

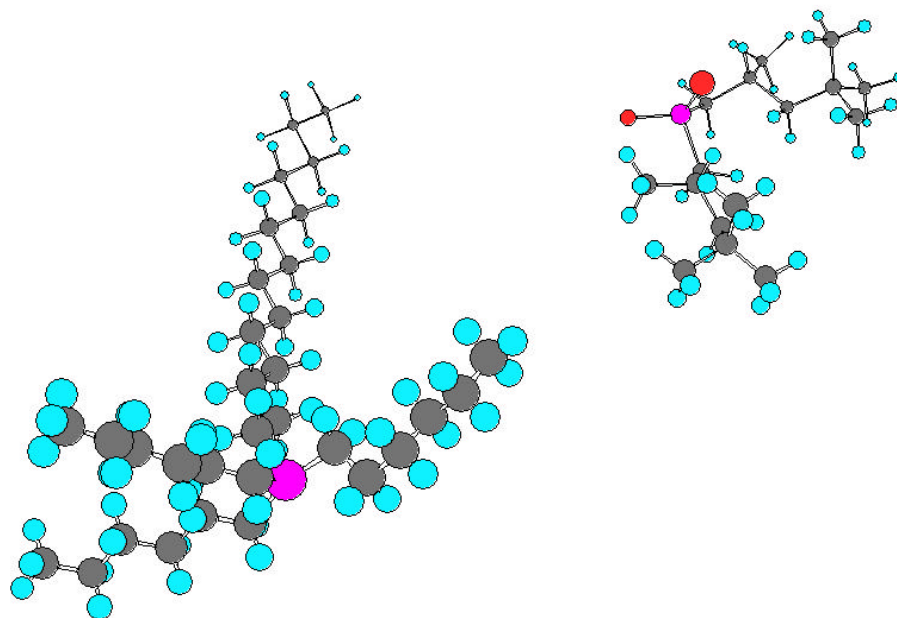
CYTEC

Technology ahead of its time™

www.cytec.com

CYPHOS® IL 104

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 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 somewhat acidic which can result in carbene formation. Phosphonium salts, on the other hand have no such acidic protons.

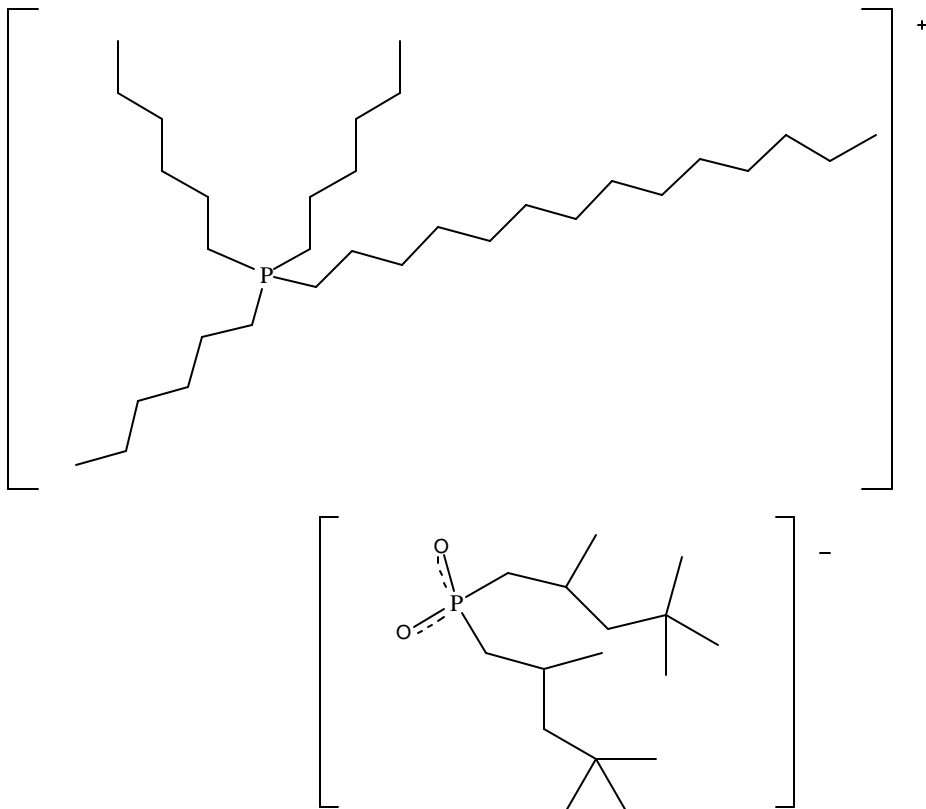
The fact that alkylphosphonium salts are, in general, less dense than water can be beneficial in product work-up steps while decanting aqueous streams which contain inorganic salt byproducts. Imidazolium salts, on the other hand are more dense than water.

Trade Name: **CYPHOS IL 104 phosphonium ionic liquid**

Chemical Name: trihexyl(tetradecyl)phosphonium bis 2,4,4-trimethylpentylphosphinate

C.A.S. Number: [465527-58-6]

Registration: None



Density and Miscibility:

CYPHOS IL 104 phosphonium liquid is a slightly viscous room temperature ionic liquid. It is less dense than water (Figure 1), is colorless to pale yellow and is immiscible with water although it is sparingly soluble in water and can dissolve up to 20.6% water. When dry, it is totally miscible with a wide range of organic solvents such as indicated in Table 1

Table 1

CYPHOS IL 104 Miscibility

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

Viscosity:

The only negative comment concerning most long alkyl chain phosphonium based ionic liquids is that they are “viscous”. While they are somewhat more viscous than typical imidazolium salts, once in service – that is, when organic substrates are added, the viscosity decreases by an order of magnitude. This is illustrated in Figure 2 in which the addition of hexane simulates a reagent or product. Additionally, the viscosity drops off exponentially with temperature. At a typical reaction of 80 to 100 °C and with the addition of 10% of a substrate, the entire system becomes very water-like.

This phenomena 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 (9).

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 104** is approximately 340 and 290 °C under dinitrogen and air respectively. (Figure 3). However, in reality, the true temperature at which an ionic liquid is thermally stable is much lower. Isothermal TGA plots for **CYPHOS IL 104** under an air atmosphere are reported in Figure 4. Based on this data, the true temperature at which the ionic liquid will be thermally stable will be approximately 150 °C. Under an inert atmosphere such as dinitrogen, the stability limit is expected to be 10 to 30 °C higher.

Applications:

CYPHOS IL 104 has been reported as a useful ionic liquid for Heck coupling reactions and for the carbonylation of iodobenzene to ethylbenzoate. (6).

Additionally, since CYANEX® 272 solvent extraction reagent (bis 2,4,4-trimethylpentylphosphinic acid) is the world standard for selective extraction of cobalt from cobalt/nickel solutions (5,7), CYPHOS IL 104 will have potential useful applications in the area of metals separation.

Analysis:

An assay procedure for CYPHOS IL 104 is currently under development. However it is expected to assay > 95% with the main impurity being tris- 2,4,4-trimethylpentyl phosphine oxide. The product will likely also contain 0.2 to 0.5% water and since it is prepared from a metathesis route from the corresponding chloride salt, it will contain up to 0.1% chloride ion.

The chloride content can be readily determined by titration with standardized AgNO₃ in a 75% 2-hydroxypropane (IPA) water medium. Karl-Fischer titration is adequate to determine residual water.

³¹P 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.

Toxicity:

Non-halide phosphonium salts containing bulky cations are relatively benign as compared to pyridinium or imidazolium salts (10). Stock et. al. have reported acetyl cholinesterase inhibitor EC₅₀ values of >2000 μM for CYPHOS IL 104 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 EC₅₀ value of 5 μM

References:

- 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) "Industrial Preparation of Phosphonium Ionic Liquids"; Christine Bradaric, Andrew Downard, Christine Kennedy, Allan Robertson, Yuehui Zhou; *Green Chemistry*, 2003, **5**, 143-152
- 5) "Preparation of Phosphonium Phosphinate Compounds for use as Polar solvents"; A. Robertson, K. Seddon; WO 2003020843
- 6) Private communication from Alwar Ramani – The Queen's University, Belfast.
- 7) "Selective Extraction of Cobalt(II) from Aqueous Solutions with Phosphinic Acid Extractants"; William A Rickelton; Allan J. Robertson; David R. Burley; US4353883
- 8) "Di-2,4,4-trimethylphenylphosphinic Acid and its Preparation"; A. Robertson; US4374780
- 9) K.R. Seddon, A. Stark, M.J. Torres; *Pure Appl. Chem.* , 2000, **72**, 2275
- 10) " Effects of ionic liquids on the acetylcholinesterase – a structure-activity relationship consideration"; F. Stock, J. Hoffmann, J. Ranke, R. Atormann, B. Ondruschka and B. Jastorff; *Green Chemistry*, 2004 **6**(6),286-290

Figure 1

CYPHOS IL 104 – Density vs. Temperature

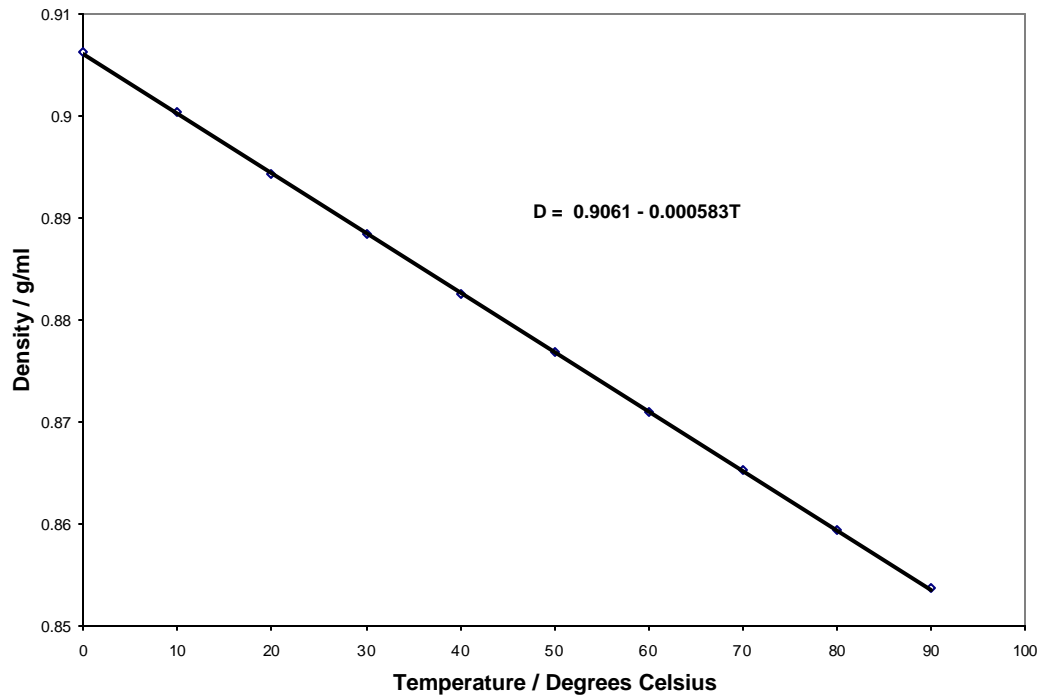


Figure 2

CYPHOS IL 104 – Effect of Solute on Viscosity

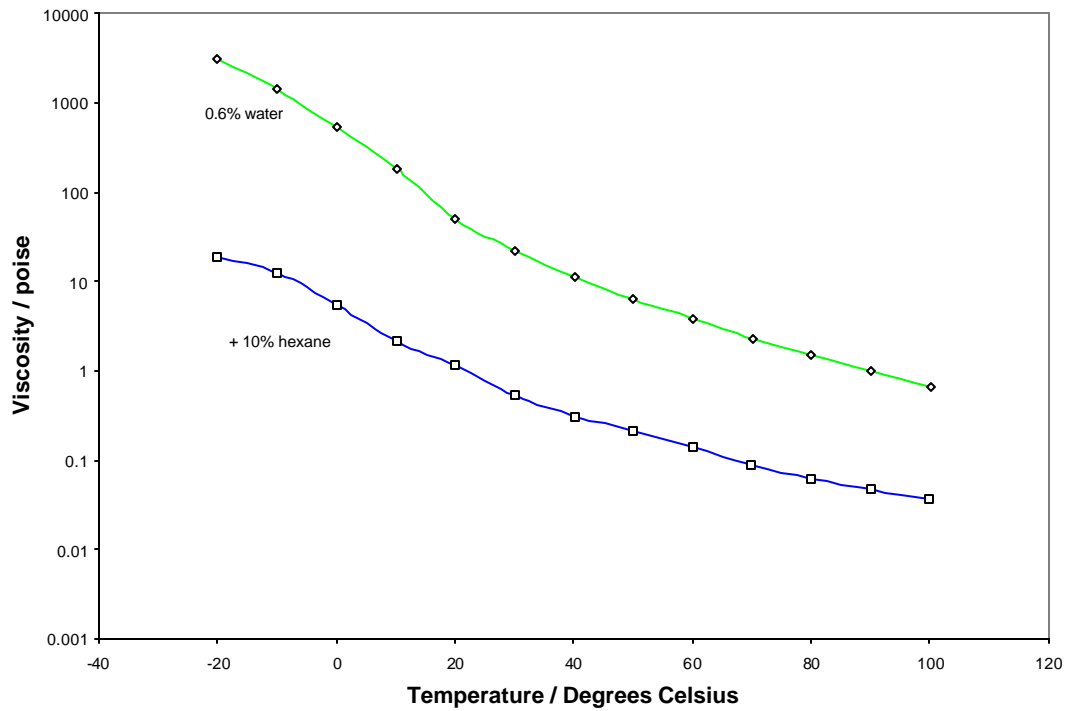


Figure 3

CYPHOS IL 104 – Standard TGA Plots under Air and N₂

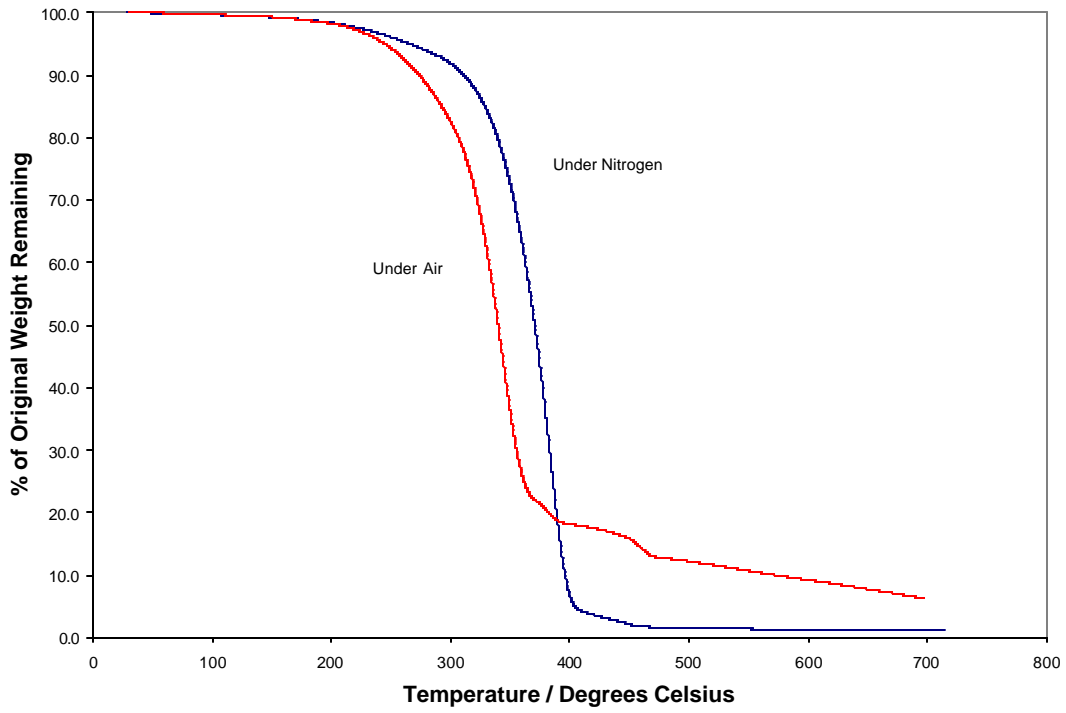
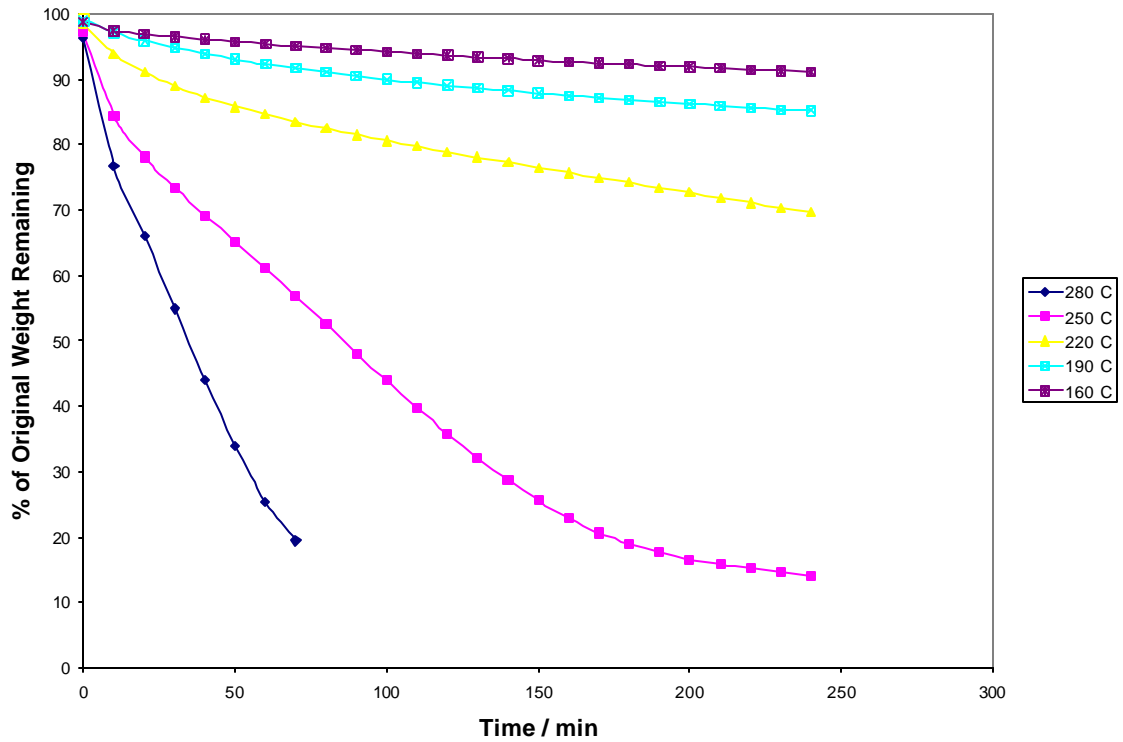


Figure 4

CYPHOS IL 104 – Isothermal TGA Plots under Air



Important Notice: The information and statements in this data sheet are believed to be reliable but are not to be construed as a warranty or representation for which we assume legal responsibility or as an assumption of a duty on our part. Users should undertake sufficient verification and testing to determine the suitability for their own particular purpose of and information or products or vendors referred to within. **NO WARRANTY OF FITNESS FOR A PARTICULAR PURPOSE IS MADE.** Nothing in this data sheet is to be taken as permission, inducement or recommendation to practice any patented invention without a license.

Trademark Notice: The ® indicates a Registered Trademark in the United States and the TM or * indicates a Trademark in the United States. The mark may also be registered, the subject of an application for registration or a trademark in other countries.

Last updated: September 2, 2005