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Use of Linear Solvation Energy Relationships for Modeling Responses from Polymer-Coated Acoustic-Wave Vapor Sensors

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The applicability and performance of linear solvation energy relationships (LSERs) as models of responses from polymer-coated acoustic-wave vapor sensors are critically examined. Criteria for the use of these thermodynamic models with thickness-shear-mode resonator (TSMR) and surface-acoustic-wave (SAW) vapor sensors are clarified. Published partition coefficient values derived from gas−liquid chromatography (GLC) are found to be consistently lower than those obtained gravimetrically, in accordance with previous reports, suggesting that LSERs based on GLC-derived partition coefficients will not provide accurate estimates of acoustic-wave sensor responses. The development of LSER models directly from polymer-coated TSMR vapor sensor response data is demonstrated and a revised model developed from SAW vapor sensor response data, which takes account of viscoelastic changes in polymeric coating films, is presented and compared to those developed by other methods.

The similarity between the partitioning phenomena governing polymer-coated thickness-shear-mode resonator (TSMR) and surface-acoustic-wave (SAW) vapor sensor responses and the retention of vapors in gas−liquid chromatography (GLC) has spawned a number of efforts to apply GLC retention models to acoustic-wave (AW) sensor responses.[1−13] The most promising of these are based on linear solvation energy relationships (LSERs).[6,14−24] LSER models of vapor−polymer interactions evolved from the early studies of solvatochromic phenomena by Kamlet et al.[14] and have been extensively explored by Abraham et al. for a wide range of solubility-related phenomena in GLC.[15−23] The application of LSERs to AW sensor responses was first suggested by Grate et al.[1,8] in the late 1980s and formally described in the excellent conceptual paper by Grate and Abraham in 1991.[2] Since then, Grate et al.[3−5,24−27] and others [6,28−30] have applied LSERs and related concepts to sensor response estimation models and coating selection strategies for TSMR and SAW sensor arrays.

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While some of the limitations of applying LSER models to AW sensor responses have been discussed in previous reports,[4,29,30] a number of issues have not been addressed or addressed only in passing. Their application to modeling SAW sensor responses has been approached in different ways[4,6] and justified under assumptions that may or may not be applicable to such devices. Their derivation directly from TSMR response data has not yet been reported. In this article, we critically examine the thermodynamic basis for LSERs, the applicability of GLC-derived LSERs to AW sensors, and the derivation of LSER models directly from TSMR and SAW sensor responses.

LSER Model. The LSER model portrays partitioning as a linear combination of five component interactions between a sorbed vapor-phase analyte and a sorbent phase at equilibrium:[2,3,24,25]

$$\log K = c + rR_2 + s\pi_2^{\mathrm{H}} + a\sum\alpha_2^{\mathrm{H}} + b\sum\beta_2^{\mathrm{H}} + l\log L^{16} \quad (1)$$

where K is the "infinite-dilution" partition coefficient of the analyte in the sorbent matrix (e.g., a polymer) and R_2, π_2^{H}, $\sum\alpha_2^{\mathrm{H}}$, $\sum\beta_2^{\mathrm{H}}$, and $\log L^{16}$ are characteristic descriptors of the solute (analyte) vapors, called solvation parameters. The coefficients r, s, a, b, and l are the corresponding sorbent-phase parameters, referred to here as solvation coefficients, complementing those of the vapors with respect to each interaction, and c is a regression constant comprising residual components not described by the other terms in the equation.

K is defined as the ratio of vapor concentration in the sorbent (polymeric) phase, C_{poly}, to that in the gas phase, C_{vap}, at equilibrium: $K = C_{\mathrm{poly}}/C_{\mathrm{vap}}$. R_2 is a measure of polarizability, this interaction being more significant when solute π electrons (or lone electron pairs) are involved.[16,17,19,31] π_2^{H} represents contributions of the solute dipolarity to the overall interaction via dipole−dipole and dipole−induced dipole interactions.[14,16,19,31] $\sum\alpha_2^{\mathrm{H}}$ represents the hydrogen bond acidity,[21] $\sum\beta_2^{\mathrm{H}}$ the hydrogen bond basicity,[22] and $\log L^{16}$, a combination of dispersion forces and "cavity formation" as reflected in the partition coefficient of the analyte vapor in hexadecane.[16,17]

Using eq 1 and the known solvation parameters of a group of solvents, the corresponding solvation coefficients r, s, a, b, and l of sorbent polymers can be derived, for example, by measuring GLC specific retention volumes, computing the corresponding K values from the retention volumes, and then regressing the vapor solvation parameters onto those K values.[20] (Note that the coefficient a represents hydrogen bond *basicity* and b represents hydrogen bond *acidity* of the polymer). Polymer solvation coefficients thus derived, in turn, can be used to estimate K values via eq 1 for untested vapors whose solvation parameters are known.

To the extent that polymer-coated AW sensor responses are governed by the mass of vapor sorbed into the polymer layer, they depend on K and hence should be predictable for such vapors. Alternatively, the AW sensor responses can be used to derive LSER coefficients directly,[6] provided that the sensor response mechanisms are properly understood, the sensor coating thickness is properly controlled, and vapor concentrations approach infinite dilution.

LSER solvation parameters have been determined for thousands of small organic molecules.[18] A subset of these was used by Abraham et al. in GLC experiments at 298 K to derive solvation coefficients for 14 polymers and GLC stationary phases.[3,4,20] Importantly, this is the only compilation of GLC-derived polymer solvation coefficients determined at a temperature low enough to be relevant to practical polymer-coated AW vapor sensor operation and modeling.

Thermodynamics. Most of terms in eq 1 can be related directly to Gibbs free energies.[16] α_2^{H}, β_2^{H}, and $\log L^{16}$ represent thermodynamic equilibrium constants that vary in proportion to $e^{-\Delta G/RT}$, where ΔG is the change in Gibbs free energy.[16,17,21,23] L^{16} is the partition coefficient of the analyte in hexadecane,[16] and the basicity and acidity terms are essentially $\log K$ values for the 1:1 complexation of hydrogen acids/bases against a given reference hydrogen base/acid in tetrachloromethane[21,22] (with regard to acidity/basicity, we point out that it might prove advantageous to use the more broadly applicable Lewis acid/base concept, rather than parametrizing the acid/base interactions only via proton-based bonding).

However, R_2 and π_2^{H} do not have such a direct relationship with ΔG. R_2 is derived from that portion of the molar refraction of the solute in excess of that of a hydrocarbon molecule of approximately the same characteristic volume (see eq 14 in ref 16).[14,16,19] π_2^{H} originated as a spectroscopically determined solvent parameter, π_2^*, which, as Abraham et al. remarked, "is certainly not a Gibbs-related quantity".[16] The most recent set of π_2^{H} values was determined by a combination of methods using several previously published GLC retention data sets collected at elevated temperature.[31] In many cases, $\pi_2^{\mathrm{H}} \approx \pi_2^*$. Although it was asserted that these π_2^{H} values are Gibbs energy-related,[31] the relationship is not obvious and the relevance of values determined from high-temperature GLC retention data to models of interactions at lower temperatures is also unclear.

It has been suggested that the regression constant, c, has thermodynamic meaning, corresponding to the contribution to sorption represented by a compound having solute parameters that are all equal to zero, such as the inert gas krypton.[3] However, interactions of such compounds with a polymer would occur through dispersion forces and should be subsumed by the $l \log L^{16}$ term of eq 1. In fact, the thermodynamic significance of the c term, if any, is indeterminate. It is the quantity remaining after the best least-squares fit is obtained by multilinear regression. It should also contain the factor 1/2.303 since ΔG is related to $\ln K$ rather than $\log K$ as used in eq 1; similarly, the factor 1/2.303 must be included in the coefficient of any of the other terms of eq 1 whenever a relationship to thermodynamic factors is examined. If the five terms in eq 1 successfully captured all of the thermodynamically relevant components of the vapor−sorbent-phase interaction, then the c term should be zero.

The thermodynamics of solute sorption in bulk polymers generally involve the following contributions:[32−34] (1) combinatorial entropy (Flory−Huggins lattice theory[35]), (2) free-volume effects

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resulting from the differences in the structures of the small solutes and the polymer chains,[32] (3) interactional enthalpy, and (4) elastic factors that depend on the polymer structure. The latter are normally negligible for liquid or rubbery amorphous polymers and are small even for glassy or crystalline polymers at low levels of vapor sorption.[33,34,36] In most cases, vapor sorption is endothermic, meaning that entropy drives the sorption process.[33,34,36] Yet, log L^{16} is the only solvation parameter that accounts explicitly for entropic factors (i.e., cavity formation). Equation-of-state effects, which arise from changes in free volume between the pure polymer and the polymer−vapor mixture, are not explicitly accounted for in the model. Furthermore, the solvation parameters are not all independent variables, but exhibit a degree of covariance that varies with the specific parameters.[16] To the extent that the terms in eq 1 are correlated, log K cannot be represented as a simple linear combination of these terms. Thus, the mathematical form of the LSER model might suggest a higher level of precision than is attainable in practice. Nonetheless, the model is a useful, if only approximate, representation of the thermodynamics of the sorption process.

AW Sensor Responses. It has been recognized for some time that responses of polymer-coated TSMR and SAW sensors to vapor sorption can arise from both gravimetric and viscoelastic changes in the polymer coating film, depending on the high-frequency polymer shear modulus and on the acoustic thickness of the polymer film prior to, and during, vapor exposure.[4,6,37−43] Since there are no provisions in the LSER model for viscoelastic effects, their influence on AW sensor responses must be accounted for separately. That is, strictly speaking, the LSER model is only applicable to the gravimetric (i.e., mass-loading) changes reflected in the AW sensor response.[4] As discussed below, an additional term can be included to account for viscoelastic effects and responses interpreted meaningfully in the context of the LSER model provided certain conditions are met.

Parts a−c of Figure 1 illustrate the important boundary conditions dictating the influences of gravimetric and viscoelastic effects on polymer-coated TSMR and SAW sensors. In reality, there is a continuum among these regions rather than the sharp boundaries depicted.[39−41]

When the coating thickness is small relative to the acoustic wavelength (in the polymer), the film moves synchronously with the underlying AW sensor substrate and it is referred to as acoustically thin (see Figure 1a, quadrants 1 and 4).[39] For TSMRs with acoustically thin polymer coatings, responses reflect only gravimetric changes in the polymer film, regardless of the polymer shear modulus (Figure 1c, quadrants 1 and 4).[40] This is because the motion imparted by the TSMR displaces the entire film parallel to the surface of the substrate and the film is minimally deformed by the wave motion.

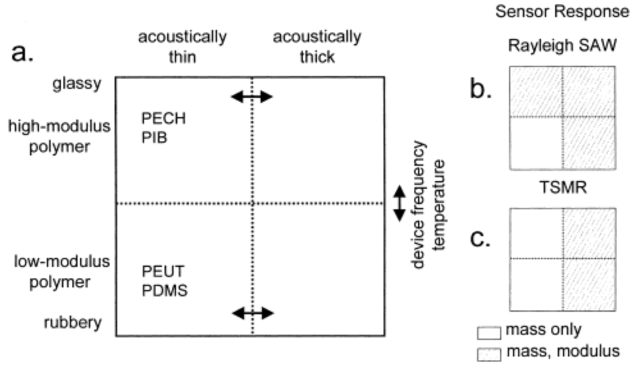

Figure 1. Classification scheme for factors affecting responses of polymer-coated AW sensors: (a) generalized diagram of relevant polymer properties. The borderline between acoustically thick and thin films depends on the initial polymer modulus, the temperature, and the device parameters (PIB, poly(isobutylene); PECH, poly(epichlorohydrin); PDMS, poly(dimethylsiloxane); PEUT, poly(etherurethane)). Importance of mass and modulus changes for (b) SAW sensors employing Rayleigh waves and (c) TSMR sensors.

For SAW devices with acoustically thin films, responses are solely gravimetric only if the shear modulus of the polymer is very low (i.e., $<10^7$ N/m^2) at the frequency of sensor operation (Figure 1b, quadrant 4). This condition is met for low-molecular-weight poly(dimethylsiloxane) (PDMS) and certain other liquid or rubbery polymers.[38,42] More typical polymers have shear moduli above this limiting value at AW sensor operating frequencies (e.g., in the range of 10^7−10^9 N/m^2),[39,43] and responses from SAW sensors with acoustically thin coatings reflect a combination of gravimetric and viscoelastic changes in the polymer (Figure 1b, quadrant 1). This is because the Rayleigh wave generated at the SAW sensor surface has a surface-parallel component of displacement in the direction of propagation that reverses every half-wavelength, causing a periodic contraction and expansion in the film that is sensitive to the viscoelasticity of the film material and influences the wave velocity (and, hence, frequency) for polymers that are more glassy in character at the temperature and frequency of operation. For such materials, vapor sorption invariably changes the free volume of the polymer film,[44] which leads to a change in its viscoelasticity (i.e., modulus) and a consequent viscoelastic contribution to the SAW response.

The following equation, which is analogous to that in ref 45, describes the relationship between the thermodynamic partition coefficient, K, and the responses from AW sensors with acoustically thin coatings:

$$mK = K_{\mathrm{AW}} = \Delta f_{\mathrm{vap}}\rho_{\mathrm{poly}}/\Delta f_{\mathrm{poly}}M_{\mathrm{vap}}C_{\mathrm{vap}} \qquad (2)$$

where Δf_{vap} (Hz) is the frequency shift (sensor response) measured upon exposure to a vapor at concentration C_{vap} (mol/L), Δf_{poly} (Hz) is the frequency shift measured upon initial deposition of the polymer film, M_{vap} (kg/mol) is the molar mass

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of the analyte vapor, and ρ_{poly} (kg/L) is the polymer density. For solely gravimetric responses (TSMRs, and SAWs with low-modulus polymers), K equals K_{AW}; i.e., the thermodynamic partition coefficient is identical to that determined by the AW device. The variable m can be considered an amplification factor that reflects the influence of modulus contributions to polymer-coated AW sensor vapor responses.[4,6] For acoustically thin films, m is independent of vapor concentration and has been expressed in the context of SAW sensor responses recently by Grate and Zellers as follows:[44]

$$m = 1 + f_L(\rho_{poly}/\rho_L)S_e \tag{3}$$

where f_L is the fractional free volume associated with the sorbed vapor (in its condensed liquid state), ρ_L is the density of the sorbed vapor in its liquid state, and S_e is the sensitivity (i.e., frequency shift) of the SAW device to the volume expansion accompanying vapor sorption within a unit mass of polymer film. Since f_L can, to a first approximation, be considered constant among different small organic molecules, and S_e will be constant for a given polymer coating, m varies as the ratio of the densities of the polymer and sorbed vapor.[44] Assuming a unit-density polymer, this ratio will range from about 0.6 to 1.7 for most common solvent vapors, and m will hence vary from about 1.6 to 2.7, which is supported by experimental evidence where gravimetric contributions are properly determined.[38,44] Thus, m will vary with both the polymer and vapor being considered and has a value of unity for film-coated TSMRs and SAWs exhibiting no modulus contributions.

If the thickness of the coating film is greater than a few percent of the acoustic wavelength (i.e., acoustically thick), then cross-film stress gradients can become important, the responses from both TSMR and SAW sensors will be larger than predicted by eq 2, and m is no longer independent of concentration (Figure 1b and c, quadrants 2 and 3). As the film thickness approaches a value where the phase shift of the acoustic wave is $\pi/2$, the film passes through a resonance and the frequency shows a significant inflection. In the case of the SAW, an approximate guideline for maintaining an acoustically thin film is that the film thickness, h, must meet the following criterion:[39]

$$h \ll |G|/f_0 v_0 \rho_{poly} \tag{4}$$

where $|G|$ is the complex shear modulus of the polymer, f_0 is the sensor operating frequency, and v_0 is the SAW velocity (3.16 km/s for quartz). Since $|G|$ is a measure of film stiffness, softer (i.e., rubbery or liquid) polymer films must be kept proportionally thinner than stiffer (glassy) films to avoid stress-related anomalies associated with the onset of the acoustically thick regime. Unfortunately, h is difficult to specify a priori because $|G|$ depends on the temperature, frequency of operation, interfacial stresses in thin films, and vapor-specific variables, such as density and plasticizing capability.[39,40,44] Limits on polymer layer thicknesses for ST-quartz SAW sensors can be determined more precisely for different assumed values of |G| from expressions in refs 39 and 40.[49]

It is important to appreciate that an acoustically thin film can be rendered acoustically thick by virtue of the reduction in modulus caused by increases in free volume accompanying vapor sorption.[39,44] This factor is much more important than swelling per se, which is on the order of just a few percent typically.[40,41,43]

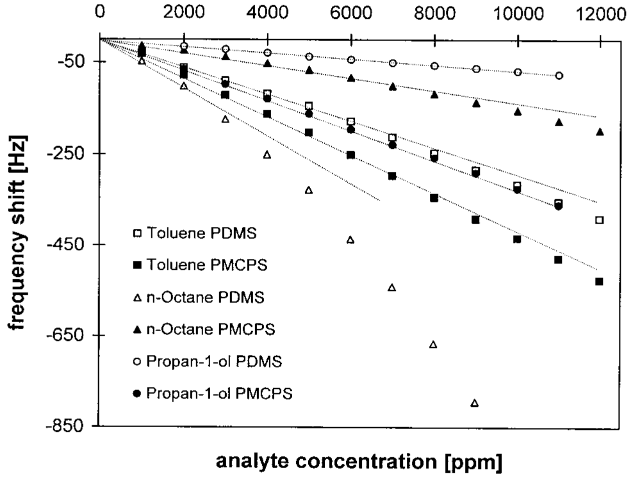

Figure 2. Sensor responses of TSMRs coated with PDMS and PMCPS upon exposure to *n*-octane, toluene, and propan-1-ol at 303 K over a larger concentration range (polymer acronyms defined in the text).

Vapor Concentration Range. For AW devices with acoustically thin polymer coatings, plotting Δf_{vap} versus C_{vap} should yield a straight line that intersects the origin and whose slope is proportional to K in accordance with eq 2.[42] Most polymers suitable for use as sensor coatings yield linear sorption isotherms in the low-concentration range, where Henry's law holds. At higher concentrations, positive deviations from Henry's law are expected and are considered typical of vapor sorption behavior in rubbery polymers.[33,34] As shown in Figure 2, it is difficult to establish general guidelines specifying the concentration range over which Henry's law behavior might be observed.

Figure 2 presents responses from two different polymer-coated TSMRs (acoustically thin films of PDMS and poly[methyl(cyanopropyl)siloxane] (50% cyanopropyl substituents, PMCPS) exposed to three different vapors (*n*-octane, toluene, propan-1-ol) over a fairly large vapor concentration range at 303 K. The shapes of the isotherms differ among the vapor/sensor pairs. The PDMS/*n*-octane isotherm deviates from linearity at a lower concentration (5−6% of the vapor saturation) and to a much greater extent than that of the PMCPS/*n*-octane isotherm, while deviations from linearity for toluene are similar for the two sensors. Both of the propan-1-ol isotherms remain linear over the entire concentration range tested (>20% saturation). (Note that 10% of saturation at 303 K corresponds to 2430 ppm of *n*-octane, 4830 ppm of toluene, and 3780 ppm of propan-1-ol). Similar behavior has been observed with different types of sensors (i.e., SAW, TSMR, capacitors, traditional balances) coated with various polymers, indicating that *the effect is independent of the transduction mechanism operating in the sensor*.[33,34,46,47]

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There is no uniform correlation between the initial slope of the isotherm and the onset of nonlinearity. In the high-concentration regimes, it is not possible to derive meaningful partition coefficients and there is a tendency toward overestimation. These data suggest that vapor concentrations be constrained to <3% of the saturation concentration in order to derive reliable estimates of K. Polymers with specific or preferential sorption sites can exhibit dual-mode sorption isotherms,[48] making the derivation of meaningful K values are even more difficult.

Determination of Polymer Solvation Coefficients and LSER Models by GLC. In deriving polymer solvation coefficients from GLC measurements for use in LSER models of AW sensor responses, it is assumed that bulk sorption governs both GLC retention and sensor responses and that concentrations approach infinite dilution. In GLC experiments, although injection volumes are usually adjusted to avoid overloading the column stationary phase, actual vapor concentrations within the stationary phase along the column length are not measured and may reach locally high values, particularly at low operating temperatures. This, in turn, may lead to distortions in eluting peaks and consequent errors in infinite-dilution K values. Temperature must also be controlled to relate GLC-derived LSER models to AW sensors, since the relative importance of the various component interactions between vapors and polymers, which dictate the polymer solvation coefficient values, change to differing degrees with temperature.[6,19] Substrate differences (i.e., a granular solid support versus a polished flat surface) and matrix differences (e.g., dry, inert gas carrier versus humid air) may also affect coefficient determinations.[6,43]

Table 1 presents a comparison of GLC-derived K values and those derived from gravimetric measurements for three polymers and each of several vapors.[49] The K_{GLC} values considered here are a subset of those compiled by Abraham et al.[3,4,20,43,50] from GLC experiments conducted at 298 K. The K_{GRV} values were determined from the mass changes measured in thin films of polymers cast on thin glass substrates that were suspended from the weighing arm of an electronic microbalance and exposed to the vapors at 296 K.[49] The polymers considered are polyisobutylene (PIB), polyepichlorohydrin (PECH), and poly(triphenylmethylsiloxane) (OV-25) (see ref 4 for structures). In all cases, $K_{GLC} < K_{GRV}$, and, on average, K_{GLC} is ~60% smaller.

Grate et al. reported limited data indicating similar discrepancies between GLC-derived K values and those derived by other methods,[38] but the strength of the trend revealed here was not evident in their data. This problem undoubtedly accounts for the absence, to date, of any reports demonstrating accurate predictions of AW sensor responses on the basis of GLC-derived LSER models. The fact that accurate predictions of *relative* AW sensor responses among a series of vapors have been demonstrated[5,45] and that the solvation coefficients are generally consistent with those derived by other methods (see below) suggests that the apparent negative bias in the GLC-derived K values and LSER models from refs 3, 4, and 20 may be the result of a systematic error in the determinations, which would principally affect the regression coefficient, c. In any case, in light of the findings presented here it is clear that AW sensor modeling efforts that have relied on these GLC-derived K values and/or LSER models will need to be revisited.[3−5,24,43,45]

Table 1. Discrepancies among Partition Coefficients Derived from GLC Retention Data GLC (K_{GLC}) and by Direct Gravimetric Measurements (K_{GRV}) for Several Polymer−Vapor Pairs

polymer	vapor	K_{GRV}/K_{GLC}
PIB	toluene	1.79
	m-xylene[a]	1.55
	isooctane	2.70
	butan-2-one	1.56
	n-butyl acetate[a]	1.11
	1,2-dichloroethane	1.92
	trichloroethene[a]	1.92
	average	1.79 ± 0.49
PECH	toluene	1.30
	m-xylene[a]	1.34
	butan-2-one	1.35
	n-butyl acetate[a]	1.39
	1,2-dichloroethane	1.47
	trichloroethene[a]	2.33
	average	1.53 ± 0.40
OV-25	toluene	1.42
	m-xylene[a]	1.70
	butan-2-one	1.79
	n-butyl acetate[a]	1.44
	1,2-dichloroethane	1.54
	trichloroethene	1.54
	tetrachloroethene	1.63
	average	1.58 ± 0.14
all	grand average	1.64 ± 0.37

[a] For these combinations, K_{GLC} values were calculated from GLC-derived LSER models in ref 20.

Determination of Polymer Solvation Coefficients and LSER Models from TSMRs. The derivation of polymer solvation coefficients directly from TSMR sensor responses has not been reported previously. To this end, analyses were performed on a data set of responses to 27 vapors from two identical arrays of TSMRs coated with acoustically thin films of the following polysiloxanes (see Figure 3): PDMS, PMCPS, PMPS, PMAPS (8% aminopropyl groups), PMiPCAS (10% acid groups), and CSVAL (10% valine groups).[36] These polysiloxanes have extremely low moduli and exhibit static glass transition temperatures in the range of 150 K.[47,51,52] For experimental details, see refs 36 and 53.

Each TSMR array consisted of six discrete AT-cut quartz crystals with gold electrodes operating at 10 MHz and coated to a thickness of 150−200 nm ($\Delta f_{poly} = 10-15$ kHz) on each face. Dry air was used as the carrier gas. Response isotherms were linear, and K values were calculated (via eq 2) from the slopes over concentrations ranging up to 2% of saturation for each vapor.[42] Table 2 presents the average K values obtained from the two TSMR sensor arrays. The differences between duplicate determinations of K were <10% in all cases and were typically less than 5%. Agreement with K values for benzene and toluene in PDMS reported by Baltussen (i.e., 419 and 1106, respectively) is excel-

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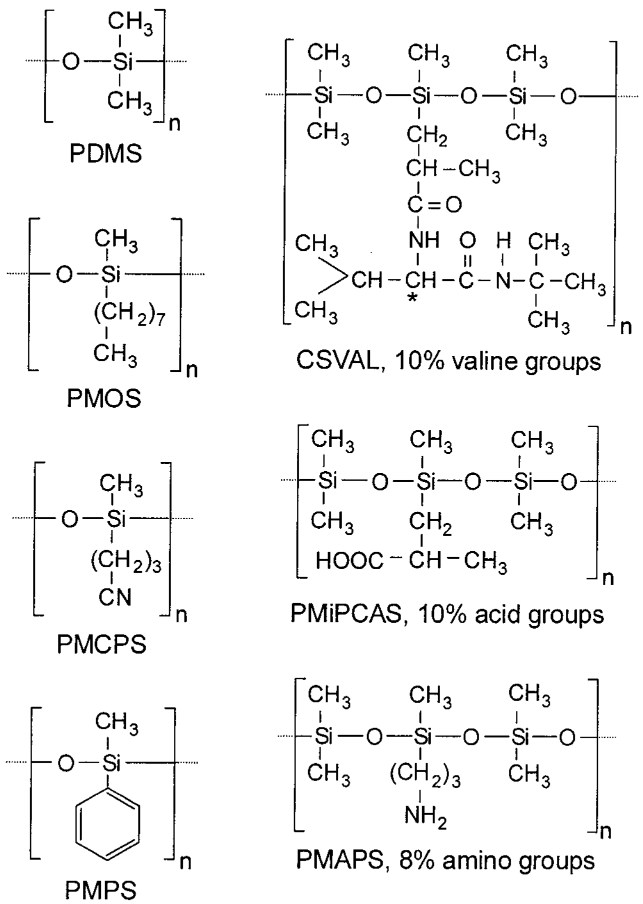

Figure 3. Systematically side-chain-modified polysiloxanes: poly(dimethylsiloxane) (PDMS, nonpolar), poly(methyloctylsiloxane) (PMOS, nonpolar), poly[methyl(cyanopropyl)siloxane] (PMCPS, dipolar, weakly basic), poly(methylphenylsiloxane) (PMPS, polarizable, nonpolar), poly[methyl(aminopropyl)siloxane], 8% amino groups (PMAPS, dipolar, basic), poly[methyl(isopropylcarboxylic acid)siloxane], 10% acid groups (PMiPCAS, dipolar, acidic), and poly[methyl(2-carboxy(D-valinyl-*tert*-butylamide)propyl)siloxane], 10% valine groups (Chirasil-Val, CSVAL, slightly dipolar, slightly basic).

lent.[54] In addition, the TSMR-derived K values for PIB or PECH in Table 2 are very close to those obtained by the gravimetric method reported in the previous section (e.g., PIB/toluene: $K_{TSMR} = 1030$, $K_{GRV} = 1010$; PECH/toluene: $K_{TSMR} = 1480$, $K_{GRV} = 1550$).

The K values from Table 2 were combined with published vapor solvation parameters[23] to calculate the polymer solvation coefficients by eq 1. Data for water, *n*-butylamine, acetic acid, and propionic acid were not included in the regression because of their tendency to aggregate in the vapor phase.[55] Table 3 presents the resulting polymer solvation coefficients and the corresponding statistics. The t statistic was used to determine the statistical significance of the solvation coefficients. Statistically nonsignificant polymer solvation coefficients and their errors are represented in parentheses in Table 3. The F statistic was used to assess whether the regression equation is a useful predictor of log K.[57] All of the F statistics were found to exceed this critical value for the six LSERs developed.

The polarizability coefficient r is not statistically significant for any of the polymers, as found previously for LSERs derived from SAW sensor responses for other polymers (see below and ref 6). Apparently, the polarizability interactions are captured in the s coefficient (dipole/induced dipole) and/or in the l coefficient (dispersion: induced dipole/induced dipole). If the rR_2 term is eliminated from the LSER there is little change in the coefficients of determination, R^2, and standard errors of the estimates, $SE_{\log K}$. Furthermore, the F statistics actually increase upon elimination of rR_2 (data not shown). The regression constant, c, is small in all cases, as expected, and is not statistically significant (we accepted a maximum standard error of 50% to consider a parameter statistically significant).

Performing the regression by forcing $c = 0$ and also omitting the rR_2 term gave the results shown in Table 4. The R^2 values decrease slightly, $SE_{\log K}$ values do not change significantly, and the F statistics decrease slightly, but remain measurably higher than those in Table 3 (full equation). For the polymers included in this study, we conclude that the polarizability term and the regression constant do not add significantly to the predictive capability of the model. Direct comparison of these TSMR-derived solvation coefficients with those derived by GLC is not possible since GLC retention data were not available. However, several of the polymers used here are similar in structure to those for which GLC (and SAW sensor) data are available, and they are discussed in the next section.

In general, the LSER coefficients in Table 4 are consistent with the structures of the polymers, with the possible exception of the unexpectedly high a coefficient for PDMS, which should interact exclusively via dispersive interactions. Vapor−substrate interactions may be contributory in this case. The fit of the LSER model to the data for PMiPCAS is poorer than that for the other polymers. Although this polymer is acidic, as evidenced by the K values for pyridine and butylamine in Table 2, the b coefficient is not significant (Table 3). The large a coefficient (hydrogen bond basicity) was not expected either. These unusual hydrogen-bonding coefficients most likely arise from the dipolarity and amphoteric nature of the COOH group, but they also call into question the validity of the LSER approach: there is a sufficient number of adjustable parameters such that an unequivocally acidic polymer can be described by a large coefficient of basicity and a negligible coefficient of acidity.

Analysis of variance reveals that the log L^{16} parameter is the predominant independent variable, accounting for most of the variance in the data. The importance of dispersive interactions has been reported previously for other vapor−polymer systems[5,6] and reveals an interesting trend in the errors in modeled K values. Back-calculation of K values from the TSMR-based LSERs developed here results in significantly larger errors for vapors with large dipole moments, hydrogen-bonding strengths, or both coupled with small log L^{16} values. The following vapors and the

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(55) For strongly hydrogen-bonding vapors, such as carboxylic acids and amines, the effective molecular masses and, hence, effective concentrations are increased by aggregation in the gas phase.[56] Partition coefficients calculated under the assumption of ideal gas behavior[4] thus will be positively biased. This, in turn, will lead to errors in the determination of the polymer solvation coefficients via eq 1. Since the extent of this effect on the vapor concentration and chemical properties of such vapors is difficult to determine, they should be excluded from the test set.[16]

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Table 2. TSMR-Derived *K* Values for Five Polysiloxanes at Infinite Dilution

polymer	*K* values					
	PDMS	PMCPS	PMPS	PMAPS	PMiPCAS	CSVAL
n-hexane	350	80	140	220	190	250
n-heptane	800	160	350	520	480	590
n-octane	2200	360	950	1400	1200	1600
n-nonane	5300	800	2500	3300	2850	3950
n-decane	10800	1700	5300	6600	5850	8000
cyclohexane	420	140	270	300	280	330
benzene	400	560	430	470	400	350
toluene	1200	1300	1200	1300	910	1000
o-xylene	3700	4300	4300	4400	2900	3300
m-xylene	3200	3200	3300	3600	2400	2800
p-xylene	3100	3100	3300	3500	2500	2700
trichloromethane	260	660	330	470	300	310
tetrachloromethane	450	320	450	410	370	400
tetrachloroethene	1600	1300	1900	1700	1400	1700
1,2-dichloroethane	270	890	430	500	430	290
ethanol	180	1000	130	450	730	440
propan-1-ol	250	1630	250	790	1100	800
propan-2-ol	100	620	100	290	380	300
butan-1-ol	570	3900	670	2100	2600	2100
pentan-1-ol	1500	8800	1600	5400	5700	6000
propionaldehyde	45	170	65	100	90	55
butyraldehyde	110	380	160	260	160	150
acetone	90	470	120	240	170	110
cyclohexanone	4700	22000	11500	12500	6700	5600
diethyl ether	90	65	55	80	70	75
anisole	3200	8500	5600	5400	3500	3200
ethyl acetate	270	500	290	400	330	260
acetonitrile	<30	830	130	270	400	85
benzonitrile	8900	78000	28000	34000	16300	11400
ethanethiol	90	180	85	130	150	120
thiophene	600	1200	800	800	750	610
pyridine	970	5000	1800	2400	3400	1460
n-butylamine[a]	570	3200	440	2100	11100	3900
acetic acid*	1700	35000	3400	13800	16000	17000
propionic acid[a]	11500	95000	20000	47000	54000	65000
water[a]	<30	800	440	210	1300	140

[a] Omitted from multiple regressions used to derive LSER models due to gas-phase aggregation (see text and ref 56).

Table 3. Polymer Solvation Coefficients Determined by Using the LSER Model: Full Equation

polymer	*c*	*r*	*s*	*a*	*b*	*l*	R^2	$SE_{\log K}$	*F*
PDMS	(0.18)[a]	(−0.05)	(0.21)	0.99	(0.10)	0.84	0.969	0.127	155
standard error	(0.13)	(0.18)	(0.20)	0.23	(0.23)	0.03			
PMCPS	(−0.12)	(0.02)	1.65	2.71	0.38	0.72	0.981	0.107	258
standard error	(0.11)	(0.13)	0.14	0.19	0.17	0.03			
PMPS	(−0.20)	(−0.03)	0.97	1.11	(0.10)	0.86	0.983	0.101	285
standard error	(0.12)	(0.13)	0.13	0.18	(0.16)	0.03			
PMAPS	(−0.01)	(−0.23)	0.97	1.99	(0.24)	0.83	0.975	0.109	205
standard error	(0.10)	(0.14)	0.14	0.19	(0.18)	0.03			
PMiPCAS	(0.13)	(−0.16)	0.79	2.36	(0.28)	0.77	0.939	0.163	80
standard error	(0.15)	(0.20)	0.22	0.29	(0.26)	0.04			
CSVAL	(0.02)	(0.05)	(0.23)	2.22	0.46	0.85	0.974	0.112	197
standard error	(0.11)	(0.14)	(0.16)	0.20	0.18	0.03			

[a] Values in parentheses are not statistically significant (standard error larger than 50% of the actual value) but are included for comparison.

range of errors in modeled *K* values among the six coatings serve to illustrate the trend: 1,2-dichloroethane (25−50%), trichloromethane (15−25%), ethanol (30−50%), pyridine (15−30%), the aldehydes (30−60%), etc. In contrast, for vapors with larger log *L*[16] values (i.e., >2.5) the accuracy of modeled *K* values is consistently greater (errors are consistently ≤15%). The strength of this trend is noteworthy as it indicates that the LSER model is inherently less accurate for polymer−vapor interactions that are not dominated by dispersive forces. This can be explained by the directional nature of the remaining interaction forces (i.e., hydrogen bonding or dipole−dipole) that may involve entropic factors that are not expressed in the model or enthalpic factors that violate the assumption of linear superposition.

Determination of Polymer Solvation Coefficients and LSERs from SAW Sensors. Patrash and Zellers[6] were the first to apply the LSER modeling approach suggested by Grate and Abraham[2] to experimental SAW sensor response data. At the time, LSER coefficients for the polymer coatings they used had not been determined at their test temperature of 298 K. While the importance of polymer modulus changes on SAW sensor re-

Table 4. Polymer Solvation Coefficients Determined Using the Simplified LSER Model Where the Regression Constant, *c*, and the Polarizability Term, rR_2, Have Been Omitted

polymer	*s*	*a*	*b*	*l*	R^2	$SE_{\log K}$	*F*
PDMS	(0.18)[a]	1.05	(0.23)	0.89	0.966	0.128	191
standard error	(0.12)	0.21	(0.18)	0.01			
PMCPS	1.65	2.66	0.31	0.69	0.978	0.106	326
standard error	0.09	0.18	0.14	0.01			
PMPS	0.92	0.99	(0.01)	0.80	0.979	0.107	314
standard error	0.09	0.18	(0.14)	0.01			
PMAPS	0.77	1.91	0.40	0.82	0.972	0.111	245
standard error	0.09	0.18	0.14	0.01			
PMiPCAS	0.67	2.37	0.46	0.80	0.936	0.161	102
standard error	0.13	0.27	0.21	0.02			
CSVAL	0.27	2.25	0.43	0.85	0.974	0.109	263
standard error	0.09	0.18	0.14	0.01			

[a] Values in parentheses are statistically not significant (standard error larger than 50% of the actual value) but are included for comparison.

Table 5. Comparison of LSER Solvation Coefficients Determined by GLC and from SAW Sensor Response Data at 298 K

		polymer solvation coefficients					
polymer	method	c^d	*r*	*s*	*a*	*b*	*l*
OV-25	SAW[a]	0.363		0.962	0.605	0.351	0.763
OV-25	GLC[b]	−0.846	0.177	1.287	0.556	0.440	0.885
PMPS	TSMR[c]	(−0.20)		0.97	1.11		0.86
PIB	SAW[a]	0.416			0.875	0.275	0.869
PIB	GLC[b]	−0.766	−0.077	0.366	0.180	0.000	1.016
PDMS	TSMR[c]	(0.18)			0.99		0.84
OV-275	SAW[a]	−0.134		1.88	3.03	0.616	0.615
SXCN	GLC[b]	−1.630	0.000	2.283	3.032	0.516	0.773
PCMPS	TSMR[c]	(−0.12)		1.65	2.71	0.38	0.72

[a] Reference 6. [b] Reference 20. [c] From Table 2, presented here to facilitate comparisons. [d] Values in parentheses are not statistically significant, but are included for comparison.

sponses was known from the earlier work of Grate et al.[43] and Martin and Frye,[37] the magnitudes of the modulus contributions were not known. Therefore, they determined LSER solvation coefficients for the polymers from K_{AW} values derived directly from the SAW sensor responses.

Under the assumption that the modulus-related contributions to the responses are directly proportional to the number of sorbed analyte molecules, K_{AW} should be proportional to the true thermodynamic *K* (i.e., $K_{AW} = mK$; see eq 2). Since eq 1 represents *K* as a log term, log *m* becomes an added term on the left-hand side of eq 1 that can be brought to the right-hand side.

Using the expression for *m* in eq 3 leads to the following modified model that combines the thermodynamic components of the LSER model with the nonthermodynamic components associated with the swelling-induced modulus changes:

$$\log K_{SAW} = 2.303 \log m + [rR_2] + s\pi_2^H + a\sum\alpha_2^H + b\sum\beta_2^H + l \log L^{16} \quad (5)$$

where *m*, as defined above, comprises terms related to the vapor (f_L/ρ_L) and to the polymer ($\rho_{poly}S_e$). This revision to the LSER model accounts for the vapor specificity of the modulus contributions to the SAW sensor response. The polarizability term is in brackets for the reasons already discussed (i.e., statistical nonsignificance).

For a given polymer, $\rho_{poly}S_e$ will be a constant. As discussed above, f_L does not vary greatly among common solvent vapors and can also be assumed constant. For a unit-density polymer and for experiments aimed at deriving polymer solvation coefficients via eq 5, ρ_{poly}/ρ_L will have an average value near unity. Thus, to a first approximation, the modulus term, 2.303 log *m*, can be treated as a constant, c_{SAW}, that replaces the regression coefficient, c_{GLC}, derived from GLC. With this term added to account for modulus contributions, the polymer solvation coefficients determined from SAW sensor response data by eq 5 should be equivalent to those determined from TSMR, gravimetric, and GLC data.

In Table 5, LSER coefficients reported by Patrash and Zellers are compared to those from Abraham et al.[3,4,20] for the two polymers common to both studies. A third comparison is presented between the structurally similar polymers poly[(bis(allylcyano)siloxane] (OV-275, from SAW sensor response data[6]) and poly[(bis(cyanopropyl)siloxane] (SXCN, from GLC retention data[3,4,20]). Coefficients for the three structurally analogous polysiloxanes derived from the TSMR response data in Table 4 are also included in Table 5 for comparison.

Some interesting trends emerge. First, the regression constant from the SAW sensor response data (c_{SAW}) is larger than c_{GLC} in all cases. If the argument presented in the preceding paragraph holds, then $c_{SAW} = 2.303 \log m$, with $m = 3.3$ and 3.4 for PIB and OV-25, respectively, and $m = 4.5$ for OV-275 (vs SXCN). These factors are remarkably close to the empirical correction factors reported by Grate et al. (3.63, 2.95, and 4.24, respectively) in attempting to reconcile these SAW response data with GLC-derived LSER model predictions.[4] The fact that these amplification factors are larger than expected (vida infra) is attributed to the use of GLC-derived solvation parameters to estimate the true K.

Second, note the similarities among the values of *s*, *a*, *b*, and *l* for OV-25: differences range from only 9−25% for SAW versus GLC-derived values. The *s* and *l* coefficients for the structurally analogous PMPS from the TSMR data are also similar to those of OV-25. The fact that the OV-25 *r* coefficient from the SAW data is statistically nonsignificant is consistent with the PMPS model from the TSMR data but differs from that for OV-25 determined by GLC. The significant *b* coefficients observed in both models for OV-25 have been attributed to hydroxyl groups associated with impurities in the commercial material.[50] The fact that the PMPS *b* coefficient is not significant reflects the absence of such hydroxyl-containing impurities. Comparing c_{SAW} for OV-25 to the statistically nonsignificant, negligibly small regression constant for PMPS, we find that $m = 1.79$. This amplification factor is consistent with these both being relatively low-modulus films and with estimates of amplification factors for other liquid SAW sensor coatings reported by Patrash and Zellers.[6] Coefficients for the three polysiloxanes with alkylcyano side chains are also remarkably similar, despite their minor structural differences. Collectively, these results indicate that introducing *m* as a constant for deriving LSER coefficients of polymeric SAW sensor coatings is reasonable. Furthermore, they establish that thermodynamically relevant polymer solvation coefficients can be derived from SAW sensor response data.

For PIB, the coefficients do not correlate quite as well as for the preceding coatings. While the *l* coefficient is similar in both cases, none of the other coefficients agree very well. This can be attributed to differences in the influence of the substrate (i.e., a solid support in the case of GLC versus a SiO_x passivation layer in the case of the SAW device) and to the determination of SAW sensor responses in an atmosphere of air at 50% relative humidity. Interactions of vapors, particularly polar vapors, with the substrate have been documented previously for PIB-coated SAW sensors,[43] and were noted by Patrash and Zellers to be the most likely cause for discrepancies in trends in their data for lower alcohols.[6] This factor, together with the presence of a low concentration of sorbed water vapor in the PIB could account for the significant *a* and *b* values observed in the SAW-sensor derived solvation coefficients. Grate et al. have shown that silanizing the sensor substrate prior to coating deposition can minimize such substrate effects.[58]

It is interesting to note that even the GLC-derived LSERs yield a significant value for the PIB *a* coefficient, despite experiments being run in an inert atmosphere, and also yield nonzero values of *r* and *s*, none of which would be expected for PIB. No explanation for these anomalous coefficient values could be found in the original reports.[3,4,20,27] This suggests that the solid support upon which the stationary phase was coated may play a significant role in vapor retention.

The coefficients for PDMS from the TSMR data are included in Table 5 because PDMS is expected to provide values similar to those of PIB. The *l* coefficients are similar, as expected, and the large *a* coefficient for PDMS provides evidence for substrate effects in the AW sensor responses, as mentioned above. The lack of a significant *b* coefficient can be attributed to running in a dry, inert atmosphere, similar to the GLC testing conditions. The lack of a significant *s* value is consistent with the SAW-derived value for PIB and with expectations and is in contrast to the nonzero GLC-derived PIB *s* coefficient, which appears to be due to external factors.

Although the preceding analyses establish that valid polymer solvation coefficients can be derived from SAW responses by approximating *m* as a constant in eq 5, to obtain accurate SAW response estimates requires that *m* be evaluated. This, in turn, requires estimates of ρ_{poly}, ρ_L, f_L, and S_e. The former two quantities are easily obtained, and approaches to obtaining the latter two quantities are discussed in refs 43 and 44. With such information at hand for a range of polymers and solvents, the ability to predict SAW sensor responses via LSER modeling is straightforward.

In summary, caution must be exercised in applying LSER models to the prediction of responses from AW sensors. The LSER method is an empirical approach to modeling thermodynamic relationships and is thus dependent upon the underlying measurements (e.g., GLC retention volumes or AW sensor responses) used to derive the model parameters. The validity of those measurements must be carefully assessed with regard to the target application. The mathematical form of the LSER suggests greater accuracy in predicting vapor−polymer *K* values than is generally attainable. Where dispersive interactions predominate in the vapor sorption process, LSER models can perform with reasonable accuracy (i.e., <15% error in predicting *K* values), but when oriented interactions are predominant the accuracy tends to degrade. Analyses presented here confirm earlier anecdotal data[38] indicating that the GLC-derived LSER models reported in refs 3, 4, and 20 and exploited elsewhere[5,26,45] have a systematic negative bias and appear useful only for predicting *relative* AW sensor responses. A modification to the LSER model, which accounts quantitatively for the influence of swelling-related modulus effects on SAW sensor responses, has been proposed here, and it has been shown that thermodynamically relevant solvation coefficients can then be derived directly from TSMR (no regression constant necessary) and SAW (regression constant necessary, if modulus contributions occur) sensor response data. These approaches to AW-sensor LSER model development are valid provided that coating thicknesses are properly controlled and that vapor concentrations are maintained at values low enough to ensure ideal behavior. Further evidence presented here suggests that the rR_2 term in the standard LSER equation can be omitted without significant loss in model performance. While polymer solvation coefficients derived from GLC, TSMR, or SAW response data are in general agreement, idiosyncrasies attributable to vapor interactions with solid support materials, sensor substrates, sorbed water vapor, or other factors unrelated to the polymer can influence the coefficient values.

A final comment is warranted on LSERs for modeling responses to vapor mixtures, which has not been attempted in any study of which we are aware. We anticipate that translation of data between GLC and AW sensors will be problematic for many vapor mixtures. Vapors within mixtures that are resolved chromatographically will interact with the stationary phase individually. In contrast, with AW sensors vapor mixtures interact with the polymeric coating simultaneously (i.e., in "batches") and such interactions may not be independent. For vapors whose sorption is governed predominantly by dispersive interactions, there may be minimal effect, but for vapors exhibiting directed interactions, there are likely to be significant differences between results from GLC and those from AW sensors because the assumption of linear superposition of component interactions is not likely to hold. This topic requires further study to characterize the influence of such factors on LSER modeling of AW sensor responses.

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