Centrale Marseille

StéRéO

Green Solvents

Low-Transition-Temperature Mixtures (LTTMs): A New Generation of Designer Solvents

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Apr. 08, 2013

Introduction

Introduction

The disadvantage of the conventional organic solvents

- known to be toxic
- dangerous for large-scale applications
- expensive to dispose as waste

In order to solve the problem

- water, glycerol, poly(ethylene glycol), perfluorinated solvents, ethyl lactate, supercritical fluids, or ionic liquids(Ils), and so on.

The disadvantage of ionic liquids

1.The hazardous toxicity and the very poor biodegradability of most ionic liquids

2.Ionic liquids with high purity are required

3.The high price of common ionic liquids

Introduction

To overcome the high price and toxicity of ionic liquids

In 2003, **Abbott** presented a new type of green solvents
the low-transition-temperature mixtures (LTTMs)

LTTMs can be prepared by mixing natural high-melting-point starting materials, which form a liquid by hydrogen-bond interactions.

Among them, deep-eutectic solvents (DESs) were presented as promising alternatives to conventional ionic liquids.

The advantage of **DESs**

- cheap and easy to prepare from natural and readily available starting materials, biodegradable, and renewable

Introduction

Definition of DESs

DESs is a fluid generally composed of two or three cheap and safe components that are capable of self-association, often through hydrogen bond interactions, to form a eutectic mixture with a melting point lower than that of each individual component.

syntheses

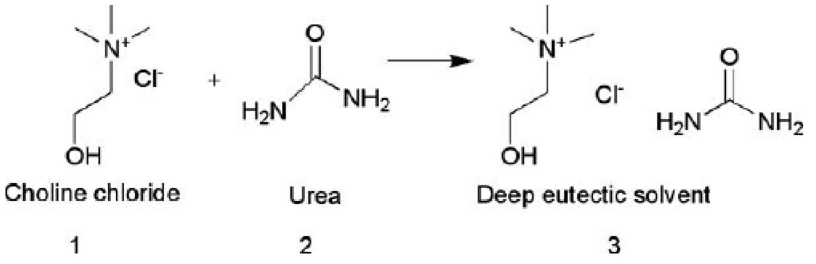
properties

applications

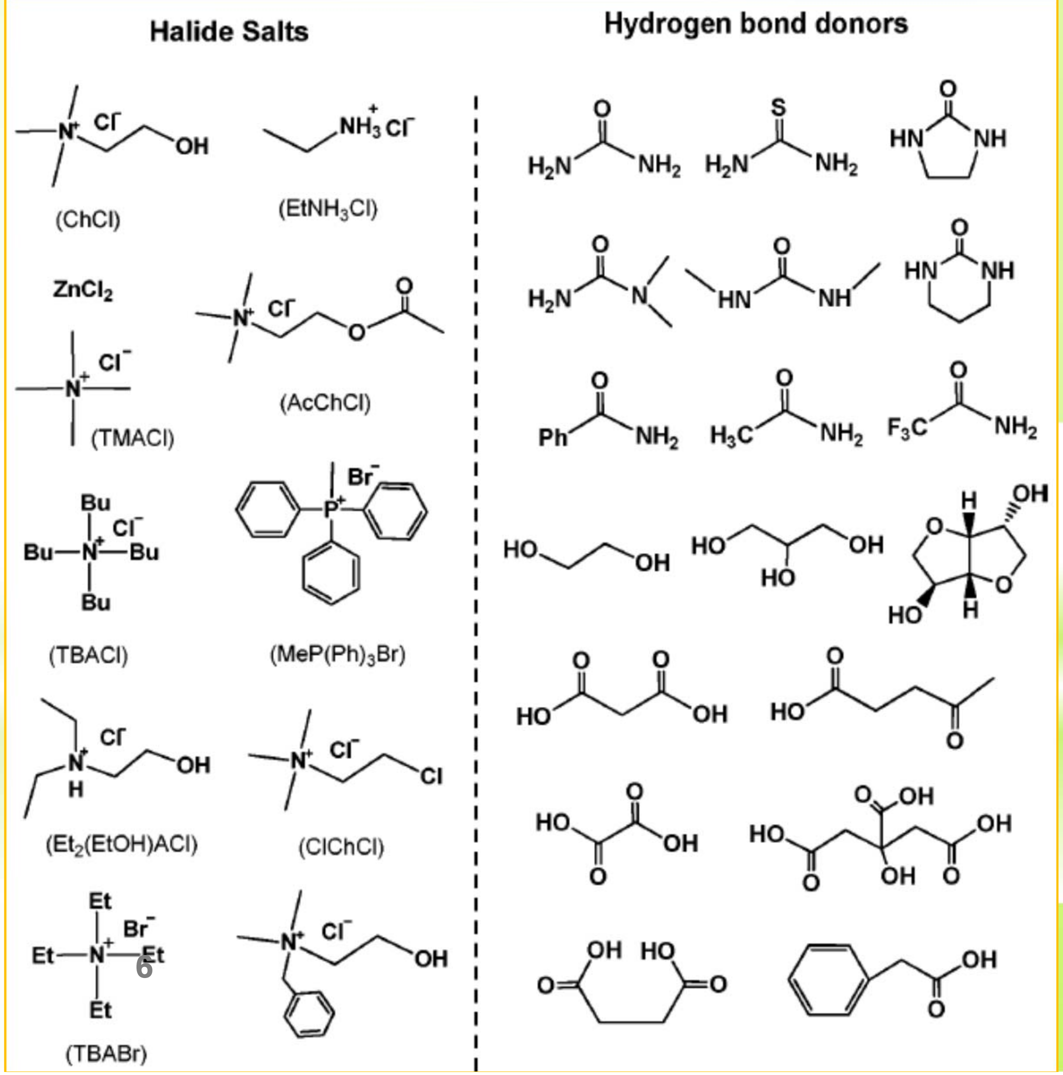
Syntheses

DES is obtained by mixing a **quaternary ammonium salt** with **metal salts** or **a hydrogen bond donor(HBD)** that has the ability to form a complex with **the halide anion of the quaternary ammonium salt**.

- Typical structures of the halide salts and hydrogen bond donors used for DES syntheses.



Scheme 1 Preparation of deep eutectic solvent.



Syntheses

In 2007, Abbott and co-workers defined DESs using the general formula $R_1R_2R_3R_4N^+X^-Y^-$.

Type I DES Y = MClx, M = Zn, Sn, Fe, Al, Ga

Type II DES Y = $MClxyH_2O$, M = Cr, Co, Cu, Ni, Fe

Type III DES Y = R_5Z with Z =-$CONH_2$, –COOH, –OH

Type IV DES = metal chlorides (e.g. $ZnCl_2$) mixed with different HBDs such as urea, ethylene glycol, acetamide or hexanediol

Synthesis of DESs is 100% atom economic, easy to handle and no purification is required, thus making their large-scale use feasible.

Physicochemical properties

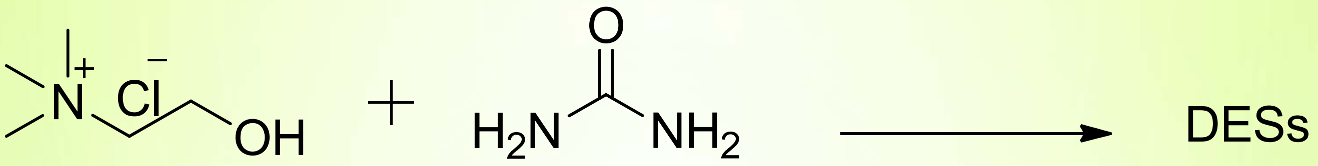
DESs are chemically tailorable solvents since they can be designed by properly combining various quaternary ammonium salts (e.g. ChCl) with different hydrogen bond donors (HBD). Hence, task-specific DESs with different physicochemical properties can be prepared.

- **Freezing point (T_f)**
- **Density**
- **Viscosity**
- **Polarity**
- **Conductivity**

Physicochemical properties

Freezing point (T_f)

DESs are formed by mixing two solids capable of generating a new liquid phase by self-association via hydrogen bonds. This new phase is generally characterized by a lower freezing point than that of individual constituents.



melting point 302 °C | melting point 133 °C | freezing point 12 °C

ratio 1 : 2

For all reported DESs, their freezing points are below 150 °C. Generally, DESs with a freezing point lower than 50 °C are more attractive since they can be used as inexpensive and safe solvents in many fields.

Physicochemical properties

Freezing point (T_f)

Abbott and co-workers proposed that the freezing point of HBD-salt eutectic mixtures should be dependent on

(1) the lattice energies of DESs

(2) the way how the couple anion–HBD interacts

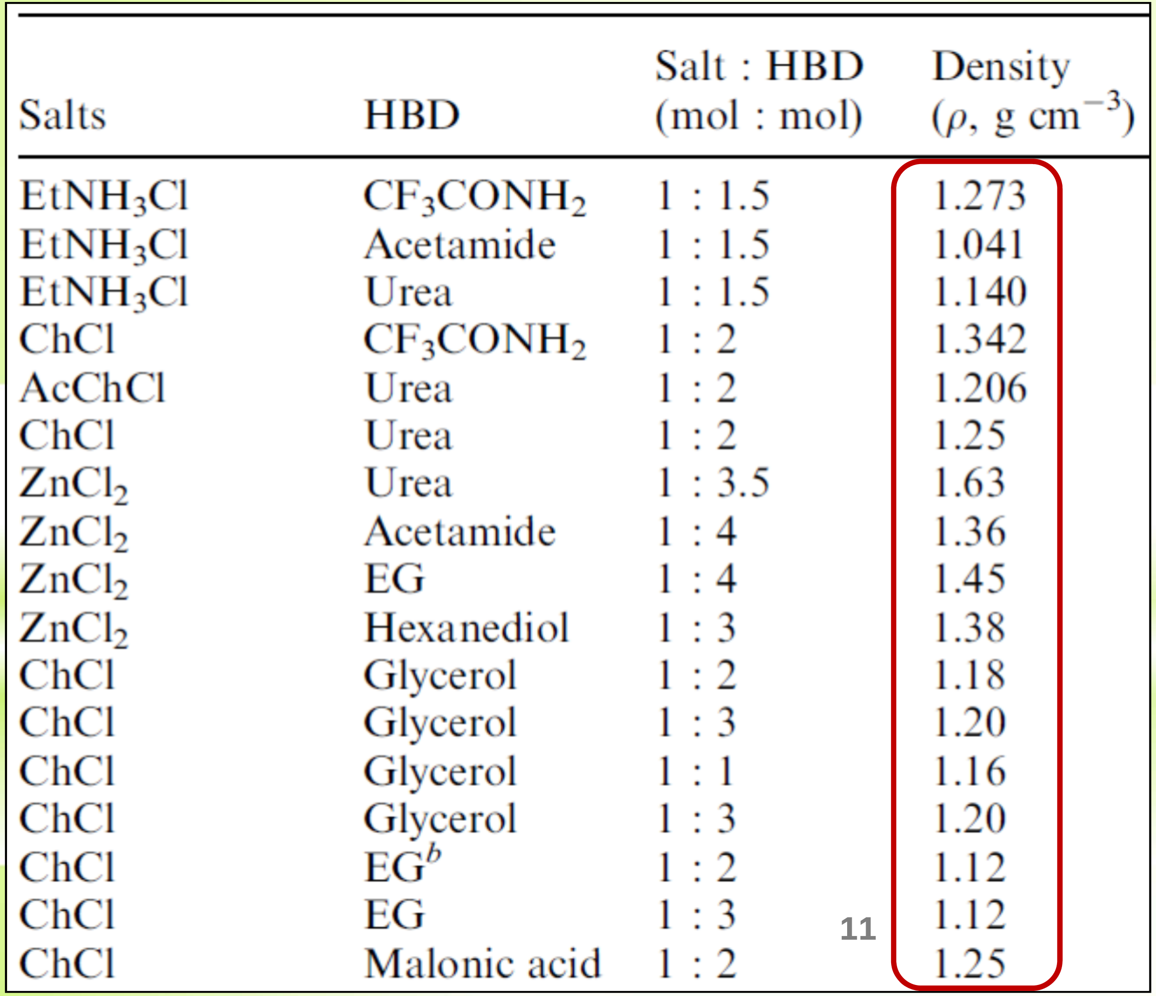
(3) the entropy changes arising from the formation of a liquid phase

Q. Zhang, K. Vigier, S. Royer, F. Jerome, *Chem. Soc. Rev.*, 2012, **41**, 7108–7146.

Physicochemical properties

Density

The density is one of the most important physical properties for a solvent. Densities of DESs are determined by means of a specific gravity meter.



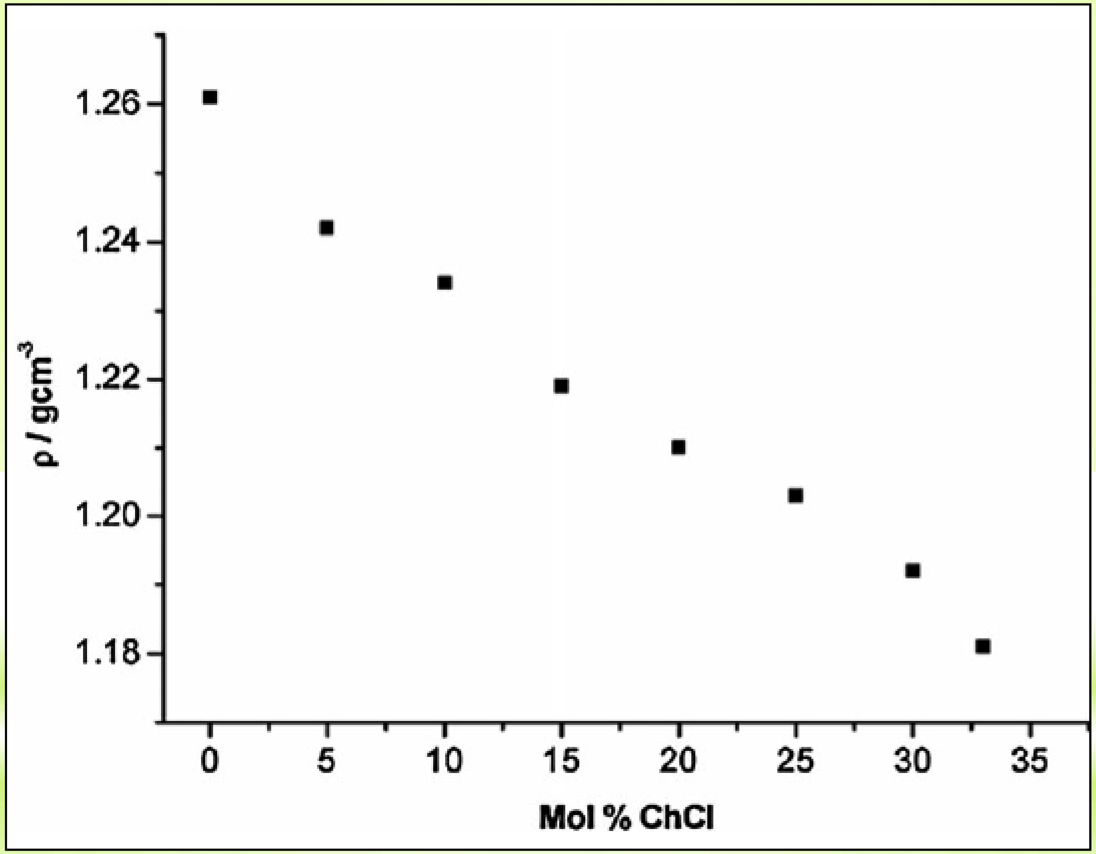
Salts	HBD	Salt : HBD (mol : mol)	Density (ρ, g cm^{-3})
$EtNH_3Cl$	CF_3CONH_2	1 : 1.5	1.273
$EtNH_3Cl$	Acetamide	1 : 1.5	1.041
$EtNH_3Cl$	Urea	1 : 1.5	1.140
ChCl	CF_3CONH_2	1 : 2	1.342
AcChCl	Urea	1 : 2	1.206
ChCl	Urea	1 : 2	1.25
$ZnCl_2$	Urea	1 : 3.5	1.63
$ZnCl_2$	Acetamide	1 : 4	1.36
$ZnCl_2$	EG	1 : 4	1.45
$ZnCl_2$	Hexanediol	1 : 3	1.38
ChCl	Glycerol	1 : 2	1.18
ChCl	Glycerol	1 : 3	1.20
ChCl	Glycerol	1 : 1	1.16
ChCl	Glycerol	1 : 3	1.20
ChCl	EG[b]	1 : 2	1.12
ChCl	EG	1 : 3	1.12
ChCl	Malonic acid	1 : 2	1.25

Most of DESs exhibit higher densities than water.

Physicochemical properties

Density

The density of a glycerol/ChCl DES as a function of the molar composition.



The organic salt/HBD molar ratio has an obvious effect on the densities of DES.

1. A. P. Abbott, G. Capper and S. Gray, ChemPhysChem, 2006, 7, 803–806.
2. C. Agostino, R. C. Harris, A. P. Abbott, L. F. Gladden and M. D. Mantle, Phys. Chem. Chem. Phys., 2011, 13, 21383–21391.

Physicochemical properties

Viscosity

Except for ChCl–ethylene glycol(EG) eutectic mixture, most of the DESs exhibit relatively high viscosities (>100 cP) at r.t. The high viscosity of DESs is often attributed to the presence of an extensive hydrogen bond network between each component, which results in a lower mobility of free species within the DES.

The high viscosity of DES should be dependent on

(1) the large ion size

(2) small void volume of most DESs

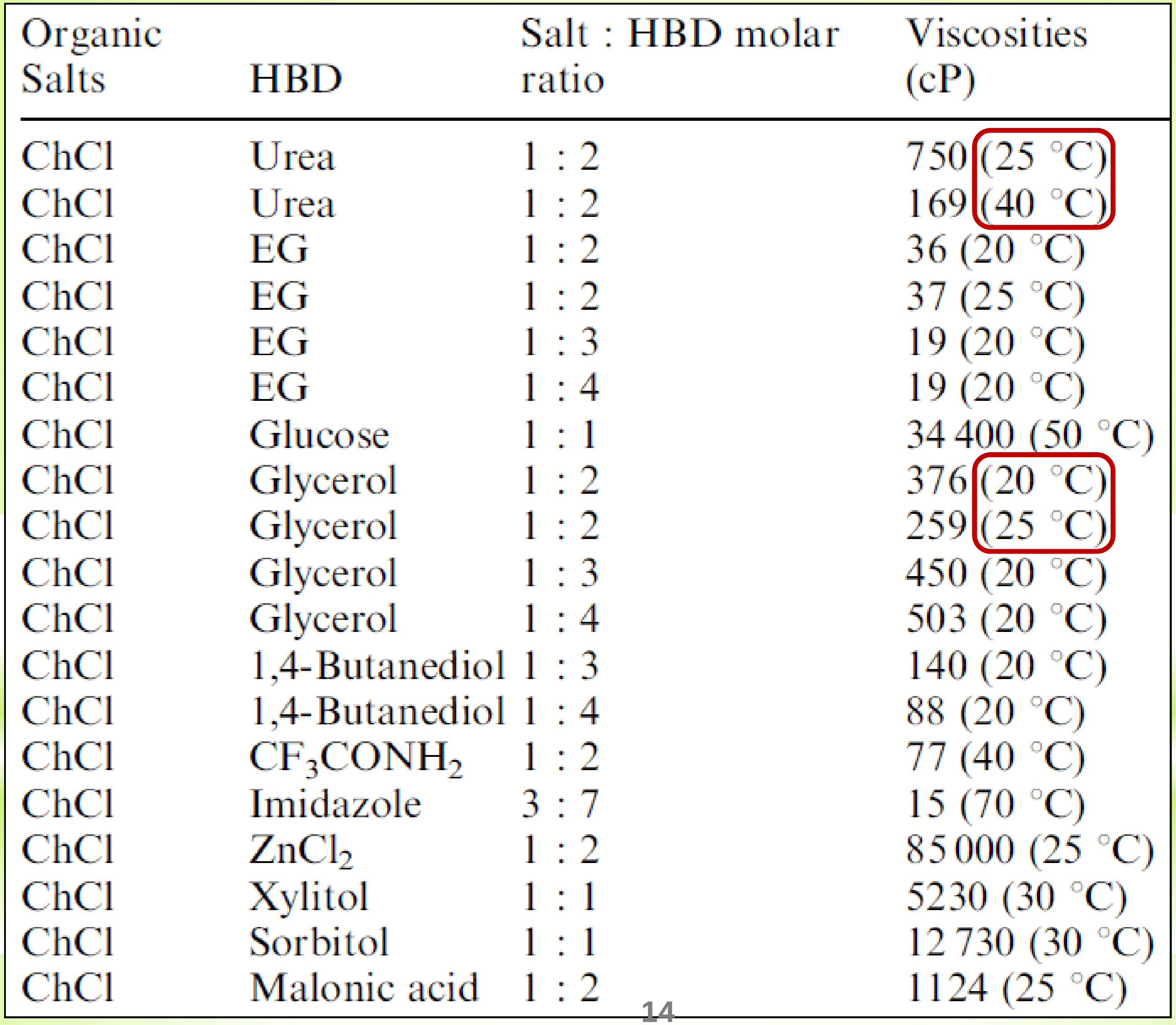
(3) electrostatic

(4) van der Waals interactions

Physicochemical properties

Viscosity

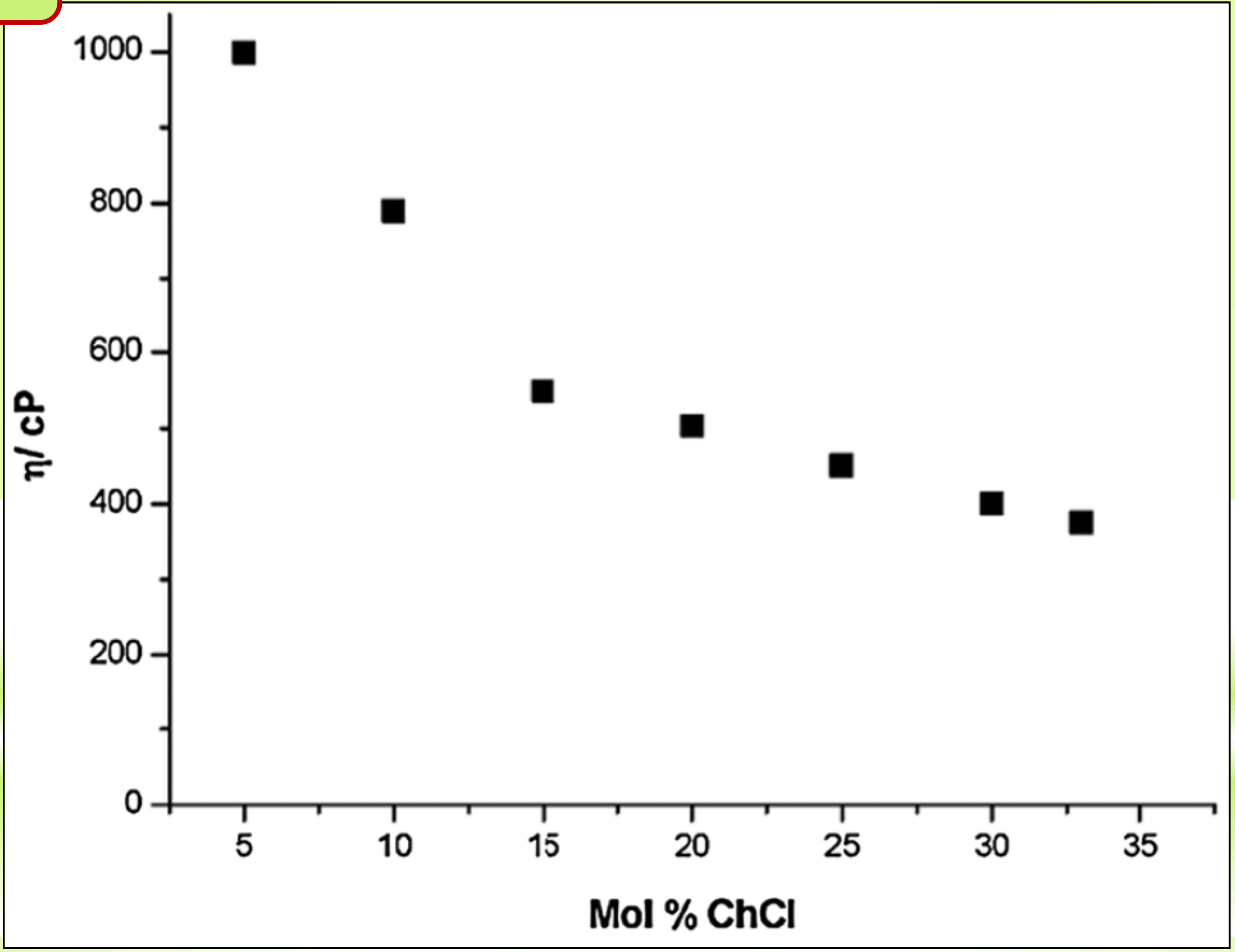
The viscosity data of common DESs at different temperatures.



Organic Salts	HBD	Salt : HBD molar ratio	Viscosities (cP)
ChCl	Urea	1 : 2	750 (25 °C)
ChCl	Urea	1 : 2	169 (40 °C)
ChCl	EG	1 : 2	36 (20 °C)
ChCl	EG	1 : 2	37 (25 °C)
ChCl	EG	1 : 3	19 (20 °C)
ChCl	EG	1 : 4	19 (20 °C)
ChCl	Glucose	1 : 1	34 400 (50 °C)
ChCl	Glycerol	1 : 2	376 (20 °C)
ChCl	Glycerol	1 : 2	259 (25 °C)
ChCl	Glycerol	1 : 3	450 (20 °C)
ChCl	Glycerol	1 : 4	503 (20 °C)
ChCl	1,4-Butanediol	1 : 3	140 (20 °C)
ChCl	1,4-Butanediol	1 : 4	88 (20 °C)
ChCl	CF_3CONH_2	1 : 2	77 (40 °C)
ChCl	Imidazole	3 : 7	15 (70 °C)
ChCl	$ZnCl_2$	1 : 2	85 000 (25 °C)
ChCl	Xylitol	1 : 1	5230 (30 °C)
ChCl	Sorbitol	1 : 1	12 730 (30 °C)
ChCl	Malonic acid	1 : 2	1124 (25 °C)

Physicochemical properties

Viscosity



An increase of the ChCl/glycerol molar ratio results in a decrease of the DES viscosity.

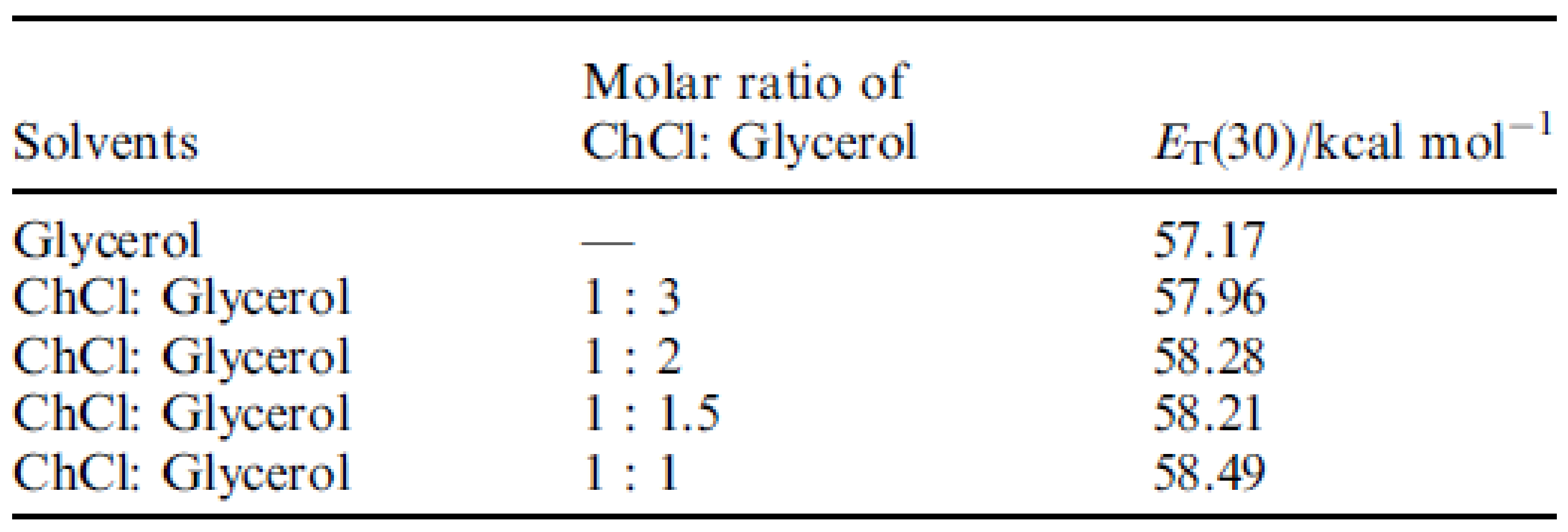
Physicochemical properties

Polarity

Polarity of a solvent can be evaluated by its polarity scale, E_T (30), which is the electronic transition energy of a probe dye (e.g. Reichardt's Dye 30) in a solvent.

$$E_T(30)(\text{kcal mol}^{-1}) = h_{CU\ max}N_A$$
$$= (2.8591 \text{ x } 10^{-3})U_{max}(\text{cm}^{-1})$$
$$= 28591/\lambda_{max}$$

h = Planck's constant
$υ_{max}$ = wave number
N_A = Avogadro's constant

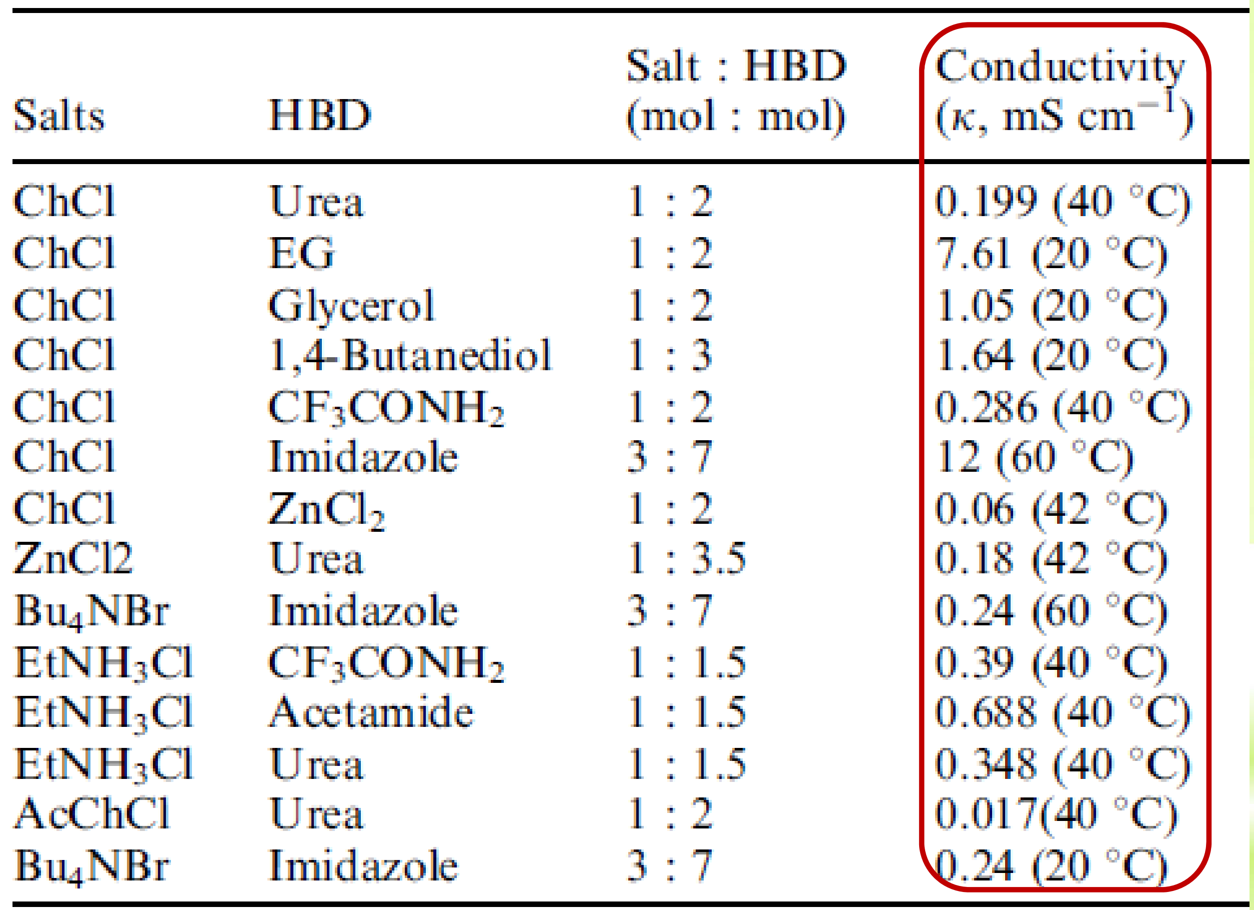


Solvents	Molar ratio of ChCl: Glycerol	$E_T(30)$/kcal mol^{-1}
Glycerol	—	57.17
ChCl: Glycerol	1 : 3	57.96
ChCl: Glycerol	1 : 2	58.28
ChCl: Glycerol	1 : 1.5	58.21
ChCl: Glycerol	1 : 1	58.49

A roughly linear increase of E_T(30) with the ChCl concentration was observed.

Physicochemical properties

Ionic conductivity



Salts	HBD	Salt : HBD (mol : mol)	Conductivity (κ, mS cm^{-1})
ChCl	Urea	1 : 2	0.199 (40 °C)
ChCl	EG	1 : 2	7.61 (20 °C)
ChCl	Glycerol	1 : 2	1.05 (20 °C)
ChCl	1,4-Butanediol	1 : 3	1.64 (20 °C)
ChCl	CF_3CONH_2	1 : 2	0.286 (40 °C)
ChCl	Imidazole	3 : 7	12 (60 °C)
ChCl	$ZnCl_2$	1 : 2	0.06 (42 °C)
ZnCl2	Urea	1 : 3.5	0.18 (42 °C)
Bu_4NBr	Imidazole	3 : 7	0.24 (60 °C)
$EtNH_3Cl$	CF_3CONH_2	1 : 1.5	0.39 (40 °C)
$EtNH_3Cl$	Acetamide	1 : 1.5	0.688 (40 °C)
$EtNH_3Cl$	Urea	1 : 1.5	0.348 (40 °C)
AcChCl	Urea	1 : 2	0.017(40 °C)
Bu_4NBr	Imidazole	3 : 7	0.24 (20 °C)

Ionic conductivities of part DESs at different temperatures

Conductivities of DESs generally increase significantly as the temperature increases due to a decrease of the DES viscosity.

Summary

As compared to another solvent, DESs have notable advantages stemming from

(1)their convenient synthesis (100% atom economy)

(2)their very low price since most of DESs can be prepared from readily accessible chemicals

(3)their low toxicity, especially DESs derived from ChCl and renewable chemicals

Although components of DESs are potentially reactive chemicals, their auto-association by a hydrogen bond drastically limits their reactivity, allowing their use in many fields of research.

CO_2 solubility

Dissolution in DESs

Combination of CO_2 with green DES systems has a great potential for a variety of chemical processes (separation and purification of gas, chemical fixation of CO_2, catalysis, etc.).

In 2008, Han and co-workers determined the solubility of CO_2 in a ChCl/urea DES at different temperatures, pressures and with different ChCl/urea molar ratio.

$$k_H = \lim_{x_1 \to 0} \frac{f_1}{x_1} \approx \frac{P_1}{x_1}$$

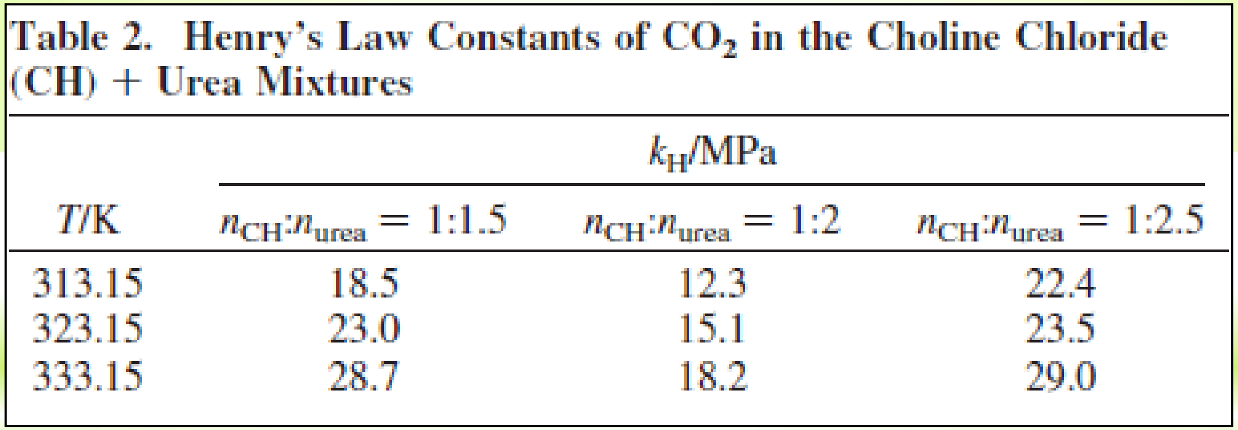


Table 2. Henry's Law Constants of CO_2 in the Choline Chloride (CH) + Urea Mixtures

	k_H/MPa		
T/K	$n_{CH}:n_{urea}$ = 1:1.5	$n_{CH}:n_{urea}$ = 1:2	$n_{CH}:n_{urea}$ = 1:2.5
313.15	18.5	12.3	22.4
323.15	23.0	15.1	23.5
333.15	28.7	18.2	29.0

The solubility of CO_2 (x_1) in ChCl/urea DES depends on three factors:

(1) x_1 values increased with increase in the CO_2 pressure (solubility of CO_2 is more sensitive to the pressure in the low-pressure range)

(2) x_1 values decreased with increase in the temperature whatever the pressure

(3) the ChCl/urea molar ratio has a significant effect on x_1 values

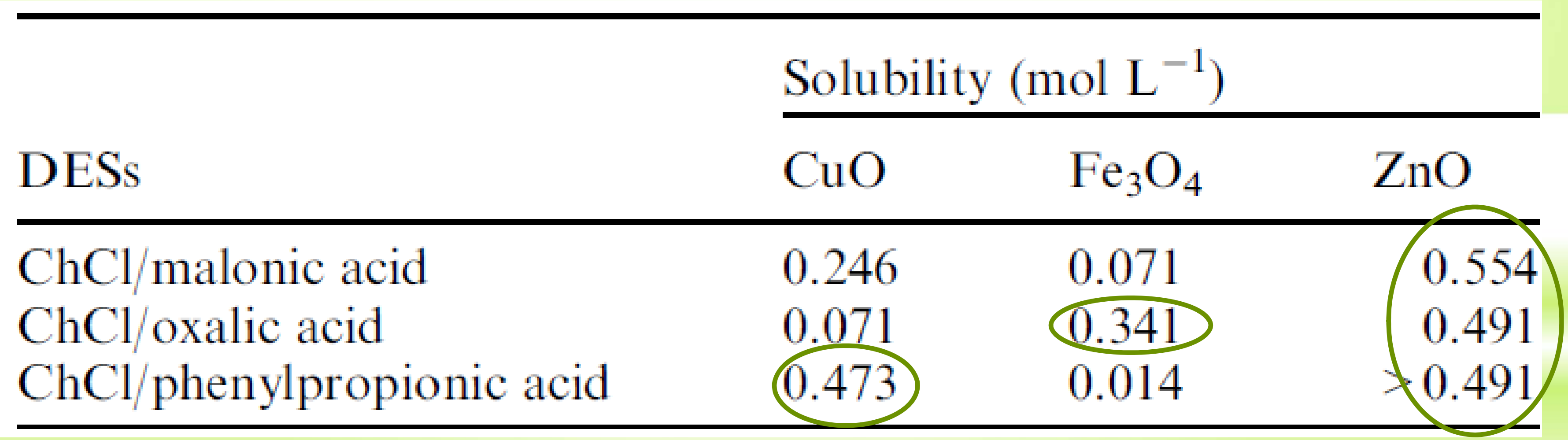
(e.g. at the same temperature and pressure, the ChCl-urea(1 : 2) eutectic mixture exhibits higher x_1 values than DES with a ChCl/urea molar ratio of 1 : 1.5 and 1 : 2.5)

Dissolution in DESs

Dissolution of metal oxides

DESs are capable of donating or accepting electrons or protons to form hydrogen bonds which confers them excellent dissolution properties.

DESs are capable of dissolving various metal oxides, thereby opening a “green” strategy for the separation and recycling of metals, a key point in electrochemistry technology.



	Solubility (mol L^{-1})		
DESs	CuO	Fe_3O_4	ZnO
ChCl/malonic acid	0.246	0.071	0.554
ChCl/oxalic acid	0.071	0.341	0.491
ChCl/phenylpropionic acid	0.473	0.014	>0.491

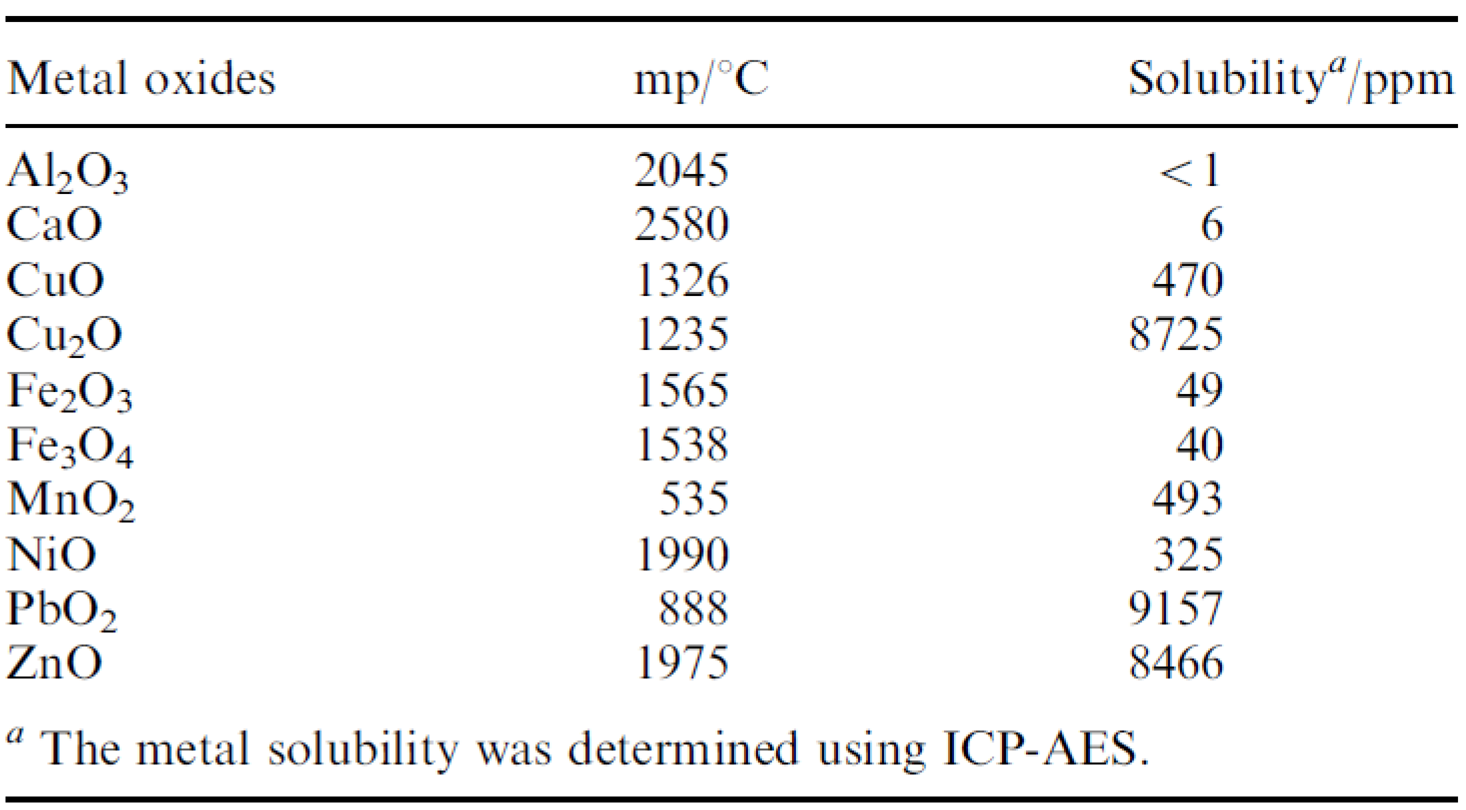
Solubility of ZnO, CuO, and Fe_3O_4 in three DESs at 50 °C

A. P. Abbott, D. Boothby, G. Capper, D. L. Davies and R. K. Rasheed, J. Am. Chem. Soc., 2004, 126, 9142-9147.

Dissolution in DESs

Dissolution of metal oxides

Solubility of metal oxides in a ChCl/urea (1 : 2) at 60 °C



Metal oxides	mp/°C	Solubility[a]/ppm
Al_2O_3	2045	< 1
CaO	2580	6
CuO	1326	470
Cu_2O	1235	8725
Fe_2O_3	1565	49
Fe_3O_4	1538	40
MnO_2	535	493
NiO	1990	325
PbO_2	888	9157
ZnO	1975	8466

[a] The metal solubility was determined using ICP-AES.

Dissolution of metal oxides in ChCl/urea DES is mainly governed by the complexation abilities of urea and the chloride anion.

Summary

Many DESs have excellent dissolution properties for CO_2, inorganic salts, and organic molecules

Many DESs can selectively dissolve different metal oxides, which thus provide great potential for the selective recovery of pure metals, especially in electrochemistry

Catalysis in DESs

Base-catalyzed reactions

Electrophilic substitution of 1-aminoanthra-9,10-quinone derivatives in ChCl/urea (1 : 2).

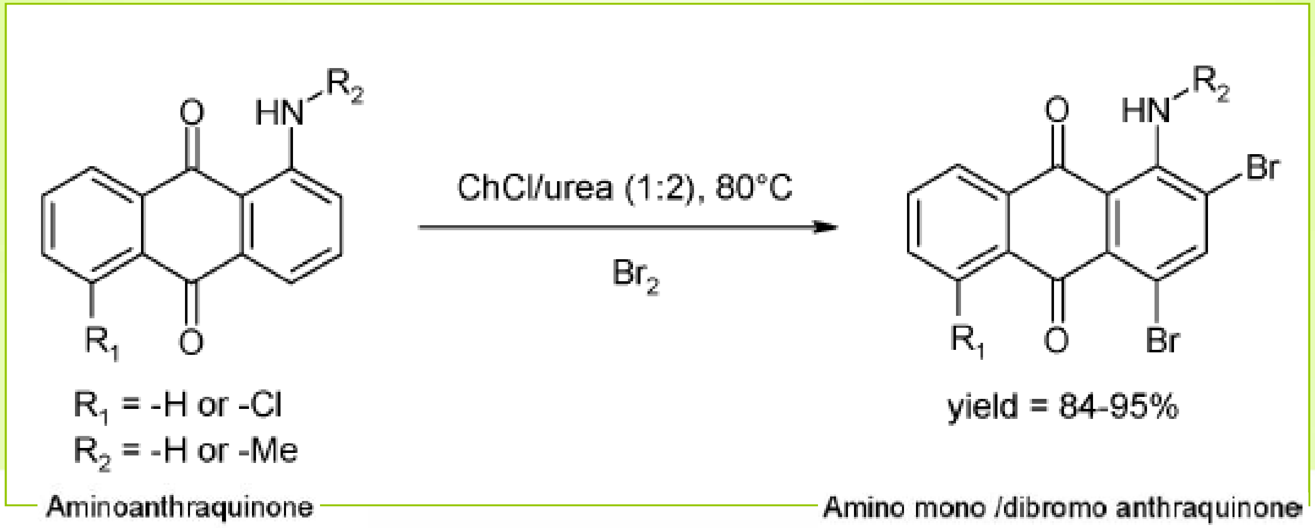


Table 2 Bromination of 1-aminoanthra-9,10-quinone derivative using organic solvents using 2.5 equivalent of bromine at 20-30 °C

Entry	Solvent	Reaction time (hr.)	Yield (%)[a]	HPLC Purity (%)
1	Methanol	10-12	75	95
2	Chloroform	10-12	70	92
3	Deep eutectic solvent	2-3	95	97

[a] Isolated by filtration.

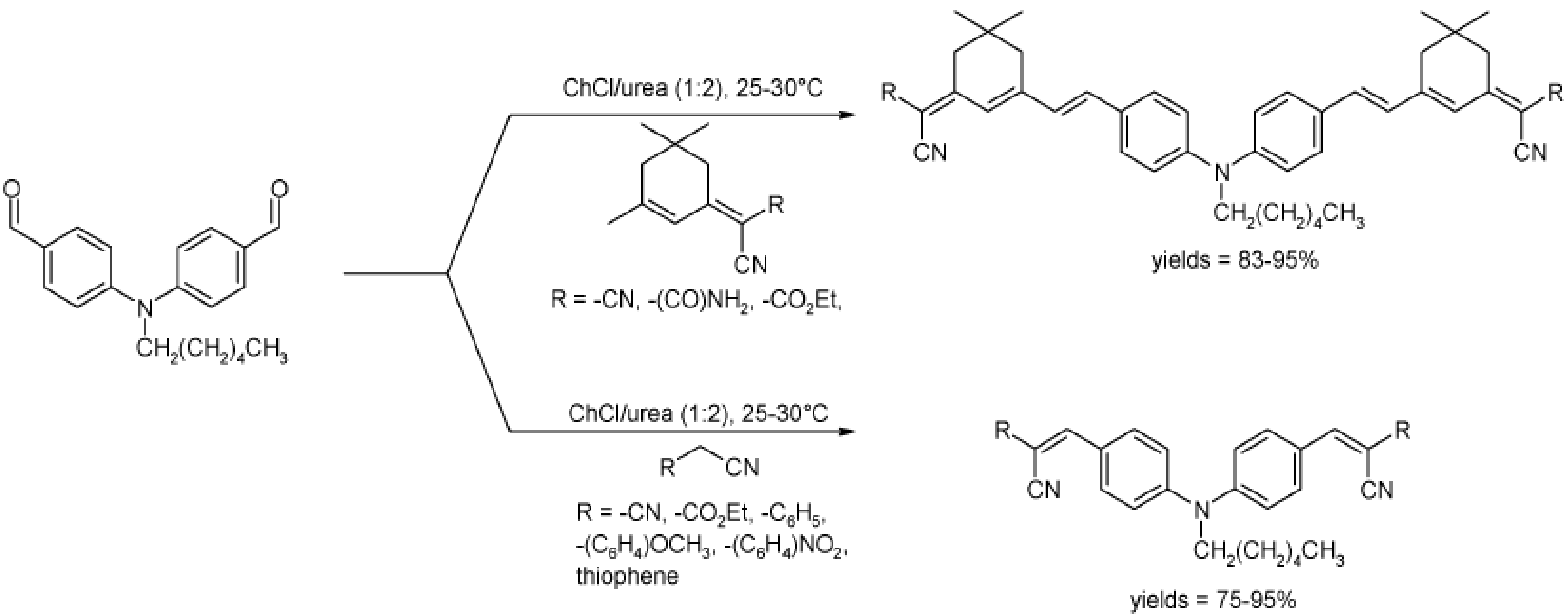
this rate enhancement might be attributed to the basic nature of the DES and/or to the ability of urea to stabilize transition states

S. B. Phadtare and G. S. Shankarling, Green Chem., 2010, *12*, 458-462.

Catalysis in DESs

Base-catalyzed reactions

Base-catalyzed Knovenagel in the ChCl–urea (1 : 2) system.



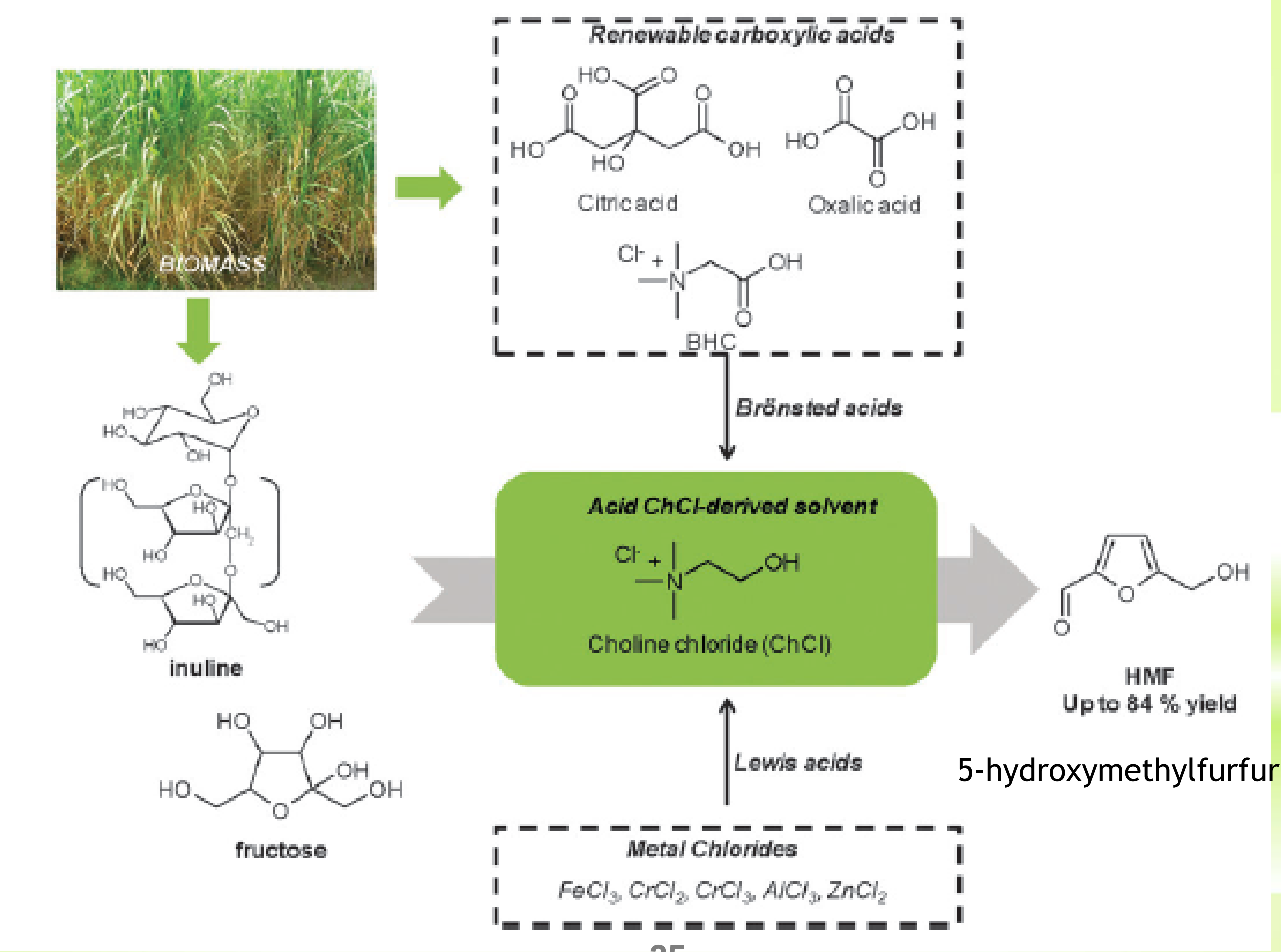
This DES was successfully recycled five times thanks to the easy isolation of the products of the reaction from the DES phase.

P. M. Pawar, K. J. Jarag and G. S. Shankarling, Green Chem.,2011, *13*, 2130–2134.

Catalysis in DESs

Acid-catalyzed reactions

Acid-catalyzed dehydration of inulin and fructose in ChCl-derived DES.



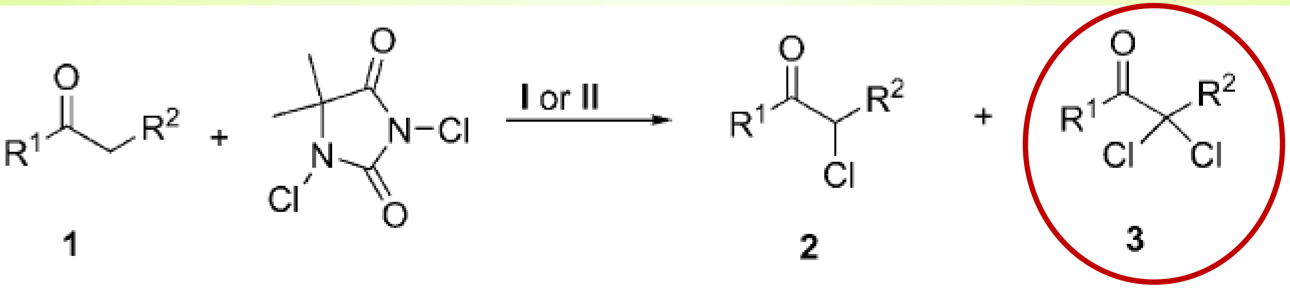
5-hydroxymethylfurfural

S. Hu, Z. Zhang, Y. Zhou, J. Song, H. Fan and B. Han, Green Chem., 2009, *11*, 873–877.

Catalysis in DESs

Acid-catalyzed reactions

Selectively prepare α-mono or α,α-dichloro ketones and β-ketoesters



I: SiO_2,MeOH,reflux,1h; Yield: **2a~2l**(86~98%)

II: DES, rt, 45 min.; Yield: **3a~3l**(86~95%)

1a: R^1=phenyl, R^2=H
1b: R^1=*p*-Cl-phenyl, R^2=H
1c: R^1=*p*-Br-phenyl, R^2=H
1d: R^1=*p*-Me-phenyl, R^2=H
1e: R^1=*p*-NO_2-phenyl, R^2=H
1f: R^1=*m*-NO_2-phenyl, R^2=H
1g: R^1=4'-Br-biphenyl, R^2=H
1h: R^1=*p*-OMe-phenyl, R^2=H
1i: R^1=Me, R^2= -COOEt
1j:R^1=benzoyl, R^2= -COOEt
1k: R^1=*p*-NO_2-benzoyl, R^2= -COOEt
1l:R^1= *t*-butyl, R^2=H

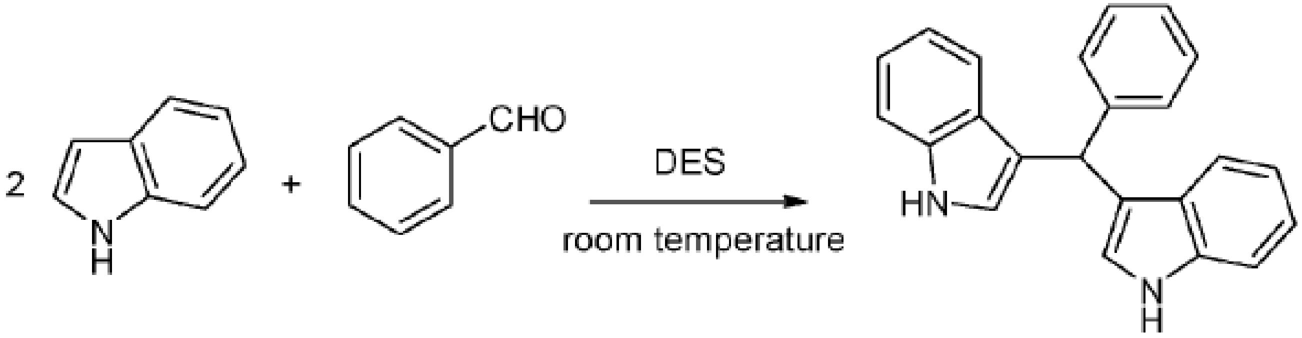
Using a DES (choline chloride:*p*-TsOH = 1:1) as the solvent and stirring for 45 min at r.t., α,α-dichlorinated products were selectively obtained in 86–95% yield.

Z. Chen, B. Zhou, H. Cai and X. Zou, Green Chem., 2009, *11*, 275–278.

Catalysis in DESs

Acid-catalyzed reactions

Synthesis of bis(indolyl)methane in acid derived ChCl DESs.



DES	ChCl/SnCl_2	ChCl/ZnCl_2	ChCl/ZnCl_2/SnCl_2	ChCl/SnCl_2/H_2O	ChCl/SnCl_2/PE*
Molar ratio	1:2	1:2	1:1:1	1:2:3	1:2:3
Yields (%)	80	64	70	85	85

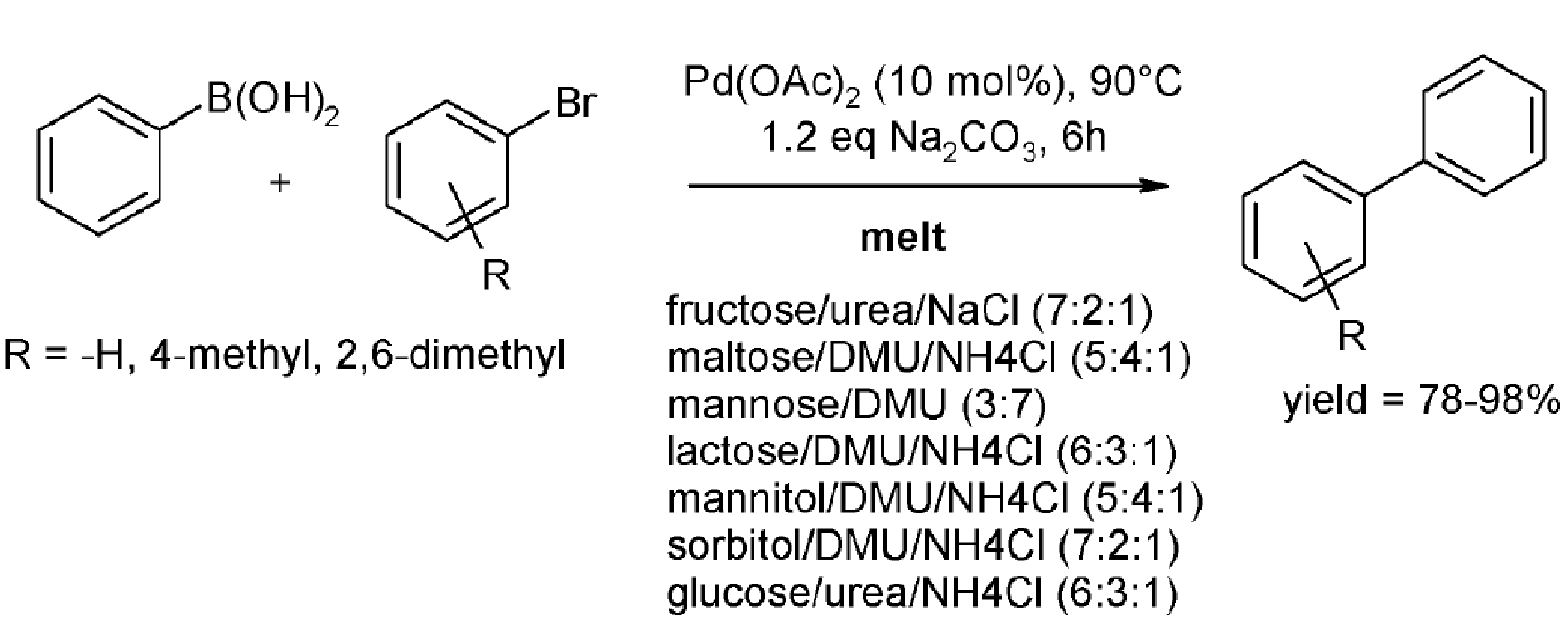
* polyethylene glycol

N. Azizi and Z. Manocheri, Res. Chem. Intermed., 2012, DOI:10.1007/s11164-011-0479-4.

Catalysis in DESs

Transition-metal-catalyzed reactions

Palladium-catalyzed Suzuki coupling in various carbohydrate-urea-inorganic salts eutectic mixtures.



Pd(OAc)$_2$ (10 mol%), 90°C
1.2 eq Na_2CO_3, 6h

melt

fructose/urea/NaCl (7:2:1)
maltose/DMU/NH4Cl (5:4:1)
mannose/DMU (3:7)
lactose/DMU/NH4Cl (6:3:1)
mannitol/DMU/NH4Cl (5:4:1)
sorbitol/DMU/NH4Cl (7:2:1)
glucose/urea/NH4Cl (6:3:1)

R = -H, 4-methyl, 2,6-dimethyl

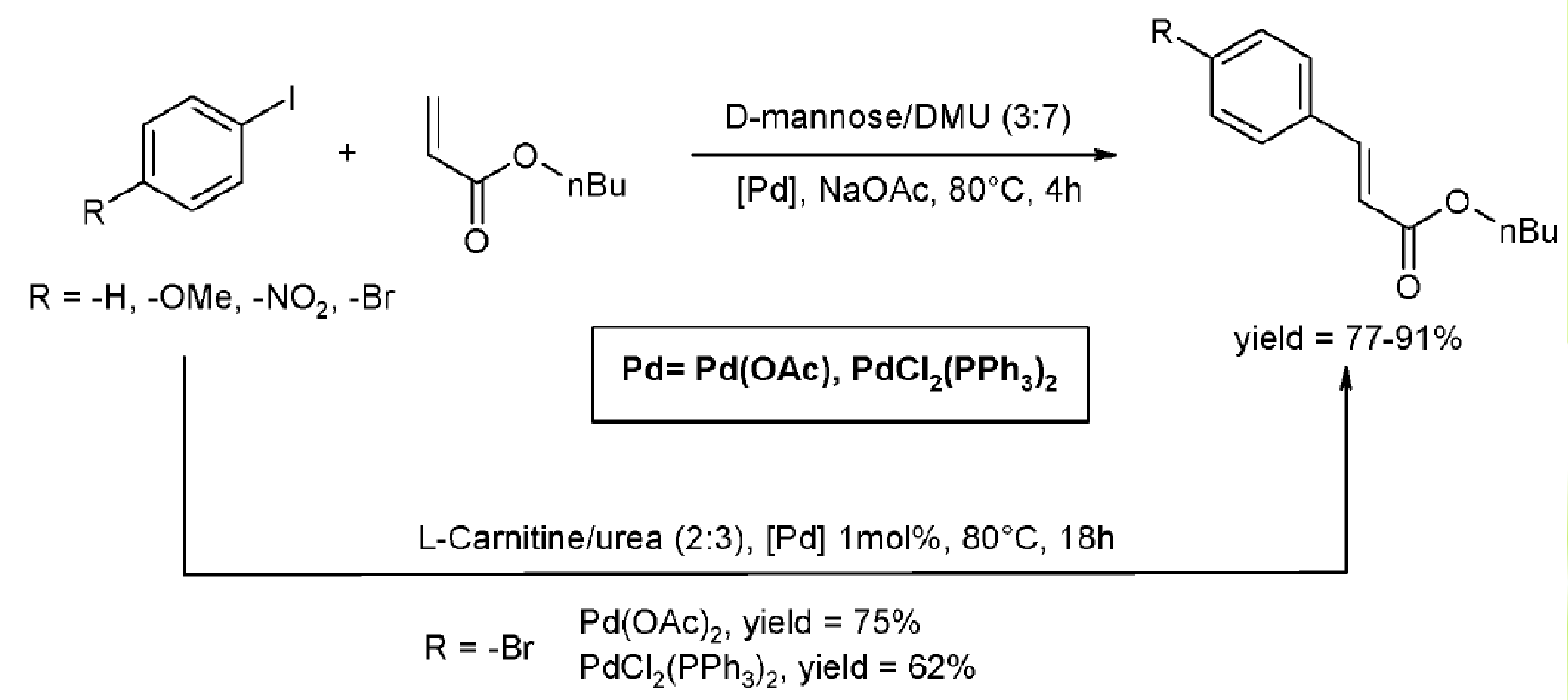
yield = 78-98%

G. Imperato, S. Hoger, D. Lenoir and B. Konig, Green Chem., 2006, 8, 1051-1055.

Catalysis in DESs

Transition-metal-catalyzed reactions

Palladium-catalyzed Heck coupling in D-mannose/*N*,*N*-dimethylurea melts.

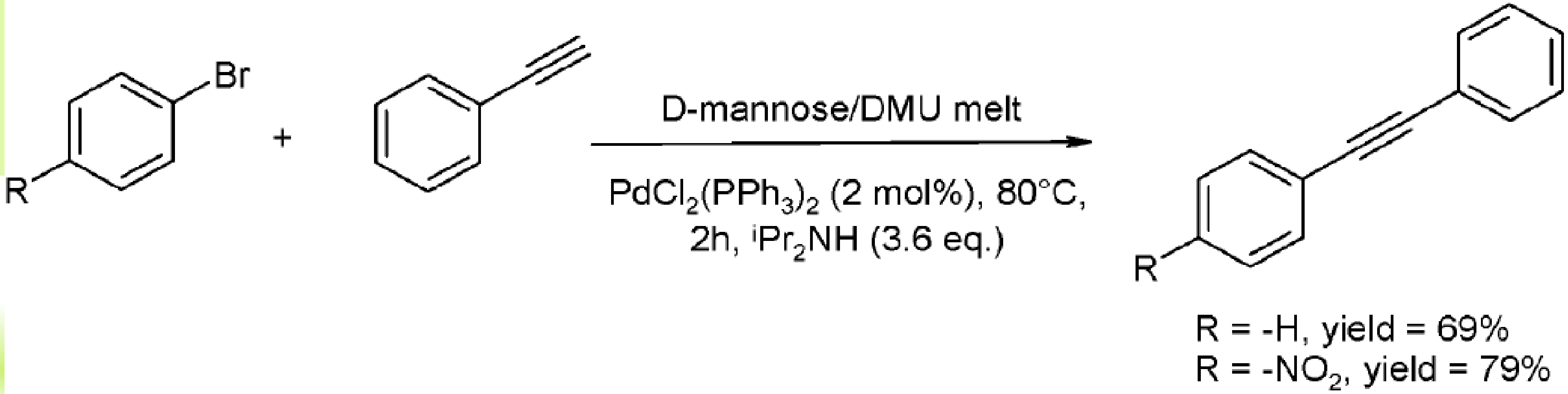


F. Ilgen and B. Konig, Green Chem., 2009, *11*, 848-854.

Catalysis in DESs

Transition-metal-catalyzed reactions

Sonogashira coupling in D-mannose/ *N*,*N*-dimethylurea melts.

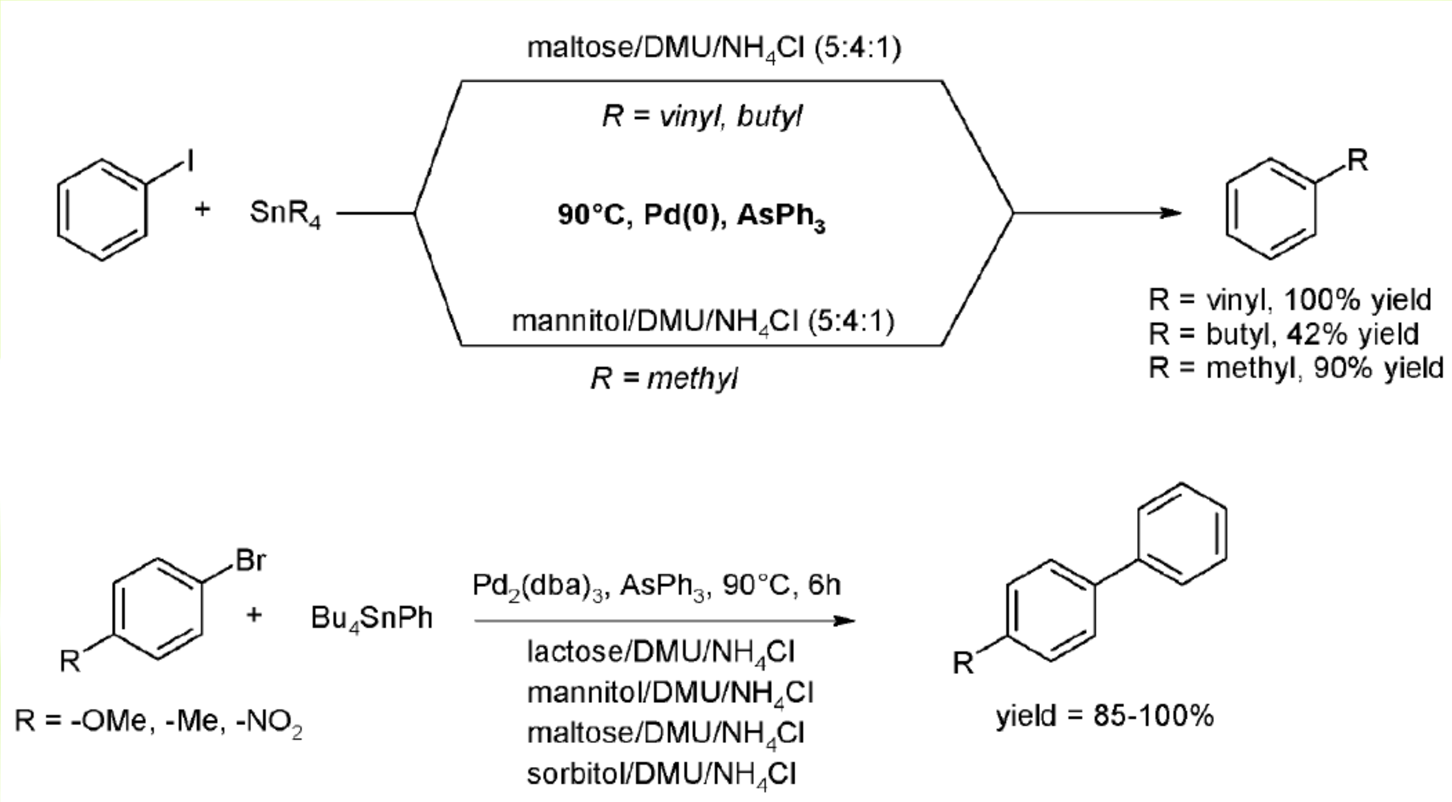


F. Ilgen and B. Konig, Green Chem., 2009, *11*, 848–854.

Catalysis in DESs

Transition-metal-catalyzed reactions

Palladium-catalyzed Stille coupling of aryl bromide and iodide with alkyl and aryl stannate in polyol/ *N*,*N*-dimethylurea /NH_4Cl melts.

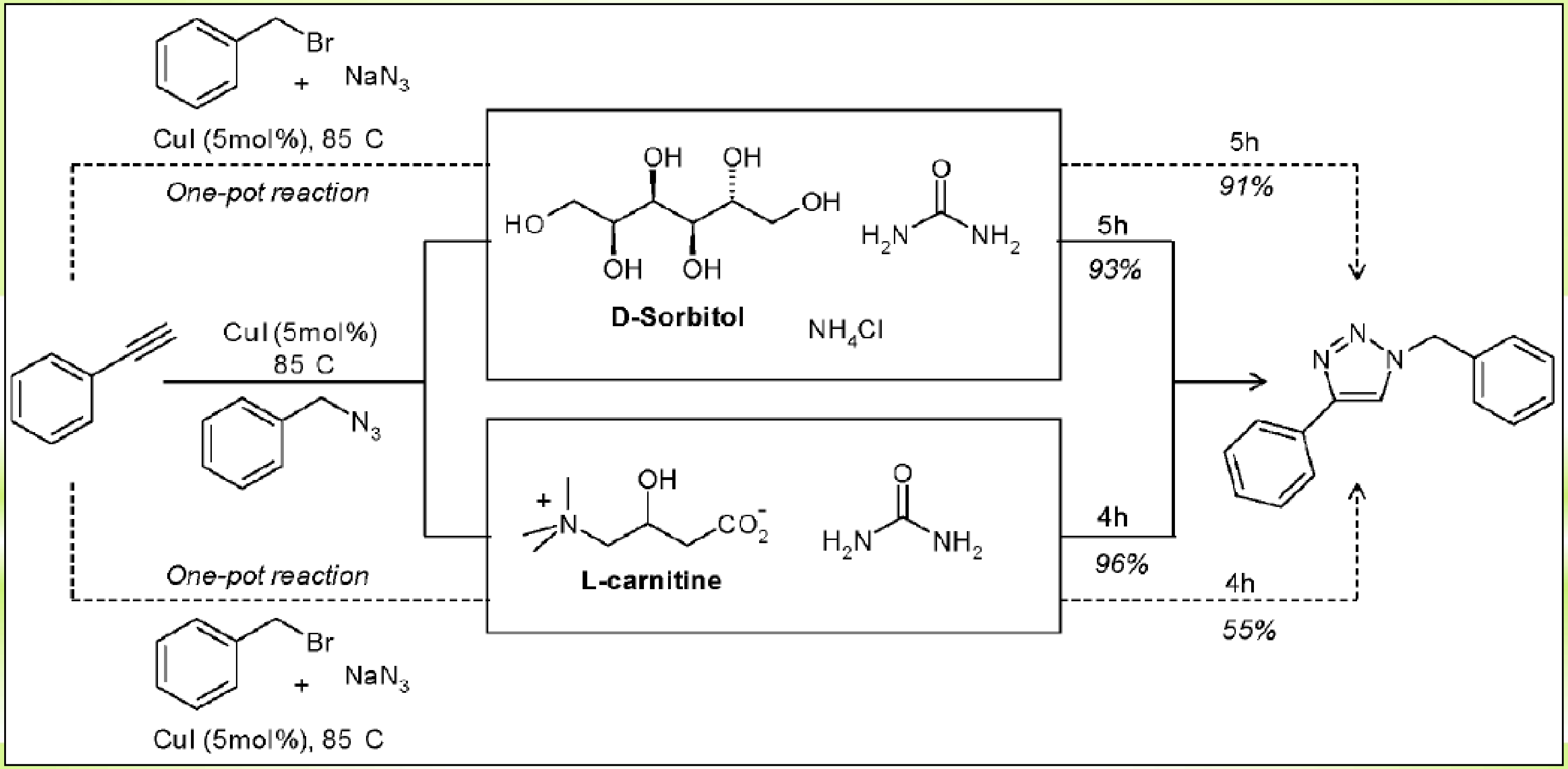


G. Imperato, R. Vasold and B. Konig, Adv. Synth. Catal., 2006, *348*, 2243–2247.

Catalysis in DESs

Transition-metal-catalyzed reactions

Cu-catalyzed azide-alkyne 1,3-dipolar cycloaddition in D-sorbitol/urea/NH_4Cl or L-carnitine/urea melts.

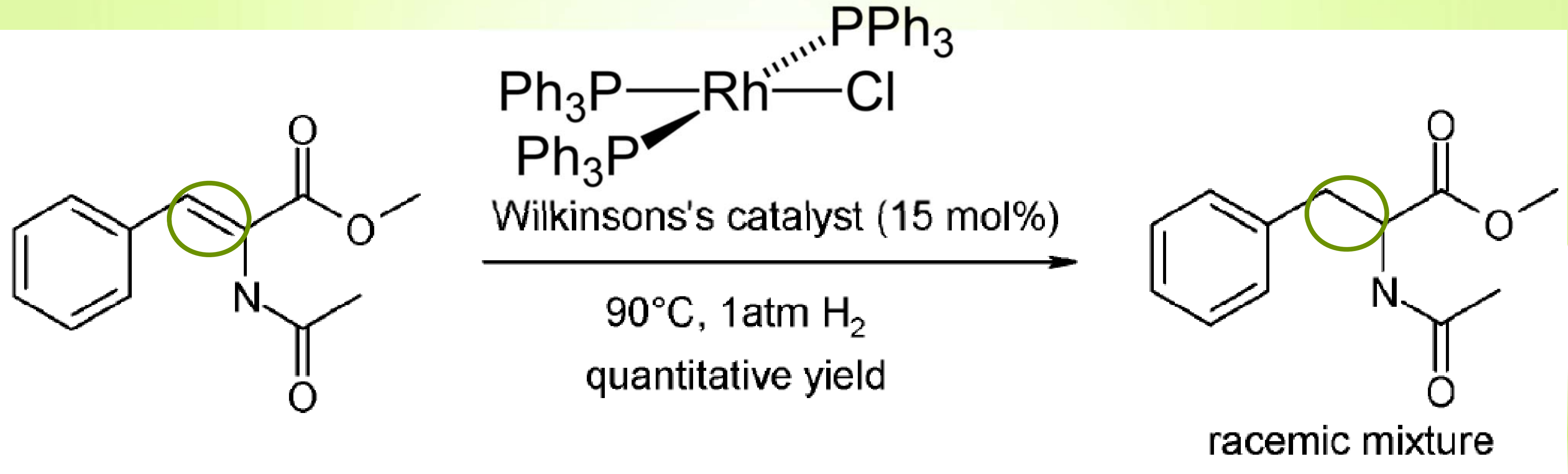


F. Ilgen and B. Konig, Green Chem., 2009, *11*, 848-854.

Catalysis in DESs

Transition-metal-catalyzed reactions

Catalytic hydrogenation of methyl α-cinnamate in citric acid/ *N*,*N*-dimethylurea (2 : 3).



G. Imperato, S. Hoger, D. Lenoir and B. Konig, Green Chem., 2006, *8*, 1051–1055.

Biocatalysis in DESs

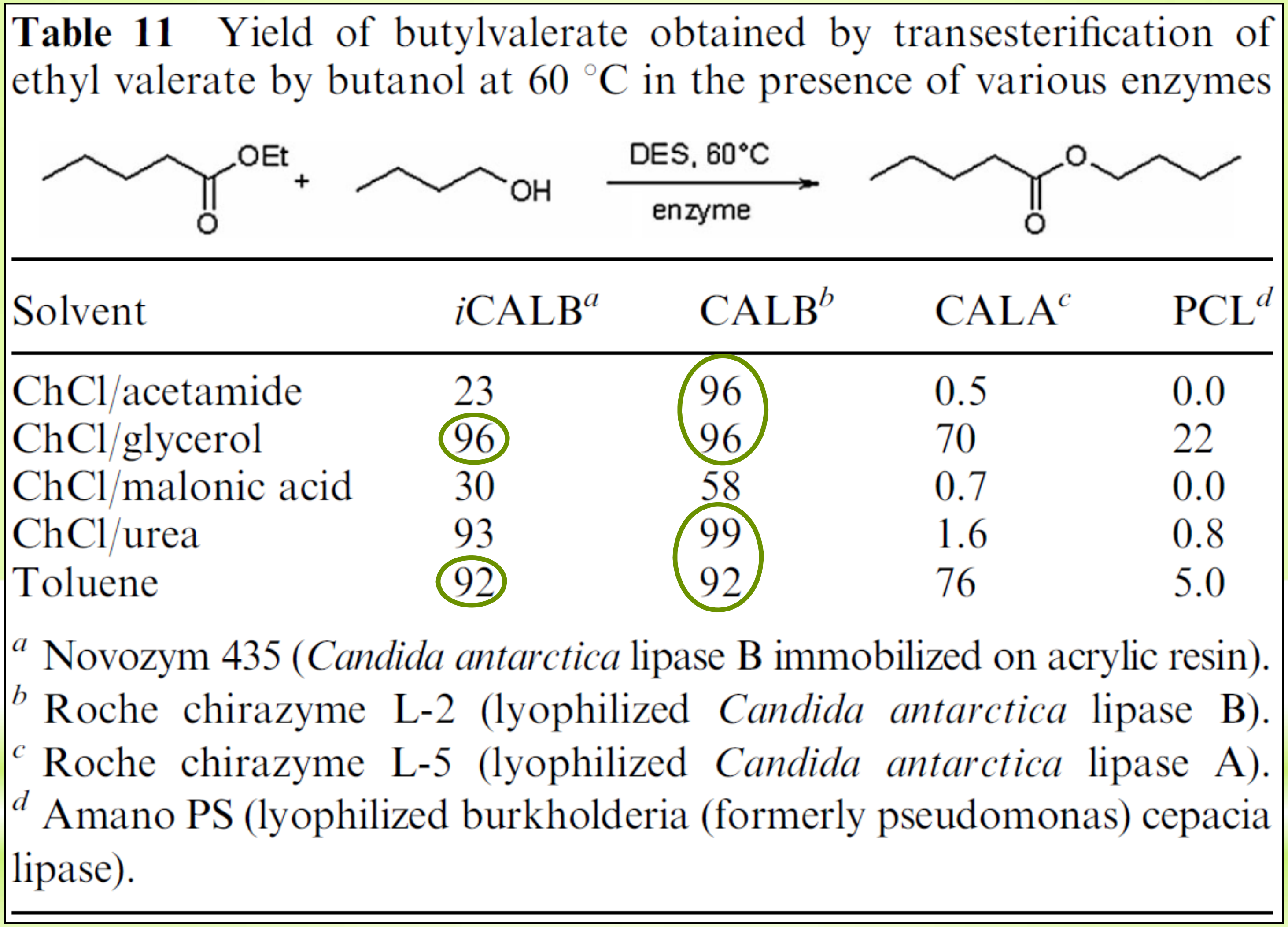


Table 11 Yield of butylvalerate obtained by transesterification of ethyl valerate by butanol at 60 °C in the presence of various enzymes

Solvent	*i*CALB[a]	CALB[b]	CALA[c]	PCL[d]
ChCl/acetamide	23	96	0.5	0.0
ChCl/glycerol	96	96	70	22
ChCl/malonic acid	30	58	0.7	0.0
ChCl/urea	93	99	1.6	0.8
Toluene	92	92	76	5.0

[a] Novozym 435 (*Candida antarctica* lipase B immobilized on acrylic resin).
[b] Roche chirazyme L-2 (lyophilized *Candida antarctica* lipase B).
[c] Roche chirazyme L-5 (lyophilized *Candida antarctica* lipase A).
[d] Amano PS (lyophilized burkholderia (formerly pseudomonas) cepacia lipase).

1. activity of enzymes in selected DES was similar to that observed in toluene
2. demonstrating the potential of DESs for biotransformations

J. T. Gorke, F. Srienc and R. J. Kazlauskas, Chem. Commun., 2008, 1235–1237.

Biocatalysis in DESs

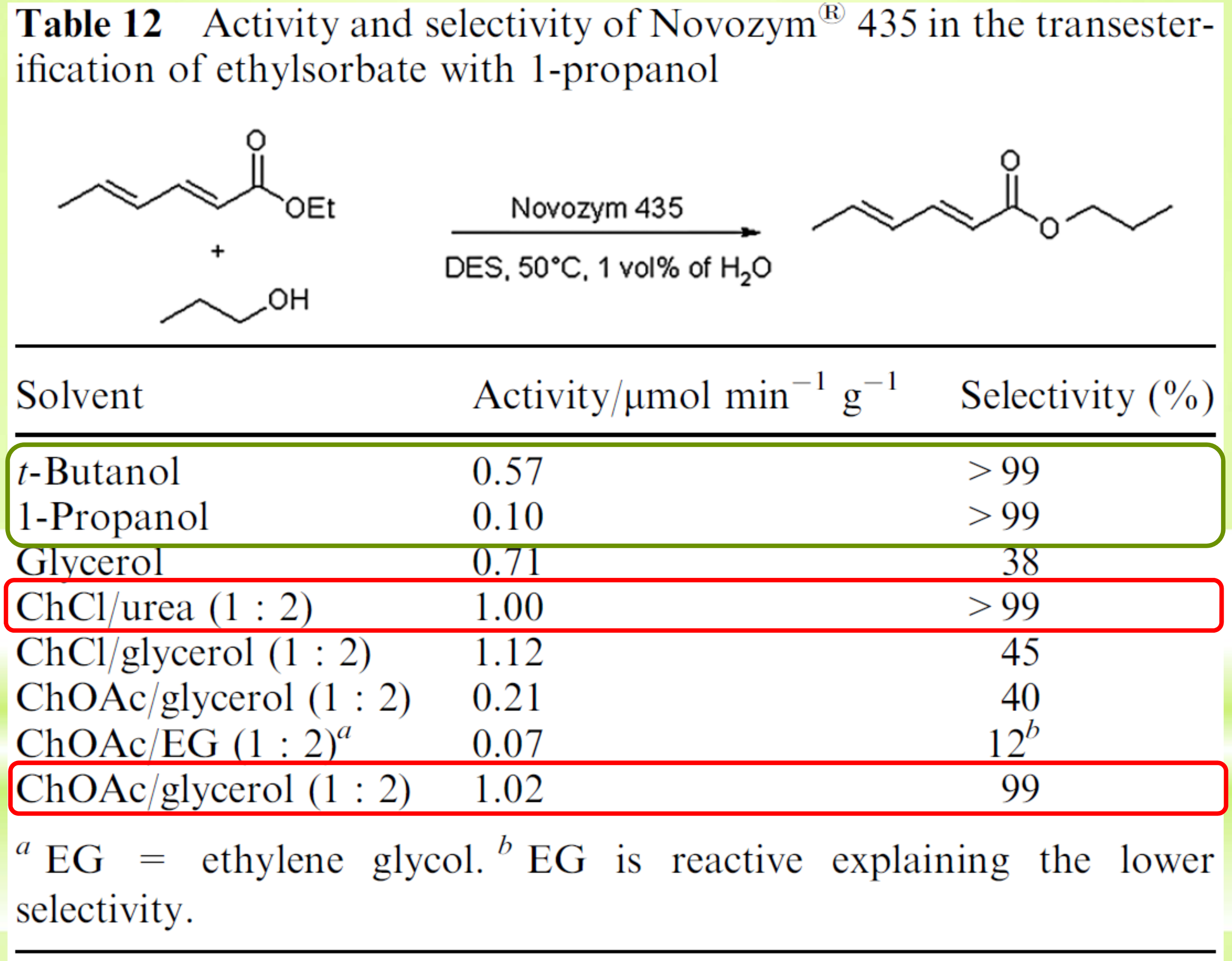


Table 12 Activity and selectivity of Novozym® 435 in the transesterification of ethylsorbate with 1-propanol

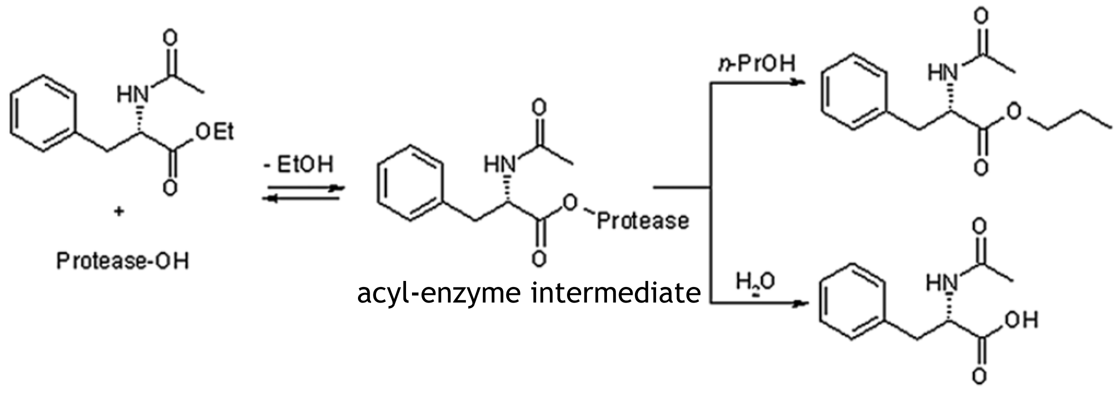
Solvent	Activity/μmol min^{-1} g^{-1}	Selectivity (%)
t-Butanol	0.57	> 99
1-Propanol	0.10	> 99
Glycerol	0.71	38
ChCl/urea (1 : 2)	1.00	> 99
ChCl/glycerol (1 : 2)	1.12	45
ChOAc/glycerol (1 : 2)	0.21	40
ChOAc/EG (1 : 2)[a]	0.07	12[b]
ChOAc/glycerol (1 : 2)	1.02	99

[a] EG = ethylene glycol. [b] EG is reactive explaining the lower selectivity.

H. Zhao, G. A. Baker and S. Holmes, Org. Bio. Chem., 2011, *9*, 1908–1916.

Biocatalysis in DESs

Table 13 Activities of subtilisin and α-chymotrypsin in glycerol-derived DESs



Solvent	Protease^a	Water content (v/v)%	Activity/ μmol min^{-1} g^{-1}	Sel. (%)
t-Butanol	S/Chit	2	0.50	29
ChOAc/glycerol (1 : 1.5)	S/Chit	2	0.42	99
ChOAc/glycerol (1 : 1.5)	S/Chit	3	0.40	99
ChOAc/glycerol (1 : 1.5)	S/Chit	4	0.90	99
ChCl/glycerol (1 : 2)	Free α-C	2	0.028	99
ChCl/glycerol (1 : 2)	α-C/Chit	2	0.031	99
ChCl/glycerol (1 : 2)	α-C/Chit	3	0.75	99
ChCl/glycerol (1 : 2)	S/Chit	3	2.90	98

[a] 50 °C, S = subtilisin, α-C = α-chymotrypsin, Chit = chitosan.

Indicating that glycerol-derived DESs were very attractive for biocatalytic reactions involving more sensitive enzyme than lipase

1. H. Zhao, G. A. baker and S. Holmes, J. Mol. Cat. B: Enzymatic, 2011, *72*, 163–167.
2. M. C. Gutierrez, M. L. Ferrer, L. Yuste, F. Rojo and F. delMonte, Angew. Chem., Int. Ed., 2010, *49*, 2158–2162.

Summary

The remarkable stability of enzymes in DESs has been recently highlighted in a scientific correspondence.

Some authors have hypothesized that the formation of natural DESs from chemicals that are present at high concentration in living cells may contribute to explain

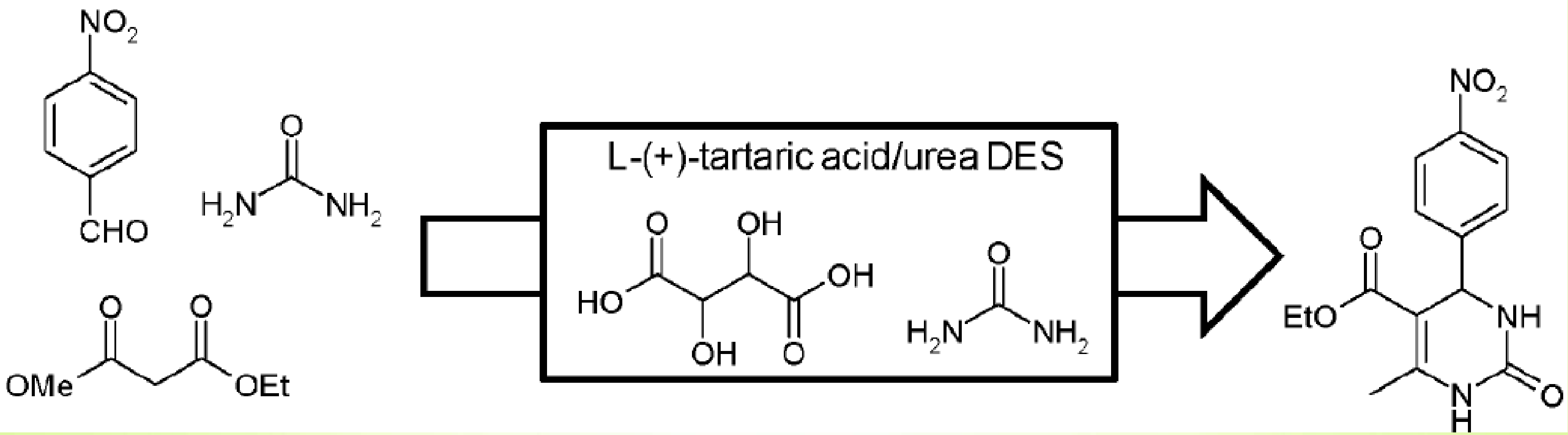
(1) mechanisms and phenomena that are nowadays difficult to understand

(2) the resistance of living organisms under extreme conditions

Y. H. Choi, J. van Spronsen, Y. Dai, M. Verbene, F. hollmann, I. W. C. E. Arends, G. J. Witkamp and R. Verpoorte, Plant Physiol., 2011, *156*, 1701–1705.

Organic synthesis in DESs

Example of Biginelli reaction performed in acid L-(+)-tartaric acid/DMU (3 : 7) DES.



dihydropyrimidinone
(DHPM)

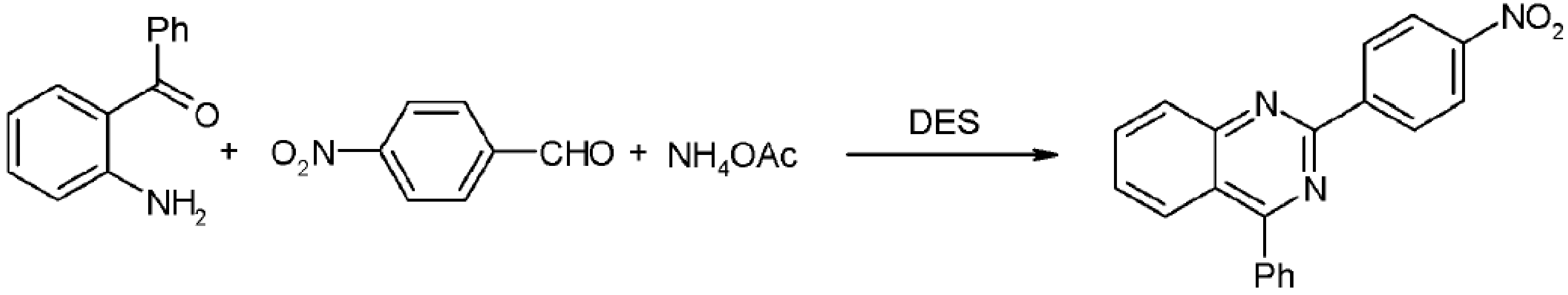
Urea was used in this example not only as a reactant but also as a component of the DES.

Ex: in a citric acid/DMU (2 : 3) DES, p-4-nitrobenzaldehye, ethylacetoacetate and DMU were selectively assembled at 65 °C to the desired DHPM which was obtained with 90% yield.

S. Gore, S. Baskaran and B. Konig, Green Chem., 2011, 13, 1009–1013.

Organic synthesis in DESs

Table 14 Three component reactions of 2-amino-benzophenone, 4-nitrobenzaldehyde and ammonium acetate in various DESs

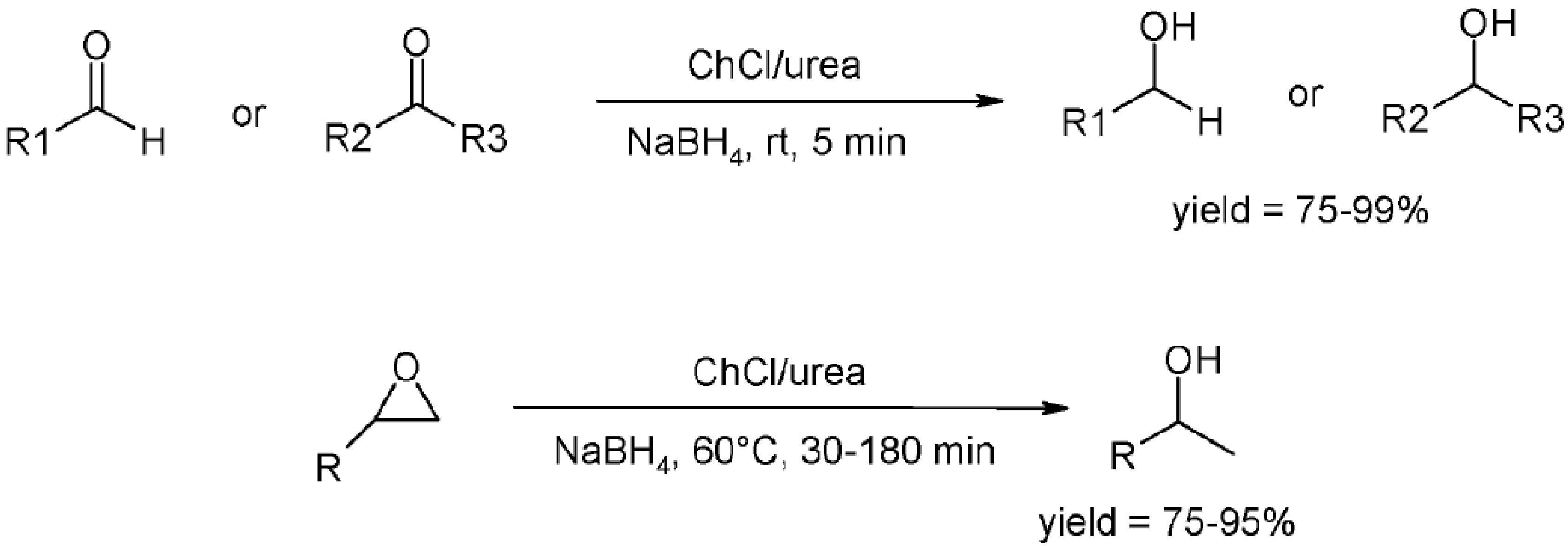


Melt	T/°C	Yield (%)
Citric acid/DMU (4 : 6)	65	85
Fructose/DMU (7 : 3)	71	75
Tartaric acid/DMU (3 : 7)	70	82
Tartaric acid/ChCl (5 : 5)	90	89
Mannose/DMU/NH4Cl (5 : 4 : 1)	89	82
Lactose/DMU/NH4Cl (5 : 4 : 1)	88	86
Maltose/DMU/NH4Cl (5 : 4 : 1)	84	92

This work exhibited a broad substrate scope and products of the reaction were conveniently isolated from the DES either by crystallization or by extraction with ethyl acetate, allowing the DES to be recycled.

Organic synthesis in DESs

Reduction of aldehydes and epoxides by $NaBH_4$ in ChCl/urea.



F.-P. Ma, G.-T. Cheng, Z.-G. He and Z.-H. Zhang, Aust. J.Chem., 2012, *65*,409-416.

Summary

In the field of catalysis and organic synthesis, it is clear that DESs will definitely contribute to the design of eco-efficient processes. The possibility to

(1) selectively and conveniently extract products of the reaction from the DESs phase

(2) adjust the pH of DESs

(3) dissolve not only organic and inorganic salts but also transition metal-derived complexes or nanoparticles

(4) recycle these media is among the most promising advantages of DESs

Outlook

Promising results were found for different fields of applications.

However,

the field of separation technology is still far from being fully explored. Deeper studies on the interactions and building principles are needed in order to gain insight into the properties of these solvents and to find new applications.

DESs can be regarded as a poorly toxic and biocompatible lipotropic agent, thus opening a new strategy for the vectorisation of pharmaceutical ingredients in the human body.

DES’s low ecological footprint and attractive price will definitely contribute to the industrial emergence of this new medium in a close future.

Thanks for your attention!