Experimental report

25/07/2022

Proposal: **6-03-456**

Council: 4/2020

Title: Investigating the Liquid Structureof Ionic Liquids containing Basic Anions used in Gas Capture Applications

Research area: Soft condensed matter

This proposal is a resubmission of 9-10-1636

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Samples: Dodecane
(C32H68P)(Cl)
(C32H68P)(C2S2NO4F6)
(C32H68P)(C2H2N3)
(C32H68P)(C7H13O2)
(C16H36P)(C2H2N3)
(C16H36P)(C7H13O2)
dodecane-d

Instrument	Requested days	Allocated days	From	To
D22	2	2	26/05/2021	27/05/2021
			01/09/2021	02/09/2021

Abstract:

Ionic Liquids (ILs) have been the subject of extensive investigation into alternative flue gas sorbents as a substitute for toxic and volatile aqueous alkanolamines. This is due to their inherent properties such as a low vapour pressure, high thermal stability, and high gas uptake capacity, which can be modified through altering the cation-anion pairing. The effect of the absorption of a gas on IL structure has received little attention, to date. Dispersions of IL provide a potentially attractive route for applications involving CO2 capture/ reduction.

The aim of this study is to determine the structure-property relationship of the ILs and the effect of CO2 uptake as dispersions (initially as 5% v/v in dodecane). Studies will be performed with anions known to chemically absorb CO2, e.g. [124-Triz] and [HexO], in comparison to anions that physically absorb CO2 ([NTf2] and Cl). The absorption of other contaminant gases (SO2 and NOx) will also be investigated.

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Objective

The objective of this work was to explore the absorption mechanism of different acidic gases found in flue gas (CO_2, NO_2, and SO_2) by various ionic liquids (ILs) via small angle neutron scattering (SANS) and elucidate the effect of IL structure (particularly the anion) on the physical and chemical absorption of gases. The temperature was also varied to investigate the gas desorption process. Previous studies have shown that flue gas impurities (SO_2 or NO_x) can influence the recyclability of the gas capture process. Therefore it is of interest to understand the structure of the species formed after gas absorption and desorption, and whether this process is reversible. The ILs were chosen based on their known interaction with acidic gases.

Experimental

Contrast matched solutions of [P_{66614}][NTf_2], [P_{66614}][HexO], [P_{66614}][Benzim], and [P_{66614}][NO_3] in h/d-toluene and/or h/d-cyclohexane were prepared (depending on solubility) and were saturated with CO_2, NO_2, and SO_2. The effect of changing the cation structure was also studied with [P_{4444}][HexO] saturated with NO_2 in d-toluene. An instrument configuration was used with λ=6 Å, sample to detector distance D=17.6 m, collimation C=17.6 m, with exposure times ranging from 600 to 900s. The experiments were initially run at 25 °C then increased initially to 50 °C then to 90 °C before being decreased back to 25 °C. Due to Covid19, the researchers were only able to attend the experiment virtually (split over two days).

Preliminary Results and Discussion

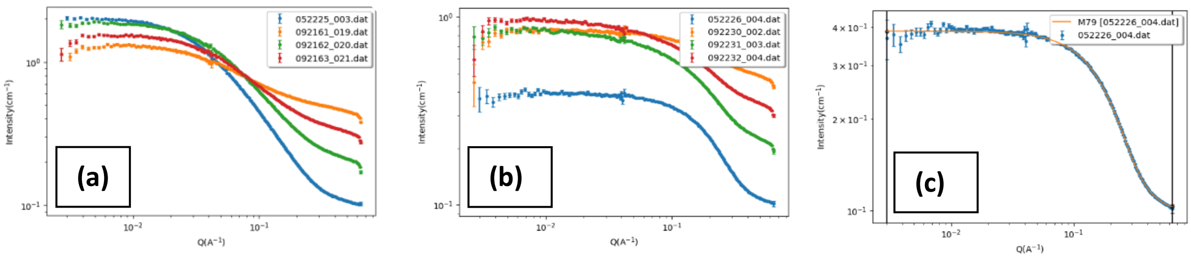

Figure 1: Examples of the neutron scattering results generated from SASView. (a) [P_{66614}][HexO], (b) [P_{66614}][NTf_2], where: IL in solvent (BLUE), IL+SO_2 (ORANGE), IL + NO_2 (GREEN), IL + CO_2 (RED). (c) [P_{66614}][HexO] at 25°C cylindrical fit with a goodness of fit of χ^2 = 2.11

Figure 1a shows an IL, [P_{66614}][NTf_2], that is known to interact physically with acidic gases. The blue line depicts the pure IL, which at a low Q matches the green IL + NO_2 line then diverges as at higher Q-values. Figure 1b shows the absorption of the gases by [P_{66614}][HexO] at 25 °C. It can be observed in the high Q region that the absorption of acidic gases changes the structure of the IL in solution. This is reflected in the initial fittings where the IL when fitted as a cylinder has a fit at χ^2 = 2, whereas the gas saturated samples had a $\chi^2 \approx 40$, suggesting that the cylinder model is not a good fit and alternative models are required for these samples.

Previous studies have shown that [P_{66614}][NTf_2] does not absorb as much NO_2 as [P_{66614}][HexO]. The differences shown between Figure 1a and 1b demonstrate the ILs absorb the gases in different ways. Similarly, studying [P_{66614}][Benzim], an IL known to interact strongly chemically with acidic gases, should enable the nature of the interaction (physical versus chemical absorption). Furthermore, investigating the effect of temperature will demonstrate whether the gas absorption process is reversible based on whether the structure returns to its initial state after heating.

Figure 1c shows an example cylindrical fitting of [P_{66614}][HexO] with NO_2 at 25ºC. In the initial experiment, the [P_{66614}][NTf_2] was fitted to a length of 122 Å. With the introduction of gas to the IL it decreased in length to 86 Å, 108 Å, and 97 Å for SO_2, NO_2, and CO_2 respectively. However, [P_{66614}][HexO] increased in length starting at 23 Å then increasing to 26 Å, 33 Å, and 35 Å for SO_2, NO_2, and CO_2 respectively. An interesting observation which held true for both ILs with all the gases is the effect of temperature on the molecules. As the temperature increases, the IL decreases in length and as it cools down, the IL returns to a similar length it initially started at.

Future Work

Further analysis of the data is being performed in order to yield a better χ^2 value and to obtain more accurate information regarding the structure of the ILs (+gas) in solution, including applying a 'structure factor' which improves the fit. However, since some of the scattering patterns are complex, applying the most appropriate fit has proved challenging and so computational modelling (molecular dynamics) is being performed to simulate the systems explored and will allow for a comparative approach with the SANS data to increase the reliability and accuracy of the results.

It is expected that this work will result in 2-3 publications, investigating the effect of IL structure on the physical or chemical absorption of different gases, and the recyclability of the gas capture process. Understanding the influence of flue gas impurities such as SO_2 and NO_x is key for the application of ILs as CO_2 capture sorbents on an industrial scale, as well as aiding the understanding of the electrochemical utilisation of CO_2 by ILs.

Acknowledgement

The University of Manchester and Infineum Teams wish to thank Dr. Lionel Porcar (ILL) for his help with this experiment. In particular with preparation and running of samples.