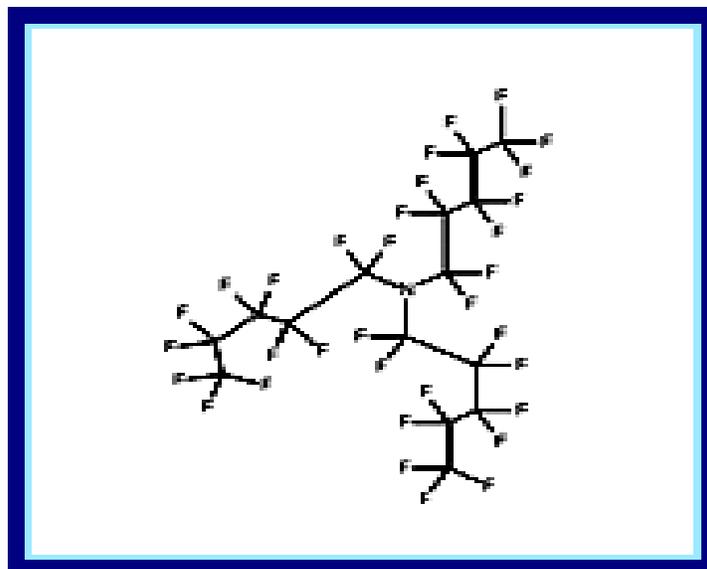


Solute Partitioning in Industrial Fluorinated Solvent FC-70
(Perfluorotripentylamine)

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Objective

This experiment is part of a larger study on transport properties (permeability, partition and diffusion) of Teflon AF, stable fluorinated membranes. Our part of the study focuses on headspace gas chromatography (HSGC) experiments to investigate the partition coefficients between two phases to help understand 'intermiscibility' effects.

Background

This particular experiment investigates organic solutes infinite dilution activity coefficients and their relative changes as concentration increases in fluorinated solvent. Simultaneous experiments were conducted in chloroform (CHCl_3) to compare the results. Industrial solvent FC-70 (Perfluorotripropylamine) was chosen because of its highest stability and selectivity for fluorine compounds, a property that is very important in organic synthesis and Teflon chemistry. FC-70 is compatible with sensitive materials (including metals, plastics and elastomers). FC-70 is used for solvent extraction of fluorine compounds. It is non-flammable, non-toxic and leaves no residue upon evaporation.

Vapor phase concentration of any complex system can be studied if the solute is sampled and measured by a gas chromatographic technique. The headspace gas chromatography (HSGC) developed by Dr. Abul Hussam is such a technique. The inherent sensitivity of modern capillary gas chromatographic technique combined with a computer controlled gas sampling, injection, sample equilibration, and data handling techniques allows very precise and accurate measurement of partition coefficients, infinite dilution activity coefficients and other solution based thermodynamic properties. The HSGC precisely samples 10^{-12} mols out of 10^{-4} mols. Vapor pressure of extremely diluted solutions can be studied accurately. The only limitation is that the solute must be present in the vapor phase >0.1 torr.

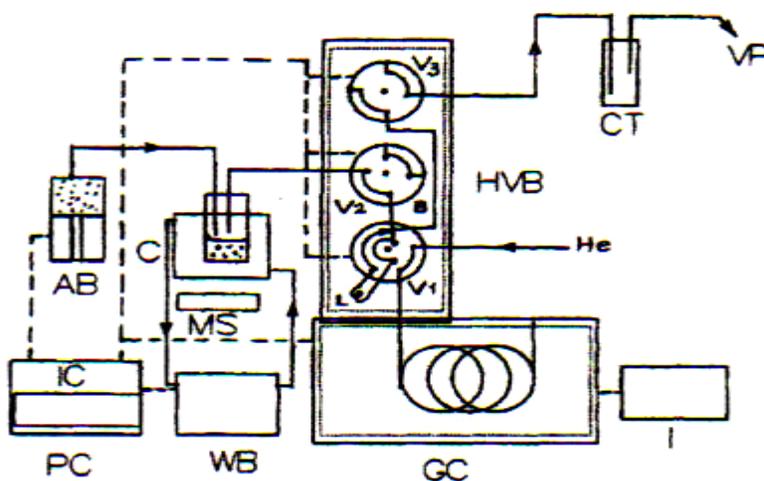


Figure 1.

Block diagram of the headspace gas chromatograph. PC, Personal computer; IC, interface controller; WB, water bath; GC, Gas Chromatograph; I, integrator; MS, magnetic stirrer; C, cell; AB, autoburet; HVB, heated valve box (thermostated to 165 °C); CT, cold trap; VP, vacuum pump; L, sampling loop; V1, six-port gas sampling valve; V2 and V3, four-port sample selection valves; and B, ballast. Fused silica vapor transfer line between C and V2 is also thermostated to 165 °C. Solid lines indicate fluid transfer tubing, and dashed lines indicate electrical connections.”

The three valves in the heated valve box (HVB) are V1, a six-port gas sampling valve, and V2 and V3, four-port sample selection valves.

As shown in the vapor loading position, a 50 μL of vapor can be sampled from the thermostated cell and injected on a fused silica capillary column without sample splitting. Critical sample transfer lines are made of fused silica to maintain inertness and reduce sample adsorption. The computerization allowed a precise control of valve activation, temperature of thermostatic cell, activation of the autoburet, control of solute- solvent ratio, the GC and the integrator at all times. This excellent sampling precision is rarely achieved by manual GC or commercial HSGC.

Experimental

Initially industrial grade fluorinated solvent (FC-70) was loaded into the sample cell (C) and a mixture of four known concentrations (solute stock solution) was loaded into the pre-calibrated autoburet (AB). The autoburet was programmed to add precise amount of the known stock solution. Critical sample transfer lines were made of fused silica (5% phenyl, 95% methyl silicon) to maintain inertness and reduce sample adsorption. After sample equilibration the vapor was sampled, injected on the column, and analyzed by the GC. This procedure may continue after each aliquot addition to obtain a series of concentration dependent peak areas which will be applied to calculate vapor pressure. The data was then analyzed in the appropriate models to calculate infinite dilution activity coefficients, vapor-liquid (or solid) partition coefficients, transfer free energies of solutes from one phase to another phase, hydrogen bond donor acceptor equilibrium constants etc. It should be noted that a single experiment can be used to obtain such properties for many solutes at a time.

Experimental Protocol:

- Autosyringe was calibrated and programmed to add $2.68 \times 10^{-3}\text{g}$ in 10s intervals
- 30 additions, 5 blank and two replicate runs for each addition
- 15 s sampling time
- 15 s residence time
- 300 s injection time
- 20 min equilibration time

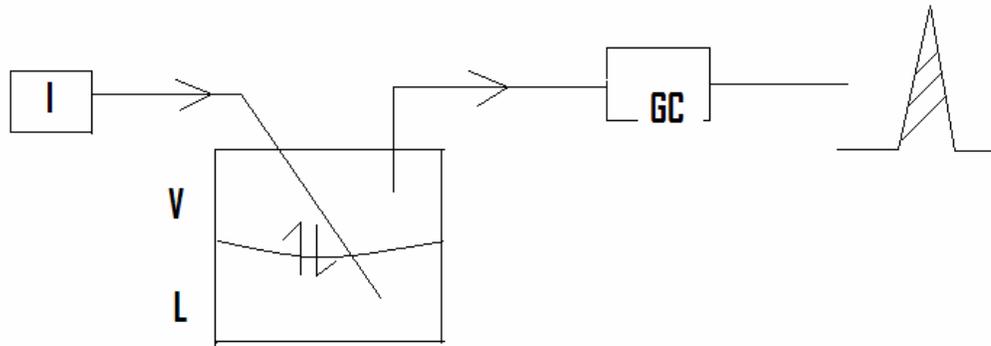


Figure 2.

Simple schematic diagram of gas - liquid equilibration. I, sample injector; V, vapor phase; L, liquid phase; GC, gas chromatograph

Results and Discussion

Activity Ratio Method:

$$A_o \propto P_o$$

$$PV = nRT \quad A \propto n_i \propto P_i$$

$$\gamma_i = (p_i / p_o)(1/x_i) = (A_i / A_o)(1/x_i)$$

Activity coefficient (γ) for each addition can be calculated using the above relationship. The plot against the mole fractions determines the infinite dilution activity coefficient of each solute.

Table 1.

Infinite dilution activity coefficients of solutes in chloroform and FC-70 at 25°C. The results are based on the intercept of activity coefficient vs solute mole fraction as shown in the graphs

| Solute | γ^{∞} Chloroform Pure | γ^{∞} Chloroform with FC-70 | γ^{∞} FC-70 Neat | γ^{∞} FC-70 with chloroform |
|-------------------------|---|---|------------------------------------|--|
| Pentafluoronitrobenzene | 1.225 | 3.35 | 16.3 | 12.7 |
| Nitrobenzene | 1.5 | 3.15 | 103.4 | 63.1 |
| Toluene | 0.147 | 0.88 | 12.2 | 12.45 |
| Trifluorotoluene | 0.42 | 2.76 | 5.9 | 6.0 |

$\gamma^{\infty} = 1 \rightarrow$ solute interaction in the whole solvent

$\gamma^{\infty} < 1 \rightarrow$ Attractive Solute – Solvent interaction

$\gamma^{\infty} > 1 \rightarrow$ Repulsive Solute – Solvent interaction

Increasing $\gamma^{\infty} \rightarrow$ Repulsive Solute – Solute (dissociation)

Decreasing $\gamma^{\infty} \rightarrow$ Attractive Solute – Solute (association)

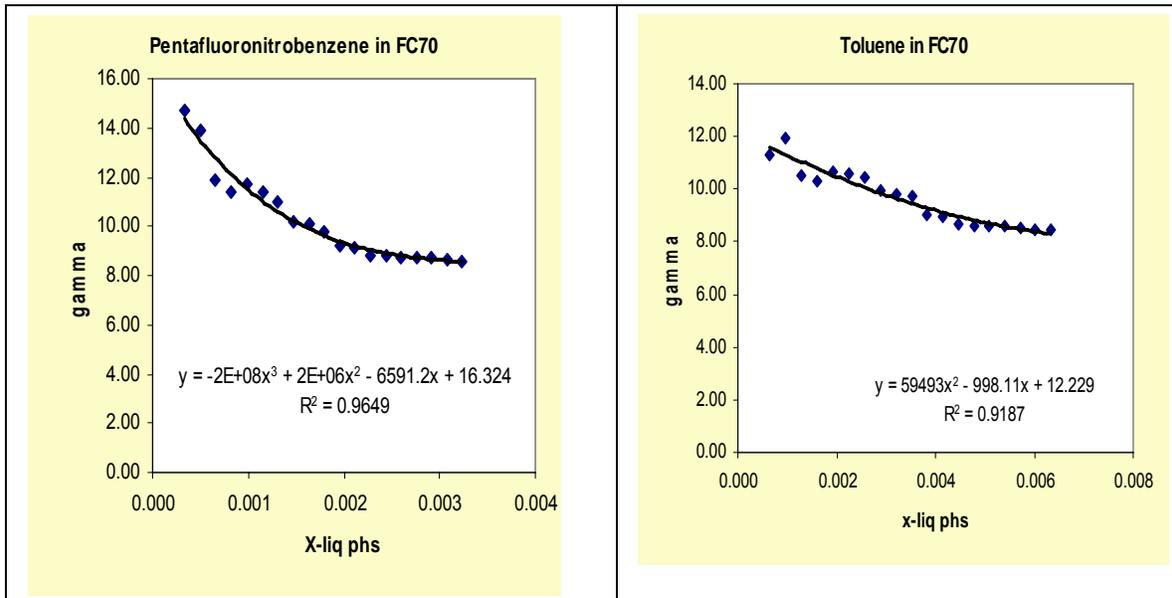


Figure 4.
Solute in FC-70

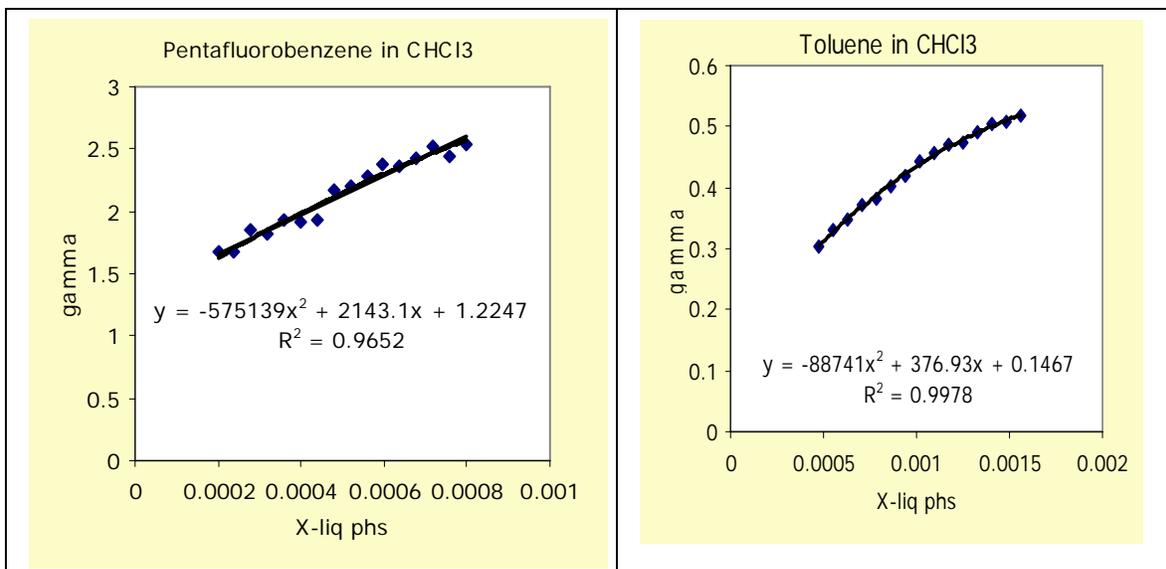


Figure 5.
Solutes in CHCl₃

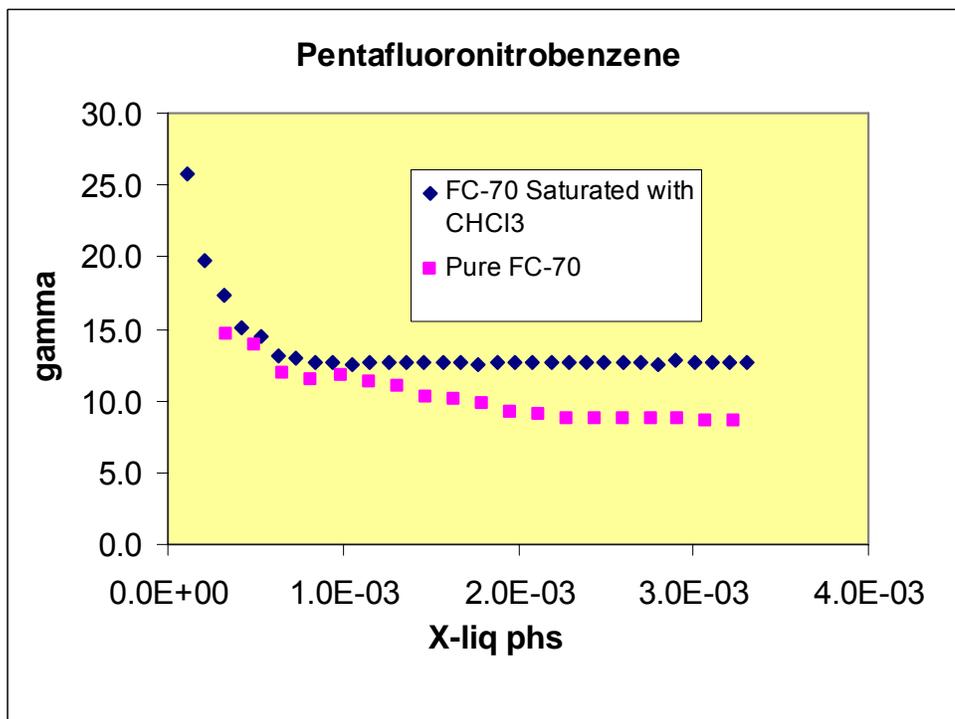


Figure 6.
The effect of CHCl₃ in FC-70

Conclusion

Infinite dilution activity coefficients (γ^{infinity}) were obtained from the extrapolation of data near saturation region. The general trend shows that the activity coefficients change rapidly at low mole fraction and become more constant in the millimole fraction region. This behavior cannot be attributed to the loss of solute due to sampling. For example, in a mixture containing 10^{-4} mols of toluene in chloroform, the headspace sampling removes 10^{-10} mols from the vapor phase. This is about a millionth fraction lost in sampling even for the most volatile toluene. The sample graphs in figure 6 show the entire data set. There is $\sim 10\%$ error in reproducibility except for nitrobenzene which is slightly higher. The initial values may indicate surface effects on activity coefficient. The up and down trends in initial values may indicate repulsive and attractive surfaces, respectively. If this is true, then nitrobenzene appears to be attractively interacting and pentafluoronitrobenzene is repulsively interacting with the surface of FC-70. On the other hand the bulk activity coefficients indicate the opposite behavior. It appears that the halogens in both solvents dominate the surface and thus repel all Lewis electrons and possibly the aromatic ring electrons. Comparing neat and mutually saturated solvents show that FC-70 solubility in chloroform has significantly affected the γ^{infinity} . Whereas, FC-70 saturated with chloroform did not change the γ^{infinity} except for nitrobenzene. The properties of fluoruous solvent FC-70, investigated in this experiment improve the understanding of fluoruous membrane transport system.