



High solubility of Victorian brown coal in 'distillable' ionic liquid DIMCARB



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HIGHLIGHTS

- The solubilisation of Victorian brown coal in DIMCARB was studied for the first time.
- The coal achieved high solubility in the 'distillable' IL at room temperature.
- The yields were superior compared to those achieved using conventional methods.
- A particularly high yield of 62.9% was achieved for the LIGHT lithotype.
- DIMCARB can selectively 'dissolve' aliphatic compounds.

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ABSTRACT

Ionic liquids formed by association of carbon dioxide (CO₂) with low molecular weight secondary amines to form carbamate salts (e.g. N,N-dimethylammonium N',N'-dimethylcarbamates, or DIMCARB) as solvents have been identified as 'distillable' as they reform their volatile precursor components upon heating at relatively low temperature and, thus, can be recovered by condensation. DIMCARB was selected for the solubilisation of a number of Victorian brown coals including Loy Yang coal, a dark, a medium light and a light lithotype and a Yallourn woody coal. The coal was mixed with DIMCARB at a mass ratio of 1:20 for 24 h at room temperature. The soluble product was recovered by centrifugation followed by acid washing to remove residual DIMCARB. The solubilisation yields achieved were between 10% and 63% in the order of woody coal < dark lithotype < medium light lithotype < Loy Yang < light lithotype. The soluble and non-soluble products were characterised by FTIR, NMR and pyrolysis GC–MS. Results revealed a positive correlation between the solubility and aliphatic content in the coals. Polycyclic aliphatic and aromatic compounds, specifically the triterpenoid group, were selectively dissolved by DIMCARB.

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1. Introduction

The abundant brown coal deposits in the State of Victoria, Australia have provided cheap energy resources for decades. However, increasing concerns about carbon dioxide emission and the increasing price of petroleum products are stimulating the search for diversified brown coal end-uses, such as producing higher quality fuels or chemicals by solubilisation. Conventional solubilisation of brown coal includes simple extraction by organic solvents, such as dichloromethane and methanol, solubilisation by reactive solvents, such as pyridine, and alkaline digestion [1].

These methods are often carried out under harsh conditions (e.g. high temperature and pressure) [2], use lengthy procedures [3] or consume non-recoverable chemicals (e.g. in the case of alkaline digestion).

Ionic liquids (ILs) have attracted considerable attention in recent years as potential alternatives to conventional organic solvents in a variety of synthetic, catalytic and electrochemical and biomass processing applications. Research has found that these ILs are able to extract plant materials such as cellulose and lignin [4–6] and to assist the dispersion of bituminous coals [7,8]. However, due to their generally low vapour pressure and high boiling points compared to organic solvents, traditional ILs for solubilisation are often problematic in terms of separating soluble products from the bulk mixture and recovering the non-volatile ILs for further use or disposal [9].

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A series of 'distillable' ILs synthesised by mixing CO₂ with a secondary amine have similar properties to conventional ILs, but can be easily recovered by dissociation to the respective amine and CO₂ at relatively low temperature and then be re-associated by condensation [9,10]. They can be readily synthesised at low cost and in bulk at a laboratory scale [11]. As early as in the 1950s these ammonium carbamates were used as solvents in patented processes to dissolve oils or aromatic hydrocarbons [12–14]. More recently it was reported that the simplest form in this series N,N-dimethylammonium N',N'-dimethylcarbamates, or DIMCARB, was used to extract tannins and curcuminoids from plant materials [15,16]. A preliminary study showed that, among a number of such ILs in the series, DIMCARB achieved the highest solubilisation yield of a Victorian brown coal (VBC) [17].

The objectives of this study were to compare the solubilisation behaviour of different types of VBC including a Loy Yang coal, three Loy Yang lithotypes and a Yallourn woody coal in DIMCARB and to determine the characteristics of the soluble materials.

2. Material and methods

2.1. Materials

The coal samples selected were a run-of-mine Loy Yang coal and three lithotypes, dark, medium light and light, also collected from the Loy Yang mine. The woody coal was handpicked from the Yallourn mine where it appeared to be a large section of tree trunk. Proximate and ultimate analyses of the samples were carried out by HRL Technology, Pty. Ltd., Australia based on standard methods and the results are listed in Table 1. For solubilisation tests, the samples were milled and sieved. The fraction with particle sizes less than 1.4 mm was selected and stored in a sealed container for subsequent treatment.

DIMCARB was synthesised in the laboratory using dry ice pellets, instead of gaseous CO₂ as commonly reported [11,18], and dimethylamine gas. Dry ice pellets of a desired amount (200–400 g) were placed in a three-neck flask which was placed in an ice-water bath. Gaseous dimethylamine (>99%, Sigma–Aldrich) was transferred to the bottom of the flask through a glass tube fitted on one of the side necks. The flow of dimethylamine gas was adjusted to maintain a constant thin mist of DIMCARB, which was condensed through two serially connected coil condensers mounted on the centre neck of the flask. The condensing water was maintained at 5 °C. As the dry ice was spent the mist inside the flask became cleared, indicating the end of the process. The flow of dimethylamine was maintained for a further 1 min to ensure that no excess dry ice remained. After the contents in the flask reached room temperature, the product was weighed before being stored in a dry, clean glass container.

Commercial DIMCARB purchased from Sigma–Aldrich Australia was also used for comparison purposes.

Based on the results of elemental analysis the laboratory synthesised product and the commercial DIMCARB were found to

consist of dimethylamine and CO₂ at a molar ratio of 2.1 to 1 and 2.0 to 1, respectively. Proton and ¹³C NMR analysis of both materials gave identical spectra.

2.2. Solubilisation process

Raw coal sample with a dry mass of 0.5 g was mixed with 10 g DIMCARB in a sealed centrifuge tube for 24 h at room temperature using a magnetic stirrer. The mixture was then centrifuged for 50 min at 4000 rpm. After the supernatant was transferred to a clean beaker, a 0.5 M hydrochloric acid (HCl) solution was added slowly until the pH was around 4. The precipitates ('the soluble') were then filtered under vacuum through a glass fibre filter (0.5 μm) and rinsed thoroughly with deionised water until the pH of the filtrate was 7. The non-soluble material ('the residue') in the centrifuge tube was subjected to the same treatment as the soluble. Both the soluble and the residue were then dried in an oven at 105 °C under nitrogen for 4 h before being cooled in a desiccator and weighed.

2.3. Characterisation of solubilisation products

Dried samples of coal and solubilisation products (solubles and residues) were subjected to elemental analysis and analyses by Fourier transform infrared spectroscopy (FTIR), solid state ¹³C nuclear magnetic resonance spectroscopy (SS ¹³C NMR) and pyrolysis–gas chromatography–mass spectrometry (Py–GC–MS).

Elemental analysis was carried out by Campbell Microanalytical Laboratory, University of Otago, New Zealand, using a CHN analyser. A PerkinElmer RX 1 spectrometer was used for FTIR analysis of the samples as KBr discs. SS ¹³C NMR spectra were collected by cross-polarisation magic-angle spinning (CPMAS) at 100.6 MHz on a Bruker Avance 300 (7.05 Tesla magnet) with a 4 mm multinuclear solid state probe at room temperature. Spin rate was 10,000 Hz; SW 30,000 Hz (296 ppm); acquisition time 25 ms, a 3 s delay and a 2 ms contact time.

Py–GC–MS analysis was carried out on a Chemical Data Systems (CDS) 1000 coil pyroprobe unit connected to a GC–MS (CP8400 GC and Saturn 2200 ITMS; Varian Inc.) fitted with a capillary column (VF-5 ms 30 m × 0.25 mm ID and 0.25 μm film thickness). The GC–MS was operated under a constant flow of helium carrier gas (1 mL/min) with the column held at 0 °C for 3 min; then ramped to 80 °C at 6 °C/min; to 200 °C at 8 °C/min and finally to 325 °C at 10 °C/min with a 15 min holding time. A quartz tube holding an accurately weighed sample of approximately 0.50 mg with a quartz wool plug at each end was inserted into the platinum heating coil of the pyroprobe. The sample was subjected to thermal desorption at 340 °C (1 °C/ms ramp with 40 s dwell time) to release volatiles through the GC–MS, producing the first chromatogram, followed by flash pyrolysis to 720 °C to produce fragments from the pyrolytic cleavage of the residual solid, thus generating the second chromatogram.

Table 1
Properties of selected coal samples.

Coal	Moisture %	Proximate analysis (% db ^a)			Ultimate analysis (% daf ^b)				
		Ash	Volatile	Fixed C	C	H	N	S	O ^c
Loy Yang (LY)	59.1	3.5	49.5	47.2	63.4	4.5	0.60	0.60	30.9
Yallourn Woody (YLWD)	59.2	1.8	52.6	45.6	67.1	5.2	0.25	0.44	27.0
Loy Yang dark (DARK)	34.5	0.7	49.0	50.3	66.7	4.3	0.69	0.30	28.3
Loy Yang medium light (MLIGHT)	26.0	0.7	49.7	49.6	67.2	4.4	0.65	0.32	27.8
Loy Yang light (LIGHT)	44.6	0.7	57.5	41.8	70.1	5.7	0.59	0.26	23.6

^a Dry basis.

^b Dry ash free basis.

^c Calculated by difference.

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