

Deep Eutectic Solvents Formed between Choline Chloride and Carboxylic Acids: Versatile Alternatives to Ionic Liquids

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Abstract: Deep Eutectic Solvents (DES) can be formed between a variety of quaternary ammonium salts and carboxylic acids. The physical properties are significantly affected by the structure of the carboxylic acid but the phase behavior of the mixtures can be simply modeled by taking account of the mole fraction of carboxylic acid in the mixture. The physical properties such as viscosity, conductivity, and surface tension of these DES are similar to ambient temperature ionic liquids and insight into the cause of these properties is gained using hole-theory. It is shown that the conductivity and viscosity of these liquids is controlled by ion mobility and the availability of voids of suitable dimensions, and this is consistent with the fluidity of other ionic liquids and molten salts. The DES are also shown to be good solvents for metal oxides, which could have potential application for metal extraction.

Introduction

Eutectic mixtures of salts have been extensively utilized to decrease the temperature for molten salt applications. In the extreme, ambient temperature molten salts have been formed by mixing quaternary ammonium salts with metal salts.^{1–5} This type of ionic liquid can be viewed as a deep eutectic resulting from the formation of complex anions, e.g., Al_2Cl_7^- and Zn_2Cl_5^- , thus decreasing the lattice energy and decreasing the freezing point of the system. Work in this area has focused on chloroaluminate salts of imidazolium and pyridinium chloride.^{1–3} A variety of different anions are formed in solution the ratios of which vary with the changing aluminum chloride composition. The depression of freezing point at the eutectic composition is as much as 190 °C. These ideas have recently been extended to other chlorometalate salts including those formed from ZnCl_2 , SnCl_2 , and FeCl_3 .^{4,5} The resultant molten salts have the advantage that they are not water sensitive, although they are, in general, more viscous than their aluminum analogues. Mixtures of zinc chloride with substituted quaternary ammonium salts such as choline chloride have large depressions of freezing point (up to 270 °C). They have been shown to have potential for large-scale applications, such as zinc electroplating,⁶ batteries⁷ as well as catalysts for Diels Alder reactions.⁸ It has also recently been shown that these ideas can be extended to other metals by using hydrated salt mixtures.⁹

To circumvent the use of metals in ionic fluids a variety of closed shell anions have been synthesized and these have been the main focus of ionic liquids research over the past decade.^{1–3} Again studies have centered on imidazolium based cations with a range of anions including BF_4^- , PF_6^- , and $(\text{CF}_3\text{SO}_2)_2\text{N}^-$. While these solvents show excellent solubility for a wide range of solutes and unusual miscibility with molecular liquids their widespread application will be limited by toxicological, economic and purity issues. Since none of these ionic liquids have yet been registered their general use as solvents may be restricted.

We have recently shown that the principle of creating an ionic fluid by complexing a halide salt can be applied to mixtures of quaternary ammonium salts with a range of amides.¹⁰ The charge delocalization is achieved through hydrogen bonding between the halide anion with the amide moiety. It was shown that a eutectic mixture of choline chloride with urea gave a liquid with a freezing point of 12 °C. This liquid was found to have interesting solvent properties that are similar to ambient temperature ionic liquids and a wide variety of solutes were found to exhibit high solubilities.¹⁰ While the depression of freezing point is less than analogous chlorometalate systems, there is a wide range of amides that can be used to form these eutectic mixtures. To differentiate these liquids from ionic liquids the term Deep Eutectic Solvents (DES) has been adopted.

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Unlike the room-temperature ionic liquids, these eutectic mixtures are easy to prepare in a pure state. They are nonreactive with water, many are biodegradable and the toxicological properties of the components are well characterized. The use of urea to form eutectics with alkali metal halides that have melting points of $<150\text{ }^{\circ}\text{C}$ has been known for a considerable time^{11,12} and a few reports also exist for adducts of urea with other metal salts.^{13,14}

This principle is not limited to amides, but can be applied to a wide variety of other hydrogen bond donors such as acids, amines and alcohols. In the current work, we focus on mixtures of carboxylic acids with choline chloride and characterize their phase behavior, fluidity, and conductivity as a function of composition and acid type. Optimizing fluidity is of key importance to the design of ionic liquids, as they tend to be more viscous than molecular liquids. It is shown that the fluid properties of these Deep Eutectic Solvents is linked to the size of the mobile species and the availability of holes of appropriate dimensions to allow mobility. This idea is found to be valid not only for other ionic liquids but also for molecular liquids and high-temperature molten salts.

Experimental Section

Choline chloride (ChCl) (Aldrich 99%) was recrystallized from absolute ethanol, filtered, and dried under vacuum. Oxalic, malonic, adipic, phenyl acetic, phenylpropionic, tricarballic, and citric acids (all Aldrich $>99\%$) and succinic acid (BDH $>99\%$) were dried under vacuum prior to use. The eutectic mixtures were formed by stirring the two components at $100\text{ }^{\circ}\text{C}$ until a homogeneous colorless liquid was formed. The liquids were cooled at a rate of $1\text{ }^{\circ}\text{C min}^{-1}$ and the freezing point was taken as the temperature at which the first solid began to form. The viscosity was determined using a Brookfield DV-E viscometer fitted with a thermostated jacket. The conductivity and its temperature dependence were determined using a Jenway 4071 conductivity meter with temperature and conductivity probes (probe cell constant = 1.01 cm^{-1}). Refractive index measurements were made using Bellingham and Stanley refractometer, which was calibrated using dichloromethane and toluene as reference standards. A Kruss K11 tensiometer equipped with a thermostated jacket, was used for the surface tension experiments. The solubility measurements were made by stirring an excess of metal oxide in the DES for 3 days at $50\text{ }^{\circ}\text{C}$. The resultant solutions were diluted with an equivalent volume of 0.1 M HCl , filtered and then analyzed using ICP-AES. The equilibrium geometry and volumes of the ions and hydrogen bond donors were calculated using a Hartree-Fock method utilizing an STO-3G model provided by commercially available software.¹⁵

Results and Discussion

Phase Behavior. Figure 1 shows the phase diagram for mixtures of choline chloride with phenylacetic and phenylpropionic acids as a function of composition. It is apparent that a eutectic is formed at a composition of 67 mol % acid which is similar to the eutectic recently reported for the choline chloride-urea system.¹⁰ It can be inferred that to form the eutectic two carboxylic acid molecules are required to complex each chloride ion. It is thought that the protons and carboxylate anions are extensively associated in the liquids. The addition of sodium

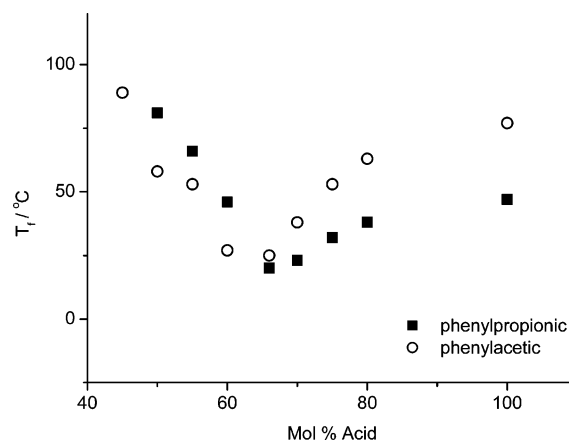


Figure 1. Freezing points of choline chloride with phenylpropionic and phenylacetic acids as a function of composition.

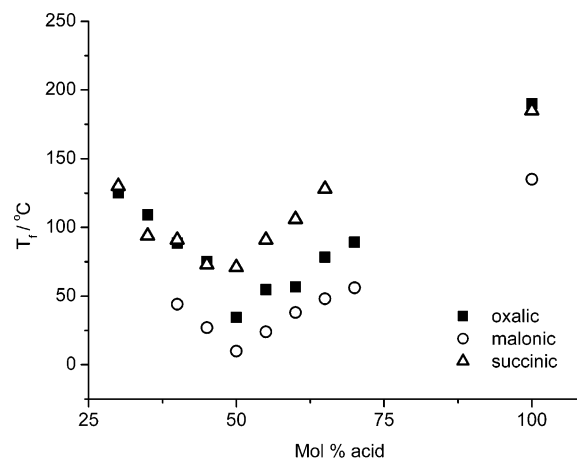


Figure 2. Freezing points of choline chloride with oxalic, malonic, and succinic acids as a function of composition.

bicarbonate to an oxalic acid/choline chloride mixture, for example, causes a brief, minor effervescence, possibly due to residual water, but after a few minutes the solid remains unreactive for several weeks in the liquid. If the acid did dissociate, then the choline salt and HCl would be formed and it is highly unlikely that the carboxylate salt of the choline cation would be liquid at ambient temperatures. Hence, we conclude that the chloride ion is complexed by the associated acid in a manner analogous to the urea/choline chloride system reported previously.¹⁰

Figure 2 shows the phase diagrams for a range of dicarboxylic acids. For these systems, the eutectic occurs at 50 mol % acid suggesting a 1:1 complex between the acid and chloride ion, or bridging acids between neighboring chloride ions. The tricarboxylic acids citric and tricarballic acid have a eutectic composition in the region 30–35 mol % acid. These exhibit the rheology of gels and presumably have extensive bridging of the acids between neighboring chloride ions. Table 1 shows the freezing point of the eutectic mixtures for the systems shown in Figures 1 and 2 as well as a variety of other carboxylic acids. The depression of freezing point (with respect to an ideal mixture of the two components) for a number of these eutectic systems is extremely large; the oxalic acid-choline chloride system, for example, is $212\text{ }^{\circ}\text{C}$. This depression of freezing point is even larger than that reported recently for the choline chloride-urea system ($178\text{ }^{\circ}\text{C}$)¹⁰ but not as large as the choline chloride-zinc chloride system ($272\text{ }^{\circ}\text{C}$)⁴ due to the covalent bonds formed

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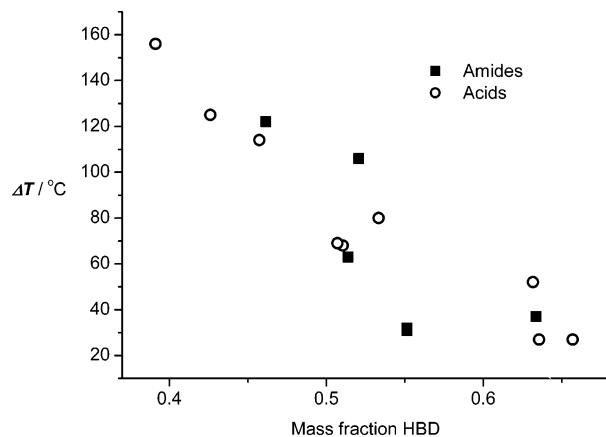


Figure 3. Freezing point depression for the eutectic mixtures listed in Table 1 and reported in the literature¹⁰ as a function of mass fraction of HBD.

Table 1. Freezing Point Temperature, T_f and Refractive Index of Various ChCl: Acid DES at the Eutectic Composition Together with the Molecular Volumes V and Melting Points, T_m^* of the Pure Acids

acid	$T_f/^\circ\text{C}$	$T_m/^\circ\text{C}$	refractive index	$V/\text{\AA}^3$
adipic	85	153	1.490	171.5
benzoic	95	122	1.415	141.5
citric	69	149	1.502	194.2
malonic	10	135	1.478	110.1
oxalic	34	190	1.480	89.3
phenylacetic	25	77	1.526	161.9
phenylpropionic	20	48	1.522	182.6
succinic	71	185	1.487	129.9
tricarballic	90	159	1.483	184.3

in the metal chloride case. The data in Table 1 show no correlation between the freezing point of the mixtures and the freezing points of the pure acids. No correlations were observed between the freezing point of the mixtures and the enthalpy of formation or fusion of the pure acids. What is, however apparent from the data in Table 1 is that in general the lower the molecular weight of the acid the larger the depression of freezing point.

The freezing point of the HBD–salt mixtures will be dependent upon the lattice energies of the salt and HBD and how these are counteracted by the anion–HBD interaction and the entropy changes arising from forming a liquid. For a given quaternary ammonium salt, the lattice energy of the HBD will be related to the anion–HBD interaction and hence to a first approximation the depression of freezing point will be a measure of the entropy change. Figure 3 shows the depression of freezing point as a function of the mass fraction of acid in the mixture. Data presented previously on amides has been added to this plot to show the applicability of this ideal to a wide range of HBD mixtures with ChCl.

Table 1 also lists the refractive index values of the eutectic mixtures. All of the DES have large values, which are comparable with other ionic liquids. The refractive index is related to the electronic polarizability of the medium¹⁶ and hence the DES with a phenyl moiety have the higher refractive indexes since the aromatic ring will be very polarizable.

The Kamlet and Taft polarity parameters have been determined for a range of imidazolium based ionic liquids. They

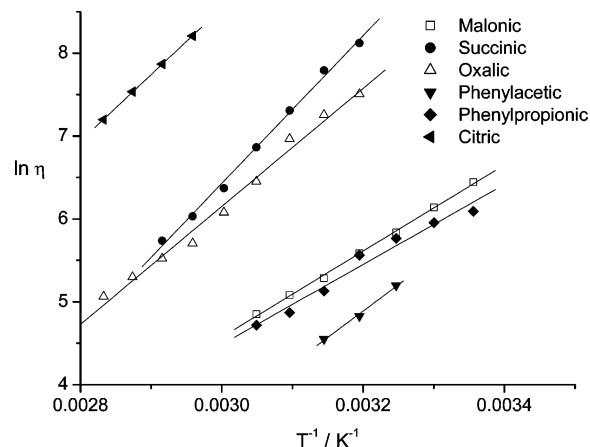


Figure 4. Plot of log viscosity vs. reciprocal of temperature for a variety of DES.

were found to have high polarizability, π^* , parameters (between 0.88 and 1.3) due to the high degree of conjugation in the cation. The hydrogen bond donating properties, α , range from 0 to 1.2 and the hydrogen bond accepting properties, β , range from 0.4 to 1.0.³ The Kamlet and Taft parameters were determined for the 1 malonic acid: 1 choline chloride mixture at 25 °C and the values were found to be $\pi^* = 0.41$, $\alpha = 3.92$ and $\beta = 0.40$. The π^* and β values are consistent with what would be expected for malonic acid, i.e., moderate polarizability and hydrogen bond acceptor properties but the α value is very high even compared to other carboxylic acids (e.g., acetic acid $\alpha = 1.12$).¹⁷

Viscosity. The viscosity of the DES listed in Table 1 change significantly as a function of temperature, the hydrogen bond donor type and mixture composition as shown in Figure 4. The viscosity values were found to cover the range 50 to 5000 cP, which is similar to those observed with ionic liquids. The change in viscosity, η with temperature can be described by the expression¹⁸

$$\ln \eta = \ln \eta_0 + \frac{E_\eta}{RT} \quad (1)$$

where η_0 is a constant and E_η is the energy for activation of viscous flow. Figure 4 shows that all of the data obey eq 1 well ($r > 0.989$). We have recently shown that the E_η for ionic liquids are considerably larger than conventional liquids and high-temperature molten salts.⁹ Ionic liquids also do not obey the empirical relationship between E_η values and the melting point of high-temperature molten salts, T_m

$$E_\eta = 3.74 RT_m \quad (2)$$

observed by Bockris.¹⁹ Figure 5 shows that a roughly linear relationship exists between E_η and, T_m but the constant of proportionality is 23.0. We have previously suggested that the difference in viscosity between ionic liquids and molten salts arise from the large ion to hole radius ratio in the latter.^{5,9} A good linear correlation is observed between $\ln \eta_0$ and E_η values

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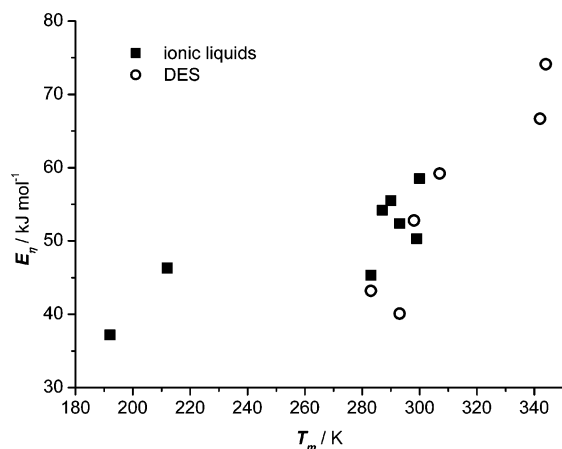


Figure 5. Energy for activation of viscous flow as a function of ionic liquid freezing point.

($r = -0.918$) (see Supporting Information for data). This could be expected since the Eyring equation²⁰ shows that

$$\eta_0 = kN_A/V \quad (3)$$

where k and N_A are the Boltzmann and Avogadro constants, respectively, and V is the molar volume of the liquid. Hence η_0 is related to the volumes of the ions and the voids in a manner similar to E_η .

Surface Tension. The surface tension of the malonic acid: choline chloride (1:1) and phenylacetic acid: choline chloride (2:1) were found to be 65.68 and 41.86 mN m⁻¹, respectively. The values are larger than most molecular solvents, but are comparable to imidazolium based ionic liquids and high-temperature molten salts, e.g., KBr $\gamma = 77.3$ mN m⁻¹ at 900 °C,²¹ *n*-butyl-methylimidazolium (BMIM) BF₄ $\gamma = 38.4$ mN m⁻¹ at 63 °C.²²

In high-temperature molten salts, hole theory has been used to explain the mobility of ions. It can be shown that in a molten salt the radius of the average-sized void, r , is related to the surface tension of the liquid, γ , by the expression¹⁸

$$4\pi \langle r^2 \rangle = 3.5 \frac{kT}{\gamma} \quad (4)$$

where k is the Boltzmann constant, and T is the absolute temperature. In the 1:1 malonic acid: ChCl DES the average void radius is 1.32 Å while the radius of the Choline⁺ ion is 3.29 Å. By contrast for KBr at 900 °C the average void radius is 2.1 Å, whereas the cation radius is 1.3 Å,^{18,21} and for BMIM BF₄ the average void radius is 1.57 Å, whereas the cation radius is 3.55 Å. This explains the significant disparity between the properties of molten salts and ionic liquids viz. the ratio of ionic radius to void radius is large for ionic liquids and approximately unity for molten salts making ionic motion considerably easier in the latter case. It also shows why the liquid properties of DES are similar to those of ionic liquids.

We propose that E_η is proportional to the ion-to-hole ratio, although this is difficult to quantify because of the lack of significant surface tension data on ionic liquids that is required to obtain the dimensions of the holes in the liquid. For the few

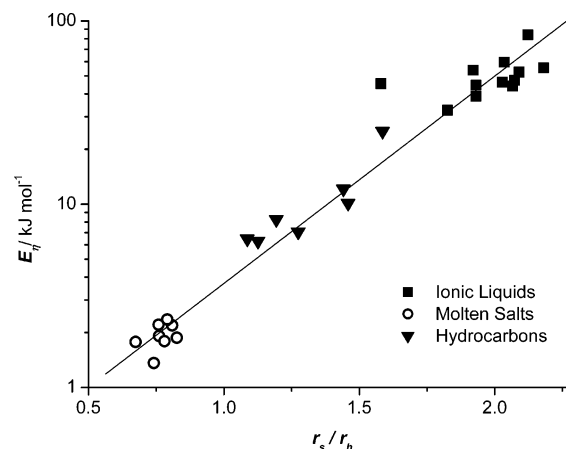


Figure 6. Energy for activation of viscous flow as a function solvent to hole radius ratio.

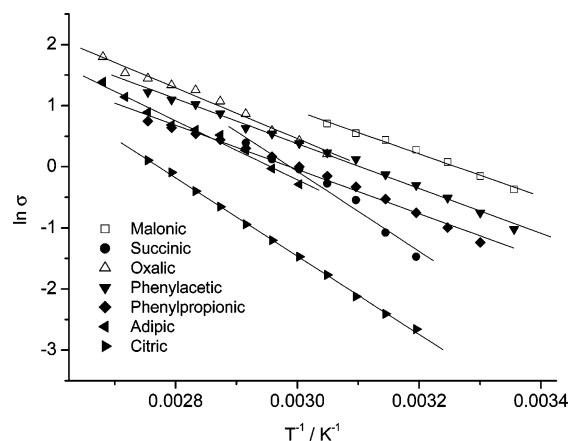


Figure 7. Plot of log conductivity vs. reciprocal of temperature for a variety of DES.

ionic liquids where both viscosity and surface tension data are available this idea can be tested. The ion/solvent radii were calculated using molecular modeling software.¹⁵ Figure 6 shows a plot of E_η vs. ion: hole radius ratio for some of the data in Figure 4 and a few high-temperature molten salts.^{5,9,18,21,23–25} Note that the ion size is taken as the geometric mean of the anion and cation, i.e., $(r_+ r_-)^{1/2}$. It is clear that the large E_η values are characteristic of ionic liquids and result from the energetics of cavity formation and enlargement, which controls ionic movement. This is an important result as it links the properties of high-temperature molten salts with room-temperature ionic liquids. Figure 6 also shows the E_η data for a number of conventional hydrocarbon liquids,²⁶ e.g., benzene, cyclohexane and pentane. It can be seen that the E_η data for these solvents are collinear with the ionic solvents showing that the movement of all of these fluids as related to the ease of solvent transfer into vacant sites, which in turn is related to the dimension of the vacant sites.

Conductivity. The DES listed in Table 1 have conductivities in the range 0.1 to 10 mS cm⁻¹ changing with composition and

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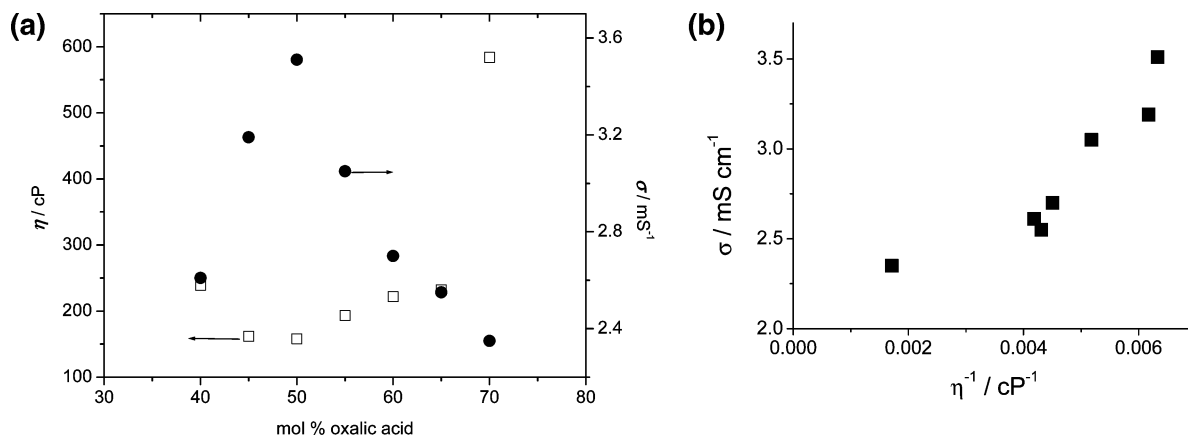


Figure 8. (a) Plot of conductivity and viscosity as a function of composition for the oxalic acid: choline chloride system. (b) Conductivity as a function of fluidity for the data in (a).

temperature. These values are again similar to imidazolium based ionic liquids² and similar to the urea: choline chloride DES.¹⁰ Analogous to the viscosity data, conductivity of ionic liquids have been fitted to¹⁹

$$\ln \sigma = \ln \sigma_0 - \frac{E_A}{RT} \quad (5)$$

where E_A is the activation energy for conduction. Figure 7 shows the data for all of the DES fit Equation 5 accurately. The values for E_A range from 29 to 54 kJ mol⁻¹ (see Supporting Information for details) and like the corresponding E_η values they are larger than those for molten salts. A strong negative correlation is seen to exist between E_A and E_η ($r = -0.936$).

Figure 8a shows the conductivity and viscosity of the oxalic acid: choline chloride system at 45 °C as a function of composition. It can be seen that a maximum in the conductivity and a minimum in the viscosity are observed at the eutectic composition (50 mol % acid). Figure 8b shows a near linear correlation between the conductivity and the reciprocal of viscosity and this is despite the mole fraction of quaternary ammonium salt in the mixture changing from 30 to 70 mol %. This plot shows that the identity of the charge carriers remains approximately constant over this composition range. It is therefore evident that it is not the number of charge carriers that control the conductivity, but rather their mobility. This reinforces the ideas proposed above that the limitation for ionic movement is the availability of voids of suitable dimensions and charge transport is hence governed by the density of voids and not the density of charged species. This has important ramifications for the design of future ionic fluids since clearly increased ionic mobility can be obtained using smaller ions in liquids with larger voids. This can and has been achieved with fluids of lower surface tension obtained using highly fluorinated anions such as PF₆⁻ and (CF₃SO₂)₂N⁻.

Figure 9 shows the correlation between σ and η^{-1} for a range of DES at their eutectic compositions as a function of temperature. Approximately linear correlations are observed for all of the systems, although the slopes are markedly different. If the charge carrying species were simply the choline and chloride ions, then all of the systems would be expected to have similar slopes. The largest slope is observed for the oxalic acid mixtures while the slopes of phenylpropionic and phenyl acetic acids are considerably smaller. It has previously been shown that for a

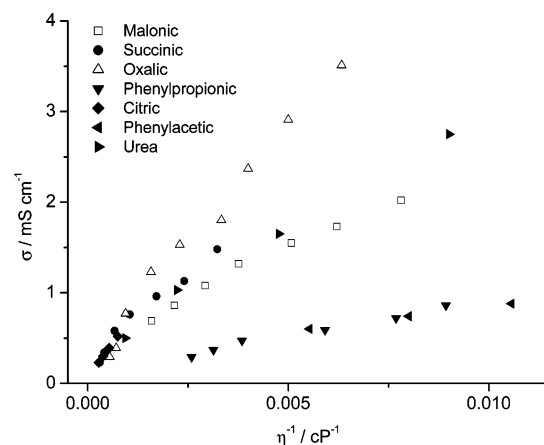


Figure 9. Conductivity as a function of fluidity for the data in Figures 4 and 7.

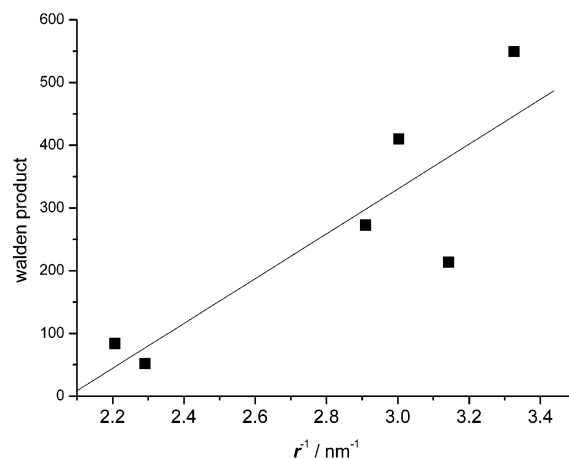


Figure 10. Plot of the Walden product as a function of the complex radius with the line of best fit to the data.

range of ionic liquids the Walden product is inversely proportional to the radius of the diffusing ions.

Figure 10 shows that the Walden product is proportional to the reciprocal of the radius of the complexed ion, assuming that the diacids complex in a 1:1 ratio, whereas the monoacids complex in a 2:1 ratio. This confirms that the chloride ions migrate with their complexing ligands, and hence, the hydrodynamic radius for the monoacids is larger than that of the diacids. It could be argued that the protons from the carboxylic acid play a significant role in the charge transport in these media,

Table 2. Solubility of ZnO, CuO, and Fe₃O₄ in Three DES at 50 °C

	solubility/mol dm ⁻³		
	CuO	Fe ₃ O ₄	ZnO
1 malonic acid: 1ChCl	0.246	0.071	0.554
1 oxalic acid: 1ChCl	0.071	0.341	0.491
2 phenylpropionic acid: 1ChCl	0.473	0.014	>0.491

but since the data published previously for the ChCl:urea system¹⁰ are consistent with those for the acids, it provides more evidence that the protons are not labile.

Ionic liquids have been shown to be interesting because of their tunable solvent properties and this has been demonstrated for a wide range of inorganic and organic solutes.³ It has previously been shown that a wide range of solutes exhibit high solubility in the choline chloride: urea DES.¹⁰ In principle the DES should be tunable by varying the hydrogen bond donor and to some extent their mole ratio in the mixture. Table 2 shows the solubility of ZnO, CuO, and Fe₃O₄ in 3 DES at 50 °C. High solubilities could be achieved for all three oxides however, the most important observation is that the solubility of each oxide is markedly different in each DES even to the extent that the order of solubility changes. For example, Fe₃O₄ is most soluble in the oxalic acid: choline chloride mixture, whereas it is a factor of 20 times less soluble in the phenylpropionic acid mixture. In contrast, CuO shows the opposite behavior and this suggests that solvents can be designed to preferentially extract one metal oxide with respect to another. This could have potential applications to mineral extraction or metal oxide processing. The majority of the more ionic transition metal oxides have been found to be soluble in a DES although the

more covalent metal oxides such as aluminates and silicates are insoluble in all DES studied to date. This suggests that metal ions could be extracted from an aluminosilicate matrix without dissolving the matrix. Metals such as copper can be recovered electrochemically from the DES with high current efficiencies using bulk electrolysis.

Conclusions

Deep Eutectic Solvents can be formed between a range of carboxylic acids and choline chloride. Their physical properties and phase behavior are similar to ionic liquids and are dependent upon the number of acid functionalities, the aryl/alkyl substituents and the composition of mixture. Charge transport in these mixtures is predominantly controlled by ionic mobility, which is in turn affected by the viscosity of the liquid. The viscosity of the fluids is affected by the large ion: hole-size ratio and a simple relationship is demonstrated between the activation energy for viscous flow and the ratio of the ion to void radius. This is shown to be valid not only for a variety of ionic liquids and high-temperature molten salts, but also for molecular hydrocarbon solvents. The ease of synthesis, availability and biodegradability of the components makes these deep eutectic solvents versatile alternatives to ionic liquids.

Acknowledgment. The authors would like to acknowledge Scionix Ltd. for funding this work.

Supporting Information Available: Summary of Data Used to Produce Figure 6 and fit parameters for the data in Figure 4 to eq 1, and those in Figure 7 to eq 5. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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