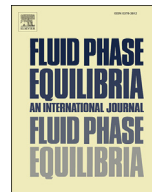




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## Thermodynamics of phase transfer for polar molecules from alkanes to deep eutectic solvents

Andrew P. Abbott\*, Azhar Y.M. Al-Murshedi, Odeh A.O. Alshammari, Robert C. Harris, Jalil H. Kareem, Idrees B. Qader, Karl Ryder

Department of Chemistry, University of Leicester, Leicester LE1 7RH, UK

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## ABSTRACT

Deep eutectic solvents (DESs) have been used for the purification of oils and the extraction of active ingredients from natural products but little is known about the mechanism of the extraction process. In this study a variety of molecular solutes are dissolved in alkanes and the thermodynamics of transfer into six DESs have been quantified. It is shown that the transfer of most solutes into the DES is endothermic and driven by entropy. The largest partition coefficients were demonstrated by the liquids with the lowest surface tensions and this is thought to arise because the enthalpy of hole formation controls the rate of solute transfer. Accordingly, it was shown that the size of the solute has an effect on the partition coefficient with smaller solutes partitioning preferably into the DES. As expected, solutes capable of strongly hydrogen bonding partitioned much better into the DES as the enthalpy of transfer was negative.

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### 1. Introduction

Deep Eutectic Solvents, DESs, are mixtures of Lewis and Brønsted acids and bases which produce low melting point systems due to complex formation [1,2]. The eutectic formation is endothermic and the process is driven by the large entropy change of going from two ordered solids to a more disordered liquid.

DESs have been primarily used for a wide variety of metal processing applications such as electrolytic, immersion, electroless deposition and electropolishing. This is due to their high solubility of metal salts, conductive nature and relatively wide electrochemical windows. They have however also been shown to be suitable solvents for a number of other processes such as liquid-liquid extraction, synthesis and gas capture. A review by Smith et al. [3], has covered this extensively.

One area where DESs are receiving the most interest is in their use as specific extractants. The first reported application was in the purification of biodiesel to extract excess glycerol and water from the reaction mixture. A Lewis basic mixture (1:1) of choline chloride and glycerol were used to complex polar species from crude biodiesel [4].

A variety of studies have investigated the extraction of sulfur containing compounds from alkanes using ionic liquids and deep eutectic solvents. This has been proposed as a methodology to enable desulfurization of oil [5–12]. Despite numerous groups studying the partition coefficients of thiophenic compounds no calculations have been made for the thermodynamics of phase transfer. It has also been used for the extraction of phenolic compounds from olive oil [13]. The use of ionic liquids and DESs for natural product extraction has also recently been reviewed [14–16]. Ionic liquids and DESs have both been shown to be candidates for extraction of a wide variety of natural product types, such as phenolic compounds, anthraquinones, flavonoids, alkaloids, essential oils, carbohydrates and lignin. They can be tailored towards specific extraction tasks by making slight variations to the anions, cations and hydrogen bond donors (HBDs). Ionic liquid and DES extraction processes have also been used in conjunction with microwave and ultrasound techniques to enhance extraction rates and some exhibit enhanced extraction efficiency compared to some organic solvents [14,16]. Efficient recovery of the natural products from ionic liquids and DESs has been carried out using supercritical fluid, anti-solvent precipitation, recrystallization and back extraction techniques.

In the current study the thermodynamics for the extraction of a range of compounds from alkanes is studied. Initially 3 thiophenic compounds are extracted from decane with six DESs. This study is

\* Corresponding author.

E-mail address: [apa1@le.ac.uk](mailto:apa1@le.ac.uk) (A.P. Abbott).

then extended to investigate the extraction of iodine followed by a variety of alkanes with different functional groups to determine the importance of hydrogen bonding in enabling selective extraction.

## 2. Experimental

All materials and reagents employed in this work were used as received and their sources and purities are listed in Table 1:

The deep eutectic solvents were prepared using similar approaches described by literature methods [1–5]. The hydrogen bond donor (HBD) and salt are mixed with respect to the specified HBD: salt molar ratio at a particular mixing speed and temperature until a clear homogeneous liquid phase was produced. Choline chloride (ChCl): ethylene glycol (EG) was prepared by mixing ChCl with EG in a 1:2 M ratio. The mixture was stirring in a flask and placed on a hot plate, magnetic stirrer at c.a. 80 °C and 500 rpm for at least 3 h until a colourless homogeneous liquid was formed. For ChCl: 1,4-butanediol (1,4 BG), ChCl: 1,5-pentandiol (1,5 PG), ChCl: glycerol (Glyc) the same preparation method was used as for 1 ChCl: 2 EG except the salt: HBD molar ratio which was 1:3, 1:3.5, 1:2 respectively. For ChCl: oxalic acid dihydrate (OxA DH) and ChCl: Urea, the solids were mixed together in a stoichiometric ratio of 1:2 and heated to 50 °C and were stirred until a homogenous colourless liquid was formed.

All partition coefficients and physical properties were measured at 1 atm pressure. A solution of Th was prepared in decane ( $6.24 \times 10^{-2}$  mol kg<sup>-1</sup> in 2.0 g decane) and then extracted at two different temperatures (25 and 35 °C) with 2.0 g of DES, at a stirring rate of 700 rpm for 60 min. The same conditions and experiments were repeated with BT and DBT. The S-content with respect to Th, BT, and DBT in decane was measured by GC-FID with a fused silica capillary column (PE Elite-5, 29.45 m long, 0.25 mm in diameter) connected to gas chromatograph (Perkin Elmer Autosystem XL) using the Totalchrom software. The operational temperature of the FID was 320 °C, and that of the injector was 310 °C. For the first 3 min, the temperature of column was set at 50 °C, increased to 300 °C at a rate of 15 °C min<sup>-1</sup>, kept at 300 C for 2 min. Helium was the carrier gas at a flow rate of 1 ml min<sup>-1</sup>. The quantities of S-compounds in a model fuel were determined from peak areas

**Table 1**  
Sample provenance.

Compound	Source and purity
choline chloride,	Sigma-Aldrich ≥99%
ethylene glycol	Sigma-Aldrich ≥99%
1,5-pentan-diol,	Sigma-Aldrich ≥99%
1,4-butan-diol,	Sigma-Aldrich ≥99%
n-decane,	Sigma-Aldrich ≥99%
thiophene (Th),	Sigma-Aldrich ≥99%
dibenzothiophene (DBT),	Sigma-Aldrich ≥99%
butanoic acid,	Sigma-Aldrich ≥99%
pentanol,	Sigma-Aldrich ≥99%
ethyl acetate,	Sigma-Aldrich ≥99%
2-pentanone,	Sigma-Aldrich ≥99%
cyclohexane and	Sigma-Aldrich ≥99%
urea	Sigma-Aldrich ≥99%
oxalic acid dihydrate	Fisher > 99%
glycerol	Fisher > 99%
hexane	Fisher > 99%
cyclohexane	Fisher > 99%
iodine	Fisher > 99%
benzothiophene (BT)	Alfa Aeser > 98%
curcumin	Naturex > 95%
β-carotene	Sigma Aldrich ≥ 93%
N,N,-dimethyl-4-nitroaniline	Sigma Aldrich > 99%
4-nitroaniline	Sigma Aldrich > 99%
Reichardt's dye ET30	Sigma Aldrich > 90%

corresponding to these sulfur species on the gas chromatography. According to the GC setup, the retention time chromatograms for Th, BT and DBT were around 3.14, 9.88 and 14.70 min respectively.

For the iodine extraction experiments, a hexane solution was prepared ( $1.19 \times 10^{-3}$  mol kg<sup>-1</sup> of iodine in 7.0 g hexane) and this was extracted at two different temperatures (25 and 35 °C) with 1.0 g of DES, at a stirring rate of 500 rpm for 5 min. The hexane layer was analysed by UV–Vis spectroscopy using a Shimadzu model UV-1601 spectrophotometer and the amount extracted was determined using a calibration plot.

Solutions of butanoic acid (0.12 mol kg<sup>-1</sup> in 2.0 g cyclohexane), 1-pentanol (0.14 mol kg<sup>-1</sup> in 2.0 g cyclohexane), 2-pentanone (0.04 mol kg<sup>-1</sup> in 2.0 g cyclohexane) and ethyl acetate (0.03 mol kg<sup>-1</sup> in 2.0 g cyclohexane) were prepared, then extracted at two different temperatures (25 and 40 °C) with 2.0 g of DES, at a stirring rate of 500 rpm for 120 min. The concentration of these solutes were determined using GC-FID in a similar manner to that described for Th.

Solutions of curcumin ( $4.29 \times 10^{-4}$  mol kg<sup>-1</sup> in 5.0 g decane) and β-carotene ( $1.79 \times 10^{-4}$  mol kg<sup>-1</sup> in 5.0 g decane) were prepared, then extracted at two different temperatures (26 and 38 °C) with 5 g of 1 ChCl: 2 EG as DES, at a stirring rate of 500 rpm for 60 min. The decane layer was analysed by Shimadzu model UV-1601 spectrophotometer to monitor the concentration of curcumin and β-carotene.

The solvatochromic parameters ( $\alpha$ ,  $\beta$  and  $\pi^*$ ) were calculated for each of the DESs used in this study. This was done by measuring the UV–Vis spectra of 3 indicator dyes in each DES of interest. The total concentration of dye in the DES was kept low (~1–2 mM) to avoid any solute-solute interactions being observed. It was previously shown that the single set probe approach was suitable for measuring these parameters in DES and so this technique was employed in this work [17]. To calculate  $\pi^*$ , the following formula was used with the data obtained from the indicator molecule 4-nitroaniline:

$$\pi^* = \left( v_{\text{solvent}} - v_{\text{cyclohexane}} \right) / \left( v_{\text{dmsO}} - v_{\text{cyclohexane}} \right) \quad (1)$$

$\alpha$  values were calculated using Reichardt's dye ET30 and  $\pi^*$  values

$$\alpha = ((30) - 14.6(\pi^* - 0.23) - 30.31) / 16.5 \quad (2)$$

$\beta$  values were calculated from the data obtained for 4-nitroaniline and N,N-dimethyl-4-nitroaniline

$$\beta = 0.9 \left( \Delta v_{\text{cyclohexane}} - \Delta v_{\text{solvent}} \right) / \left( \Delta v_{\text{cyclohexane}} - \Delta v_{\text{propan-1-ol}} \right) \quad (3)$$

Viscosity measurements were obtained as a function of temperature using a Brookfield DV-E Viscometer (Brookfield Instruments, USA) fitted with an IKA-Werke TC1 thermocouple. A variety of spindles (LV1, LV2 and LV3) were used with rotation rates of 5–200 rpm to obtain appropriate viscosity data. A Krüss Tensiometer model K9MK1 was used to measure the surface tension data for all liquids. The pressure was taken as atmospheric pressure ( $0.101 \pm 0.002$  MPa).

## 3. Results and discussion

### 3.1. Extraction of organosulfur species by type III DESs

DESs have been studied for the extraction of sulfur containing compounds from mineral oil. Most sulfur in oil is in the form of

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