

Study of Sorption/Desorption of Water and Organic Vapors on Poly(ethylene maleate)-Based Sensor-Coating Materials Using an Automated Gravimetric Analyzer

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Received 23 January 2002; accepted 12 August 2002

ABSTRACT: Hydrophobic comonomers bisphenol-A and hexafluorobisphenol-A were incorporated as diol components in the sensor-coating material poly(ethylene maleate) (PEM), resulting in modified polymers, HCPEM and HFPEM, respectively. To assess the suitability of these polymers as sensor interfaces, the sorption/desorption isotherms and kinetics of water and a range of volatile organic vapors were obtained over the entire relative pressure range of 0.1 to 1.0, using an automated intelligent gravimetric sorption analyzer. The extent and rate of sorption of organic vapors were higher in the modified polymers compared to those of the parent polymer. Sorption hysteresis was observed at high relative pressures, especially with water and other hydrogen-bonded polar organic vapors. Polarizable vapors

like toluene and benzene were sorbed more than nonpolarizable cyclohexane vapors. The sorption results were interpreted in terms of semiempirical models based on concepts of thermodynamic interaction parameter, partition coefficient, and linear solvation energy relationship. The study reveals the potential of sorption/desorption isotherms and kinetics in characterizing the sorption properties of coating materials that are used as an interface in acoustic wave sensors. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 1760–1767, 2003

Key words: poly(ethylene maleate); sorption; kinetics (polymer); coatings; sensors

INTRODUCTION

Poly(ethylene maleate) (PEM) is a dipolar basic unsaturated polyester useful for sensing many organic vapors, including organophosphorous (OP) compounds,^{1–3} widely employed as pesticides or chemical warfare agents. It has therefore achieved considerable significance as a coating (interface) material for surface (SAW) or bulk acoustic wave (BAW) devices. The polymer film coated on a piezoelectric surface of these devices collects and concentrates vapor molecules from the gas phase by sorption. The sensor responds to the change in mass or viscoelastic properties of the film as the vapor is sorbed. Over the past decade, hydrogen bond acidic polymers, such as fluoropolyol (FPOL) and its copolymers, with polysiloxanes (BSP-3, SXFA, etc.) have been favored^{2–5} over PEM because of their superior sensitivity toward OP compounds and higher hydrophobicity. However, PEM is much more economically synthesized because of simpler procedures and cheaper precursor monomers. It was therefore considered worthwhile to overcome the relative demerits of PEM by incorporating polarizable and hydrophobic comonomers, such as bisphenol-A and

hexafluorobisphenol-A in the main chain (Fig. 1) to obtain modified polymers HCPEM and HFPEM, respectively.

The suitability of a polymer as a sensor-coating material needs to be assessed in terms of sensitivity and selectivity toward the analyte vapor, besides rapidity and reversibility of response. Qualitative guidance in the selection of coatings can be obtained through considerations of polymer and vapor physicochemical properties affecting the magnitude of solubility interactions⁶ or by use of principal components or cluster analysis⁷ of sensor calibration data. The analogy between the partitioning phenomenon that governs the response of polymer-coated sensors and the separation of analytes in gas-liquid chromatography (GLC) also provides a method for screening of coating materials. The partition coefficient (K) determined from the retention volume of the vapors on a polymer column in GLC (K_{GLC}) is a useful measure of equilibrium vapor-polymer solubility at a given temperature. The K_{GLC} values were correlated to the partition coefficients of analyte vapors on a polymer-coated acoustic wave device (K_{SAW}).^{1,3,6,7} On average, K_{SAW} values were about four times greater^{6–8} than those of K_{GLC} . Increased sensor responses were attributed to changes in the polymer modulus accompanying swelling by the vapor.^{6–8} However, the data on high frequency polymer moduli and the effect of vapor sorption on moduli are not available for many

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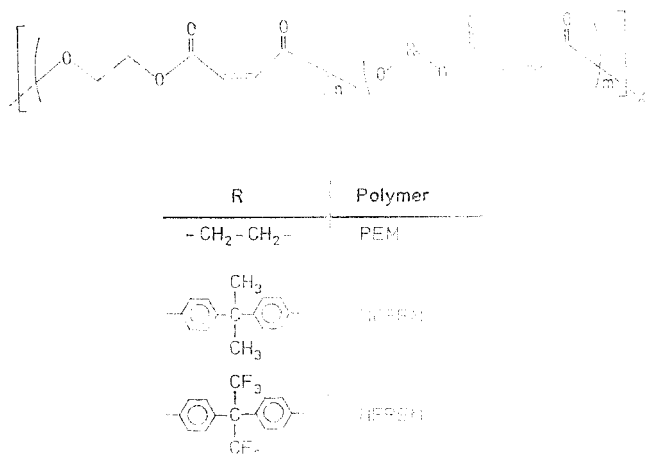


Figure 1 Poly(ethylene maleate) PEM, and modified polymers (HCPEM and HFPEM).

sensor-coating materials. Hence, a convenient, rapid, and reliable method for accurately predicting sensor responses has not yet emerged.

Our objective was therefore to investigate the possibility of using sorption/desorption isotherms for selection and performance evaluation of coating materials. Our other aim was to check the applicability of available semiempirical models for estimating sensor responses to organic vapors, in describing the sorption characteristics. We sought to quantify sorption of various classes of vapors and understand the interaction responsible for vapor sorption, thereby facilitating tailoring of the polymers for a high sensitivity and selectivity toward the desired analyte vapors. To acquire information on the effects of both chemical nature and concentration of the sorbate vapors, on the rate and extent of sorption in the polymer, we investigated sorption/desorption kinetics and isotherms for various vapors on PEM and its derivatives. A computer-assisted intelligent gravimetric analyzer (IGA; Hiden Analytical Ltd., UK) was used to obtain vapor sorption/desorption isotherms over a wide range of vapor concentrations encompassing the partial pressure (p/p_0) range from 0.1 to 1.0. The sorption results were analyzed in terms of various semiempirical models and the linear solvation energy relationship.

EXPERIMENTAL

Materials

PEM was synthesized from maleic anhydride and ethylene glycol (mol ratio 1 : 1.1) by acid catalyzed condensation reaction according to the standard method.¹⁰ Bisphenol-A (0.2 mol) along with ethylene glycol (0.9 mol) was used as the diol component for synthesis of HCPEM. In HFPEM, hexafluorobisphenol-A (0.2 mol) was the comonomer with ethylene glycol (0.9 mol). The number-average molecular weight M_n , esti-

mated using acetylation of hydroxyl end groups,^{9,10} ranged from 3000 to 4000. The spectroscopic and thermal characterizations of these polymers were reported previously.¹⁰

The adsorbates acetone, toluene, benzene, cyclohexane, and methanol (supplied by Qualigens, India) were of HPLC grade and dried before use using molecular sieves or anhydrous sodium sulfate.

Sample preparation

Because the polymers were viscous liquids, to avoid uncertainties in the mass-transfer phenomenon resulting from uneven thickness of the sample film, immobilization of the polymer on an inert support was preferred. Polymer (15%) was loaded onto Chromosorb DMCS (acid washed, 100–120 mesh; Analabs, US) using a dilute solution in acetone. The immobilized polymer was dried to constant weight and also outgassed for 24 h at 0.01 mbar and 80°C using the IGA system.

Determination of sorption/desorption isotherms

The sorption/desorption characteristics of water vapor and various other organic vapors on the immobilized polymers were acquired using the IGA system from Hiden Analytical UK. A 35- to 40-mg sample of immobilized polymer (corresponding to 5.4–6.0 mg of neat polymer) was placed in a stainless steel sample bucket of fine mesh and exposed to predetermined concentrations of analyte vapor. The partial pressure of the vapors was automatically computed by the system using Antoine's equations.¹¹ The temperature was maintained at 30°C using a Hubber Ministat (Hubber, Germany), with an accuracy of $\pm 0.01^\circ\text{C}$.

RESULTS AND DISCUSSION

The IGA system constitutes a conventional microbalance head (sensitivity, $\pm 1.0 \mu\text{g}$) mounted in a stainless steel vacuum-pressure reactor. Gas pressure is adjusted by means of conventional (shutoff or leak) valves driven by high resolution stepping motors. The IGA method exploits the relaxation behavior of the material after pressure changes to simultaneously evaluate kinetic parameters and the asymptotic uptake. The procedure adopted for the measurement of an incremental isotherm is a two-stage process once thermal equilibrium has been established. The pressure is controlled to establish a new set point without undue disturbance of the balance. The second stage involves recording of mass, temperature, and pressure as a function of time. The time dependency of mass change is analyzed according to the linear driving force model (function F_1), to determine the asymptotic uptake.¹¹

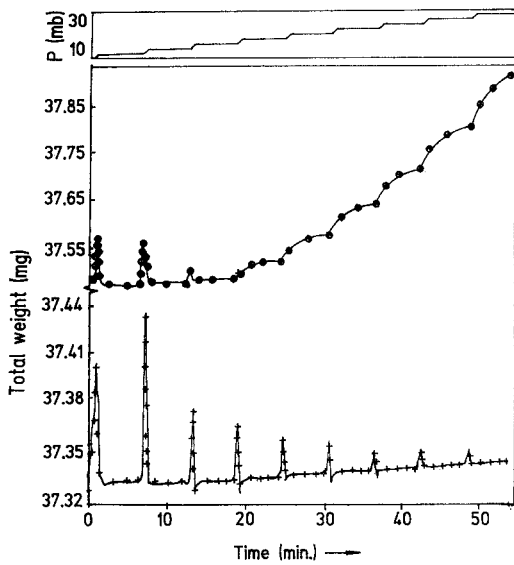


Figure 2 Sorption kinetics for water vapor on PEM (—●—) and HCPM (—+—).

At low vapor activity, the time required to approach sorption equilibrium is prohibitively long, even for the thinnest feasible film samples; measurements were thus made on powdery samples, for which the diffusion path is much shorter and the consequent sorption time is much more accessible.

Sorption/desorption of water vapor

Water vapor is known to have a competitive effect on the adsorption of pollutants/contaminants from air/gas streams.^{2-5,12} This can adversely affect the performance of a sensor-coating material. PEM and its derivatives were therefore assessed for uptake of water vapors at $30.0 \pm 1^\circ\text{C}$ in the relative pressure range 0.05 to 0.99 (absolute pressure 0.995 to 41.99 mbar) using 8.0 pressure steps of range 5 mbar. The representative kinetics of sorption are plotted in Figure 2, whereas

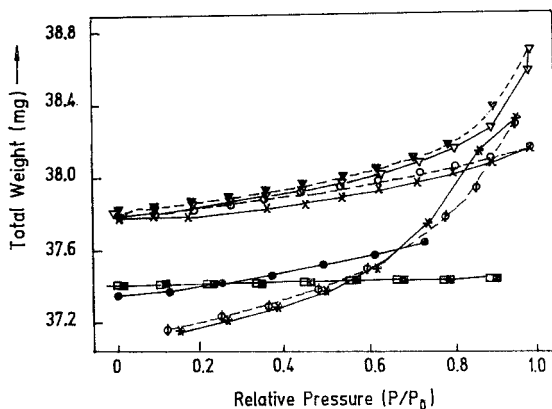


Figure 3 Sorption isotherms for water vapor on PEM-based polymers.

the corresponding sorption isotherms are shown in Figure 3. Because the experiments were carried out at a temperature much higher than the glass-transition temperature (T_g) of the polymers ($\sim 6-8^\circ\text{C}$), these macromolecules are assumed to be in a rubberlike state, yielding homogeneous vapor-polymer solution. Hence, the sorption mechanism involves swelling and dissolution, involving exchange of places of vapor molecules and units or segments, of flexible macromolecules. When a polymer chain is sufficiently flexible, such rearrangements are possible from the very first portions of an absorbed gas or vapor¹² (i.e., from the lowest values of its pressure p_1). Therefore, sorption isotherms on elastomers and flexible polymers are

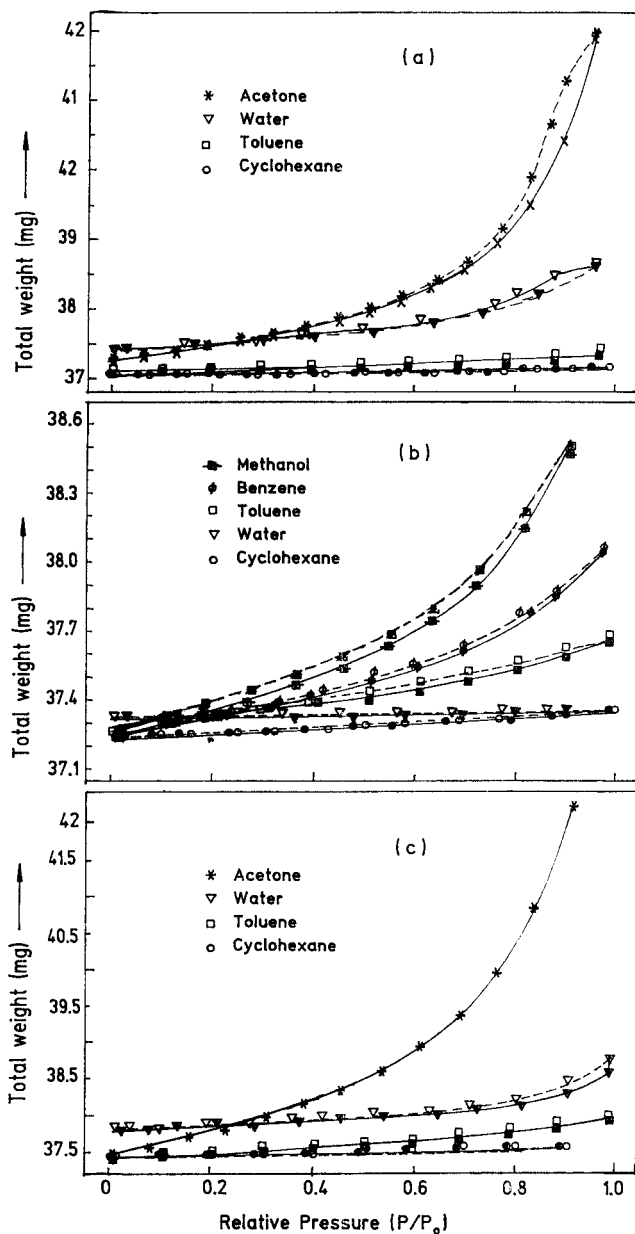


Figure 4 Vapor sorption/desorption isotherms on (a) PEM, (b) HCPM, and (c) HFPEM.

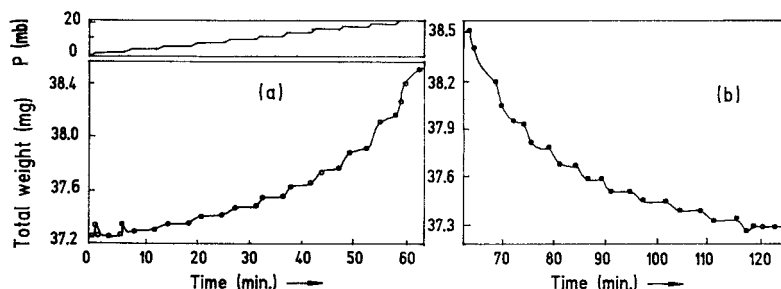


Figure 5 HCPeM-Methanol: (a) sorption kinetics, (b) desorption kinetics.

concave toward the abscissa axis in the entire range of p/p_0 .

It is also observed that the sorption kinetics and isotherms depend not only on the nature of the polymer but also on the concentration of the vapors. In general the mass uptake of water vapors by the polymers was about 3%. The extent of sorption was highest (3.22%) in PEM and least in HCPeM (0.21%). The dipolar (ester and ether) linkages in these polymers favor polar-polar interactions with water. The hydrophobicity of the bisphenol moiety in HCPeM lowers the extent of these interactions. We expected that perfluorination of $-\text{CH}_3$ groups would increase the hydrophobicity attributed to the water-repellant effect of fluorine. However, it was observed that the sorption of water vapors in HFPEM was nearly three times that in HCPeM. This may be a consequence of both reduced molecular interaction and steric effect induced by $-\text{CF}_3$ groups, which hinder the close packing of polymer chains, resulting in an increase in free volume and thus facilitating uptake of individual water molecules. Space-filling models have also shown¹² that perfluorination of the methyl groups transforms the bisphenol residue into a rigid segment; the interchain separations in these rigid bulky polymers appear to be large enough to permit relatively free movement of permeants below a certain size.

The rate of desorption of water vapors was in general found to be slower than the sorption rate. This was more pronounced at higher vapor concentrations ($p/p_0 > 0.5$), resulting in high pressure hysteresis in PEM and HFPEM. The hysteresis is attributed to clustering of water molecules.¹² These clusters are less mobile than individual molecules, so desorption is slower. Although HCPeM exhibits no hysteresis, it is conspicuous in HFPEM. The limited segmental motion in HFPEM (higher T_g), resulting from the restricted torsional motion of the phenyl rings around a $-\text{C}(\text{CF}_3)_2$ linkage, possibly inhibits the rate of desorption of water clusters.

Two subsequent sorption/desorption cycles recorded for HFPEM are also shown in Figure 3. The extent of sorption as well as the hysteresis, especially at higher concentrations, was larger in the second

cycle. Probably, water vapor sorbed in the first run plasticizes the polymer,¹² thus subsequently facilitating a higher sorption. During the first cycle, hysteresis was observed over the entire activity range, whereas in the second run, hysteresis was more pronounced at higher vapor concentrations. The temperature dependency of water sorption in HFPEM was as expected; although the rate of sorption increased, the extent of sorption decreased with an increase in temperature, which results from the enhanced kinetic energy and hence the higher mobility of sorbate molecules.

Sorption/desorption of organic vapors

Figure 4(a) depicts the sorption/desorption isotherms of acetone, toluene, and cyclohexane, compared to that of water, on PEM. The extent of sorption of these vapors follows the order acetone $>$ water $>$ toluene $>$ cyclohexane. In general, when the interactions between the polymer and the sorbate vapor are substantial, the sorption isotherm approaches the y -axis. At low relative pressures, the vapor uptake is small because of the weak polymer-sorbate forces; once a molecule is sorbed, however, the adsorbate-adsorbate forces promote the sorption of further molecules, in a cooperative process, so that the isotherms become convex to the pressure axis.¹² For inert vapors, the isotherm is closer to the x -axis. This is also evident in the sorption isotherms for organic vapors in the polymers HCPeM [Fig. 4(b)] and HFPEM [Fig. 4(c)].

Because of the dipolarity in the PEM-based polymers, it is understandable that the polar vapors such as acetone and methanol would be sorbed more than nonpolar vapors, like toluene and cyclohexane. The modified polymers HFPEM and HCPeM sorbed acetone and toluene vapors to a slightly greater extent than did PEM; greater free volume in modified polymers facilitates higher sorption than that of PEM. The representative sorption/desorption kinetics for a polar vapor (methanol) and a nonpolar vapor (toluene) on one of the modified polymers (i.e., HCPeM) are depicted in Figures 5 and 6, respectively. The rate of sorption was calculated from the slope of the initial linear region of such kinetics and is tabulated in Table

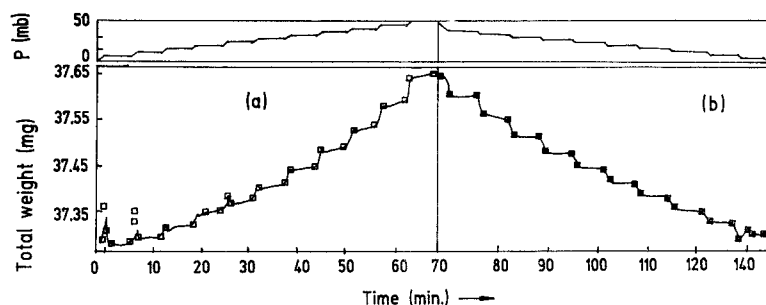


Figure 6 HCPem-Toluene: (a) sorption kinetics, (b) desorption kinetics.

I. It is observed that the polar vapors are sorbed at a faster rate than the nonpolar vapors. The extent of sorption of toluene vapors in the polymers HCPem and HFPEM was almost comparable, although the rate of sorption was 1.3 times in HFPEM ($6.5 \times 10^{-3} \text{ mg min}^{-1}$) compared to that in HCPem. Furthermore, it is also observed that the sorption kinetics for vapors that have an affinity for the polymer, for instance methanol, can be clearly distinguished from those of inert vapors, like toluene, based on a higher rate of sorption and the smooth profile of the plot.

Solubility parameters and relative partition coefficients

The relative importance of structural features in enhancing the extent or rate of sorption is difficult to quantify. We sought to rationalize the sorption isotherms in terms of the concepts of polymer-solution chemistry, and semiempirical models available for estimating response of sorption-based sensors to organic vapors. The simplest description of polymer-vapor interactions is based on solubility parameters. The solubility parameter of a substance is defined as the square root of the molar vaporization energy per unit volume and, as such, is a measure of cohesive energy

(or enthalpy).^{9,12} In general, the more similar the solubility parameter values of two materials, the lower their heat of mixing and the greater their mutual solubility. The values of solubility parameters were estimated using molecular group-contribution methods.^{9,12,13}

Snow and Wohltjen¹ compared the responses of a PEM-coated SAW sensor to five vapors to those estimated from the solubility parameters of the polymer and vapors. The order of sensor responses agreed reasonably well with expectations. The authors defined a relative partition coefficient K_r (atm^{-1}) that can be used to compare the partitioning of different vapors in a given polymer, at a given temperature¹:

$$K_r = 1/p_s \exp[V_s(\delta_p - \delta_s)^2/RT] \quad (1)$$

where p_s is the saturation vapor pressure for a solute vapor of molar volume V_s , R is the gas constant, and T is the absolute temperature; δ_p and δ_s are the solubility parameters of the polymer and sorbate, respectively. These parameters were either obtained from published literature or calculated using standard formulae.^{9,12,13} We applied the above model to determine K_r for the sorption of organic vapors on PEM-based poly-

TABLE I
Rate of Vapor Sorption on PEM-Based Polymers

System ^a	Pressure range		Rate of sorption ($\times 10^3 \text{ mg/min}$)
	(mb)	(p/p_0)	
PEM-Water (S)	20-27.2	0.47-0.64	9.62
HCPem-Water (S)	20-27.2	0.47-0.64	0.30
HFPEM-Water (S)	20-27.2	0.47-0.64	6.94
PEM-Toluene (S)	20-30	0.34-0.5	3.05
HCPem-Toluene (S)	20-30	0.34-0.5	4.69
HCPem-Toluene (D)	20-30	0.34-0.5	5.07
HFPEM-Toluene (S)	20-30	0.34-0.5	6.56
HCPem-Benzene (S)	50-100	0.30-0.60	9.32
HCPem-Cyclohexane (S)	78-100	0.46-0.59	1.71
HCPem-Methanol (S)	45-80	0.19-0.35	8.55
HCPem-Methanol (S)	100-150	0.44-0.66	22.0
HCPem-Methanol (D)	100-150	0.44-0.66	21.4

^a S, sorption; D, desorption.

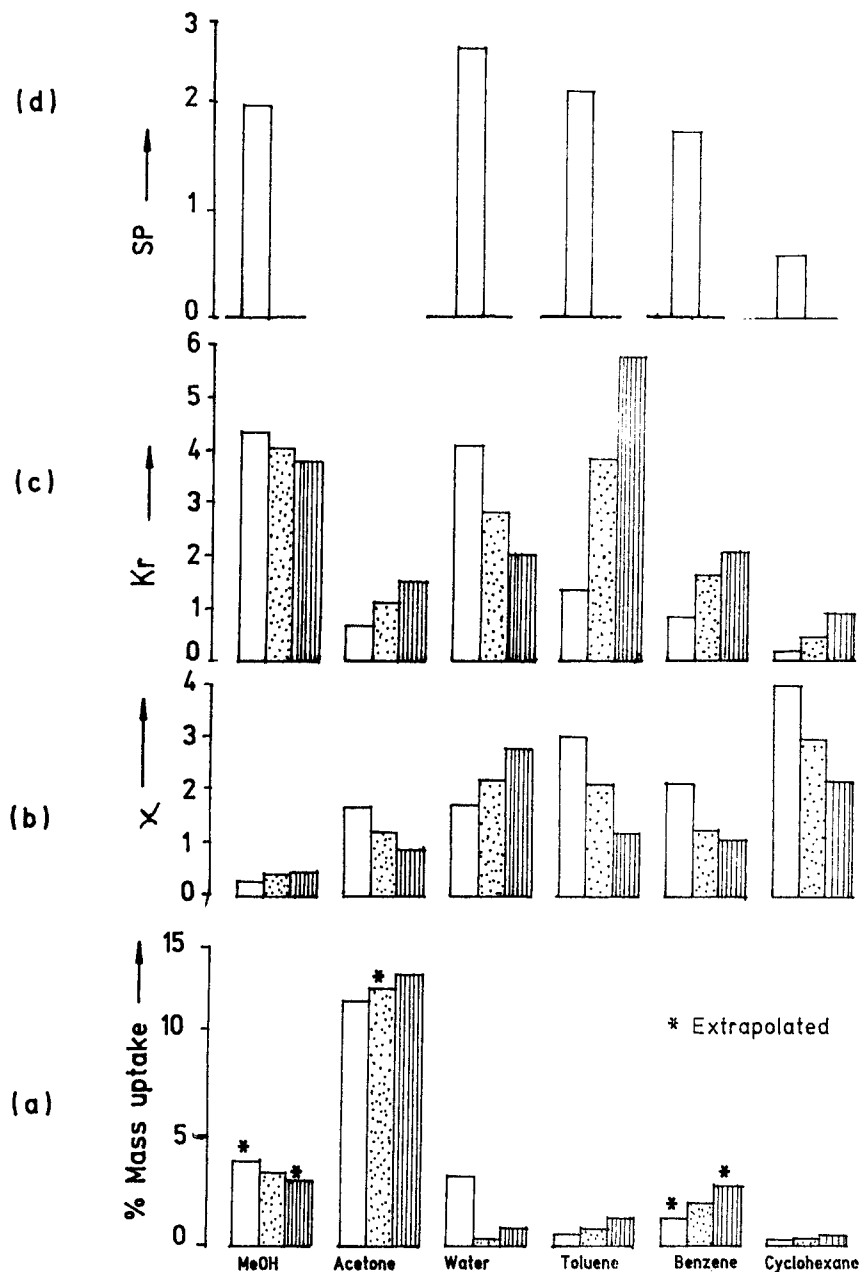


Figure 7 Bar graph depicting (a) %mass uptake, (b) χ , (c) Kr, and (d) SP for PEM, HCPEM, and HFPEM for water and organic vapors.

mers. As observed from Figure 7, the predicted order of sorption is well approximated for nonpolar vapors such as toluene and cyclohexane. For acetone and water, where oriented chemical interactions such as hydrogen bonding are predominant, the theoretical assumptions break down, and discrepancies between the expected and observed sorption behaviors are noted.

Although a number of more complex approaches^{12,13} have been developed that expand the solubility parameter concept to account for such interactions, a better correlation of sorption can be in terms of the Flory-Huggins thermodynamic interaction parameter

χ , which is a measure of heat of mixing of the sorbed molecules with the polymer.^{9,12} In other words, it corresponds to the energy change that occurs when a mole of solvent (sorbate, in this case) molecules is removed from the pure solvent and immersed in an infinite amount of pure polymer. It therefore has a dual nature, being related both to the cohesive energy density (i.e., energy of interaction) and entropy of mixing. The parameter is calculated from the following equation^{9,12}:

$$\chi = (V_s/RT)(\delta_p - \delta_s)^2 + \chi_s \quad (2)$$

TABLE II
Physicochemical Parameters for Analyte Vapors and PEM-Based Polymers

Chemical	V (cm ³ /mol)	δ (J/cm ³) ^{0.5}	P_s (mb)	Parameter ^a				
				R	π_2^*	α	β	$\log L$
Water	12.3	47.81	42.3	0.00	0.43	0.65	0.00	0.26
Methanol	21.7	29.52	226.9	0.28	0.44	0.43	0.47	0.97
Acetone	39.0	19.77	392.4	—	—	—	—	—
Toluene	59.5	18.35	51.09	0.61	0.55	0.00	0.14	3.34
Benzene	48.4	18.7	165.7	0.61	0.59	0.00	0.00	2.80
Cyclohexane	61.4	16.7	170.1	0.30	0.00	0.00	0.00	2.91
PEM	77.7	28.95	—	-1.03	2.75	4.23	0.00	0.86
HCPEM	103.1	26.98	—	—	—	—	—	—
HFPEM	115.1	25.49	—	—	—	—	—	—

^a The parameter values for PEM denote the corresponding regression coefficients, r , s , a , b , l .

where V_s is the molar volume of the sorbate, obtained from literature or calculated using standard formulae; χ_s is an "entropic" correction term used to account for orientational effects and specific interaction between the vapor and the polymer, and is often assumed constant,¹² with a value of 0.35. A higher value of χ (>1.0) implies limited sorption, whereas $\chi < 0.5$ indicates a high degree of sorption. Furthermore, the higher the χ , the less pronounced the convexity of the sorption isotherm.

As observed from Figure 7, for PEM-based polymers, cyclohexane has the highest χ (>2.0) and is sorbed the least. The trend in χ values justifies the observed sorption trends; for instance, for HCPEM, χ increases in the order methanol < benzene < toluene < water < cyclohexane; the extent of sorption is just in the reverse order, as mentioned above. For a nonpolar vapor such as toluene, χ is highest (2.998) for PEM and lowest (1.552) for HFPEM; the value for HCPEM is intermediate. These values are in conformity with the observation that the extent of sorption of toluene in the modified polymers is greater than that in the parent polymer PEM; hence, an estimate of extent of sorption can be made based on χ .

Linear solvation energy relationship

Besides polarity and the thermodynamic interaction parameter, the polymer-sorbate interactions also include such forces as Lewis acidity, van der Waal's interactions, and dispersive forces.^{6-9,12} Linear solvation energy relationships (LSER) have been widely used⁶⁻⁸ to determine the relative contribution of these forces, especially to explain the coating response on SAW devices or the partitioning of solute vapors in various polymers during gas chromatography. Although the LSER is empirical, correlations have been established between solvation parameter scales and fundamental physical and thermodynamic quantities. We chose Abraham's LSER equation^{6,7} given below, to

analyze the observed sorption isotherms in terms of polymer-sorbate interactions:

$$SP = C + rR + s\pi^* + a\alpha + b\beta + l \log L \quad (3)$$

where SP denotes a solute (vapor, in this case) property, whereas C is a regression constant with a value of -1.653 for PEM. The coefficients r , s , a , b , and l refer to the strengths of various interaction forces in affecting vapor solubility in a given polymer. The coefficient r reflects the ability of the polymer to interact with n - or π -electrons. The value of s quantifies the polymer dipolarity; a and b represent the hydrogen-bond basicity and acidity, respectively. The ability of the polymer to separate adjacent members of a homologous series is indicated by l . The corresponding terms R , π^* , and L represent vapor properties that complement those of the polymer. R is the polarizability parameter, reflecting the ability of a vapor to interact with a polymer through n - or π -electrons. π^* is indicative of dipolarity-polarizability and is roughly proportional to the molecular dipole moment for compounds having a single strongly polar functional group. α and β denote hydrogen-bond acidity and basicity, respectively. L is the Ostwald solubility coefficient (same as partition coefficient) on n -hexadecane at 298 K and provides a measure of cavity formation and dispersive forces.^{6,7} In some cases, certain terms may be eliminated because the interactions they characterize do not contribute significantly to overall sorption.

To implement the LSER model in the present application, the solvation parameter coefficients for each coating material must be known. These coefficients are reported for PEM¹ and are given in Table II, but are not available for HCPEM and HFPEM. We thus applied the LSER model only to PEM. As seen from Table II, SP is least for cyclohexane with a value of 0.5520, whereas for toluene and water it is 2.1341 and 2.5030, respectively. Thus, it is reasonable to assume a higher extent of sorption for a larger value of SP . The

$\log K_{\text{GLC}}$ values in the PEM column, reported elsewhere,¹ also concur with the sorption trends predicted on the basis of SP values. In a recent review,⁸ Grate suggested that inclusion of kinetic data in addition to equilibrium data would add variance and dimensionality not indicated by the LSER formalism. Such an approach will be adopted for future studies.

CONCLUSIONS

1. From the characterization of the sorption properties of polymers, it is evident that the sensitivity of PEM toward polar or nonpolar analyte vapors may be improved by incorporation of bisphenol comonomers, which enhance the free volume, hydrophobicity, and polarizability of the parent polymer. Because PEM-based polymers are more sensitive to polar compounds, they can be exploited for sensing and monitoring the presence of these chemicals in the environment.
2. The extent of sorption of volatile organic chemicals in PEM and its derivatives is well approximated in terms of semiempirical models based on solubility parameters, partition coefficient, thermodynamic interaction parameter, or linear solvation energy relationship.
3. The sorption isotherms and kinetics provide information on the extent and rate of sorption for a wide range of analyte vapors and thereby facilitate the selection of sensitive sensor-coating materials. The desorption isotherms, on the other hand, provide important information regarding the reversibility of the material. The sorption hysteresis is indicative of irreversible sensor response.

4. The sorption method is therefore proposed as a convenient alternative to GLC or SAW-based methods of screening the coating materials, which require the generation and individual calibration of a dynamic vapor stream for each partition coefficient to be determined. The proposition gains further support from the concurrence of the sorption results with the semiempirical models used for estimating partition coefficients.

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