Density, Viscosity and Conductivity of Tetra-alkyl Phosphonium Ionic Liquids

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The density, viscosity and conductivity of nine commercially available tetra-alkyl phosphonium ionic liquids (ILs) are presented. The effect of cation volume and symmetry, anion volume, and temperature are observed. The Vogel-Tamman-Fulcher (VTF) equation is used to calculate the theoretical glass transition temperature (T_0) and the activation energy of conductivity $E_{a,\Lambda}$. The conductivity of three halo-aluminate ionic liquid systems for mole fractions up to 0.7 $AlCl_3$ is reported.

Introduction

Hurley and Weir were some of the early investigators into the uses of ionic liquids (ILs). They successfully electrodeposited aluminium at room temperature from solutions of ethyl pyridinium bromide (EPB), aluminium chloride and toluene or benzene (1). Unfortunately, the pyridinium cation had the disadvantage of being relatively easy to reduce. To overcome this limitation, Wilkes *et. al.* developed a class of ionic liquid cations based on dialkyl-imidazolium salts in an effort to create a battery with an aluminum metal anode and a chlorine cathode (2). The most promising of these salts was the 1-ethyl-3-methylimidazolium chloride [EMIM][Cl]. Phosphonium ionic liquid cations are also very stable and are considerably less expensive than imidazolium ILs (3). They are also understudied compared to both pyridinium and imidazolium. It is believed that phosphonium-types are good alternatives to other ILs in many situations and thus deserve further research (4).

The ionic liquid / chloro-aluminate equilibrium varies with concentration of $AlCl_3$. The two main equilibrium reactions are described in Equations 1 (5):

$$Cl^- + AlCl_3 = [AlCl_4]^- \qquad [1a]$$

$$[AlCl_4]^- + AlCl_3 = [Al_2Cl_7]^- \qquad [1b]$$

Experimental

Cytec Phosphonium Ionic Liquids

The focus of this study was to determine the density, viscosity and conductivity of phosphonium ionic liquids. Some basic information regarding the ionic liquids tested is presented in Table I. Cytec Inc. provided the ionic liquids.

TABLE I. Molecular weight (MW), purity, melting point (T_{mp}) and upper limit of the safe operating temperature in an air environment of phosphonium ionic liquids (6).

CYTEC IL #	Cation	Anion	MW g/mol	Purity %	T_{mp} °C	Upper limit °C
101	$[(C_6H_{13})_3P(C_{14}H_{29})]^+$	Cl^-	519.3	93-95	-50	140
102	$[(C_6H_{13})_3P(C_{14}H_{29})]^+$	Br^-	563.8	96-98	0	150
105	$[(C_6H_{13})_3P(C_{14}H_{29})]^+$	$N(CN)_2^-$	549.9	97	<20	175
109	$[(C_6H_{13})_3P(C_{14}H_{29})]^+$	$N(SO_2CF_3)_2^-$	764.0	98	<20	180
110	$[(C_6H_{13})_3P(C_{14}H_{29})]^+$	PF_6^-	628.9	98	50	120
111	$[(C_6H_{13})_3P(C_{14}H_{29})]^+$	BF_4^-	570.7	97	37	140
164	$[(C_4H_9)_4P]^+$	Cl^-	294.9	97	80	180
167	$[(C_4H_9)_3P(C_{14}H_{29})]^+$	Cl^-	435.2	95-99	45	180
482	$[(C_8H_{17})_4P]^+$	Br^-	563.8	94-97	40-45	-

Sample Preparation

All of the samples were prepared in a Vacuum Atmosphere Co. Glove box (HE Series) under a dry nitrogen atmosphere (< 10 ppm O_2, H_2O). $AlCl_3$ (99.99% pure) from Alfa Aesar was used to prepare the binary mixtures.

Density

The density of the neat ionic liquids was measured using a 25 mL glass pyncometer. The temperature was adjusted using a water bath. The density equations presented are a combination of correlations determined by Cytec Inc. and experimental data points from this work. The results using this procedure were in close agreement with the values of Cytec.

Viscosity

The viscosity experiments were performed outside the glove box using a Cannon-Frenske type capillary viscometer. The temperature of the experiment was controlled using an oil bath. The samples were dried for 4 hours at temperatures ranging from 120-155 ºC in a dry nitrogen environment prior to testing.

Conductivity

The conductivity was measured using a Jenway conductivity meter with an "enterprise" probe (cell constant = 1 cm^{-1}). To maintain the nitrogen atmosphere, dry nitrogen (< 10 ppm O_2, H_2O) was used to purge the test tube continuously via two needles in the stopper (Figure 1). The samples were dried for 4 hours at 140 ºC under a constant dry nitrogen purge prior to testing.

The temperature during the conductivity experiments was regulated using a heated and agitated oil bath. A time lapse of 55 minutes in between measurements was found to be adequate to ensure steady state conditions. The temperature measurements were made by a combination of the Jenway in-line thermocouple (up to 105 °C) and the heating bath thermocouple for temperatures above 105 °C. A second thermocouple (not depicted) immersed in the test solution in some of the experiments was used to establish a relationship between the heating bath and the test solution at higher temperatures. The conductivity data presented in this paper are reported from statistical analysis and fitting between 6-10 steady state data points, usually with a third order polynomial.
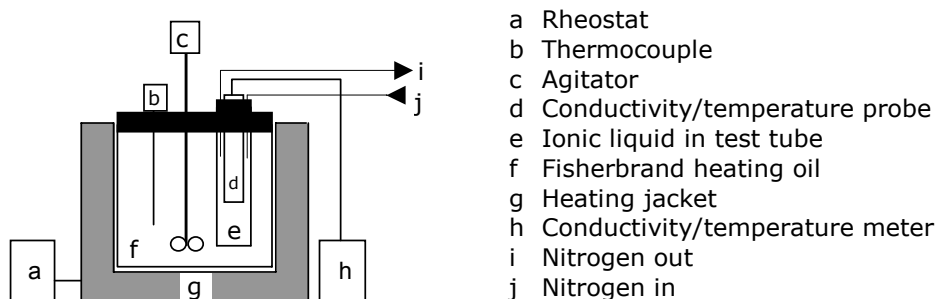
a Rheostat
b Thermocouple
c Agitator
d Conductivity/temperature probe
e Ionic liquid in test tube
f Fisherbrand heating oil
g Heating jacket
h Conductivity/temperature meter
i Nitrogen out
j Nitrogen in

Figure 1. Conductivity measurement experimental setup.

<u>Experimental Error</u>

Six repeat experiments of the conductivity of IL 101 and IL 101 : AlCl$_3$ mixtures (0.6 mole fraction AlCl$_3$) were conducted to evaluate the experimental error. The mean conductivity results of IL 101, 95% confidence interval, and standard error as a percentage of the mean are shown in Table II.

TABLE II. Experimental errors in the conductance measurements, based on 6 repeat experiments.

Solution	T. ºC	Mean Conductivity mS/cm	95% Confidence Interval		Standard Error % of Mean
IL 101 $[(C_6H_{13})_3P(C_{14}H_{29})]^+Cl^-$	25	0.0074	0.0067 -	0.0082	5.3
	50	0.0390	0.0321 -	0.0459	9.1
	75	0.1252	0.1186 -	0.1319	2.7
	100	0.2958	0.2839 -	0.3076	2.0
	125	0.5801	0.5616 -	0.5986	1.6
	150	1.0079	0.9762 -	1.0397	1.6
IL 101 + 0.6 M.F. AlCl$_3$ $[(C_6H_{13})_3P(C_{14}H_{29})]^+Cl^-$ + 0.6 Mole Fraction AlCl$_3$	25	0.0867	0.0804 -	0.0931	3.8
	50	0.4257	0.4051 -	0.4464	2.5
	75	0.9840	0.9269 -	1.0411	3.0
	100	1.8450	1.7408 -	1.9493	2.9
	125	3.0922	2.9397 -	3.2447	2.5
	150	4.8088	4.6109 -	5.0068	2.1

Results and Discussion

<u>Impurities</u>

To identify possible impurities, the samples were digested in a solution of H$_2$O$_2$ and H$_2$SO$_4$ at elevated temperature; the solution was then analyzed by ICP. TABLE III lists the most prominent impurities in the samples. As seen below, sodium was present in higher concentrations in some of the samples. One significant source of sodium contamination was during the preparation of ionic liquids, as the ILs with anions other than chloride and bromide required an anion metathesis reaction. Despite washing, some sodium salts remained in the IL. The higher levels of aluminium in IL 110 and 111 may be due to dissolution of aluminium during production as both of these ionic liquids contain fluorine compounds and possibly small amounts of hydrofluoric acid.

TABLE III. Ionic liquid metal impurity content.

IL	Impurity (mg/kg)				
	Al	**Ca**	**Cu**	**Fe**	**Na**
101	55	61	5	34	154
102	47	451	102	61	716
105	42	222	62	34	445
109	27	82	19	42	203
110	3665	339	40	164	9901
111	1629	490	14	101	4285
164	74	89	8	71	448
167	<0.2	31	12	<0.03	394
482	65	74	16	82	383

There were other impurities present in the ionic liquids, some of these are listed in Cytec chemical information sheets and are summarized in Table IV. In the halo-aluminate ionic liquids there was likely trace amounts of aluminium oxy-chlorides or bromides, for example $AlOCl_2^-$ (7).

TABLE IV. Known impurities (5).

IL	Impurities		
101	0.1 - 0.4% tetradecene isomers	0.1-0.5% HCl	0.1-1.2% $[PR_3H]^+$ Cl^-
102	0.1 - 0.4% tetradecene isomers	0.1-0.5% HBr	0.1-1.2% $[PR_3H]^+$ Br^-
105	0.5% Cl^-	0.3% H_2O	
109	< 0.1% Cl^-	0.1% H_2O	
110	< 0.1% Cl^-		
111	< 0.1% Cl^-		
164	0.1-0.6% HCl		0.1-1% $[PR_3H]+$ Cl^-
167	0.2-0.5% tetradecene isomers	0.2 to 1.2% HCl 0.1-0.3% H_2O	0.1 to 1.5% $[PR_3H]^+$ Cl^-

Density

Linear relationships of density and temperature are shown Figure 2, the equations are provided in Table V. The temperature range for the density measurements of IL 164 was small due to its high melting point and the use of a water bath heat source.
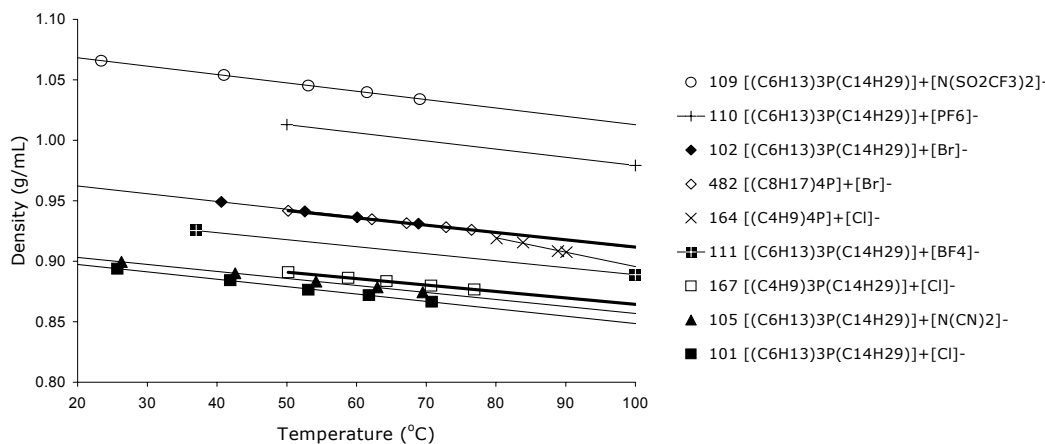

Figure 2. Effect of temperature on the densities of phosphonium ionic liquids.

Viscosity

Phosphonium ionic liquid viscosity is somewhat higher than that of their ammonium counterparts (4). The kinematic viscosity (υ) of the ILs generally decreased with increasing anion volume (Figure 3). Exceptions were IL 102 (Br⁻) and IL 111 (BF₄⁻)

whose viscosities were slightly higher than IL 101 (Cl⁻) and IL 110 (PF₆⁻) respectively. Values for the ion volumes are presented in Figures 13 and 14.
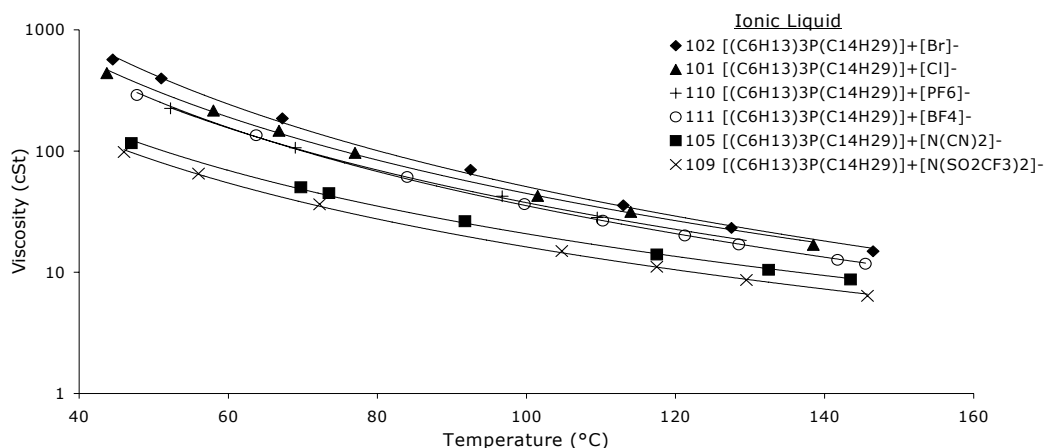

Figure 3. Effect of temperature on the kinematic viscosity of tetradecyl(trihexyl) phosphonium ionic liquids.

The kinematic viscosities of the chloride ionic liquids with smaller cations appeared to be higher at temperatures < ca. 120 ºC but decreased as the temperature increased (Figure 4). The higher viscosity at lower temperature may be due to the fact that liquid ranges studied for IL 164 and IL 167 are much closer to their melting points than for IL 101.
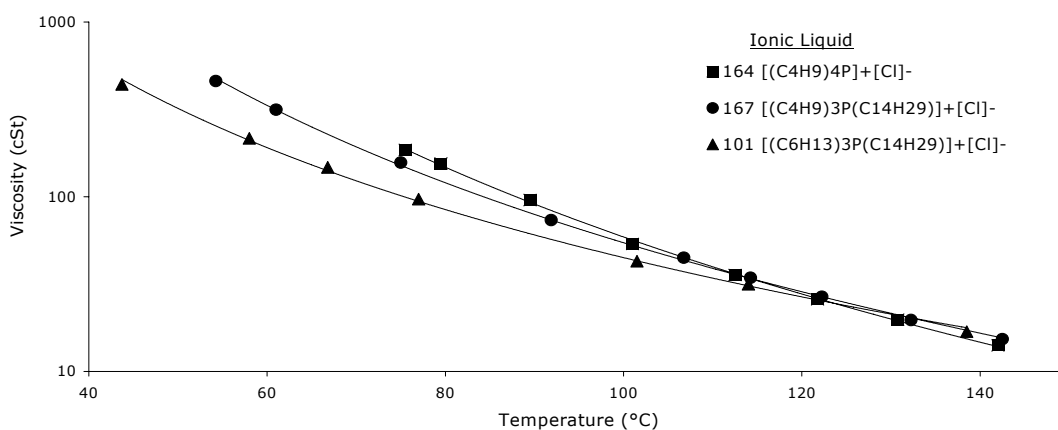
Figure 4. Effect of cation type and temperature on phosphonium ionic liquids with chloride anions.

In Figure 5, the viscosity of two ionic liquids with the same chemical composition but different structures and nearly identical density are compared. The difference between the two was the symmetry of the cation; IL 482 was composed of four octyl chains while IL 102 was composed of three hexyl chains and one tetradecyl chain. Asymmetry in the cation resulted in a decreased viscosity.
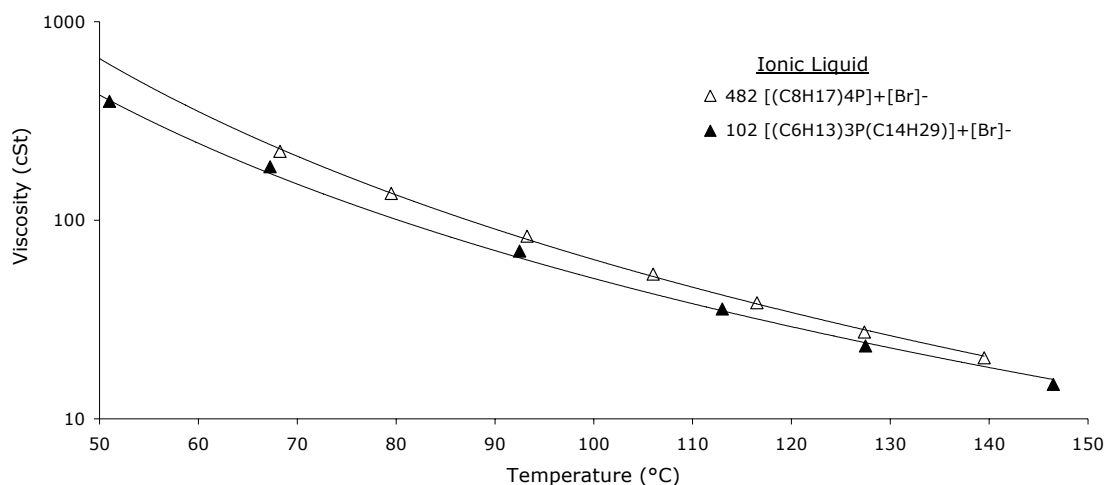
Figure 5. Effect of cation symmetry on the kinematic viscosities of bromide phosphonium ionic liquids.

Conductivity

In the tetradecyl(trihexyl)phosphonium series tested, a larger anion generally resulted in higher conductivity (Figure 6). The only exception, $N(CN)_2^-$, was more conductive than would be expected. Larger anions have a less localized charge, reducing ion interaction that may hinder migration. Diaw *et. al.* recently reported that with 1-butyl-3-methlylimidazolium ionic liquids, having a PF_6^- anion resulted in a more viscous and less conductive ionic liquid than the BF_4^- anion (8). They attributed this to stronger cation-anion interactions. In this situation, with a tetradecyl(trihexyl) phosphonium ionic liquid, the PF_6^- anion system was more conductive than BF_4^-.
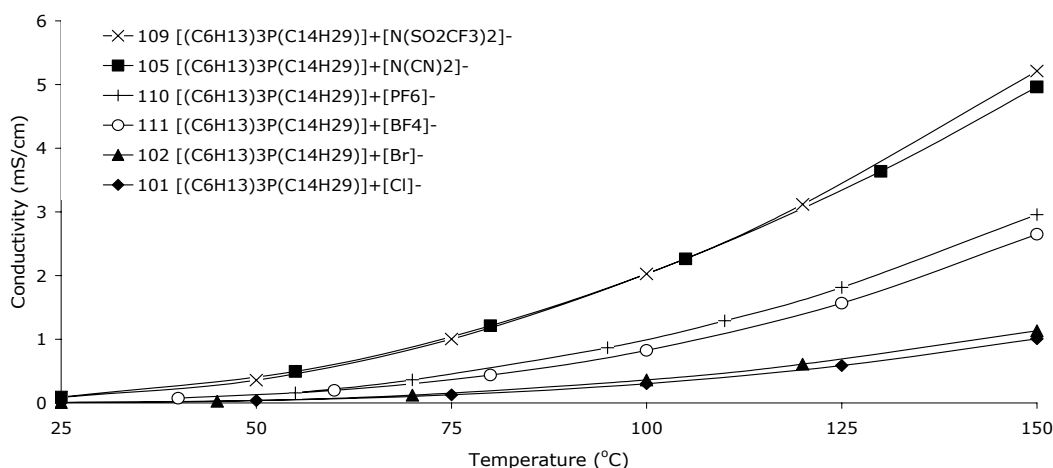

Figure 6. Effect of anion type on the conductivity of tetradecyl(trihexyl) phosphonium ionic liquids.

Cation type also heavily influences the conductivity, and contrary to the general anion effect, a smaller cation leads to increased conductivity (Figure 7). The tetrabutyl phosphonium chloride (IL 164) was the most conductive, followed by tetradecyl(tributyl) phosphonium chloride (IL 167) and tetradecyl(trihexyl) phosphonium chloride (IL 101).

The small cation size also results in higher melting points, 80, 45 and −50 ºC for ILs 164, 167 and 101 respectively (Table I).
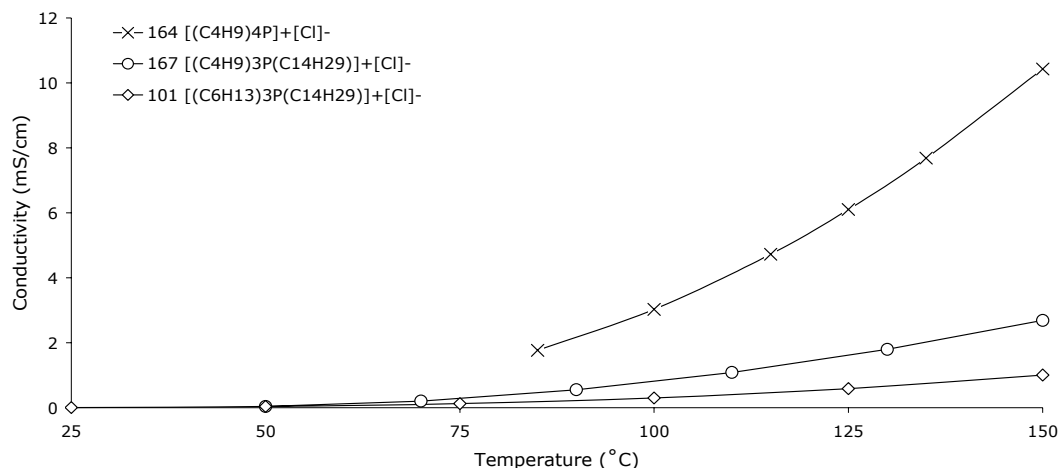
Figure 7. Effect of cation type on the conductivity of chloride phosphonium ionic liquids.

The cation symmetry also influenced the conductivity as shown in Figure 8 where two ionic liquids of identical molecular weight and density are compared. The asymmetric cation of IL 102 resulted in a slight increase in conductivity at higher temperatures. The asymmetry also reduced the melting point from 43 to 0 ºC (Table I).
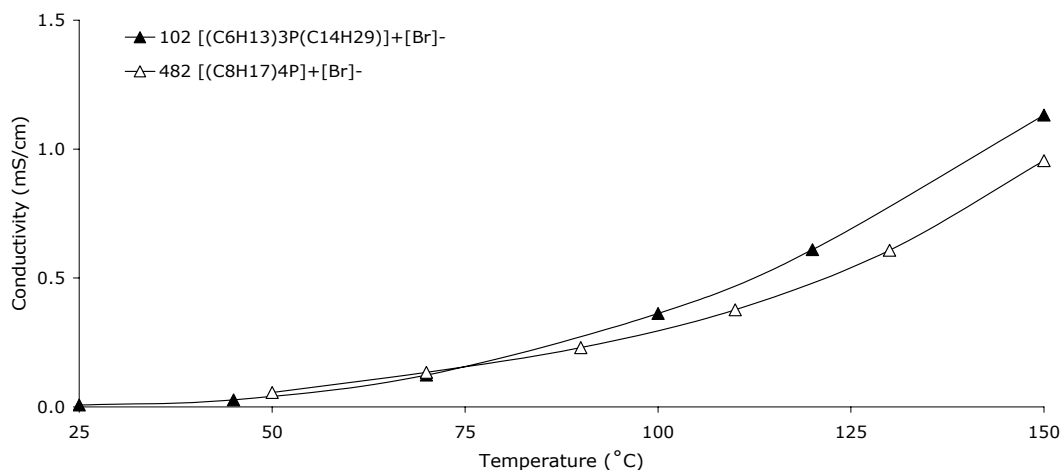
Figure 8. Effect of cation symmetry on the conductivity of bromide phosphonium ionic liquids.

A summary of density functions, along with conductivity, viscosity and Walden products of ionic liquids at select temperatures are shown in Table V. The dynamic viscosity (η in cP) is calculated from the kinematic viscosity (υ in cSt) using the density (σ in g/mL).

$$\eta = \upsilon \cdot \sigma \qquad [2]$$

The Walden product is the product of the dynamic viscosity and molar conductivity. Ideally, the Walden product would be independent of temperature; for the most part this is the case. The exceptions are that the Walden products of IL 110, 164, 167 and 482 vary significantly with temperature (Table V).

TABLE V. Summary of the density functions as well as the conductivity, viscosity and Walden product of the ionic liquids at select temperatures.

IL	Density (σ) g/mL (T in ºC)	Conductivity (κ) mS/cm		Molar Conductivity (Λ) S·cm²/mol		Kinematic Viscosity (υ) cSt		Dynamic Viscosity (η) cP		Walden Product ($\eta \cdot \Lambda$) cP·S·cm²/mol	
	ºC→	*50*	*100*	*50*	*100*	*50*	*100*	*50*	*100*	*50*	*100*
101	.914-.00059T	.037	.303	.022	.184	320	44.8	283	38.3	6	7
102	.970-.00065T	.040	.362	.024	.226	427	50.9	401	46.1	10	10
105	.915-.00058T	.394	2.03	.244	1.30	107	20.8	94.4	17.8	23	23
109	1.08-.00069T	.357	2.03	.260	1.53	84.3	16.2	88.3	16.4	23	25
110	1.05-.00068T	.101	.998	.063	.641	258	37.6	261	36.8	16	24
111	.947-.00058T	.124	.826	.077	.530	266	35.5	244	31.5	19	17
167	.918-.00053T	.040	.798	.020	.402	635	54.5	566	47.1	11	19
482	.972-.00060T	.056	.295	.034	.182	650	63.3	612	57.7	21	11
	ºC→	*85*	*100*	*85*	*100*	*85*	*100*	*85*	*100*	*85*	*100*
164	1.015-.00119T	1.77	3.03	.571	.997	115	58.8	105	53	60	52

VTF Fitting

The Vogel-Tammann-Fulcher (VTF) equation can be used to describe the conductivity of molten salts as a function of temperature, Equation 3 (9).

$$\Lambda = AT^{-1/2}\exp[-B/(T-T_0)] \qquad [3]$$

Here, Λ is the molar conductivity (S·cm²/mol), A and B are constants, T is the temperature (Kelvin) and T_0 is the temperature at which the transport function goes to zero. The molar conductivity was calculated from the measured conductivity using Equation 4.

$$\Lambda = \text{K} \cdot MW/\sigma \qquad [4]$$

K is the measured conductivity (S/cm), MW is the molecular weight (g/mol) and σ is the density (g/mL). Lu and Dreisinger estimated the T_0 of the BMIC : $AlCl_3$ ionic liquid system at various $AlCl_3$ concentrations by fitting a linear plot to conductivity data (10). Sanders *et. al.* showed that T_0 values estimated by fitting the conductivity data are comparable to both T_0 estimated by viscosity and experimental values of the glass transition temperature (T_g) for the $AlBr_3$-MeEtimBr system (11). Figure 9 shows the linear fit that is obtained when optimized by varying T_0.
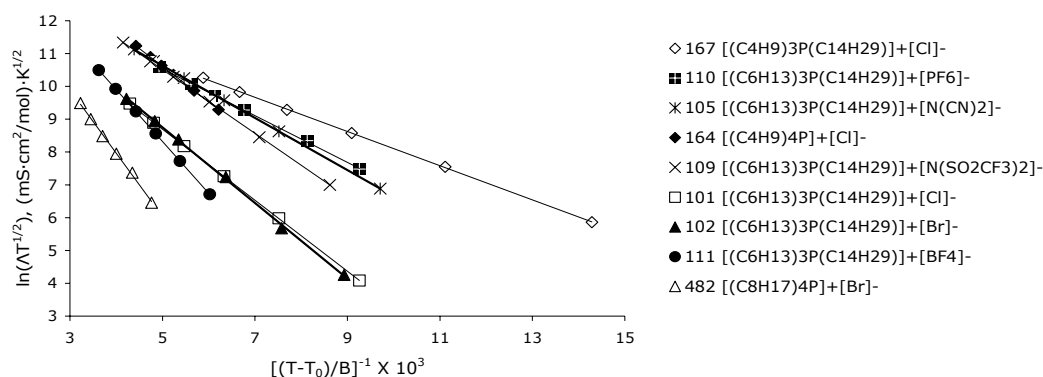

Figure 9. VTF equation parameters, T_0 was the variable to optimize a linear fit and B is the slope of the line.

Once T_0 and B are identified, the temperature dependent activation energy of conductivity ($E_{a,\Lambda}$) can be calculated. By differentiating Equation 4 with respect to T ($\partial \ln\Lambda/\partial T$) and knowing that $E_{a,\Lambda} = RT^2(\partial \ln\Lambda/\partial T)$ where R is the rate constant (8.31 J/mol·K), Equation 5 may be derived (12) as:

$$E_{a,\Lambda} = -RT/2 + RT^2B/(T-T_0)^2 \qquad [5]$$

Table VI summarizes the B and T_0 values derived by fitting the conductivity results to the VTF equation, and the activation energy of conductivity at select temperatures. The theoretical glass transition temperatures were found to be between 33 and 202 ºC lower than the melting points of the ionic liquids. The standard error of T_0 with a 95% confidence interval was found to be +/- 9.4% of the mean based on six repeat experiments of IL 101. The activation energy of conductivity decreased with increasing temperatures for all of the ionic liquids.

TABLE VI. VTF equation parameters (B and T_0) and $E_{a,\Lambda}$ at selected temperatures.

| IL	B	T_0 ºC	T_{mp} ºC	$E_{a,\Lambda}$ (kJ/mol)				
				50 ºC	75 ºC	100 ºC	125 ºC	150 ºC
101	1082	-83	-50	52.9	43.5	37.2	32.7	29.4
102	1650	-87	0	76.1	63.1	54.4	48.2	43.5
105	795	-78	<20	41.9	34.0	28.8	25.2	22.5
109	973	-91	<20	42.3	35.4	30.7	27.3	24.7
110	711	-53	50	58.0	43.5	35.0	29.4	25.5
111	1577	-126	37	44.0	39.1	35.5	32.8	30.6
167	521	-20	45	92.0	57.9	41.6	32.4	26.6
164	1089	-76	80	-	59.3	47.9	40.5	35.3
482	1927	-160	40-45	37.7	35.0	32.8	31.1	29.6

Conductivity of Chloro-aluminate Mixtures
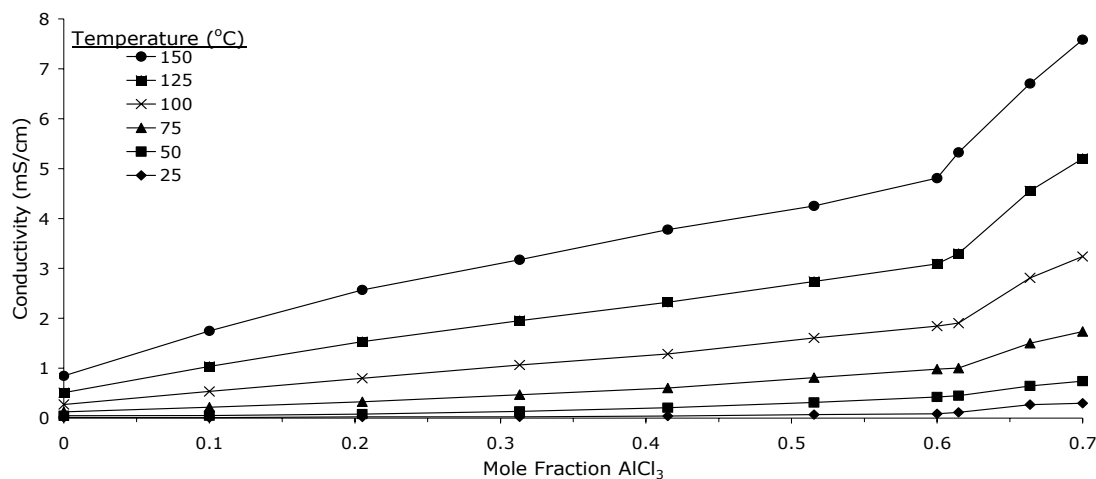
Figure 10. Conductivity of the $AlCl_3$: IL 101 system as a function of temperature and $AlCl_3$ concentration.

The conductivity of halo-aluminate ionic liquids was also investigated as a function of temperature and concentration of $AlCl_3$. The increased conductivity of halo-aluminate ionic liquids with $AlCl_3$ concentration is likely due to the increased mobility of $AlCl_4^-$ and $Al_2Cl_7^-$ compared with Cl^-. This enhanced mobility of larger anions is counter

intuitive if considering only the size, but can be rationalized by the decreased effect of cation-anion pairing or bonding due to the lower charge density as suggested by Fannin *et. al.* (13). In the case of IL 101 (tetradecyl(trihexyl) phosphonium chloride), the conductivity generally increased with increasing mole fraction $AlCl_3$ suggesting that ionic interaction is limiting the conductivity at all concentrations tested (Figure 10). There was some undissolved $AlCl_3$ in the experiments at 0.7 mole fraction $AlCl_3$, upon heating to elevated temperatures the $AlCl_3$ bubbled out of the solution as $AlCl_3$ (g).

The $AlCl_3$: IL 164 system exhibited the highest conductivity of all the ionic liquid systems tested in this work (Figure 11). Similar to $AlCl_3$: IL 101, the conductivity generally increased with increasing $AlCl_3$ concentration. The relatively small tetra-butyl cation of IL 164 allows high conductivity throughout most of the concentration range. An exception was the formation of an intermediate phase at the neutral melt composition (0.5 mole fraction $AlCl_3$) at which a solid was present at temperatures below about 130 ºC. An increase in conductivity at the nearby compositions of 0.45 and 0.55 mole fraction $AlCl_3$ was observed at elevated temperatures.
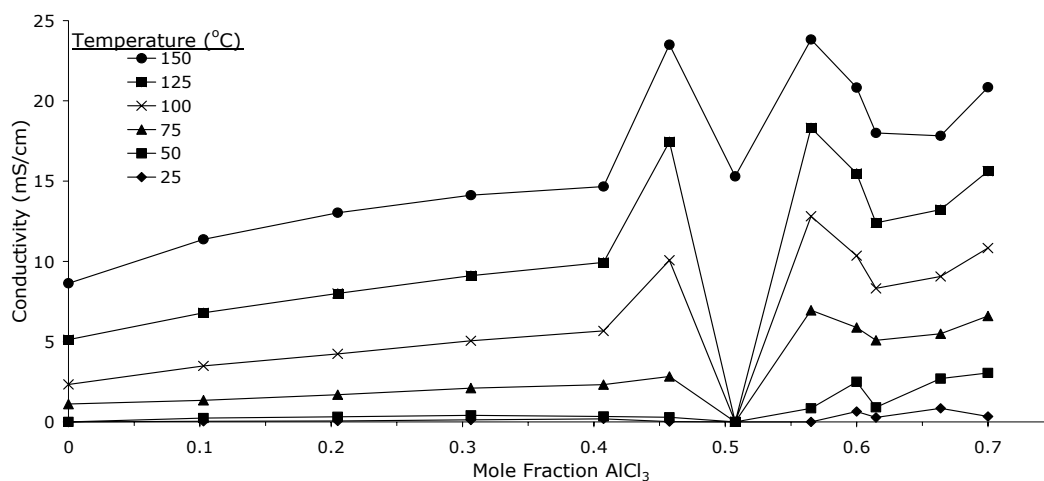

Figure 11. Effects of $AlCl_3$ concentration and temperature on conductivity of the $AlCl_3$: IL 164 system.
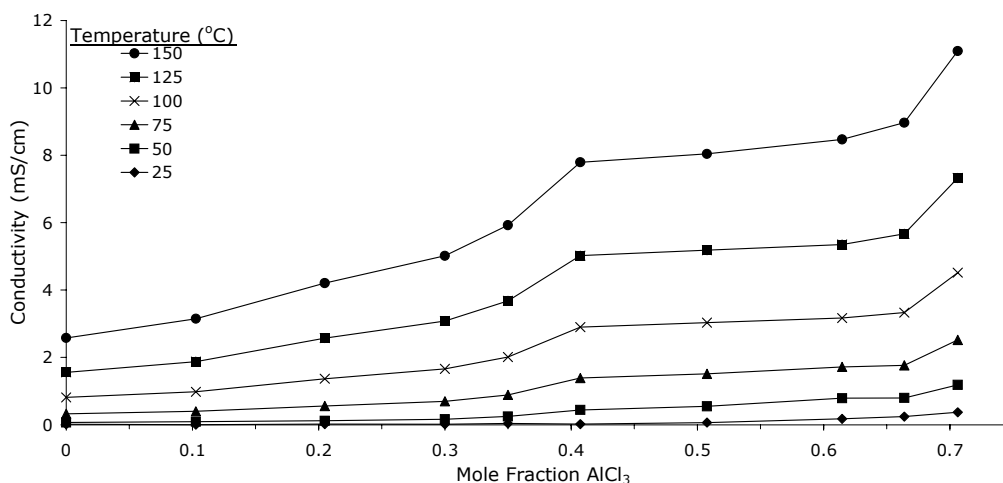

Figure 12. Conductivity of the $AlCl_3$: IL 167 system as a function of temperature and $AlCl_3$ concentration.

   IL 167 was similar to IL 101 in that the conductivity generally increased with increasing additions of $AlCl_3$ (Figure 12).   The conductivity was relatively constant between 75 and 100 ºC for $AlCl_3$ mole fractions from ca. 0.4-0.6. A significant increase in the conductivity at elevated temperatures and $AlCl_3$ concentrations greater than ca. 0.67 mole fraction was also noticed.

   The effects of anion and cation volume on the conductivity are summarized in Figures 13 and 14. The anions were considered to be $Al_2Cl_7^-$ and $AlCl_4^-$ at 0.67 and 0.5 mole fraction $AlCl_3$ respectively. The ion volumes presented were taken from a consistent set of data or calculated using a generalized linear equation from the literature (14).
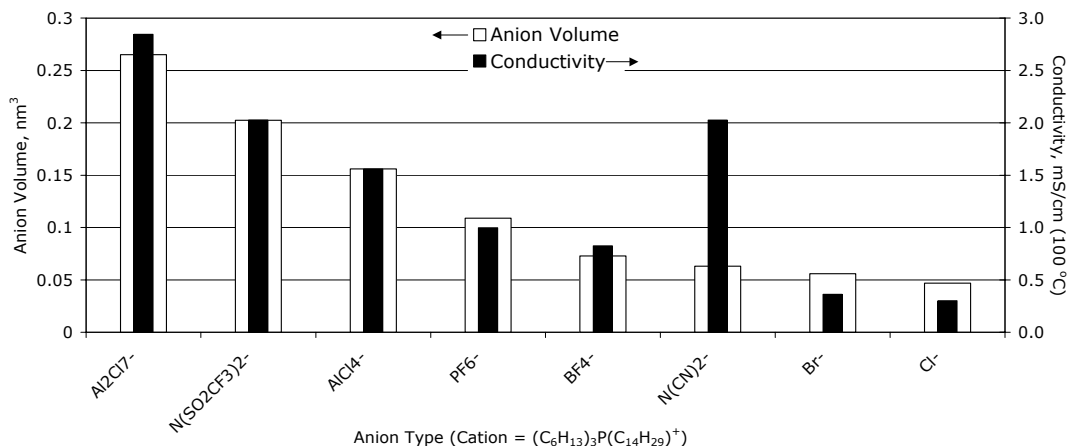

Figure 13.   Effect of anion volume on the conductivity of tetradecyl(trihexyl) phosphonium ionic liquids.
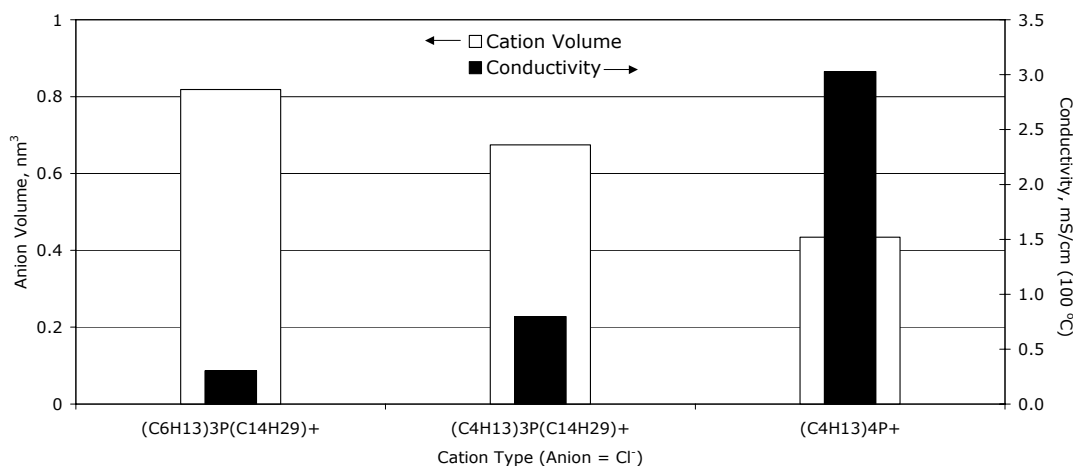

Figure 14. Effect of cation volume on the conductivity of phosphonium chloride ionic liquids.

Conclusions

The properties of commercially available tetra-alkyl phosphonium ionic liquids were studied. The conductivity increased with decreasing cation volume and increasing anion volume. Asymmetry in the cation resulted in a slight decrease in viscosity and an increase in conductivity at elevated temperatures. An intermediate phase with a relatively high

melting point was identified in the tetra-butyl phosphonium chloride : AlCl$_3$ system at 0.5 mole fraction AlCl$_3$.

Acknowledgments

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