



# Ambient temperature solubilisation of brown coal in ammonium carbamate ionic liquids



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## HIGHLIGHTS

- The solubilisation of a Victorian brown coal in three ammonium carbamate ionic liquids (ILs) was studied.
- Single step solubilisation yields of ILs were comparable to 1 M NaOH solution.
- Total solubility of Loy Yang coal in DIMCARB at ambient temperature was 66.5%.
- Less polar ILs DACARB and DPCARB were more selective for triterpenoid compounds.

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## ABSTRACT

Coal solubilisation is often a necessary step for the alternative utilisation of the cheap and abundant brown coal resources in the State of Victoria, Australia, such as producing high quality fuel or chemicals. A series of ionic liquids (ILs), ammonium carbamates, formed by the association of carbon dioxide (CO<sub>2</sub>) with low molecular weight secondary amines, were investigated as solvents for the solubilisation of Victorian brown coal. The ionic liquid was mixed with a Loy Yang coal at a mass ratio of 20 to 1 (dry basis) for 24 h at ambient temperature. The solubilisation yields of the coal using three such ILs from dimethyl-, diallyl- and dipropyl- amines, respectively, were between 18% and 23%. Repeated solubilisation of the coal with fresh solvent achieved higher yields, with the highest at 66% by the carbamate formed from dimethylamine (DIMCARB). The variations in chemical structure between the products were compared by elemental analysis and a variety of spectroscopic techniques (FTIR, Solid State <sup>13</sup>C NMR and Py-GC-MS). The soluble products of the initial solubilisation were more aliphatic than their parent coal. The less polar ILs formed from diallyl- and dipropyl- amines (DACARB and DPCARB) appeared to be more selective for high molecular weight triterpenoids than DIMCARB. Subsequent treatment tended to dissolve more aromatic components.

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## 1. Introduction

Ionic liquids (ILs) in recent years have attracted considerable attention as potential alternatives to conventional organic solvents in a variety of synthetic, catalytic and electrochemical applications. There have been reports that ILs are capable of dissolving biopolymers such as cellulose and lignin [1–3] and assisting in the dispersion of bituminous coals [4]. However, due to their low vapour pressure, these ILs are not distillable using conventional solvent distillation techniques, often resulting in difficulties in separating soluble products from the bulk mixture and recovering the IL for further use or disposal. In addition, the thermal decomposition of

the ILs (often at high temperatures) could prove problematic if the extract decomposes at temperatures below that of the IL decomposition [5].

Our focus is on a series of ILs produced from CO<sub>2</sub> reacted with aliphatic secondary amines. Those formed from dialkylamines, i.e. the N,N-dialkylammonium N',N'-dialkylcarbamates, are called dialcarbs [6]. They have similar properties as traditional ILs but can be easily recovered at low temperature by dissociation to the respective amine and CO<sub>2</sub>, which can then be re-associated by condensation [5,7]. These ILs can be readily synthesised at low cost in bulk, at a laboratory scale. Recently a series of dialkylcarbamates have been synthesised and employed for the extraction of curcumin from turmeric [8].

Victorian brown coal has provided an abundant and cheap energy resource for the State of Victoria, Australia, for decades.

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However, with the increasing price of petroleum products, there may be an opportunity to diversify its end-use into new sustainable applications. Traditional solubilisation of brown coal employs non-reactive solvents, such as chloroform or toluene, or reactive solvents, such as pyridine, aliphatic amines and aqueous alkaline solution [9]. These methods either are carried out under harsh conditions (e.g. high temperature and pressure) [10] to achieve high yields or consume large quantities of non-recoverable chemicals (e.g. in the case of aqueous alkaline digestion). Supercritical fluids have been used for oil extraction from biomass [11–13]. The technique requires operations under elevated temperatures and pressures and often suffers from low yields when being applied to coal samples [14]. The properties of the ‘distillable’ ILs may provide a more cost effective and environmental friendly method for the isolation of valuable chemicals from coal.

In a previous study using DIMCARB for the solubilisation of a variety of Victorian brown coal samples, a first using this series of ILs for coal solubilisation, yields of 10–63% were obtained [15]. A selective extraction of polycyclic triterpenoid components from the coals by DIMCARB was observed. The present study further investigates the solubility of a Victorian brown coal sample across a series of ‘distillable’ dialcarbs and characterises the chemical properties of their soluble and insoluble products. The selectivity of these ILs is further examined.

## 2. Material and methods

### 2.1. Materials

The coal used was run-of-mine Loy Yang coal (LY) from the Latrobe Valley, Australia. The properties of the sample (as received) are listed in Table 1. Preliminary tests showed lower solubilisation yields using dried coal samples than using wet samples. Hence, the raw coal sample was milled and sieved and the fraction of less than 1.4 mm was selected for subsequent use without any further treatment. Moisture content was measured frequently over the course of the experiment and calculations were adjusted accordingly.

ILs including N,N-dimethylammonium N',N'-dimethylcarbamate (DIMCARB), N,N-diallylammonium N',N'-diallylcarbamate (DACARB), N,N-dipropylammonium N',N'-dipropylcarbamate (DPCARB), N,N-diethylammonium N',N'-diethylcarbamate (DECARB) and N,N-bisethylhexylammonium N',N'-bisethylhexylcarbamate (DBCARB) were synthesised in the laboratory and were screen tested.

DIMCARB was synthesised using the method described previously [15]. The other alkyl carbamates were prepared by mixing the corresponding amine with dry ice at a 2:1 M ratio. Small pieces of dry ice were added into pre-weighed amine in a flask which was placed in an ice-water bath. A stopper was immediately inserted to prevent any vapour from escaping. The contents were stirred on a magnetic stirrer until the dry ice is fully dissolved. The flask was then wiped dry and weighed on a balance. More dry ice was added as needed until the 2:1 M ratio was reached.

Preliminary results showed that the solubility of the coal in the only hydrophobic IL, DBCARB, was very low ( $\leq 2\%$ ). DECARB is

easily solidified at room temperature, which then not only requires the dissolution process to be carried out at elevated temperature but also results in difficulties in separating and removing the solidified IL from the sample. Therefore, these ILs were not further investigated. The properties of the ILs and the screening results are provided as [supplementary information \(Table S1\)](#).

### 2.2. Solubilisation process

Coal solubilities were measured using two methods: a single step solubilisation to measure solubility at 1:20 coal to IL ratio and repeated extraction to measure total solubility.

For the single step solubilisation, the coal sample with a dry mass of 0.5 g was treated with 10 g of the selected IL (including a mixture of DIMCARB and water at 2:1 mass ratio) following the same procedures as described in our previous work [15]. As a comparison, alkaline digestion was carried out by replacing the IL with the same amount of a 1 M NaOH solution. The solubilisation and post-treatment procedures were the same as that using the ILs, except that the solid products were rinsed with weakly acidic water (pH 3–4) instead of deionised water.

The total solubility of the coal in each solvent was determined by repeatedly treating the non-soluble residue with fresh solvent after removing the soluble layer by centrifugation. After the first step where 10 g of the IL or the NaOH solution was used, in each following step, 3–5 g of fresh solvent was mixed with the residue for 24 h. This was repeated until the yield was less than 2%. The post-treatment for the soluble layer of each step and the final residue followed the same procedures as for the single step solubilisation process.

The soluble and non-soluble products of the single step solubilisation (1:20) were termed ‘S soluble’ and ‘S residue’, respectively, whereas those of the repeated extraction were termed ‘R soluble’ and ‘R residue’, respectively. It should be noted that the term ‘soluble’ is loosely used here since based on the observation in our previous study the ‘soluble’ materials are in fact colloidal in nature [15].

### 2.3. Characterisation of solubilisation products

The dried samples of coal and solubilisation products (residues and solubles) were analysed by Fourier Transform Infrared spectroscopy (FTIR), Solid State  $^{13}\text{C}$  Nuclear Magnetic Resonance Spectroscopy (SS  $^{13}\text{C}$ -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 CNH analyser.

A PerkinElmer RX 1 spectrometer was used for the FTIR analysis of the KBr disks of the samples. SS  $^{13}\text{C}$ -NMR spectra were collected on a Bruker Avance 400 (9.4 Tesla magnet) with MAS at 100.6 MHz and a 4 mm multinuclear solid state probe at room temperature and processed using Brukers Topspin 3.1 program. Spin rate was 10000 Hz; SW 30000 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  $\times$  0.25 mm ID and 0.25  $\mu\text{m}$  film thickness). 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  $^{\circ}\text{C}$  (1  $^{\circ}\text{C}/\text{ms}$  ramp with 40 s dwell time) to release volatiles followed by flash pyrolysis to 720  $^{\circ}\text{C}$  to produce fragments from the pyrolytic cleavage of residual macromolecules. The GC–MS was operated under a constant flow of helium carrier gas (1 mL/min). The column temperature

**Table 1**  
Properties of the Loy Yang coal studied.

Moisture (%)	Proximate analysis (% db <sup>a</sup> )			Ultimate analysis (% daf <sup>b</sup> )				
	Ash	Volatile	Fixed C	C	H	N	S	O <sup>c</sup>
52–55	3.5	49.5	47.2	63.4	4.5	0.6	0.6	30.9

<sup>a</sup> Dry basis.

<sup>b</sup> Dry ash free basis.

<sup>c</sup> By difference.

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