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SOLUBILITY PROPERTIES OF SILOXANE POLYMERS FOR CHEMICAL SENSORS

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Introduction

Many chemical sensors rely on a sorbent material to collect and concentrate analyte molecules at the sensor's surface where they can be detected.[1] Ideally, this sorbent material will impart the chemical sensor with both sensitivity and selectivity for the target species. If the sensor is to be reversible, then the species must also desorb from the material or be actively removed by some process such as catalytic destruction. Polymer materials offer many attractive features for chemical sensing. Organic compounds are readily sorbed in a reversible fashion, selectivity can be altered by varying the chemical structure, and polymer materials can be processed into thin films.

In this paper, we will discuss the factors that govern the sorption of vapors by organic polymers. The approach described has been applied in the past for the design and selection of polymers for acoustic wave sensors.[1-6] However, the principles apply equally well to the sorption of vapors by polymers used on optical chemical sensors. For example, the polymer could be applied as a thin film to a planar waveguide, as the cladding along the length of an optical fiber, or to the end of an optical fiber. Species sorbed into the polymer could then be detected by a change in an optical signal.

Absorption and the Partition Coefficient

In this paper, we will focus on absorption of vapors into the bulk of polymer materials. This is to be distinguished from adsorption, where the sorbed species resides only on the surface of a material. Absorption is dependent on the strengths of various fundamental interactions between the absorbed species and the sorbent material, and can be modeled using solubility concepts.

The thermodynamic measure of the equilibrium distribution of a vapor between the gas phase and a sorbent polymer phase is given by the partition coefficient, K:

$$K = C_S / C_V \quad (1)$$

As shown in Figure 1, C_S represents the concentration of the vapor absorbed in the polymer, and C_V represents the concentration of the vapor in the gas phase.

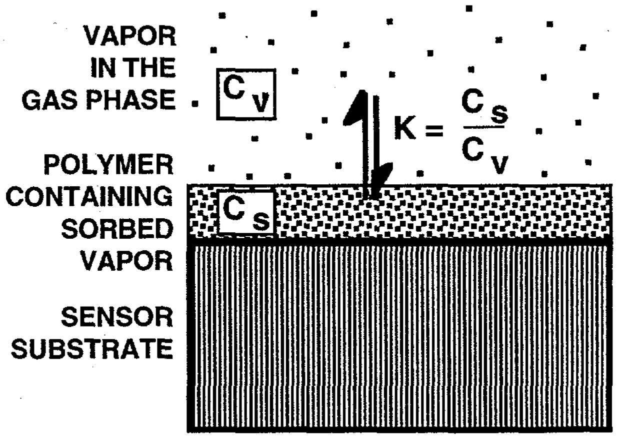

Figure 1. Illustration showing the absorption of vapor from the gas phase into a sorbent polymer phase.

Since a chemical sensor's response to a given gas phase vapor concentration depends on the amount of vapor sorbed by the sorbent polymer, the goal in creating a sensitive chemical sensor is to design or select a polymer with a favorable partition coefficient for the vapor of interest. This principle can be shown more explicitly in equations 2-4:

$$Q = f(C_V) \qquad (2)$$

$$Q = f(C_S) \qquad (3)$$

$$Q = f(KC_V) \qquad (4)$$

Equation 2 corresponds to a typical laboratory experiment where the analytical signal, Q, of the sensor is measured in response to the test gas phase vapor concentration. However, the sensor's response is actually a function of the concentration of the analyte in the sorbent layer on the sensor's surface, as shown in equation 3. Equation 4 follows from equation 3 and equation 1. Equation 4 is a general relationship that shows how sensor responses depend on the partition coefficient. Other aspects of the sensor's response, which depend on the transduction mechanism of the particular type of sensor, are accounted for by the function operating on KC_V in equation 4.

Solubility Model for Absorption

The absorption process involves the initial adsorption of vapor molecules on the polymer surface, followed by dissolution of the adsorbed molecules into the bulk of the polymer. Therefore, the vapor can be regarded as the solute, and the sorbent polymer as the solvent. The dissolution process can be examined in terms of three conceptual steps. A cavity must form in the solvent through the breaking of solvent-solvent interactions; this process is endoergic. Then the monomeric solute fills the cavity with concomitant reorganization of solvent around the cavity. Finally, attractive interactions develop between the solute and the solvent. These are by definition solubility interactions; they are exoergic and favor sorption.

The types of solubility interactions that develop between neutral organic species and polymers include dispersion interactions (also known as London forces or induced-dipole/induced-dipole interactions), dipole/induced-dipole interactions (also known as induction interactions), dipole/dipole interactions (also known as orientation interactions), and hydrogen-bonding interactions. (The general term van der Waals interactions includes dispersion, induction, and orientation interactions, as well as electrostatic interactions involving charges and polarizable or dipolar species.) Between any particular vapor and polymer, the interactions that develop will depend on the particular properties of the vapor and polymer, including their polarizability, dipolarity, hydrogen-bond basicity, and hydrogen-bond acidity. These properties are known as solubility properties, and they are determined by chemical structure. In all but the simplest sorption processes, multiple interaction types occur simultaneously.

Given this conceptual framework, it follows logically that it should be possible to model sorption processes in terms of the solubility properties of the interacting species. To this end, a set of solvation parameters have been developed that describe the particular solubility properties of individual solute molecules.[7] These are used in linear solvation energy relationships (LSERs) that model the sorption process as a linear combination of terms representing particular interactions. For the absorption of vapors into a particular polymer, the relationship takes the form given in equation 5:

$$\log K = c + r R_2 + s \pi_2^H + a \Sigma\alpha_2^H + b \Sigma\beta_2^H + l \log L^{16} \qquad (5)$$

The parameters R_2, π_2^H, $\Sigma\alpha_2^H$, $\Sigma\beta_2^H$, and $\log L^{16}$ are solvation parameters that describe the solubility properties of the solute vapors. Examples for selected solute vapors representing various chemical classes are given in Table 1. Specifically, R_2 is a calculated excess molar refraction parameter that provides a quantitative indication of polarizable n- and π-electrons;[8] π_2^H measures the ability of a molecule to stabilize a neighboring charge or dipole;[9] $\Sigma\alpha_2^H$ and $\Sigma\beta_2^H$ measure effective hydrogen-bond acidity and basicity, respectively;[7] and L^{16} is the gas-liquid partition coefficient of the solute on hexadecane at 25°C (determined by gas-liquid chromatography).[10] (L is the symbol for the Ostwald solubility coefficient, which is defined identically to the partition coefficient

Table 1. Solvation Parameters for Various Organic Vapors

	Polarizability	Dipolarity/ Polarizability	Acidity	Basicity	Dispersion/Cavity
Solute	R_2	π_2^H	$\Sigma\alpha_2^H$	$\Sigma\beta_2^H$	$\log L^{16}$
n-Hexane	0.000	0.00	0.00	0.00	2.668
Isooctane	0.000	0.00	0.00	0.00	3.106
Dichloromethane	0.387	0.57	0.10	0.05	2.019
Tetrachloromethane	0.458	0.38	0.00	0.00	2.823
Trichloroethene	0.52	0.37	0.08	0.03	2.997
Diethyl ether	0.041	0.25	0.00	0.45	2.015
Butanone	0.166	0.70	0.00	0.51	2.287
Ethyl acetate	0.106	0.62	0.00	0.45	2.314
Acetonitrile	0.237	0.90	0.07	0.32	1.739
Triethylamine	0.101	0.15	0.00	0.79	3.040
N,N-Dimethylacetamide	0.363	1.33	0.00	0.78	3.717
Methanol	0.278	0.44	0.43	0.47	0.970
Ethanol	0.246	0.42	0.37	0.48	1.485
Hexafluoropropan-1-ol	-0.240	0.55	0.77	0.10	1.392
Triethyl phosphate	0.000	1.00	0.00	1.06	4.750
Benzene	0.610	0.52	0.00	0.14	2.786
Toluene	0.601	0.52	0.00	0.14	3.325

as in equation 1.) The L^{16} parameter is a combined measure of dispersion interactions that increase L^{16} and the cost of creating a cavity in hexadecane leading to a decrease in L^{16}. These solvation parameters have been determined for some 2000 compounds and have been tabulated in recent papers.[7,11] With the exception of R_2, the solvation parameters are all derived from thermodynamic measurements of equilibrium phenomena.

The coefficients in equation 5, s, r, a, b, and l, characterize the properties of the polymer that are complementary to those of the vapor. For each polymer under consideration, these coefficients and the constant, c, are determined by regressing measured partition coefficients of a diverse set of vapors against the solvation parameters for those vapors. Usually, the required partition coefficients are determined by a well established method based on gas chromatographic measurements.[12] The r-coefficient provides a measure of polymer polarizability. This coefficient is normally slightly positive, but can be negative if the polymer contains fluorine atoms. The s-coefficient is related to the polymer dipolarity/polarizability. The a-coefficient measures the sorbent phase hydrogen-bond basicity that interacts with the solute hydrogen-bond acidity, while the b-coefficient measures the sorbent phase hydrogen-bond acidity that interacts with the solute hydrogen-bond basicity. The l-coefficient is a combined measure of dispersion interactions that tend to increase l and cavity effects that tend to decrease l.

Once an LSER equation for a polymer has been determined, it can be used for a number of purposes. The coefficients provide a measure of the polymer's solubility properties. The values of the individual terms, $r\,R_2$, $s\,\pi_2^H$, $a\,\Sigma\alpha_2^H$, $b\,\Sigma\beta_2^H$, and $l \log L^{16}$, can be calculated for specific vapor/polymer pairs, and these indicate the contributions of particular interactions to the overall sorption process. This aids in understanding which interactions are most important. Finally, partition coefficients can be predicted for any vapor whose solvation parameters are known.

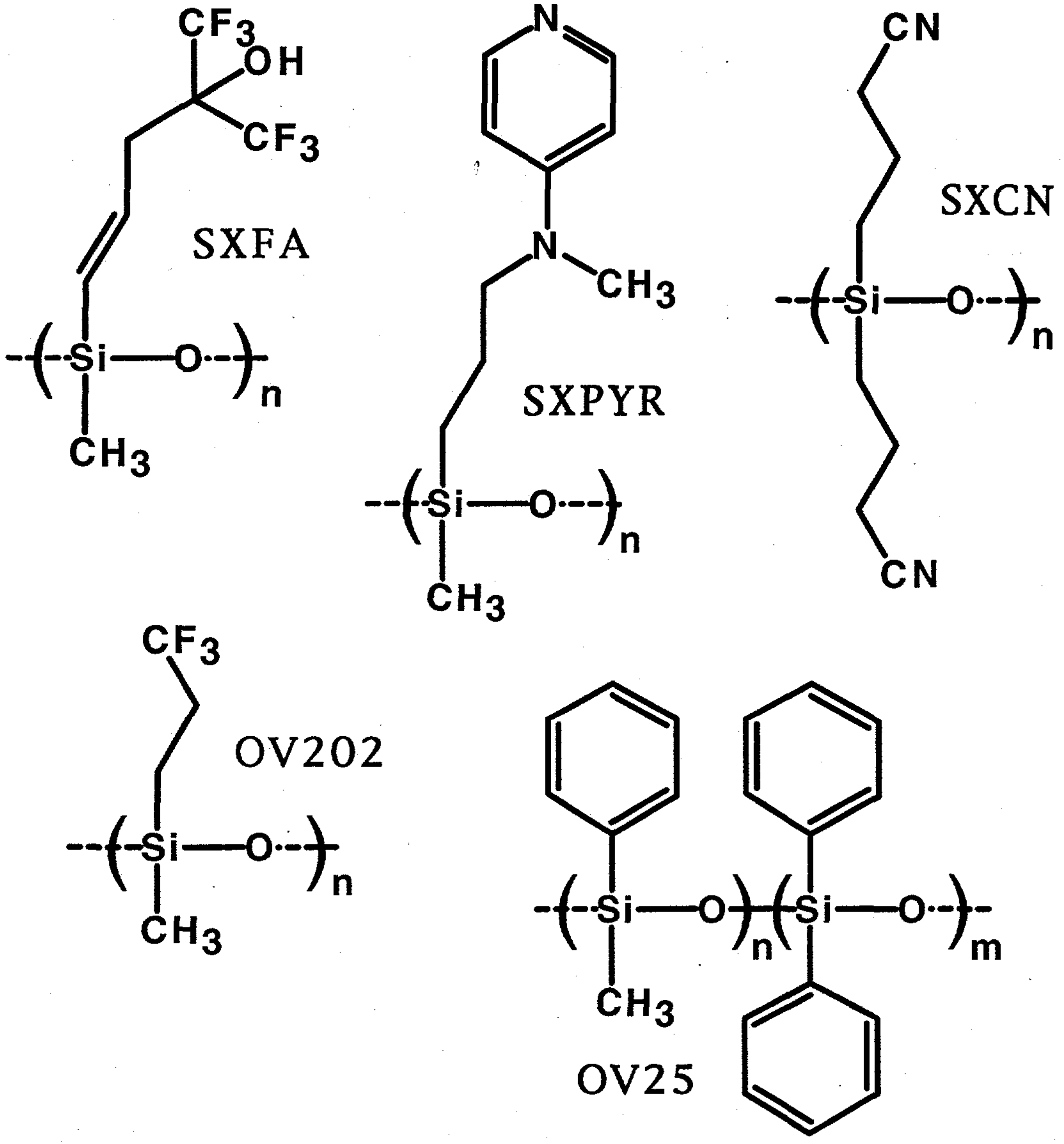

Figure 2. Repeat units of the structures of five siloxane polymers.

Table 2. LSER Coefficients for Five Substituted Siloxane Polymers [a]

	Polarizability	Dipolarity/ polarizability	Basicity	Acidity	Dispersion/ cavity	Constant
Polymer[a]	r	s	a	b	l	c
SXFA	-0.417	0.602	0.698	4.250	0.718	-0.084
SXPYR	-0.189	2.425	6.780	0.000	1.016	-1.938
SXCN	0.000	2.283	3.032	0.516	0.773	-1.630
OV202	-0.480	1.298	0.441	0.705	0.807	-0.391
OV25	0.177	1.287	0.556	0.440	0.885	-0.846

[a] The structures of these polymers are shown in Figure 2.

Example Siloxane Polymers

LSER relationships have been determined for a variety of polymers and other sorbent materials.[3,4,13] For illustrative purposes, we have selected a set of siloxane polymers for consideration. The sorbent properties of siloxane materials can be varied by the particular organic functional groups pendant to the chain, while the polymer backbone remains constant. Siloxane polymers are usually elastomeric which provides rapid and reversible vapor sorption. In addition, polysiloxanes are already in use on optical fibers: polydimethylsiloxane is a well-known fiber optic cladding material. The structures of the five polysiloxanes we will discuss are shown in Figure 2. The LSER coefficients for these polymers are given in Table 2.

The first polymer in Table 2, SXFA, has pendant hexafluoroisopropanol groups. These groups result in strong hydrogen-bond acidity, as indicated by the large b-coefficient. By contrast, the pendant aminopyridyl groups of SXPYR result in strong hydrogen-bond basicity, as indicated by the large a-coefficient. These groups are also dipolar, resulting in a large s-coefficient. SXCN is also basic and dipolar as a result of the pendant nitrile groups. Many organic functional groups are both dipolar and basic. Nitrile groups represent strong dipolarity with only moderate basicity. Hence, the a-coefficient of SXCN is only about half that of SXPYR. OV202 is a well-known chromatographic stationary phase with trifluoropropyl groups. This phase provides moderate dipolarity without significant basicity (moderate s-coefficient and small a-coefficient). The last polymer, OV25, is also a chromatographic stationary phase. It is a nonpolar phase whose pendant phenyl groups afford a polarizability that is greater than that of simple polydimethylsiloxane. Polarizability is indicated by the positive r-coefficient and moderate s-coefficient.

The individual interaction terms for each of five vapors on each of the five polymers have been calculated and these are listed in Table 3. These calculations show which interactions are most important between particular vapor/polymer pairs. Isooctane is a nonpolar hydrocarbon capable only of dispersion interactions. On all polymers the only non-zero interaction term for isooctane is the $l \log L^{16}$ term. Dispersion interactions play an important role in the sorption of all vapors and the $l \log L^{16}$ term is significant for all vapor/polymer pairs. Trichloroethene is more polarizable and dipolar than isooctane; as a result, the $s\,\pi_2^H$ term becomes significant depending on the dipolarity and polarizability of the polymer. Triethylamine is a basic vapor with minimal dipolarity. This results in a significant hydrogen-bonding interaction with SXFA, the only hydrogen-bond acidic polymer among the five polysiloxanes being considered. This is apparent in the large value of the $b\,\beta_2^H$ term for this vapor/polymer pair. Triethyl phosphate is still more basic, resulting in an even larger $b\,\beta_2^H$ term for sorption into SXFA. Triethyl phosphate is also quite dipolar, resulting in significant dipole/dipole interactions with SXPYR and SXCN. Ethanol is a vapor that is both hydrogen-bond basic and hydrogen-bond acidic. As a result it has hydrogen-bonding interactions with both acidic and basic polymers. This results in a large $a\,\alpha_2^H$ value for ethanol/SXPYR, and a large $b\,\beta_2^H$ term for ethanol/SXFA.

Table 3 also presents the partition coefficients calculated for each vapor/polymer pair. In general, dispersion interactions are always a significant driving force for sorption and thus play a major role in determining overall partition coefficients. In this regard, the $\log L^{16}$ values of vapors are very important in determining overall sorption. Dipole/dipole interactions and hydrogen-bonding interactions are also important if the vapor and polymer have complementary properties that promote these interactions.

Sensing Basic Vapors

We are particularly interested in the detection of basic vapors such as organophosphates. From the

Table 3. Calculated Interaction Terms for Five Vapors Sorbed by Each of Five Polymers

	Polarizability $r R_2$	Dipolarity/ polarizability $s \pi_2^H$	Hydrogen-bonding $a \Sigma\alpha_2^H$	Hydrogen bonding $b \Sigma\beta_2^H$	Dispersion/ cavity $l \log L^{16}$	Partition coefficient $\log K$
SXFA						
Isooctane	0	0	0	0	2.23	2.15
Trichloroethene	-0.22	0.22	0.06	0.13	2.15	2.26
Triethyl phosphate	0	0.60	0	4.51	3.41	8.43
Triethylamine	-0.04	0.09	0	3.36	2.18	5.50
Ethanol	-0.10	0.25	0.26	2.04	1.07	3.43
SXPYR						
Isooctane	0	0	0	0	3.16	1.22
Trichloroethene	-0.10	0.90	0.54	0	3.04	2.45
Triethyl phosphate	0	2.43	0	0	4.83	5.31
Triethylamine	-0.02	0.36	0	0	3.09	1.50
Ethanol	-0.05	1.02	2.51	0	1.51	3.05
SXCN						
Isooctane	0	0	0	0	2.40	0.77
Trichloroethene	0	0.84	0.24	0.02	2.32	1.79
Triethyl phosphate	0	2.28	0	0.55	3.67	4.87
Triethylamine	0	0.34	0	0.41	2.35	1.47
Ethanol	0	0.96	1.12	0.25	1.15	1.85
OV202						
Isooctane	0	0	0	0	2.51	2.12
Trichloroethene	-0.25	0.48	0.04	0.02	2.42	2.32
Triethyl phosphate	0	1.30	0	0.75	3.83	5.49
Triethylamine	-0.05	0.19	0	0.56	2.45	2.77
Ethanol	-0.12	0.55	0.16	0.34	1.20	1.74
OV25						
Isooctane	0	0	0	0	2.75	1.90
Trichloroethene	0.09	0.48	0.04	0.01	2.65	2.43
Triethyl phosphate	0	1.29	0	0.47	4.20	5.11
Triethylamine	0.02	0.19	0	0.33	2.69	2.40
Ethanol	0.04	0.54	0.21	0.21	1.31	1.47

analysis above, it is clear that a hydrogen-bond acidic polymer such as SXFA will be most effective at sorbing such compounds. A variety of other hydrogen-bond acidic materials that might also serve the same function have been described in other publications and might also be considered in this application.[3,4,14]

The partition coefficient for triethyl phosphate/SXFA is the largest in Table 3. Two major factors contribute to this. First, triethyl phosphate has a larger log L^{16} value than any of the other vapors. This results in large partition coefficients on all the polymers. Second, triethyl phosphate is a particularly strong hydrogen-bond base, and SXFA is a particularly strong hydrogen-bond acid. This results in very strong hydrogen-bonding. The partition coefficient of triethyl phosphate on SXFA is three orders of magnitude greater than its partition coefficient on any of the nonhydrogen-bond acidic polymers.

We are currently developing fiber optic sensors where the cladding serves as a sorbent layer to collect and concentrate analyte vapors. These sorbed vapors will be detected and identified spectroscopically. Solubility models are being used as described above to guide the design of polymeric cladding materials for particular vapors.

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