

Ionic Liquid Extractions of Soil Organic Matter

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Abstract

The ionic liquids dimethylammonium dimethylcarbamate (DIMCARB) and 1-butyl-3-methylimidazolium chloride (Bmim Cl) can solubilise soil organic matter. Soil extractions with these materials showed that the organic matter recovered showed chemical properties that were consistent with humic substances. These extracts had a slightly different organic composition than the humic acids extracted using the traditional International Humic Substances Society (IHSS) method. The ionic liquids also solubilised some inorganic matter from the soil. Humic acids recovered with alkali were also partially soluble in the ionic liquids. DIMCARB appeared to chemically interfere with organic extract, increasing the level of nitrogen in the sample. It was concluded that the ionic liquid Bmim Cl may function as a useful solvent for SOM, and may be used to recover organic matter of a different character to that obtained with alkali

Key Words

Ionic liquids, humic substances, soil organic matter, extraction, characterisation

Introduction

The term 'ionic liquid' refers to a specific group of organic salts that melt at or below room temperature. These are called 'room temperature ionic liquids' (RTILs) or simply 'ionic liquids' (ILs). Ionic liquids have been investigated for their ability to dissolve and extract natural organic compounds (Zhao *et al.* 2005), proteins (Fujita *et al.* 2005), carbohydrates (Liu *et al.* 2005) and lignin (Tan *et al.* 2009). Given that soil organic matter (SOM) is likely to contain all of these compounds, or at least fragments of them, it is reasonable to conclude that ionic liquids may solvate part, if not all of the organic matter in soil.

The ionic liquid dimethylammonium dimethylcarbamate or 'DIMCARB', was chosen for study as a potential SOM extractant. Unlike other ionic liquids, DIMCARB is able to be removed by distillation thus providing a means of recovering extracted material from the ionic liquid. The ionic liquid 1-butyl-3-methylimidazolium chloride or 'Bmim Cl' was also chosen because this material has been used to dissolve cellulose and is commercially available (Swatowski *et al.* 2002).

Method

Soil Preparation

Dalmore clay soil, a peaty clay with up to 17.6% organic matter from the Koo-Wee-Rup area in Victoria, was used in this study. After removing of organic debris, the soil was dried in a vacuum oven at 40 C overnight to remove free water. A fine grind of this sample was prepared for extraction.

Humic Acid Extraction

A standard International Humic Substances Society (IHSS) method (Swift, 1996) for extracting humic materials with alkali solution was followed, with a modification of the final step to "clean up" the humic acids by removing inorganic matter.

Whole soil (200 g) yielded 3.42g of dried humic acids. The sample of humic acid was washed six times in concentrated HCl (32% w/w), followed by washing in distilled water. After each washing, recovery of the humic acids was achieved by centrifugation. Waste acids were neutralised and discarded. After washing in acid, washing in water was repeated until pH increased to the point where the humic acids would start to redissolve. The recovered humic acid was air dried and stored in a dessicator (1.92 g).

Synthesis of DIMCARB

DIMCARB was synthesised following a method published by Kreher *et al* (2004).

Dimethylamine and carbon dioxide gases were fed to a three neck RBF resting in ice bath and connected to a 1.5ft spiral condenser from which DIMCARB was collected as a distillate.

Soil Extraction with DIMCARB

A sample of soil (50 g) was combined with DIMCARB (250 ml) in a stoppered conical flask, and stirred overnight at room temperature. The Soil / DIMCARB mixture was transferred to 30 ml glass centrifuge tubes and centrifuged. The supernatant was decanted and vacuum filtered through glass filter paper. Filtered extracts were combined, placed under high vacuum to boil off and collect the DIMCARB. The mass of dry soil extract recovered was 1.42 g.

IL extraction with Bmim Cl

Two 1 g samples of acid washed soil (HCl) were prepared. One sample was placed in a vacuum oven (110°C for 2 hrs) to remove water, this was labelled 'oven dry soil'. The other sample was allowed to equilibrate with moisture in the air and was labelled 'air dry soil'. Both samples were then treated with the following extraction method. Bmim Cl (20 g) was melted and dried in vacuum oven (110°C for 4 hrs). Using a high speed glass centrifuge tube, soil (1 g) was added to of molten Bmim Cl (10 g). This was then sonicated (70°C for 4 hours). Whilst still hot, the mixture was centrifuged (20,000 rpm for 30 mins). The supernatant was recovered and deionised water (10 ml) was added. This was shaken and then allowed to stand overnight. Precipitated solids were settled using high speed centrifugation (as above), and the supernatant poured off and set aside. The remaining solids were washed in deionised water, centrifuged, and the supernatant discarded. This step was repeated three times to remove the ionic liquid. The sample was then freeze dried.

The two dried organic extracts weighed 0.15 g (oven dry soil), and 0.12 g (air dry soil).

Results and Discussion

DIMCARB Extract

The dark brown solid recovered from the DIMCARB extraction (1.42 g) represented 2.84% of the original soil sample. Thermal gravimetric analysis showed this to have an ash content of 21.8%. The extraction recovered 1.11 g of organic matter (OM), or 22.9% of all the OM in the soil sample (4.85 g OM in 50 g of soil). The solid state carbon-13 nuclear magnetic resonance of whole soil, humic acid (obtained by the traditional IHSS method) and DIMCARB extract are shown in Figure 1. While the differences are not striking, the DIMCARB extract does appear to show more prominent O-alkyl absorbance than the humic acid extract. The carboxyl region is prominent, and consistent with a humic substance spectrum. Elemental analysis of this organic extract showed a higher level of nitrogen was present in the DIMCARB extract (~ 4%) compared with the humic acid extract (~2%).

Bmim Cl Extract

The solid state carbon-13 nuclear magnetic resonance of whole soil, humic acid (obtained by the traditional IHSS method) and the two Bmim Cl extracts are shown in Figure 2. As with the DIMCARB extract, the O-alkyl absorbance region is more prominent than the humic acid extract. The spectra of both extracts are consistent with a humic substance spectrum. TGA results showed 66.1% ash was present in the 'air dry' sample and 72.5% ash for the 'oven dry' sample and use of this ionic liquid carried considerable quantities of ash along with the organic matter. Further investigation to de-ash the organic matter is required.

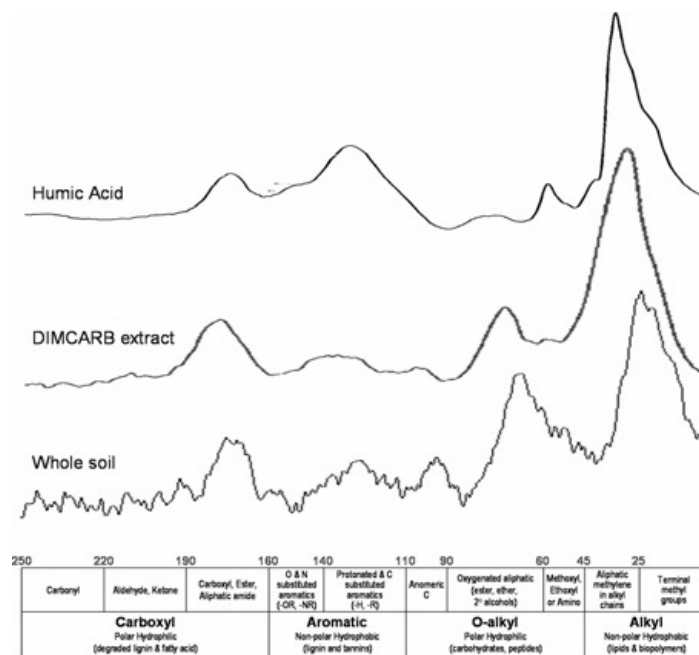


Figure 1. Solid State ^{13}C NMR spectra and chemical shift assignments (ppm) for Humic Acid, DIMCARB extract and whole soil.

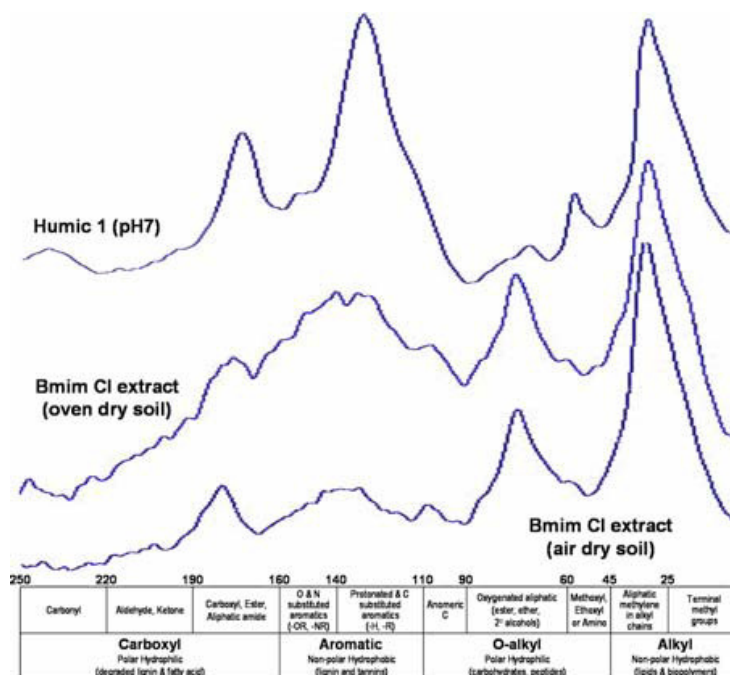


Figure 2. Solid State ^{13}C NMR spectra for humic acid (pH 7), and extracts of soil obtained with Bmim Cl.

Conclusion

The dimethylammonium dimethylcarbamate (DIMCARB) extraction of an organic matter rich soil was found to give a good yield of OM, and contained organic carbon types that seemed to be more representative of the SOM. However, it was also determined by microanalysis that DIMCARB is a reactive medium that interacts with the SOM and changes it chemically through the addition of nitrogen.

The second extraction solvent investigated utilised the ionic liquid, 1-butyl-3-methylimidazolium chloride (Bmim Cl). Experimental evidence indicated that this ionic liquid is capable of solvating and extracting SOM. The Bmim Cl extracts were found to contain an excellent representation of the types of organic carbon found in SOM, with higher oxygenated alkyl content than the humic acids recovered with alkali. The extracts were, however, very high in ash content, although this issue may be addressed by further developing the method.

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