

Determination of Polymer-Solvent Interaction Parameters Using Piezoelectric Crystals, with Reference to the Sorption of Chemical Warfare Agents

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SYNOPSIS

Polymeric materials which show sensitivity to certain classes of organic vapors and give minimal responses from interferents are being sought for use as coatings on piezoelectric mass detection devices. The present work illustrates some simple methods for the determination of fundamental properties such as polymer-solvent interaction parameters and diffusion constants, and relates these to the sensitivity and response time of the sensor. Polymers with a controlled variation in crosslink density were exposed to a variety of common solvents and vapors covering a range of solubility parameters. Seven non-crosslinked amorphous polymeric materials were also assessed for their suitability as selective coatings for the detection of a range of chemical warfare vapors. Gross differences in the response characteristics of coated crystals immersed in liquids can be predicted, and an approximate guide to the relative rates of solvent penetration can also be obtained. More accurate predictions are hampered by the lack of knowledge of the specific interactions which occur within polymer-solvent pairs. Crosslinking the polymer film to enable operation in strongly solvating liquids has the effect of reducing the extent of swelling to a larger degree than expected on the basis of existing theories. The operation of coated crystals in the gas phase at very high vapor concentrations leads to a dual site adsorption process which can be described by the BET equation. At much lower vapor concentrations Henry's law appears to determine the response, and a simple solution model developed from partition theory for stationary phases in gas-liquid chromatography can be used to interpret the sensitivity of three non-crosslinked amorphous polymeric films to DMMP, GA, GB, and GD. While adequately describing the responses of the organophosphorus esters, the model is not as satisfactory in predicting the interactions with HD. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

In recent times attention has been directed toward the development of chemical sensors for the determination of trace levels of organic compounds in vapors and liquids. Among the many types of sensors which have been demonstrated to be useful for the continuous monitoring of environmental pollutants are coated piezoelectric crystals.¹ These devices have been in use for around 25 years and it is accepted that the vibrating crystal undergoes a change in its natural oscillation frequency following sorption of

molecules by a layer of polymeric material upon the crystal surface. Detection limits around 10^{-12} g for a 15 MHz crystal have been estimated and the Sauerbrey expression² has been shown to quantitatively describe the behavior:

$$\Delta F = -k_1 F_0^2 \Delta m / A \quad (1)$$

where ΔF is the frequency change, k_1 is a constant dependent on the crystal and the coating sensitivity and mass, F_0 is the natural oscillation frequency, Δm is the change in mass following sorption by the coating and A is the surface area.

The key factor in determining the performance of the device as a sensor is the manner in which the crystal coating and the target molecules interact,

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namely the nature of the proportionality constant, k_1 . Although it is unlikely that a particular film will respond exclusively to any given vapor, polymeric materials which show sensitivity to certain classes of organic vapors and give minimal responses from interferents are being sought. A recent article³ provides a detailed literature review and a discussion on coating selection strategies for sorption detectors.

Piezoelectric crystals have been applied with some success as a sensitive means of following the interactions between polymers and gases. For example, the oxidative degradation that occurs when extremely thin films of elastomers deposited on a quartz microbalance are exposed to ultraviolet (UV) light has been successfully monitored.⁴ Using surface acoustic wave devices, which exhibit a similar frequency-mass relationship to piezoelectric crystals, the uptake of water vapor by polyimide and cellulose acetate butyrate films has been determined and the results interpreted in terms of the enthalpy and entropy of sorption.⁵ Vapor sorption isotherms using crystals coated with poly(isobutylene) in hydrocarbons and chlorinated methanes have also been measured⁶ and the calculated polymer-solvent interaction parameters have been found to be in reasonable agreement with previously published values determined by using gas chromatography and a quartz-helix vapor sorption apparatus.

Until recently, measurements were performed almost exclusively in the gas phase because it was often assumed that a quartz crystal would not reliably oscillate when immersed in a liquid due to the large energy losses at the interface between phases. Consequently little information has been reported on the application of these devices to the determination of polymer-solvent/solute solubility parameters where the interaction takes place in the liquid phase. In our earlier work,⁷ a study was undertaken to determine some of the variables which influence the resonant frequency of 10-MHz AT-cut quartz crystals immersed in liquids. The sorption characteristics of crystals coated with films of poly(ethylenimine) were also investigated and it was shown that Fick's diffusion law appears to govern the rate of uptake of solute by the polymer. Furthermore, both the rate of sorption, and the equilibrium mass uptake by the coating were found to be strongly dependent on the chemical compositions of the materials involved. The potential therefore exists for a rapid and general means of measuring the interaction between film-forming polymers and solvents or solutes. In particular the method affords the possibility of simultaneous determination of both the kinetic and thermodynamic factors in-

involved in sorption, using only microgram quantities of material.

The present report describes some measurements aimed at assisting in the selection and tailoring of polymeric coatings for piezoelectric crystal sensors. The main objective is to illustrate a simple method for the determination of fundamental properties such as polymer-solvent interaction parameters and diffusion constants, and to show how these relate to the sensitivity and response time of the sensor. In the first set of experiments, polymers with a controlled variation in crosslink density were exposed to a variety of common solvents and vapors covering a range of solubility parameters. In addition, a further seven non-crosslinked polymeric materials were assessed for their suitability as selective coatings for the detection of a range of chemical warfare agents and the results interpreted in terms of the gas-liquid partition theory for stationary gas chromatography phases. In particular, the blister agent *bis*-(2-chloroethyl) sulfide (HD, mustard), the nerve agents ethyl-*N,N*-dimethyl phosphoramidocyanidate (GA), methyl isopropyl phosphonofluoridate (GB), methyl pinacolyl phosphonofluoridate (GD), and the simulant dimethyl methyl phosphonate (DMMP) were studied and recommendations are made on the most appropriate coatings for their detection.

EXPERIMENTAL

The apparatus and technique for measurement of the oscillation frequency of low-temperature coefficient 10-MHz AT-cut quartz crystals immersed in liquids has previously been described.⁷ The electrical device used to measure frequency consisted of an oscillator circuit with one reference and one working crystal and a circuit to measure the difference in frequency. A frequency-to-digital signal converter interfaced to an XT microcomputer enabled data to be logged at chosen intervals and plotted as a function of time. Collection of frequency values with a precision of 0.1 Hz for the dry crystal was achieved by these means.

The majority of gas phase measurements were performed using 8 MHz AT-cut crystals mounted into a 1.5 cm³ PTFE cell situated in a thermostated cabinet ($30 \pm 0.1^\circ\text{C}$), housing a diffusion tube vapor generator of the design described by Fortuin.⁸ Crystals mounted in the PTFE cell were purged for 3-4 h with dry nitrogen until constant frequency shifts were obtained. Variations in the concentrations of each of the test vapors were achieved by altering the flow rate of dry nitrogen over the diffusion tube or

by using diffusion tubes of different dimensions. These concentrations were determined by passing the vapor stream into 2 cm³ of diethyl phthalate and analysing the resulting solution by gas chromatography. A Varian 3700 GC equipped with a flame photometric detector was used, operating in the sulfur mode for HD and phosphorus mode for GA, GB, GD, and DMMP. The column was 0.5 m long and 3.1 mm ID, packed with 5% OV101 on Chromasorb. The injection port and detector temperatures were set at 350 and 230°C, respectively, and the column was operated isothermally at 180°C. The carrier gas was nitrogen at a flow rate of 35 ml min⁻¹ and peak areas were determined using a Varian 4270 integrator.

In the case of gas phase sorption experiments in which relatively highly controlled partial vapor pressures were required, the coated crystal was sealed with silicone rubber in a vacuum line and a measured vapor pressure of solvent admitted to the system. Uptake of vapor was generally too rapid to enable kinetics to be measured and therefore only the equilibrium degree of swelling could be reliably determined in these experiments. For moisture uptake measurements, the relative humidity was set by exposing the coated crystal to the vapors above an appropriately saturated salt solution.

In order to produce coatings with a variation in crosslink density without varying the chemical composition, diglycidyl ether of bisphenol A (DGEBA), with an epoxy equivalent weight of 175, was reacted with stoichiometric amounts of mixtures of aniline and di-amino diphenylmethane (DDM), to give a series of networks in which the only significant structural variable is the concentration of bonds linking the chains.⁹ The structure is shown in Table I and numerical values of the crosslink densities were calculated from the amine/diamine ratio as previously described.⁹ To enable the preparation of a thin coating of this polymer on the crystal surface, the unreacted resin/amine mixture was dissolved in dichloromethane (1% w/v) and an approximate 1 μl aliquot applied with a microliter syringe to the center of the crystal, and spread to cover the entire silver electrode. In situations where a film did not form uniformly, additional solvent was applied until an approximately even layer was obtained, determined by eye using the surface gloss as a guide. Some trial and error was involved in this process; however, in subsequent work the application of liquid using a Sprite Airbrush has been found to assist in the production of more uniform thin films. Uniformity of film thickness was not considered to be a critical factor in determining the equilibrium

uptake of vapor or liquid since the fractional increase in frequency following sorption should be the same at any position on the crystal surface and for any thickness below a limiting value. The resin was allowed to dry and cure at ambient temperature overnight then postcured at 60°C for 4 h and 170°C for 1 h under a nitrogen atmosphere. For the soluble non-crosslinked polymers, the coating method involved the application of the droplet of solution followed by baking at 100°C for 10 min. Crystal loadings, measured by the frequency change solely due to the coating, were typically in the range 8–30 kHz.

The seven polymeric materials investigated were polyphosphazene (PNF), polyethylene maleate (PEM), Hypalon 20, Thiokol LP-31, OV-101, OV-215 and Viton E-430. All are either rubbery solids or viscous liquids with glass transition temperatures below room temperature. OV-215 and OV-101 are gas-liquid chromatography stationary phases. PNF, Hypalon 20, and Viton E-430 are commercially available rubbers. LP-31 is a polysulfide sealant prepolymer and PEM was synthesized using literature methods.¹⁰ Hydrophobicity, chemical similarity to the five test vapors and relative solubility parameters were used as a basis for the selection of these materials. Their structures and solubility parameters where available are given in Table I. Table II lists the solubility parameters and volatilities of the test vapors at 30°C.

Uptake of solvent by the epoxy-coated crystals was measured as a function of time by immersing the coated crystal in the thermostatically controlled liquid and logging the frequency at 0.5 s intervals. Many of the crosslinked polymer films were reused for several experiments since it was found that the solvent could be rapidly desorbed with a hot air blower without disturbing the integrity of the film.

RESULTS AND DISCUSSION

Crosslinked Polymer Coatings

Non-crosslinked polymers are not suitable for use as coatings for crystals intended for use in liquid-phase applications in which a variety of organic solvents may be involved because there is a likelihood of unstable oscillation due to excessive solvation or, in some cases, complete dissolution of the film. Crosslinked polymer coated crystals were therefore used for solution measurements, and the data were interpreted in terms of frequency change, expressed as a percentage of the original coating load, as a function of time and at equilibrium.

Table I

Coating	Structure	Solubility Parameter MPa ^{1/2}
Poly(phosphazene)	$\begin{array}{c} \text{CH}_2\text{CF}_3 \\ \\ \text{O} \\ \\ (-\text{P}=\text{N}-)_n \\ \\ \text{O} \\ \\ \text{CH}_2(\text{CF}_2)_3\text{CF}_2\text{H} \end{array}$	20.5
Poly(ethylenemaleate)	$\begin{array}{c} \text{O} \quad \quad \quad \text{O} \\ \quad \quad \quad \\ (\text{O}-\text{C} \quad \quad \quad \text{C}-\text{O}-\text{CH}_2\text{CH}_2)_n \\ \backslash \quad / \\ \text{C}=\text{C} \end{array}$	19.8
Hypalon 20	$\begin{array}{c} \text{CH}_2 \quad \quad \quad \text{CH}_2 \quad \quad \quad \text{CH}_2 \\ \quad \quad \quad \quad \quad \quad \\ (\text{CH}_2)_x (\text{CH})_y (\text{CH})_z \\ \quad \quad \quad \\ \text{Cl} \quad \quad \quad \text{SO}_2\text{Cl} \end{array}$	
Thiokol LP-31	$(-\text{S}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{S}-)_n$	
Viton E-430	$\begin{array}{c} \text{CF}_3 \\ \\ \text{CH}_2 \quad \quad \quad \text{CF} \quad \quad \quad \text{CF}_2 \\ \quad \quad \quad \quad \quad \quad \\ (\text{CH}_2)_x (\text{CF})_y (\text{CF}_2)_y \end{array}$	19.5
OV-101	$\begin{array}{c} \text{CH}_3 \\ \\ (-\text{Si}-\text{O}-)_n \\ \\ \text{C}_6\text{H}_4 \end{array}$	
OV-215	$\begin{array}{c} \text{CH}_3 \\ \\ (-\text{Si}-\text{O}-)_n \\ \\ (\text{CH}_2)_2\text{CF}_3 \end{array}$	
DGEBA/DDM/aniline	$\begin{array}{c} \text{R} \quad \quad \quad \text{R} \\ \quad \quad \quad \\ (-\text{N}-)_x (-\text{N}-)_y \\ \quad \quad \quad \\ \text{C}_6\text{H}_4 \quad \quad \quad \text{C}_6\text{H}_5 \\ \\ \text{CH}_2 \\ \\ \text{C}_6\text{H}_4 \\ \\ \text{N} \\ \\ \text{R} \end{array}$ $\text{R} = -\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-\text{O}-\text{C}_6\text{H}_4-\text{CH}(\text{CH}_3)-\text{C}_6\text{H}_4-\text{O}-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-$	21.5–23.5

Table II Thermodynamic Parameters for CW Agents and a Simulant

Property	Vapor				
	DMMP	GA	GB	GD	HD
Vapor conc. at 30°C (g m ⁻³)	9.3	0.86	29.8	5.6	1.5
Solubility parameter (MPa ^{1/2})	21.7	18.8	18.6	17.2	21.9

The rate of uptake of mass by a polymer sheet exposed to a liquid is generally described by Fick's equation for diffusion¹¹ as follows:

$$M(t)/M(\infty) = 1 - (8/\pi^2) \sum_{n=0}^{n=\infty} (1/(2n+1)^2) \times \exp[-D(2n+1)^2\pi^2t/4L^2] \quad (2)$$

where $M(t)$ is the mass taken up by the film at time t , $M(\infty)$ is the equilibrium mass uptake by the film, L is the film thickness and D is the diffusion coefficient.

The linear portion of the sorption curves can be approximated by the following equation:¹²

$$M(t)/M(\infty) = 2(Dt/\pi L^2)^{1/2} \quad (3)$$

It has also been shown that for coated AT quartz

crystals the film thickness is related to the frequency by the following expression:¹³

$$L = N_q \rho_q \Delta F_c / \rho_c F_0^2 \quad (4)$$

where N_q is the quartz crystal frequency constant (1.668×10^5 Hz cm), ρ_q is the quartz density (2.69 g cm⁻³), ρ_c is the density of the coating and ΔF_c is the frequency change due to the coating alone.

Experimental sorption results were analyzed by plotting fractional mass uptake against $t^{1/2}$. Determination of D was made by least-squares fitting the rising part of the sorption curve to eq. (3), using the film thickness calculated from eq. (4). Data for epoxy-coated crystals immersed in a variety of common organic solvents are given in Table III. Figures 1 and 2 show typical experimental results obtained using a homologous series of solvents (CH₃CO₂R, R = Me, Et, *n*-Pr and *n*-Bu), at several tempera-

Table III Experimental Solvent Uptake and Diffusion Constant Measurements for DGEBA/DDM/Aniline Network Polymers Coated on a 10 MHz Crystal Immersed in a Variety of Organic Liquids

Solvent	% Mass Uptake		Diffusion Constant (cm ² /s)	Viscosity (cP, 20°C)	Solubility Parameters (MPa ^{1/2})			
	Expt.	Calc. ^a			δ	δ_d	δ_p	δ_h
$X_c = 3.417$ mol/kg								
Chloroform	32.9	29	9.2×10^{-12}	0.58	19.0	17.9	3.1	5.7
Dichloromethane	30.9	32	1.8×10^{-10}	0.42	21.2	17.8	6.4	6.1
Dioxane	18.7	21	2.2×10^{-11}	1.37	20.2	18.2	1.8	7.4
Ethylacetate	14.7	9	2.2×10^{-10}	0.46	18.6	15.2	5.3	9.2
Propylacetate	11.5	13	1.3×10^{-10}	0.59	18.0	15.6	4.3	7.8
Acetone	10.2	6	3.4×10^{-9}	0.33	20.0	15.5	10.4	7.0
Acetonitrile	9.4	2	2.8×10^{-9}	0.36	21.5	15.4	18.0	6.1
Butylacetate	7.6	13	5.2×10^{-11}	0.73	17.4	15.7	3.7	6.4
<i>n</i> -Pentanol	6.9	5	2.3×10^{-10}	3.68	22.3	16.0	4.5	13.9
Methanol	5.8	1	1.3×10^{-9}	0.60	29.6	15.2	12.3	22.3
Toluene	3.2	8	6.0×10^{-11}	0.59	18.2	18.0	1.4	2.0
$X_c = 2.571$ mol/kg								
Methylacetate	19.2		4.0×10^{-10}	0.38	19.6	115.5	7.2	7.6
Ethylacetate	16.3		4.8×10^{-11}	0.46	18.6	15.2	5.3	9.2
Propylacetate	14.4		7.6×10^{-12}	0.59	18.0	15.6	4.3	7.8
Butylacetate	12.7		2.7×10^{-12}	0.73	17.4	15.7	3.7	6.4

^a Calculated by assuming mass uptake $\propto 1/[(\delta_d - \delta_{Pd})^2 + (\delta_p - \delta_{Pp})^2 + (\delta_h - \delta_{Ph})^2]$ (see text).

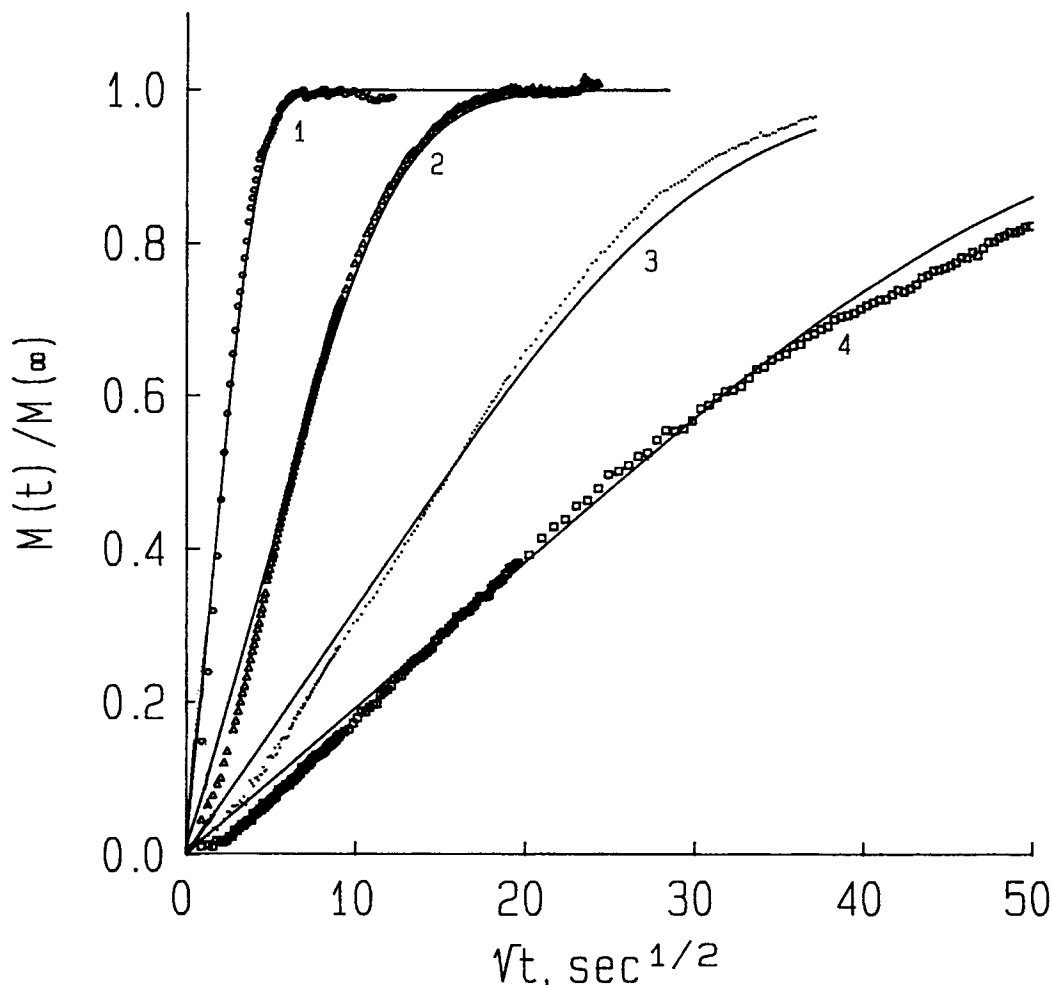


Figure 1 Experimental and calculated sorption curves for a 10 MHz crystal coated with DGEBA/DDM/aniline network polymer ($X_c = 2.571$ mol/kg), immersed in (1) methylacetate, (2) ethylacetate, (3) propylacetate, and (4) butylacetate at 22°C.

tures, and also the predicted diffusion behavior using eq. (2) with $n = 100$.

For glassy crosslinked polymers, including those in the present study, the sorption curves are in some instances non-Fickian. This feature has been observed for the sorption of penetrants by many polymers below their T_g ¹² and is related to the inability of the polymer chains to relax during the time scale of diffusion. In these cases the diffusion coefficient which is calculated using eq. (4) represents at best an empirical approximation.

For crosslinked polymers above T_g the equilibrium swelling is given by the following expression:¹⁴

$$X_c V_1 = -(\ln(1 - V_2) + V_2 + V_2^2 x_1) / (V_2^{1/3} - V_2/2) \quad (5)$$

where V_1 is the molar volume of the solvent, X_c is

the concentration of effective network chains, V_2 is the volume fraction of polymer and x_1 is the polymer-solvent interaction parameter whose value is given by

$$x_1 = \beta + V_1(\delta_1 - \delta_2)^2 / RT \quad (6)$$

where β is a lattice constant, usually 0.35, R is the gas constant, T is the temperature and δ_1 and δ_2 are the Hildebrand solubility parameters for the solvent and polymer respectively.

The maximum uptake of solvent by the polymer should occur when $\delta_1 - \delta_2$ is close to zero (i.e., the solubility parameters for the solvent and polymer are matched). Tables of solubility parameters for solvents are readily available and the values listed in Tables I to III are those which are generally accepted as reliable.¹⁵ Solubility parameters for

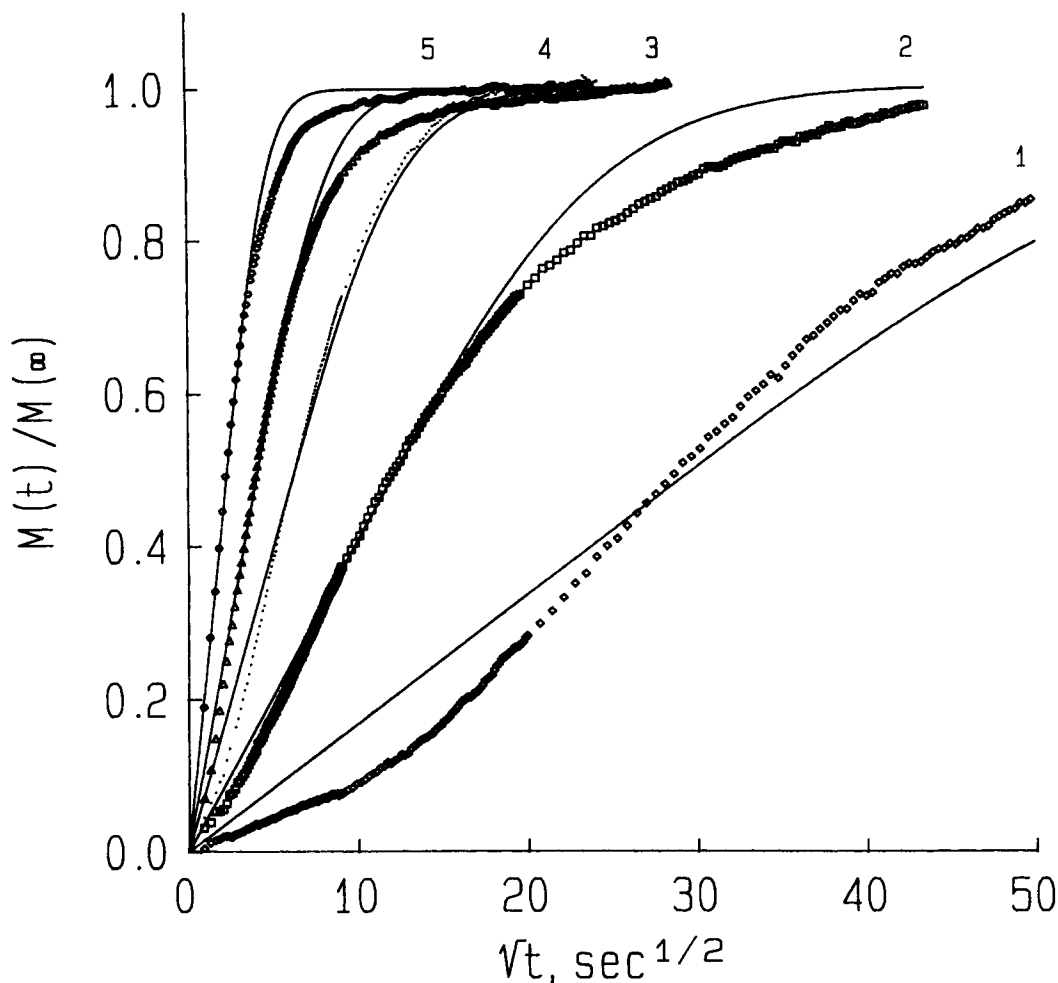


Figure 2 Experimental and calculated sorption curves for a 10 MHz crystal coated with DGEBA/DDM/aniline network polymer ($X_c = 2.571$ mol/kg), immersed in ethylacetate at the following temperatures: (1) 2°C, (2) 11°C, (3) 22°C, (4) 30°C, and (5) 40°C.

DMMP and the CW agents were taken from Dillon et al.¹⁶ The estimation of solubility parameters for the polymer component can be achieved using additivity techniques involving the molar attraction constants for the groups which comprise the repeat units in the polymer chain. For the DGEBA-DDM epoxy system these values have been calculated previously¹⁵ and range from 21.5 to 23.5 MPa^{1/2}, depending on the additivity method employed. The results in Table III show that the mass increase at equilibrium following immersion of the coated crystals in the solvents is only loosely related to the solubility parameter difference. For example, chloroform and dichloromethane are the most effective swelling agents, yet *n*-pentanol, which has a similar solubility parameter to both the polymer and the two chlorinated solvents, is a very poor swelling agent. However, within a series of homologous com-

pounds such as the alkyl acetates, the observed trend is that as the solubility parameter difference increases, the degree of swelling decreases. The same type of behavior has previously been reported for the solvent swelling of epoxy networks using a different method of measurement.^{15,17} In reality there are many parameters which must be used to adequately categorize solvent behavior. These include indices of hydrogen bonding, dipolar bonding, and dispersion forces. Bidimensional solubility maps have been constructed using these parameters,^{15,18,19} but even when large numbers of solvents have been examined the method is only able to predict with any degree of certainty gross differences in swelling characteristics. The major shortcoming of these generalized approaches is that they are not able to take into consideration specific interactions, that occur by virtue of the shape and conformation of

the polymer molecule, and the degree of accessibility of the groups which most strongly interact. However, if the solubility parameter is redefined in terms of components due to dispersion forces (δ_d), polar groups (δ_p) and hydrogen bonds (δ_h), then the polymer-solvent interaction parameter listed in eq. (6) may be considered to be proportional to $(\delta_d - \delta_{Pd})^2 + (\delta_p - \delta_{Pp})^2 + (\delta_h - \delta_{Ph})^2$, where the subscript P refers to the solubility parameter component for the polymer.¹⁸ Furthermore, if, as a first approximation, the mass uptake is taken to be inversely proportional to the multicomponent solubility parameter difference function, then a multiple nonlinear regression analysis using the values listed in Table III enables the following solubility parameters for the DGEBA/DDM network polymer to be calculated: $\delta_{Pd} = 20.7$, $\delta_{Ph} = 6.6$, and $\delta_{Pp} = 4.9$. The calculated mass uptakes listed in Table III have been determined using these polymer solubility parameters. These are included to give an indication of the predicted relative trend and are purely an empirical correlation. The data show that the refined solubility parameters are of much greater predictive use than the Hildebrand values and enable gross differences in swelling capacity to be explained.

Prediction of the diffusion constant is also hampered by a similar lack of a unified theory taking into account all the factors involved. Fedors²⁰ has proposed a semiempirical relation, eq. (7), which describes the limiting diffusion coefficient, D_0 , of a small amount of pure solute in pure solvent.

$$D_0 = 4.5 \times 10^{-9} (V_1^* - V_1)^{3/2} / \eta_1 V_1^{*4/3} (V_2^* - V_2^0)^{1/2} \quad (7)$$

The subscript 1 refers to the solvent and 2 is for the solute, V_2^0 is the partial molar volume of the solute and V^* and V are the molar volumes at the critical temperature and at T , respectively, and η is the viscosity. The equation was found to give reasonable predictions for low-molecular weight solutes in low-molecular weight solvents, and for polymers diffusing in organic solvents. However, it has been reported by other workers that the relationship does not give a good correlation with data for small molecules diffusing in polymers.²⁰ The only positive correlation involving the diffusion coefficient that can be found for the polymer-solvent pairs listed in Table III is that, with several exceptions, as the viscosity of the solvent increases, the velocity of penetration decreases. This is to be expected given that the viscosity reflects the overall size and shape of the solvent molecule.

The temperature dependence of the diffusion coefficient follows an Arrhenius relationship, which has been shown by other workers to apply to a wide range of polymers and penetrants.¹⁹ Values of D , calculated from the data in Figure 2 for the DGEBA/DDM/aniline system ($X_c = 2.571 \text{ mol kg}^{-1}$) immersed in ethylacetate, give a linear activation energy plot with a slope of 39.4 kJ mol^{-1} (correlation coefficient -0.993), in reasonable agreement with other similar systems.¹⁹

The effect of varying the crosslink density on the equilibrium degree of swelling is illustrated in Figure 3. The four solvents were chosen to cover a wide range of solubility parameters, and it is apparent for all of these systems that as the level of crosslinking decreases, the degree of swelling increases, in qualitative agreement with the predictions of eq. (5). Figure 3 also shows fits of eq. (5) to the data using values of x_1 calculated for the lowest crosslink density coating exposed to each of the four solvents. The data clearly indicate that the uptake of solvent at the high crosslink densities is much less than predicted by theory. Equation (5) was originally developed for rubbers by assuming that the configurations adopted by each chain between crosslink points obey Gaussian chain statistics.¹⁴ This assumption fails to hold at high levels of crosslinking and the effect has been quantified previously for the epoxy networks using measurements of the modulus above T_g in conjunction with the rubber elasticity equation.²¹ At present there is not available a more precise theory to describe the swelling properties of networks.

Sorption isotherms in the vapor phase were determined for a selection of the crosslinked coatings using chloroform and water as the adsorbates. Typical adsorption isotherm data are shown in Figure 4. Figure 5 shows some of the data plotted according to the BET equation, i.e.,

$$m = ab(p/p^0)/(1 - (p/p^0)) \times (1 - (p/p^0)(1 - b)) \quad (8)$$

where m is the % sorption, p is the partial pressure, p^0 is the saturation vapor pressure, and a and b are semiempirical constants.

The BET equation is known to be most applicable below a relative pressure of 0.6,²² and the data in Figures 5 and 6 show that the materials do not obey Henry's law at these vapor concentrations. The adsorption of water by a wide range of polymers, including epoxy coatings, has been studied by other workers^{22,23} and the BET equation describes the up-

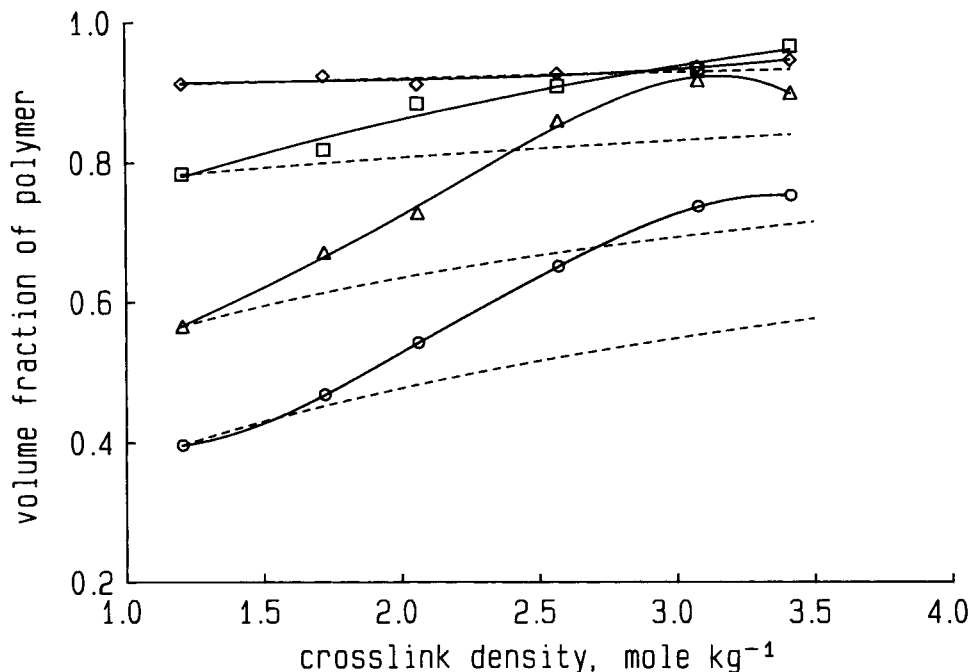


Figure 3 Equilibrium solvent uptake as a function of crosslink density for DGEBA/DDM/aniline polymers coated on 10 MHz crystals immersed in the following solvents: (○) chloroform, (△) ethylacetate, (□) toluene, and (◇) methanol. The dotted lines represent the theoretical predictions described in the text using the following values of x_1 : chloroform, 0.28, ethylacetate, 0.57, toluene, 1.08, and methanol, 1.72.

take of vapor in many of these examples. With less hydrophilic materials, such as the vinyl polymers, the isotherm data are not all that well represented by BET theory.²⁴

The derivation of the BET equation is based on the concept that sorbed solvent molecules are present in one of two states; either strongly localized or in a liquid like form.²⁵ The initial sorption of vapor occurs by specific interactions between strongly interacting groups, and as these sites become saturated the more loosely bound solvation process occurs. Provided the concentration of vapor is several orders of magnitude below the saturation pressure then it can be shown that the BET isotherm is approximately the same in mathematical form as Henry's law, and only the strongly binding sites are involved in sorption. In such a situation the vapor is not randomly distributed throughout the polymer and it becomes difficult to make predictions based on thermodynamic models. In practical terms this means that the application of coatings such as these for the determination of high concentrations of solvent vapors, or even as ambient humidity sensors, requires that the adsorption isotherm be known accurately before the device can be calibrated.

Non-crosslinked Polymer Coatings

Figure 6 shows the response expressed in terms of frequency decrease, of a crystal loaded with 17 kHz of PNF challenged with different concentrations of DMMP. Vapor equilibration which is indicated by a steady frequency shift is in all cases achieved in less than 2 minutes. Along with the six other coatings, PNF exhibited a reversible response to all test vapors with desorption times being comparable to absorption times. These times, however, were also affected by volumetric flow rates across the crystal surface. Flow rates greater than 200 cm³ min⁻¹ lead to equilibration times of less than 1 minute, whereas with flow rates less than 100 cm³ min⁻¹ these times were extended up to 6 minutes. As the dead volume between the vapor switching valve and the cell is 2 cm³ this behavior is most likely a result of vapor sorption-desorption on the tubing walls.

The sensitivity of each coating was determined by plotting equilibrium frequency shifts against vapor concentration for each vapor. All plots exhibited a linear correlation between frequency shift and vapor concentration over the range 2–35 mg m⁻³ suggesting that all sorption processes obey Henry's law.

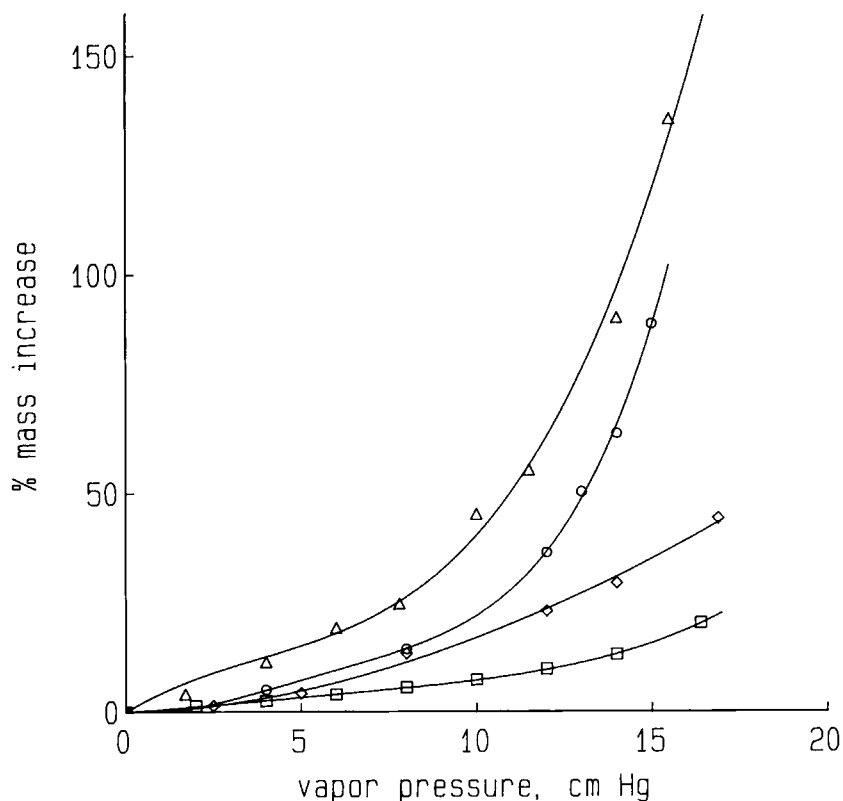


Figure 4 Sorption isotherms at 22°C for DGEBA/DDM/aniline network polymers coated on 10 MHz crystals exposed to chloroform vapors. The coatings were prepared with the following crosslink densities (mol/kg): (□) 3.417, (◇) 2.571, (○) 1.721, and (△) 1.206.

The slope of each plot was divided by the coating mass, expressed in kHz, to give a normalized sensitivity. The normalized sensitivity for each coating-vapor combination is presented in Table IV. No single coating exhibits an exceptionally large response to a particular vapor while giving meager responses to others. The coatings showing the greatest response to the organophosphorus esters are PEM, PNF, and Viton, whereas these are relatively insensitive to HD. The two sulfur-containing coatings, Hypalon 20 and LP-31, are more sensitive to HD than the organophosphorus esters. These results suggest that some degree of specificity may be obtained with coatings which are structurally similar to the test vapors of interest.

The measured sensitivity of PEM to DMMP is slightly less than that determined with a 112 MHz surface acoustic wave device ($1.2 \text{ Hz kHz}^{-1} \text{ mg}^{-1} \text{ m}^3$) in which coating deposition was performed with an aerosol brush.²⁶ Coatings prepared by this method may exhibit greater sensitivity in comparison to continuous films since droplets afford a greater surface area for vapor sorption.

The partition coefficient, K_p , commonly used in

gas-liquid chromatography to describe the dissolution of vapors into condensed phases has been employed to interpret equilibrium sorption of common organic vapors onto coated surface acoustic wave microsensors.²⁷ For vapor sorption processes which can be described by the regular solution model, which assumes all intermolecular interactions are due to dispersion forces only, K_p is given by the relationship shown below.¹⁰

$$K_p = (RT/M_c p^0) \exp(-V_1(\delta_1 - \delta_2)^2/RT) \quad (9)$$

where M_c is the molecular weight of the repeat unit of the coating, p^0 is the solvent vapor pressure and the remaining parameters are the same as those defined for eqs. (5) and (6).

Using eq. (9), partition coefficients for all vapors in the three most effective coatings i.e., PNF, PEM, and Viton, are calculated and presented, for comparative purposes, relative to each value for DMMP in Table V. Values in parenthesis refer to experimental normalized sensitivities for each coating relative to DMMP. With the exception of HD there is good agreement between expected and actual responses of each of these coatings to all vapors. Since

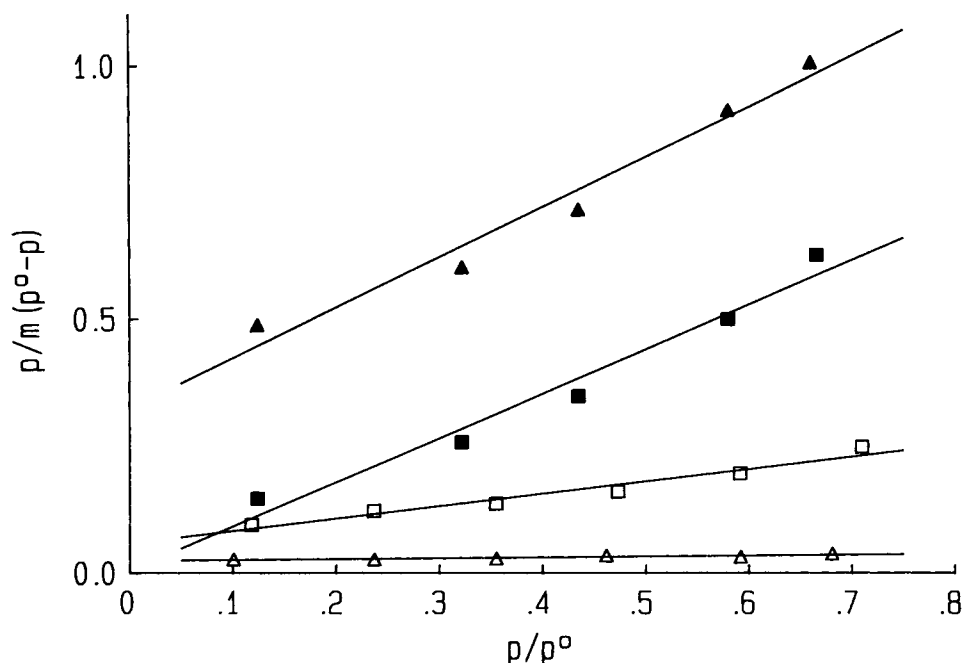


Figure 5 Sorption data at 22°C plotted according to the BET isotherm for DGEBA/DDM/aniline network polymers coated on 10 MHz crystals exposed to chloroform vapor (unfilled symbols) and water vapor (filled symbols). The coatings were prepared with the following crosslink densities (mol kg^{-1}): (\square , \blacksquare) 3.417 and (\triangle , \blacktriangle) 1.206.

the solubility parameter and volatility of HD and GA are similar, a particular coating would be expected to give near equal responses to HD and GA.

This discrepancy may arise from the presence of specific interactions involving S and Cl atoms on HD and heteroatoms in each polymeric film, there-

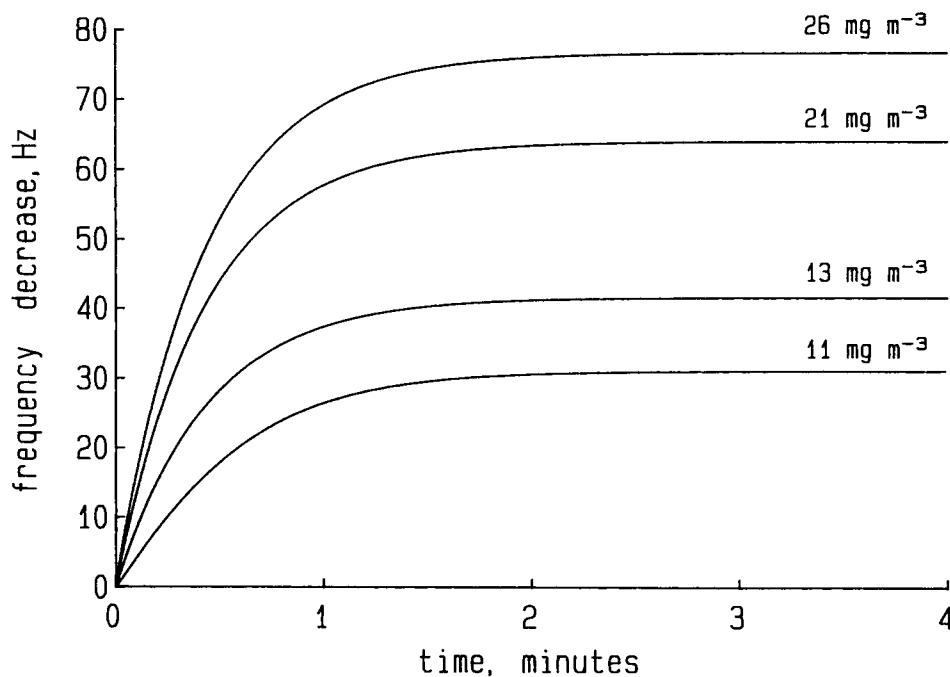


Figure 6 Frequency shift versus time plots for a PNF-coated crystal challenged with several concentrations of DMMP.

fore invalidating the assumptions on which the model is based.

A CW detection system based solely on one or more of these coated crystals would be unable to detect low concentrations ($< 0.1 \text{ mg m}^{-3}$) of CW agents. Improved sensitivity, selectivity, and response time may be obtainable by using an array of coated devices which is interfaced to a microprocessor.²⁶

An alternative approach to the interpretation of coating responses from vapor sorption may be found using Kamlet's comparison method²⁸ in which the magnitude of each specific interaction (H bond donor, acceptor, dipole-dipole) is assessed by the assignment of a solvatochromic parameter. Values of these parameters for low-molecular weight organic molecules are readily found in the literature, however, the unavailability of these parameters for complex high-molecular weight compounds renders the interpretation of the results in this investigation impossible.

CONCLUSIONS

Gross differences in the response characteristics of coated crystals immersed in liquids can be predicted and an approximate guide to the relative rates of solvent penetration can also be obtained. More accurate predictions are hampered by the lack of knowledge of the specific interactions which occur between polymer-solvent pairs such as hydrogen and dipolar bonding and shape factors. Crosslinking the polymer film to enable operation in strongly solvating liquids has the effect of reducing the extent of swelling in a manner which is not well described by existing theories. The operation of coated crystals in the gas phase at very high vapor concentrations leads to a dual site adsorption process which can be

Table IV Normalized Sensitivities of Coating Materials Exposed to Test Vapors

Coating	Response to Vapor ($10^{-2} \text{ Hz KH}_2^{-1} \text{ mg}^{-1} \text{ m}^3$)				
	DMMP	GA	GB	GD	HD
PNF	19.3	87.4	15.6	38	1.1
PEM	53.8	72.1	7.5	45	9.2
VITON	23.2	128.9	5.8	8.6	1.8
LP-31	1.4	14.7	1.0	0.7	28.6
HYPALON 20	3.8	14.9	0.7	7.4	18.0
OV-101	4.8	16.4	0.8	5.9	4.5
OV-215	9.7	25.2	1.5	12.1	4.9

Table V Relative Theoretical and Experimental (in Brackets) Partition Coefficients for Test Vapors with PNF, PEM, and VITON

Coating	Vapor				
	DMMP	GA	GB	GD	HD
PNF	1 (1)	10.5 (4.5)	0.30 (0.81)	1.4 (1.6)	4.4 (0.06)
PEM	1 (1)	11.1 (7.8)	0.32 (0.14)	1.5 (0.9)	9.3 (0.17)
VITON	1 (1)	11.3 (5.6)	0.32 (0.25)	1.6 (0.37)	6.1 (0.08)

predicted adequately by the BET equation. At much lower vapor concentrations Henry's law is operational and a simple solution model which applies to gas-liquid chromatography stationary phases can be used to interpret the responses of three non-cross-linked amorphous polymeric films to DMMP, GA, GB, and GD. While adequately describing the responses of the organophosphorus esters, the model is less satisfactory in predicting the interaction with HD.

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