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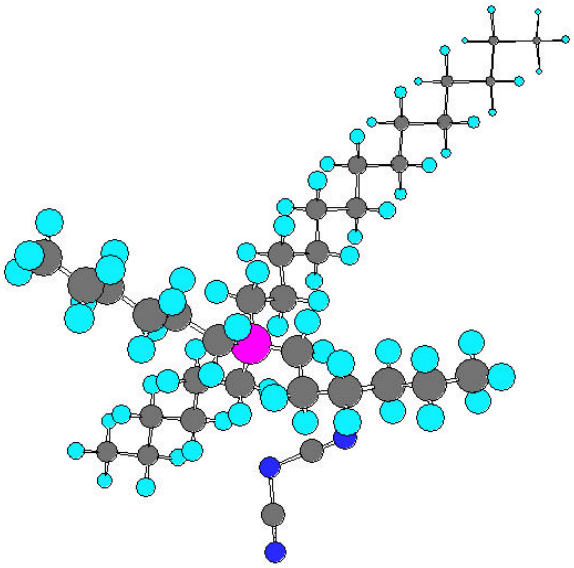
CYPHOS® IL 105

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.

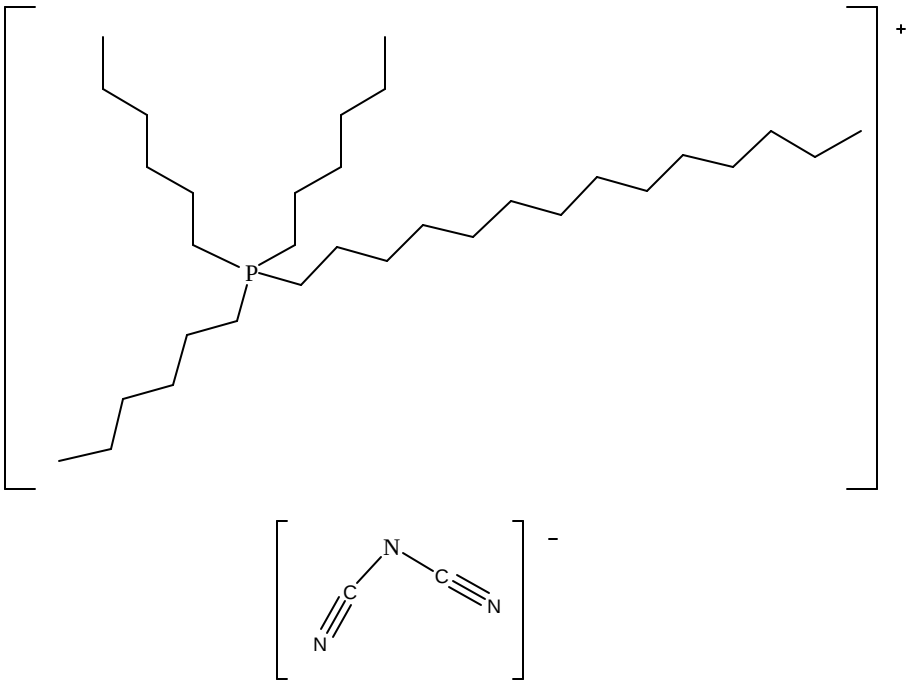
The fact that alkylphosphonium salts are, in general, less dense than water can be beneficial in product work-up steps while decanting aqueous streams which contain inorganic salt byproducts. Imidazolium salts, on the other hand are more dense than water.

Trade Name: **CYPHOS IL 105 phosphonium ionic liquid**

Chemical Name: tetradecyl(trihexyl)phosphonium dicyanamide

C.A.S. Number: None

Registration: None



Miscibility:

CYPHOS IL 105 phosphonium ionic liquid will form two phases with water. When fully saturated, it can dissolve up to 3.1% water. It is miscible with common organic solvents such as those listed in Table 1.

Table 1

CYPHOS IL 105 Miscibility

Diluent	Miscible
water	No
hexane	Yes
toluene	Yes
2-hydroxypropane (IPA)	Yes
diethylether	Yes
tetrahydrofuran	Yes
dichloromethane	Yes

Viscosity:

CYPHOS IL 105 phosphonium ionic liquid is a liquid at room temperature and has a viscosity which is an order of magnitude lower than that of other phosphonium salts. In general, the dicyanamide anion in combination with any onium cation will result in salts with lower viscosities (6). The addition of substrates will have a dramatic influence on the further reduction of the system viscosity. This is simulated in Figure 1 by the addition of hexane. As with all materials, viscosity also decreases exponentially with temperature. Consequently, at typical reaction temperatures of 80 to 100 °C. and in the presence of a reactant and/or reaction product, the viscosity will be very water-like.

This phenomenon is not unusual. In addition to changing the anion and carbon chain length, small amounts of solutes – diluents or otherwise - have a profound effect on the viscosity as well as the density of ionic liquids (5).

Thermal Stability:

Typically standard TGA plots are used to determine relative thermal stability of ionic liquids. Heating rates of 5 to 10 °C per minute either under an inert atmosphere or under oxidative conditions such as air are usually reported. Under these conditions, the onset for weight loss for CYPHOS IL 105 is approximately 390 and 310 °C under dinitrogen and air respectively. (Figure 2). However, in reality, the true temperature at which an ionic liquid is thermally stable is much lower. Figures 3 and 4 are isothermal TGA plots under dinitrogen and air respectively. The respective safe operating temperatures would appear to be 175 and 215 °C.

Applications:

Bio-transformations are often limited to the concentration of either the substrate or products due to toxicity effects on either the enzymes or organisms. For example, 1500 mg/l of phenol is toxic to Pseudomonas putida. However, the bio-degradation can be

carried out in a two phase system such as CYPHOS IL 105/(aqueous phenol), in which the phenol will partition into the IL phase at a concentration which is non-toxic to P. putita. This organism is totally compatible with CYPHOS IL 105 and is thus able to consume the phenol from the aqueous phase as it gradually partitions into the IL phase (9).

Analysis:

An assay procedure for CYPHOS IL 105 is currently under development, however, it will typically assays 97% based on phosphorus ^{31}P NMR. Because CYPHOS IL 105 is derived from the corresponding chloride salt (4) and based on limited production data, the chloride and water content are 0.5 and 0.3% respectively. It is expected that the chloride content will be reduced in the future.

The chloride content can be readily determined by titration with standardized $AgNO_3$ in a 75% 2-hydroxypropane (IPA) water medium. Karl-Fischer titration is adequate to determine residual water.

^{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.

LC/MS is the most universal tool to identify and quantify cations and anions (10).

Toxicity:

Non-halide phosphonium salts containing bulky cations are relatively benign as compared to pyridinium or imidazolium salts (8).Stock et. al. have reported acetyl cholinesterase inhibiter EC_{50} values of >2000 µM for CYPHOS IL 105 as compared to values of 28-30 µM and 13-189 µM for pyridinium and imidazolium salts. The latter and in particular the pyridinium salts are not unlike the known acetyl cholinesterase inhibitor Aldicarb which has an EC_{50} value of 5 µM

References:

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

3) Green Chemistry April, 2002

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8) " Effects of ionic liquids on the acety lcholinesterase – a structure-activity relationship considerstion"; F. Stock, J. Hoffmann, J. Ranke, R. Atormann, B. Ondruschka and B. Jastorff; Green Chemistry, 2004 6(6),286-290

9) "Phosphonium ionic liquids for degradation of phenol in a two-phase partioning bioreactor"; Environmental Biotechnology; 2005, 67, 131-137; M.D. Baumann, A.J. Daugulis and P.G. Jessop

10) "Development of an LC/MS Analytical Procedure for Ionic Liquids with Emphasis on Phosphonium Ionic Liquids"; 1st International Congress on Ionic Liquids, June 19-22, 2005, Salzburg, Austria; T.T. Chang and M.J. Piquette (also posted on www.cytec.com/business/phosphine)

Figure 1

Effect of Solute of CYPHOS IL 105 Viscosity

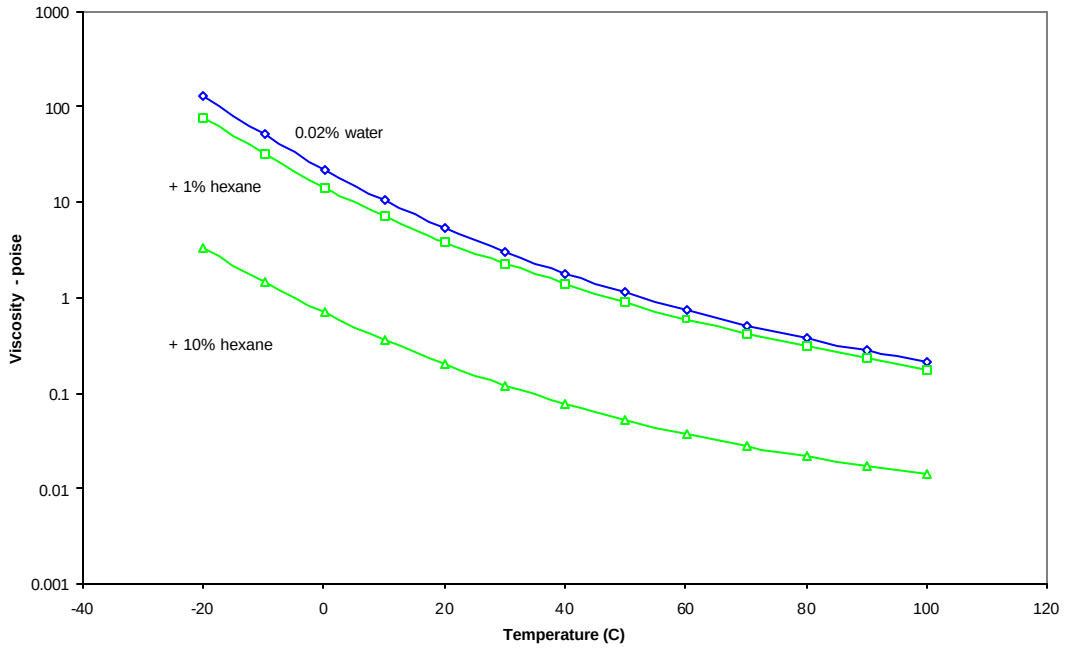


Figure 2

CYPHOS IL 105 – Standard TGA Plots under Air and N_2

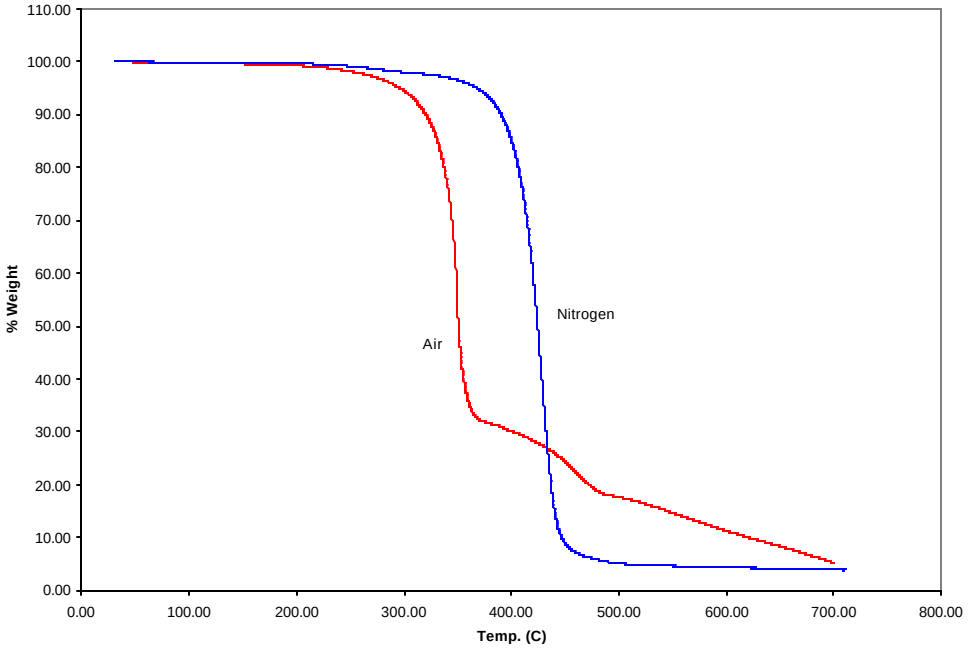


Figure 3

CYPHOS IL 105 – Isothermal TGA Plots under Air

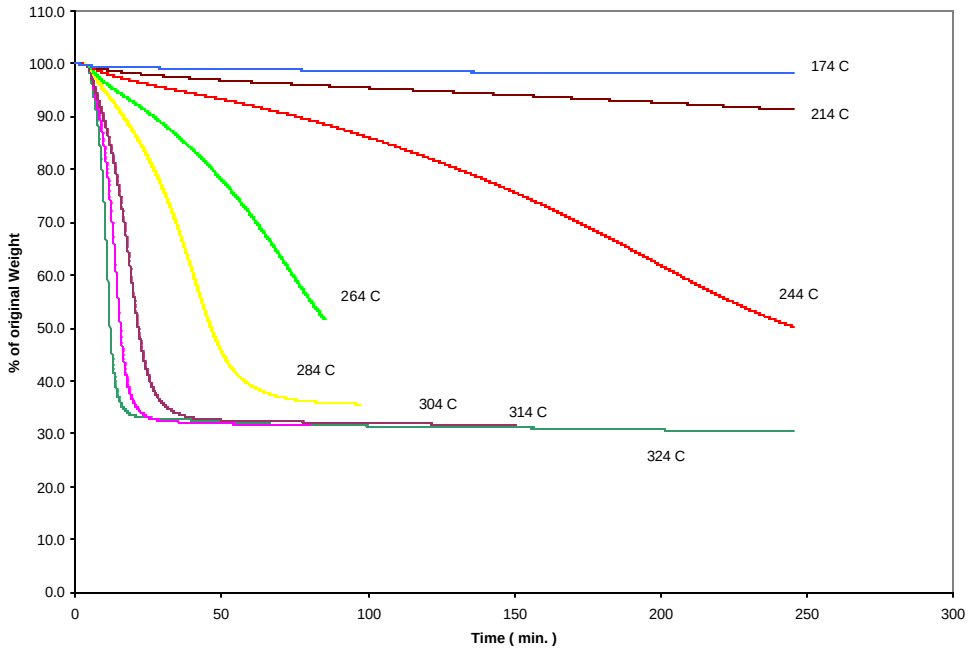
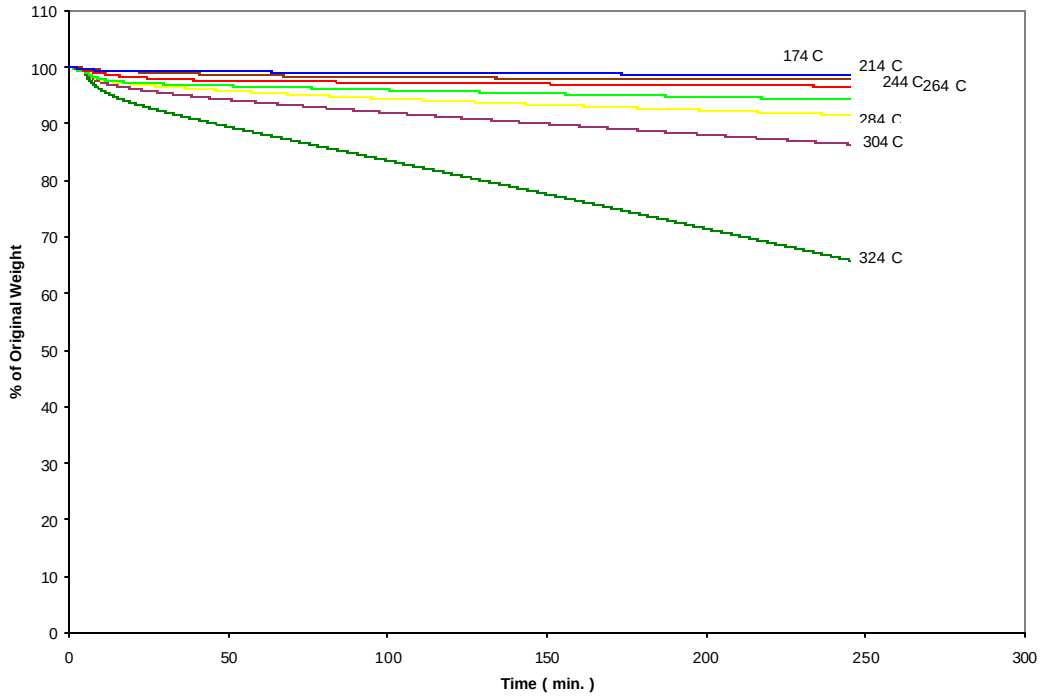


Figure 4

CYPHOS IL 105 – Isothermal TGAs under N_2



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