% NOHM-I-PEI based aqueous fluid showed the lowest. It is believed that when the NOHMs loading was as low as 5 wt.%, which was less than the critical concentration \( C^* \) as determined in Chapter 4, more amine sites were available for carbon capture. When the concentration of NOHM-I-PEI increased
to 20 wt.% (C≥C*) and 50 wt.% (C>C*), the formation of the hierarchical structures of NOHMs, as confirmed in Chapter 6, blocked a number of amine sites for carbon capture, leading to the lowered amine efficiency.

Figure 7.7. CO₂ capture normalized by the mass of NOHMs in NOHM-I-PEI based aqueous fluids (a) without KHCO₃ and (b) with 0.1 M KHCO₃ at different concentrations of NOHM-I-PEI under atmospheric pressure and at room temperature.
7.3.1.2. Effect of salt

The effect of salt on the carbon capture performance of NOHMs-based fluids was investigated as shown in Figure 7.8. For 5 wt.% and 20 wt.% NOHM-I-PEI based aqueous fluids, no observable difference was seen until 100 min and 15 min, respectively. However, afterwards, both the carbon capture capacity and capture kinetics witnessed a reduction. The 5 wt.% NOHM-I-PEI based aqueous fluids underwent a less significant reduction compared to the 20 wt.% NOHM-I-PEI based aqueous fluids. Thus, in order to minimize the negative impact of salt on the capture performance using NOHMs-based fluids, a lower concentration of salt and a smaller amount of NOHMs loading are preferred.

The reduction of carbon capture capacity and kinetics is believed to be a result of the interactions between salt ions and NOHMs, as indicated from the NMR study of the interaction between salt ions and NOHMs in Chapter 6. Such interaction may lead to a competition between salt cations, $K^+$, and $CO_2$ to the basic amine sites of NOHM-I-PEI. Additionally, salt may also induce a change of polymer configurations in the system (Rajendran et al., 2007), affecting the carbon capture performance. The salt-induced polymer configuration change needs further investigation.
Figure 7.8. Effect of salt on CO$_2$ capture by NOHMs-based fluids at the concentration of NOHM-I-PEI of (a) 5 wt.% and (b) 20 wt.%.

7.3.1.3. Effect of physical solvent additive

Since N-methyl-2-pyrrolidone (NMP) possesses a tertiary amine in the chemical structure that can interact with CO$_2$, NMP was proposed as a possible fluid additive to further enhance the carbon capture performance of NOHMs-based fluids. Even though
some additional tertiary amines were incorporated into the system, both the carbon capture kinetics and capacity decreased dramatically when the secondary fluid was changed to either water/NMP mixture or pure NMP. As shown in Figure 7.9, the carbon capture capacity of 5 wt.% NOHM-I-PEI based aqueous fluids could reach 0.48 mmol/g-fluids at 300 min, but this carbon capacity at the same time scale decreased to 0.21 mmol/g-fluids and 0.05 mmol/g-fluids when the secondary fluids were water/NMP (1:1) and pure NMP, respectively. Similar behavior was also observed for 20 wt.% NOHM-I-PEI based fluids. The addition of NMP into the NOHMs/water system significantly increased the viscosity of the system as presented in Chapter 4. Thus, a limited mass transfer and the unavailability of amine sites due to a possible formation of a NOHMs-NMP complex accounted for this reduction in carbon capture capacity and sorption kinetics.
Figure 7.9. Effect of NMP on the CO$_2$ capture performance by NOHMs-based fluids at the concentration of NOHM-I-PEI of (a) 5 wt.% and (b) 20 wt.%.

7.3.2. Existing forms of CO$_2$ within NOHMs-based fluids

FTIR was utilized to determine the existing forms of CO$_2$ by analyzing and comparing the absorption peaks of different components in NOHMs-based fluids. As summarized in Table 7.1, within non-aqueous NOHM-I-PEI based fluids, carbamate was detected due to the chemisorption of CO$_2$ by the abundant amine groups on the tethered PEI polymers.
Meanwhile, CO\textsubscript{2} dissolved by physisorption was also present in the system. In the aqueous NOHM-I-PEI based fluids, bicarbonate was formed because of the further reaction between carbamate and water. Carbonate/bicarbonate couple was also detected from the weak interaction between water and CO\textsubscript{2}. However, this reaction can be negligible since the solubility of CO\textsubscript{2} in water is only 34 mmol/L-water at 25\textdegree C and 1 atm (Crovetto, 1991). The pH of NOHM-I-PEI based fluids was measured to be ~11. It was determined that under this pH, carbonate was more prevalent than bicarbonate.

In NOHM-I-HPE based fluids, no carbamate was detected and the existence of other species, such as dissolved CO\textsubscript{2}, was identified to be similar as NOHM-I-PEI. The only amine group on the HPE polymer was used to tether onto the silica nanoparticle and no spare amines were available for the reaction with CO\textsubscript{2}.

Among various forms of carbon dioxide in NOHMs-based fluids, the electrochemical conversion of carbamate has been rarely reported, and the role of the amine functional groups in tuning the reaction is still not definitive (Ertem et al., 2013). Bicarbonate has been investigated for electrochemical conversion to formate (Spichiger-Ulmann and Augustynski, 1985). It was further concluded that dissolved CO\textsubscript{2} was the electroactive species from the dissociation of bicarbonate, and such dissociation was a slow process (Hori and Suzuki, 1983; Zhong et al., 2016). Hori et al. elucidated that when electrochemical conversion was operated in the bicarbonate electrolyte under CO\textsubscript{2} bubbling, the electroactive CO\textsubscript{2} was primarily the dissolved CO\textsubscript{2} from CO\textsubscript{2} bubbling, but not from the dissociation of the existing bicarbonate ions (Hori and Suzuki, 1983).
Indeed, the quantification of each species in NOHMs-based fluids from CO₂ capture is needed in future studies.

Table 7.1. CO₂ existing forms within various NOHMs-based fluids.

<table>
<thead>
<tr>
<th></th>
<th>Aqueous (in H₂O)</th>
<th>Non-aqueous (in mPEG)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOHM-I-PEI</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(CO₂)</td>
<td></td>
<td>(CO₂)</td>
</tr>
<tr>
<td>(HCO₃⁻)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(CO₃²⁻)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Carbamate)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NOHM-I-HPE</td>
<td></td>
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<tr>
<td>(CO₂)</td>
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<td>(CO₂)</td>
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<td>(HCO₃⁻)</td>
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<tr>
<td>(CO₃²⁻)</td>
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</table>

7.3.3. Combined carbon capture and conversion to CO

NOHM-I-HPE based aqueous fluids, doped by 0.1 M KHCO₃, were chosen for this particular combined carbon capture and conversion study. The following considerations have been made: (1) dissolved CO₂ via physisorption has been identified as the primary electroactive species, (2) water is able to provide protons for electrochemical conversion and is miscible with NOHM-I-HPE, and (3) 0.1 M has been determined as the optimal
concentration for KHCO₃ to promote the electrochemical conversion of CO₂ (Zhong et al., 2017).

A loading of 5 wt.% NOHM-I-HPE was selected because 5 wt.% is smaller than the critical concentration of NOHM-I-HPE based aqueous fluid so that significant overlapping of NOHMs could be avoided as mentioned in Chapter 4, and salt has a minimal impact on the carbon capture performance at this NOHMs loading.

In order to produce CO, two types of cathodes were employed. One selected cathode was polycrystalline silver electrode (Hori, 2008). Silver has been found to be selective towards CO production due to that it has a weak binding energy to the reaction intermediate (CO) (Hori, 2008; Kortlever et al., 2015). The other selected cathode was a pyridinic-N doped porous carbon electrode, BAX-M-950, which has also proven selective on the electrochemical conversion of CO₂ to CO (W. Li et al., 2017). Both cases were investigated using the 5 wt.% NOHM-I-HPE based aqueous fluid in comparison with the conventional 0.1 M KHCO₃ electrolyte.

When polycrystalline silver was used as the electrocatalyst, CO was the major gaseous product. As presented in Table 7.2, the average CO production rate using NOHM-I-HPE based fluid was $2.4 \times 10^{-10}$ mol/s at the current density of -1.33 mA/cm², and the H₂/CO ratio was 24. In contrast, 0.1 M KHCO₃ electrolyte exhibited an average CO production rate of $1.5 \times 10^{-10}$ mol/s and a H₂/CO ratio of 28. This 60% improvement for CO production and the reduced H₂/CO ratio were achieved with the addition of only 5 wt.% NOHM-I-HPE in a closed reactor system. Further modification of the H₂/CO ratio can be
realized with the reverse water gas shift reaction and H₂/CO separation to adjust the needed syngas ratio for synthetic fuel production via Fischer-Tropsch reactions.

It is worth noting that this electrochemical conversion experiment was carried out without continuous CO₂ bubbling. After CO₂ saturation in NOHMs-based fluids, the electrolysis was conducted with a tightly sealed electrochemical cell to ensure that the converted CO₂ was from the captured CO₂. Thus, the reaction rate was limited compared to other works that focused on electrocatalysis with continuous CO₂ bubbling (Hori, 2008). Indeed, this production rate of CO needs further improvements with the advancement in electrocatalysts, the enhanced mass transfer of CO₂ from the bulk fluid to the electrode surface, and the coupling with the continuous CO₂ bubbling during electrolysis.

An alteration in reaction selectivity was observed on the pyridinic-N doped porous carbon electrode, BAX-M-950. When NOHM-I-HPE based fluids were employed, the faradaic efficiency for CH₄ production remained similar, but the faradaic efficiency for CO production was significantly suppressed from 24% in 0.1 M KHCO₃ electrolyte (W. Li et al., 2017) to 1.0% in NOHM-I-HPE based aqueous fluid.
Table 7.2. Electrochemical reduction of CO$_2$ on polycrystalline Ag (1.35 cm$^2$) and pyridinic-N doped porous carbon electrode (W. Li et al., 2017) at -1.4 V (vs Ag|AgCl)

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Polycrystalline Ag</th>
<th>Pyridinic-N doped porous carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrolyte</td>
<td>Average CO production rate [mol/s]</td>
<td>Faradaic efficiency of CO [%]</td>
</tr>
<tr>
<td>0.1 M KHCO$_3$</td>
<td>$1.5 \times 10^{-10}$</td>
<td>28</td>
</tr>
<tr>
<td>5 wt.% NOHM-I-HPE based aqueous fluids</td>
<td>$2.4 \times 10^{-10}$</td>
<td>24</td>
</tr>
</tbody>
</table>

7.3.4. Integrity of NOHMs-based fluids over multiple cycles

In Chapter 5, the electrochemical stability of NOHMs-based fluids was determined in the absence of CO$_2$ reduction. In this chapter, three consecutive cycles of combined carbon capture and conversion on polycrystalline silver electrode were carried out to test the integrity of NOHM-I-HPE based aqueous fluids. FTIR and TGA were employed to characterize the re-dried fluids as shown in Figure 7.10. It demonstrates that structural changes barely occurred to NOHM-I-HPE based fluids after carbon capture and subsequent electrochemical treatments. The absorption peaks at 1630 cm$^{-1}$ and 1530 cm$^{-1}$ in the FTIR spectrum and the maintained decomposition temperature up to ~300°C depicted that the ionic bonding between the HPE polymers and the linkers on nanoparticle surface still remained intact.

NMR was conducted for bulk fluids as presented in Figure 7.11. It can be inferred that NOHMs-based fluids stayed intact without any observable changes in chemical shifts. The
peak at 161 ppm corresponded to the bicarbonate ion of the salt, and the peaks from 10 to 80 ppm were identified to be from NOHM-I-HPE.

The impact of O\(_2\) (air) on NOHM-I-HPE during the electrochemical conversion of CO\(_2\) was also evaluated with air bubbling. The electrochemical conversion was still able to proceed without observable structural changes of NOHM-I-HPE. With this integrity, electrochemical conversion of CO\(_2\) can be realized without damaging NOHM-I-HPE.

On the other hand, NOHM-I-PEI is able to increase the CO\(_2\) solubility to a higher value than NOHM-I-HPE, but a number of challenges exist for NOHM-I-PEI based fluids with the current single-cell electrochemical set-up. First, electrochemical conversion of the carbamate, as a result of chemical reaction between NOHM-I-PEI and CO\(_2\), is difficult and has been rarely reported. Second, a possible degradation of NOHM-I-PEI was indicated from the color change to yellow after electrolysis for 20 min. It is believed that the tethered PEI polymers are subject to the reaction with the O\(_2\) from the oxygen evolution reaction on the anode.
Figure 7.10. (a) FTIR spectrum and (b) TGA plot for the re-dried NOHM-I-HPE based aqueous fluids over 3 cycles of combined carbon capture and subsequent electrochemical conversion on polycrystalline silver.
7.3.5. Roles of NOHMs in capture and electrochemical conversion of CO$_2$

The NOHMs-mediated carbon capture and conversion are evaluated in terms of CO$_2$ concentration, pH of the fluids and the formation of a possible complex between a certain reaction species and NOHMs.

The incorporation of NOHMs is able to increase the CO$_2$ solubility in the electrolyte. A 5 wt.% NOHM-I-PEI based aqueous fluid has demonstrated a CO$_2$ solubility (0.46 mmol/g-fluids) that is 10 times higher than that of the 0.1 M KHCO$_3$ electrolyte (0.044 mmol-CO$_2$/g-fluids) as shown in Figure 7.12. Even with the addition of 5 wt.% NOHM-I-HPE, designed for physisorption of CO$_2$, the dissolved CO$_2$ concentration in the bulk can be increased to 0.052 mmol-CO$_2$/g-fluids, higher than that for 0.1 M KHCO$_3$ electrolyte,
and 0.034 mmol-CO$_2$/g-fluids for pure water (Crovetto, 1991) at room temperature. However, the local concentration of CO$_2$ near the electrode surface is still to be determined using specific techniques, such as NMR spectroscopy.

The pH value of the fluid will affect the availability of protons for the electrochemical conversion of CO$_2$. For example, the pH of the 5 wt.% NOHM-I-HPE based aqueous fluid doped by 0.1 M KHCO$_3$ was measured to be around 8.51, similar to the 8.47 value of the 0.1 M KHCO$_3$ electrolyte, as shown in Figure 7.12. On the other hand, the pH value of a 5 wt.% NOHM-I-PEI based aqueous fluid is around 10.41, and this higher pH value might limit the proton supply for the electrochemical conversion of CO$_2$ to hydrogenated products. Meanwhile, the interactions between protons and NOHMs might also result in a more basic local environment close to the electrode.

![Figure 7.12. Solubility of CO$_2$ and pH of various solutions. N_HPE stands for NOHM-I-HPE. N_PEI stands for NOHM-I-PEI. The NOHMs-based fluids were loading by 5 wt.% NOHMs and doped by 0.1 M KHCO$_3$.](image-url)
The possible complexation of a certain reaction species by NOHM-I-HPE in mediating the electrochemical conversion of CO$_2$ is proposed based on (1) the CO$_2$ electrochemical reaction pathways (Gattrell et al., 2006), and (2) how ILs can co-catalyze this reaction (Lim and Kim, 2017). A number of researchers have attempted to clarify the electrochemical reaction mechanisms of CO$_2$ (Gattrell et al., 2006; Kortlever et al., 2015; Schouten et al., 2011), as depicted in Figure 7.13. The interaction between the carbon atom of $CO_2$ (CO$_2^-$) and the copper electrode surface leads to the production of CO and other products (Gattrell et al., 2006; Kortlever et al., 2015; Schouten et al., 2011). Meanwhile, when oxygen atoms are interacting with the electrocatalysts, formate is expected to form (Gattrell et al., 2006; Kortlever et al., 2015; Schouten et al., 2011).

Figure 7.13. Reaction pathways for electrochemical conversion of CO$_2$ (Gattrell et al., 2006; Kortlever et al., 2015; Schouten et al., 2011).

As shown in Figure 7.14, a NOHM$s$-CO$_2$ complex can be formed within the boundary layer. The interactions between the carbon atom of the reaction species $CO_2$ (CO$_2^-$) and the ether groups on NOHM-I-HPE are believed to promote a certain reaction pathway and inhibit other reaction routes. This complexation within the boundary can occur through a
single NOHM at an extremely low concentration of NOHMs, or through the NOHMs aggregation at higher concentrations. Such complexation has also been observed in ILs-assisted electrochemical conversion of CO₂. An anion-CO₂ complex was proposed by Snuffin et al. in an EMIMBF₃Cl-based electrolyte (Snuffin et al., 2011). The CO₂ in the BF₃-CO₂ complex exhibited a longer C=O bond length, and this weakened C=O bond was believed to facilitate the subsequent electrochemical conversion. Rosen et al. suggested that an EMIM-CO₂ complex was able to lower the activation energy of the reaction pathway for CO production with the mediation of [EMIM][BF₄] (Rosen et al., 2011). It was further found that the EMIM⁺ cation could stabilize the CO₂⁻ intermediate and inhibit the dimerization of CO₂, thus promoting the production of CO (Sun et al., 2014; Yuanqing Wang et al., 2015).

Another possibility, as illustrated in Figure 7.14, was that the captured CO₂ would desorb first from NOHM-I-HPE at the boundary layer and then diffuse to the catalyst surface. The distance from the desorption position to the catalyst surface and the readiness of desorption are supposed to influence the subsequent electrochemical conversion of the desorbed CO₂. This two-step mechanism was also proposed by Tanner et al. in the roles of ILs in electrochemical conversion of CO₂ (Tanner et al., 2016).
It is believed that the dominance of the two schemes can be tuned by the types and concentrations of NOHMs. A higher concentration of the NOHMs, that have a higher affinity to CO$_2$, is supposed to induce a higher possibility of the formation of a NOHMs-CO$_2$ complex. Indeed, the relative contributions of the two mechanisms at different conditions will be investigated in the future work.

7.4. Conclusions

Nanoparticle Organic Hybrid Materials (NOHMs)-based fluids were designed for combined carbon capture and conversion. The carbon capture performance can be tuned by the concentration of NOHMs, and the presence of salt and physical solvents. It was determined that the 30 wt.% NOHM-I-PEI based aqueous fluid exhibited an optimal
balance between sorption kinetics and capture capacity. A combined carbon capture and conversion using NOHMs-based fluids was carried out in order to produce syngas under polycrystalline silver. With the addition of only 5 wt.% NOHM-I-HPE, the production of CO was enhanced by 60% compared to 0.1 M KHCO$_3$ electrolyte. On the other hand, when a pyridinic-N doped porous carbon electrode was used, the production of CO was greatly suppressed. The NOHM-I-HPE based fluid has also exhibited excellent robustness over multiple cycles of combined carbon capture and electrochemical conversion. It was determined that the incorporation of NOHMs could lead to an increased concentration of CO$_2$ in the fluid with a tunable pH adjustment. Additionally, NOHMs might also form a complex with the reaction species $\text{CO}_2$ ($\text{CO}_2^-$) to further influence the reaction pathways. This novel study of combined carbon capture and conversion using nanoscale hybrid aqueous fluids under ambient conditions will be followed by a further improvement of fluids design, a better compatibility of electrocatalysts and a deeper understanding of the reaction mechanism.

In this scenario, carbon capture can be pulled by the electrochemical conversion. By tuning the structures of NOHMs-based fluids, the binding energy to CO$_2$ and the existing forms of carbon can be altered and selected, and thus the carbon capture kinetics, transport and conversion rate can be accordingly modified and controlled. NOHMs-based fluids are believed to have provided to an innovative pathway for carbon management with a potentially reduced energy penalty and carbon footprint.
Chapter 8

Encapsulation of Nanoscale Hybrid Materials for Carbon Capture with Enhanced Mass Transfer

This chapter is based on the following manuscripts to be submitted:

“Fabrication and characterization of encapsulated NOHMs for CO$_2$ capture with enhanced mass transfer” (Wei Yu, Ming Gao, Tao Wang, and Ah-Hyung Alissa Park)

“Encapsulation of Nanoscale Hybrid Materials in a Lab-on-chip Device for Carbon Capture” (Wei Yu, Dongyang Wang, Ming Gao, Tao Wang, Kun Liu, Qiao Lin, and Ah-Hyung Alissa Park)
Abstract

An alternative way of utilizing NOHMs and NOHMs-based fluids in carbon capture will be introduced in this chapter. The high viscosity of neat NOHMs, and the relative higher viscosity of NOHMs-based fluids compared to MEA-based solvents are subject to a resulting mass transfer in carbon capture. Thus, the microencapsulation of NOHMs and NOHMs-based fluids with a high specific surface area is proposed using a micro-capillary device. The CO₂ absorption kinetics using encapsulated NOHMs-based fluids has been improved by 30 times compared to non-encapsulated NOHMs-based fluids. Furthermore, cyclic tests of CO₂ absorption and desorption of dried encapsulated NOHMs present a maintained CO₂ capture capacity. The microencapsulation of NOHMs and NOHMs-based fluids has provided an alternative approach in making use of the highly viscous water-lean solvents, which is promising in scaling up with various reactor systems, such as the fluidized bed reactor.
8.1. Introduction

The continuously increasing anthropogenic CO₂ emission has caused a pressing climate change concern, and worldwide researchers are developing various technologies and protocols to tackle this urgent challenge. Carbon Capture, Utilization and Storage (CCUS) has been proposed as a global effort to realize efficient carbon management. Amine-based aqueous solvents, such as monoethanolamine (MEA) (Alie, 2004; Gouedard et al., 2012; Rochelle, 2009; Voice, 2013), have been utilized in post-combustion CO₂ capture with a high capture capacity and fast sorption rate. However, the CO₂ capture process with amine scrubbing technology is energy-intensive, primarily due to the energy consumption by the large amount of water. Therefore, water-lean carbon capture solvents have been designed and developed (Heldebrant, Koech, Glezakou, et al., 2017), such as Ionic Liquids (ILs) (Bates et al., 2002; H. Davis, Jr., 2004; Jianmin Zhang et al., 2006; X. Zhang, Zhang, Dong, Zhao, Zhang, Huang, et al., 2012), CO₂BOLs (Heldebrant et al., 2011, 2009; Heldebrant, Koech, Ang, et al., 2010; Mathias et al., 2013; Phan et al., 2008), and Nanoparticle Organic Hybrid Materials (NOHMs) (Lin and Park, 2011; Lin et al., 2013; Y. Park et al., 2012; Petit et al., 2012). These water-lean solvents have exhibited a smaller specific heat capacity and a lower vapor pressure than water. Moreover, a high degree of freedom in molecular design and system innovation can be achieved thanks to the chemical tunability of these water-lean solvents.

Liquid-like Nanoparticle Organic Hybrid Materials (NOHMs) are a novel class of nanoscale hybrid materials, designed for various applications, such as CO₂ capture.
NOHMs have shown excellent thermal stability, near zero vapor pressure and high chemical tunability (Lin and Park, 2011; Petit, Lin, et al., 2013). Yet, NOHMs, similar to other anhydrous carbon capture solvents, share a high viscosity (Heldebrant, Koech, Rousseau, et al., 2017) up to $10^4$ cP (Petit, Bhatnagar, et al., 2013). In previous chapters, NOHMs-based fluids have been developed with tunable carbon capture kinetics. However, the viscosities of NOHMs-based fluids were measured still to be higher than that of the conventional amine-based carbon capture solvents, such as MEA-based solvents (Amundsen et al., 2009). A high viscosity can lead to limited mass transfer in CO$_2$ capture and compromise the applications of the materials in conventional reactors such as a bubbling reactor (Crowther and Henion, 1985).

Microencapsulated sorbents are a new class of gas separation materials consisting of (1) liquid solvents for carbon capture and (2) a polymer shell, such as silicone polymers (Stolaroff et al., 2016) equipped with an excellent CO$_2$ permeability and mechanical strength. The encapsulation of viscous solvents can provide the liquid solvents with the physical behavior of solid sorbents (Vericella et al., 2015). Low viscosity solvents, such as carbonate solutions (Vericella et al., 2015), have been successfully encapsulated (Utada et al., 2005), demonstrating a rapid CO$_2$ absorption and desorption rate thanks to the remarkably increased liquid-gas contact area (Stolaroff et al., 2017; Vericella et al., 2015). However, the encapsulation of highly viscous solvents, such as NOHMs and NOHMs-based fluids, is challenging, regarding the flow behavior of a highly viscous liquid inside the micro-capillary tubes.
The particular interest of this chapter is to realize the encapsulation of NOHMs and NOHMs-based fluids with enhanced mass transfer for carbon capture. A micro-capillary device is developed to accomplish the encapsulation of highly viscous CO$_2$ capture solvents, NOHMs-based fluids. The encapsulated NOHMs have presented good thermal stability. The CO$_2$ capture kinetics has been greatly improved with excellent recyclability. It is believed that the encapsulation of NOHMs is a novel approach to efficient CO$_2$ capture, and can be potentially utilized in large scale applications, such as fluidized bed reactor systems (Raksajati et al., 2017).

8.2. Experimental methods

8.2.1. Materials

LUDOX SM-30 Silica (7 nm, silica suspension, Sigma-Aldrich) and branched polyethylenimine (PEI Mn 1800, Polysciences) were used for NOHM-I-PEI synthesis. NOHM-I-PEI based fluids were prepared by dispersing neat NOHM-I-PEI in DI water to prepare 10-40 wt.% NOHMs-loading solutions serving as the core of the capsules.

A photopolymerizable silicone (TEGO RAD 2650, EVONIK) mixed with 1 wt.% photoinitiator (Irgacure 1173, Sigma-Aldrich) was used as the shell material for capsule fabrication. The outer carrier fluid was made of 40 wt.% of glycerol (>99%, Sigma-Aldrich) and 60 wt.% of poly(vinyl alcohol) (1 wt.%, PVA, Sigma-Aldrich) aqueous solution.

8.2.2. Synthesis of NOHMs and NOHMs-based fluids

NOHM-I-PEI is chosen for investigation in this chapter since the tethered PEI polymers contain abundant amine functional groups, suitable for a fast uptake of CO$_2$ via
chemisorption. The chemical structure of NOHM-I-PEI is shown in Figure 8.1. Based on the previously developed synthesis methods as mentioned in Chapter 3 (Lin and Park, 2011), proton exchange was performed for a diluted silica nanoparticle suspension to exchange the sodium ions on silica nanoparticle surface with protons. Diluted PEI solution was then added dropwise into the protonated silica nanoparticle suspension under vigorous stirring. Neat NOHM-I-PEI was obtained and ready to use after H₂O and CO₂ removal at 50°C under vacuum for 3 hours.

The NOHM-I-PEI based aqueous fluid was manufactured based on the methods described in Chapter 3. After vacuum drying for 3 h, NOHM-I-PEI was mixed with water at various ratios under vigorous stirring.

![Chemical structure of NOHM-I-PEI](image)

**Figure 8.1.** The chemical structure of NOHM-I-PEI.

8.2.3. Encapsulation of NOHM-I-PEI based fluids

Encapsulated NOHMs-based fluids were produced using a micro-capillary device, as illustrated in Figure 8.2. The device was comprised of an outer square tube (CAT# 8290-100, VitroCom) and two inner round tubes (CAT# CV7087-B-100, VitroCom). The exit tip
of the inner tube was controlled to be 100-150 μm (Utada et al., 2005) by a laser puller.

Encapsulated NOHMs-based fluids were produced through the co-flow of inner, shell, and outer fluids in the device at varying flow rates from 200 to 5000 μL/h. The co-flow of inner and shell fluids was pinched off by the outer fluid. The microcapsules were then cured for 10 s under UV light of 302 nm wavelength (Pierce 3UV Lamp, Thermo Scientific). The as-fabricated NOHMs capsules were collected in a vial with diluted outer fluids to reduce osmotic swelling and shrinking. The capsules can be preserved for several months without observable deformation and NOHMs leakage. The size of the capsules was around 440 μm, and the volume ratio of the shell material to core was around 2:3.

It is known that the average diameter of a single NOHM-I-PEI is around 10 nm, whereas the size of the NOHMs aggregation is even larger as discussed in Chapter 6. Therefore, the nano-porous structure of silicone polymer is able to confine the NOHM-I-PEI inside of the capsules.

Figure 8.2. Experimental set-up for the encapsulation of NOHMs-based fluids.
8.2.4. Thermal stability of the encapsulated NOHMs-based fluids

A Labsys evo thermogravimetric analyzer (TGA) was employed to study the thermal stability of encapsulated NOHMs-based fluids. ~25 mg of the capsules was placed into the Al₂O₃ crucible. The samples were heated from 20°C to 900°C at 10 K/min. The balancing gas was N₂ at a flow rate of 20 ml/min.

8.2.5. CO₂ capture performance of encapsulated NOHMs-based fluids

The CO₂ capture performance of encapsulated NOHM-I-PEI based fluids was measured via a customized ambient pressure reactor system as shown in Figure 8.3, modified from the reactor design described in Chapter 7. The reactor was first purged by water-saturated CO₂ for 30 min. About 0.3 g of sample was placed in a four-layer mesh sample holder. The sample holder was then sealed into the reactor after CO₂ purging was complete. The valves were carefully controlled to ensure that the inside total pressure was equal to ambient pressure. A pressure transducer was used to monitor the pressure drop. The recorded pressure change was then translated to carbon capture capacity based on the ideal gas law. The CO₂ reservoir was designed with a volume far exceeding the volume of the sample holder so that the mass transfer limit of the gaseous CO₂ from the reservoir to the samples can be negligible.
The recyclability of encapsulated NOHMs in carbon capture was determined using a Labsys evo thermogravimetric analyzer (TGA). Encapsulated NOHMs-based fluids were dried first under N₂ to remove all water so that only NOHM-I-PEI remained inside the capsules. CO₂ absorption was performed at 40°C with pure CO₂ flow at 16 ml/min for 1 h. After absorption, the temperature was increased to 100°C at 10 K/min and the carrier gas was switched to N₂ at the flow rate of 20 ml/min. The sample was kept at 100°C for 1 h, followed by cooling to 40°C at 10 K/min for the next cycle. 15 cycles of carbon absorption and desorption were performed. A blank experiment using only shell material was also conducted to subtract the amount of CO₂ captured by the shell materials.

### 8.3. Results and discussion

#### 8.3.1. Thermal stability

To evaluate the thermal stability of the encapsulated NOHMs, TGA was performed for
the encapsulated 10 wt.% NOHM-I-PEI based aqueous fluid and pure shell material, respectively. Figure 8.4 shows that the shell material can stay stable up to 300°C before decomposition. Residues were left after the sample was heated to 900°C, which was believed to be Si-based materials from silicone. For the encapsulated NOHM-I-PEI based fluids, the first weight loss up to 160°C corresponded to water loss within the capsules. The subsequent gradual weight loss was attributed to the decomposition of NOHM-I-PEI. After 300°C, the weight loss came from the decomposition of both the shell material and NOHM-I-PEI. This excellent thermal stability has enabled these NOHMs capsules to be used for high temperature regeneration processes with the temperature generally lower than 150°C (T. Wang et al., 2017).

Figure 8.4. TGA results of the encapsulated 10 wt.% NOHM-I-PEI based aqueous fluids and the shell material.
8.3.2. CO$_2$ capture performance

The encapsulated NOHMs-based fluids showed a remarkable advantage over the non-encapsulated NOHMs-based aqueous solution in terms of CO$_2$ absorption kinetics. As shown from Figure 8.5, the CO$_2$ saturation time of the encapsulated NOHMs-based fluids was 30 times shorter. Encapsulation of NOHMs-based fluids imposed a negligible impact on the CO$_2$ capture capacity, in that a 4.6 mmol CO$_2$/g-NOHM-I-PEI capture capacity was reached for both carbon capture systems. The improved CO$_2$ capture kinetics of the encapsulated NOHMs-based fluids was primarily due to the enhanced specific surface area compared with the liquid bulk.

![Figure 8.5. CO$_2$ capture by encapsulated and non-encapsulated 20 wt.% NOHM-I-PEI based aqueous fluids.](image)
8.3.3. Recyclability of CO₂ absorption and desorption

The recyclability of dried encapsulated NOHM-I-PEI in carbon capture and desorption was tested via TGA between 40°C (dry CO₂) and 100°C (dry N₂) for multiple cycles as shown in Figure 8.6. A 0.37 mmol CO₂/g-NOHM-I-PEI capacity was attained for the 40 wt.% NOHM-I-PEI in capsules. This was lower than that of the encapsulated 40 wt.% NOHM-I-PEI based fluids due to the fact that the water-lean case had reduced mass transfer in carbon capture compared to the water-rich case, and tertiary amines were not able to react in water-free conditions. After 15 cycles, the capture capacity was maintained, demonstrating an excellent recyclability and stability of the capsules.

![Figure 8.6. Recyclability of CO₂ capture using dried 40 wt.% encapsulated NOHMs.](image)

8.4. Conclusions

Encapsulated NOHM-I-PEI based aqueous fluids have been achieved for the first time
using a micro-capillary device. This is pioneering in the encapsulation of highly viscous liquids, with excellent thermal stability. Enhanced mass transfer has been observed in carbon capture kinetics compared to non-encapsulated NOHM-I-PEI based fluids, thanks to the increased specific surface area of the capsules. The dried encapsulated NOHM-I-PEI exhibited a robustness in carbon capture over multiple cycles. With this innovative approach in carbon capture, the encapsulated NOHMs can be fit into different reactor systems (e.g., fixed bed and fluidized bed) with tunable parameters.

The encapsulation of NOHMs-based fluids has further enriched the application of NOHMs as a dual-purpose reactive medium for combined carbon capture and conversion. The encapsulated NOHMs-based fluids are believed to have provided a transformative route to address the challenges in CCUS.
Chapter 9

Conclusions and Future Work

9.1. Conclusions

In this study, a novel nanoscale hybrid solvent system is designed and investigated for combined carbon capture and electrochemical conversion. The fundamental properties, hierarchical structures, transport phenomena, and resultant carbon capture and conversion performance are systematically investigated.

Two types of Nanoparticle Organic Hybrid Materials (NOHMs), NOHM-I-PEI and NOHM-I-HPE, were designed and synthesized, illustrative of two major carbon capture modes (e.g., chemisorption and physisorption). In order to tackle the high viscosity challenge of NOHMs, NOHMs-based fluids were developed by mixing NOHMs with a secondary fluid (e.g., water and mPEG), doped by salts (e.g., KHCO₃ and LiTFSI).

The impacts of CO₂ loading on the fundamental physical and chemical properties of NOHMs-based fluids were evaluated. It was found that the CO₂ loading resulted in an increase in the densities of NOHMs-based fluids, and such increase was more significant in NOHM-I-PEI based fluids. This was primarily because, with the similar molecular weights of PEI and HPE polymers, NOHM-I-PEI captured CO₂ via amine-functional groups, leading to a higher capture capacity. For NOHM-I-PEI based aqueous fluids, the loading of CO₂ also induced an increase in the specific heat capacity and a decrease in the viscosity, as a result of a possible formation of intra-molecular hydrogen bonds. On the
contrary, NOHM-I-HPE based aqueous fluids witnessed a reduction in the specific heat capacity and a minimum viscosity change after carbon capture.

The different chemistries of the two NOHMs-based aqueous fluids were further investigated in terms of the viscosity-based mixing behavior. A non-linear increase of viscosity was observed with the increasing concentration of NOHMs, indicating an interaction between NOHMs in the system. NOHM-I-HPE aqueous fluids also exhibited a much higher viscosity than NOHM-I-PEI based fluids at the same mass loading of NOHMs. For example, the viscosities of NOHM-I-PEI and NOHM-I-HPE based aqueous fluids at 30 wt.% NOHMs loading were 22.6 cP and 395 cP, respectively. Such non-linear behavior was characterized by critical concentration, $C^*$. The critical concentration of NOHM-I-HPE based aqueous fluids was 0.1918 g/ml, lower than that of NOHM-I-PEI based aqueous fluids, 0.2415 g/ml. The intrinsic viscosity of NOHM-I-HPE based aqueous fluids was determined to be 9.76 ml/g, higher than that of NOHM-I-PEI based aqueous fluids, 7.65 ml/g. The results implied that the addition of NOHM-I-HPE into water would lead to a more significant contribution of viscosity to the system.

The conductivities of NOHMs-based fluids were found to be inversely related to the concentration of NOHMs. In addition, ionic conductivity of NOHMs-based aqueous fluids was measured to be orders of magnitude higher than that of NOHMs-based mPEG fluids. This indicated that salt ions might migrate through differing dominant mechanisms in different secondary fluids.

An unexpected enhancement in ionic conductivity was observed for NOHMs-based
fluids compared to untethered polymer-based fluids. For example, the conductivities for NOHM-I-PEI/water and PEI/water system at 50 wt.% loading of NOHMs and PEI were 15 mS/cm and 0.91 mS/cm, respectively. After comparing the adjusted conductivity of untethered polymer-based fluids and resolving the relative tortuosity of ion transport, it was hinted that the ionic conductivity in NOHMs-based fluids was not only connected to the viscosity effect, but it was also hypothesized to be related to a unique multi-scale structure in the system that allowed faster ion migration compared to untethered polymer-based fluids.

With this structural hypothesis, an ultra-small-angle X-ray scattering (USAXS) measurement was performed for NOHMs-based fluids to probe into this unique structure from large scale agglomerate to mid-scale aggregate, and to small scale inter-NOHMs distance (center to center). This hierarchical structure was highly tunable by changing different NOHMs and secondary fluids, and the concentrations of NOHMs.

The diffusion behavior under such multi-scale structures was then studied. Surprisingly, for certain NOHMs-based fluids, such as 10 wt.% NOHM-I-HPE based aqueous fluids, the diffusion coefficient of water was $3.43 \times 10^{-9}$ m$^2$/s, which was even higher than that of DI water, $2.99 \times 10^{-9}$ m$^2$/s. This indicated that some channels were formed by NOHMs, enabling a faster local diffusion rate of water. This diffusion behavior also confirmed the hierarchical structure of NOHMs-based fluids.

With the hierarchical structural information and diffusion behavior, it is speculated that ions primarily move in two regions of NOHMs-based fluids, NOHMs-rich region and
secondary fluids-rich region. Ions can diffuse in the secondary fluids, such as in water, through the channels formed by NOHMs, and meanwhile ions can also hop through NOHMs with a unique tortuosity in NOHMs-based mPEG fluids. Decoupled ion migration from structural relaxation is also hypothesized to facilitate the ion hopping in the NOHMs-rich region. The exact size of such channels, the relative contributions of different ion migration pathways, and the degree of decoupling of ion transport from structural relaxation are still to be determined.

The tunable carbon capture performance was then evaluated for NOHMs-based fluids, primarily through NOHM-I-PEI based aqueous fluids. The sorption kinetics was found to be dependent on both the amount of NOHMs and the viscosity of the fluids. A 30 wt.% NOHM-I-PEI based aqueous fluid has demonstrated an optimal balance between capture capacity and sorption kinetics. As the concentration of NOHM-I-PEI further increased beyond 30 wt.%, the sorption kinetics decreased due to the increased viscosity of the system. It was also found that the presence of salt has imposed a minimal impact on the capture performance in the initial 100 min for 5 wt.% NOHM-I-PEI based aqueous solutions but would lead to a more significant reduction in capture capacity and kinetics at higher NOHMs loadings. This was partially attributed to the competition between the salt cations and CO$_2$ to the amine sites in NOHM-I-PEI. Lastly, the addition of physical solvents, NMP, greatly suppressed capture capacity and reduced the sorption kinetics of NOHMs-based fluids, hypothesized to be a result of a complexation between NMP and NOHMs in the fluids.
The existing forms of CO\textsubscript{2} in NOHMs-based fluids were also determined and it was identified that dissolved CO\textsubscript{2} by physisorption was the electroactive species for electrochemical conversion of CO\textsubscript{2}. NOHM-I-HPE based aqueous fluid was then selected for the study of combined carbon capture and electrochemical conversion.

In order to produce CO, two types of electrocatalysts were employed, polycrystalline silver and a pyridinic-N doped porous carbon electrode, BAX-M-950. In comparison with 0.1 M KHCO\textsubscript{3} electrolyte, an enhancement of CO production by 60% in 20 min was observed on polycrystalline silver, and a suppression of CO production was detected on BAX-M-950 electrode using 5 wt.% NOHM-I-HPE based aqueous fluids.

These phenomena were evaluated based on the roles of NOHMs in carbon capture and conversion. In addition to the CO\textsubscript{2} concentration increase and a slight pH change of the electrolyte, it was hypothesized that certain reaction species can be complexed by NOHMs to promote CO production on polycrystalline silver and alter the reaction selectivity on the carbon-based electrode.

In the last section, another way of utilizing NOHMs and NOHMs-based fluids was investigated through encapsulation. It was found that the capture kinetics was enhanced for encapsulated NOHMs-based fluids compared to non-encapsulated NOHMs-based fluids, through the creation of an increased specific surface area for CO\textsubscript{2} capture.

9.2. Future work

The mixing behavior is fundamentally important in designing and developing the next generation NOHMs-based fluids. A wider selection of grafted polymers, secondary fluids,
and nanoparticle sizes will be conducted to deepen the understanding of the mixing rule of nanoscale hybrid materials in various solvents. A survey will be performed to identify what are the good solvents, poor solvents, and non-solvents for different kinds of NOHMs.

The evolution of the hierarchical structures of NOHMs-based fluids will be investigated to further understand the mixing rule. In-situ USAXS measurement is proposed to resolve the real-time structural information of NOHMs-based fluids at different loading of secondary fluids, such as water. A customized in-situ cell for USAXS measurements will be designed to ensure a complete mixing of NOHMs with real-time added secondary fluids.

The polymer configuration in NOHMs is one critical factor in understanding how the structures develop in NOHMs-based fluids, and in resolving the unique pathways of ion and CO$_2$ transport. The configurations of the tethered polymers (e.g., stretched and contracted, folded and coiled), the length of the tethered polymers at different compositions, and how the adjacent tethered polymers interact will be investigated for a model NOHMs-based fluid using small-angle neutron scattering (SANS).

After a more profound mixing rule of NOHMs-based fluids is revealed, a quantification of the ion migration in NOHMs-based fluids and a quantification of carbon capture and diffusion in NOHMs-based fluids are needed.

In terms of ion migration, the relative contributions of the ion transport through the NOHMs-rich region and secondary fluids-rich region will be investigated. This study can be related to the diffusion behavior study using pulsed field gradient (PFG) NMR. The time
scale of structural relaxation of NOHMs, diffusion rates of secondary fluids, and the degree of decoupling of ion transport from structural relaxation are to be determined via specific techniques, such as broad-band dielectric spectroscopy. The ion migration through the structures in untethered polymer-based fluids will also be studied to facilitate the understanding of ion migration in the structure of NOHMs-based fluids.

The detailed correlations between the carbon capture kinetics, and the viscosity behavior as well as the structural configuration of NOHMs-based fluids are to be established. The relative amount of different carbon species and their diffusion behavior will be determined, using techniques such as $^{13}$C NMR and computer simulations. The possible complexation of $CO_2 (CO_2^-)$ by different types of NOHMs at different concentrations will be investigated through density functional theory (DFT) simulations.

Lastly, a life cycle analysis (LCA) is recommended for the selected next-generation NOHMs-based fluids that possess an enhanced CO$_2$ capture and electrochemical conversion performance, to assess the overall environmental and economic impacts. In this way, the potential energy reduction and possible decarbonization are expected to be established for novel nanoscale hybrid solvent systems developed for combined carbon capture and conversion.
Reference


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Power Sources, 170(2), 460–464.


Greenhouse Gas Control, 3(2), 133–142.


Separation. *Chemical Reviews*.


Appendix

The chemical composition and structure identification were performed for NOHM-I-HPE based aqueous fluids via both $^{13}$C and $^1$H NMR spectroscopy as shown in Figure A.1 and Figure A.2. In $^{13}$C NMR spectrum, the peak at around 161 ppm corresponded to the bicarbonate ion in the fluids. The carbon atoms in NOHMs gave rise to multiple peaks from 10 to 80 ppm. Meanwhile, the peaks from 120 to 140 ppm were identified to be from the reference solution (toluene), which were not overlapping with the peaks of NOHMs.

From the $^1$H NMR spectrum, it can be seen that the peak at around 4.8 ppm referred to water in the system. Peaks from 0.9 to 4.0 ppm reflected hydrogen atoms in NOHM-I-HPE. The large peak at around 3.5 ppm was attributed to the CH$_2$ groups on the tethered HPE polymers. The CH$_3$ group on the side chain of the HPE polymer resulted in a peak at around 0.9 ppm, which was different from the terminal CH$_3$. 
Figure A.1. $^{13}$C NMR spectrum of 10 wt.% NOHM-I-HPE based aqueous fluids doped by 0.1 M KHCO$_3$.

Figure A.2. $^1$H NMR spectrum of 30 wt.% NOHM-I-HPE based aqueous fluids doped by 0.1 M KHCO$_3$. 
Table A.1. Selected cations of Ionic Liquids (ILs).

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<th>Abbreviation</th>
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<tr>
<td>1,3,4,6,7,8-hexahydro-1-methyl-2H-pyrimido[1,2-a]pyrimidine bis(pentafluoroethyl)sulfonylimide</td>
<td>MTBDH</td>
</tr>
<tr>
<td>Trihexyl(Tetradecyl)Phosphonium</td>
<td>$P_{66614}$</td>
</tr>
<tr>
<td>1-Ethyl-3-Methylimidazolium</td>
<td>EMIM</td>
</tr>
<tr>
<td>1-Butylpyridinium</td>
<td>BuPy</td>
</tr>
<tr>
<td>1-Octylpyridinium</td>
<td>OcPy</td>
</tr>
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Table A.2. Selected anions of Ionic Liquids (ILs).

<table>
<thead>
<tr>
<th>Anion</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
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<td>NO₃</td>
</tr>
<tr>
<td>Tetrafluoroborate</td>
<td>BF₄</td>
</tr>
<tr>
<td>Dicyanamide</td>
<td>DCA</td>
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<tr>
<td>Hexafluorophosphate</td>
<td>PF₆</td>
</tr>
<tr>
<td>Trifluoromethanesulfonate</td>
<td>TfO</td>
</tr>
<tr>
<td>Bis(Trifluoromethylsulfonyl)Imide</td>
<td>Tf₂N</td>
</tr>
<tr>
<td>Tris(Trifluoromethylsulfonyl)Methide</td>
<td>Methide</td>
</tr>
<tr>
<td>Imidazolium</td>
<td>Im</td>
</tr>
<tr>
<td>2-cyanopyrrolide</td>
<td>2-CNpyr</td>
</tr>
<tr>
<td>N-acetylglycine</td>
<td>Ac-Gly</td>
</tr>
<tr>
<td>N-Methylglycine</td>
<td>Me-Gly</td>
</tr>
<tr>
<td>Trifluorochloroborate</td>
<td>BF₃Cl</td>
</tr>
</tbody>
</table>