Physical Property Determination of Perfluorinated Surfactants

by

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Abstract

Fluorinated surfactants, perfluorocarboxylic acids in particular, have become increasingly popular in numerous industrial and domestic applications although little is known about their environmental fate. The purpose of the study was to measure the physical properties (vapour pressure, vp, and Henry's Law constant, K_H) of the protonated form of perfluorocarboxylic acids. In order to supplement the determination of these physical properties, a series of simple and novel methods for the separation and detection of perfluorocarboxylates and perfluoroalkyl sulfonates by ion chromatography (IC) were developed. Mixtures of perfluorocarboxylates ranging in chain length from perfluoropropionate to perfluorodecanoate, as well as perfluorohexyl sulfonate and perfluorooctyl sulfonate were separated using either an isocratic anion exchange separation method or a gradient reverse phase method. It was found that separation and method application (anion exchange vs. reverse phase) was dependent on the length of the perfluoro portion of these compounds. Anion exchange separation was appropriate for shorter chain compounds while reverse phase was better for longer chained perfluoro compounds. Once developed, the K_H was determined using an acidified water method while vp was determined using the boiling point method. Results from the physical property determination experiments show the unique attributes of the carbon – fluorine bond, and the perfluoro chain. Vapour pressure results showed little deviation with increasing perfluoro chain length while Henry's Law constant results showed an inflection in the volatility of perfluorocarboxylic acids, with a maximum value at perfluoropentanoic acid.

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Table of Contents

List of Tables

Chapter Two

Chapter Three

List of Figures

Chapter Two

Chapter Three

List of Appendices

Chapter 1

Introduction

1.1 Introduction

Recently, interest in the environmental measurement of anionic perfluorinated surfactants has increase. Two particular classes of anionic perfluorinated surfactants, the perfluoroalkyl sulfonates and perfluorocarboxylates, have received increase attention. This has primarily been based upon on the decision by the 3M Co. to discontinue the use of perfluorinated surfactants in its ScotchGard formulation[1]. According to 3M Co., this was a preemptive decision so that production and eventual release in the environment would not reach toxicologically significant levels. However, since the tendency of these chemicals to partition in the environment is unknown, toxicologically significant levels may have already been reached in certain environments. Thus, there is a clear need to determine the partitioning of these compounds in the various compartments in the environment.

1.2 Applications and Synthesis

The use of perfluorinated surfactants in both industrial and domestic applications is immense. This includes adhesives, cleaners, coatings, as a surfactant in electroplating and glass etching processes, fire – fighting foams, greases and lubricants, oil and solvent repellents in paper products, and fabric protection formulations[2]. Although the direct application of PFOS is common in fire - fighting foams and coating additives, according to 3M Co., the perfluorooctyl sulfonyl flouride (PFOS - F) is the more commonly sold form of perfluorinated surfactants. In the year 2000, production of PFOS - F for commercial sales was estimated to be at 3.6 million kilograms, while PFOS was approximately 23000 kilograms over that same period[3]. The preference of PFOS - F over its hydrolysis product, PFOS, is likely to be due to the ease of further reaction of

PFOS - F to form the intermediates N – methyl or N – ethyl perfluorooctane sulfonamide, which is a common precursor for commercial products. The synthesis of perfluorinated compounds, or compounds containing a perfluorinated portion is primarily through two processes, telomerization and electrochemical fluorination.

Electrochemical fluorination involves the application of a current to a mixture of the organic compound to be fluorinated, and hydrogen fluoride. Although this process has been well studied and is employed in industry, the exact mechanism of fluorination is still not fully understood. It is suspected that the compound follows a free radical mechanism as shown[2],

$$H^+ + F^- \xrightarrow[Ni]{\text{voltage}} F\bullet + e^- + H^+$$

$$F\bullet + RH \longrightarrow R\bullet + HF$$

$$F\bullet + R\bullet \longrightarrow RF$$

In order to overcome the large activation energy barrier of this oxidation reaction, an inorganic or organic species is commonly added to increase the conductivity of the solution so that a larger voltage can be applied. The electrochemical fluorination process can be applied to alkyl acid fluoride to produce the perfluorocarboxylic acid fluoride,

$$C_nH_{2n+1}COF + (2n+2)HF \longrightarrow C_nF_{2n+1}COF + \text{by - products}$$

Depending on these conditions, low to moderate yields are generally obtained of a mixture of branched isomers[4]. As mentioned, the acid fluorides can than be converted into their corresponding acid, salt, or a number of other surfactant derivatives based upon the individual companies formula. The formation of the alkyl radical results in the

production of a homologous series of both odd and even number perfluorocarbons[5], demonstrating the non – selective nature of this synthetic process.

In contrast to the electrochemical technique, telomerization is the process by which a compound, known as a taxogen, is catalyzed to induce a radical chain reaction with a perfluoro olefin, the telogen. Taxogens commonly used in this process are perfluoroalkyl iodide compounds due to the sensitivity of the carbon – iodide bond to photo induced hetero cleavage, or photo induced catalysis. For example, in the mechanism below, pentafluoroethyl iodide behaves as the taxogen, and reacts with tetrafluoroethylene, the telogen, to produce a mixture of only even numbered carbon perfluoroalkyl iodide compounds of various chain lengths[6],

$$CF_3CF_2I \xrightarrow{h\nu} CF_3CF_2\bullet + I\bullet$$

$$CF_2{=}CF_2 + CF_3CF_2\bullet \longrightarrow CF_3CF_2CF_2CF_2\bullet$$

$$CF_3CF_2CF_2CF_2\bullet + CF_2{=}CF_2 \longrightarrow CF_3CF_2CF_2CF_2CF_2CF_2\bullet$$

$$CF_3CF_2[CF_2CF_2]_n\bullet + CF_3CF_2I \longrightarrow CF_3CF_2[CF_2CF_2]_nI + CF_3CF_2\bullet$$

The resulting product, $CF_3CF_2[CF_2CF_2]_nI$, is than reacted with ethylene in the presence of a free radical catalyst to form the perfluoroalkylethyl iodide, which can then undergo further reaction to produce both the partially perfluorinated, as well as the perfluorinated surfactant product. Since this process only produces even numbered perfluorocarbon compounds, there is a distinction between the products produced via telomerization and electrochemical fluorination.

1.3 Toxicology

The toxicity of perfluorocarboxylates and perfluoroalkyl sulfonates has been well documented. Laboratory rat toxicity studies suggest that perfluorocarboxylates and perfluoroalkyl sulfonates behave as peroxisome proliferators[7-17]. That is, they induce enzymatic activity in the liver. One enzyme group that is particular susceptible to proliferation is cytochrome P450, a group of enzymes found primarily in the endoplasmic reticulum of liver tissue, and amongst their many functions, is the oxidation of various xenobiotics. This metabolic process is the means by which xenbiotic compounds are modified *in vivo*, which either increases or decreases its toxicity. Since cytochrome P450 exists as multiple isozymes with different substrate specificities, induction of a particular group may result in tissue specific toxicity; such is the case with perfluorooctanoate (PFOA). According to Biegel *et al.* [14], PFOA induced cytochrome P450 XIX, aromatase, which is responsible for the conversion of testosterone to estradiol. The increase in estradiol induced an increase in Leydig tumor cell production in the rats tested. It is suspected this increased Leydig cell production was associated with tumor growth by stimulating the clonal expansion of spontaneously initiated cells. Lipid metabolism has also been shown to be affected by PFOA[7,9,11-13,15]. Haughom and Spydevold[15] suggested that the observed hypolipemic effect, the increase in hepatic lipid metabolism and subsequent decrease in serum lipid levels, is the result of reduced liver activity of hydroxymethyl glutaric acid – CoA reductase, and acyl – CoA cholesterol acyltransferase in conjunction with the increase metabolism of fatty acids. Although, this effect is rarely toxic, pronounced weight loss in laboratory mice has been documented[15].

Similar findings have been published for perfluorobutanoate (PFBA) and perfluorodecanoate (PFDA) at inducing peroxisome proliferation[8,10,17]. It would appear that the carboxylate functionality is essential for these effects, as the perfluoroalkyl chain showed none of the observed effects of the perfluorocarboxylates[17]. The findings suggest that any chemical consisting of a negatively charged functional group and a metabolically inert hydrophobic tail would behave in a similar manner in causing peroxisome proliferation[17]. While the underlying patterns of toxicity for PFBA, PFDA, and PFOA are similar, the onset and duration of toxicity are dependent on the perfluoro chain length. For example, PFOA causes an acute lethality but transient toxicity, while PFDA induces a more delayed lethality and has a persistent toxicity effect[10].

PFOS appears to act under the same mechanism in inducing peroxisome proliferation as the perfluorocarboxylates. This suggests that the effect is highly dependent on the presence of a negatively charged functional group, as opposed to carboxylate moiety alone, attached to a metabolically inert hydrophobic moiety[10]. The potency of PFOS is comparable to that of PFOA, which is surprising as this suggests that PFOS – acyl CoA and PFOA – acyl CoA are both mutually formed from acyl CoA synthetase. Such non - selectivity of the synthetase is surprising as the carboxylate and sulfonate moiety are chemically different. This challenges the traditional hypothesis that the first step is the formation of the thioester between the proliferator and coenzyme A[16]. Nonetheless, the ability of PFOS to act as a peroxisome proliferator has been supported by other researchers which demonstrated a decline in serum triacylglycerols and cholesterol levels, both of which are associated with hypolipemic effects[15-17]. Comparable levels of peroxisome proliferation was observed for PFOS, and PFOA with

dosages of 0.05% w/w to male mice over a period of 5 days[16]. In contrast, PFDA was found to be far more potent, as a single dosage of 50 mg/kg to rats resulted in significant increases in liver enzyme activity.

1.4 Degradation and Persistence in the Environment

The stability of anionic perfluorinated surfactants to many harsh chemical environments is at least partially responsible for its attractiveness to many industrial applications. Indeed, the stability was demonstrated when no degradation was observed for PFOS after digestion in a HNO_3/H_2O_2 solution for 48 hours (unpublished data). Since, no degradation occurred under these extreme oxidative conditions, one would postulate that these compounds do not oxidatively degrade in the natural environment. Biodegradation studies of perfluorooctyl sulfonate resulted in similar conclusions as no degradation of PFOS was observed under both anaerobic and aerobic (reductive and oxidative) environments[18,19]. Visscher *et al.*[20] first demonstrated the reductive and oxidative degradation of TFA, the shortest homologue of the perfluorocarboxylates, in soil. However, the study has yet to be repeated. Recently, Kim *et al.*[21] demonstrated the reductive degradation of TFA by an engineered microbial community over an extended period. The direct applicability of this system to longer chained perfluorocarboxylates is unknown; however, since this suite of compounds are similar in bond strength, it is suspected that the longer chained homologues would degrade in the same fashion. It is important to note that although biodegradation of TFA was observed in the laboratory, the kinetics of such degradation in nature is probably insignificant as the presence and

growth of this microbial composition is small. Therefore, there does not appear to be a sink for these anionic perfluorinated surfactants in the environment.

1.5 Environmental Measurements

In spite of the fact that there is a large variety of use of perfluorooctyl sulfonate and the perfluorocarboxylates, in combination with their suspected persistence in the environment, the amount published data pertaining to environmental measurements is surprisingly limited. Two of these studies measured the presence of these compounds in human plasma from the 3M Co. plant workers[22-25]. The first of which was originally published in the 1970s when Guy et al.[22], measured PFOA in mg/L concentration levels. Olsen et al.[25], later measured PFOS also in the mg/L level, in the workers of the same plant as well as the workers of their fluorochemical production plant in Belgium. Recently, Hansen et al.[26], demonstrated the utility of negative ion electrospray liquid chromatography tandem mass spectrometry by measuring both PFOS and PFOA in 65 non - plant worker blood samples. Not surprisingly, the concentrations of PFOS in these general population sera samples were far less, from 6.7 to 81.5 ng/mL[26], than those of the plant workers, from 0.10 to 9.93 μg/mL[25]. In terms of the physical environment, anionic perfluorinated surfactants have been shown to be present at sites that have been contaminated by aqueous film forming foams[4,27,28]; perfluorocarboxylates and perfluoroalkyl sulfonates of varying chain lengths were measured in ground and surface water. Recently, Geisy[29,30] has measured the accumulation of PFOS in wildlife. Concentrations of PFOS from 1 – 2570 ng/mL where measured in the liver and plasma of fish, birds, and aquatic mammals throughout the world[29]. The study suggested that PFOS

is not only globally distributed, but also bioaccumulating and persisting within food chains.

1.6 Purpose

The purpose of this research was to determine the physical properties of perfluorocarboxylic acids. It is hoped that by measuring the physical properties of the perfluorocarboxylic acids, the mechanism of distribution and predictions of the environmental fate of these compounds can be made.

In chapter 2, a rapid method for detection and separation using both reverse phase and anion exchange ion chromatography with conductivity detection is described. This section details the importance of properly selecting the set of columns based upon the chain length of both the perfluorocarboxylates and perfluoroalkyl sulfonates. Because development of these methods, in part, provides the methodologies for physical property determination, it was necessary to complete this work first.

In chapter 3, the vapour pressure and Henry's Law constants for a range of perfluorocarboxylic acids (trifluoroacetic acid to perfluorooctanoic acid) were determined. The selection of the methods for physical property determination was critical for these classes of compounds. General trends observed in both the vapour pressure and Henry's Law constant measurements will be described.

The final chapter ties the results from the previous two chapters by indicating the significance of the findings to the distribution of the compound in the environment. Potential avenues for future work are presented, with importance placed on further

physical properties determinations. Included in the future works section is an introduction to a separate suite of non ionic perfluorinated surfactants, focusing primarily on their potential role in the environmental distribution of these anionic perfluorinated surfactants.

1.7 References

[1] Renner, R. *Environ. Sci. Technol.*, **2000**, 34, 371A.

[2] Kissa, E. In *Fluorinated Surfactants;* Marcel Dekker, Inc., 1994.

[3] 3M Co. SIDS Initial Assessment Report Perfluorooctane Sulfonic Acid and Its Salts, **2000**, St. Paul, MN.

[4] Moody, C.A., Kwan, W.C., Martin, J.W., Muir, D.C.G., Mabury, S.A. Accepted for publication *Anal. Chem.*

[5] Moody, C.A., Field, J.A. *Environ. Sci. Technol.*, **2000**, 34, 3864 – 3870.

[6] Haszeldine, R. N. *J. Chem. Soc.*, 1953,

[7] Ikeda, T., Aiba, K., Fukuda, K., Tanaka, M. *J. Biochem.*, **1985**, 98, 475 – 482.

[8] Vandel Heuvel, J.P. *Gen Pharmac.*, **1996**, 27, 1123 – 1129.

[9] Intrasuksri, U., Rangwala, S.M., O'Brien, M., Noonan, D. J., Feller, D. R. *Gen. Pharmac.*, **1998**, 31, 187 – 197.

[10] Reo, N.V, Narayanan, L., Kling, K.B., Adinehzadeh, M. *Toxicol. Lett.*, **1996**, 86, 1 – 11.

[11] Pastoor, T.P., Lee, K.P., Porri, M.A., Gillies, P.J. *Exp. Mol. Pathol.*, **1987**, 47, 98 - 109.

[12] Kawashima, Y., Uy-Yu, N., Kozuka, H. *J. Biochem.*, **1989**, 261, 595-600.

[13] Uy-Yu, N., Kawashima, Y., Kozuka, H. *Biochem. Pharmacol.*, **1990**, 39, 1492 – 1495.

[14] Biegel, L.B., Liu, R.C.M., Hurtt, M.E., Cook, J.C. *Toxicol. and Appl. Pharmacol.*, **1995**, 134, 18 – 25.

[15] Haughom, B., Spydevold, O. *Biochim. et Biophys. Acta.*, **1992**, 1128, 65 – 72.

[16] Sohlenius, A.K., Eriksson, A.M., Hogstrom, C., Kimland, M., DePierre, J.W. *Pharmac. & Toxicol.*, **1993**, 72, 90 - 93.

[17] Ikeda, T., Fukuda, K., Mori, I., Enomoto, M., Komai, T., Suga, T., Induction of Cytochrome P – 450 and Peroxisome Proliferation in Rat Liver by Perfluorinated Octane Sulphonic Acid (PFOS). In Fahimi, H.D., Sies, H. Peroxisomes In Biology and Medicine; Springer – Verlag Berlin Heidelberg, 1987.

[18] Remde, A., Debus, R. *Chemosphere*, **1996**, 32, 1563 – 1574.

[19] Key, B.D., Howell, R.D., Criddle, C.S. *Environ. Sci. Technol.*, **1998**, 32, 2283 – 2287.

[20] Visscher, P.T., Culbertson, C.W., Oremland, R.S. *Nature*, **1994**, 369, 729 – 731.

[21] Kim, B.R., Suidan, M.T., Wallington, T.J., Du. X. *Environ. Eng. Sci.*, **2000**, 17, 337 – 342.

[22] Guy, W.S., Taves, D.R., Brey, W.S. *Amer. Chem. Soc.*, **1976**, 475, 117 – 134.

[23] Belisle, J., Hagen, D.F. *Anal. Biochem.*, **1978**, 87, 545 – 555.

[24] Belisle, J., Hagen, D.F. *Anal. Biochem.*, **1980**, 101, 369 – 376.

[25] Olsen, G.W., Burris, J.M., Mandel, J.H., Zobel, L.R. *JOEM*, **1999**, 41, 799 – 806.

[26] Hansen, K.J., Clemen, L.A., Ellefson, M.E., Johnson, H.O. *Environ. Sci. Technol.* **2001**, 35, 766 – 770.

[27] Moody, C.A., Field, J.A. *Environ. Sci. Technol.*, **1999**, 33, 2800 - 2806.

[28] Moody, C.A., Hebert, G.N., Strauss, S.H., Field, J.A. Submitted for publication n *Environ. Sci. Technol.*

[29] Geisy, J., Kannan, K. *Environ. Sci. Technol.* **2001**, 35, 1339-1342.

[30] Kannan, K., Koistinen, J., Beckmen, K., Evans, T., Gorzelany, J., Hansen, K., Jones, P., Helle, E., Nyman, M., Giesy, J. *Environ. Sci. Technol.* **2001**, 35, 1593 – 1598.

Chapter 2

Comparison of Anion Exchange and Reverse Phase Ion Chromatography for the Determination of Perfluorinated Carboxylate and Sulfonate Surfactants

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2.1 Abstract

A series of simple and novel methods for the separation and detection of perfluorocarboxylates and perfluoroalkyl sulfonates by ion chromatography (IC) is described. Mixtures of perfluorocarboxylates ranging in chain length from perfluoropropionate to perfluorodecanoate, as well as perfluorohexyl sulfonate and perfluorooctyl sulfonate were separated using either an isocratic anion exchange (quaternary ammonium column) separation method or a gradient reverse phase (divinyl benzene column) method. Separation and method application (anion exchange vs. reverse phase) were found to be dependent on the length of the perfluoro portion of these compounds. Anion exchange separation was appropriate for shorter chain compounds while reverse phase was better for longer chained perfluoro homologues. In comparing two ion chromatography instruments, systems employing a gradient in combination with higher hydroxide concentration showed improved chromatography and faster run times.

2.2 Introduction

The wide spread use of anionic perfluorinated surfactants, in combination with their suspected persistence in the environment has lead to increased interest in their environmental measurement. One particular group of anionic perfluorinated surfactants of growing interest are the perfluorocarboxylates and the perfluorosulfonates. These compounds are components in many industrial and domestic applications including lubricants, aqueous fire fighting foams (AFFF), domestic surfactant mixtures (Scotchgard™), and as an emulsifying reagent for teflon synthesis[1].

Despite the wide use of these perfluorinated carboxylates and sulfonates, little in the way of analytical and chromatographic techniques for their detection has been

developed, due in part to the lack of suitable detectors for these compounds. Many researchers have avoided this problem by derivatizing the perfluorocarboxylate into either a fluorescent species[2] or the methyl ester for gas chromatography analysis[3,4], while direct measurement has been limited to the use of ^{19}F NMR[5]. Derivatization to the methyl ester is time consuming and has only been applied to perfluorocarboxylates. ^{19}F NMR, on the other hand, has limitations as spectral overlap of the terminal CF_3 group in mixed solution of perfluorinated surfactants hinders separation and detection of individual compounds. Recently Hansen et al.[6], used HPLC – ESMSMS for the determination of perfluorocarboxylates and perfluoroalkyl sulfonates in biological matrixes. Drawbacks of the system include its high cost, as well as extended periods of maintenance and equilibration time. The mass injected into the instrument must be in the picogram to nanogram range to ensure linearity in response as well as to minimize residual effects due to the low detection limit of the instrument. This requires sample preparation for contaminated solutions. Direct measurement of perfluorocarboxylates and sulfonates through ion chromatography with conductivity detection can overcome problems associated with these other techniques.

Ion chromatography has been previously used for the determination of small fluorinated acids in aqueous samples[7-9], however, these methods have limited applicability as strong anion exchange prevents elution of longer chained perfluorocarboxylic compounds and perfluoroalkyl sulfonates. Reverse phase chromatography, although common in application with spectroscopic detectors, has found limited use in the field of ion chromatography. The majority of its application has been focused primarily in the field of measuring long chained hydrocarbon

surfactants[10-12], while its application to perfluoro compounds has been limited[13]. In the later study, Laikhtman et al. (1998) focused on the identification and detection of industrial mixtures of perfluorinated surfactants in an acid etching bath. The chromatography in this method was poor, and no effort was made to separate the mixtures of perfluorinated compounds present as impurities, or between the two industrial perfluorinated surfactant mixtures studied.

Difficulties in the separation of perfluorocarboxylates and perfluoroalkyl sulfonate surfactants by ion chromatography are attributed to the unique properties of the perfluoro chain, and the carbon fluorine bond. The carbon fluorine bonds are traditionally characterized by a high degree of overlap between the bonding orbitals, high electronegativity of fluorine, and the presence of 3 lone pairs of electrons on the fluorine nucleus[1]. Perfluorination greatly exaggerates these effects resulting in a dual phobic characteristic. The large enthalpy of solvation from the rigid perfluoro chain greatly increases the hydrophobicity of the molecule[14]. This effect is further magnified by the size and spatial charge distribution of the perfluoro chain which creates a negative sheath along the tail of the compound[15]. This negative sheath masks the positive carbon and as a result, prevents solvation around itself. In addition, the electronegativity and the three lone pairs of electrons of the fluorine nucleus result in a repellency towards other compounds. The highly charged perfluoro chain and the presence of a sulfonate / carboxylates moiety contributes to the hydrophilicity of the molecule. Based on this competing hydrophobic / hydrophilic nature, one can manipulate the conditions to separate mixtures of perfluoro surfactants.

In the present investigation, reverse phase chromatography was used to separate between mixtures of perfluorocarboxylates and perfluoroalkyl sulfonates in natural pond water, acidic media, and soil water solutions. Limitations on the use of reverse phase ion chromatography will be discussed and the appropriateness of the application of anion exchange chromatography for this suite of compounds will be examined. To support lab studies, a method was developed on a second ion chromatography system for the determination of perfluorooctanoate in spiked pond water samples. It is important to note that the following paper describes methods developed over a series of trials based upon the chemical properties of the PFCAs. Chromatograms from these optimal methods are illustrated in this paper.

2.3 Experimental

Two ion chromatography systems were used for this study. The first was a microbore DX – 500 chromatography system (Dionex, Oakville, ON, Canada). The system includes a GP50 gradient pump, a CD20 conductivity detector, and a LC25 chromatography oven. For reverse phase separation, a polymeric divinyl benzene column (IonPac NG1 5 x 0.4 cm, Dionex) was utilized, while a quaternary ammonium based resin (AG16 5 x 0.2 cm & AS16 25 x 0.2cm, Dionex) was employed for anion exchange separation. Constant sample volumes were injected using a 25 μL loop. An ASRS Ultra (Dionex, Oakville, ON, Canada) suppressor was used in external water mode to decrease background noise and to maximize the amount of organic component in the mobile phase. The second ion chromatography system consisted of a Perkin Elmer 200 Series HPLC pump with an Alltech ERIS 1000 HP ion suppressor unit and Alltech 550 Conductivity detector. A 100 μL loop was utilized with a varying volume of injection.

An Xterra C8 silica / polymeric hybrid column (2 x 0.39 cm, Waters, Mississauga, ON, Canada) was used in this case.

Reagents and standards

The mobile phase was prepared from reagent grade *iso* – propanol, HPLC grade acetonitrile, and HPLC grade methanol purchased from Aldrich (Mississauga, ON, Canada). Standards and solvents using water were made up with 18 MΩ water from a Barnstread E-pure water deionization system (Fisher – Nepean, ON, Canada). The 0.100 *M* NaOH solution was made from a 50% (*w*/*w*) NaOH stock from Fisher (Nepean, ON, Canada). Perfluoropropionic acid 97% (PFPrA), perfluorobutyric acid 99% (PFBA), perfluoropentanoic acid 97% (PFPeA), perfluoroheptanoic acid 99% (PFHpA), perfluorooctanoic acid 98% (PFOA), and perfluorodecanoic acid 98% (PFDA) were obtained from Aldrich. Potassium perfluorooctylsulfonate 86% (PFOS) and potassium perfluorohexylsulfonate 99.9% (PFHxS) were obtained from 3M Co. (St. Paul, MN, USA), while perfluorohexanoic acid 95% (PFHxA) was purchased from Oakwood Research Chemicals (West Columbia, SC, USA).

Methods

The solvent gradients employed are given in table 1. An attempt to develop isocratic methods was made, and was successful for the anion exchange separation of short chained perfluorocarboxylates and sulfonates. Isocratic conditions allowed for faster equilibration time, as well as greater applicability to simpler chromatography systems.

Table 1: Chromatography methods for perfluoro surfactant analysis

Method	Column	Flow Rate (mL/min)	Conditions			
			Time (min)	% 0.1 M NaOH	% 70% i - PrOH / H_2O	% H_2O
Anion Exchange Mixture Separation	Weak anion exchange column: AG16 & AS16	0.40 mL/min	0.0	10	0	90
			30.0	10	0	90
Reverse Phase Mixture Separation	Polydivinyl Benzene Guard Column: NG1	0.40 mL/min	0.0	0	23	77
			5.0	0	23	77
			24.0	0	35	65
			30.0	0	35	65
			30.5	0	23	77
			35.0	0	23	77
PFOA – DX500	Polydivinyl Benzene Guard Column: NG1	0.75 mL/min	0.0	4	30	66
			3.0	4	30	66
			3.5	2	49	49
			6.5	2	49	49
			7.0	4	30	66
			13.0	4	30	66
			Time (min)	10 mM NaOH in 5% ACN, 5% MeOH, 90% H_2O		
PFOA – PE200	Xterra C8 Column	0.40 mL/min	0.0	100		
			15.0	100		

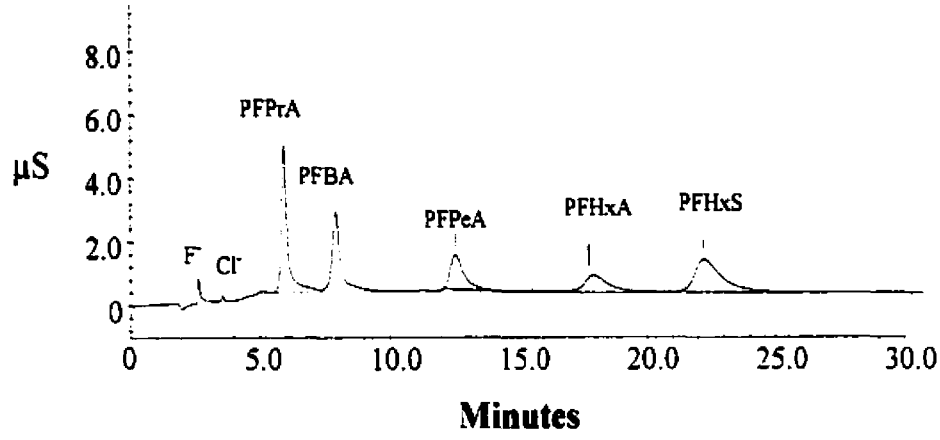

Figure 1: Chromatogram of a mixture of short chained perfluorocarboxylates and perfluorohexylsulfonate separated by anion exchange chromatography. The separation was performed on a Dionex AS16 and AG16 column using 10% of a 0.1 M NaOH solution, and 90% H_2O. The flow rate was 0.40 mL/min.

2.4 Results and discussion

Anion Exchange Chromatography

In anion exchange chromatography, the interaction between the anion exchange stationary phase and the aggregated molecule determines the retention on the column. The utility of isocratic anion exchange separation of the smaller chained perfluorocarboxylates as well as a short chained perfluoroalkyl sulfonate ranging from concentrations of 5 to 30 ppm is demonstrated in figure 1. The small initial peaks in the chromatogram are from F^- and Cl^-, respectively. These anions are not retained and are eluted from the column in the solvent front. This allows for easy and rapid detection of the perfluorocarboxylates and perfluoroalkyl sulfonate without interferences from the matrix. The utility of anion exchange separation of perfluoro acids is, however, limited

to the shorter chained molecules. With further increases in perfluoro chain length the elution time increases as well as the broadness of the peaks, as shown in figure 1. It is also important to note that there are chemical limitations on the concentration of NaOH in the solvent which can be used with the weak anion exchange column. Further increases in NaOH strength from that used is possible, however, resolution between shorter perfluoro chained carboxylates decreases under isocratic conditions. Alternatively, a gradient maybe employed with drawbacks including longer run and equilibration times. Thus, alternative methods are required for longer chained perfluorocarboxylates.

Reverse Phase Chromatography for Mixture Analysis

The use of reverse phase chromatography for the separation of longer chained perfluoro carboxylates and sulfonates is shown in Figure 2 with concentrations ranging from 15 – 60 ppm. The basis of separation in this case is the high propensity of the molecule to partition from water. The hydrophobicity of the polydivinyl benzene column provides a medium in which these compounds can partition into, and be retained by the column. Elution from the column is achieved by the gradient addition of a slightly polar organic solvent *iso* - propanol. It was found that organic solvents with a slight polarity were more efficient in comparison to non polar solvents such as hexane in eluting perfluorocarboxylates and sulfonates due to the charge associated with the carboxylate / sulfonate moiety, as well as the polarity of the C – F bond. Methanol, acetonitrile, and *iso* – propanol were tested and the latter solvent was chosen based upon background conductivity, compound resolution, and instrument maintenance requirements. Based upon both the length of the perfluoro chain as well as the negative charge bearing functional group, these compounds elute off the column. To improve

upon the chromatography of the longer chained perfluoro compounds, a more vigorous increase in the percentage of isopropanol was necessary. It resulted in decreased resolution between compounds.

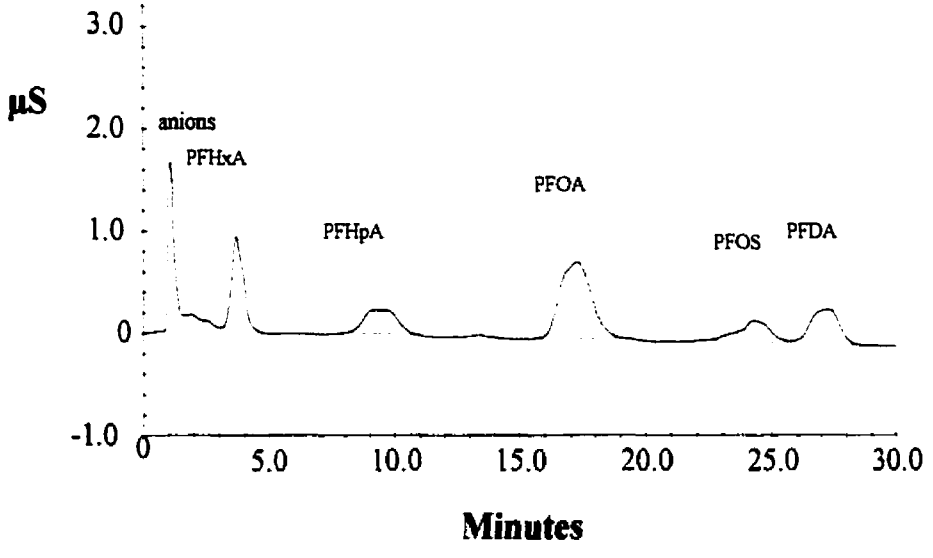

Figure 2: Chromatogram of a mixture of long chained perfluorocarboxylates and perfluorooctyl sulfonate separated by reverse phase chromatography. The separation was performed on a Dionex NG1 column using a mixture of 2 eluents: (A) 70% *i* – PrOH / H_2O solution; and (B) H_2O. The column was initial held at 23% A and 77% B from 0 – 5 minutes. A gradient was than employed so that the eluent at 24 minutes comprised of 35% A and 65% B. This was held until the 30 minute, at which point the eluent was decreased over a period of 0.5 min to 23% A and 77% B, and allowed to equilibrate until the 35 minute mark of the experimental method for subsequent runs. The flow rate was 0.40 mL/min.

Comparison of the use of gradient elution of PFOA using NG1 column on a Dionex DX500 system with isocratic elution using an Xterra C8 column on a Perkin Elmer 200 series IC pump for reverse phase separation and detection.

A chromatogram showing the separation and detection of PFOA using the Dionex DX500 system is given in Figure 3. A gradient using three solvents was employed to optimize the chromatography of PFOA. It was found that the perfluoro compound, regardless of chain length, would elute when both the percentage of isopropanol had increased and the NaOH had decreased. At that point the total conductivity of the eluent was at its lowest point as demonstrated by the depression in the chromatogram. As in traditional reverse phase chromatography, the isopropanol served to provide an organic medium for the compound to elute into, as previously discussed. However, the reason for the improvement in peak shape from the addition of hydroxide was not clear. It is suspected that hydroxide served to improve the chromatography by repelling and thus concentrating the PFOA onto the polydivinyl benzene column through increasing the ionic strength of the mobile phase. The perfluoro chain's propensity to partition out of high ionic strength water was greater in comparison to water due to the increased eletrostatic repulsion. Elution, therefore, only occurs with both an increase of organic solvent in the mobile phase as well as a decrease in NaOH concentration is made. The result was a vastly improved peak shape. Under the current method, and utilizing the 25 μL loop, a detection limit of approximately 2 ppm was obtained. An average R^2 value of 0.9942 (n=3) was obtained over a range from 2 – 250 ppm.

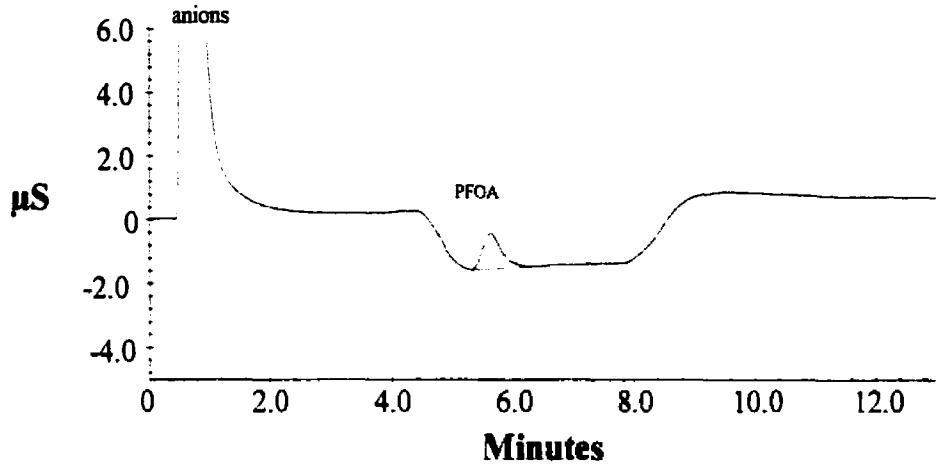

Figure 3: Chromatogram of a pond water sample containing PFOA separated using DX500 ion chromatography system. The separation was performed on a Dionex NG1 column using a mixture of 3 eluents: (A) 0.1 M NaOH; (B) 30% of a 70% *i* – PrOH / H_2O solution; and (C) H_2O. The column was held at 4% A, 30% B, and 66% C from 0 – 3 minutes. A gradient was than employed so that the eluent at 3.5 minutes comprised of 2% A, 49% B and 49% C. This was held until the 6.5 minute, at which point the eluent was decreased over a period of 0.5 min to 4% A, 30% of B and 66% C. The column was allowed to equilibrate under these conditions until the 13 minute mark of the experimental method for subsequent runs. The flow rate was 0.75 mL/min.

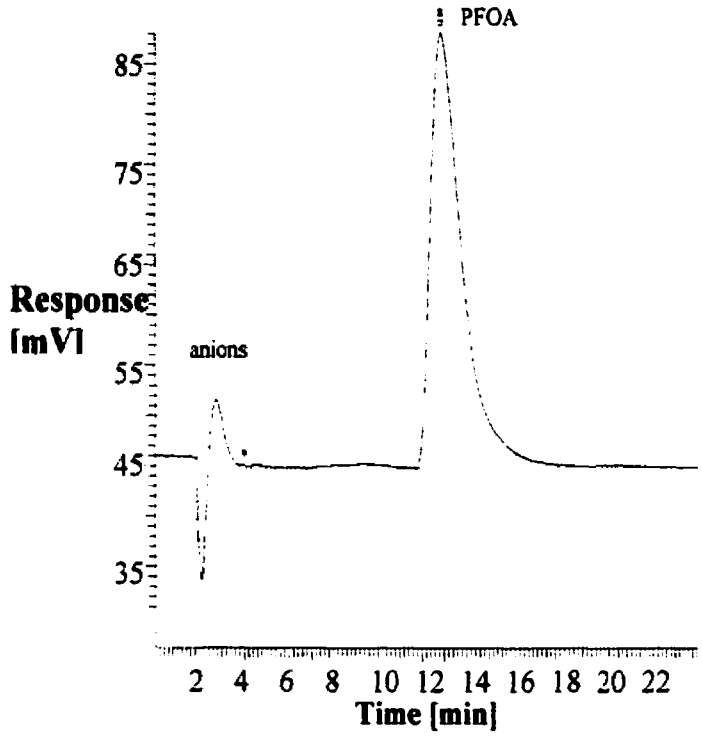

Figure 4: Chromatogram of a pond water sample containing PFOA using PE200 ion chromatography system. The separation was performed on a Xterra C8 column using 10 mM NaOH in 5% ACN, 5% MeOH, and 90% H_2O solution. The flow rate was 0.40 mL/min.

The use of an isocratic PE200 system for the elution of PFOA demonstrates the need for both a gradient system as well as a system capable of handling large percentages of organic solvent in the mobile phase. The resulting chromatogram of a synthetic field water sample using this system is shown on Figure 4. The initial large peak was associated with the presence of common ions found in solution, such as chloride, fluoride, sulphate, etc. Their elution with the solvent front indicates little retention on the C8 column, as expected since these anions are not hydrophobic in nature. The PFOA

peak elutes at approximately 13 minutes with a peak broadness of over 4 minutes in width. Due to the broadness of the peak, there are severe limitations on the limit of detection using this method. The peak broadness can be improved by increasing the percentage of organic phase in solution, however due to the use of the electrochemically regenerated ion suppressor, the percentage of organic solvent cannot exceed 10%. In addition, since the system is limited to isocratic elution, use of an ionic species to concentrate the analyte onto the column is also limited due to the instability of the XTerra column at pH>12. However, the resulting chromatogram does indicate that an isocratic system employing only 10% organic component in the mobile solvent is effective in separating and detecting PFOA from pond water solutions.

Conclusion

This paper has demonstrated a method for separation and analysis of a mixture of perfluorinated acids using both anion exchange and reverse phase ion chromatography. Rather than stating one method is better than the other, the two methods seem to compliment each other with anion exchange more appropriate for the shorter chained perfluorocarboxylates and perfluoroalkyl sulfonates, while reverse phase was found to be more suitable for the longer chained compounds. It was shown that a system that can use a gradient and tolerate a high percentage of organic solvent in the mobile phase has superior chromatography compared to a less versatile system.

Acknowledgement

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2.5 References

[1] E. Kissa, Fluorinated Surfactants, Marcel Dekker, Inc., New York, 1994.

[2] T, Ohya, N. Kudo, E. Suzuki, Y. Kawashima, J. Chromatogr. B 720 (1998) 1 – 7.

[3] J. Belisle, D. Hagen, Anal. Biochem. 101 (1980) 369 – 376.

[4] C. A. Moody, J. A. Field, Environ. Sci. Technol. 33(1999) 2800-2806.

[5] D. A. Ellis, J. W. Martin, D. C. G. Muir, S. A. Mabury, Anal. Chem. 72 (2000) 726 – 731.

[6] K. J. Hansen, L. A. Clemen, M. E. Ellefson, H. O. Johnson, Environ. Sci. Technol. As Soon As Publishable Contents (January 12, 2001).

[7] D. A. Ellis, M. L. Hanson, P. K. Sibley, T. Shahid, N. A. Fineberg, K. R. Solomon, D. C. G. Muir, S. A. Mabury, Chemosphere 42 (2001) 309 – 318.

[8] C. Sarzanini, M. C. Bruzzoniti, E. Mentasti, J. Chromatogr. A 850 (1999) 197 – 211.

[9] E.T. Urbansky, Environ. Monitoring 2 (2000) 285 – 291.

[10] S. X. Jiang, X. Liu, J. Liq. Chrom. & Rel. Technol. 20 (1997) 2053 – 2061.

[11] A. Stemp, V.A. Boriraj, P. Walling, P. Neill, JAOCS 72 (1995) 17 – 21.

[12] L. M. Nair, R. Saari-Nordhaus, J. Chromatogr. A 804 (1998) 233 – 239.

[13] M. Laikhtman, J. Rohrer, J. Chromatogr. A 822 (1998) 321 – 325.

[14] M. Abe, Curr. Opn. Coll. Int. Sci. 4 (1999) 354-356.

[15] G. Sandford, Phil. Trans. R. Soc. Land. A 358 (2000) 455 – 471.

Chapter 3

Physical Property Determination of Perfluorocarboxylic Acid

Formatted in preparation for submission to Journal of Chemical and Engineering Data

3.1 Abstract

Fluorinated surfactants, perfluorocarboxylic acids and perfluoroalkyl sulfonates in particular, have become increasingly popular in numerous industrial and domestic applications though little is known about their environmental fate. Other than trifluoroacetic acid (TFA), there are no literature values for K_d, K_H, VP, and C_{wsat} of perfluoropropionic acid (PFPrA) to perfluorooctanoic acid (PFOA). The purpose of this investigation was to measure the vapour pressure and Henry's Law constant of the protonated form of these perfluorocarboxylic acids. Vapour pressures were determined using the boiling point method, while the Henry's Law constant was determined using a modified bubble chamber. Literature values for TFA were used to validate all experimental procedures.

3.2 Introduction

Perfluorocarboxylic acids (PFCAs) are commonly used surfactants in a variety of industrial and commercial applications including lubricants, emulsifying and wetting reagents, and detergents(Kissa, 1994). Research into this suite of compounds has primarily focused upon the toxicological effects (Olson and Anderson, 1983; Kawashima et al., 1989; Intrasuksri et al., 1998; Haughom and Spydevold, 1992; Sohlenius et al., 1993; Vandel Heuvel, 1996; Biegel et al., 1995), its contamination resulting from aqueous fire fighting foams (Moody and Field, 1999; Moody et al., 2001), their presence in human plasma (Guy et al., 1976; Belisle and Hagen, 1980; Olsen et al., 1999; Hansen et al., 2001), and recently their accumulation in wildlife (Geisy and Kannan, 2001; Kannan et al., 2001), while their physical properties have not received much attention. Other than trifluoroacetic acid, which is the shortest of the PFCAs, the vapour pressure

and Henry's Law constant are not known. The lack of information is in part attributed to the difficulty in measuring the physical properties of strong acids. For example, the negative log of the dissociation constant (pKa) for acetic acid and trifluoroacetic acid are 4.74 and 0.26, respectively (Kissa, 1994). The electronegativity associated with the fluorine nucleus stabilizes the formation of the conjugate base by inductively delocalizing the negative charge towards the perfluoro chain making the perfluoro compound a much stronger acid than its hydrogen analogue. The large acid dissociation constant is problematic because the acid and conjugate base exhibit significantly different chemical and physical properties. Therefore, the design of experiments to measure physical properties of the protonated PFCA must be in a matrix in which little to no dissociation occurs. The effect on the acid dissociation constant by the perfluoro chain is one example of the unique physical properties of this suite of compounds, its effects on other physical properties are unknown. Although the measurement of the protonated form of the PFCA is unrealistic in an environmental distribution sense, as the compound is unlikely to exist in its protonated form in the natural environment, it provides the only avenue for the determination of general trends in physical properties for PFCA as a result of increasing perfluoro chain length. Therefore, measurements of the protonated form of the PFCA were undertaken.

The purpose of the study was to determine the vapour pressure (vp) and Henry's Law constant (K_H) of a range of PFCAs from trifluoroacetic acid to perfluorooctanoic acid. Although, the shorter chain perfluorocarboxylic acid are not commonly used as surfactants, they are present in industrial mixtures as an impurity. Also, obtaining the physical properties of this whole series of compounds allows for determination of the

intrinsic properties governing their partitioning behaviour. Both the vp and K_H play a critical role in the tendency of a compound to partition between aqueous and gaseous environments, and are therefore required for predicting the potential distribution of a compound. The water solubility of the perfluorocarboxylic acid was also calculated from the measured vp and K_H values.

3.3 Experimental Section

Chemicals

All perfluorocarboxylic acids of at least 97% purity were purchased from Aldrich (Mississauga, ON, Canada) with the exception of perflurohexanoic acid, which was obtained at 95% purity from Oakwood Research Chemicals (West Columbia, SC, USA). The acid solution used in the Henry's Law experiment was made from 18 MΩ water (Barnstread E-pure, Nepean, ON, Canada) and hydrochloric acid stock from Fisher Scientific Canada (Nepean, ON, Canada).

Analytical Methods

Ion chromatography was used for the analysis of PFCAs in aqueous samples because of its durability and short analysis time. The method originally described by Kwan et al. (2001) was employed. Briefly, a microbore DX - 500 system (Dionex, Oakville, ON, Canada) was used. The system includes a GP50 gradient pump, a CD20 conductivity detector, and a LC25 chromatography oven. Constant sample volumes were injected using a 25 μL loop. For TFA, PFPrA, PFBA, PFPeA, and PFHxA, an AG16 (5 x 0.2 cm, Dionex) and AS16(25 x 0.2 cm, Dionex), anion exchange column were used. The compound was eluted from the column under isocratic conditions with a mixture of

0.1 M NaOH solution, and 18 MΩ. For PFHpA and PFOA, a polymeric divinyl benzene column, IonPac NG1 (5 x 0.4 cm, Dionex), was employed. The compound was eluted using a gradient of 70% i – PrOH, 0.10 M NaOH, and 18 MΩ. Table 1 summarizes the individual methods employed for the analysis.

Table 1. Ion Chromatography Conditions for PFCA analysis.

Analyte	Flow Rate	Conditions			
		Time (min)	% 0.1 M NaOH	% 70 % *i* – PrOH / H_2O	% H_2O
TFA	0.40	0	2	0	98
		16	2	0	98
PFPrA	0.40	0	2	0	98
		24	2	0	98
PFBA	0.40	0	5	0	95
		24	5	0	95
PFPeA	0.40	0	8	0	92
		20	8	0	92
PFHxA	0.40	0	15	0	85
		19	15	0	85
PFHpA	0.75	Init	4	30	66
		0.0	4	30	66
		3.0	4	30	66
		3.5	2	47	51
		6.5	2	47	51
		7.0	4	30	66
		13.0	4	30	66
PFOA	0.75	Init	4	30	66
		0.0	4	30	66
		3.0	4	30	66
		3.5	2	49	49
		6.5	2	49	49
		7.0	4	30	66
		13.0	4	30	66

Vapour Pressure Determination of PFCAs

Vapour pressure was determined using a boiling point apparatus as described by Thomson and Douslin (1971). The apparatus involved a modified Claissen distillation head connected to a round bottom flask containing the PFCA. A Teflon stir bar was

added to provide an activated surface for the pure PFCA. A condenser was mounted on the distillation head, which in turn was connected to a ballast ball to regulate the pressure within the system. A dual line was attached to the ballast ball connecting both the vacuum system and an electronic pressure barometer. The temperature of the round bottom flask was held constant while the pressure within the apparatus was reduced until the pressure was equal to the vapour pressure of the PFCA, at which point the sample began to boil. The temperature was varied from room temperature to a maximum of 70°C (depending on the compound), and a graph of the log of the vapour pressure as a function of the temperature was generated. Vapour pressure at 25°C was than calculated from the graph.

For the vapour pressure of PFOA, a correction factor was required as the sample is a solid at room temperature. The ratio of the solid to liquid state vapour pressure was estimated by:

$$\ln (P^s_S/P^s_L) = -\Delta S_F ((T_M/T) - 1)/R \qquad (1)$$

Where P^s_S is the calculated vapour pressure of the solid sample in solid form, while P^s_L is the measured vapour pressure of the solid sample in liquid form. The equation states that with a phase change, an entropy correction factor, ΔS_F, must be taken into account which in turn is multiplied by a constant determined by the melting point of the analyte, PFOA (T_M = 329 K). Walden's rule state (Walden 1908) that many organic compounds have an entropy of fusion of approximately 56.5 J/ mol K, simplifying the equation to:

$$\ln (P^s_S/P^s_L) = -6.79 ((T_M/T) - 1) \qquad (2)$$

Henry's Law Constant Determination of PFCAs

The Henry's Law constant was determined using a derivative of a method by Bowden et al. (1995). Briefly, nitrogen was passed through a sample solution of constant temperature containing the PFCA analyte and hydrochloric acid (HCl). From the sample solution, the nitrogen gas was than bubbled through a 18 μΩ water trap solution, at which point the PFCA deprotonates, and was quantitatively recovered. Aliquots of the trap solution at four time points were taken, and the average concentration was determined using ion chromatography as described above. The cumulative effect of salting- out and Henry's Law constant (K_H^*), was determined using equation 3 (Bowden et al., 1995):

$$K_H^* = P / [PFC_x]_{sample\ solution} \qquad (3)$$

where P is the vapour pressure of the PFCA, and $[PFC_x]_{sample\ solution}$ is the concentration of the prontonated form of the PFCA. Substituting the ideal gas equation for P, the equation becomes:

$$K_H^* = \frac{n \times R \times T}{V \times [PFC_x]_{sample\ solution}} \qquad (4)$$

The volume is equivalent to the volume of gas passed through the sample volume, that is, the nitrogen flow rate (F) multiplied by the duration (t). Furthermore, the number of moles is equivalent to the concentration measured in the trap solution ($[PFC_x]_{trap}$) multiplied by the volume of the trap solution. Equation 4 becomes

$$K_H^* = \frac{[PFC_x]_{trap} \times T \times R \times V_{trap}}{F \times [PFC_x]_{sample\ solution} \times t} \qquad (5)$$

Lastly, since the concentration of the protonated form of the PFCA is a function of the acid dissociation constant, that is:

$$K_a = \frac{[PFC_x^-] \times [H^+]}{[PFC_x]_{sample\ solution}} \qquad (6)$$

The total concentration of the PFCA is the sum of its protonated form and deprotonated form, that is,

$$[PFC_x]_{tot} = [PFC_x]_{sample\ solution} + [PFC_x^-] \qquad (7a)$$

$$[PFC_x]_{tot} = [PFC_x]_{sample\ solution} \times (1 + K_a / [H^+]) \qquad (7b)$$

Substitution of equation 7b into equation 5 gives,

$$K_H^{\bullet} = \frac{[PFC_x]_{trap} \times T \times R \times V_{trap} \times (1 + K_a/[H^+])}{F \times [PFC_x]_{tot} \times t} \qquad (8)$$

Control experiments showed that neither flow rate nor duration of study affected the Henry's Law constant value indicating that the sample solution was in equilibrium with the nitrogen gas. This procedure was repeated for 3 additional temperatures from 15°C to 30°C, and the log $K_H^{\bullet}$ was plotted vs. temperature to determine the $K_H^{\bullet}$ at 25°C. As the equation indicates, the $K_H^{\bullet}$ is a function of the acid dissociation constant K_a of the PFCA. However, only the K_a of TFA, PFBA, and PFOA were available in the literature, with TFA being the strongest acid of the three. It was assumed that at the range of concentration of HCl used in the experiment (4.09 M - 6.13 M), all PFCAs were in their protonated form within the sample solution. Comparison of the experimental K_H value of TFA using this assumption versus K_H value using the K_a showed less than 10% deviation, indicating the assumption was valid. By assuming that all PFCA were protonated equation 8 simplifies to,

$$K_H^{\bullet} = \frac{[PFC_x]_{trap} \times T \times R \times V_{trap} \times V_{cor}}{\text{Flow Rate} \times [PFC_x]_{tot} \times t} \qquad (9)$$

The experiment was repeated for three or four HCl concentrations ranging from 4.26 M to 6.13 M, and this range in concentration was chosen to minimize error from partial protonation. The resulting K_H^* was then plotted in a log scale as a function of HCl concentration, so that the salt effects of chloride could be cancelled.

$$\log K_H^* = m\ [HCl] + b \qquad (10)$$

Where the intercept, b, is the Henry's Law constant of the protonated form of the PFCA. No salt effects were assumed to occur when the concentration of HCl was zero. Conceptually, when the concentration of hydrochloric acid is equal to zero, the sample solution would contain the perfluorocarboxylic acid in its protonated state in aqueous solution. Thereby, equation (10) simplifies to:

$$K_H = 10^b \qquad (11)$$

This assumption appears valid as a literature value comparison of K_H for TFA showed less than 10% deviation from the calculated activity based method by Bowden et al. (1995).

3.4 Results

Vapour pressure was determined for TFA to PFOA using the boiling point method. Pefluorohexanoic acid was omitted due to the high cost of the compound. Results of triplicate measurements and their calculate standard deviation are given in Table 2 and are summarized as a function of perfluoro chain length in Figure 1. The K_H results for TFA to PFOA with error bars indicating standard deviation from regression analysis of the plot are given in Figure 2. A sample calculation of Henry's Law constant is given in Appendix C for PFPrA. Lastly, the calculated water solubility as a function of

increasing perfluoro chain length is presented in Figure 3. A complete list of experimental values is available in the appendices.

3.5 Discussion

The accuracy and precision of the boiling point method was verified using TFA. A number of vp values of TFA are available in literature, for example Kreglewski (1962) reported a vp value of 1.50 kPa at 25°C, while Kauck et al. (1951) measured it to be 16.4 kPa at the same temperature, which is different by a full order of magnitude. Such discrepancies exemplify the difficulty associated with vp measurements of strong acids. Nonetheless, the experimental measured value seemed to be in good agreement with Kauck's results as it deviated by only 25% which is an acceptable deviation for measurements of this type (*cf.* the deviation observed when comparing Kauck results with Kreglewski*)*, in addition the measured value lye between the two literature values. The method showed a high degree of precision in replicate vp measurements (n=3, ± 3%). There was a clear decrease in vp value as chain length increased from TFA to PFBA as shown in figure 1. This is explained as a result of an increase in molecular weight (MW) associated with the

Compound	Vapour Pressure (kPa)	Standard Deviation
TFA	11.8	0.3
	12.0	
	12.3	
PFPrA	3.93	
PFBA	1.26	
PFPeA	2.75	0.54
	2.16	
	3.24	
PFHpA	1.62	0.20
	1.68	
	2.00	
PFOA	1.77	0.17
	1.53	
	1.85	

Table 2: Vapour pressure results of perfluorocarboxylic acids at 25°C.

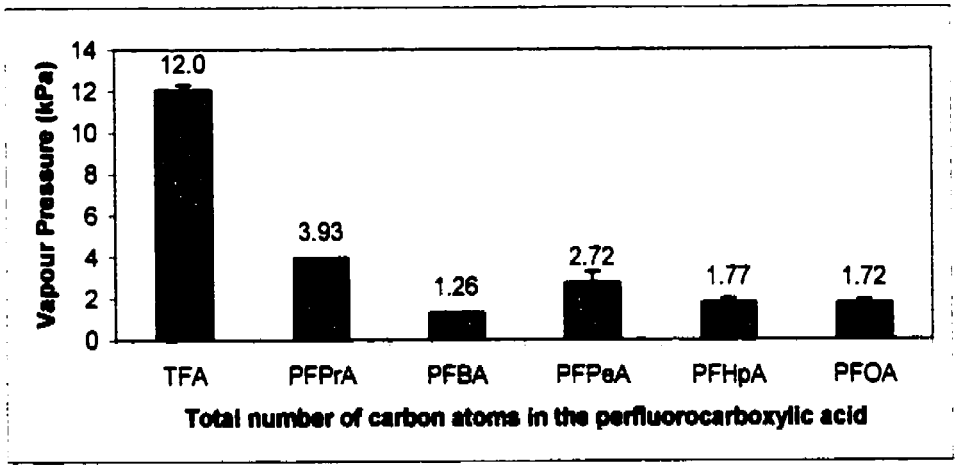

Figure 1. Vapour pressure of perfluorocarboxylic acids with increasing chain length at 25°C.

subsequent addition of a -CF_2- unit into the perfluoro chain. This trend of decrease in vp with increasing MW, appeared to be segmented between two sections, from TFA to

PFBA and PFPeA to PFOA. One possible explanation for this apparent difference would be the dimerization of the carboxylic acid moieties between adjacent compounds. If this were the case, the measured vp would be the sum of the fraction of the monomer and dimer multiplied by its corresponding vp. Since the dimer is heavier, the mixture of monomer and dimer would result in a lower vp relative to the vp of the monomer alone. This ability to dimerize is dependent on the compounds capacity to form hydrogen bonds and in the case of acetic and propionic acid, pure solutions of these compounds are thought to be completely dimerized (De Kruif and Oonk, 1979). However, dimerization does not appear to be occurring for the PFCAs, as the characteristic dependence of dimerization as a function of temperature was not observed. The linearity of the log vp vs. 1/temperature plots were good with r^2 values of 0.81 (PFPeA) or greater over an average range of 20°C, suggesting that there was no significant differences in vp of PFPrA to PFOA. The inability of PFCAs to dimerize is likely associated with the electronegativity of the perfluoro chain. The electronegativity inductively delocalize electrons towards the tail of the PFCA, hindering the formation of hydrogen at the carboxylate moiety.

Perfluorination of the carboxylic acid resulted in an increased vapour pressure relative to the hydrogen analogue. This is demonstrated by comparing the literature values of alkanoic acids measured by Ambrose and Ghiassee (1981) with the PFCA, as shown in Table 2. For example, the vapour pressure of perfluoropropionic acid was measured to be 3.93 kPa in comparison to 0.435 kPa for its hydrogen analogue. The effects on vp were counter to the increase in molecular weight as perfluropropionic acid was approximately a factor of two greater in molecular weight than propionic acid. Since

factors such as symmetry and branching were constant, the resulting increase in vp must be from either an increase in rigidity of PFPrA, or a decrease in intermolecular attraction, or a combination of the two factors. The increased rigidity is consistent with literature findings, as Abe (1999) previously described the perfluoro chain as a rigid rod – like shape with an external negative fluorine sheath. By reducing the degrees of freedom of the PFCA, its ability to distribute energy is decreased thereby increasing its vp. In terms of fluorine – fluorine interactions between adjacent PFCAs, this fluorine sheath explanation was consistent with the findings of this paper. The small size of the fluorine nucleus completely masked the positive carbon backbone. The lack of an accessible

	Perfluoro- (kPa)	Hydrogen Analogue (kPa)[a]
Acetic Acid	12.0 ± 0.3	2.08
Propionic Acid	3.93	0.435
Butanoic Acid	1.26	0.084
Pentanoic Acid	2.72 ± 0.54	0.0170
Hexanoic Acid	N/A	0.00405
Heptanoic Acid	1.77 ± 0.20	N/A
Octanoic Acid	1.72 ± 0.17	0.000221

[a] Ambrose and Ghiassee (1981)

Table 3. Comparison of the vapour pressure of perfluorocarboxylic acids with its hydrogen analogue at 25°C.

positive carbon center prevented intermolecular perfluoro – perfluoro chain attraction. This is further magnified, as there is likely a repellency effect between adjacent perfluoro

chains due to the fluorine atom. Both the rigidity and electrostatic repulsion are expected to increase as a function of increasing perfluoro chain length, thereby increasing the vp of the PFCA relative to the hydrogen analogue, counteracting the effects of the increase in molecular weight. The result is a lack of variation in vp with increasing chain length as demonstrated with PFHpA (1.77 kPa) and PFOA (1.72 kPa).

The K_H was determined based upon the assumption that the activity coefficient of the PFCA, ν_{PFCA}, was unity. This assumption was verified using TFA, as the measured value of 0.0121 Pa m^3 mol^{-1} was in good agreement with the literature result of 0.0113 Pa m^3 mol^{-1} (Bowden et al., 1995). There was a clear trend in K_H with increasing perfluoro chain length, with an inflection point at perfluorobutanoic acid (PFBA) as shown in figure 2. This inflection point can potentially be explained by calculating the water solubility (C_{sat}) from the vp and K_H results and is shown in figure 3. Water solubility

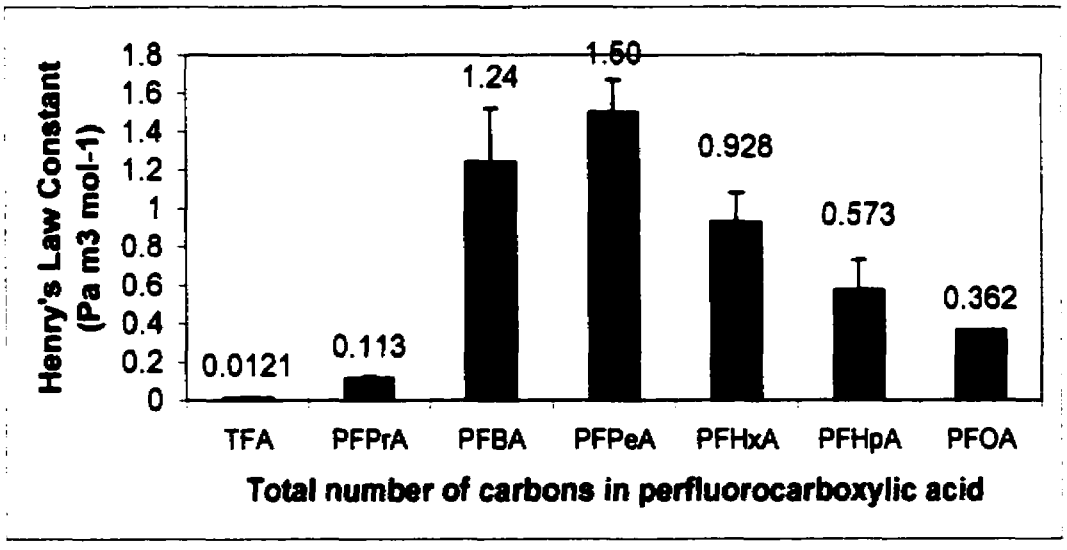

Figure 2. Henry's Law constant of perfluorocarboxylic acids at 25°C with increasing chain length.

showed relatively no change from PFBA to PFOA indicating that inflection in the Henry's Law constant was the result of an additive effect that was not clear from either the vp or the C_{sat} figures. It is important to note that the calculated water solubility value is of the protonated form of the PFCA assuming no deprotonation would occur, and no micelle formation. Although these assumptions are clearly incorrect, the lack of variation with increasing perfluoro chain length relative to its hydrogen analogue (Table 3) is worth noting. Fluorine substituted molecules in comparison with the hydrocarbon analogue generally show an increase in enthalpy of solvation as the electronegative fluorine acted as a hydrogen bond acceptor (Alkorta et al., 2000). Although, this interaction is approximately half that of oxygen – hydrogen interactions (2 kcal/mol vs. 4 kcal/mol), this does provide an explanation for the lack of variation with solubility with increasing chain length as observed, relative to the hydrocarbon analogue. That is, the perfluoro chain forms weak hydrogen bonds with water, thereby enthalpy stabilizing

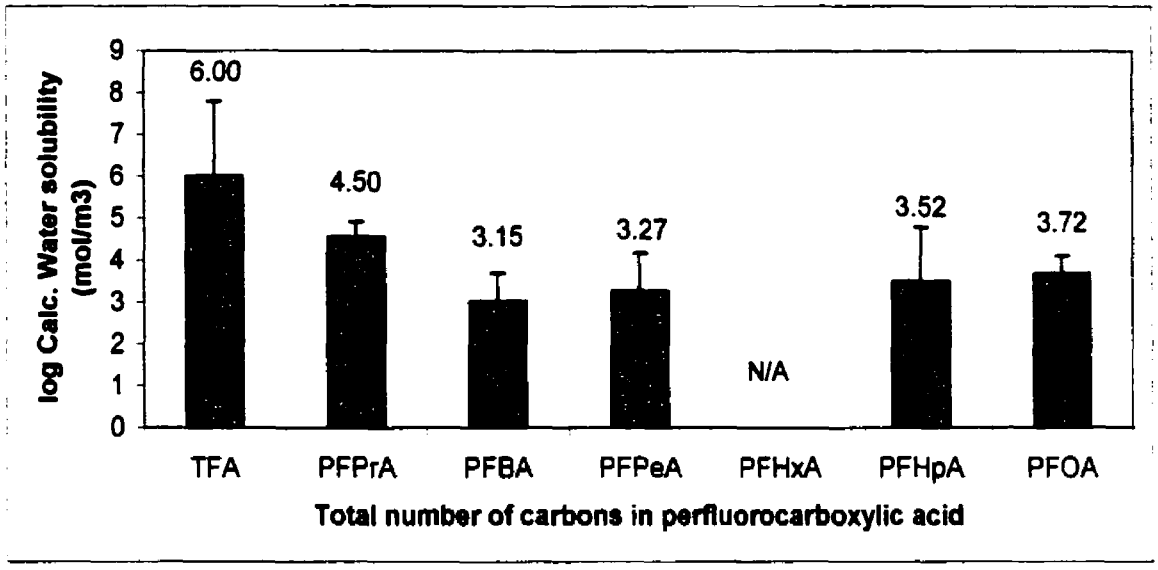

Figure 3. Calculated water solubility of perfluorocarboxylic acids with increasing chain length at 25°C.

increasing perfluoro chain length. Such interaction can further be magnified by substitution of the perfluoro chain adjacent to a carbon containing a π orbital (Ellis, 2000), as in the case of the carboxylic acid moiety. The presence of electrons in the π orbital allowed for a polarization of the electrons towards the perfluoro chain generating a dipole for increased water solvation. Conversely, the entropy effects of solvation around a rigid molecule can be described by comparing the alignment of water molecules around a rigid perfluoro molecule and its hydrocarbon analogue. In the case of the

	Perfluoro- (mol/m^3)	Hydrogen Analogue (mol/m^3)[b]
Acetic Acid	$1.00 \times 10^6 \pm 2.99 \times 10^5$	1.67×10^4
Propionic Acid	$3.14 \times 10^4 \pm 2.54 \times 10^3$	1.35×10^4
Butanoic Acid	$1.42 \times 10^3 \pm 323$	681
Pentanoic Acid	$1.87 \times 10^3 \pm 514$	245
Hexanoic Acid	N/A	88.7
Heptanoic Acid	$3.30 \times 10^3 \pm 1.21 \times 10^3$	21.7
Octanoic Acid	$5.22 \times 10^3 \pm 564$	5.47

[b] Syracuse Research Corporation, 2001

Table 4. Comparison of the water solubility of perfluorocarboxylic acids with its hydrogen analogue at 25°C.

hydrocarbon chain, free rotation allows for water to arrange itself in multiple ways surrounding the molecule, resulting in a high degree of disorder. In contrast, due to the rigidity of the perfluoro chain, water molecules must orient themselves in a particular fashion. This orientation of water around the perfluoro compound results in a relatively higher degree of order within the system. With increasing perfluoro chain length, the rigidity of the PFCA is expected to increase, thereby resulting in a decrease in entropy of the system. This thermodynamic explanation is supported by Dannenfelser and Yalkowsky (1991), who concluded that the predicted solubility of a compound is directly proportional to its symmetry number, or the number of indistinguishable positions in which a compound can be oriented. The increase in entropy of solvation with increasing perfluoro chain length would therefore decrease solubility and counter the effects of enthalpy. The result is the lack of variation in water solubility with increasing perfluoro

chain length (log C_{wsat} of 3.15 for PFBA to 3.72 for PFOA) as shown in Figure 3. The lack of significant variation in water solubility and vapour pressure indicates that the likely cause of the inflection point in the Henry's Law constant versus perfluoro chain length, is due to an additive effect that is not clearly shown in either of the C_{sat} or the vp alone.

Conclusion

Data have been reported for the vapour pressure and Henry's Law constant for a series of PFCAs from TFA to PFOA. It was shown that the vapour pressure of the perfluorocarboxylic acid was at least two orders of magnitude greater than its hydrocarbon analogue, and this was attributed to a decrease in intermolecular interaction between the perfluoro chain. Increases in chain length showed little trend in vapour pressure, as the increase in molecular weight was offset by the decrease in intermolecular interaction, and an increase in electrostatic repulsion. In terms of the Henry's Law constant, there was a distinct inflection point brought on by the increase in volatility, however little in the way of a trend can be conclusively described due to the interaction of the perfluoro chain with water. This interaction was described as enthalpy favored while entropy disfavored, and as a result, solubility with increasing perfluoro chain length showed little variation. The study demonstrates the atypical nature of perfluoro compounds, as generalized rules for predicting physical properties could not be made as the many factors governing the interaction of the perfluoro chain hinders such predictions.

Acknowledgement

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3.5 References:

Abe, M. 1999. Synthesis and Applications of Surfactants Containing Fluorine. *Curr. Opn. Coll. Int. Sci.* **1999**, 4, 354 – 356.

Alkorta, I. Rozas, I., and Elguero, J. Effects of Fluorine Substitution On Hydrogen Bond Interactions. *J. Fluor. Chem.* **2000**, 101, 233 – 238.

Ambrose, D., and Ghiassee, N. Vapour Pressures and Critical Temperatures and Critical Pressures of Some Alkanoic Acids: C_1 to C_{10}. *J. Chem. Thermodynamics* **1981**, 19, 505 – 519.

Belisle, J., and Hagen, D. A Method for the Determination of Perfluorooctanoic Acid in Blood and Other Biological Samples. *Anal. Biochem.* **1980**, 101, 369 - 376.

Biegel, L., Liu, R., Hurtt, M., Cook, J. Effects of Ammonium Perfluorooctanoate on Leydig Cell Function: *In Vitro*, *in Vivo*, and Experiment *Vivo* Studies. *Toxicol. and Appl. Pharmacol.* **1995**, 134, 18 – 25.

Bowden, D., Clegg, S., and Brimblecombe, P. The Henry's Law Constant of Trifluoroacetic Acid and its Partitioning into Liquid Water In the Atmosphere. *Chemosphere* **1995**, 32, 405 – 420.

Dannenfelser, R.M. and Yalkowsky, S.H. Database of Aqueous Solubility for Organic Non – Electrolytes. *Sci. Total Environ.* **1991**, 101/102, 625 – 628.

DE Kruif, C., and Oonk, H. Enthaplies of Vaporization and Vapour Pressures of Seven Aliphatic Carboxylic Acids. *J. Chem. Thermodynamics* **1979**, 11, 287 – 290.

Ellis, DA. Organofluorine compounds in the environment: Analysis, sources and fate. Univeristy of Toronto, Toronto, 2000.

Geisy, J., Kannan, K. Global distribution of perfluorooctane sulfonate in wildlife. *Environ. Sci. Technol.* **2001**, 35, 1339-1342.

Guy, W., Taves, D., and Brey, W. Biochemistry Involving Carbon – Fluorine Bonds. *Amer. Chem. Soc.* **1976**, 475, 117 – 134.

Hansen, K., Clemen, L., Ellefson, M., Johnson, H. Compound – Specific, Quantitative Characterization of Organic Fluorochemicals in Biological Matrices. *Environ. Sci. Technol.* **2001**, 35, 766 - 770.

Haughom, B., Spydevold, O. The Mechanism Underlying the Hypolipemic Effect of Perfluorooctanoic Acid (PFOA), Perfluorooctane Sulphonic Acid (PFOSA) and Clofibric Acid. *Biochim. et Biophys. Acta.* **1992**, 1128, 65 – 72.

Intrasuksri, U., Rangwala, S., O'Brien, M., Noonan, D.., Feller, D. Mechanism of Peroxisome Proliferation by Pefluorooctanoic Acid and Endogenous Fatty Acids. *Gen. Pharmac.* **1998**, 31, 187 – 197.

Kannan, K., Koistinen, J., Beckmen, K., Evans, T., Gorzelany, J., Hansen, K., Jones, P., Helle, E., Nyman, M., Giesy, J. Accumulation of perfluorooctane sulfonate in marine mammals. *Environ. Sci. Technol.* **2001**, 35, 1593 – 1598.

Kauck, E. and Diesslin, A. Some Properties of Perfluorocarboxylic Acids. *Ind. and Eng. Chem.* **1951**, 43, 2332 – 2338.

Kawashima, Y., Uy – Yu, N., Kozuka, H. Sex – Related Differences in the Inductions by Perfluorooctanoic Acid of Peroxisomal β - Oxidation, Microsomal 1 – Acylglcerophosphocholine Acytransferase and Cytosolic Long – Chain Acylhydrolase in Rat Liver. *Biochem. J.* **1989**, 261, 595 – 600.

Kissa, E. *Fluorinated Surfactants*. Marcel Dekker, Inc., New York, 1994.

Kreglwski, A. Vapour Pressures and Molar Volumes of Liquid Perfluoro – n – Octane Trifluoroacetic Acid, and its Anhydrife. *Bull. Acad. Pol. Sci. Ser. Sci. Chim.* **1962**, 11-12, 629 – 633.

Kwan, W., Sullivan, R., Small, J., Mabury, S. Comparison of Anion Exchange and Reverse Phase Ion Chromatography for the Determination of Perfluorinated Carboxylate and Sulfonate Surfactants. *J. Chrom. A.* 2001, Submitted.

Moody, C., Field, J. Determination of Perfluorocarboxylates in Groundwater Impacted by Fire-Fighting Activity. *Environ. Sci. Technol.*, **1999**, 33, 2800 - 2806.

Moody, C.A., Kwan, W.C., Martin, J.W., Muir, D.C.G., Mabury, S.A. Determination of perfluorinated surfactants in surface water samples by two independent analytical techniques: Liquid chromatography/tandem mass spectrometry and F-19 NMR. *Anal. Chem.*, **2001**, 73, 2200 - 2206.

Olsen, G.W., Burris, J.M., Mandel, J.H., Zobel, L.R. Serum Perfluorooctane Sulfonate and Hepatic and Lipid Clinical Chemistry Tests in Fluorochemical Prodcution Employees. *JOEM* **1999**, 41, 799 – 806.

Olson, C., Andersen, M. The Acute Toxicity of Perfluorooctanoic Acid and Perfluorodecanoic Acid in Male Rats and Effects on Tissue Fatty Acids. *Toxicol. Appl. Pharmoacol.* **1983**, 145, 285 – 293.

Sohlenius, A., Eriksson, A., Hogstrom, C., Kimland, M., DePierre, J. Perfluorooctane Sulfonic Acid is a Potent Inducer of Peroxisomal Fatty Acid β - Oxidation and Other Activities Known to be Affected by Peroxisome Proliferators in Mouse Liver. *Pharmac. & Toxicol.* **1993**, 72, 90 - 93.

Syracuse Research Corporation. Phys. Prop Database. **2001**.

Thomson, G., Douslin, D. Determination of pressure and volume. In Weissberger, A., and Rossiter, BW. 1st edition, *Physical Methods of Chemistry*, Vol. 1 – Techniques of Chemistry. Wiley – Interscience, New York, 1971.

Vandel Heuvel, J. Perfluorodecanoic Acid as a Useful Pharmacologic Tool for the Study of Peroxisome Proliferation. *Gen Pharmac.* **1996**, 27, 1123 – 1129.

Walden, P. Ubew die schmelzwrme, spezifische kohsion und molekulargrsse bei der schmelz – termperatur. *Z. Elektrochem.* **1908**, 14, 713 – 728.

Yalkowsky, S. Estimation of Entropies of Fusion of Organic Compounds. *Ind. Eng. Chem. Fundam.* **1979**, 18, 108 – 111.

Chapter 4

Conclusions and Future Work

4.1 Conclusions

The overall objective of this research was to measure the physical properties of anionic perfluorinated surfactants. However, in order to do so, a rapid ion chromatography technique was required for aqueous sample measurement to supplement physical property measurements. In chapter 3, two of these physical properties were measured, the Henry's Law constant and vapour pressure. Other than trifluoroacetic acid, there are no literature values of Henry's Law constant, and vapour pressure for the remaining perfluorocarboxylic acids. The results of indicate the unique nature of perfluorocarboxylic acids, in particular the effects of increasing perfluoro chain length.

The ion chromatography methods developed were superior in separation and peak shape in comparison to that available in literature. Methods were developed on multiple ion chromatography systems allowing for a high degree of selection for the user. The bases of separation were discussed by comparing anion exchange and reverse phase separation of mixtures of perfluorocarboxylates and sulfonates. Rather than concluding that one method was more effective than another for this suite of compounds, it was concluded that anion exchange and reverse phase chromatography would be most effective in complimentary approach. Anion exchange separation for the shorter chained perfluorinated surfactants, reverse phase for the longer chained perfluorinated surfactants. The distinction of the two was made at perfluorohexanoate, although this was somewhat arbitrary and was made on the basis of minimizing run times. The versatility of the methods provides the basis for future aqueous measurements for physical properties determination.

The Henry's Law constant and vapour pressure of the perfluorocarboxylic acid were measured. The applicability of these measurements was limited to certain environments, in particular those of manufacturing at which acidic conditions are used. The unique properties of the C – F bond and the perfluoro chain defies traditional physical properties estimates, allowing us to develop a new set of qualitative guidelines for this purpose.

Overall, the two projects were successful in reaching their goals. The results presented provide the basis for not only future physical property determination, but it also provides a set of qualitative guidelines for physical property estimation. In addition, the study demonstrates the uniqueness of anionic perfluorinated surfactants and the difficulty associated with quantitative determination.

4.2 Future Work

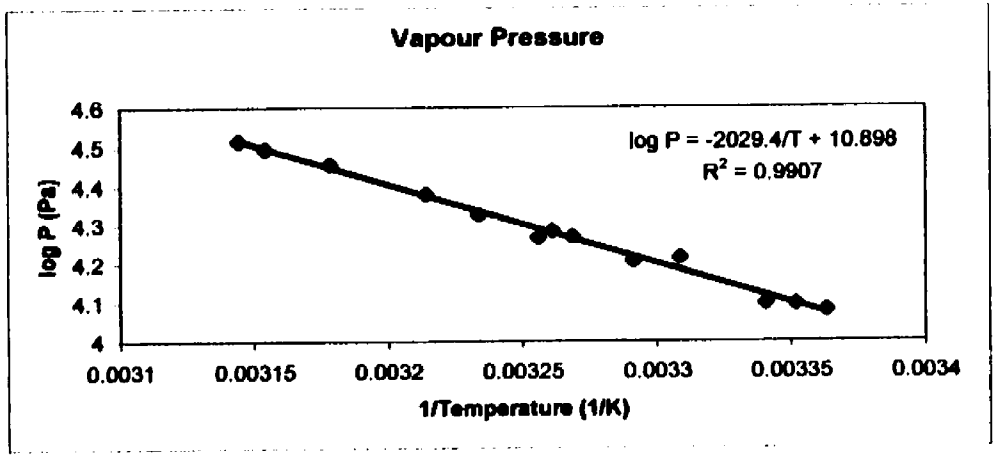
The gaseous distribution of anionic perfluorinated surfactants thus far has been focused upon the perfluorocarboxylates. However, another set of important compounds that are of particular interest is the perfluoroalkyl sulfonates in particular perfluorooctyl sulfonate (PFOS). The applicability of the distribution of PFOS in its protonated form is limited, as it is expected that the perfluoroalkyl sulfonates are vastly stronger acids than the perfluorocarboxylates. Therefore, even under harsh chemical environments, such as acid bath etching mixtures, it is suspected that there would be no significant degree of the perfluoroalkyl sulphonate in its acid form. Indicating that PFOS, and its shorter chained analogue, are distributed via an alternative mechanism, for example in the form of an amide alcohol, $C_8F_{17}SO_2N(CH_2CH_3)CH_2CH_2OH$ (PFOSA-OH). It is hypothesized that

through that PFOS and its shorter chained homologues is distributed via a non ionic form, and eventually undergoes hydrolysis to form its corresponding anion. The vapour pressure and water solubility of PFOSA-OH, $C_8F_{17}SO_2F$ (PFOS-F) have been previously measured by this researcher (unpublished data), however measuring the rate of hydrolysis is not straightforward due to the relatively low solubility of the compound in water. This obstacle can be overcome by measuring the rate of formation of PFOS using LC – MS/MS. Using this data, the potential of modeling the global distribution of PFOS as well as its non – ionic form exists.

Appendix A

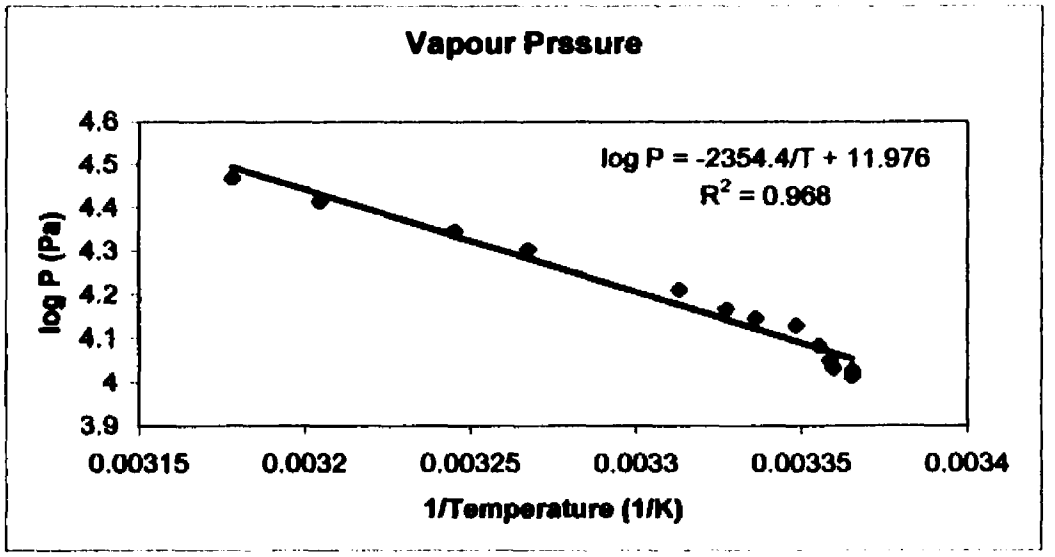
Vapour Pressure Results

Vapour Pressure Results – Trifluoroacetic Acid



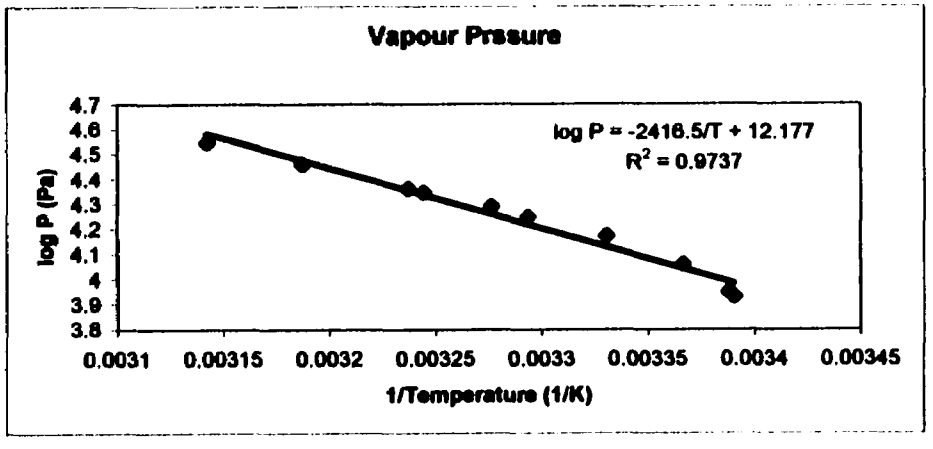
Temperature (C)	Pressure (Pa)
24.2	1.21E+04
25.2	1.25E+04
26.2	1.25E+04
29.1	1.65E+04
30.7	1.61E+04
32.8	1.87E+04
33.5	1.93E+04
34	1.86E+04
36.1	2.12E+04
38	2.40E+04
41.5	2.87E+04
43.9	3.13E+04
44.9	3.29E+04
45.6	3.39E+04

Vapour Pressure Results – Trifluoroacetic Acid



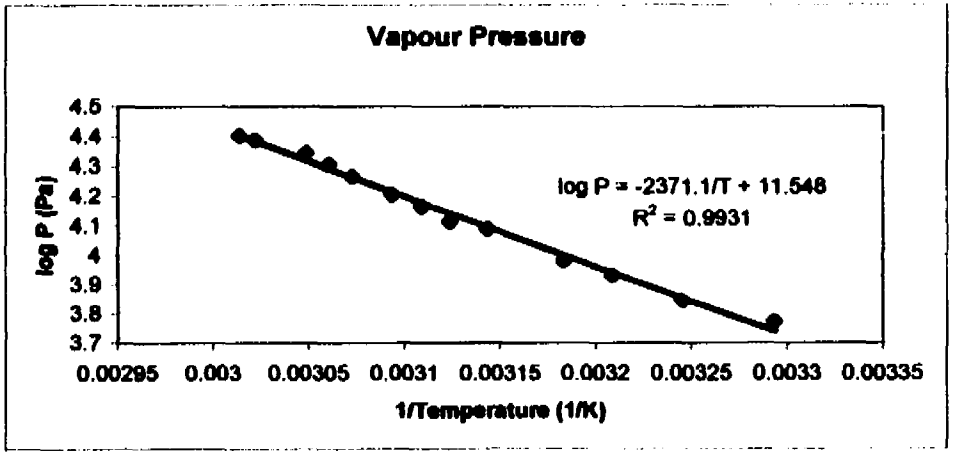
Temperature (C)	Pressure (Pa)
24	1.03E+04
24	1.06E+04
24.5	1.08E+04
24.9	1.21E+04
24.6	1.12E+04
25.5	1.35E+04
26.6	1.40E+04
27.4	1.47E+04
28.7	1.63E+04
32.9	2.02E+04
35	2.22E+04
38.9	2.60E+04
41.5	2.94E+04

Vapour Pressure Results – Trifluoroacetic Acid



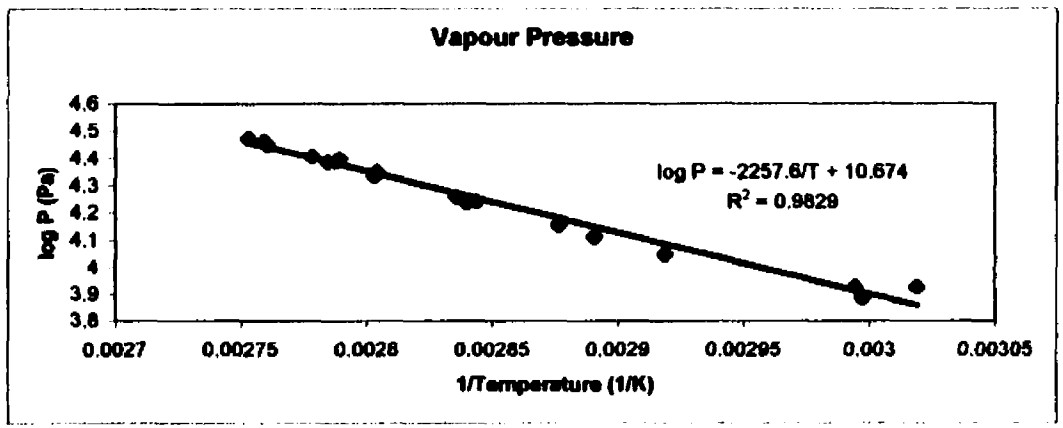
Temperature (C)	Pressure (Pa)
22	8.93E+03
21.8	8.56E+03
23.9	1.15E+04
27.1	1.49E+04
32.1	1.96E+04
30.5	1.77E+04
35.1	2.22E+04
35.8	2.30E+04
40.6	2.89E+04
45.1	3.53E+04

Vapour Pressure Results – Perfluoropropionic Acid



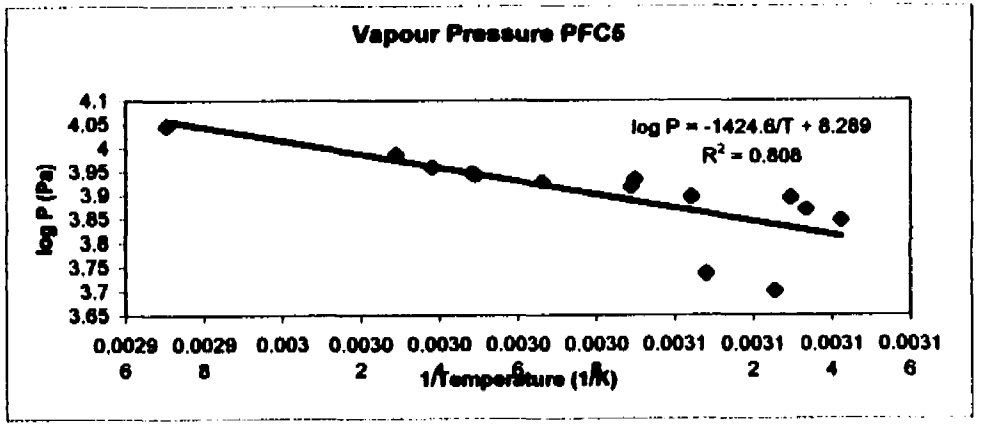
Temperature (C)	Pressure (Pa)
30.5	5.95E+03
35	7.01E+03
38.5	8.56E+03
41	9.61E+03
45	1.23E+04
47	1.30E+04
48.5	1.46E+04
50.1	1.61E+04
52.3	1.85E+04
53.6	2.03E+04
54.9	2.21E+04
57.8	2.45E+04
58.7	2.53E+04

Vapour Pressure Results – Perfluorobutanoic Acid



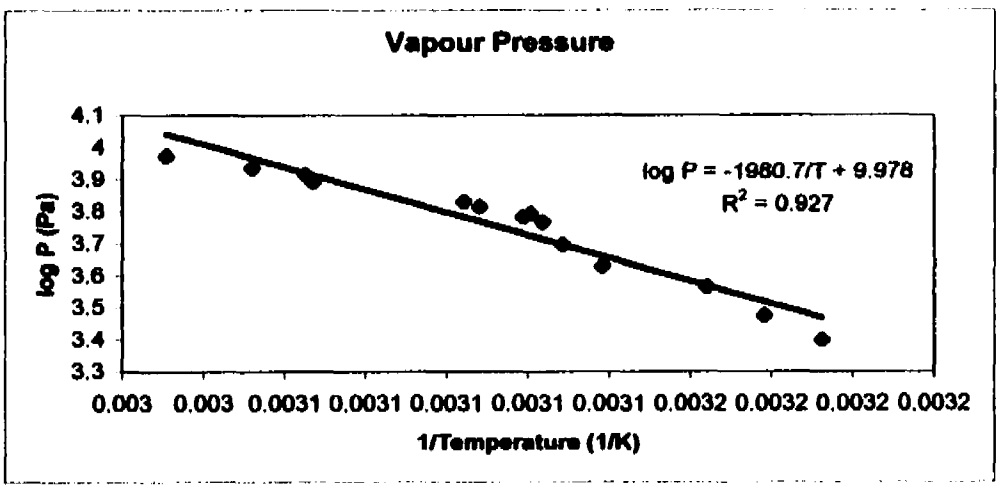
Temperature (C)	Pressure (Pa)
60.5	7.69E+03
60.8	8.48E+03
58.1	8.47E+03
69.5	1.11E+04
72.8	1.30E+04
74.5	1.43E+04
78.5	1.75E+04
79	1.73E+04
79.5	1.82E+04
83.5	2.24E+04
83.6	2.17E+04
85.4	2.51E+04
86	2.45E+04
85.6	2.46E+04
86.8	2.56E+04
89.3	2.91E+04
89.1	2.82E+04
90.1	2.98E+04

Vapour Pressure Results – Perfluoropentanoic Acid



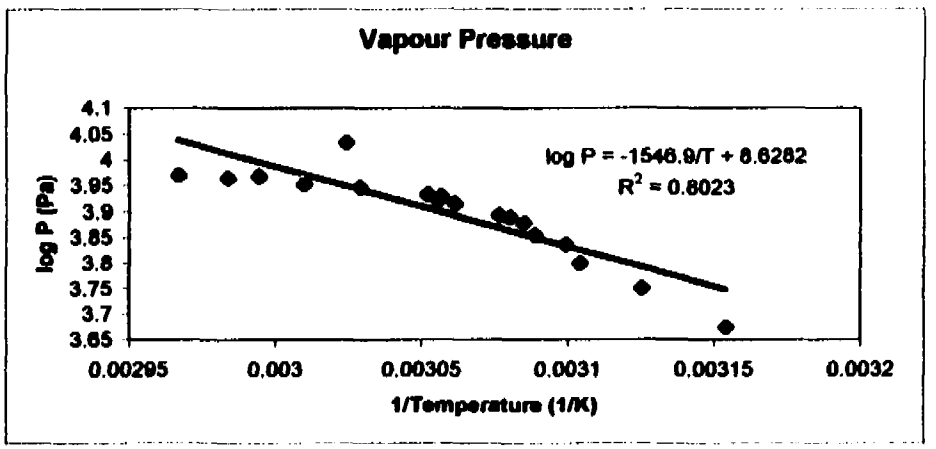
Temperature (C)	Pressure (Pa)
46.8	5.03E+03
48.6	5.45E+03
45.1	7.04E+03
46	7.43E+03
46.4	7.85E+03
49	7.89E+03
50.6	8.28E+03
50.5	8.60E+03
53	8.48E+03
54.8	8.77E+03
54.9	8.85E+03
56	9.12E+03
57	9.71E+03
63.5	1.11E+04

Vapour Pressure Results – Perfluoropentanoic Acid



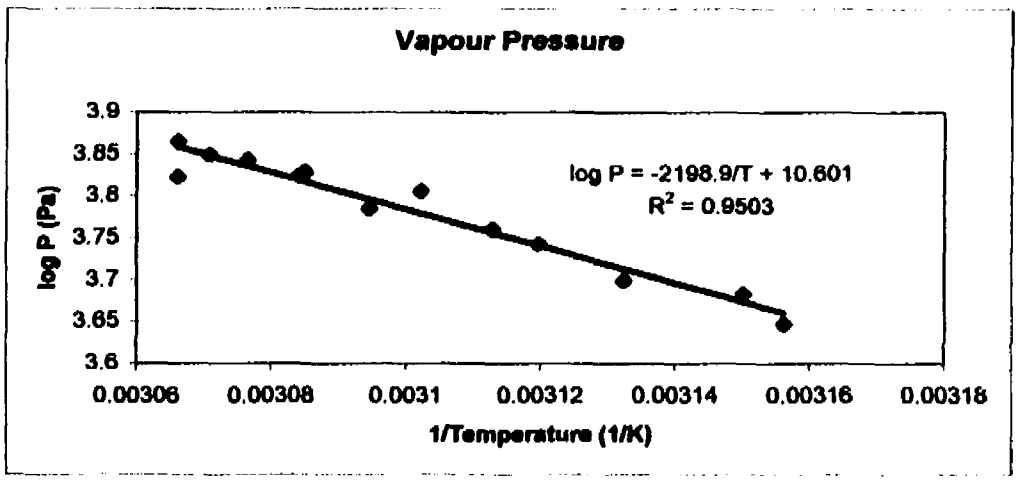
Temperature (C)	Pressure (Pa)
40.1	2.51E+03
41.5	2.99E+03
42.9	3.68E+03
45.5	4.27E+03
46.5	4.99E+03
47	5.85E+03
47.3	6.21E+03
47.5	6.05E+03
48.6	6.53E+03
49	6.77E+03
52.9	7.80E+03
53.1	8.23E+03
54.5	8.64E+03
56.8	9.43E+03

Vapour Pressure Results – Perfluoropentanoic Acid



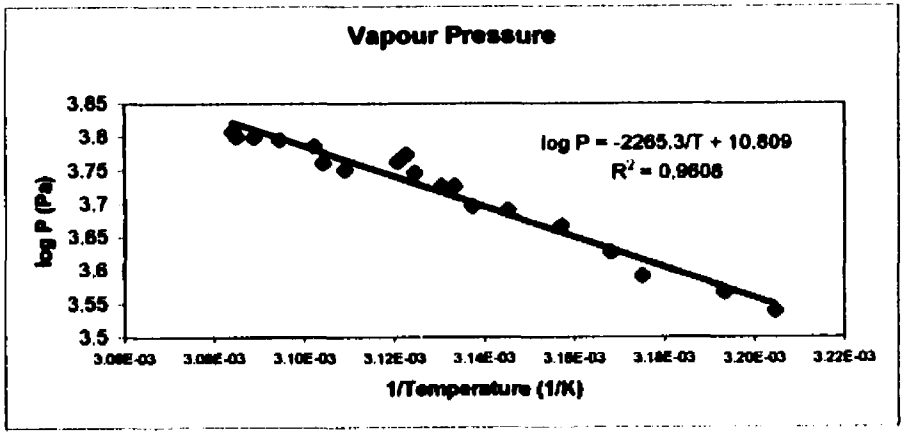
Temperature (C)	Pressure (Pa)
43.9	4.73E+03
46.8	5.65E+03
49	6.32E+03
49.5	6.88E+03
50.6	7.19E+03
51	7.57E+03
51.5	7.76E+03
51.9	7.84E+03
53.5	8.24E+03
54.1	8.37E+03
54	8.51E+03
54.5	8.57E+03
54.5	8.59E+03
57	8.87E+03
59.1	8.97E+03
60.8	9.31E+03
57.5	1.08E+04
62	9.24E+03
63.9	9.35E+03

Vapour Pressure Results – Perfluoroheptanoic Acid



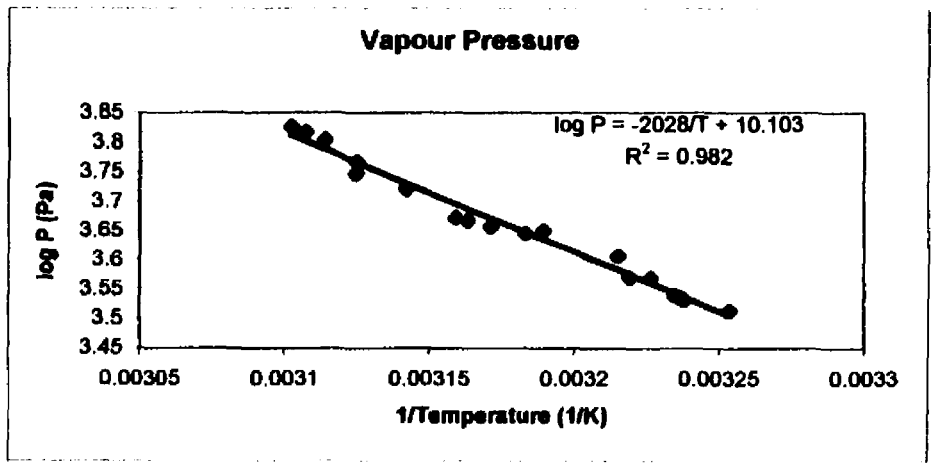
Temperature (C)	Pressure (Pa)
43.7	4.44E+03
44.3	4.83E+03
46.1	5.00E+03
47.4	5.53E+03
48.1	5.76E+03
49.2	6.40E+03
50	6.09E+03
51	6.75E+03
51.1	6.67E+03
51.9	6.97E+03
52.5	7.07E+03
53	7.35E+03
53	6.65E+03

Vapour Pressure Results – Perfluoroheptanoic Acid



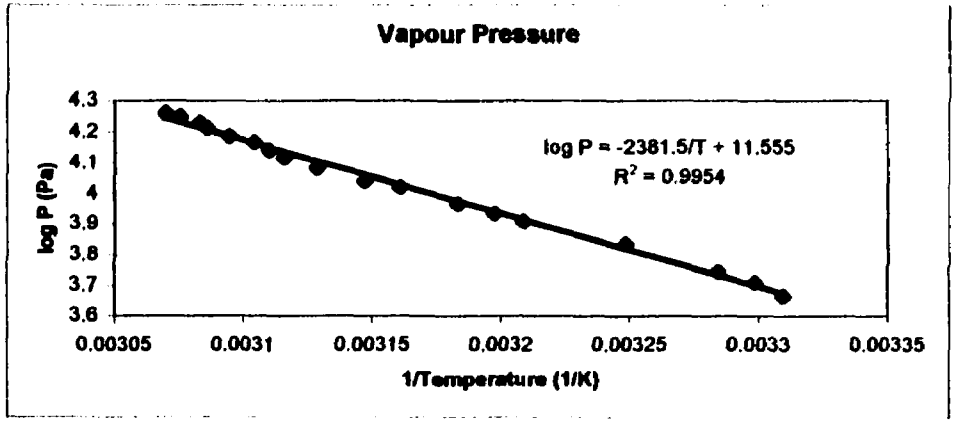
Temperature (C)	Pressure (Pa)
38.9	3.47E+03
40	3.69E+03
41.8	3.91E+03
42.5	4.24E+03
43.6	4.65E+03
44.8	4.91E+03
45.6	4.97E+03
46	5.33E+03
46.3	5.33E+03
46.9	5.59E+03
47.1	5.95E+03
47.3	5.80E+03
48.5	5.64E+03
49	5.77E+03
49.2	6.12E+03
50	6.25E+03
51	6.32E+03
50.6	6.31E+03
51.1	6.44E+03

Vapour Pressure Results – Perfluoroheptanoic Acid



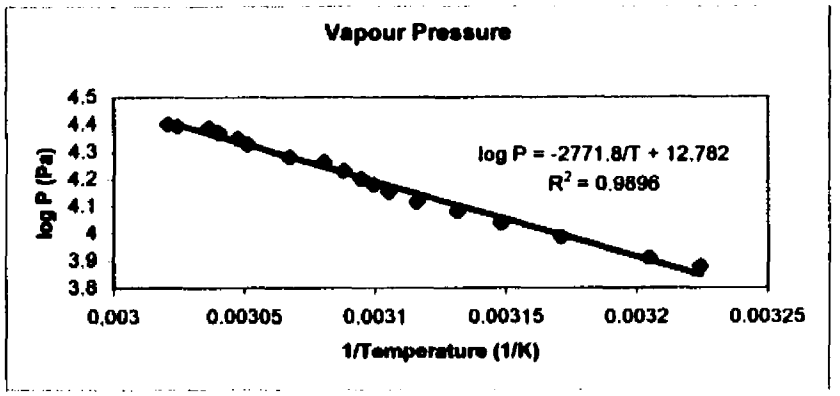
Temperature (C)	Pressure (Pa)
34.2	3.27E+03
35.7	3.40E+03
35.8	3.43E+03
36	3.47E+03
36.8	3.71E+03
37.5	3.72E+03
37.9	4.04E+03
40.4	4.48E+03
41	4.43E+03
42.2	4.55E+03
43	4.67E+03
43.4	4.71E+03
45.1	5.28E+03
46.9	5.60E+03
46.9	5.87E+03
48	6.37E+03
48.7	6.57E+03
49.2	6.71E+03

Vapour Pressure Results – Perfluorooctanoic Acid



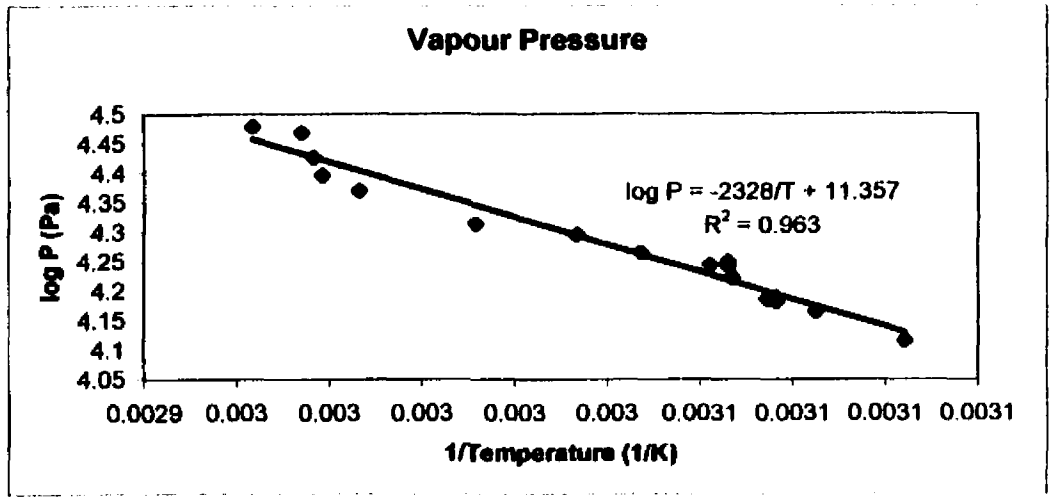
Temperature (C)	Pressure (Pa)
29	4.64E+03
30	5.13E+03
31.3	5.56E+03
34.7	6.85E+03
38.5	8.11E+03
39.6	8.61E+03
41	9.25E+03
43.2	1.05E+04
44.6	1.10E+04
46.5	1.21E+04
47.8	1.31E+04
48.4	1.38E+04
49	1.47E+04
50	1.53E+04
50.9	1.63E+04
51.2	1.70E+04
52	1.77E+04
52.6	1.82E+04

Vapour Pressure Results – Perfluorooctanoic Acid



Temperature (C)	Pressure (Pa)
37	7.56E+03
38.9	8.15E+03
42.2	9.71E+03
44.5	1.09E+04
46.2	1.21E+04
47.8	1.31E+04
48.9	1.43E+04
49.5	1.51E+04
50	1.60E+04
50.7	1.70E+04
51.5	1.83E+04
52.9	1.91E+04
54.6	2.13E+04
55	2.23E+04
55.8	2.35E+04
56.2	2.45E+04
57.9	2.53E+04
57.5	2.48E+04

Vapour Pressure Results – Perfluorooctanoic Acid



Temperature (C)	Pressure (Pa)
49	1.31E+04
51	1.46E+04
52.1	1.54E+04
52.9	1.67E+04
53.4	1.76E+04
53	1.78E+04
51.9	1.52E+04
51.9	1.55E+04
53	1.75E+04
55	1.84E+04
56.5	1.98E+04
58.9	2.06E+04
61.7	2.35E+04
62.6	2.49E+04
62.8	2.67E+04
63.1	2.95E+04
64.3	3.01E+04

Appendix B

Experimental Henry's Law Constant Results

Henry's Law Constant – Trifluoroacetic Acid

[HCl] (mol/L)	Temperature (°C)	Time (s)	$K_{II}^{\bullet}$ (Pa m^3 mol^{-1})
3.41	15	1031	0.0458
	20	905	0.0462
	25	1908.6	0.0494
	30	707	0.0557
4.26	5	304	0.0290
		1168	0.0444
		2009	0.0513
		3138	0.0545
	15	269	0.0607
		1152	0.0656
		2005	0.0630
		2764	0.0594
	20	356	0.0635
		1247	0.0591
		2242	0.0683
	25	276	0.0722
		1080	0.0636
		2110	0.0694
		2590	0.0571
	30	310	0.0676
		1087	0.0779
		1761	0.0759
5.11	15.1	956	0.0887
	25.1	1234	0.103
	35.1	750	0.120

Henry's Law Constant – Perfluoropropionic Acid

[HCl] (mol/L)	Temperature (°C)	Time (s)	K_H^* (Pa m^3 mol^{-1})	[HCl] (mol/L)	Temperature (°C)	Time (s)	K_H^* (Pa m^3 mol^{-1})
4.09	15.0	1017	1.32	5.31	15.0	1083.2	1.13
		2052.5	1.37			1922.4	0.838
		3060.2	1.10			2532.7	0.802
		4072.8	0.949			3400.3	0.877
	20.0	1315.1	0.762		20.2	1185.7	1.12
		2212.7	0.606			2132.1	1.15
		2833.7	0.577			2764.8	1.17
		4146.6	0.599			3773.2	1.21
	25.0	1020.3	0.598		25.0	1260.3	1.70
		1984.7	0.607			2123.0	1.68
		3234.4	0.812			2928.4	1.64
		4009.5	0.818			3637.1	1.77
	30.0	972.3	0.961		30.0	1181.7	2.27
		1983.2	0.942			2041.1	2.31
		2746.1	0.972			2752.6	2.40
		3756.3	0.976			3919.0	2.53
4.90	15.0	1026.0	1.69	6.13	15.2	916.4	1.93
		2392.7	1.15			1975.0	2.13
		4364.7	1.31			3197.6	1.88
		5143.8	1.50			3815.9	1.79
	20.2	828.2	2.33		20.4	2547.7	2.05
		2311.8	1.65			3370.9	1.95
		3943.9	1.16			4047.6	2.02
		4509.0	1.01				
	25.1	1001.2	1.28		25.1	901.9	1.67
		1756.9	1.49			1975.8	1.27
		2238.6	1.42			2529.5	1.57
		3101.2	1.63			2837.3	1.65
	30.0	1020.1	1.25		30.0	1181.3	2.56
		2016.1	1.68			1974.4	2.87
		3060.1	1.97			3028.2	2.92
		3967.9	2.27			3939.7	3.09

Henry's Law Constant – Perfluorobutanoic Acid

[HCl] (mol/L)	Temperature (°C)	Time (s)	K_H^* (Pa m^3 mol^{-1})	[HCl] (mol/L)	Temperature (°C)	Time (s)	K_H^* (Pa m^3 mol^{-1})
4.09	15.0	981.8	1.07	5.31	15.0	1248.8	1.12
		1791.3	1.16			1981.8	0.893
		2461.4	1.25			3111.6	0.888
						3845.1	0.882
	20.0	805.5	2.23		20.3	1099.1	1.25
		1598.4	2.29			1372.75	1.24
		2382.2	2.36			1685.5	1.44
		3200.8	2.29			2025.8	1.47
	25.0	805.4	3.00		25.0	1127.4	1.32
		1905.9	2.84			1892.1	1.54
		2445.0	2.95			2648.6	1.40
						3494.4	1.62
	30.0	787.0	1.83		30.0	1244.85	1.60
		1618.0	2.26			2324.4	1.47
		2386.4	3.35			3021.0	1.74
		3204.5	4.26			3448.9	1.82
4.90	15.0	1150.8	0.931	6.13	17.6	910	1.27
		2066.4	1.17			1509.1	1.41
		2932.0	1.03			2021.7	1.44
		3958.9	1.12			3038.6	1.70
	20.0	1077.5	1.76		23.3	1223.6	4.27
		2225.0	1.61			1937.3	4.01
		2747.9	1.63			2464.5	4.14
		3789.8	1.67			3073.6	4.37
	25.0	1026.1	2.99		30.0	791.8	5.79
		1830.4	2.59			1594.05	5.29
		2925.0	2.57			2117.1	5.58
		3530.3	2.54			2719.4	5.64
	30.0	1280.2	2.85				
		1625.4	2.40				
		2244.6	2.87				
		2724.4	3.27				

Henry's Law Constant - Perfluoropentanoic Acid

[HCl] (mol/L)	Temperature (°C)	Time (s)	K_H^* (Pa m^3 mol^{-1})	[HCl] (mol/L)	Temperature (°C)	Time (s)	K_H^* (Pa m^3 mol^{-1})
4.09	15.0	897.4	0.854	5.31	15.0	600.3	1.12
		1534.5	0.812			1245.7	1.39
		2439.7	1.02			1800.0	1.63
		3131.6	1.17			2365.7	2.01
	20.0	834.7	2.70		20.0	640.8	5.45
		1771.1	2.43			1219.9	6.04
		2369.1	2.70			1845.3	6.46
		3236.0	3.04			2404.2	6.92
	25.0	606.5	2.86		25.0	554.0	9.16
		1470.4	4.73			1148.6	13.0
		2022.9	5.02			1892.3	15.9
		2695.2	5.56			2364.6	17.6
	30.0	594.7	5.80		30.0	473.6	18.5
		1122.8	6.04			926.7	21.7
		1734.9	6.26			1465.0	23.3
		2318.2	7.05			1985.7	24.7
4.90	15.0	755.3	1.20	6.13	15.0	584.6	2.04
		1252.9	1.21			1202.0	2.97
		1857.5	1.33			1794.6	3.22
		2676.1	1.61			2367.3	4.19
	20.0	628.3	4.30		20.0	568.4	13.6
		1196.1	5.50			1217.2	17.8
		1826.8	6.09			1771.6	19.0
		2485.2	7.01			2369.2	22.2
	25.0	674.0	8.38		25.0	597.7	29.0
		1205.8	9.37			1586.7	34.0
		1683.1	9.90			2013.9	39.5
		2838.7	10.0			2396.6	33.7
	30.0	613.9	7.73		30.0	632.4	23.4
		1647.5	10.7			1201.8	27.8
		2004.2	11.0			1718.9	31.6
		2684.2	11.6			2489.2	34.5

Henry's Law Constant - Perfluorohexanoic Acid

[HCl] (mol/L)	Temperature (°C)	Time (s)	K_H^* (Pa m^3 mol^{-1})	[HCl] (mol/L)	Temperature (°C)	Time (s)	K_H^* (Pa m^3 mol^{-1})
4.09	15.0	1475.5	8.05	5.31	15.0	688.7	14.1
		2048.2	11.1			1332.6	24.7
		2996.3	15.6			2111.2	28.3
		4318.2	15.6			2839.5	23.4
	20.0	947.8	19.9		20.0	804.2	35.3
		1865.9	25.1			1477.9	49.3
		2904.3	29.2			2010.1	52.6
		3624.9	32.7			2712.0	49.0
	25.0	672.6	20.9		25.0	1001.6	67.5
		1326.6	30.2			2143.7	61.7
		2107.2	40.7			2975.5	58.8
		3015.5	39.1			4058.2	60.7
	30.0	717.5	5.45		30.0	1115.6	25.9
		1400.0	10.5			1969.7	52.3
		2175.1	15.0			2924.3	80.7
		3029.6	19.0			3946.2	144
4.90	15.0	835.7	8.35	6.13	15.0	569.3	40.8
		1492.4	10.9			1015.0	49.1
		2187.3	9.36			1497.5	57.9
		2960.2	9.96			2009.2	57.0
	20.0	816.6	12.7		20.0	483.5	45.9
		1707.7	12.9			1003.9	64.9
		2305.9	14.7			1525.6	82.2
		2972.5	14.8			1988.3	88.5
	25.0	906.9	9.46		25.0	505.5	94.1
		1564.3	13.3			1017.0	93.8
		2086.2	16.6			1966.5	92.2
		2983.0	18.8			2635.5	94.7
	30.0	780.7	44.4		30.0	741.8	62.1
		1607.2	47.6			1588.2	69.8
		2153.9	50.9			2516.0	77.9
		2936.2	60.8			3268.6	84.5

Henry's Law Constant - Perfluoroheptanoic Acid

[HCl] (mol/L)	Temperature (°C)	Time (s)	K_H^* (Pa m^3 mol^{-1})	[HCl] (mol/L)	Temperature (°C)	Time (s)	K_H^* (Pa m^3 mol^{-1})
4.09	15.0	1132.7	< MDL	5.31	15.0	952.3	2.83
		1754.1	2.74			1561.45	2.20
		2257.2	2.15			2024.7	2.12
		2717.3	1.99			2480.7	1.99
	20.0	1349.1	<MDL		20.0	682.0	<MDL
		2205.3	2.65			1117.1	1.70
		2734.4	3.62			1563.4	1.75
		3553.2	4.20			2266.0	2.38
	25.0	1318.8	<MDL		25.0	771.0	3.22
		1984.9	1.88			1449.6	2.73
		2705.2	1.77			1922.6	2.95
		3509.4	1.93			2404.0	2.97
	30.0	1375.6	<MDL		30.0	656.8	<MDL
		1884.7	1.94			1277.4	2.26
		2771.3	2.05			1797.5	2.48
		3612.3	2.16			2313.3	2.71
4.90	15.0	1167.0	5.82	6.13	15.0	867.0	<MDL
		1638.8	5.30			1832.4	3.25
		2102.1	4.54			2815.6	3.28
		2824.4	4.51			3655.2	3.13
	20.0	1082.6	<MDL		20.0	861.5	<MDL
		1683.9	6.03			1514.5	4.05
		2168.0	5.26			2120.9	4.40
		2751.7	5.80			2572.8	4.63
	25.0	1239.1	7.75		25.0	578.6	7.05
		1810.0	7.65			1036.9	5.17
		2310.6	7.80			1471.3	5.22
						2071.9	6.44
	30.0	1186.7	<MDL		30.0	860.1	7.06
		1884.9	6.33			1482.9	7.16
		2444.9	5.63			1908.4	7.55
		3027.6	5.90			2392.0	8.55

Henry's Law Constant - Perfluorooctanoic Acid

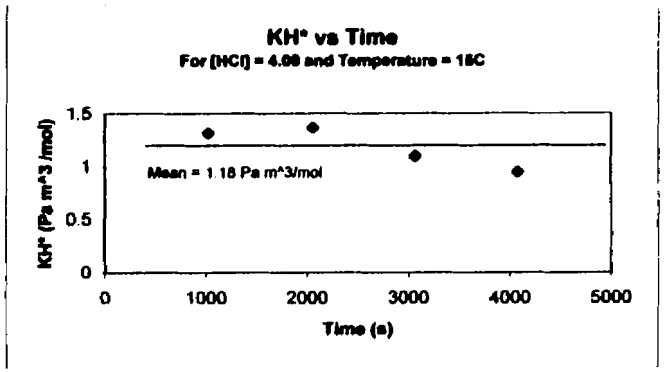
[HCl] (mol/L)	Temperature (°C)	Time (s)	K_H^* (Pa m^3 mol^{-1})	[HCl] (mol/L)	Temperature (°C)	Time (s)	K_H^* (Pa m^3 mol^{-1})
4.09	15.0	1207.8	0.213	6.13	15.0	1046.6	0.782
		2469.7	0.279			2129.1	0.807
		3494.5	0.257			3099.3	0.801
		5199.5	0.239			4059.6	0.797
	22.8	1249.8	0.572		23.0	1473.0	0.661
		2518.3	0.457			2249.9	0.599
		5095.8	0.471			3022.8	0.599
		7512.5	0.544			4384.0	0.548
	30.0	1419.3	0.644		30.0	1501.9	0.900
		2647.1	0.876			2738.6	1.09
		4742.6	0.863			3336.6	1.18
						4310.0	1.10
4.90	15.0	1791.2	0.295				
		2478.4	0.244				
		3362.2	0.280				
		5027.9	0.241				
	23.0	1671.5	0.462				
		2561.1	1.01				
		3705.9	1.57				
		4723.0	1.35				
	30.0	1610.8	0.801				
		3409.6	1.18				
		4864.0	1.70				
		6220.0	1.71				

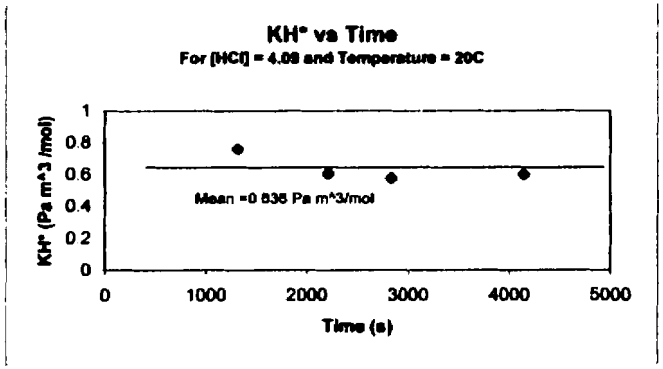
Appendix C

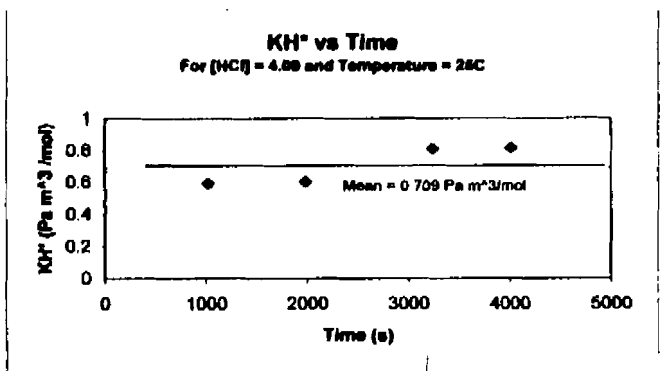
Example Calculation of Henry's Law Constant

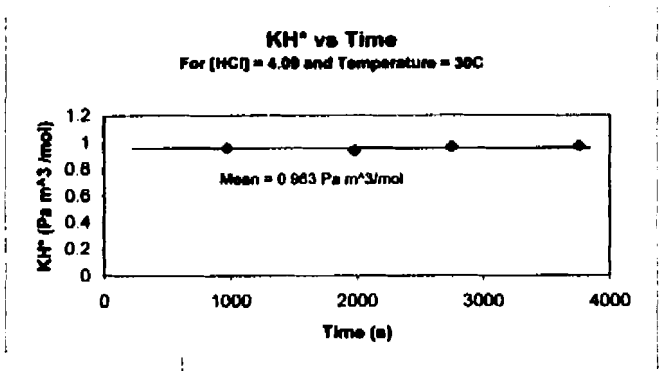
For Perfluoropropionic Acid

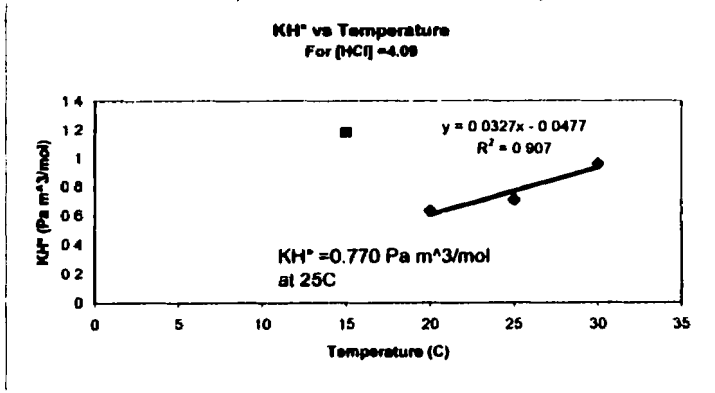
KH' of PFPrA for HCl= 4.09



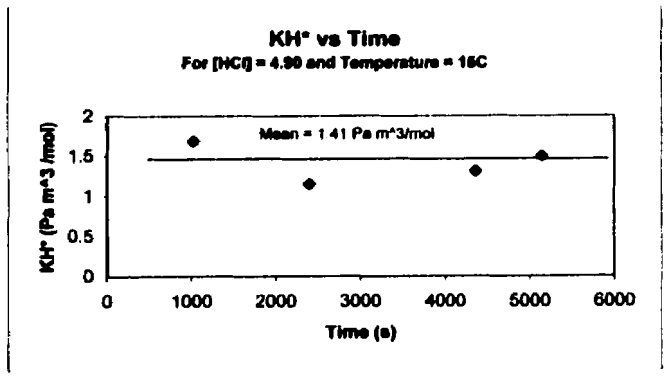


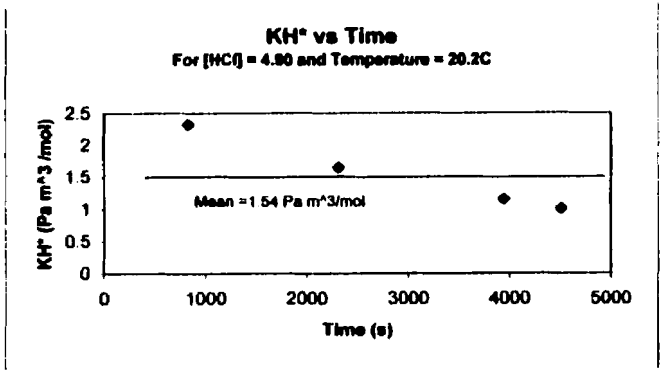


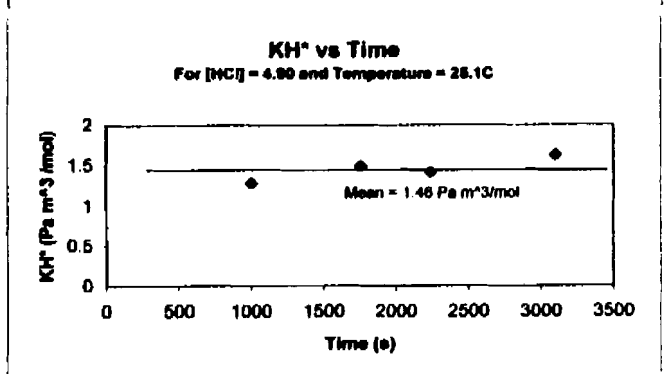


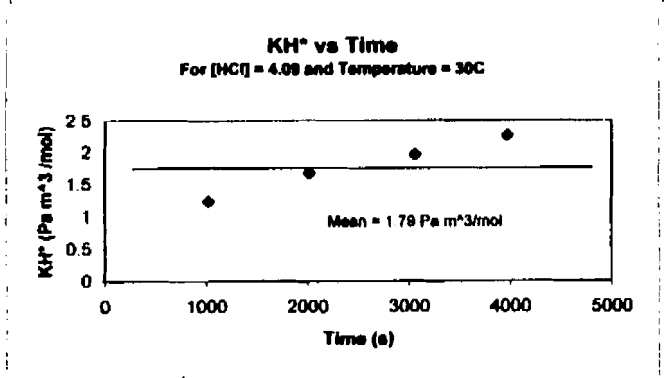


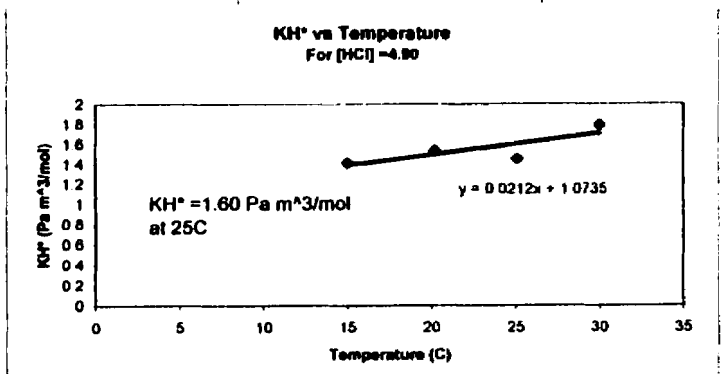
KH* of PFPrA for HCl= 4.90



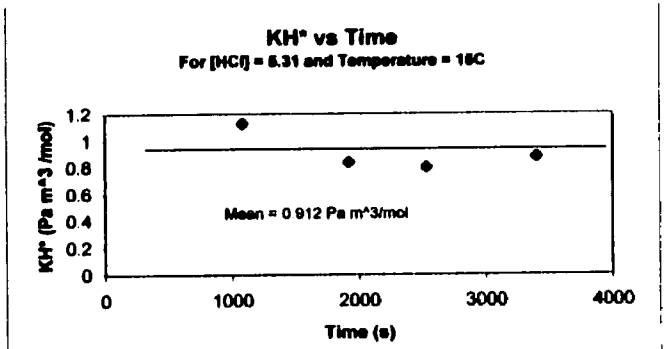


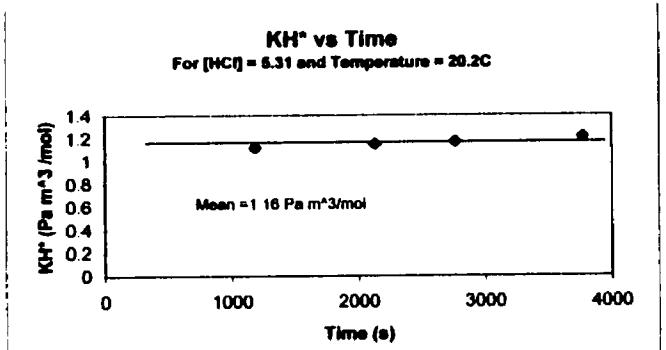


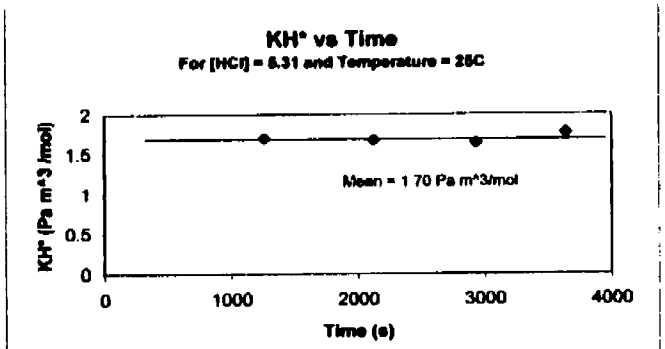


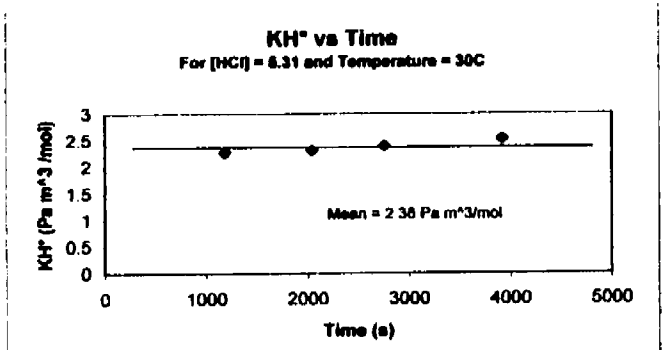


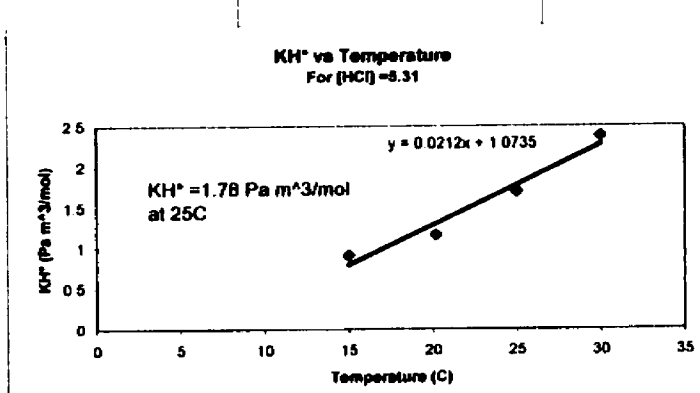
KH* of PFPrA for HCl= 5.31



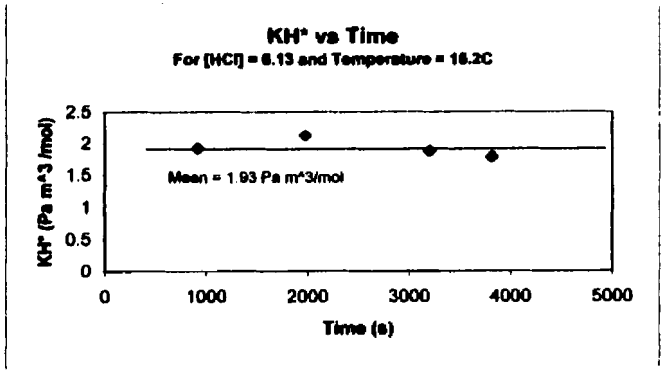


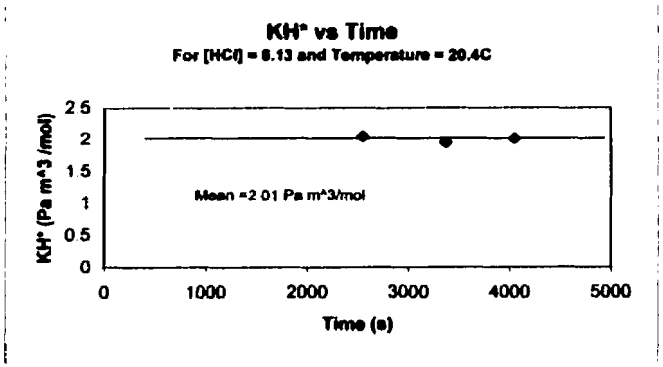


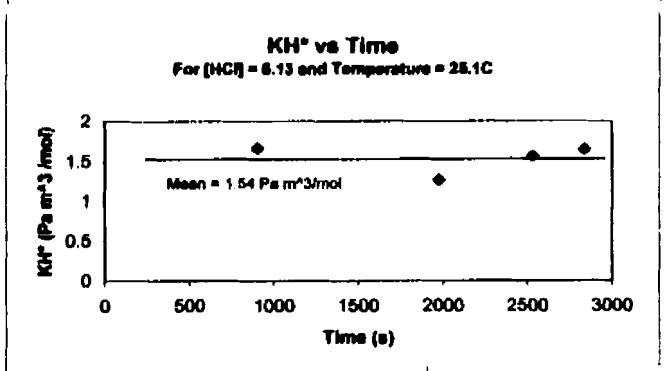


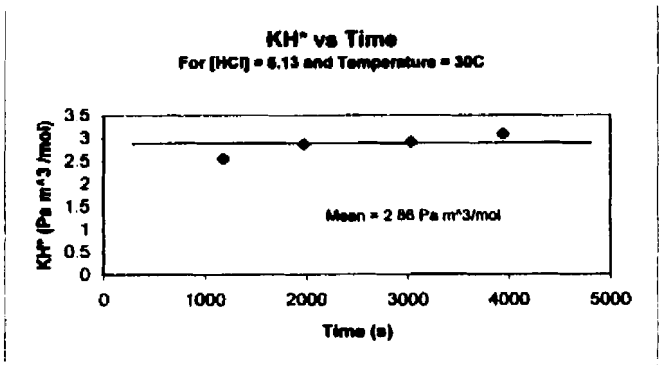


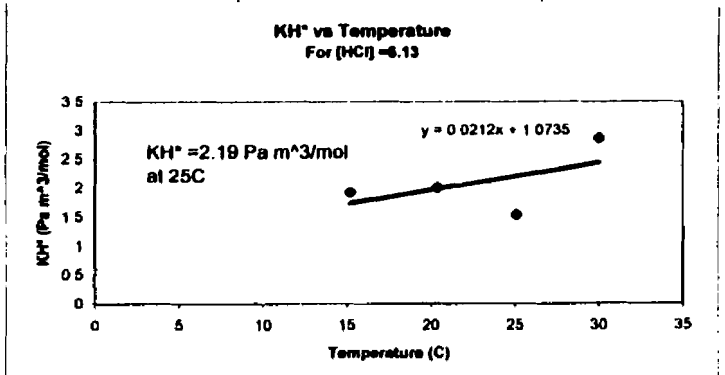
KH* of PFPrA for HCl= 6.13

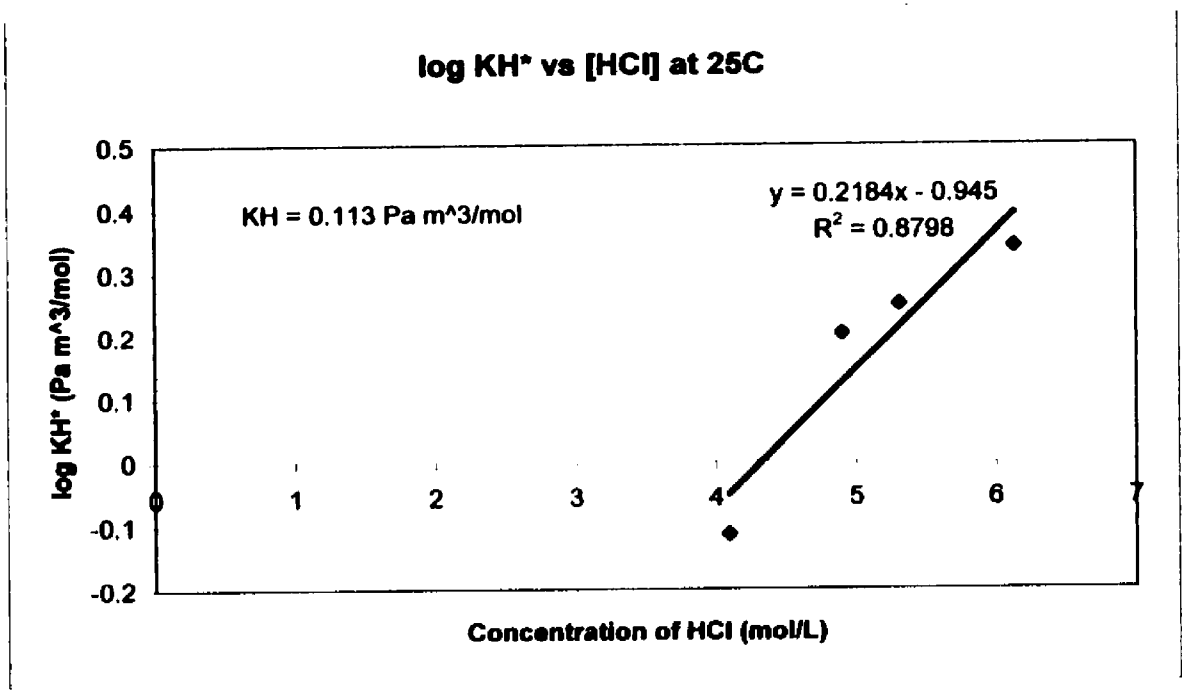











log KH* vs [HCl] at 25C
KH = 0.113 Pa m^3/mol
y = 0.2184x - 0.945
R2 = 0.8798
log KH* (Pa m^3/mol)
0.5
0.4
0.3
0.2
0.1
0
-0.1
-0.2
0
1
2
3
4
5
6
7
Concentration of HCl (mol/L)