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The Fractional Free Volume of the Sorbed Vapor in Modeling the Viscoelastic Contribution to Polymer-Coated Surface Acoustic Wave Vapor Sensor Responses

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Surface acoustic wave (SAW) vapor sensors with polymeric sorbent layers can respond to vapors on the basis of mass loading and modulus decreases of the polymer film. The modulus changes are associated with volume changes that occur as vapor is sorbed by the film. A factor based on the fractional free volume of the vapor as a liquid has been incorporated into a model for the contribution of swelling-induced modulus changes to observed SAW vapor sensor responses. In this model, it is not the entire volume added to the film by the vapor that contributes to the modulus effect; it is the fractional free volume associated with the vapor molecules that causes the modulus to decrease in a manner that is equivalent to free volume changes from thermal expansion. The amplification of the SAW vapor sensor response due to modulus effects that are predicted by this model has been compared to amplification factors determined by comparing the responses of polymer-coated SAW vapor sensors with the responses of similarly coated thickness shear mode (TSM) vapor sensors, the latter being gravimetric. Results for six to eight vapors on each of two polymers, poly(isobutylene) and poly(epichlorohydrin), were examined. The model predicts amplification factors of the order of about 1.5−3, and vapor-dependent variations in the amplification factors are related to the specific volume of the vapor as a liquid. The fractional free volume factor provides a physically meaningful addition to the model and is consistent with conventional polymer physics treatments of the effects of temperature and plasticization on polymer modulus.

All acoustic wave devices are sensitive to added surface mass, and this has served as a powerful and unifying principle for the development of acoustic wave chemical sensors. However, it is also clear that it is misleading to assume that an observed sensor response is due solely to mass loading. Other effects, such as polymer viscoelastic changes, acoustoelectric phenomena, and liquid properties such as viscosity and density, can contribute significantly to observed responses. Acoustic wave sensors have been reviewed in several articles and two books.[1−19]

In this paper, the interest is primarily in the viscoelastic contribution to polymer-coated surface acoustic wave (SAW) vapor sensor responses. Investigations of polymer-coated thickness shear mode (TSM) and SAW devices have shown that polymer viscoelastic properties can play a significant role in sensor responses under certain circumstances. Several approaches have been used in these investigations, including simultaneous measurements of velocity and attenuation, impedance analysis, independent measurements of vapor sorption or added mass, and comparisons of the responses of TSM and SAW devices.[20−29] In

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general, the ability to probe polymer viscoelastic properties with acoustic wave devices remains a subject of lively research.[30−38]

Throughout this paper it is assumed that the polymer film under consideration is observed at a temperature above the dilatometric or "static" glass transition of the polymer. Under these conditions, vapor diffusion within the film is rapid, yielding a homogeneous vapor polymer solution. In addition, the thermal expansion of the polymer is primarily attributable to "the creation of additional free volume with rising temperature".[39] Furthermore, we will consider only polymer films that are acoustically thin with and without sorbed vapor, as set out previously by Martin and Frye.[28]

Under these conditions, TSM vapor sensors respond solely on the basis of mass loading. However, SAW vapor sensors may still include a viscoelastic contribution to the observed response due to the surface wave's intrinsic sensitivity to film viscoelastic properties.[22,23,28,40] Vapor absorption increases the volume and decreases the modulus of the film. Modulus decreases in an acoustically thin film contribute to the SAW vapor sensor response in the same direction as the mass-loading response, thus amplifying the response. This mechanism for a viscoelastic contribution to SAW vapor response is dependent on "swelling-induced modulus changes".[20]

The inherent sensitivity of surface acoustic waves to viscoelastic properties is evident in thermal expansion experiments, where frequency shifts of several hundred hertz per degree of temperature change are observed as the temperatures of polymer-coated SAW devices are changed.[20,28] This sensitivity is observed even after the inherent temperature drift of the bare SAW device is removed and is due to the decrease in polymer modulus as the polymer expands with increasing temperature. Specifically, the modulus decreases because the free volume of the polymer material is increasing.

Modeling the extent of the viscoelastic contribution to polymer-coated SAW vapor sensors in the acoustically thin regime is the subject of the present paper. A factor for the fractional free volume of the vapor as a liquid is added to a semiempirical model for swelling-induced modulus changes described previously.[20] This factor provides a more realistic physical understanding of the contribution of free volume, associated with the sorbed vapor molecules, to the viscoelastic component of the response. In addition, this modification revises the estimate of the relative roles of mass loading and viscoelastic contributions and improves the predictions of the model relative to experimental data.

THEORETICAL TREATMENTS

Swelling-Induced Modulus Change Model. Acoustic wave vapor sensor responses, Δf_v, can be related to the partition coefficient, K, according to eq 1, assuming that responses are solely due to mass loading.[20,41]

$$\Delta f_v = \Delta f_s C_v K/\rho_S \qquad (1)$$

The partition coefficient gives the ratio of the concentration of vapor in the sorbent phase, C_s, to the concentration of vapor in the vapor phase, C_v. As shown in eq 2, the product of the vapor concentration in the gas phase and the partition coefficient give the vapor concentration in the polymer phase. It is the vapor sorbed into the polymer to which the sensor responds.

$$KC_v = C_s \qquad (2)$$

The remaining symbols that are in eq 1 are Δf_s, the amount of sorbent phase on the sensor surface expressed as a frequency shift, and ρ_s, the density of the sorbent phase.

The SAW response model in eq 1 was modified in 1992[20] to include a term related to swelling-induced modulus changes as in eq 3.

$$\Delta f_v = (\Delta f_s C_v K/\rho_S) + (C_v K/\rho_L)(\Delta f_s A_{SAW}/\alpha) \qquad (3a)$$

$$\Delta f_v = (\Delta f_s C_v K/\rho_S) + v_1\,(\Delta f_s A_{SAW}/\alpha) \qquad (3b)$$

In this equation, Δf_v now represents the total frequency shift on vapor sorption due to both gravimetric and swelling effects. The first term is the gravimetric effect exactly as in eq 1.

In the second term, $C_v K$ gives the concentration of vapor in the sorbent phase according to eq 2, and $C_v K/\rho_L$ gives the volume fraction increase of the sorbent phase due to vapor sorption, i.e., the amount of swelling, where ρ_L is the density of the vapor as a liquid. The factor of $C_v K/\rho_L$ is equivalent to the volume fraction of the vapor in the polymer/vapor solution, to be designated as v_1 in the polymer physics treatment below. The model is shown using v_1 in eq 3b. It is assumed in calculating the volume fraction increase due to the sorbed vapor that

$$V_v/V_s \approx V_v/(V_s + V_v) \qquad (4)$$

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where V_s and V_v are the volumes of the sorbent polymer phase and the liquid vapor.

The variable A_{SAW} in the second term of eq 3 represents the kilohertz change in frequency due to a 1 °C change in temperature per kilohertz of coating on the device surface. Values for this variable are empirically determined by measurements of the effect of polymer thermal expansion on polymer-coated SAW device frequency, correcting for the inherent temperature drift of the bare SAW device. The product $\Delta f_s A_{SAW}$ gives the frequency change per degree of temperature change for a polymer-coated SAW device. The units of A_{SAW} reduce to $°C^{-1}$, the same units as a coefficient of thermal expansion. The variable α in eq 4 is the coefficient of thermal expansion of the polymer, i.e., the fractional volume increase per degree. Thus, $\Delta f_s A_{SAW}/\alpha$ gives the frequency change due to a fractional volume increase of the polymer film, assuming that the experimentally observed frequency changes are attributable to the polymer thermal expansion that is occurring.[20]

To summarize, the second term of eq 3 uses independent knowledge of the partition coefficient of the test vapor into the polymer film to calculate the concentration of the vapor in the film and, using the density of the vapor as a liquid, to estimate the volume increase of the film due to vapor absorption. Then the effect of the volume increase on SAW frequency is empirically calibrated from thermal expansion experiments. Thus, the second term in eq 3 estimates the fractional volume increase of the film and the effect of this fractional volume increase on frequency, assuming that the volume effect of sorbed vapor is equivalent to the volume effect due to thermal expansion (free volume).[20]

In the original publication, it was noted that, in the derivation of eq 3, development of a quantitatively accurate model was not the main intention.[20] The derivation was intended to rationalize why observed responses should exceed gravimetric responses calculated from partition coefficients and eq 1 above. At that time, the prevailing belief was that SAW devices with soft organic sensing layers behaved simply as gravimetric sensors. It was also noted in the original publication[20] and subsequent descriptions[15] that the model tended to give results that overestimated observed responses. Furthermore, the model was noted to have weaknesses related to the assumptions made to estimate swelling effects. The primary weakness was the assumption that the effect of increasing the volume by vapor absorption is the same as the effect of increasing the volume by thermal expansion.[20] It is this assumption that shall be corrected in the model described below.

Conventional Polymer Physics Treatment of Plasticization. Ferry's classic treatment of polymer viscoelasticity includes a chapter on plasticization, where polymers containing a small-molecule diluent are described as solutions.[39] Polymer materials with sorbed vapor under consideration in this paper correspond to solutions containing a few weight percent or less of diluent. Ferry describes the fractional free volume of a polymer/diluent solution, f, at temperature T in terms of the polymer free volume, f_2, the volume fraction, v_1, of diluent, and a parameter, β', relating the diluent volume fraction to free volume.

$$f(T, v_1) = f_2(T) + \beta' v_1 \tag{5}$$

As Ferry explains,[39] "fractional free volumes are not quite additive, so the total fractional free volume depends on (volume) composition" according to

$$f = f_1 v_1 + f_2 v_2 + k_v' v_1 v_2 \tag{6}$$

For small amounts of diluent, as is the case for trace vapor sorption, the β' parameter corresponds to

$$\beta' = f_1 - f_2 + k_v' \tag{7}$$

In these equations, subscripts 1 and 2 refer to the diluent and polymer, respectively, which correspond to the vapor and the sorbent phase in sensor experiments. Fractional free volumes are given by f variables and volume fractions are given by v_i variables. In eq 7, the last two terms are small relative to the first, so β' is qualitatively equivalent to f_1, the fractional free volume of the diluent as a liquid. Values for β' are in the range of 0.1–0.3, according to Ferry in the third edition of his book.[39] The first edition notes that f_1 is "of the order of 0.2 for simple liquids far above their glass transition temperature".[42]

The effects of diluent concentration and temperature on polymer relaxation times, and hence polymer modulus, are given by eqs 8 and 9, respectively.

$$\log a_c = -(1/2.303)\{\beta' v_1/[f_2\,(f_2 + \beta' v_1)]\} \tag{8}$$

$$\log a_T = -\{B/(2.303 f_g)\}\{[\alpha_f\,(T - T_g)]/[f_g + \alpha_f(T - T_g)]\} \tag{9}$$

Equation 8 describes the shift factor, a_c, used in assessing the effect of the diluent concentration on polymer modulus. It is entirely analogous to the shift factor, a_T, conventionally used in assessing the effect of temperature on polymer modulus, as given in eq 9. The subscript g in eq 9 refers to a reference temperature taken as the glass transition temperature. B is a constant on the order of unity. The parameter α_f gives the thermal expansion of free volume relative to the total volume. This fractional volume increase is equivalent to the polymer thermal coefficient if the expansion is attributable entirely to increasing free volume.

The key feature of eqs 8 and 5 is that the volume fraction of the diluent, v_1, is modified by the coefficient β'. Comparing the effect of diluent volume fraction with the effect of thermal expansion, it should be noted that the free volume increase associated with thermal expansion directly affects modulus. However, the volume increase due to the addition of the diluent, or sorbed vapor, affects the modulus only to the extent that it is modified by β'. This aspect of conventional polymer physics motivates a revision to the swelling-induced modulus change model in eq 3 using either β' or f_1 to modify v_1.

Viscoelastic Models Related to SAW Sensors. In Martin's treatment of viscoelastic effects and film resonance as they relate to polymer-coated SAW sensors, the effect of diluent on modulus was modeled as a volume effect, following the approach of Ferry,

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and then combined in an equation including the effects of both temperature and diluent volume.[28]

$$F(T, V_1) = F(T) + \chi V_1 \tag{10}$$

$$\log a_T = -\{B/(2.303\, F_o)\}\{[\alpha_f(T - T_o) + \chi V_1]/[F_o + \alpha_f(T - T_o) + \chi V_1]\} \tag{11}$$

Martin's equations, given here as eqs 10 and 11, are reproduced using his symbols, where the subscript of 0 refers to a reference temperature. Equation 10 is identical to Ferry's eq 5 above, such that F refers to fractional free volume ($F = f$), V_1 is the volume fraction of diluent ($V_1 = v_1$), and Martin's plasticizing parameter, χ, is equivalent to Ferry's β'. The symbol for the thermal expansion coefficient of the polymer, attributable primarily to free volume increase, is unchanged. Martin's plasticizing parameter was treated as an empirically determined parameter, and no physical interpretation was given.[28,43]

The factor of $[\alpha_f(T - T_o) + \chi V_1]$ in Martin's combined equation for the shift factor, incorporating both temperature and diluent effects, emphasizes again that the volume fraction of diluent is not treated identically to the volume fraction increase of free volume due to thermal expansion. Instead, the volume fraction of diluent is modified by the plasticizing parameter, which reduces the impact of the total diluent volume fraction.

Martin also described relationships for the film thickness, h, and density, ρ, of polymer films with sorbed vapor according to eqs 12a and 13a, where C is the molar concentration of vapor in the film (moles of sorbed vapor permilliliter of polymer), V is the molar volume of the vapor as a liquid (moles per milliliter), and m is the molecular weight (grams per mole) of the vapor. The h_o and ρ_o terms indicate values for the polymer film with no sorbed vapor. For small vapor volume fractions, these relationships can be expressed according to eqs 12b and 13b.

$$h(\mathrm{C}) = h_o\,(1 + CV) \tag{12a}$$

$$h(C) = h_o(1 + V_1) \tag{12b}$$

$$\rho(C) = (\rho_o + Cm)/(1 + CV) \tag{13a}$$

$$\rho(C) = (\rho_o + C_vK)/(1 + V_1) \tag{13b}$$

It should be noted that the vapor volume fraction $V_1 = v_1 = C_vK/\rho_L$ is present in eqs 11, 12, and 13, and thus all these equations contain vapor-specific information related to the vapor's density as a liquid.

Revised Swelling-Induced Modulus Change Model and Physical Interpretation. The model in eq 3 uses a calculated volume fraction of the vapor and an empirically determined volume effect based on thermal expansion to estimate the effect of the vapor on the modulus. From the treatments by Ferry and Martin, it is apparent that the entire volume fraction of the diluent cannot be treated as equivalent to an increase in fractional free volume due to thermal expansion. Only some fraction of the diluent volume fraction should be regarded as equivalent to "thermal expansion free volume"—that fraction being defined by the β' coefficient in Ferry's treatment or the equivalent χ parameter used by Martin. Therefore, the fractional volume increase due to vapor sorption in the model in eq 3 should be modified by β' as shown in eq 14.

$$\Delta f_v = (\Delta f_s C_v K/\rho_S) + \beta'(C_v\, K/\rho_L)(\Delta f_s A_{SAW}/\alpha) \tag{14a}$$

$$\Delta f_v = (\Delta f_s C_v K/\rho_S) + \beta' v_1(\Delta f_s A_{SAW}/\alpha) \tag{14b}$$

Equation 14b is the same as eq 14a except that v_1 is substituted for C_vK/ρ_L to show the similarity to the polymer physics treatments in eqs 5 and 8.

The physical meaning of the β' coefficient as set out by Ferry will now be examined.[39]

Ferry notes that in eq 7 the last term k_v' is of the order of -0.01 and in the second term f_2 is of the order of 0.025 and that both these terms are small compared to the first term, f_1, which is approximately 0.2. Given this simplification, it follows that β' is approximately equal to f_1, the fractional free volume of the diluent. This is a physically meaningful quantity that shall be used in the revised model for SAW response. Strictly speaking, β' is slightly less than f_1 based on the typical values just noted. In conventional polymer physics treatments, β' is often taken as an adjustable parameter when modeling particular polymer/diluent pairs.

The meaning of Martin's plasticization parameter, χ, Ferry's β' coefficient, and the influence of diluent vapor on polymer modulus is clear: the total free volume in the polymer containing diluent vapor molecules is the free volume of the polymer plus the free volume associated with the vapor. Therefore, it is not the entire volume fraction of the diluent, v_1, that influences modulus. It is the portion of the volume fraction of vapor that is free volume, given by f_1v_1 or $\beta'v_1$, that influences the modulus; this free volume can be treated the same as free volume added by thermal expansion. This interpretation addresses the primary weakness of the original swelling-induced modulus change model (eq 3) in a logical and physically meaningful way. Using this approximation, the model in eq 14 can be modified to eq 15, where f_L is the same as f_1.

$$\Delta f_v = (\Delta f_s C_v K/\rho_S) + f_L(C_v K/\rho_L)(\Delta f_s\, A_{SAW}/\alpha) \tag{15a}$$

$$\Delta f_v = (\Delta f_s C_v K/\rho_S) + f_1 v_1(\Delta f_s A_{SAW}/\alpha) \tag{15b}$$

Like eq 14b, eq 15b uses notation to show the similarity to the polymer physics treatments in eqs 5 and 8. However, the present model can be distinguished from polymer physics treatments in the fact that β' is normally treated as an adjustable parameter, whereas f_L is not treated as an adjustable parameter in eq 15.

It is apparent that the revision of the model in eq 3 with the fractional free volume of the vapor as a liquid significantly decreases the predicted contribution of modulus effects. Assuming a value of f_L that is of the order of 0.2, the modulus term is one-fifth as large as previously suggested by eq 3.

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(43) Martin used a single value of 0.083 for χ when modeling the effects of pentane and trichloroethylene in poly(isobutylene). This fitted parameter was found using a thermal expansion coefficient of 0.00025 for the polymer.

Amplification Factor Due to Modulus Effects. Equation 15 can be rearranged so that the total response can be expressed as

$$\Delta f_v = n\{\Delta f_s C_v K/\rho_S\} \tag{16}$$

where

$$n = 1 + f_L(\rho_S/\rho_L)(A_{SAW}/\alpha) \tag{17}$$

The variable n can be regarded as the amplification factor, giving the ratio of the observed response to the gravimetric response. The second term in eq 17 gives the ratio of the modulus contribution to the mass contribution in eq 15. The parameters in this ratio consist of those that are vapor-dependent, f_L and ρ_L, and those that are strictly polymer-dependent, ρ_S, A_{SAW}, and α.

It is worth noting that accurate values of partition coefficients are not necessary for prediction of the relative roles of mass and modulus contributions using the model given by eqs 15, 16, and 17.

RESULTS AND DISCUSSION

Comparison with Experimental Results. Determining the portion of an observed SAW vapor sensor response that is attributable to a modulus change generally requires some independent method to determine the mass loading of the polymer film. In the initial work on the swelling-induced modulus change model, infinite dilution partition coefficients determined by gas–liquid chromatography (GLC) were used.[20] More recent work using the responses of gravimetric TSM sensors has provided partition coefficient values at finite vapor concentrations.[22,23] Values determined by this approach will be used in the present paper. Comparison of TSM and SAW vapor sensor responses to determine the gravimetric component of the SAW response was originally demonstrated by Martin and Frye.[28]

Experimental values of the amplification factor were determined according to eq 18, using data published previously.[22,23]

$$n = K_{SAW}/K_{TSM} \tag{18}$$

The parameters K_{SAW} and K_{TSM} are apparent partition coefficients calculated from observed responses according to eq 1. Conversion of sensor responses to apparent partition coefficients is a convenient way to normalize the data, recognizing that these represent thermodynamic partition coefficients only if the sensor's response is entirely gravimetric. The assumption of gravimetric TSM vapor sensor responses was supported experimentally by impedance analyzer measurements and by consideration of the conditions for obtaining acoustically thin performance.[22]

Table 1 provides a list of test vapors, the vapor abbreviations used in this paper, and relevant properties such as the densities and fractional free volumes of the vapors as liquids. Numerical values for K_{SAW} and K_{TSM} for each of several vapors on poly(isobutylene), PIB, and poly(epichlorohydin), PECH, are given in Table 2. With the exception of one column of K_{SAW} values for PIB, these values are all taken from reference 22 which provides a detailed experimental description. The SAW results reported for PIB in reference 22 and in the third column of data in Table 2 were determined from a sensor that was silanized with 1,3-diphenyl-1,1,3,3-tetramethyldisilazane to reduce surface hydroxyl concentration prior to application of the polymer film.[44] This reduces the extent to which interfacial adsorption contributes to the observed SAW responses, which are otherwise assumed to be due entirely to bulk absorption in the polymer. Use of this silanizing reagent to reduce interfacial adsorption has been described previously.[45]

Table 1. Vapor Abbreviations and Parameters

vapor	abbrev	fractional free vol as a liquid, f_L	density as a liquid, ρ_L
n-hexane	HEX	0.275	0.64
benzene	BZN	0.204	0.872
toluene	TOL	0.198	0.859
dichloromethane	DCM	0.234	1.325
carbon tetrachloride	CTC	0.239	1.584
methyl ethyl ketone	MEK	0.237	0.785
cyclohexane	CHX	0.223	0.777
chloroform	CLF	0.235	1.455

Table 2. Polymer-Coated Acoustic Wave Sensor Data Normalized as *K* Values

vapor	PIB K_{TSM}	PECH K_{TSM}	PIB[a] K_{SAW}	PIB[b] K_{SAW}	PECH[b] K_{SAW}
HEX	186	43	506	528	100
BZN	315	648	701	743	1173
TOL	1000	1673	2302	2282	3096
DCM	70	238	161	162	451
CTC	358	287	623	634	422
MEK	112	712	307	386	1760
CHX	401		847		
CLF	193		391		

[a] SAW device silanized with 1,3-diphenyl-1,1,3,3-tetramethyldisilazane to reduce surface hydroxyl concentration prior to application of the polymer film. [b] Polymer film applied to unsilanized silica surface.

Interfacial adsorption is expected to be most significant when a SAW sensor with a very nonpolar polymer, such as PIB, is tested against polar vapors that can hydrogen bond to surface silanol or siloxy groups. The experimentally observed K_{SAW} values for several vapors on PIB using an unsilanized sensor provided in the fourth column of data in Table 2 are in excellent agreement with those derived from a silanized sensor, except those for methyl ethyl ketone. Methyl ethyl ketone is a base that is expected to hydrogen bond to surface silanols. These results support the notion that interfacial adsorption can contribute to polymer-coated SAW responses.[46] The important point with regard to this study is that when interfacial adsorption makes a significant contribution to the SAW response, experimental amplification factors calculated

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(44) This point was not specified in the Faraday Transactions paper, which focused primarily on the experimental details of the TSM measurements.

(45) McGill, R. A.; Grate, J. W.; Anderson, M. R. In *Interfacial Design and Chemical Sensing*; Mallouk, T. E., Harrison, D. J., Eds.; ACS Symposium Series 561; American Chemical Society: Washington, DC, 1994; pp 280–294.

(46) The plausibility of this mechanism is supported by unpublished results from Grate's laboratory at PNNL, where continuous films of poly(dimethylsiloxane) on SAW devices were found to give calibration curves to MEK that are insensitive to PDMS thickness at low concentrations and curved concave downward in the form similar to a Langmuir isotherm. At higher concentrations, linear absorption behavior dominates, but the total response at higher concentration includes the nonlinear adsorption effect.

Table 3. Comparison of Calculated and Experimental Amplification Factors for PIB[a]

	ρ_S/ρ_L	*n*, calcd,[b] $f_{L = 0.2}$	*n*, calcd,[c] $f_{L\ \mathrm{variable}}$	*n*, exptl,[d,e] $K_{SAW/KTSM}$	*n*, exptl,[d,f] K_{SAW}/K_{TSM}
HEX	1.44	2.73	3.37	2.72	2.84
BZN	1.06	2.27	2.29	2.23	2.36
TOL	1.07	2.29	2.27	2.30	2.28
DCM	0.69	1.83	1.98	2.30	2.31
CTC	0.58	1.70	1.83	1.74	1.77
MEK	1.17	2.41	2.67	2.74	3.45
CHX	1.18	2.42	2.58	2.11	
CLF	0.63	1.76	1.89	2.02	

[a] Poly(isobutylene) $\rho_S = 0.92$, $A_{SAW}/\alpha = 6$. [b] $n = 1 + (f_L/\rho_L)(\rho_S A_{SAW}/\alpha)$. [c] f_L taken from Table 1. [d] Amplification factor, *n*, calculated from K_{SAW} and K_{TSM} values as described in the text. [e] K_{SAW} data were derived from a SAW device silanized with phenyldimethyl groups to reduce surface hydroxyl concentration and reduce adsorption of polar vapors at the silica interface. [f] Amplification factors from SAW sensor data where the SAW device was not silanized.

Table 4. Comparison of Calculated and Experimental Amplification Factors for PECH[a]

	ρ_S/ρ_L	*n*, calcd,[b] $f_{L = 0.2}$	*n*, calculated,[c] $f_{L\ \mathrm{variable}}$	*n*, exptl,[d] K_{SAW}/K_{TSM}
HEX	2.13	2.91	3.63	2.33
BZN	1.56	2.40	2.43	1.81
TOL	1.58	2.42	2.41	1.85
DCM	1.03	1.92	2.08	1.89
CTC	0.86	1.77	1.92	1.47
MEK	1.73	2.56	2.85	2.47

[a] Poly(epichlorohydrin) $\rho_S = 1.36$, $A_{SAW}/\alpha = 4.5$. [b,c,d] See Table 3.

according to eq 18 are expected to exceed those predicted by theoretical models that assume the entire SAW response is due to absorption in the polymer.

Experimental amplification factors found for each of several vapors (see Table 1) on poly(isobutylene), PIB, and poly(epichlorohydin), PECH, are given in Tables 3 and 4. Using K_{SAW} and K_{TSM} taken from reference 22,[22] amplification factor values range from 1.5 to 2.7. Experimental amplification factors are not constant for all vapors on a single polymer; they are vapor-dependent. Using SAW response data from an unsilanized sensor, a value of 3.45 is calculated for MEK on PIB, in contrast to a value of 2.74 on the silanized PIB-coated SAW sensor. Otherwise, amplification factors for other vapors on PIB-coated SAW sensors are in good agreement, whether the sensor is silanized or not. Only the amplification factors of the silanized PIB-coated SAW sensor will be used for comparisons with theoretical predictions.

Theoretical amplification factors, *n*, have been calculated for the same vapors on PIB and PECH using eq 17, and these results are also included in Tables 3 and 4. The A_{SAW}/α values were taken from the original publication on the swelling-induced modulus model.[20] The fractional free volume of the vapor was handled in two ways. In the first, it was assumed to be 0.2 for all vapors, a value that is reasonable on the basis of three considerations: it is the value indicated by Ferry, it is at the midpoint of the range for β', and it is consistent with the magnitude of calculated fractional free volumes for vapors (see Table 1).[42] In the second approach, individual fractional free volume values for each vapor were used. Fractional free volumes for particular liquids can vary depending on the method used to determine them.[47-49] The values for fractional free volumes in Table 1 were calculated from the difference between molar volumes at 298 K and intrinsic molar volumes, both values taken from tabulations by Marcus.[47]

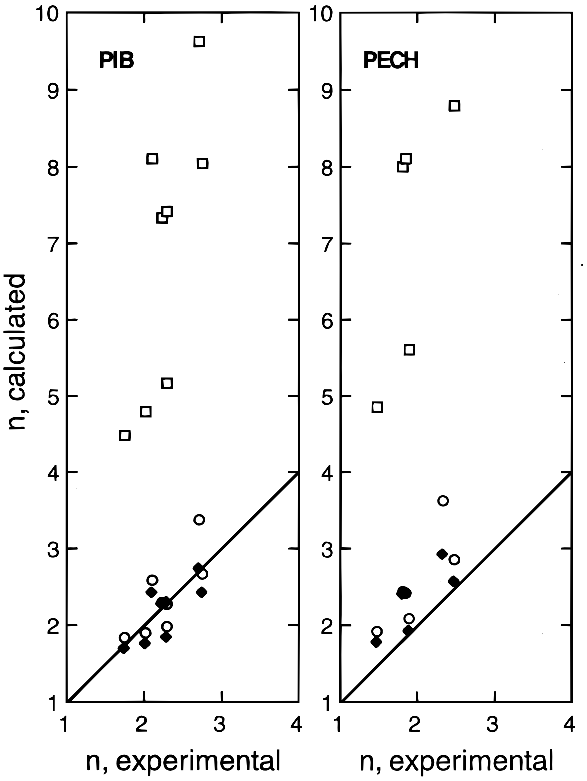

Figure 1. Plots of predicted amplification factors, *n*, against experimental values determined from the ratio of normalized observed SAW sensor responses to normalized gravimetric TSM sensor responses. Predicted values of *n* were calculated using either a fractional free volume value of 0.2 for all vapors (solid diamonds) or the vapor-specific fractional free volume values given in Table 1 and described in the text (open circles). In addition, the plot shows the values calculated if the fractional free volume factor is not included in the model (open squares).

The predicted amplification factors are of the correct magnitude compared with the experimental values. As observed experimentally, the exact values are dependent on the vapor properties (Table 1). If ρ_S/ρ_L is assumed to be one for all vapor polymer pairs (i.e., vapor density is not considered) and the fractional free volume is assumed to be 0.2 for all vapors, the amplification factors are calculated to be 2.2 for PIB and 1.9 for PECH. If the fractional free volume factor is not included in the calculation (i.e., calculations according to eq 3), calculated amplification factors are much larger and not in agreement with the experimental data under consideration.

Comparisons of calculated and experimental amplification factors are shown graphically in Figure 1, with a line of slope 1 drawn to show where perfect agreement should occur. Calculated values are shown for constant fractional free volume of 0.2 (solid diamonds) and vapor-specific fractional free volumes (open circles). In addition, results for the original model without the f_L

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(47) Marcus, Y. *The Properties of Solvents*; John Wiley and Sons: New York, 1998.

(48) Hildebrand, J. H.; Scott, R. L. *The Solubility of Nonelectrolytes*, 3rd ed.; Dover Publications: Toronto, Canada, 1964.

(49) Bagley, E. B.; Scigliano, J. M. *Polym. Eng. Sci.* **1971**, *11*, 177–181.

term are shown (open squares). Predictions made including an f_L term, in accordance with the model in eqs 15 and 17, are clearly in much better agreement with the experimental amplification factors than predictions made without including the f_L term. Using a constant fractional free volume, the only source of vapor-dependent variation in the model is the vapor density as a liquid. Vapors from liquids with higher densities are predicted to have lower amplification factors than those from liquids with lower densities. The results for PIB generally support this trend, with data scattered about the agreement line. The results for PECH are generally above the agreement line, but still support the overall trend. In both cases, vapors from dense liquids, such as chlorinated hydrocarbons, plot toward the lower left and vapors from less dense liquids, such as aliphatic hydrocarbons, plot toward the upper right along the agreement line. In general, the plots show that vapor-dependent variations in the amplification factor that are observed experimentally are also approximated by the model.

The use of vapor-specific fractional free volume values did not significantly improve the correlation between calculated and experimental results. Using K_{TSM} values for the mass loading and either approach for the fractional free volume, the revised model predicts amplification factors with average errors of about 10% for PIB and 20−30% for PECH.

Instead of using the model in eq 15 that includes a fractional free volume parameter, it is possible to use eq 14 with the β' parameter. The latter can be treated as an adjustable fitting parameter. Individual β' parameters were calculated for each vapor on each polymer so that the model predicts exactly the experimentally found amplification factors. The average of the fit β' parameters for the eight vapors on the PIB-coated SAW sensor was 0.22. Using this average as a single β' value for calculating the predicted amplification factors for all the vapors on PIB yields little overall improvement in prediction errors compared to using a single f_L value of 0.2. The average of the differences between predicted and experimental amplification factors was still about 10%. However, the predicted amplification factors on PECH were systematically above the agreement line in Figure 1. An average β' value of 0.15 was calculated for the six vapors on PECH as just described. Using this β' value, predicted amplification factors are systematically lower than those predicted using $f_L = 0.2$, and the prediction errors are improved. The average of the differences between predicted and experimental amplification factors was about 10%. It should be noted that β' will collect any systematic biases caused by errors in the polymer density, polymer coefficient of thermal expansion, or polymer A_{SAW} value when it is treated as an adjustable parameter.

Relative Contributions of Mass-Loading and Modulus Effects. In the original model (eq 3) it was noted that the magnitude of the modulus contribution depended primarily on the magnitude of A_{SAW}/α and secondarily on the ratio of the sorbent polymer phase density to the liquid density, ρ_S/ρ_L.[20] For the polymers considered, A_{SAW}/α values were in the range of 4 to 6. Assuming that the density ratio is of the order of 1, the original model predicted that n should be of the order of 5−7.

In the revised model, the influence of A_{SAW}/α is modified by the fractional free volume of the vapor as a liquid, f_L. Taking f_L to be 0.2, the value of $f_L A_{SAW}/\alpha$ would be of the order of about 1 for the polymers considered. This yields $n = 2$ when the ratio of sorbent phase density to vapor density as a liquid is 1. This appears to be a reasonable approximation for polymers such as poly(isobutylene) and poly(epichlorohydrin) in light of the experimental results based upon TSM sensor measurements published previously[22,23] and presented in Tables 3 and 4. Incorporation of the fractional free volume factor into the model brings amplification factors that were much too large down to reasonable values in comparison with these experimental values, as illustrated in Figure 1.

Vapor Dependence. The revised model and the original swelling-induced modulus change model predict that the modulus effect should be vapor-dependent as a result of variations in the vapor's density as a liquid. In the revised model, however, A_{SAW}/α is multiplied by f_L, resulting in a value of $f_L A_{SAW}/\alpha$ that is about 1 when the value of A_{SAW}/α is in the range of 4−6. Then the ratio of the modulus contribution to the mass contribution is approximately the ratio ρ_S/ρ_L and the amplification factor, n, is approximately $(1 + \rho_S/\rho_L)$. The results in Tables 3 and 4 which are shown in Figure 1 support the prediction that the amplification factor should be vapor-dependent in a manner approximately predicted by the vapor-density dependence. (It is actually more intuitive to think in terms of vapor specific volume rather than vapor density since the modulus effect is volume-dependent. The amplification factor, which is a ratio of modulus to mass effects, increases with vapor specific volume as a liquid, which is a ratio of volume to mass. However to be consistent with the equations above, vapor density will continue to be the property discussed, referring always to the density of the vapor as a liquid.)

In the first comparison of TSM and SAW vapor sensor results, Martin and Frye reported that the gravimetric contributions to observed PIB-coated SAW sensor responses to pentane and trichloroethylene were 40 and 67%, respectively.[28] These values correspond to n values of 2.5 for pentane vs 1.5 for trichloroethylene. Given densities of 0.92, 0.63, and 1.46 g/mL for poly(isobutylene), pentane, and trichloroethylene, respectively, the ρ_S/ρ_L density ratios for poly(isobutylene)/pentane and poly(isobutylene)/trichloroethylene are of the order of 1.5 and 0.6, respectively. Assuming that the value of $f_L A_{SAW}/\alpha$ is about 1 as discussed above, these density ratios result in predicted amplification factors, n, of 2.5 and 1.6, in excellent agreement with the experimental results. Thus, the dependence on vapor density shown in Martin and Frye's data, and accounted for by vapor volume factors in their theoretical model, is also predicted by the revised swelling-induced modulus change model.

The revised model also predicts that the modulus effect will also be vapor-dependent to the extent that fractional free volume depends on the particular vapor. The initial attempt in this paper to include vapor-specific fractional free volume values did not significantly improve the correlation relative to using the vapor density as the sole vapor dependent parameter. It is worth noting that changing f_L from 0.2 to 0.25 produces a change in that calculated amplification factor of only about 10−15%. Uncertainties in generating diluted vapor streams for the TSM and SAW measurements are typically a few to several percent, which can be a major contributor to the uncertainties in the K values determined. The experimental amplification factors will have an uncertainty that is the sum of the uncertainties for the two measurements. Using the β' parameter in eq 14, the effect is vapor-dependent to the extent that β' is vapor-dependent, the values of which are primarily dependent on vapor fractional free volume at low vapor concentrations, as already discussed.[39]

Polymer Dependence. It has been noted previously that the extent to which modulus changes contribute to observed SAW sensor responses depends on the initial modulus of the polymer.[20,22] Furthermore, it has been shown in comparisons with similarly coated TSM vapor sensors that polymers assumed to have low initial modulus values and yet still be acoustically thin, (poly(dimethylsiloxane) and poly(butadiene), did not show a viscoelastic amplification.[22] The present model does not directly address this point. The sensitivity to modulus decreases is empirically incorporated in the A_{SAW} value. An inaccurate value for A_{SAW} would lead to systematic bias in model predictions for a set of vapors on a given polymer.

The model does predict a dependence on the polymer thermal expansion coefficient. These generally do not vary a great deal from polymer to polymer, but the specific value assigned to a polymer may vary depending on the source. An inaccurate value could lead to systematic errors in model prediction. Furthermore, it is predicted that increasing polymer density contributes to a greater relative modulus contribution. Polymer density values fall generally in a range from about 0.9−1.4 g/mL. Again, an inaccurate value would lead to systematic bias in model predictions.

Discussion. The original swelling-induced modulus change model predicted amplification factors for polymers such as PIB and PECH in the range of 5−7.[20] This prediction was recognized to overestimate the modulus effect, and a smaller amplification factor was suggested on the basis of experimental measurements. Infinite dilution partition coefficients derived from GLC experiments were used to estimate the actual gravimetric contribution to observed responses. It was found that amplification factors determined on this basis were quite variable among the vapor/polymer pairs considered, but they were always greater than one and typically in the range of 3−6. It was suggested that $n = 4$ might be used as a "rule of thumb" for the amplification factor in order to simplify the model.[20] This simplification eliminated the need to measure A_{SAW} values and eliminated the influence of vapor density. Empirically, this approach was found to be useful when infinite-dilution GLC partition coefficients (or partition coefficients calculated from linear solvation energy relationship (LSER) models based in GLC partition coefficients) were used in estimations, although smaller amplification factors in the range of 2 to 4 were indicated for a range of polymers.[21]

Mass and modulus contributions to SAW responses were subsequently reexamined for a variety of polymers, including PIB and PECH, using TSM sensor responses, to determine the mass loading of the polymers.[22] Partition coefficients determined from TSM sensor responses were compared with independent literature data as well. The K_{TSM} values appeared to be reasonable by comparison with literature data, and were generally larger than the GLC values used previously. Using the K_{TSM} values, the amplification factor was estimated to be "2 rather than 4".[22] It was also shown that the amplification factor may be 1 (i.e., no modulus contribution) for polymers assumed to have a low initial modulus in the acoustically thin regime. The modulus change contribution to observed SAW sensor responses remained significant for polymers such as PIB and PECH, if not necessarily always "predominant" for every vapor/polymer combination.

The fractional free volume factor is a physically meaningful addition to the swelling-induced modulus change model that results in a satisfying agreement with experimental results based on gravimetric K_{TSM} values. This factor addresses an assumption in the original model in a way that is consistent with conventional polymer physics treatments of concentrated polymer solutions (plasticized polymers). Therefore, the original concept behind the swelling-induced modulus change model was correct in treating the modulus term as a volume effect that can be modeled by comparison with thermal expansion. It is simply necessary to divide the added diluent vapor volume into free volume and occupied volume and only treat the free volume as influencing the modulus, as shown in this paper. Furthermore, the addition of the fractional free volume term results in the emergence of the vapor density factor (i.e., the specific volume of the vapor as a liquid) as a useful physical parameter describing vapor dependence of the amplification factor according to this model.

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