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Glycerol eutectics as sustainable solvent systems†

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In this work the use of glycerol as a hydrogen bond donor in Deep Eutectic Solvents is studied. The physical properties of choline chloride mixtures with glycerol are quantified and it is shown that eutectic mixtures can circumvent some of the difficulties of using glycerol as a solvent *viz*. high viscosity and high melting point. The solvent properties are characterised using polarity parameters and the values are similar to other ionic liquids although it is shown that this procedure is a poor method of characterising Lewis basicity. The application of these liquids to the esterification of glycerol is used as a demonstration of the ability to tune a reaction with the quaternary ammonium halide acting as a quasi-protecting group. The liquids represent a sustainable way of preparing non-toxic, tuneable solvent systems.

Introduction

Glycerol is a by-product of a range of hydrolysis and *trans*esterification processes of oils and fats most notably in the soap and biodiesel manufacturing industries. Glycerol has some uses principally as viscosity modifiers and freezing point suppressants however with annual production in excess of 1 million tonnes p.a. the market is saturated. The fact that glycerol is poorly combustible means that it cannot even be used as a fuel and it is regarded by many to be a waste product. One of the limiting factors with its use as a bulk solvent is its high viscosity and high boiling point making it difficult to separate species by filtration or distillation. A recent review¹ has assessed the use of glycerol as a green solvent.

We have recently shown that the addition of a stoichiometric equivalent of a quaternary ammonium salt to glycerol forms a deep eutectic solvent (DES) and decreases the viscosity of the liquid. This mixture was shown to be useful for the purification of biodiesel.² DESs are mixtures of hydrogen bond donors with simple halide salts which produce liquids which have physical and solvent properties that are comparable with ionic liquids.^{3,4} DESs have been used for a variety of applications including metal deposition, metal oxide processing, metal dissolution and a variety of synthetic processes. The majority of systems studied to date have been based on choline chloride $HOC_2H_4N^+(CH_3)_3Cl^-$ (ChCl) because it is non-toxic and readily available as a bulk commodity chemical. Its common use stems in part from its simple manufacture; an efficient gas phase reaction between trimethylamine, ethylene oxide and HCl. This means that the Sheldon E factor⁵ for this salt is close to zero because almost no waste products are formed during this reaction. The combination of the salt with glycerol produces a liquid which is non-flammable and non-toxic; the mixture can even be prepared from food-grade components.

In the current work we characterise the physical properties of these liquids and use them to propose an improved model for the mobility of species in ionic liquids. We also demonstrate that the chemical properties of these liquids are different from bulk glycerol by characterising the solvatochromic parameters and demonstrate that esterification reactions of glycerol produce significantly different product distributions.

Experimental

Synthesis of 1:2 ChCl: glycerol system

ChCl (Aldrich 99%) was recrystallised from absolute ethanol, filtered and dried under vacuum. Glycerol (Aldrich 99%) was used as received. The eutectic mixtures were formed by stirring the two components at ~80 °C until a homogeneous colourless liquid was formed.

Physical property measurements

The viscosity of the various ChCl:glycerol mixtures were measured using a Brookfield DV-E Viscometer fitted with a thermostated jacket and the conductivity of these systems was measured using a Jenway 4071 Conductivity Meter conductivity probe. Surface tension and density measurements were carried

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[†] Electronic supplementary information (ESI) available: Tables of data used in Figures 2, 3 and 6 together with the full data used to create Table 4 in the form shown in Figure 8.See DOI: 10.1039/c0gc00395f

 Table 1
 Peak elution time of reagents and products of esterification reactions using GPC

Reagent/Product	Lauric Acid	Mono Ester	Di Ester	Tri Ester
Elution Time/min	14.7	14.2	13.3	12.9

out using a Krüss Tensiometer K9 with a platinum plate which was connected to a thermostated water bath. All readings were taken after 25–30 min at each temperature to ensure the system was at equilibrium. For clarity error bars have been omitted from most plots but these are typically less than $\pm 3\%$ of the given value.

Solvatochromism experiments

All UV-Vis measurements were carried out using a Shimadzu model UV-1601 spectrophotometer to measure the solvatochromic shift of the different indicator dyes in the visible absorbance spectrum. The program UV PROBE was used to obtain the maximum absorbance of the UV-Vis spectra of the solvatochromic dyes in each system. Sample concentration was kept in the range of 10^{-5} – 10^{-6} mol dm⁻³ in order to reduce any possible solute–solute interactions being observed.

Esterification experiments

The progression of the esterification reactions was measured by gel permeation chromatography (GPC). The GPC used was a Polymer Laboratories PL-GPC 220 with two PLgel 5 μ m 50 Å columns. The analysis was carried out at 40 °C at a flow rate of 1 cm³ min⁻¹. The solvent used was dry THF. Each sample vial contained 0.02 g of product and was dissolved in 1.25 mL of dry THF. Under this setup the elution times of the reagents and products are shown in Table 1. As would be expected the product yields were less reproducible than the physical measurements but values of the equilibrium constant are ±10% of the values quoted.

Diffusion coefficient studies

The Pulsed Field Gradient NMR experiments were carried out with a Bruker DMX 300 equipped with a diffusion probe capable of producing magnetic field gradient pulses up to 11.6 T/m. The measurements were performed over the temperature range from 298 K to 333 K, with increments of 5 K using a Bruker Variable Temperature unit, BVT 300. Samples were prepared in 5 mm NMR tubes filled with liquid to a height of approximately 20 mm. For each temperature, the sample was left for 15 min before starting the measurement, to achieve thermal equilibrium. Diffusion measurements were carried out using the PGSTE pulse sequence (Fig. 1), holding the gradient pulse duration, δ , constant and varying the magnetic field gradient strength, g, for 16 points. A homospoil gradient between the second and the third 90° radiofrequency pulse (RF) was applied in order to destroy any unwanted residual magnetization on the transverse plane. The observation time, Δ , was set to 50 ms. Typical values of δ were 3 and 4 ms. The numerical values of the diffusion coefficient, D, were obtained by fitting the NMR signal decay to the echo attenuation equation, given by:

$$\mathbf{E} = \exp\left[-D\gamma^2 g^2 \delta^2 \left(\Delta - \frac{\delta}{3}\right)\right] \tag{1}$$

where γ is the gyromagnetic ratio of the nuclei being studied (*i.e.*, ¹H in this case).

Results

Physical properties of glycerol with ChCl

The high viscosity of glycerol (1200 cP at room temperature) makes its use as a solvent very difficult. However, due to its low toxicity and ready availability, it could make an ideal solvent. The addition of a salt has a significant effect upon the fluid properties. Fig. 2 shows the effect of ChCl on the viscosity, η , of



Fig. 1 PGSTE pulse sequence showing gradient pulse duration, δ , echo time, τ , storage interval, T, homospoil gradient (crosshatched pattern) and observation time, Δ .



Fig. 2 Plot of temperature versus viscosity as a function of ChCl composition for glycerol (a) and a plot of all viscosities at 298 K (b).

glycerol as a function of composition and temperature. It can be seen that the viscosity decreases as the salt concentration increases which is in direct contrast to diol based systems where the viscosity increases as salts are added.⁶ It is worth noting that the addition of 33 mol% ChCl decreases the viscosity of glycerol by a factor of 3. Whilst this is higher than most molecular solvents it is similar to many ionic liquids and DESs.

The addition of 33 mol% ChCl significantly decreases the freezing point of glycerol from 17.8 °C down to -40 °C circumventing one of the problems with the use of the pure liquid. Fig. 3 shows the corresponding conductivity of the systems shown in Fig. 2. DESs have been studied in depth previously and many have shown a correlation between molar conductivity and fluidity.⁶



Fig. 3 Plot of temperature *versus* conductivity as a function of ChCl composition for glycerol systems.

This trend is more obvious when the viscosity is taken at one temperature and compared as a function of molar percentage composition of ChCl (Fig. 2 (b)). Like most ionic liquids the viscosity-temperature profiles follow an Arrheniuslike behaviour. The change in viscosity, η with temperature can be described by the expression;⁷

$$\ln \eta = \ln \eta_0 + \frac{E_\eta}{RT} \tag{2}$$

where η_{θ} is a constant and E_{η} is the energy for activation of viscous flow. The values of E_{η} are in the range 54.7 for 5% ChCl to 45.1 kJ mol⁻¹ for 33%. Analogous to the viscosity data, conductivity of ionic liquids have been fitted to;⁸

$$\ln \sigma = \ln \sigma_0 + \frac{E_\Lambda}{RT} \tag{3}$$

where E_A is the activation energy for conduction. The values of E_A are in the range –38.5 for 5% ChCl to –27.9 kJ mol⁻¹ for 33%. These values are in line with other ionic liquids and DESs.^{9,10} The values of E_η and E_A are always of opposite sign and of similar magnitude since there is an inverse relation between the two parameters (see eqn (8)). The values for DESs and ionic liquids are significantly larger than most molecular solvents and molten salts due to their abnormally high viscosity and low free volume.⁴

The effect of the salt upon the structure of the liquid can be more clearly seen by measuring the liquid density. The amount of free volume can be determined using a hard sphere model. Using the density data shown in Fig. 4 the molar volume V_m can be calculated using

$$V_m = M_r / \rho \tag{4}$$

where M_r is the relative molar mass of the liquid calculated from

$$M_r = x_{ChCl} M_{ChCl} + x_{HBD} M_{HBD}$$
(5)

where x is the mole fraction and M the relative molar mass of the two components. The actual volume occupied by the components can be calculated in a similar manner *i.e.*

$$V_{comp} = (x_{ChCl} V_{ChCl} + x_{HBD} V_{HBD})N_A$$
(6)



Fig. 4 Density of the glycerol systems as a function of molar composition of the system in terms of ChCl.

where V is the molecular volume of the component and N_A the Avogadro constant. Using this approach the fractional molar free volume can be obtained using;

$$V_{free} = (V_m - V_{comp}) / V_m \tag{7}$$

Fig. 4 shows the raw density data for the ChCl:glycerol systems. As well as a decrease in viscosity, ChCl also decreases the density which causes an increase in free volume. The change in V_{free} with mole fraction ChCl can be observed in Fig. 5 (a). Glycerol is a viscous liquid because of the lack of free volume caused by the extent of hydrogen bonding. The fluidity $(1/\eta)$ of the liquid is related to the free volume of the liquid (Fig. 5 (b)).

We have previously proposed a new model that explains the mechanism of motion in an ionic liquid which fits the behaviour of DESs. It proposed that the mechanism of charge transfer is limited by the migration of holes through the liquid. Since the fraction of suitably sized holes in ambient temperature ionic liquids is very low the holes can be assumed to be at infinite dilution. The molar conductivity, Λ , can therefore be described by combining the Stokes–Einstein and Nernst– Einstein equations (eqn (8))¹¹

$$A = z^{2} F e/6 \pi \eta (R_{+} + R_{-})$$
(8)

where z is the charge on the ion, R is the species radius, F the Faraday constant and e is the electronic charge. This has been shown to be valid for a range of ionic liquids. Recent work by Zhao *et al.*¹² suggested that hole theory for ionic liquids could be modified to account for parts of an ion moving and the ions being non-spherical. This is a useful procedure and results in an improvement to the calculated viscosities.

An alternative analysis of mobility in ionic liquids has used NMR measurements to calculate self diffusion coefficients, D. These differ from those calculated using the Stokes–Einstein equation (eqn (9)).

$$D = kT/6\pi\eta R \tag{9}$$

This difference between the calculated radius and the hard sphere radius was ascribed to changes in ionic character, termed "ionicity", resulting from ionic association.^{13–16} In the current work we aim to show that the disparity between the values is due to the identity of the mobile species.

The diffusion coefficient for Ch^+ and glycerol was determined as a function of temperature using Pulsed Field Gradient NMR and these data are shown in Table 2. From eqn (9), if the fluid behaves like a Newtonian fluid then the radius of the diffusing species can be calculated and these are shown in columns 4 and 5. The values are considerably below the hard sphere radius of Ch^+ (3.29 Å) and glycerol (3.00 Å).

It has previously been suggested that the movement of holes in an ionic liquid aids in mass transport. The average size of the void, r_H , in the liquid can be determined from the surface tension of the liquids as described in eqn (10).

$$4\pi < r_H^2 > = 3.5 \frac{kT}{\gamma} \tag{10}$$



Fig. 5 Plot of (a) free volume vs. mole composition of ChCl and (b) free volume vs. $1/\eta$.

Table 2 Measured and calculated diffusion coefficients derived from PFG NMR and hard sphere models

T/K	$D_{meas}\times 10^{11}/m^2s^{-1}$		Rª/Å		$r_{H}{}^{b}/\text{\AA}$	$D^{e} \times 10^{11} / m^{2} s^{-1}$		$D^d \times 10^{11} / m^2 s^{-1}$	
	$\overline{Ch^+}$	Glycerol	Ch+	Glycerol	Hole	Ch+	Glycerol	Hole	
298	0.38	0.52	2.33	1.69	1.54	0.25	0.28	0.55	
303	0.51	0.70	2.43	1.75	1.56	0.36	0.39	0.75	
308	0.66	0.92	2.57	1.88	1.58	0.49	0.54	1.02	
313	0.86	1.17	2.65	1.89	1.60	0.67	0.73	1.37	
318	1.07	1.50	2.64	1.88	1.62	0.86	0.95	1.75	
323	1.40	1.97	2.58	1.88	1.64	1.12	1.23	2.25	

^{*a*} Calculated using eqn (9) with the D values in columns 2 and 3. ^{*b*} Calculated using eqn (10). ^{*c*} Calculated using hard sphere radii (Ch⁺ = 3.26 Å and glycerol = 3.00 Å) from molecular simulation.⁴ ^{*d*} Calculated using $r_{H}^{#}$.

where k is the Boltzmann constant and γ is the surface tension at temperature T. Surface tension could be expected to follow similar trends to viscosity since it is a measure of how strong the intermolecular forces are in the liquid, similar to the measure of viscosity. It is reasonable to expect that as viscosity increases with an increase in the molar composition of ChCl, the surface tension should increase as the molar composition of ChCl increases. A plot of surface tension as a function of temperature can be seen in Fig. 6. The surface tensions of the various compositions show a linear correlation with temperature as with other ionic liquids. The values are similar in magnitude to tetrafluoroborate and hexafluorophosphate salts but higher than bistriflamide analogues.^{17,18} As would be expected from the viscosity and free volume results, the surface tensions decrease as more ChCl is added to the system. This is further evidence that the ChCl is breaking up the intermolecular forces of the glycerol as described above. The average size of the hole was calculated using eqn (10) and these are shown in Table 2 as a function of temperature. These values are similar in size to the radius of the diffusing species calculated using the data in Table 2 and eqn (9). While it has previously been suggested that diffusion occurs via ions moving from one vacancy to another it is clear that this model needs to be refined. The data presented here show that the mobility of holes themselves are the dominant factor in controlling mass transfer in ionic liquids. It is clearly not suitable to claim that the holes are the only factor affecting mass transport in ionic liquids since this would mean that all species would diffuse at the same rate. It is clear however that



Fig. 6 Plot of temperature *versus* surface tension for the glycerol systems.

the size of the hole dominates the mechanism of mass transport. Subsequent results with second generation ionic liquids will show that this generic model fits the diffusion of both charged and uncharged species in ionic liquids.¹⁹

Chemical properties of glycerol with ChCl

Solvent polarity. The polarity of a solvent can be characterised using semi-empirical linear free energy relationships. The use of solvatochromic parameters allows an insight into solvation and local density, and has been particularly useful in an understanding of the solvent properties of supercritical fluids.²⁰⁻²² The two most commonly used scales are the $E_{T}(30)$ polarity scales of Dimroth and Reichardt^{23,24} and the multi parameter scale of Kamlet and Taft.^{25,26} To calculate the π^* , α and β values three indicator probe molecules were used. The molecules used to investigate these parameters were Reichardt's Dye 30, 4-nitroaniline and N,N-dimethyl-4-nitroaniline. For this work, the solvents investigated were standardized around these single probe sets. This is common practice with many workers in the field. Other workers in this field however favour the use of several probes and then average the values obtained. The disadvantage of using many probes is that considerable effort is required to derive parameters for any new solvent. The single probe set approach has the advantage of being experimentally less involved, but also the data obtained will be comparable with published literature.27

By using Reichardt's Dye 30, a value for $E_T(30)$ can be calculated using eqn (11).

$$E_T(30) (\text{kcal mol}^{-1}) = h_{CUmax} N_A = (2.8591 \times 10^{-3})$$

$$U_{max} (\text{cm}^{-1}) = 28591 / \lambda_{max}$$
(11)

In addition to the $E_T(30)$ scale, there is a normalised scale, the E^{N_T} scale. The normalised value for a solvent is calculated using eqn (12);

$$E_T^N = \frac{E_T(solvent) - E_T(TMS)}{E_T(water) - E_T(TMS)} = \frac{E_T(solvent) - 30.7}{63.1 - 30.7}$$
(12)

To calculate π^* the eqn (13) was used with the data obtained from the indicator molecule 4-nitroaniline

$$\pi^* = (v_{\text{solvent}} - v_{\text{cyclohexane}}) / (v_{\text{dmso}} - v_{\text{cyclohexane}})$$
(13)

 α values were calculated using $E_T(30)$ data and 4-nitroaniline π^* data using eqn (14)

$$\alpha = (E_T(30) - 14.6 (\pi^* - 0.23) - 30.31)/16.5$$
(14)

 Table 3
 Solvent polarity parameters for glycerol: ChCl mixtures

Solvent	$E_T(30)/\text{kcal mol}^{-1}$	$E^{\scriptscriptstyle N}{}_{\scriptscriptstyle T}$	π*	α	β
Glycerol	57.17	0.817	0.956	0.882	0.658
ChCl: Glycerol 1:3	57.96	0.841	0.970	0.914	0.657
ChCl:Glycerol 1:2	58.58	0.860	0.984	0.937	0.657
ChCl: Glycerol	58.21	0.849	0.980	0.921	0.658
ChCl: Glycerol 1:1	58.49	0.858	1.003	0.923	0.658

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

$$\beta = 0.9 \left(\Delta v_{\text{cyclohexane}} - \Delta v_{\text{solvent}} \right) / \left(\Delta v_{\text{cyclohexane}} - \Delta v_{\text{propan-1-ol}} \right)$$
(15)

The data in Table 3 shows that the choline chloride based DES's exhibit a polarity that is similar to RNH_3^+X^- and $\text{R}_2\text{NH}_2^+\text{X}^-$ ionic liquids with discrete anions.²⁸ It can also be seen that the addition of choline chloride increases the $E_T(30)$, π^* and α parameters of the system. The changes in these parameters as a function of choline chloride concentration can be seen in Fig. 7.

Fig. 7 shows a roughly linear increase in $E_T(30)$ with ChCl concentration. Extrapolating this trend to 100% ChCl gives a value of approximately 59 kcal mol⁻¹ which is comparable to that for ethylammonium nitrate²⁸ which is reasonable. Similar trends are observed for π^* and α , although the parameters are relatively insensitive to changes in polarity. The β parameter in particular does not appear to show significant changes with increasing chloride concentration. To some extent this is not surprising since the number glycerol OH groups present are in excess to the indicator solute and will act as a better hydrogen bond donor. This suggests that in high polarity solvents, solvatochromic indicators are insensitive to compositional changes because solvent–solvent interactions.

Esterification of glycerol

To demonstrate the different chemical properties of ChClglycerol mixtures the esterification of glycerol with lauric acid was chosen as a model experiment. The aim of this work was to determine the effect of hydrogen bonding of Cl⁻ to the OH moieties on glycerol. It was envisaged that the strength of the H-bonding would affect the reactivity of glycerol and this could change the product distribution of the reaction.

The esterification of the triol can be broken down into three elementary equilibria. Analysis of such a complex process is clearly complicated and here only a simple qualitative analysis is carried out. Attempts to fit all of the data were unsuccessful. The scheme for this reaction is as follows:

$$[glycerol] + [lauric acid] \rightleftharpoons [monoester] + [water] K_1 = \frac{[monoester][water]}{[lauric acid][glycerol]}$$
(16)

$$[monoester] + [lauric acid] \rightleftharpoons [diester] + [water] K_2 = \frac{[diester][water]}{[monoester][lauric acid]}$$
(17)

$$[\text{diester}] + [\text{lauric acid}] \rightleftharpoons [\text{triester}] + [\text{water}] K_3 = \frac{[\text{triester}][\text{water}]}{[\text{diester}][\text{lauric acid}]}$$
(18)

The plots shown in Fig. 8 show the progression of the esterification of lauric acid in various ChCl: glycerol mixtures and also pure glycerol. In each system, 60 cm³, (0.82 mol) of glycerol was used and the corresponding molar amount of ChCl needed to make up the desired ratio was added. It should be noted that the addition of ChCl changes the volume of the system and so the data have not been analysed in terms of the concentration, but rather the number of moles of each reagent. In each case the acid catalyst added was trifluoroacetic acid (6 cm³, 0.078 mol). In these systems 0.1 moles of lauric acid was added. The reactions were all carried out at 150 °C, in a sealed



Fig. 7 Variation of $E_{\tau}(30)$ (a), π^* , α and β (b) with mole fraction of ChCl in glycerol.



Fig. 8 Esterification data of 0.1 moles of lauric acid in various ChCl: glycerol DES mixtures.

vessel. As lauric acid and the respective esters are poorly soluble in glycerol and the glycerol based DESs, aliquots were taken from the top organic layer after being allowed to phase separate, which at this temperature was liquid. The isomeric form of the mono- and di-esters were not investigated in the analysis. Only the formation of the mono- and di-esters were investigated.

The data in Fig. 8 show that the addition of ChCl does have a marked effect on the product distribution of the reaction. These systems are operating in large excess of glycerol, with a greater than 8:1 ratio of glycerol: lauric acid. The mono-ester would be the most abundant product predicted due to the large excess of glycerol. This is indeed the case with pure glycerol where negligible amounts of di- and tri-esters formed. It also shows that after 8 h there is still approximately 70% of the free acid remaining. This is a surprising result since there is such a large amount of glycerol available for the lauric acid to react with but this could be due to the high viscosity of the system.

The 1:1 ChCl: glycerol mixture shows a faster consumption of the lauric acid than the pure glycerol system, resulting in a much greater formation of the mono-ester. It should be noted that approximately twice as many moles of products are made when ChCl is added which clearly negates any effect of dilution. The 1:1.5 and 1:2 systems show similar overall conversion to the monoester but noticeably the monoester concentration goes through a maximum due to its use in eqn (17). The concentration of the diester is significantly increased with respect to both the pure glycerol and the 1:1 ChCl systems. The rate of consumption of the lauric acid follows $1:2 \approx 1:1.5 > 1:1 >$ glycerol. This could be due to the *pseudo* site inhibition, where the interaction between the glycerol OH moieties interact with the Cl⁻ from ChCl, but a more logical explanation is that the process is mass transport controlled.

The results shown in Fig. 8 indicate that the addition of choline chloride alters the product distribution of the esterifcation of glycerol and lauric acid. The 1:2 mixture shows that it is possible to form the di-ester product in relatively large amounts considering that the initial ratio of glycerol: lauric acid is very high. Deviating to a ratio of 1:1.5 does not appreciably alter this product distribution, however changing the ratio to 1:1, the product distribution more closely resembles that of the of the

Table 4Equilibrium constants for the formation of the mono-, di- andtri- esters for all ChCl based systems

Ratio of ChCl:glycerol	Lauric acid/mol L ⁻¹	\mathbf{K}_1	\mathbf{K}_2	K ₃
1:3	0.2	1.038	1.26	0.053
	0.3	1.053	1.080	0.13
	0.4	1.28	0.97	0.14
	0.6	0.64	2.58	1.41
1:2	0.1	1.43	0.79	0.11
	0.2	0.24	0.66	0.026
	0.3	0.40	1.36	0.174
	0.4	1.01	1.83	0.22
	0.6	0.44	1.91	0.78
1:1.5	0.1	0.48	0.21	0.021
	0.2	0.006	0.16	0.005
	0.3	0.31	0.70	0.070
	0.4	0.97	1.40	0.17
	0.6	0.90	0.77	0.290
1:1	0.1	0.077	0.007	0.005
	0.2	0.58	0.34	0.040
	0.3	0.44	0.50	0.061
	0.4	0.52	0.61	0.082
	0.6	0.41	1.11	0.74
No ChCl	0.2	1.58	0.41	0.02
	0.3	2.43	0.79	0.04
	0.4	2.24	0.62	0.04
	0.6	2.14	1.11	0.15

pure glycerol system. There are likely to be many factors governing how these reactions progress; the addition of ChCl to glycerol lowers the viscosity, which would increase the mass transport in the system however it also acts as a diluent of the glycerol.

The experiments shown in Fig. 8 were repeated at four different initial lauric acid concentrations; 0.2, 0.3, 0.4 and 0.6 mol L⁻¹. The results are given summarised in Table 4 and full details are provided in the ESI[†]. The K values in Table 4 are apparent equilibrium constants based on the number of moles of species in solution. Although there is a relatively complex relationship between the concentrations of ChCl and lauric acid upon the product distribution, it can be concluded that the ChCl leads to a considerably higher proportion of product in the form of the diester whereas pure glycerol results predominantly in the monoester. It can also be seen that almost no tri-ester forms. Most importantly in the 1:1.5 mixture the di-ester was effectively the only product formed. The supplementary information shows that most systems have reached equilibrium within 8 h however all systems were left for 24 h to obtain an equilibrium value. Where the data point taken after 24 h differs significantly from that after 8 h the last data point was ignored. However in most cases the tri-ester was still being formed at a slow rate due to the back reactions of eqn (16) and (17) yielding more acid. While there is some fluctuation in the K_3 values the trend compared to K_1 and K_2 are constant.

In the equimolar ChCl: glycerol mixture the rate of conversion decreases and the monoester is the favoured product. The same trend was observed using 0.1 moles of free acid. This suggests there is a *pseudo* site inhibition effect from the Cl⁻ interacting with the OH moieties that occurs at high ChCl concentrations.

The 1 : 1 system shows a faster rate of formation of the monoester than in the 0.2 M system, as would be expected since the amount of lauric acid is greater. In all of the ChCl containing systems the amount of di-ester formed is approximately constant (0.01 mol). This is significantly higher that the pure glycerol system. All of the systems containing ChCl are slow to reach equilibrium, again because the tri-ester appears to form slowly and removes di-ester from the system.

Increasing the lauric acid concentration to 0.4 moles results in a similar product distribution to that found with 0.3 moles and as Table 4 shows the equilibrium constants for pure glycerol remain relatively similar. As the lauric acid concentration increases the data for the ChCl containing systems approach equilibrium. The equilibrium constants are shown in Table 4. In all of the pure glycerol systems the equilibrium constants are in the order $K_1 > K_2 > K_3$ whereas for the ChCl containing mixtures the order is $K_2 > K_1 > K_3$. The only way in which the equilibrium can be driven to the right is if one of the components is removed or more accurately if it decreases its activity in the system. One possible explanation for the data observed in Table 4 is that the presence of ChCl causes a decrease in the activity of water due to hydrogen bonding between the chloride anion and the water molecules.

One complication is that the reaction is carried out at 150 °C which would normally be enough to drive the water from the reaction vessel however in these experiments the reaction vessel was closed and so the ChCl would also affect the concentration of water vapour in the headspace. Nevertheless, inspection of the data in Table 4 suggests that both K_2 and K_3 increase as the ChCl concentration increases which supports this idea. Furthermore the central premise of this work was that ChCl could act as a *pseudo*-site inhibitor. This could either prevent esterification, which is clearly not the case, or it could reduce the activity of glycerol in eqn (16). If this were the case, then diand tri-esterification would be preferred, which is indeed what appears to occur.

The results for the system containing 0.6 mol L^{-1} of ChCl superficially support all of the discussions above. The concentration of the mono-ester is up to ten times larger than that observed in some of the ChCl containing systems. Given that glycerol is still present in a large excess it is important to notice that the overall lauric acid concentration is approximately the same at the end of each experiment. While this could be viewed in terms of decreased glycerol activity in the ChCl an alternative view could be that the ChCl breaks up the structure of the glycerol and therefore actually enables further reaction on the OH moieties that could normally be inter-molecularly hydrogen bonded. It is probably a mixture of both effects that lead to the observed product distribution.

Equilibrium constants have been calculated for the ChCl based systems, and are shown in Table 4. An additional point worth discussing at this juncture is that the choline cation contains an OH moiety which in principle could be esterified. Despite numerous experiments no such esters were observed. Bell *et al.* also studied esterification reactions in choline based ionic liquids and deep eutectic solvents. The choline cation was found to be very unreactive and it was only when strong Lewis acids such as $ZnCl_2$ were present with acetic anhydride that any significant acylation took place.²⁹

Conclusion

The work here has shown that by adding ChCl to glycerol there is a marked reduction in the viscosity, whereas in the case of several previously reported ChCl : diol mixtures the viscosity increases.⁵ This is due to the 3D intermolecular H-bond interactions in glycerol that are broken up on addition of ChCl resulting in a less ordered system. This is also backed up by the density data which decreases as ChCl is added, where this is not true for the diol systems. As would be expected the conductivity increases as a function of ChCl addition due to more charge carrying species being made available in an increasingly more fluid solvent.

Several polarity parameters; E^{N}_{T} , α , β and π^{*} have been obtained for the first time for several alcohol based DESs. The data has provided information on the relative polarity of these systems, which suggests that they are similar to RNH₃⁺X⁻, R₂NH₂⁺X⁻ and imidazolium ionic liquids, which is not surprising given the similarity in the structure of ChCl. There is a linear increase in the E^{N}_{T} , π^{*} and α values of the glycerol based DESs as the ChCl concentration is increased.

By performing esterification of glycerol it has been shown that at low fatty acid concentrations and high ChCl concentrations the monoester can be selectively produced at a significantly higher rate than in pure glycerol. Solventless esterification of glycerol and lauric acid was carried out using ChCl with the intention of using its hydrogen bonding interaction with glycerol to behave as a potential site inhibitor to selectively form monoor di-ester products. The work has shown that the addition of ChCl to the system actually encourages the reaction to progress further towards the di-ester product, as opposed to the pure glycerol system which encouraged only mono-ester formation. It is thought that because ChCl breaks up the 3-D structure of glycerol, this actually works in favour of the esterification reaction as it can further react with glycerol molecules already esterified. It is also possible that ChCl is interacting with water molecules produced in the reaction, effectively removing them from the equilibrium, which in turn helps drive the reaction forward. The ChCl also decreases the viscosity of the liquid and at low acid concentrations it is suggested that the process is mass transport controlled when the system has not reached equilibrium.

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