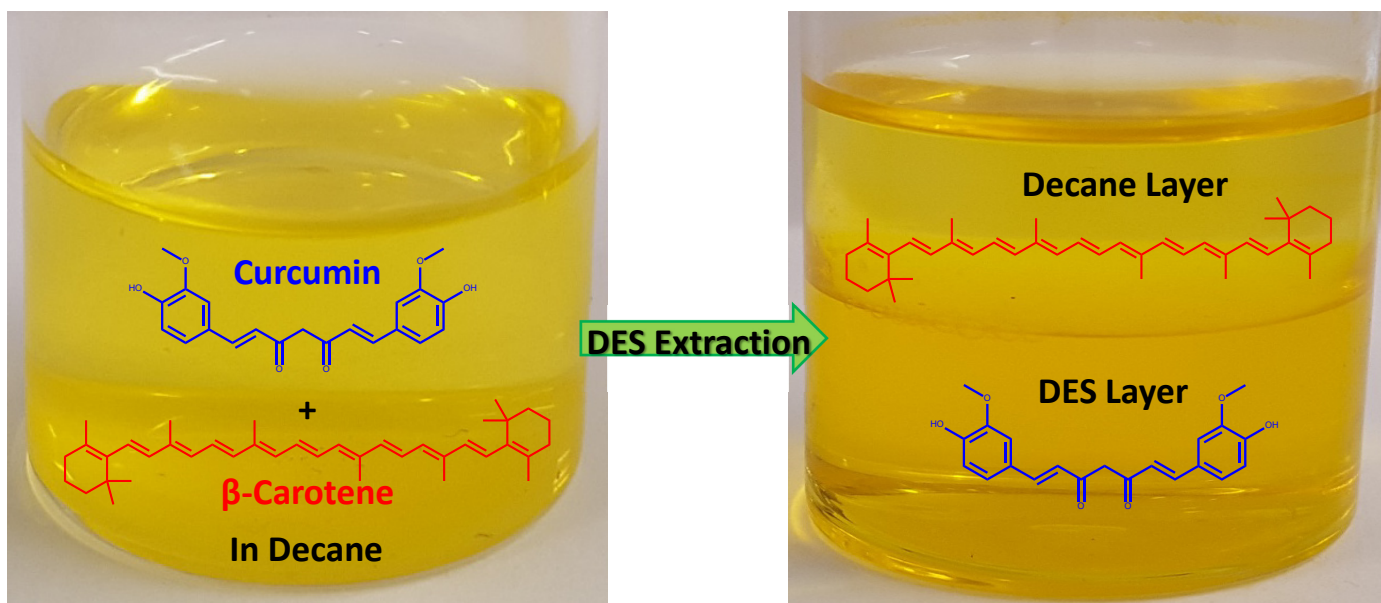# Thermodynamics of Phase Transfer for Polar Molecules from Alkanes to Deep Eutectic Solvents

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

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Graphical Abstract

Thermodynamics of Phase Transfer for Polar Molecules from Alkanes to Deep Eutectic Solvents

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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 controlling 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.

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 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, 6, 7, 8, 9, 10, 11, 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 [14,15,16]. 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 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.

Experimental

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

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%

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 molar ratio. The mixture was stirring in a flask and placed on a hot plate, magnetic stirrer at c.a. 80 ºC and 500 rpm for at least 3 hours until a colourless homogeneous liquid was formed. For ChCl: 1,4-butanediol (1,4 BG), ChCl: 1,5-pentanediol (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 ºC 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 (6.24×10^{-2} mol kg^{-1} in 2.0 g decane) and then extracted at two different temperatures (25 and 35 ºC) 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 ºC, and that of the injector was 310 ºC. For the first three minutes, the temperature of column was set at 50 ºC, increased to 300 ºC at a rate of 15 ºC min^{-1}, kept at 300 C for 2 min. Helium was the carrier gas at a flow rate of 1 ml min^{-1}. The quantities of S-compounds in a model fuel were determined from peak areas 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 (1.19×10^{-3} mol kg^{-1} of iodine in 7.0 g hexane) and this was extracted at two different temperatures (25 and 35 ºC) 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^{-1} in 2.0 g cyclohexane), 1-pentanol (0.14 mol kg^{-1} in 2.0 g cyclohexane), 2-pentanone (0.04 mol kg^{-1} in 2.0 g cyclohexane) and ethyl acetate

(0.03 mol kg^{-1} 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 x 10^{-4} mol kg^{-1} in 5.0 g decane) and β-carotene (1.79 x 10^{-4} mol kg^{-1} 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 (α, β and π*) 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 π*, the following formula was used with the data obtained from the indicator molecule 4-nitroaniline:

$$\pi^* = (\nu_{solvent} - \nu_{cyclohexane})/(\nu_{dmso} - \nu_{cyclohexane}) \qquad (1)$$

α values were calculated using Reichardt's dye ET30 and π* values

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

β values were calculated from the data obtained for 4-nitroaniline and N,N-dimethyl-4-nitroaniline

$$\beta = 0.9 (\Delta\nu_{cyclohexane}-\Delta\nu_{solvent})/(\Delta\nu_{cyclohexane}-\Delta\nu_{propan-1-ol}) \qquad (3)$$

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).

Results and Discussion

Extraction of Organosulfur Species by Type III DESs

DESs have been studied for the extraction of sulphur containing compounds from mineral oil. Most sulfur in oil is in the form of thiophene (Th), benzothiophene (BT) and dibenzothiophene (DBT). All of these compounds are polarisable and should be good hydrogen bond acceptors through the sulfur moiety on the heterocyclic ring. The thermodynamics of Th partition can be determined by measuring the partition coefficient of the compound between the DES and oil phase as a function of temperature.

These parameters were determined at 298 and 308 K using the Gibbs and Van't Hoff equations [18]

$$\Delta G = -RTlnK_p \tag{4}$$

$$\ln\left(\frac{K_2}{k_1}\right) = -\frac{\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{5}$$

$$\Delta S = (\Delta H - \Delta G)/T \tag{6}$$

where, R is the universal gas constant, T is the absolute temperature, K_p is the value of partition coefficient at equilibrium defined as:

$$K_p = \frac{(molality\ of\ Th)_{in\ DES}}{(molality\ of\ Th)_{in\ decane}} \tag{7}$$

The decane layer was analysed by GC and the data are shown in **Table 2**.

It can be seen that Th partitions more favourably in the alkane layer than the DES. The solute also partitions more favourably into the DES at higher temperature showing that the enthalpy of transfer is positive. It is interesting to note that the enthalpy of formation of the DESs themselves is also endothermic. If it is assumed that actual hydrogen bond formation is exothermic then it must be assumed that the enthalpy of breaking up the H-bonding in the DES to enable a hole for the solute to fit into must be endothermic.

Table 2: *Partition coefficients and Gibbs energy change for Th partition from decane to DESs (T ± 0.5ºC). The standard uncertainties are standard deviations made from 3 replicate GC-FID measurements*

DES	K_p at		ΔG (kJ mol^{-1}) at		ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1}) at 25 ºC
	25 ºC	35 ºC	25 ºC	35 ºC		
Th						
1 ChCl: **3.5** 1,5-PG	0.46 ± 0.02	0.52 ± 0.007	+1.9 ± 0.1	+1.7 ± 0.04	+9.0 ± 2.1	+23.8 ± 7.4
1 ChCl: **3** 1,4-BG	0.39 ± 0.007	0.45 ± 0.03	+2.3 ± 0.04	+2.1 ± 0.15	+10.4 ± 3.2	+27.1 ± 5.1
1 ChCl: **2** EG	0.30 ± 0.002	0.35 ±0.0008	+3.0 ± 0.02	+2.6 ± 0.04	+13.2 ± 0.5	+34.0 ± 1.7
1 ChCl: **1** OxA DH	0.10 ± 0.007	0.16 ± 0.01	+5.6 ± 0.16	+4.8 ± 0.2	+31.2 ± 0.9	+85.9 ± 3.4
1 ChCl: **2** Glyc	0.09 ± 0.01	0.14 ± 0.004	+6.0 ± 0.3	+5.0 ± 0.07	+35.0 ± 5.9	+97.4 ± 7.3
1 ChCl: **2** Urea	0.06 ± 0.002	0.14 ± 0.01	+7.2 ± 0.08	+5.0 ± 0.2	+70.8 ± 3.2	+213.5 ± 11.1
BT						
1 ChCl: **3.5** 1,5-PG	0.49 ± 0.01	0.55 ± 0.03	+1.8 ± 0.05	+1.5 ± 0.1	+10.0 ± 2	+27.5 ± 7.1
1 ChCl: **2** Glyc	0.07 ± 0.05	0.11 ± 0.14	+6.5 ± 1.2	+5.6 ± 0.3	+32.2 ± 8.1	+86.2 ± 8.5
DBT						
1 ChCl: **3.5** 1,5-PG	0.31 ± 0.05	0.32 ± 0.1	+2.9 ± 0.4	+2.9 ± 0.7	+2.3 ± 3.1	-2.3 ± 0.3
1 ChCl: **2** Glyc	0.043 ± 0.02	0.05 ± 0.01	+7.8 ± 0.8	+7.6 ± 0.4	+11.7 ± 2.8	+13.1 ± 4.2
Iodine						
1 ChCl: **2** EG	11.79 ± 0.18	15.30 ± 0.34	-6.1 ± 0.03	-7.0 ± 0.05	+19.9 ± 0.5	+88.0 ±1.2
1 ChCl: **2** Glyc	19.87 ± 0.41	43.59 ± 1.11	-7.4 ± 0.1	-9.7 ± 0.06	+60.0 ± 1.1	+226.2 ± 3.9
1 ChCl: **2** Urea	25.08 ± 0.20	40.40 ± 0.60	-8.0 ± 0.2	-9.2 ± 0.3	+36.4 ± 0.3	+148.9 ± 0.4

± quantity is the standard deviation of 3 replicate measurements

In all DESs tested ΔG for transfer of Th was positive but small and the partition is driven by the increase in entropy presumably occurring through breaking up the structure of the DES. The formation of the DESs is also driven by entropy in going from organised crystalline solids into a less organised liquid.

To try to understand the equilibria between the two phases it is important to consider the thermodynamic factors which change when species are transferred. To transfer a thiophene molecule from the oil to the DES, energy will be required to create a cavity

into which it can be accommodated but some energy will be recovered through the solvation of the solute in the DES.

While **Table 2** shows that the lower values of K_p tend to occur with the more viscous DESs the partition coefficients were measured as a function of time and stirring rate and it was found that under the experimental conditions the systems were at equilibrium. **Table 3** shows some of the physical properties of the liquids tested at 25 ºC and it can be seen that K_p values do not simply correlate with viscosity. **Table 3** also lists the polarity parameters for the DESs used. There are numerous methods of determining solvent polarity but one of the most commonly used, particularly with DESs is the Kamlet-Taft solvent parameters [19-23]. The π* scale is normalised to produce a scale from 0.00 for cyclohexane to 1.00 for dimethyl sulfoxide. The use of other indicator molecules with hydrogen bond donating and accepting abilities enables similar normalised scales to be developed for the hydrogen bonding ability of the solvent. These scales rely on linear solvation energy relationship (LSER) which has the generalised form

$$XYZ = XYZ_0 + s\pi* + b\beta + a\alpha \tag{8}$$

where XYZ and XYZ_0 are solvent-dependent properties for a given solvent and a standard reference solvent respectively. XYZ could represent reaction rates, equilibrium constants or a position/intensity of spectral absorption. The α term is a measure of the hydrogen bond donor properties β is the hydrogen bond acceptor property and π* is the polarisability/ dipolarity parameter. The terms s, a and b are constants obtained from experiment.

The data for the DESs used **Table 2** are shown in **Table 3**. Note that no parameters could be determined for **1** ChCl: **2** OxA DH which did not form a complex with Reichardt's Dye 30. It can be seen that the polarity of all of the DESs is high. The polarisability parameter is comparable to that for DMSO (1.0) and is comparable to a wide range of imidazolium based ionic liquids [23]. The hydrogen bond donor properties are also high and comparable with molecular solvents such as methanol (0.93) and water (1.17). The α values are considerably higher than imidazolium based ionic liquids which is not surprising given the relatively acidic protons on both choline and the HBDs of the DESs.

The β parameters are also relatively high which again is not surprising given the relatively basic nitrogen and oxygen functionalities in the HBDs.

The results from **Table 3** show that the polarity parameters are all very similar and no trend is seen with the extraction efficiency. Thiophenic species are polarisable molecules with hydrogen bond acceptor ability through the relatively basic sulfur moiety. It would therefore be expected that the solvent with the highest polarisability and hydrogen bond donor capacity would be the best solvent. This is however not the case and while DESs are in general good solvents for Th partition is not controlled by solvent polarity.

Table 3: *Viscosities, surface tensions and Kamlet and Taft solubility parameters for the DESs used in Table 2 at 298 ± 0.5 K. The standard uncertainties are standard deviations made from 3 replicate measurements*

DES	1 ChCl: 3.5 1,5-PG	1 ChCl: 3 1,4-BG	1 ChCl: 2 EG	1 ChCl: 2 Glyc	1 ChCl: 1 OxA DH	1 ChCl: 2 Urea
Viscosity (cP)	110 ± 0.4	94 ± 0.8	40 ± 0.04	296 ± 1.6	767 ± 3.9	849 ± 0.2
π*	0.96 ± 0.03	0.93 ± 0.02	0.96 ± 0.001	0.96 ± 0.04	-	0.98 ± 0.02
α	0.89 ± 0.03	0.96 ± 0.02	1.02 ± 0.02	1.04 ± 0.06	-	1.05 ± 0.02
β	0.61 ± 0.03	0.42 ± 0.002	0.33 ± 0.007	0.32 ± 0.01	-	0.30 ± 0.04
Surface tension / mN m⁻¹	47.5 ± 0.17	55.8 ± 0.12	56.5 ± 0.3	68.7 ± 0.45	60.8 ± 1	71.6 ± 0.12
Hole radius / Å	1.55 ± 0.003	1.47 ± 0.002	1.42 ± 0.004	1.37 ± 0.004	1.26 ± 0.012	1.29 ± 0.001

± quantity is the standard deviation of 3 replicate measurements

Figure 1 shows a plot of enthalpy of phase transfer (**Table 2)** as a function of surface tension (**Table 3**) and it can be seen that that there is a good correlation between the two parameters. The surface tension is a measure of the inter-molecular/ionic forces in the liquid and are an indicator of the energy required to form a void in the liquid. This correlation suggests that the enthalpy of transfer for Th is governed by the ability to form a hole of sufficient dimensions for the solute to fit in.
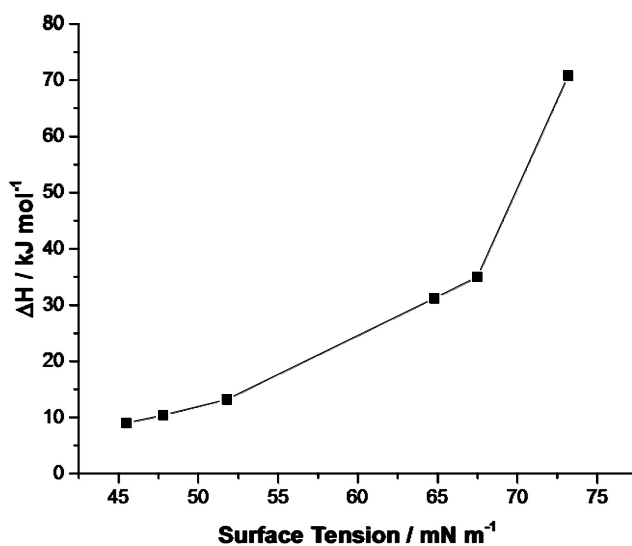
Figure 1: Plot of measured surface tension of different DESs vs the calculated ΔH of transference of Th from decane to DES at 298 K.

It has previously been shown that the energy of hole formation is very important at controlling diffusion and conductivity so it is not surprising that it should also be involved in the thermodynamics of solvation and phase equilibria [17].

It can be seen that **1** ChCl: **3.5** 1,5-PG, **1** ChCl: **3** 1,4-BG and **1** ChCl: **2** EG have lower surface tensions than the other liquids which correlates with the extraction efficiency shown in **Table 2**. Toh et al., revealed that low surface tension allows the extractant to form an emulsion owing to the mechanical excitation, hence growing the interfacial area and capability of extraction [24]. A low surface tension decreases the cohesive forces at the interface, hence increasing liquid solubilisation. The average void radius ‹r› can be related to the surface tension (γ) by the equation **6**: [25]

$$4\pi < r^2 >= \frac{3.5kT}{\gamma} \tag{9}$$

where k is the Boltzmann constant. The average void radius in the liquids tested are shown in **Table 3**. It can be seen that the average radius in all cases is significantly smaller than that needed to accommodate the solute. The solutes are all non-spherical but approximations of their radii in the plane of the molecule are; Th = 5.2 Å, BT = 6.9 Å,

DBT = 8.0 Å. It is clear that their dimensions are considerably larger than the hole radii listed in **Table 3** so a significantly larger hole will need to be made to accept the solute.

Effect of solute size

If the thermodynamics of phase transfer for Th are controlled by the energetics of hole formation then it would be expected that the closely related compounds, BT and DBT should be energetically harder to transfer as they are larger. **Table 2** shows that this is indeed the case

Figure 2 shows this graphically for the sulfur extraction efficiency of the three compounds in **1** ChCl: **3.5** PG and **1** ChCl: **2** Glyc. It can clearly be seen that as it becomes harder to create a void and as the solute gets larger the extraction efficiency decreases.
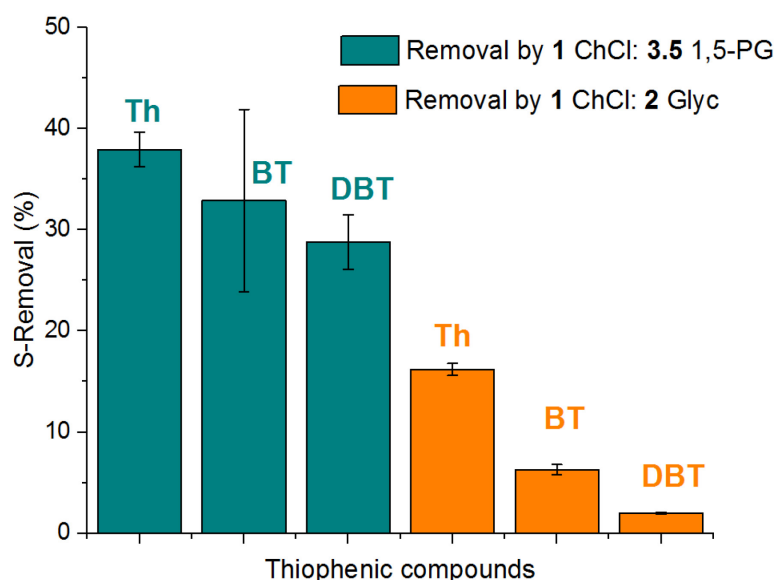

Figure 2: *Extraction of Th, BT and DBT from decane by **1** ChCl: **3.5** 1,5-PG and **1** ChCl: **2** Glyc at 298 ± 0.5 K.*

To see the effect of the solute polarity on phase transfer the above experiments were repeated using iodine as a solute. Iodine is an important solute in DESs as it has been used extensively as an electrocatalyst and a good oxidising agent [26]. Molecular iodine is apolar and dissolves readily in non-polar solvents such as decane. It does, however also form complexes with chloride anions, I_2Cl^-, and forms stable solutions in DESs. **Table 2** shows that despite being non-polar iodine partitions preferentially into the DES, in some

cases decolouring the organic phase almost completely. Interestingly the enthalpy of transfer to the DES is still endothermic showing that entropy is still driving the transfer of iodine to the polar phase. The enthalpy of transfer is more endothermic in **1** ChCl: **2** Urea and **1** ChCl: **2** Glyc than in **1** ChCl: **2** EG and yet iodine partitions preferentially into the DESs with the higher surface tension which is opposite to that seen for Th. It is evident in this case that the enthalpy of hole formation is less important in governing partition of the solute but the complex formed, I_2Cl^- is better at breaking up the structure of the DES than Th because the entropy of transfer is much higher for I_2.

Effect of solute hydrogen bonding

If the solute being transferred to the DES has a larger enthalpy of interaction with the DES than that between the chloride and the HBD of the DES then the transfer should be exothermic and the partition coefficient should be significantly larger than that observed for less polar solutes such as those listed in **Table 2**. To test this idea, the transfer of four aliphatic solutes with different functional groups was tested from cyclohexane to **1** ChCl: **2** EG. The results are shown in **Table 4**.

*Table 4: Partition coefficients and Gibbs energy change for functional groups partition from cyclohexane to **1** ChCl: **2** EG (T ± 0.6 °C). The errors are quoted as standard deviations made from 3 replicate GC-FID measurements.*

Solute	K_p at		ΔG (kJ mol^{-1})		ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
	25 °C	40 °C	25 °C	40 °C	at 25 °C	at 25 °C
Butanoic acid	100	100	--	--	--	--
1-Pentanol	1.22 ±0.02	0.95 ± 0.02	-0.5 ± 0.04	+0.1 ± 0.06	-12.7 ± 0.3	-44.4 ± 3.1
Ethyl acetate	0.10 ± 0.01	0.20 ± 0.06	+5.5 ± 0.3	+4.0 ± 0.7	+38.4 ± 3.6	+110.3 ± 12.3
2-Pentanone	0.02 ± 0.02	0.04 ± 0.02	+9.4 ± 1.5	+8.4 ± 1.1	+30.0 ± 6.4	+69.0 ± 5.7

± quantity is the standard deviation of 3 replicate measurements

The four solutes chosen were butanoic acid, 1-pentanol, ethyl acetate and 2-pentanone as they all have approximately the same size but clearly the first two are strong hydrogen bond donors whereas the last two are significantly weaker. The data in **Table 4** show that the butanoic acid is extensively completely transferred to the DES whereas the

corresponding alcohol lies predominantly in the DES. The enthalpy of transfer cannot be calculated by this method but it is fair to assume that it is exothermic as is that for 1-pentanol. It is interesting to note that the transfer of 1-pentanol causes a slight ordering of the DES unlike the other solutes. For both ethyl acetate and 2-pentanone the enthalpy of transfer is endothermic but the partition coefficient is very much into the alkane phase rather than the DES.

The extraction of natural products has been shown to preferentially extract the polar constituents and the reason for this is examined using two solutes; curcumin and β-carotene. Both are large, highly conjugated molecules but the former has phenolic moieties capable of H-bonding whereas the latter has no polar functional groups. The partition coefficients between decane and **1** ChCl: **2** EG are shown in **Table 5**. It can be seen from **Figure 3** that as expected from the above results, curcumin partitions predominantly into the DES phase whereas β-carotene has negligible H-bonding ability and remains in the alkane phase.
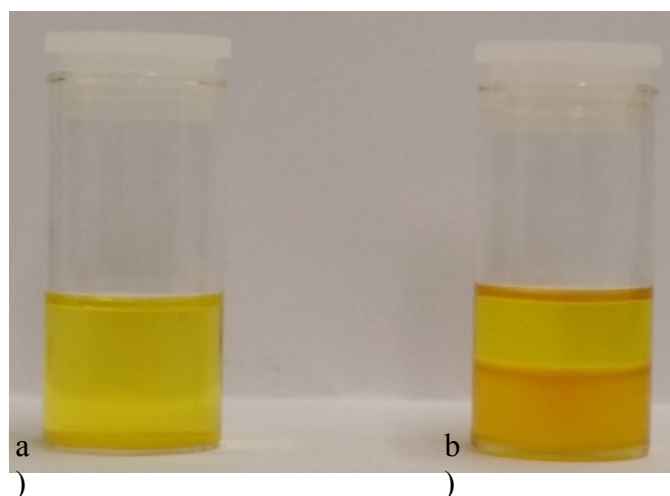

Figure 3: *a) Curcumin and β-Carotene in decane, b) upper decane layer containing 100% β-carotene and lower **1** ChCl: **2** EG layer containing 100% curcumin after liquid-liquid extraction of a) using **1** ChCl: **2** EG*

Table 5: *Partition coefficients and Gibbs energy change for curcumin and β-carotene partition from decane to **1** ChCl: **2** EG (T ± 0.5 °C). The standard uncertainties are standard deviations made from 3 replicate UV-vis spectra*

Substance	K_p at		ΔG (kJ mol^{-1})		ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1}) at 26 ºC
	26 ºC	38 ºC	26 ºC	38 ºC		
Curcumin	4.06 ± 0.33	8.16 ± 0.38	-3.5 ± 0.2	-5.4 ± 0.1	+45.9 ± 2.1	+164.9 ± 6.5
β-Carotene	0.13 ± 0.0008	0.06 ± 0.003	+5.0 ± 0.01	+7.2 ±0.1	-52.8 ± 2.3	-192.8 ± 7.7

<u>+</u> quantity is the standard deviation of 3 replicate measurements

High solubilities have previously been observed for large molecules such as lignin [27] and vegetable tans [28] in DESs. This presumably because of the large enthalpy of solvation resulting from the solute having a large number of hydroxyl functional groups.

Conclusion

The extraction of a range of solutes from alkanes to a variety of DESs was studied. It was found that in general the largest partition coefficients were obtained for the liquids for the lowest surface tensions as these will be the easiest to form a cavity in. From this it was concluded that the partition of solutes is governed by hole formation. This tends to make the transfer of solutes to DESs endothermic which means that it is the entropy change which enables transfer presumably because the solute breaks up the structure of the DES. The endothermicity of transfer naturally means that larger partition coefficients will be obtained for most solutes at higher temperatures. It was also found that the size of the solute was important at governing the partition coefficient; the larger the solute the more energy is required to make a hold and the lower is the enthalpy for transfer.

Partition into DESs is greatest where the enthalpy of solvation is exothermic. This clearly occurs when the solute is strongly hydrogen bonding and to achieve this the hydrogen bond formed between the solute and the chloride of the DES will have to be larger than that between the chloride and the HBD of the DES. It was shown therefore that the order for K_p was butanoic acid > 1-pentanol > ethyl acetate > 2-pentanone.

Acknowledgements

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