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Ken Mullen

Keith Carron

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**Ken Mullen and Keith Carron
Department of Chemistry
University of Wyoming
Laramie, Wyoming**

Adsorption of Chlorinated Ethylenes at 1-Octadecanethiol-Modified Silver Surfaces

Ken Mullen[†] and Keith Carron^{*}

Department of Chemistry, University of Wyoming, Laramie, Wyoming 82071-3838

The adsorption of chlorinated ethylenes at octadecylthiol-modified surface-enhanced Raman spectroscopy (SERS) substrates was examined. It was found that the adsorption could be followed with SERS and the adsorption isotherms could be fit to a Frumkin isotherm. In order to better understand variations in the isotherms between substitutions of the chlorinated ethylenes, an isotherm that utilizes an adsorption parameter analogous to the Hildebrand solubility parameter was developed. The adsorption parameters were found to qualitatively follow the solubility parameters. The detection limits were calculated and range from 2086 ppm for *trans*-1,2-dichloroethylene to 12.6 ppm for tetrachloroethylene. A linear free-energy relationship was found for the log *K*, adsorption equilibrium constant, and the log *S*, aqueous solubility, of these compounds. This relationship allows one to predict the detection limit for low aqueous solubility organic compounds.

This work is a continuation of experiments directed at developing analytical techniques for in situ monitoring of groundwater contaminants using optical fibers and surface-enhanced Raman spectroscopy (SERS).¹ In a previous study of benzene, xylenes, and naphthalene on 1-octadecanethiol-(ODT-) coated silver substrates, we demonstrated that reasonable detection limits of 1–10 ppm and excellent spectral selectivity could be achieved.² In this report, we are describing results of a similar study carried out with chlorinated ethylenes on ODT-modified surfaces.

In situ detection of chlorinated ethylenes is important due to their presence in the environment from dry cleaning, extraction, and degreasing applications. They are classified as dense nonaqueous-phase liquids (DNAPLs) and have been reported to have peculiar solubility behavior.³ DNAPLs often show solubilities far below expected levels.⁴ This disparity has been attributed to improper sampling due to spatial heterogeneity of DNAPL plumes, loss of analyte during pumping, and dilution of the sample in the collection process.⁵ Since the expected levels at sites are above our detection limits, our method of in situ monitoring should overcome the

ambiguity in environmental measurements of DNAPL contaminants.

We have demonstrated very good sensitivity and selectivity for metal ions and pH using SERS fiber optic probes.^{6,7} Metal ions and protons are detected with coatings composed of known indicators. These "active" coatings chemically react or bind the analyte and flag its presence through characteristic changes in the Raman spectrum of the coating. By combining resonance Raman and SERS, we are able to achieve excellent sensitivities (<1 ppb).

The principle behind our in situ organic sensor is a "static" chromatographic system. Our substrates are coated with a bonded phase that mimics the C-18 coating used in reverse-phase bonded-phase chromatography. The function of this coating is to concentrate hydrophobic organics at the SERS interface. The degree of concentration is related to the adsorption coefficient for the organic species of interest. Resolution of species in solution can be achieved spectroscopically through characteristic Raman bands of the analyte. Quantification of the analyte is possible by measuring the intensity of an analyte Raman band relative to a Raman band of the coating material.

Ex situ work in the detection of organics with SERS is largely based on spotting solutions onto a SERS active substrate. After evaporation of the solvent, the SERS signal is collected. This technique has shown very high sensitivity and selectivity for many organic compounds. Laserna et al reduced Ag(I) ions with NaBH₄ onto filter paper.⁸ They were able to detect nanomole quantities of 9-aminoacridine, 1-nitropyrene, and 1,10-phenanthroline. Vo-Dihn and co-workers carried out extensive studies of the spotting technique and also reported nanomole detection limits for a variety of hazardous organic compounds.^{9,10} Resonantly enhanced compounds can be detected with attomole sensitivity.¹¹

In the course of our analysis, we felt it was necessary to provide a physical description of the unexpected behavior of chlorinated ethylenes at ODT surfaces. Our surfaces are nonporous, homogeneous interfaces and should produce either a Langmuir-type or a Frumkin-type of isotherm.¹² We found

[†] Present address: Los Alamos National Labs, CLS-1, MS 6740, P.O. Box 1663, Los Alamos, NM 87544.

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that all four of the chlorinated ethylenes examined did fit a Frumkin isotherm and that the positive Frumkin parameter suggested that attractive forces exist between the chlorinated ethylenes. While this result in itself is not surprising, the large variation in the Frumkin parameter between compounds was unexpected.

This led us to develop an adsorption model that utilizes the concept of an adsorption parameter that is analogous to the Hildebrand solubility parameter.¹³ The approach is similar to that of Snyder's solvent strength parameter.¹⁴ Snyder's solvent strength parameter is useful in predicting adsorption chromatographic partition coefficients with oxide surfaces. The explicit assumption in the solvent strength parameter model is that the dominant interaction is between the solvent and the surface. However, in our case, the solvent water has little affinity for the hydrophobic surface, and the dominant forces are between solute molecules not between water and the surface. We found that tabulated solubility parameters accurately predicted the unusual behavior, and the tabulated values are fairly close to our measured adsorption parameter. The advantage of our approach is that, as a first approximation, adsorption parameters can be related to tabulated tables of solubility parameters. As more adsorption data are collected, consistent adsorption parameters should be established, and their exact relationship to solubility parameters can be found. Since we found that chlorinated ethylenes exhibit nonlinear behavior at very low fractional coverages (<2%), the development of a predictive model such as proposed here can help anticipate undesirable chromatographic effects.

EXPERIMENTAL SECTION

The SERS spectra in this study were obtained with 2.0-mm-thick silver foil (99.9%, Aldrich) etched with 30% nitric acid. The largest enhancements were found when the silver was polished with 0.3 μm of alumina (Buhler) prior to etching. This leads to a surface which appears homogeneous and white after etching.

1-Octadecanethiol (98%) (ODT) and reagent-grade chlorinated ethylenes (CEs) were purchased from Aldrich and used without further purification. The etched silver substrates were soaked in a 1 mM ethanolic solution of ODT for 24 h. After being soaked, the substrates were rinsed with ethanol and allowed to air dry. This forms a durable, self-assembled monolayer of ODT on the SERS substrate.

The fractional coverage, θ , was determined by measuring Raman spectra of a known bulk mixture of a CE and ODT to determine the relative intensity of the C=C stretching frequency to the 1295- cm^{-1} band of ODT. This ratio was used to find the number of CE molecules per ODT molecule on the surface. We used Porter's value of 4.2×10^{14} molecule/

cm^2 for the coverage of ODT on silver.¹⁹ The saturated monolayer coverage of the CE was found from the density of the liquid and assuming spherical molecules. Dividing the surface coverage by the calculated saturated monolayer coverages produces θ . This method assumes that intensities on the surface are the same as those in the bulk. This assumption is not completely valid since molecular orientation relative to the surface can change intensities observed. However, the bands chosen for the coverage determination appeared not to change drastically from the bulk intensities. However, given this ambiguity, the coverages should be considered as approximate.

The Raman spectra were collected in rigidly held cuvettes. This ensured that the same position on the surface was excited by the laser beam for the series of dilutions. The cuvette was capped with a septum to prevent evaporation of the chlorinated ethylenes. The range of analyte concentrations was obtained by standard dilutions of a saturated solution. The concentrations of saturated solutions were taken from ref 15. The solubilities are 6300 ppm, *trans*-1,2-dichloroethylene (t-DCE); 3500 ppm, *cis*-1,2-dichloroethylene (c-DCE); 1100 ppm, trichloroethylene (TCE); and 150 ppm, perchloroethylene (PCE).

A Spectra Physics 2025 Kr⁺ laser provided 647-nm light for Raman excitation. The laser power was set at 40 mW, and 500-s integration times were used to collect spectra of ODT-coated silver. Higher powers were found to cause irreversible damage to the substrate. The damage resulted in a decrease in the SERS signal. The intensity of the spectrum of the ODT coating was monitored throughout the measurement of the isotherm to ensure that no damage occurred. Raman spectra of the neat liquid samples were obtained with 100 mW and 200-s integration times. The spectra were dispersed with a HR-320 ISA spectrograph with a 1200 g/mm grating. The spectrograph was fitted with a Photometrics CCD9000 detector cooled to -102 °C. The slits were set at 30 μm , which corresponds to 7 cm^{-1} resolution. The Raman spectra were taken with *p*-polarized light using 90° scattering. The collection optics consisted of an f1.8 camera lens set up with a magnification to f# match with our f5.0 spectrograph. The Raman scattered light was collimated and passed through a 647-nm holographic Raman cutoff filter to remove the elastically scattered or reflected laser light.

RESULTS AND DISCUSSION

Raman Spectra of Chlorinated Ethylenes. The small number of atoms and the high symmetry of chlorinated ethylenes lead to fairly simple Raman spectra.¹⁶ Figure 1 shows the Raman spectra of the four chlorinated ethylenes in the 1100–1650- cm^{-1} region used in this study. The strong Raman band around 1580 cm^{-1} is mostly due to the C=C stretch. In PCE, only the C=C stretch is observed in the region studied. The less substituted CEs show a band between 1185 and 1272 cm^{-1} that contains C-H bending motion. In c-DCE and t-DCE, only one band is observed due to the symmetric C-H bending. The asymmetric C-H bending mode is not Raman active in their respective C_{2v} and C_{2h} symmetries. TCE, C_3 symmetry, has two C-H bending frequencies at 1229

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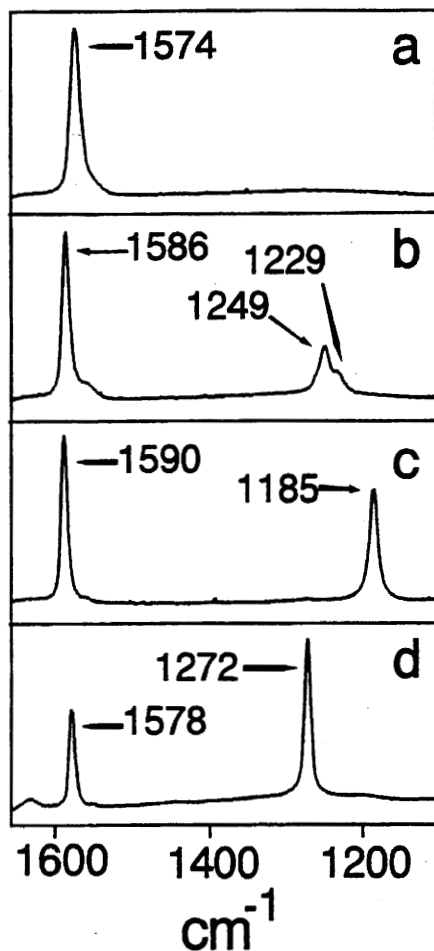


Figure 1. Neat Raman spectra of CEs: (a) PCE, (b) TCE, (c) *c*-DCE, (d) *t*-DCE.

and 1249 cm^{-1} due to Raman activity of both the symmetric and the asymmetric C–H bending.

Figure 2 shows Raman spectra of ODT in the 1100–1650- cm^{-1} region. The spectra contain a single strong band due to the CH_2 wag at 1295 cm^{-1} and a triplet composed of CH_2 and CH_3 deformations.¹⁷ The similarity between solid ODT in this region and the surface spectrum is indicative of a highly structured self-assembled monolayer. Upon melting or mixing of ODT with a solvent, the triplet structure of ODT breaks down into an unresolved doublet. We have observed that poorly formed monolayers and monolayers exposed to high concentrations of benzene also have a doublet structure. We propose that these bands can be used to indicate the degree of intercalation of adsorbate into the monolayer. A thorough study of these peaks and the intercalation of benzene into the ODT is in progress. We have proven the intercalation of benzene and alkylbenzenoids by measuring the distance dependence of material on various carbon length alkythiols in comparison with *tert*-butylbenzene, which due to its bulky steric properties does not intercalate. In this study, the triplet structure was constant even at the highest coverages (35%). We conclude, therefore, that CEs are being adsorbed to the surface of the ODT.

The strong 1295- cm^{-1} band of ODT was chosen as our internal standard for this work. Since it is much stronger than the C=C stretch of the adsorbed chlorinated ethylenes,

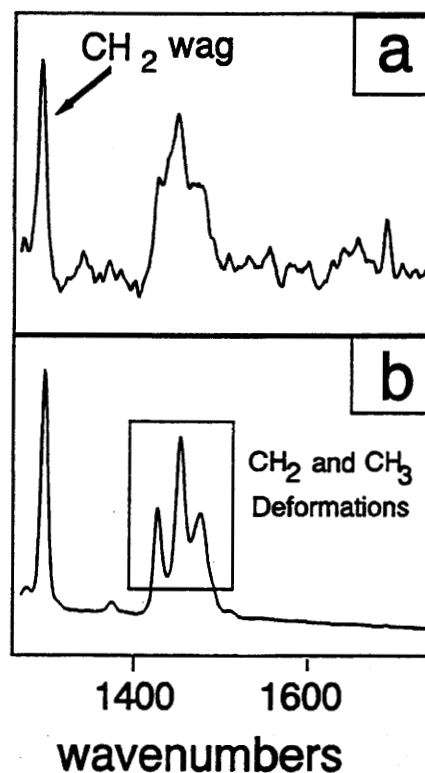


Figure 2. Raman spectra of ODT: (a) SERS spectrum of an ODT monolayer on silver, (b) Raman spectrum of solid ODT.

its contribution to S/N will be neglected. No correlation between the concentration of chlorinated ethylenes and the intensity of this peak was observed.

Isotherms for Adsorption of Chlorinated Ethylenes on ODT. The isotherms for the adsorption of CEs onto self-assembled ODT surfaces provide a calibration curve for determining unknown CE concentrations in aqueous solutions and indicate the nature of the adsorption process. For example, the analysis of adsorption isotherms of pyridine on silica-coated SERS substrates by Simpson and Harris provided detailed information about the sites of adsorption and multilayer formation.¹⁸ Isotherms of the chlorinated ethylenes used in this study are illustrated in Figure 3. Two distinct characteristics of the isotherms observed for CEs on ODT surfaces are that saturation of the surface is never achieved and that the process is non-Langmuirian.

The isotherms could be fit to a Frumkin isotherm:

$$\theta = \frac{k_0 e^{2g\theta} C}{1 + k_0 e^{2g\theta} C} \quad (1)$$

where k_0 is the adsorption coefficient, C is the solution concentration of the adsorbate, and g is the Frumkin parameter. The g values found for PCE, TCE, *c*-DCE, and *t*-DCE are 1.8, 5.25, 1.4, and 3.5, respectively. The positive values are indicative of attractive forces between the adsorbed molecules. The magnitude of the g values gives an indication of the strength of the attractive energy. While the Frumkin isotherm yielded information about the adsorption process and the magnitude of intermolecular forces between the adsorbed molecules, it did not explain or predict the differences in the cohesive energies for the different chlorinated ethylenes. For this reason, we applied an isotherm based on tabulated

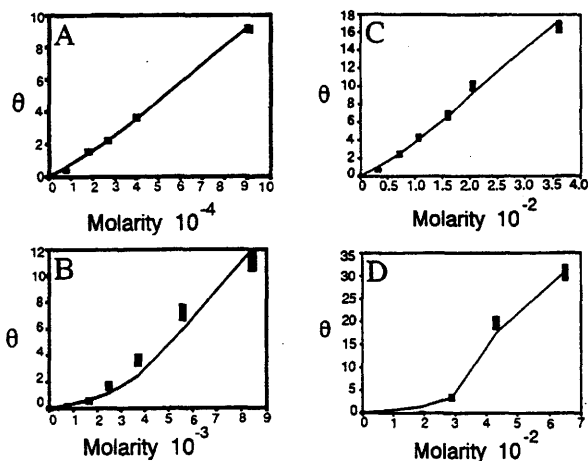


Figure 3. Isotherms of PCE (A), TCE (B), c-DCE (C), and t-DCE (D). Error bars are based on the random noise associated with the CE peak. The lines are drawn from a best fit to eq 4. The parameters of the fit are listed in Table 1.

solubility parameters to determine if TCE and t-DCE would be predicted to have much larger attractive forces than PCE and c-DCE.

To develop our isotherm, we start with the chemical potentials of solution and interface:

$${}^i\mu_s = {}^i\mu_s^\circ + RT \ln {}^i a \quad (2)$$

$${}^i\mu_i = {}^i\mu_i^\circ + RT \ln \frac{f\theta}{1-f\theta} \quad (3)$$

where ${}^i\mu_s$ and ${}^i\mu_i$ are the chemical potentials of the solution and interface, respectively. ${}^i\mu_s^\circ$ and ${}^i\mu_i^\circ$ are the standard chemical potentials of the solution and interface with standard states of ${}^i a = 1$ and $f\theta = 0.5$, respectively. ${}^i a$ is the activity of component i , θ is the fractional coverage of i , and f is the activity coefficient for i at the interface. Since the CEs have very low solubilities, the solution activity coefficient is constant over the range of dilutions used in this work. Given that the activity coefficient is constant, we will use the simplification that ${}^i a$ can be replaced with ${}^i C$.

If f is 1, this analysis leads to a Langmuir isotherm; otherwise, the form of the isotherm is

$$\theta = \frac{1}{f} \frac{k' C}{1 + k' C} \quad (4)$$

The value of f can be approximated by the Hildebrand-Satchard equation²⁰

$$RT \ln f = {}^i V (\delta_a - \delta_i)^2 j \phi^2 \quad (5)$$

where ${}^i V$ is the molar volume of component i , δ_a is the adsorption parameter for component i , δ_i is the interfacial Hildebrand parameter, and $j\Phi$ is the volume fraction of component j :

$$j\phi = \frac{m(1-\theta)}{m(1-\theta) + \theta} \quad (6)$$

where m is given by

$$m = {}^j V / {}^i V \quad (7)$$

j corresponds to the solvent and i is the solute. $j\Phi$ leads to the

Table 1. Molecular Parameters for Determination of Chlorinated Ethylene Adsorption Parameters

	δ_a^a	k^b	f_0	${}^i V^c$	${}^i \delta_a$
PCE	22.6	162 ± 8	2.33	101	19.1
TCE	19.0	70 ± 12	20.4	90	18.8
c-DCE	22.4	8.4 ± 0.3	2.71	76	19.8
t-DCE	18.9	11.3 ± 3	13.9	77	18.8

^a In $\text{MPa}^{1/2}$. ^b In $(\text{molarity})^{-1}$. ^c In cm^3/mol .

coverage dependence of the isotherm described by eq 4. We have assumed that δ_i is the geometric mean of Hildebrand parameters of the interfacial components, which in this case are water and octadecane.²¹ The δ values for water and octadecane are 48 and 16.4 $\text{MPa}^{1/2}$.²⁰ This leads to a δ_i of 28.1 $\text{MPa}^{1/2}$ for the ODT/water interface. The ${}^i \delta_a$ values for the CEs are PCE (19.1 $\text{MPa}^{1/2}$), TCE (18.8 $\text{MPa}^{1/2}$), c-DCE (19.8 $\text{MPa}^{1/2}$), and t-DCE (18.8 $\text{MPa}^{1/2}$).²⁰ In our analysis, we varied ${}^i \delta_a$ and k to fit the data points. The values for ${}^i \delta_a$ that we found are PCE (22.6 $\text{MPa}^{1/2}$), TCE (19.0 $\text{MPa}^{1/2}$), c-DCE (22.4 $\text{MPa}^{1/2}$), and t-DCE (18.9 $\text{MPa}^{1/2}$). These data are tabulated in Table 1. It can be seen that qualitatively the adsorption parameters match the solubility parameters with PCE and c-DCE being larger than TCE and t-DCE. The quantity $({}^i \delta_a - \delta_i)^2$ represents the difference in the intermolecular forces between like molecules and unlike molecules. A large value of $({}^i \delta_a - \delta_i)^2$ means that the unlike molecules (in this case solute molecules and solvent molecule/interface) prefer to remain separated and the like molecules will be attracted to each other.

The solvent parameter can be separated into components that reflect the molecule's ability to interact through dispersion forces, Keesom forces, Debye forces, or hydrogen bonding.²² In the case of PCE and TCE, the larger ${}^i \delta$ values for PCE can be seen from the tabulated values of $\delta_{\text{dispersion}}$, δ_{polar} , and $\delta_{\text{hydrogen bonding}}$. PCE has 5.5% more dispersion energy, 101% more polar energy, and 55% less hydrogen-bonding energy than TCE.²⁰ The role of hydrogen bonding is difficult to predict in hydrocarbon/aqueous systems. However, from the dispersion and the polar contributions, it is apparent that PCE interacts most strongly with a water/alkane interface, i.e., $(\text{PCE}\delta - \delta_a) < (\text{TCE}\delta - \delta_a)$. Likewise TCE will be more prone to interact with itself. As more studies are carried out and probes of the interfacial adsorption interaction parameters are found, a better description of the interface should be established.

A linear free-energy relationship between the adsorption coefficient and the solubility can be used to predict the adsorption coefficient of new compounds on ODT-coated silver surfaces. This formula is useful as it allows one to predict detection limits of other organic analytes. Assuming ideal behavior, the chemical potential of a pure solute in equilibrium with a saturated aqueous solution can be written as

$${}^i \mu_{\text{sat}} = {}^i \mu_s^\circ + RT \ln S \quad (8)$$

where ${}^i \mu_{\text{sat}}$ is the chemical potential of the saturated solution, ${}^i \mu_s^\circ$ is the chemical potential at 1 molar concentration, and S is the solubility in molarity. One may also write the equilibrium

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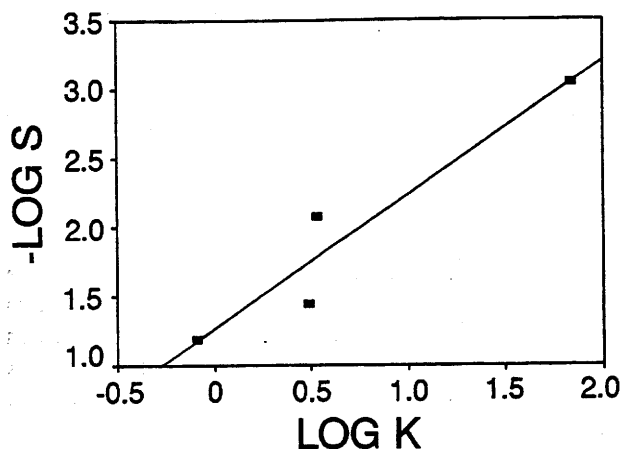


Figure 4. Plot of the linear relationship between $\log S$ and $\log K$ for CE on ODT surfaces. The R^2 for this plot is 0.92.

at the interface as

$${}^i\mu_s^\circ + RT \ln {}^iC = {}^i\mu_i^\circ + RT \ln [\theta/(1-\theta)] \quad (9)$$

This can be rearranged to produce a Langmuirian adsorption coefficient:

$$K = \frac{\theta}{{}^iC(1+\theta)} \quad (10)$$

In order to find the Langmuirian adsorption coefficient from our data, we take k/f in eq 4 in the limit of θ to 0. Combining eqs 8–10, one finds that a plot of $-\log S$ vs $\log K$ is shown in Figure 4. Equation 11

$$-\log S = \log K + \frac{{}^i\mu_i^\circ - {}^i\mu_{sat}^\circ}{2.3RT} \quad (11)$$

shows that the slope should be 1 and the intercept is related to the energy of adsorption required to form 0.5 monolayers from a saturated solution. Linear regression of our data shows that $-\log S = 0.996 \log K + 1.22$. The positive value for the y -intercept is reflected in the θ equal to less than 0.5 coverage found for CEs on ODT-coated surfaces for saturated aqueous solutions of CEs.

Detection Limits for Chlorinated Ethylenes. The detection limit for CEs can be found from the isotherms. Two methods were used in this study.²³ One method is given by

$$DL = 3\sigma/m \quad (12)$$

where DL is the detection limit, σ is the standard error of y estimate, and m is the slope. This method was used for *c*-1,2 and PCE since they are fairly linear. The value of the standard error in the y -intercept was found by using

$$\sigma_y = \left[\frac{\sum_{i=1}^N (mX_i - y_i)^2}{N-2} \right]^{1/2} \quad (13)$$

where N equals the number of observations and $N-2$ equals the degrees of freedom.

The second method was used for *t*-DCE and TCE. These isotherms display strong nonlinearity at low concentrations, and a line through 0 will underestimate the detection limit. In this case, we calculated the standard deviation of the blank

Table 2. Detection Limits for Chlorinated Ethylenes
detection limit (ppm)

	method 1	method 2
PCE	12.6	14.3
TCE		257
<i>c</i> -DCE	300	260
<i>t</i> -DCE		2086

Table 3. Molecular Parameters for *p*-Dichlorobenzene

${}^iV^a$	${}^i\delta^b$	f_o	S^c	Γ_{sat}^d	DL ^e
119	19.8	27	79	2.4×10^{14}	4.2

^a cm^3/mol . ^b $\text{MPa}^{1/2}$. ^c ppm. ^d molecule/ cm^2 .

spectrum (ODT in water) at the Raman frequency used for analysis, $\sim 1580 \text{ cm}^{-1}$. Using the equation for the isotherm, we found which concentration would produce a signal three times larger than the standard deviation of the blank, N_{blank} . For our system, we found N_{blank} to be 1.5, and our reference peak averaged 500 count/s. The ratio of $3N_{\text{blank}}$ to the reference peak was taken to find R_{min} . R_{min} , 0.009, is the minimum detectable ratio. When R_{min} is placed into the equation for the isotherm, the detection limit can be found. Fractional coverages were converted back into peak ratios for this calculation. This procedure was also applied to *c*-DCE and PCE, and good agreement was found between the two methods. The detection limits are listed in Table 2.

Equation 11 allows us to make predictions about the use of SERS to detect organic material in groundwater. It follows from eqs 4 and 11 that

$$R = F \frac{\Gamma_{sat}}{\Gamma_{ODT}} \left[\frac{fKS}{1+fKS} \right] \quad (14)$$

where R is the ratio of an analyte Raman band to a surface coating Raman band, F is the relative differential Raman cross-section for the analyte Raman band and the reference Raman band of the surface, f is the surface activity coefficient, KS is the product of infinite dilution adsorption coefficient and the solubility (0.0546), Γ_{ODT} is 4.8×10^{14} molecule/ cm^2 , and Γ_{sat} is the monolayer coverage of the analyte. Our analysis of detection limits indicated that we can detect any R value down to 0.009.

In order to illustrate the utility of eq 14, an example of *p*-dichlorobenzene will be worked out. The relevant parameters are listed in Table 3.²⁰ The activity coefficient at 0 coverage is given by eq 5 at $\Phi = 1$ is 27. The bracketed term in eq 12 is equal to θ and for *p*-dichlorobenzene is 58%. We include an iteration to account for the true activity coefficient at non-zero coverage and find that the exact value of θ is 34%. From the molar volume, we find that Γ_{sat} is 2.4×10^{14} molecule/ cm^2 . If one assumes equal Raman cross-sections for the analyte and ODT peak, this leads to an R value of 0.17. We determined an instrumental detection limit of $R = 0.009$ so that the detection limit for *p*-dichlorobenzene will be $79 \text{ ppm} \times 0.009/0.17$ for 4.2 ppm.

The major conclusion from this analysis is that most compounds will be easily detectable given that KS is a constant, the δ values for low aqueous solubility (lipophilic) compounds rarely exceed $22 \text{ MPa}^{1/2}$, and molar volumes are typically on

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the order of 100–200 cm³/mol. The low detection limits should include environmental contaminants such as PAHs and PCBs that have very low aqueous solubilities (consequently large *K*'s).²⁴

CONCLUSIONS

We have demonstrated that chlorinated ethylenes in aqueous solutions can be detected using SERS and self-assembled monolayers of ODT. The detection limits are not exceptional. However, for in situ monitoring, this approach could alleviate many of the problems associated with sample collection of DNAPLs. This work also allowed us to develop a predictive scheme for the detection limit of other organic compounds.

An isotherm based on solubility parameters was developed, and reasonable agreement between tabulated solubility parameters and calculated adsorption parameters was found. The use of solubility parameters is not new and has been applied to chromatographic systems. The difference between this work and earlier models is that we have modeled our process as adsorptive and not partitioning.²² Our isotherms clearly showed that a concentration-dependent sorption coefficient is required, and spectra of the monolayer indicated

that partitioning did not occur. Should this approach prove to be a general method for the determination of isotherms, its value will be that of a very large number of molecules.

There is still much ambiguity about the sorption process at self-assembled monolayers. For example, aromatic compounds appear to partition into the monolayer, while the chlorinated ethylenes do not.^{2,25} Aromatic compounds exhibit a large sorption coefficient, and the partitioning may be a general phenomena at high coverages. Future work will be devoted to better understanding the sorption process and to expand our adsorption parameters into individual interaction components. SERS will be an excellent tool for this work since it can follow dispersive effects through Raman band shifts,²⁶ orientational interactions through relative Raman intensities of in-plane and out-of-plane vibrations,²⁷ and hydrogen bonding through known hydrogen bond strength correlations and line-width measurements.²⁸

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