

Phosphonium-Based Ionic Liquids Analogues and Their Physical Properties

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New ionic liquids analogues, that is, deep eutectic solvents (DESs), have been successfully synthesized. These DESs have been synthesized by the reaction of phosphonium-based salts with different hydrogen bond donors. Many of these DESs have melting temperatures lower than 100 °C. Preliminary laboratory results showed that these DESs can be used in different applications, for example, electrochemical processes, separation of sugars, and so forth. Melting temperature, density, viscosity, pH, conductivity, and dissolved oxygen content of the novel phosphonium-based DESs were measured as a function of temperature. It was found that the type of the salt and hydrogen bond donor and the mole ratio of both compounds have a paramount effect on the studied properties.

Introduction

Ionic liquids (ILs) are compounds that typically contain organic cations and inorganic anions with unique properties, low melting temperature (<100 °C), wide liquid phase range, high thermal stability, nonflammability, and very low vapor pressure.^{1,2} Over the past few years there has been a dramatic increase in research related to the use of ILs as potential replacements for organic solvents in chemical processes.^{3–6} The growing interest about ILs in regards to Green Chemistry and Engineering has largely been a result of the fact that they have no measurable vapor pressure, thus they do not emit volatile organic compounds (VOCs).^{7,8} Ionic liquids also have a diversity of potential applications.^{9–18}

While useful in the fine chemical industry, applications of ILs in the pharmaceutical industry and food industry have been very limited due to issues with toxicity, purity, and high costs.¹⁹ Recently, ionic liquids analogues, known as deep eutectic solvents (DESs), have been recognized as an alternative to traditional solvents and ILs themselves.²⁰ They are a combination of a salt and a hydrogen-bond donor (HBD), in which a new compound is formed, usually having much lower melting temperature than the components of the combination. DESs are advantageous because they can be easily prepared in high purity at low cost, and their components are biodegradable and possess low toxicity. Moreover, most DESs are nonreactive with water.²¹

The first generation DESs were based on mixtures of quaternary ammonium salts with hydrogen donors such as amines and carboxylic acids. The deep eutectic phenomenon was first described for a mixture of choline chloride and urea with a 1:2 mole ratio, respectively. Choline chloride has a melting temperature of 302 °C and that of urea is 133 °C while the eutectic mixture melts as low as 12 °C.²² This DES is able to dissolve many metal salts like lithium chloride (solubility 2.5 mol·L⁻¹) and copper(II) oxide (solubility 0.12 mol·L⁻¹). In this capacity, these solvents are used for metal cleaning prior

to electroplating. Because the solvent is conductive, it also has a potential application in electropolishing. Organic compounds such as benzoic acid (solubility 0.82 mol·L⁻¹) also have great solubility and this even includes cellulose. Compared to ordinary solvents, eutectic solvents also have a very low VOC and are nonflammable. Other deep eutectic solvents of choline chloride are formed with malonic acid at 0 °C, phenol at -40 °C, and glycerol at -35 °C.²²

Abbott et al.¹⁹ reported that eutectic mixtures of salts were utilized to decrease the temperature for molten salt applications. For the sake of illustration, they reported that ambient temperature molten salts can be formed by mixing, for example, quaternary ammonium salts with metal salts, and called the resultant compound as an ionic liquid analogue or deep eutectic mixture. This eutectic is a result of the formation of complex anions, for example, Al₂Cl₇⁻ and Zn₂Cl₅⁻, thus decreasing the lattice energy and decreasing the freezing temperature of the system.

Chen et al.²¹ described two methods of nucleophilic fluorination to prepare α -fluoroacetophenones from α -bromoacetophenones by using KF with PEG-400 or tetra-butylammonium fluoride with ZnF₂. They also developed a novel method for a one-pot fluorination to prepare α -fluoroacetophenones directly from acetophenones in DES. Morrison et al.²³ investigated possible uses of DES in solubilizing poorly soluble compounds for enhanced bioavailability in early drug development such as toxicology studies. They found that for five poorly soluble model compounds, solubility in DES is 5 to 22 000 folds higher than that in water. They concluded that DESs can be a promising vehicle for increasing exposure of poorly soluble compounds in preclinical studies.

Industrial applications of DESs are very promising. DESs were applied as a medium for the deposition of Zn, Cr, Sn, Cu, and Ag metals in the electro- and electroless plating of metals.^{24,25} Its application for the electropolishing of stainless steel was also studied whereby a DES composed of choline chloride and ethylene glycol showed three main advantages over the commercial alternative: (i) high current efficiencies are obtained; (ii) gas evolution at the anode/solution interface during polishing is negligible; and (iii) the liquid used is comparatively

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benign and noncorrosive compared to the current aqueous acid solutions.²⁶ DESs have been also tested as a reaction media for the synthesis of Lanthanide-organic frameworks. It was found that DESs can act as unusual reaction media by serving as template-delivery agents in a controlled manner and can as well be used for the synthesis of materials that cannot be prepared using other standard techniques.²⁷

All the work that has been published in the literature was on ammonium-based DES. Taking into consideration the important effect of the type of salt on the physical and chemical properties of the DESs, in this work we synthesized a novel class of DESs based on phosphonium salts with different hydrogen bond donors. To design any process involving DESs on an industrial scale, it is necessary to know a range of physical properties including melting temperature, viscosity, density, etc. In this work, we measured melting temperature, density, viscosity, pH, conductivity, and dissolved oxygen content of a selected class of the phosphonium-based DESs as a function of temperature.

Experimental Section

Chemicals. All the chemicals used were supplied by Merck Chemicals (Darmstadt, Germany), were of high purity (> 99 %), and were used without any further purification. The water mass fraction of these chemicals as per the manufacturer's guide is $< 10^{-4}$.

Synthesis of DESs. The original method of DES synthesis reported by Abbott et al.²⁸ was used to synthesize the DESs. A jacketed cup with mechanical stirrer was used to mix both the salt and hydrogen-bond donor. The mixing time and temperature were set to be a minimum of 3 h and 70 °C, respectively, while observing the formation of a homogeneous colorless liquid. However, some DESs had not shown a colorless liquid even after long hours of mixing at temperatures as high as 100 °C. All synthesis procedures were done at atmospheric pressure. A precipitate was formed after cooling down some of the synthesized DESs. In this case, the DES was filtered under vacuum to get rid of the precipitate.

The above procedure was repeated for different salt to hydrogen-bond donor mole ratios to determine the value that gives the DES with the lowest melting temperature.

The synthesis experiments were conducted in a glovebox with tight humidity control of less than 1 ppm water.

Physical Properties. All synthesized DESs were stored in well-sealed laboratory vials and were kept in a dehumidifier chamber with temperature control or in a desiccator over silica gel. Utmost precautions were taken for isolating the DESs from air moisture and contaminants.

Anton Paar DMA 4100 Density Meter (U-Tube) was used for measuring the densities at various temperatures. The temperature range for this density meter was (25 to 85) °C.

Freezing temperatures were measured using a Mettler Toledo Differential Scanning Calorimetry (DSC) device. The equipment's measurement accuracy was tested by measuring samples of known freezing points.

Conductivities of the DESs were measured at a range of temperatures using Eutech Cyberscan Con 11 hand-held meter. The variation of the temperature was done by using a water-bath with temperature control. The meter was calibrated by measuring the conductivities of aqueous solutions of KCl at different concentrations.

The pH of the synthesized DESs was measured at different temperatures using Eutech Cyberscan pH 300 hand-held meter. The variation of the temperature was achieved using a water-

Table 1. Uncertainties of Measurements Estimated for This Research

property	estimated uncertainty
density	$\pm 0.0001 \text{ g}\cdot\text{cm}^{-3}$
freezing temperature	$\pm 0.19 \text{ }^{\circ}\text{C}$
conductivity	$\pm 70 \text{ }\mu\text{S}\cdot\text{cm}^{-1}$
pH	± 0.04
nD	± 0.0027
viscosity (relative)	(3 to 5) % of measured value
dissolved oxygen	$\pm 0.03 \text{ mg}\cdot\text{L}^{-1}$

bath with temperature control. The meter was calibrated by standard pH buffer solutions.

Refractive indices of the DESs were measured at a range of temperatures using Mettler Toledo RE 40D Refractometer. This meter has a built-in method for calibration using deionized water. The calibration was done automatically before each test.

The viscosities of the DESs were measured at a range of temperatures using Brookfield R/S plus Rheometer. The temperature variation was achieved using external water-bath. The meter was calibrated using zero-calibration method.

Dissolved oxygen for the DESs was measured at a range of temperatures using Eutech DO600 hand-held meter. The variation of the temperature was achieved using a water-bath with temperature control. The meter was calibrated with sodium sulfide hydrate saturated solution.

Table 1 shows a summary of the estimated uncertainties.

Results and Discussion

Novel DESs based on methyltriphenylphosphonium bromide and benzyltriphenylphosphonium chloride as salts and glycerin, ethylene glycol, and 2,2,2-trifluoroacetamide as HBD were synthesized for several mole ratios of salt/HBD. The melting temperatures for the resulting DESs are shown in Figure 1. As can be seen from the figure, the salt to HBD mole ratios that give the DES with the lowest melting temperature depends on both the salt and the HBD. The DESs that gave the lowest melting temperature for different salt/HBD combinations are listed in Table 2 along with their abbreviations. In this table, the salt/HBD mole ratio represents the ratio of salt used (in moles) to that of the hydrogen bond donor in a particular DES combination.

Because of the variation of melting temperatures of the DESs studied in this research, their physical properties were measured at different ranges of temperatures, as all the measurements were

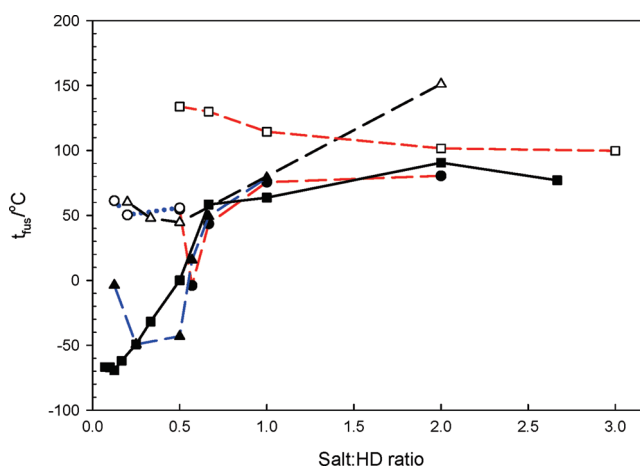


Figure 1. Freezing temperatures of phosphonium-based DESs as a function of salt/HBD mole ratio. ●, methyl salt/glycerine; ▲, methyl salt/ethylene glycol; ■, methyl salt/2,2,2-trifluoroacetamide; ○, benzyl salt/glycerine; △, benzyl salt/ethylene glycol; and □, benzyl salt/2,2,2-trifluoroacetamide.

Table 2. Compositions and Abbreviations for DESs Used in This Work

salt	hydrogen-bond donor	mole ratio (S/HBD)	abbreviation
methyltriphenylphosphonium bromide	glycerine	1:1.75	DES 1
methyltriphenylphosphonium bromide	ethylene glycol	1:4	DES 2
methyltriphenylphosphonium bromide	2,2,2-trifluoroacetamide	1:8	DES 3
benzyltriphenylphosphonium chloride	glycerine	1:5	DES 4
benzyltriphenylphosphonium chloride	ethylene glycol	1:3	DES 5
benzyltriphenylphosphonium chloride	2,2,2-trifluoroacetamide	3:1	DES 6

Table 3. Freezing Temperatures for the Studied DESs

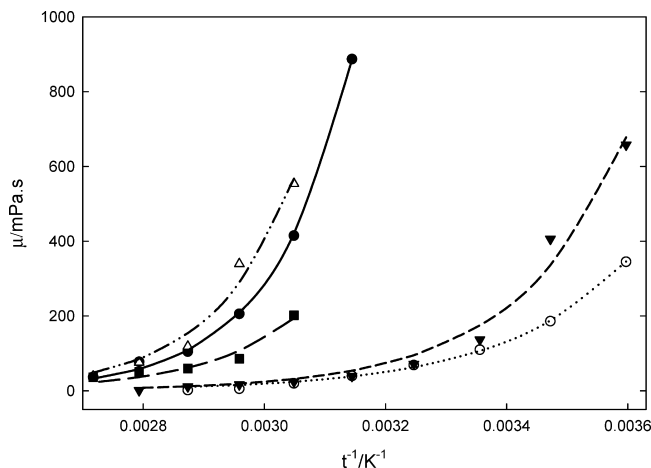
DES	$t_{fus}/^{\circ}\text{C}$
1	-4.03
2	-49.34
3	-69.29
4	50.36
5	47.91
6	99.72

done for the liquid phase. Thus, the physical properties of methyltriphenylphosphonium bromide-based DESs, which mostly have a melting temperature lower than 0 °C, were measured from (5 to 95) °C except for the refractive index and the density, which were measured within the range of (15 to 65) °C and from (25 to 85) °C, respectively, due to equipment limitations. On the other hand, the physical properties of benzyltriphenylphosphonium chloride-based DESs, which have relatively high melting temperatures, were measured at temperatures at least 5 °C higher than their melting temperatures. Because the operating temperatures of the density meter used are limited between 25 °C and 85 °C, DESs 4 and 5 were not measured for their density due to their high melting temperatures. Other than melting temperature, the physical properties of DES 6 were not measured because of its high melting temperature, as shown in Table 3.

It was found that the melting temperature of all the synthesized DESs is a function of the mole ratio of salt to hydrogen bond donor as shown in Figure 1. For example, for methyltriphenylphosphonium bromide + 2,2,2-trifluoroacetamide system the melting temperature of the mixture changes from as high as 91 °C at 1:2 to -69 °C at 1:8 salt/HBD mole ratio. It should be noted that the melting temperature of methyltriphenylphosphonium bromide is 231 °C while that for 2,2,2-trifluoroacetamide is 73 °C.

For the DES composed of methyltriphenylphosphonium bromide and ethylene glycol, the eutectic temperature occurs at a mole ratio of 1:4 with a melting temperature of -50 °C. This DES is characterized by having a low viscosity of about 5.4 mPa·s at 65 °C. When glycerine was used as HBD with the same salt, the eutectic temperature occurs at a mole ratio of 1:1.75 with a melting temperature of -4 °C. The decrease in the amount of the HBD needed for making the DES can be attributed to the larger number of hydroxyl groups in glycerine compared to that in ethylene glycol. However, the viscosity of this DES is about 16.6 mPa·s at 65 °C, which is higher than that for the corresponding one with ethylene glycol. Being liquids at or below 100 °C makes these DESs IL analogues that share many characteristics with ILs and at the same time they are less expensive, easy to synthesize, and highly pure.

The mole ratio of salt/HBD has a great influence on the viscosity of the DESs as can be seen in Figure 2. It should be noted that the value of the viscosity of the DES at the eutectic temperature is not necessarily the minimum as can be inferred from Figure 2. So in some practical applications where the viscosity is very important,

**Figure 2.** Dynamic viscosity, μ , of phosphonium-based DESs as a function of salt/HBD as a function of temperature t at the range of (278 to 368) K with the Arrhenius fit curves. ●, ○, ▲, and ■ refer to DES1, DES2, DES3, DES4, and DES5, respectively. Curves, eq 1.**Table 4. Regression Parameters for Viscosity and Density^a**

DES	μ_0	E_μ	SSE
	mPa·s	Pa·L·mol ⁻¹	
1	$2.281 \cdot 10^{-8}$	$6.446 \cdot 10^7$	$4.585 \cdot 10^{-10}$
2	$8.184 \cdot 10^{-6}$	$4.058 \cdot 10^7$	$1.823 \cdot 10^{-4}$
3	$1.148 \cdot 10^{-6}$	$4.668 \cdot 10^7$	$7.589 \cdot 10^{-9}$
4	$7.786 \cdot 10^{-8}$	$6.193 \cdot 10^7$	$4.051 \cdot 10^{-9}$
5	$4.158 \cdot 10^{-7}$	$5.443 \cdot 10^7$	$9.347 \cdot 10^{-10}$

DES	κ_0	E_κ	SSE
	mS·cm ⁻¹	Pa·L·mol ⁻¹	
1	47842.94	26.52	$3.44 \cdot 10^{-2}$
2	1214.79	15.80	$7.42 \cdot 10^{-2}$
3	2123.98	15.94	2.21
4	$6.87 \cdot 10^{-4}$	-8.29	$6.34 \cdot 10^{-9}$
5	$9.99 \cdot 10^{-33}$	-180.96	$2.54 \cdot 10^{-2}$

^a μ_0 and κ_0 are constants of regression for viscosity and conductivity, respectively, E_μ and E_κ are activation energies of viscosity and conductivity, respectively, and SSE is the sum of squared errors.

an optimum value for the salt/HBD ratio that gives reasonable values for both melting temperature and viscosity should be chosen. The viscosities of the 5 DESs where all fitted using Arrhenius-like formula as shown below

$$\mu = \mu_0 e^{\left[-\frac{E_\mu}{RT}\right]} \quad (1)$$

where μ is the viscosity, μ_0 is a constant, E_μ is the activation energy, R is the gas constant, and T is the temperature in Kelvin. The regression correlation coefficients were of values higher than 0.94. Values of μ_0 and E_μ are shown in Table 4 along with the sum of squares of deviations.

Both the pH and dissolved oxygen (DO) in the synthesized DESs were measured as a function of temperature and are plotted in Figures 3 and 4, respectively. The pH of the DES1 was around 7 and did not change much with the change of temperature. On the other hand, the pH of DES2 was very low, acidic, and increased with temperature. It seems that the type of the HBD has a strong effect on determining the acidity of the DES. The solubility of molecular oxygen in DESs was much smaller than that in familiar ILs.²⁹ Solubility of oxygen in ILs or DESs is an important parameter for applications involving oxidative reactions. In this case the IL or DES can be used as

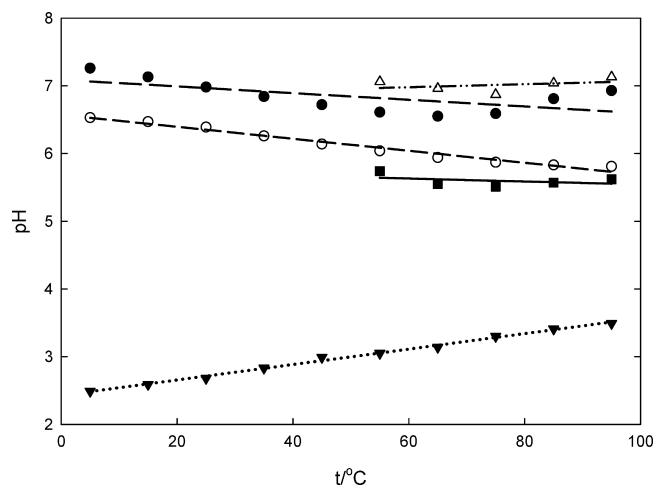


Figure 3. pH for selected phosphonium-based DESs as a function of temperature t at the range of (5 to 95) °C. ●, ○, ▼, △, and ■ refer to DES1, DES2, DES3, DES4, and DES5, respectively. Lines, eq 4.

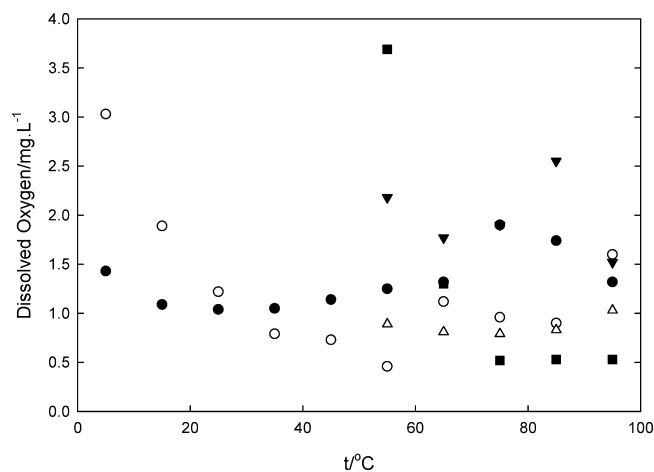


Figure 4. Dissolved oxygen in selected phosphonium-based DESs as a function of temperature t at the range of (5 to 95) °C. ●, ○, ▼, △, and ■ refer to DES1, DES2, DES3, DES4, and DES5, respectively.

a solvent and sometimes as a reactant. In general, it was noticed that the DO values for all tested DESs were much smaller than those reported for familiar ILs. The solubility of molecular oxygen in DESs involving benzyltriphenylphosphonium chloride-based salts showed very little variation with temperature. In this case, the DO is stable within the application range of temperature. On the other hand, the DESs involving methyltriphenylphosphonium bromide-based salts were very sensitive to the temperature variations ((0.3 to 3) $\text{mg}\cdot\text{L}^{-1}$ and (1 to 2) $\text{mg}\cdot\text{L}^{-1}$ for the ethylene glycol and glycerol-based HBD, respectively). In these cases, the DO sensitivity should be taken into consideration when dealing with such applications involving dissolved oxygen at different temperatures.

Density measurements were done for the methyltriphenylphosphonium bromide-based DESs only, as mentioned earlier. The behavior here was linear as expected. The variation of DES density with temperature is shown in Figure 5. The results for these three DESs were fitted by a linear relationship as follows

$$\rho/\text{g}\cdot\text{cm}^{-3} = a(t/^{\circ}\text{C}) + b \quad (2)$$

where ρ is the density, t is the temperature, and b is a constant that depends on the type of DES. The values of a and b for the tested DESs are shown in Table 5.

Table 5. Values of Parameters a and b Used in Equation 2

DES	a	b
1	-0.0007	1.25
2	-0.0011	1.42
3	-0.0007	1.31

As for the electrical conductivity, the behavior of the DESs was different for those of methyltriphenylphosphonium bromide-based DESs than from benzyltriphenylphosphonium chloride-based DESs. While DES1, DES2, and DES3 showed increasing conductivities with increasing temperatures, the electrical conductivity of DES4 and DES5 decreased with the increase of temperature, as shown in Figure 6. In addition, the conductivity of DES4 and DES5 did not change considerably at temperature range from (70 to 95 °C). Once again, Arrhenius-like equation was used to fit the behavior as shown below

$$K = K_0 e^{\left[-\frac{E_K}{RT}\right]} \quad (3)$$

where K is the conductivity in $\text{mS}\cdot\text{cm}^{-1}$, K_0 is a constant, E_K is the activation energy of conductivity, and R is the gas constant. Regression correlation coefficients were similar in their

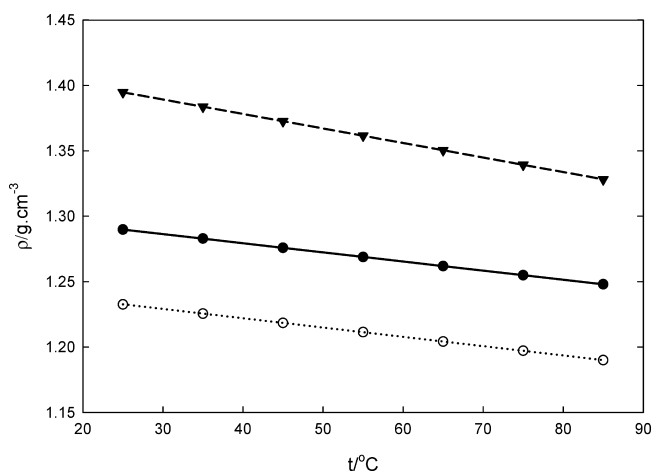


Figure 5. Densities, ρ , of methyltriphenylphosphonium bromide-based DESs as a function of temperature t at the range of (5 to 95) °C. ●, ○, and ▼ refer to DES1, DES2, and DES3, respectively. Lines, eq 2.

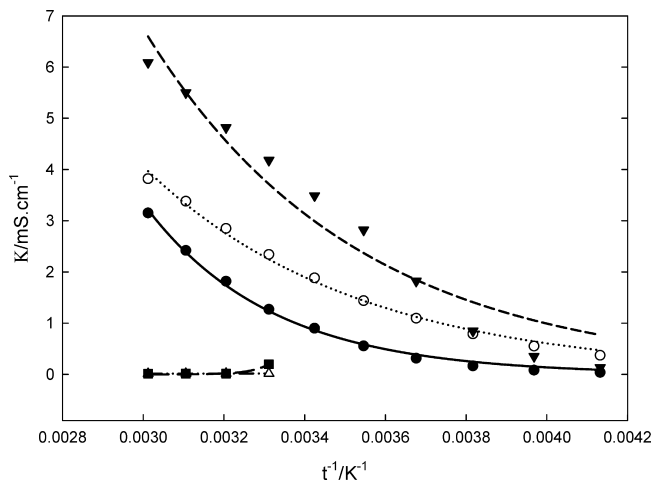


Figure 6. Conductivities, K , of selected phosphonium-based DESs as a function of temperature t at the range of (278 to 368) K with the Arrhenius fit. ●, ○, ▼, △, and ■ refer to DES1, DES2, DES3, DES4, and DES5, respectively. Curves, eq 3.

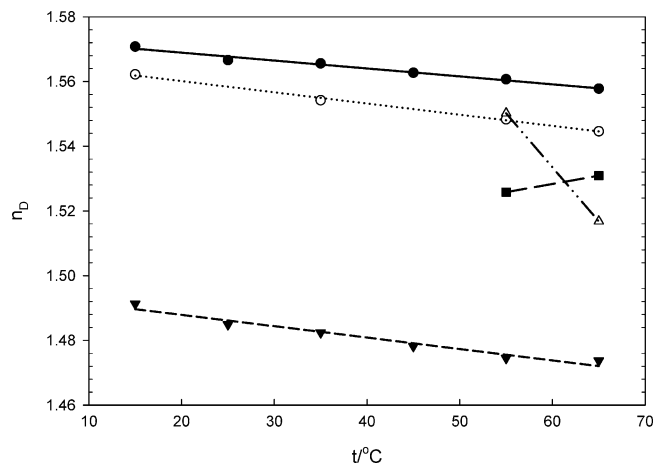


Figure 7. Refractive indices for selected phosphonium-based DESs as a function of temperature t at the range of (15 to 65) °C. ●, ○, ▼, △, and ■ refer to DES1, DES2, DES3, DES4, and DES5, respectively. Lines, eq 4.

Table 6. Values of Parameters a and b for Equation 4

DES	n_D		pH	
	$a \cdot 10^4$	b	$a \cdot 10^4$	b
1	-2.446	1.5738	-49	7.0887
2	-3.456	1.567	-89	6.571
3	-4.526	1.4947	114	2.4267
4	-33.4	1.7339	22	6.847
5	5.1	1.4997	-22	5.763

range of values with those of the viscosity's regression, that is, > 0.94 . Values of K_D , E_K , and sums of square errors are shown in Table 4.

The relatively high conductivities of methyltriphenylphosphonium bromide-based DESs make them good candidates for electrochemical applications, for example, electrodeposition, electrofinishing, and so forth.

Finally, the refractive indices (n_D 's) were measured at different temperatures. n_D is an important property of any application involving optical properties of the medium. It is used to calculate the focusing power of lenses and the dispersive power of prisms. Since n_D is a fundamental physical property of a substance, it is often used to identify a particular substance, confirm its purity, or measure its concentration. Mostly, it is used to measure the concentration of a solute in an aqueous solution.

Typically, the values of the refractive indices are expected to decrease while increasing the temperature because temperature affects the density of the substances, which in turn, affects their refractive indices. All the DESs showed the expected behavior except DES5, which showed an increase in its value at 65 °C compared to that at 55 °C; see Figure 7.

Refractive index is proportional to the square roots of electrical permittivity and magnetic permeability. These factors may change with temperature, but not linearly, and therefore the refractive index does not have a simple relationship with temperature.

Both of n_D and pH behaviors were fitted linearly, as the normal behavior is expected to be linear disregarding the acute deviation of some measurements from linear behavior. Table 6 shows the parameters needed for fitting the behavior by the general equation

$$Y = a(t/^\circ\text{C}) + b \quad (4)$$

where Y is n_D or pH, t is temperature in °C, and a and b are constants that vary according to the type of DES. As n_D and pH are unitless properties, a and b are unitless parameters.

Conclusion

A novel class of DESs has been synthesized by the reaction of phosphonium-based salts with different hydrogen bond donors. Many of these DESs have melting temperatures lower than 100 °C, which makes them ILs analogues. Physical properties including melting temperature, density, viscosity, conductivity, pH, refractive index, and dissolved oxygen content were experimentally measured for these novel DESs.

It was found that the type of the hydrogen bond donor has a great influence on the physical behavior of the DES. 2,2,2-Trifluoroacetamide as a hydrogen bond donor had always dragged the physical behavior of the DES far compared to other HBD. The effect of temperature on the measured physical properties was discussed in detail. A straight line equation was used to fit the density, n_D , and pH profiles, while Arrhenius equation was used to fit both viscosity and conductivity profiles. Preliminary results, not shown in this work, showed possible application of these DESs in liquid–liquid extraction and the separation of sugars.

Supporting Information Available:

Tables of the freezing point, viscosities, conductivities, pH, densities, dissolved oxygen content, and refractive indices. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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