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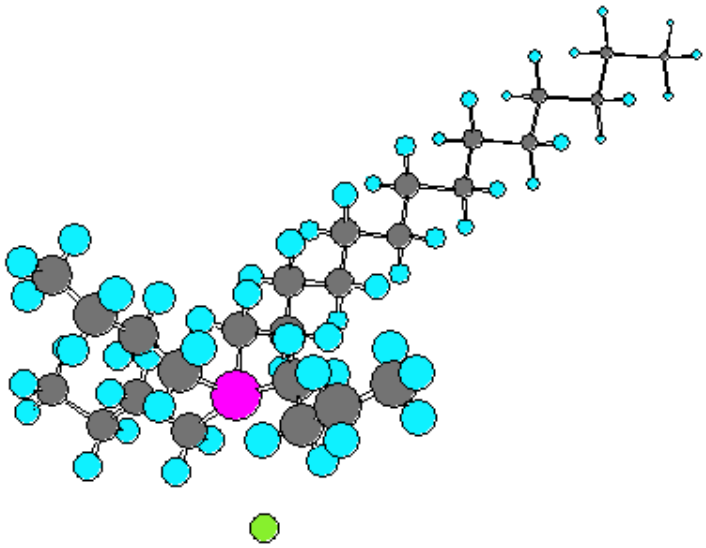
CYPHOS® IL 167

Phosphonium Ionic Liquid



Introduction:

Why consider a "phosphonium" ionic liquid?

Soon after the discovery that certain nitrogen based room temperature liquid salts were found to be useful as battery electrolytes (1a,1b,), interest in these and similar salts as novel fluids and solvents developed. There were a scant number of papers during the 1980s and early 1990s but mainly due to the efforts of the group at The Queen's University – Belfast, headed up by Professor Ken Seddon, there has been an exponential rise in interest and number of publications in the last 7 to 8 years. (2) Indeed, almost an entire issue of Green Chemistry (3) has been devoted to ionic liquids.

Perhaps one of the most influential publications to direct industrial attention to ionic liquids was a feature article entitled "Designer Solvents" in C&E News – March 30,1998 in which Ken Seddon, Robin Rogers, Tom Welton, Helene Olivier and others elaborated on the potential of ionic liquids. While the article dealt almost entirely with nitrogen based ionic liquids, there was a brief reference by Ken Seddon which alluded to the fact that phosphonium salts are also a potential source of numerous ionic liquids. This brief reference to phosphonium ionic liquids is very much representative of the current fraction of publications relating to phosphonium based ionic liquids. With the exception of several papers and patents by George Parshall in the mid 1970s using stannate and germanate salts and John Knifton et al in the early 1990s which centre on the use of molten tetrabutylphosphonium bromide as an ionic solvent, almost the entire volume of ionic liquid literature deals with nitrogen based systems and in particular, those based on 2-methylimidazolium salts.

There was a good reason for the lack of phosphonium based ionic liquid publications – availability of the starting material! While Cytec has been commercially producing phosphine derivatives since 1971, it was not until 1990 that tributylphosphine was produced on a large commercial scale. Since that time, not only has tetrabutylphosphonium chloride and bromide become available in multi ton scales, many other trialkylphosphines and the corresponding quaternary phosphonium salts are or can be manufactured on a large scale.

The phosphonium cation contains four substituents and the various combinations along with the multitude of various available anions represents an enormous number of possible salts. Even when one restricts the cation to the generic formula – $[PR_3R']^+$, the number is still very large. Of course, not all such phosphonium salts are liquid at room temperature, but by a judicious selection of R and R' as well as the appropriate anion, there are many phosphonium salts which are in fact liquid at room temperature and many more which fall within the broad general definition of ionic liquids as salts which are low melting – that is less than 100 °C.

There are several reasons why one might consider a phosphonium ionic liquid. The most important one for those contemplating an industrial process is availability and cost. Phosphonium salts can meet both of these demands – already Cytec is manufacturing phosphonium salts on a multi ton scale and because of the high volumes, costs will be relatively low. For commercial products, chemical inventory registration is also part of the availability equation. While, most of the possible phosphonium ionic

liquids are still not registered, several are already listed on EINECS, TSCA, EEC, AICS, PICCS and DSL.

Ionic liquids, in general, are not going to be outrageously expensive, but they will not be in the same league as toluene, 2-hydroxypropane (IPA) or tetrahydrofuran (THF). This means that to be economically viable, they must be chemically as well as thermally very stable for multiple recycle use. Even 0.5 to 1% decomposition can lead to major losses after 10 to 20 cycles. Not only will there be solvent losses but there will also be contamination of the ionic liquid solvent and/or products with decomposition byproducts.

In this regard, phosphonium salts are much more thermally stable than the corresponding ammonium salts and even have an edge on imidazolium salts. This is very important for processes which operate at temperatures greater than 100 °C. In addition to being slightly less thermally stable, the imidazolium cation contains protons which are not entirely inert. They are some what acidic which can result in carbene formation. Phosphonium salts, on the other hand have no such acidic protons.

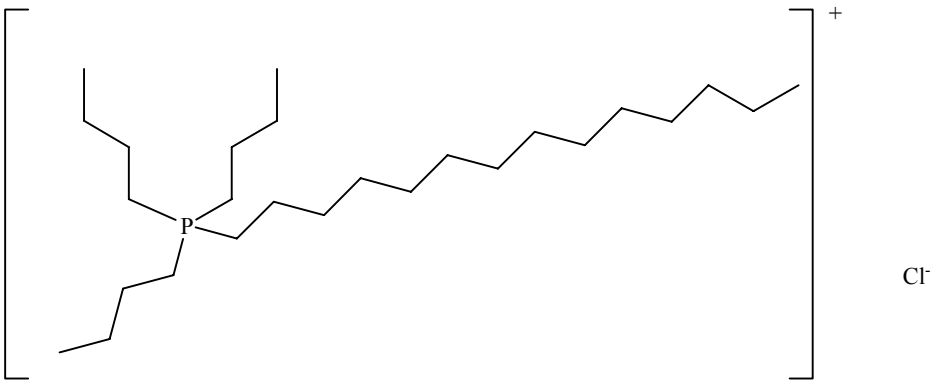
The fact that alkylphosphonium salts are, in general, less dense than water can be beneficial in product work-up steps while decanting aqueous streams which contain inorganic salt byproducts. Imidazolium salts, on the other hand are more dense than water.

Trade Name: …… **CYPHOS IL 167**

Chemical Name: …….. tetradecyl(tributyl)phosphonium chloride

C.A.S. Number: …… [81741-28-8]

Registration: ……. EINECS (279-808-2), AICS, DSL, EEC, PICCS



CYPHOS IL 167 is a low melting solid (Mp 45 °C).

Viscosity:

The viscosity of CYPHOS IL 167 as a function of temperature is presented in Figure 1. The viscosity is moderately low – especially in the 80 to 120 °C temperature range.

As well as temperature effects, the addition of any substrate will have a dramatic effect on viscosity reduction. This demonstrated also in Figure 1 in which the viscosity/temperature relationship is plotted for 10% solutions of hexane, toluene and water.

Miscibility:

It is hydroscopic and very soluble in water (>50 % at 20 °C) as well as a variety of polar organic solvents such as 2-hydroxypropane (IPA) , toluene, methanol, ethanol and tetrahydrofuran (THF). However, due to its high water solubility, it is unlikely that a triphasic system will form on the addition of water and a non polar solvent such as hexane.

Thermal Stability:

Typically standard TGA data is reported to indicate the thermal stability of ionic liquids. As long as the experimental conditions are the same – heating rate, atmosphere over the sample and sample size - such data is only a good measure of relative thermal stability.

Using a 10 °C/min heating rate, the onset of weight loss for CYPHOS IL 167 under an air atmosphere is approximately 310 °C while under an atmosphere of dinitrogen, the "apparent" decomposition temperature increases to approximately 250 °C.

However, a more realistic measure of thermal stability is determined by isothermal TGA studies. Under these conditions, the sample is held at various constant temperatures for an extended period of time, during which any weight loss is observed. Figures 2 and 3 depict weight changes for CYPHOS IL 167 under dinitrogen and air atmospheres respectively.

Based on the data in Figures 2 and 3, it would appear that the true upper limit for thermal stability will be approximately 200 °C under a dinitrogen atmosphere. This decreases slightly to about 180 °C under an air atmosphere. This is consistent with most other phosphonium based ionic liquids. It is expected that for most applications, these upper temperature limits will be more than adequate.

Applications:

While there is little or no application data available for CYPHOS IL 167, there is no reason to suspect that in the molten state, it cannot be used much like CYPHOS IL 101 as a solvent for a variety of organic reactions.

The thermal stability should be identical but with a slightly viscosity and a slightly higher density at any given temperature.

With the addition of $AlCl_3$ or transition metal salts such as $FeCl_3$, $TiCl_3$ or $CuCl_2$, various tetradecyl(tributyl)phosphonium ionic liquids with complex metal halide anions can be formed. Using the proper solvent (usually acetone) the chloride anion can be converted via metathesis to hexafluorophosphate or tetrafluoroborate. (1)

Availability:

Most importantly, CYPHOS IL 167 is listed on all the major chemical inventories and is currently manufactured on a multi ton scale.

Analysis:

CYPHOS IL 167 typically assays > 96% $[PR_3R']^+ Cl^-$ - R = butyl and R' = tetradecyl - with the main impurities being 0.2 to 1.2% HCl and 0.1 to 1.5% $[PR_3H]^+ Cl^-$ – R = butyl. The product will also contain 0.1 to 0.3% water and 0.2 to 0.5% tetradecene isomers. Titration with standardized $AgNO_3$ in a 75% aqueous 2-hydroxypropane (IPA) solvent will yield the total chloride content. This result when combined with a

corresponding NaOH titration will yield the $[PR_3H]^+ Cl^-$, HCl and $[PR_3H]^+ Cl^-$ content. The volatile content (tetradecene isomers) are determined by an internal standard G.C. analysis of an octane extract. The assay can also be determined by a potentiometric titration with standardized dodecylsulfate solution.

^{31}P NMR is generally not suitable for precise analysis. However, the distinctive signal at +33 ppm can be useful for qualitative analysis.

While electrospray mass spectral analysis (ESMS) is generally not available in every laboratory, this also a very useful tool for both quantitative and qualitative analysis.

Figure 1

Viscosity of CYPHOS IL 167 as a Function of Temperature

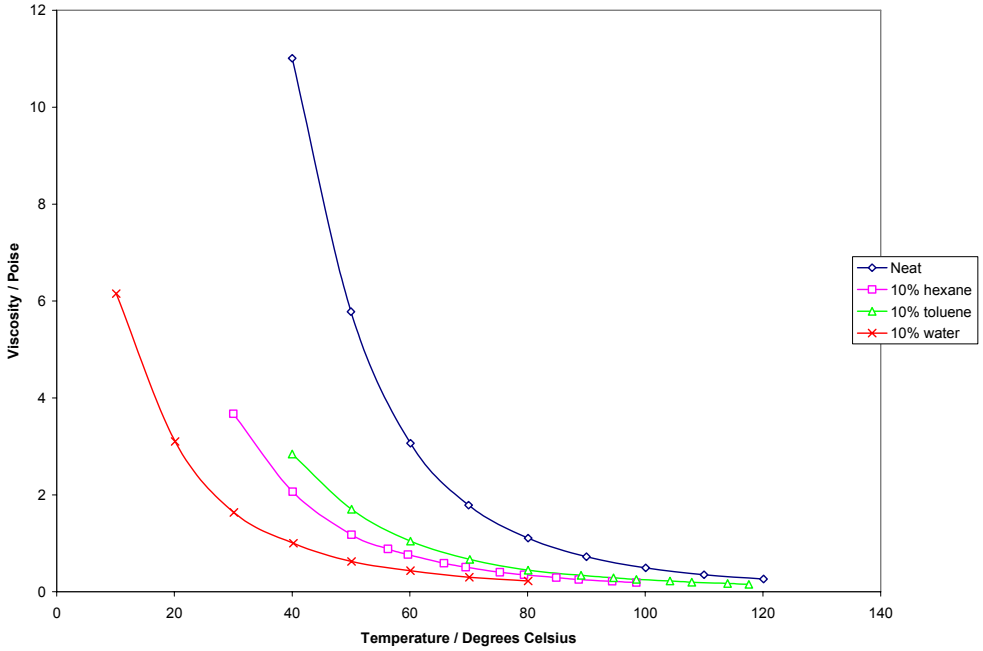


Figure 2:

Isothermal TGA of CYPHOS IL 167 Under a Dinitrogen Atmosphere

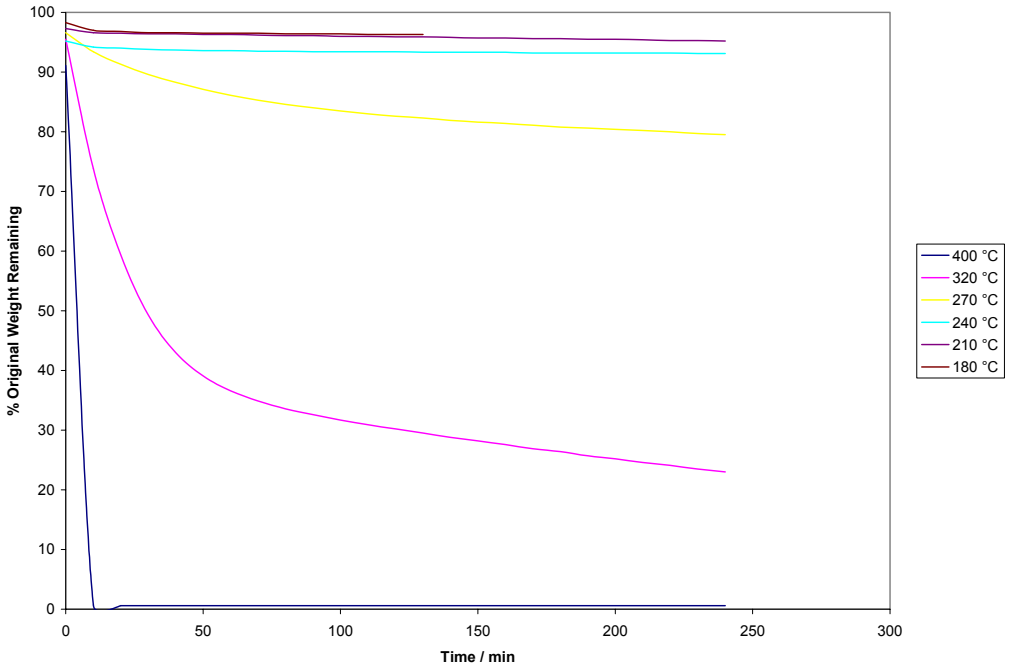
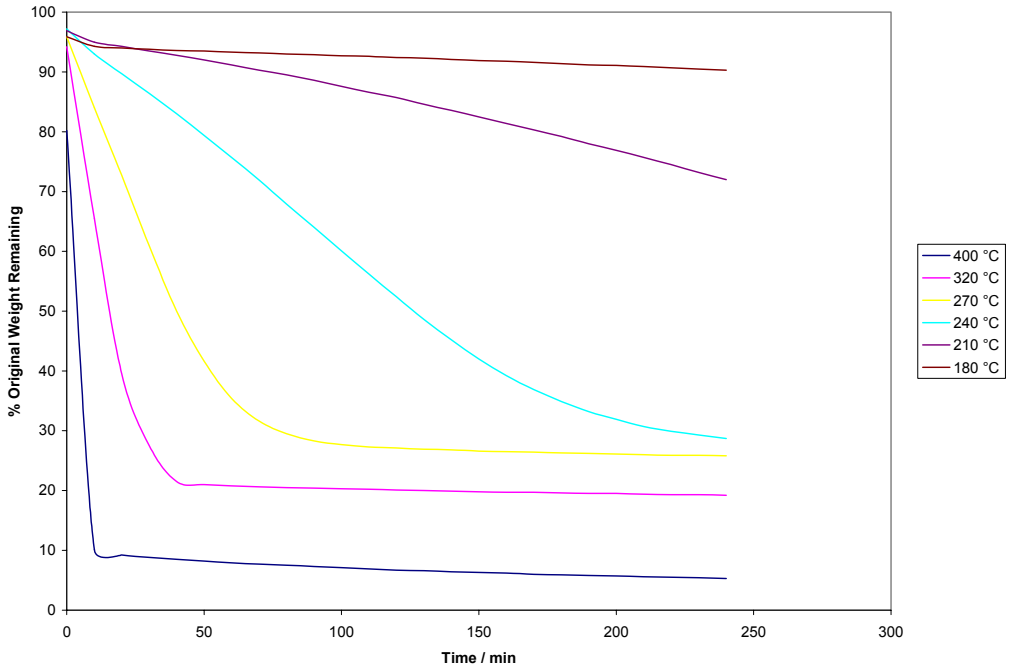


Figure 3:

Isothermal TGA of CYPHOS IL 167 Under an Air Atmosphere



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1a) Fannin, A .A, Jr; King, L. A.; Levisky, J. A.; Wilkes, J. S.; J. Phys. Chem., 1984, **88**, 2610-2614

1b Fannin, A. A. Jr; Floreani, D. A.; King, L. A.; Landers, J. S.; Piersma, B. J.; Stech, D. J.; Vaughn, R. L.; Wilkes, J. S.; and Williams, J. L., J. Phys. Chem. 1984, **88**, 2614-2621

2) "Forward", Professor Ken Seddon, Green Chemistry April, 2002.

3) Green Chemistry April, 2002

4) "Phosphonium Salts"; A Robertson; WO 01/87900 A1

5)"Industrial Preparation of Phosphonium Ionic Liquids"; Christine Bradaric, Andrew Downard, Christine Kennedy, Allan Robertson, Yuehui Zhou; Green Chemistry, 2003, **5**, 143-152

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