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Measuring Molecular Diffusion Through Thin Polymer Films with Dual-Band Plasmonic Antennas

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ABSTRACT: A general and quantitative method to characterize molecular transport in polymers with good temporal and high spatial resolution, in complex environments, is an important need of the pharmaceutical, textile, and food and beverage packaging industries, and of general interest to the polymer science community. Here we show how the amplified infrared (IR) absorbance sensitivity provided by plasmonic nanoantenna-based surface enhanced infrared absorption (SEIRA) provides such a method. SEIRA enhances infrared (IR) absorbances primarily within 50 nm of the nanoantennas, enabling localized quantitative detection of even trace quantities of analytes and diffusion measurements in even thin polymer films. Relative to a commercial attenuated total internal reflection (ATR) system, the limit of detection is enhanced at least 13-fold, and as is important for measuring diffusion, the detection volume is about 15 times thinner. *Via* this approach, the diffusion coefficient and solubility of specific molecules, including L-ascorbic acid (vitamin C), ethanol, various sugars, and water, in both simple and complex mixtures (e.g., beer and a cola soda), were determined in poly(methyl methacrylate), high density polyethylene (HDPE)-based, and polypropylene-based polyolefin films as thin as 250 nm.

KEYWORDS: plasmonics, nanoantennas, surface-enhanced infrared spectroscopy, organic molecules, polymer, diffusion

uantitative determination of diffusion and solubility of molecules in polymers is important for applications including drug delivery,¹⁻³ desalination,⁴ fuel cells,⁵ flow batteries,⁶ food and beverage packaging,⁷ and separation processes.⁸ Making such determinations particularly challenging is that the physical properties of polymers depend on factors including polymer molecular weight, polydispersity, degree of chain alignment, processing history, film thickness, and their current environment. Swelling a polymer even a few percent with small molecules can significantly change its melting and/or glass transition temperatures, strongly influencing its properties,9-11 making it difficult to predict the behavior of polymers in real-world environments.^{12,13} As such, methods which accurately measure transport and dissolution of specific molecules in polymers and specifically in thin polymer films, in chemically complex environments are important for numerous applications.¹

Fourier transform infrared (FTIR) spectroscopy provides a nondestructive label-free approach for the identification and characterization of molecules based on their chemical-bond-specific absorption features.¹⁵ Because the IR absorbances of most molecules are relatively weak, approaches including grazing angle and internal reflection methods, for example, attenuated total reflectance (ATR),¹⁶ which increase the effective path length of light within the polymer, and the development of high power IR laser light sources have been

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utilized.^{17–19} However, these methods probe considerable thicknesses, for example, up to a few μ m above the substrate for ATR, and are thus not appropriate for determining localized chemical concentrations with a depth resolution on the order of 100 nm, such as required to quantify diffusion of molecules into thin polymer films. While confocal Raman can provide a high lateral spatial resolution, it can be very difficult to determine the exact z position of the focal spot, and from more fundamental perspective, the focal volume is rather elongated in z, typically to greater than 500 nm, even when a high NA objective is used, making confocal Raman nonideal for probing diffusion in thin polymer films. Here we show that by leveraging the local electric field enhancement associated with the excitation of plasmonic resonances that we can characterize diffusion in films at least as thin as 250 nm. A particularly attractive aspect of utilizing plasmonic resonances is the enhanced sensitivity to vibrational and electronic states in the near (10s to no more than 100 nm) vicinity of the resonant element. Common examples of plasmonically enhanced molecular detection include surface-enhanced fluorescence, $^{20-22}$ surface-enhanced Raman spectroscopy (SERS), $^{23-27}_{23-27}$ and surface-enhanced infrared absorption (SEIRA).^{28–35} A significant difference between quantitative SERS (which operates using visible light) is that it requires ~ 10 nm control of the characteristic dimensions of the resonant features, while SEIRA, which operates using IR light, only requires control of the characteristic dimensions of the resonant element on the order of a few 100 nm. It is useful to note that SEIRA and SERS detect different vibrational modes, and in that sense are complementary.

As previously demonstrated, the cross-section of specific IR absorption bands can be enhanced up to 5 orders of magnitude by SEIRA, 29,36-39 providing quantitative sensitivity to mM and below chemical concentrations. This allows monitoring dynamic processes such as molecular binding events with ultrahigh sensitivity.^{40–43} Here we additionally take advantage of the fact that substrates can be patterned with antennas of various length,^{32,44} and thus resonant frequencies, to enable concurrent detection of multiple IR resonances from the exact same region of the substrate. Attractively, large-area subas well as samples that benefit from gratingstrates⁴⁵ enhancement can easily be manufactured.⁴⁶ Because SEIRA is only sensitive to molecules within ~ 100 nm of the gold nanoantenna (see our 1/e skin depth calculations and experimental data on thin polymer films later in this manuscript), it is particularly useful for studies of even thin polymer films. It is this attractive combination of spatially localized high sensitivity and quantitative nature, which enables SEIRA to quantitatively and concurrently measure diffusion and solubility of small molecules in three important thin polymer films, specifically CANVERA 1110, a commercial HDPE-based polyolefin coating being used to coat food and beverage containers, EXP-4599, a Dow Chemical polypropylene-based polyolefin coating, and poly(methyl methacrylate) (PMMA).

RESULTS AND DISCUSSION

We start by patterning an array of single or dual-band resonant nanoantennas designed to provide strong IR absorption enhancement over a spectral range from about 800 cm⁻¹ to 2000 cm⁻¹ on an IR-transparent substrate. The substrate is coated with the polymer of interest, and then exposed to a solution containing the molecule(s) of interest (Figure 1).



Figure 1. SEIRA spectroscopy. (a) Scanning electron microscope image of an array of CNAs. Scale bar is 5 μ m. (b) Experimental and simulated reflectance of the CNA coated substrate in air. Dashed blue and purple lines are simulated reflectance spectra for x- and y- polarized light, respectively. (c) and (d) show the calculated electric field distributions at (c) 1340 cm⁻¹ and (d) 1770 cm⁻¹. (e) Cross-sectional schematic illustrating diffusion of a mixture of molecules into a polymer coated on a CNA (not to scale).

Initially, only absorption bands from the polymer are observed, as molecules have not diffused into the near-field of the nanoantennas. Over time, the IR reflectivity of the substrate begins to evolve, as molecules diffuse into the sensing region of the nanoantennas. By monitoring specific IR band absorptions, in conjunction with appropriate background subtraction and calibration experiments as we detail here, we quantitatively monitor the dissolution and diffusion of the molecules of interest into the polymer. In this report, we focus on simple mixtures such as alcohol-water, L-ascorbic acid-water, and sugar-water solutions, and also, as a proof-of concept, show this approach works for monitoring the interactions of complex systems with polymer coatings including a cola soda, beer, and dog food. The polymers investigated were PMMA, HDPE, polypropylene. PMMA provides a well-known standard, EXP-4599 and CANVERA are polyolefin-based coatings being adapted by the food and beverage coating industry due to their low cost and the fact that they replace coatings containing chemicals of increasing human health concerns. Understanding diffusion and analyte solubility in these coatings is of practical importance and showing the method described here works for these three rather different chemistries is a strong indication the method will work for many polymer chemistries.

Calibration experiments demonstrate a linear relationship between the integrated absorbance band and analyte concentration, enabling diffusion coefficients and analyte

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Figure 2. SEIRA calibration and determination of L-ascorbic acid-water solution diffusion in polymer coatings. (a) Chemical structure of Lascorbic acid. (b) Reflectance spectra of antenna array in air (green solid line) and water (blue solid line). The black dashed line in (b) is the shifted air reflectance curve. The difference of air-shifted curve and reflectance of the antenna array immersed in water indicates absorbance of water (solid red line). The absorbance is displayed at the bottom of the panel (gray shaded region) with units indicated by the scale bar. (c) Reflectance spectra of antenna array immersed in water (dashed black line) and in a 200 mM L-ascorbic acid-water solution (solid blue line). The absorbance of L-ascorbic acid (calculated by eq 1) is displayed at the bottom of the panel (solid red line). For reference, a scaled $(\times 5)$ absorbance spectrum is displayed as the gray-shaded region with units indicated by the scale bar. (d) Following the approach to determine the absorbance spectra in (c), the absorbance spectra of 0 to 100 mM L-ascorbic acid solutions are plotted. (e) Integrated and peak absorbance as a function of L-ascorbic acid concentration. Equations of the lines are y = 0.0278x (blue) and y = 0.0664x (red). Black dashed line indicates 3 times standard deviation of averaged noise spectra. The x coordinate of the intersection of the black dashed line and the red line is the SEIRA LOD for L-ascorbic acid. (f) Absorbance spectra of water and 5 mM L-ascorbic acid in water. (g-i) Differential reflectance spectra over time as a 1 M L-ascorbic acid-water solution diffuses into CANVERA 1110, PMMA and EXP-4599. Cyan blocks indicate L-ascorbic acid C-O and C-O-C absorption bands. Red blocks indicate water H-O-H absorption band. (j-l) Concentration of Lascorbic acid over time at the bottom of the polymer films calculated from the integrated absorbance of the C-O and C-O-C bonds. (mo) Concentration of water at the bottom of the polymer film over time calculated from the integrated absorbance of the H–O–H bond. In j-o, except l, experimental data are fit to a Fickian model.

concentrations to be quantitatively determined. We find that SEIRA provides over an order of magnitude enhancement

sensitivity (~13 fold) over ATR. 47 This, in combination with the fact SEIRA is sensitive only to molecules within about 100



Figure 3. Comparison of spectroscopy on a SEIRA chip, on a bare substrate, and using ATR. (a) Absorbance spectra of 200 mM ethanol in water, and a water background on a CNA-coated region of the substrate (SEIRA-active region). (b) Integrated absorbance and peak absorbance for 0 to 100 mM ethanol from the CNA coated region of the substrate. (c) Absorbance spectra of 200 mM ethanol in water, and a water background on a bare region of the substrate. (d) Integrated absorbance and peak absorbance for 200 to 5000 mM ethanol on the bare region of the substrate. (e) Absorbance spectra of 200 mM ethanol in water, and a water background measured using ATR. (f) Integrated absorbance for 20 to 1000 mM ethanol as measured by ATR. Equations of the fitted lines are (b) y = 0.0105x (blue) and y = 0.035x (red) and (d) y = 0.183x (blue) and y = 0.047x (red) (f) y = 0.00202x (red) and y = 0.00828x (blue). (g) Electric field intensity distribution around a CNA. (h) Field intensity as a function of distance along the direction of green arrow in (g). (i) Electric field intensity as a function of distance along the direction of distance along the direction of green arrow in (i).

nm of the nanoantenna, enables transport measurements can be made on analyte penetration, even at low concentration, into thin polymer coatings (coatings studied here were 250 nm to 5 μ m thick). In particular for the thinner films, such a measurement is difficult via ATR since ATR probes a depth of at least 500 nm, and generally at least one μ m above the substrate.

Plasmonic Nanoantenna Design and Calibration. A $200 \times 200 \ \mu m^2$ array of Cross-shaped gold NanoAntennas (CNAs) was patterned on a CaF2 substrate (see Methods and Figure 1 for details). While other substrates could be used, the low refractive index of CaF2 enhances the sensitivity (see Methods for details).⁴⁸ By tuning the length of each arm, the CNA can be defined to exhibit a dual band resonance which can be tuned to match the analyte absorption band of interest. Simulated and experimental reflectance spectrum of an array of CNAs are shown in Figure 1b. The resonance peaks at 1340 and 1770 cm⁻¹ are generated by the longer and shorter arms, respectively (Figure 1c-d). The fact that the two CNAgenerated field enhancement factors are large and roughly equal is advantageous as it allows for concurrent monitoring of different molecular species,49,50 even with lateral spatial resolution.⁵¹ Note the reflectance spectra in Figure 1 are measured in air. Once coated with polymer, the resonance bands red-shift about 200 cm⁻¹ due to the increase in the refractive index of their environment, matching them as intended with the absorption bands of interest. We note, the substrate could contain arrays of antenna of different length to increase the number of absorption bands that would be enhanced, however, this would come at a cost of sensitivity to a given absorption band.

First, the relationship between the intensity of absorption bands of interest and the analyte concentration was determined. Figure 2a,b present the reflectance spectra of the CNA in air and deionized water. In water, relative to in air, the antenna resonance redshifts 137 cm⁻¹ (the peak envelope in Figure 2a), and a strong H–O–H scissoring absorption coming from water is found between 1550 and 1720 cm^{-1} . The effect of the water vibrational band is clearly visible in the plasmonic reflectance spectra. The gray-shaded region displays the extracted absorbance signal. For the 200 mM L-ascorbic acid water solution, C-O and C-O-C stretching is observed between 1040 and 1210 cm^{-1} (Figure 2c). Specifically, there are two pronounced peaks at approximately 1050 and 1150 cm⁻¹ which are used to evaluate the presence of L-ascorbic acid in water. Since water is the dominant constituent (~99%) of this solution and does not have a sharp absorption in this spectral region, we use the water spectrum as an internal standard to determine the relationship between IR absorption and analyte concentration.

SEIRA calibration was accomplished by measuring the reflectance spectra of 5 to 100 mM L-ascorbic acid aqueous solutions. These spectra were then subtracted by the pure water spectra to correct the background (Figure 2d). The computed absorbance signal can be calculated by,⁵²

$$A = -\log_{10}(R_{analyte}/R_{water})$$
(1)

where A is the absorption, and R_{analyte} and R_{water} are the reflectance spectra of the L-ascorbic acid water solution and water spectrum, respectively. The integrated absorbance over the absorption band of interest (e.g., the C–O and C–O–H region, 1040–1210 cm⁻¹) are then calculated and plotted as a function of the concentration (Figure 2e). The integrated

absorbance scales linearly with L-ascorbic acid concentration, in agreement with the Beer–Lambert law, especially for relatively low concentrations.⁵³ Five measurements were made at each concentration. These measurements enable determination of the sensitivity and sensing range of the system and provide the calibration necessary to quantitatively measure the concentration of a molecule in the vicinity of the antenna element.

SEIRA Limit of Detection and Sensitivity Relative to a Bare Substrate and ATR-Mode Spectroscopy. The SEIRA limit of detection (LOD) was determined from the signal-tonoise ratio (SNR) at various concentrations of L-ascorbic acid. The peak absorbance at 1210 cm⁻¹ is taken as the signal amplitude (S). Spectra collected from water are used to provide the noise amplitude as there are no water absorptions in this region. The spectrum of a high concentration of Lascorbic acid (100 mM) was first recorded. The spectral region for calculating the noise was set to $900-1250 \text{ cm}^{-1}$ so that it was centered at the peak maximum in the L-ascorbic acid spectrum and included wavenumbers on either side of the peak position where the peak intensity was 1% or greater of the peak maximum. The calculated noise amplitude (N) of the water background, determined to be 2.99×10^{-2} mOD, is the standard deviation (SD) of five averaged water spectra at the same band (the average of each water spectra is first determined, and then the SD of these five numbers is determined). The relationship between S and L-ascorbic acid concentration is shown as the red line in Figure 2e. Through a linear fit to this data and N, the SNR as a function of L-ascorbic acid can be determined. The limit of detection for L-ascorbic acid is determined to be 1.35 mM, using as the cutoff a SNR of 3. To show an example at a slightly higher concentration than this, a 5 mM L-ascorbic acid spectra and a water spectra are plotted on the same graph in Figure 2f (calculated SNR of 22.86).

Even if nanoantennas are not present, IR reflection from an interface changes if the optical properties of the material on either side of the interface change. Thus, along with comparing SEIRA with ATR, it was also necessary to compare the optical response of a region on the substrate containing nanoantennas with a region on the substrate without nanoantennas, under the same imaging conditions (Figure 3). A substrate containing a CNA patch is exposed to a mixture of ethanol and water. Reflection measurements (around the C-O stretching band of ethanol at 1040-1120 cm⁻¹) were then taken from the CNAcontaining region of the substrate and a bare region of the substrate, and compared with spectra taken using a ZnSe crystal on a commercial ATR-FTIR system (Thermo-Nicolet NEXUS 670) (Figure 3a-f). For 200 mM ethanol, the calculated standard deviation of the water background is 2.99 $\times 10^{-2}$ mOD using SEIRA, 7.76 mOD without SEIRA and 7.5 \times 10⁻² mOD using ATR, and the SNR is 223 with and 11.11 without SEIRA and 21.3 for ATR. Absorbance spectra for ethanol concentrations of 5-100 mM within the SEIRA region, 40-5000 mM outside the SEIRA region, and 20-1000 mM for ATR are included as Supporting Information (SI) Figure S1a-c. The LOD within the SEIRA region is 2.17 mM, outside the SEIRA region it is 128 mM and it is 27.43 mM for ATR (Figure 3b,d,f). For all experiments, spectra were collected for 90 s over the spectral window of 3000-500 cm^{-1} with a nominal spectral resolution of 8 cm^{-1} . These measurements indicate SEIRA provides an at least 13-fold



Figure 4. SEIRA-based vs substrate reflection-based measurements for diffusion into CANVERA 1110. Reflectance as a 50 wt % ethanolwater solution diffuses into CANVERA 1110. (a) SEIRA-based. (b) Substrate reflection-based. Concentration of ethanol over time at the bottom of the polymer films calculated from the integrated absorbance of the C–O region using (c) SEIRA, and (d) the substrate reflection. Concentration of water at the bottom of the polymer film over time calculated from the integrated absorbance of the H–O–H region using (d) SEIRA, and (f) the substrate reflection. In c–f, experimental data are fit to a Fickian model. In c and d, the standard deviation of data points from 2500 to 4500 s (orange area) vs the diffusion curve is calculated to quantify the experimental deviation for SEIRA and the substrate reflectance methods.

enhancement in the LOD relative to a commercial ATR system.

An important quantitative difference between SEIRA and ATR is the thinner volume probed by SEIRA. Figure 3g-j show the nearfield electric field distributions around the lateral arm of the CNA and the s-polarized and p-polarized evanescent field produced by ATR (ZnSe crystal) as calculated via the FDTD method (Lumerical). The variation of the field normal to the substrate (the direction important for a diffusion measurement) at 1000 cm⁻¹ is plotted in Figure 3h,j. Using both methods, the field decays exponentially above the substrate. The calculated skin depth (depth at which the field intensity has fallen to 1/e) is 40 nm for SEIRA and 620 nm (980 nm) for s-polarization (p-polarization) ATR. See this reference⁵⁴ for a calculator for the penetration depth in ATR, which also indicates a minimum detection thickness of order 600 nm, even for high angles of incidence. The SEIRA skin depth was also confirmed experimentally as shown in SI Figures S8 and S9. A strong H-O-H scissoring absorption from H₂O was observed when a 90 nm PMMA film was coated on the substrate (which results in a ~ 30 nm PMMA film above the CNAs). The absorption intensity was \sim 50% of that

when H_2O was placed directly on the CNAs, which agrees qualitatively with the skin depth calculation presented in Figure 3h,j. Once the PMMA thickness above the CNAs was 125 nm, the H-O-H scissoring absorption reduced considerably, and was similar for both this and a 150 nm thick film. Some of the remaining water signal is probably due to water absorbed by the PMMA film, but we cannot also rule out defects or pinholes on the PMMA film, so do not quantitatively analyze this data. As both FDTD and the experimental on the ultrathin PMMA film show, SEIRA is sensitive to a much smaller thickness than ATR, which as we show is important in quantitative investigation of analyte diffusion into thin polymer coatings.

Solubility and Diffusion of L-Ascorbic Acid, Ethanol, And Water in Polymer Films. *Via* SEIRA, L-ascorbic acid transport and concentration within CANVERA 1110, EXP-4599, and PMMA films of different thicknesses was investigated (Figure 2). Differential absorbance spectra at 3 min intervals for 60 min after exposure of polymer coating to the aqueous L-ascorbic acid solution are shown in Figure 2g-i. For all spectra, absorption is referenced to spectra taken for each polymer after exposure to water and immediately before

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Figure 5. SEIRA-measured diffusion into CANVERA 1110 films of varying thickness. (a) Concentration of ethanol over time at the bottom of 0.5, 2.5, and 5 μ m thick CANVERA 1110 polymer films calculated from the integrated absorbance of the C–O region using SEIRA. (b) Concentration of water at the bottom of the polymer film over time calculated from the integrated absorbance of the H–O–H region using SEIRA. (c) Apparent thickness dependent diffusion coefficient of water and ethanol into CANVERA 1110.

the L-ascorbic acid water solution is introduced thus the use of the term 'differential absorbance spectra'. As the same nanoantenna array patch is monitored for each experiment, spectra collected immediately before analyte-containing solution is added serves as the background, and it was not necessary to perform the baseline correction used in Figure 2b,c. This same background subtraction approach was used for all the polymer films investigated to subtract absorbances due to the polymer. The integral over the characteristic region serves as a proxy for the L-ascorbic acid and water concentration. Using the calibration curve shown in Figure 2e, the absorbance signal vs time can be converted into a concentration vs time (Figure 2j-o). The blue and red blocks on Figure 2g-i highlight the spectral regions of the specific Lascorbic acid C-O and C-O-C absorption bands (1040- 1210 cm^{-1}) and water H–O–H scissoring band (1550–1720 cm⁻¹) of interest. Since the volume of analyte uptake by the polymer film is small, spectral shifts in the plasmonic resonance due to changes in the refractive index of the polymer film as analyte penetrates can be neglected. By focusing on particular absorption bands, transport of specific molecules in the polymer coatings can be monitored. Using a Fickian model, the diffusion coefficient of a penetrant into the polymer films can be obtained from the SEIRA data, starting with the following equation:55

$$S(t) = \int_0^{z_d} u(z, t) dz = \overline{C} + \frac{1}{z_d} \sum_{n=0}^\infty \frac{A_n L}{\lambda_n} e^{-\frac{-\lambda_n^2 D}{L^2} t} \sin\left(\frac{\lambda_n z_d}{L}\right)$$
(2)

S(t) indicates concentration of analyte penetrant by the film as a function of time t, and \overline{C} is the equilibrium concentration. L is half of the thickness of polymer film and z_d is the depth of material sampled by instrument, which is set as 100 nm for all measurements throughout the paper (~twice the skin depth). See SI Note 2 for the definition of λ_n and A_n . The diffusion coefficient, D is the only adjustable fitting parameter in eq 2. The specific function used and fitting procedure are included in the SI Notes. The diffusivity of analyte in the polymers can be determined by regressing the experimental data (concentration versus time) to the solution of Fick's law with the initial and boundary conditions defined by the experiment. We note, the approximation of $z_d = 100$ nm will result in errors in determination of D for an ultrathin film (e.g., less than about 250 nm), as it probably results in an under-approximation of the distance a molecule must traverse before it is detected (twice the skin depth is probably an overapproximation of the sensing thickness). As the films become thicker, and certainly by a thickness of 500 nm, the effect of this approximation is insignificant.

There are two observable absorption bands (C–O, C–O–C at 1040–1210 cm⁻¹ and H–O–H at 1550–1720 cm⁻¹) for the L-ascorbic acid water solution within the SEIRA region (1000–1800 cm⁻¹). For CANVERA 1110 and PMMA, the transport behavior for both L-ascorbic acid and water obey Fick's law, while only a water signal is observed in the EXP-4599 coating. Apparently, L-ascorbic acid does not diffuse into the EXP-4599 coating to a detectable level (Figure 21). As a check of the quantitative accuracy of the analyte concentration as measured by SEIRA, we note the measured saturated water content of PMMA is ~0.35 M (Figure 2n), which is in the middle of the range found for commercial PMMA, 0.13M–0.52M.⁵⁶

Similar measurements are carried out for 50 wt % ethanolwater diffusion into CANVERA 1110 with SEIRA and from an antenna-free region of the substrate (Figure 4 and SI Figure S2), as well as PMMA, and EXP-4599 with SEIRA (SI Figure S2). Differential reflectance spectra for 50 wt % ethanol-water diffusion in CANVERA 1110 over 75 min with and without SIERA are plotted in Figure 4a,b. Clearly the characteristic peaks associated with ethanol and water absorption are clearer when SEIRA is used. The analyte concentration vs time as determined with and without SEIRA are shown in Figure 4c-f. As extracted from the SEIRA data, the ethanol diffusion coefficient, 1.54×10^{-10} cm²/s, was approximately 1.5 times faster than the water diffusion coefficient, 1.09×10^{-10} cm²/s. Similar trends are seen even from the substrate reflectivity (antenna-free region), but there is significant scatter in the data due to the equilibrium concentration of both ethanol and water in the polymer being near the limit of detection. The standard deviation of data relative to the fit from 2500 to 4500 s (orange area) is calculated to quantify the difference between the SEIRA and substrate reflectance curves, respectively. It is found that the standard deviation is 0.57 mM and 33.1 mM for SEIRA and substance reflection measurements, respectively. The FTIR stability, the concentration of the analyte, and the duration of the measurement sets the minimum measurable value of D for a given film thickness; in our experiments, we generally could measure $D = 1.54 \pm 0.018 \times 10^{-10} \text{ cm}^2/\text{sec}$ for



Figure 6. SEIRA-measured diffusion of sugars into 250 nm thick CANVERA 1110 films. (a) Chemical structures of glucose, maltose and maltrotriose. (b) Absorbance spectra of 200 mM glucose, maltose and maltrotriose water solutions. (c) Plot of diffusion coefficients as a function of molecular weight. SEIRA-determined concentration evolution of glucose (d), maltose (e) and maltrotriose (f) vs time at the bottom of a 250 nm thick CANVERA 1110 polymer film calculated from the integrated absorbance of the C–O and C–C regions.

SEIRA and $D = 1.30 \pm 0.53 \times 10^{-10} \text{ cm}^2/\text{sec}$ on the bare substrate.

Ethanol and water diffusion data into the PMMA and EXP-4599 coatings are indicative of rather complex interactions. While the concentration of ethanol in CANVERA 1110 starts to saturate (to ~62 mM) after 75 min, the ethanol concentration in the bottom of the PMMA film is still increasing roughly linearly (to ~33.4 mM) for at least 75 min (SI Figure S2a,b). In the EXP-4599 coating, we observe an exponentially increasing C–O (ethanol) band (Figure S2c) for at least 75 min. By 75 min, the ethanol uptake of EXP-4599 is at least 300 mM. The time-resolved water concentration for the same three coatings is shown in Figure S 2d–f. Unlike for ethanol, the water concentration in all three polymer coatings stabilizes after ~15 min.

Solubility and Diffusion in Thin Polymer Coatings. The ability of SEIRA to probe a very thin volume with high sensitivity makes it well-suited to investigating diffusion in thin polymer coatings. We demonstrate this first by monitoring 1 M

ethanol-water solution diffusion into 0.5 μ m, 2.5 μ m, and 5 μ m thick CANVERA 1110 coatings. Figure 5 and SI Figure S3 show the differential reflectance spectra and concentration evolution plots as a function of time for these three coating thicknesses. For the 5 μ m thick CANVERA 1110 coatings, the ethanol and water diffusion coefficients are 0.97×10^{-10} cm²/s and 1.31×10^{-10} cm²/s, respectively. As the coating thickness decreases, the apparent diffusion coefficient decreases slightly, but this may only be an artifact of there being fewer meaningful data points in the fit. In comparison to a 50 wt % solution (9.6 M ethanol) (Figure 4), the diffusion coefficient is slightly smaller for ethanol but slightly larger for water, perhaps because the polymer is less swollen by ethanol (the equilibrium ethanol concentration in the polymer is about 15 mM when exposed to 1 M ethanol, vs about 62 mM when exposed to 9.6 M ethanol). Our measurements on thickness and molecular weight dependence provide an initial demonstration of the capability for measuring diffusion in thin polymer coatings with the limitation that to obtain our desired LOD, each data point

b

а



Figure 7. SEIRA-measured diffusion of Coca-Cola and Diet Coke into CANVERA 1110, PMMA, and EXP-4599. (a) Chemical structures of fructose and glucose. (b) Integrated absorbance and peak absorbance calibration plot for 0 to 100 mM fructose. The equations of the fitted lines are y = 0.018x (blue) and y = 0.046x (red). Black dashed line indicates 3 times standard deviation (SD) of averaged noise spectra. The x coordinate of the intersection of the black dashed line and the red line is the limit of detection for SEIRA measurements of fructose. (c,d) Fructose and glucose concentration over time in CANVERA 1110 after exposure to Coca Cola and Diet Coke. (e,f) Fructose and glucose concentration over time in PMMA, and EXP-4599 after exposure to Coca Cola.

requires a 90 s integration, which we followed by a 90 s idle time. This 180 s time step sets an upper bound to the measurable diffusion constant.

Investigation of diffusion into even thinner films requires systems with slower diffusion. Here we investigate diffusion of 200 mM aqueous solutions three sugars with increasing molecular weights (glucose, maltose and maltrotriose) into a 250 nm thick CANVERA 1110 coating. Note, 250 nm is well above the SEIRA probe depth, but significantly below the ATR probe depth. Each data point was collected for 75 s and the idle time between measurements was set to zero. Figure 6a provides the chemical structures of glucose, maltose and maltrotriose. All three molecules consist of the same sugar subunit. Figure 6b and SI Figure S4a show the absorbance spectra for the 200 mM solutions and the calibration curve. As expected, the C–O and C–C region $(1000-1150 \text{ cm}^{-1})$ absorption peaks increase with the number of sugar subunits. Figure 6c plots the diffusion coefficient against molecular weight as determined from the concentration evolution as a function of time (Figure 6d–f). The associated differential reflectance spectra are shown in SI Figure S4b–d. Not surprisingly, we find the diffusion coefficients are roughly linear with molecular weight in agreement with the Stokes–Einstein relation.⁵⁷

SEIRA Spectroscopy of Sugar in Coca-Cola Diffusion through Polymer Coatings. As a proof-of concept example of using SEIRA for a complex food product, we studied the transport of a sugar from Coca-Cola into the polymer coatings. In Coca-Cola, there are 39 g of sugar per 355 mL. Previous reports have indicated the sweetener in Coca-Cola is about 60% fructose and 40% glucose by weight.⁵⁸ Since they are chemically similar, we do not attempt to discriminate them. Figure 7a gives the chemical structures of fructose and glucose.^{59,60} Figure 7b and SI Figure S5a show the integrated absorbance and peak absorbance plots as a function of concentration. The calculated limit of detection of SEIRA for the fructose/glucose mixture is 0.66 mM. Differential reflectance spectra demonstrate fructose/glucose enters CANVERA 1110 coating in Figure 7c. It is observed that the concentration of fructose and glucose saturate at 4 mM. A SEIRA study using Diet Coke was performed to determine the contribution of caffeine to the measured signal. Both Diet Coke and Coca-Cola contain caffeine, which has a C-N bond with an absorption band at 995-1191 cm⁻¹, which overlaps the absorption band of fructose and glucose. SI Figure S5b provides reflectance spectra of Coca-Cola and Diet Coke measured with SEIRA. Note, the sugar in Coca-Cola is replaced with an artificial sweetener; aspartame in Diet Coke and aspartame also could contribute the absorption at the band of 1000-1100 cm⁻¹ due to its C-O bond. However, in SI Figure S5b, we show the peak in the band of $1000-1100 \text{ cm}^{-1}$ as measured with SEIRA for Diet Coke is very weak relative to the peak observed for Coca-Cola. This is probably because the combined concentration of aspartame (180 mg/12 oz) and caffeine (46 mg/12 oz) is small in Diet Coke (aspartame is approximately 200 times sweeter than sucrose). Differential reflectance spectra for Diet Coke diffusion into CANVERA 1110 are provided in Figure 7d. No observable signal is detected. Because the concentration of caffeine is similar in Coca-Cola (11.89 ppm) and Diet Coke (12.76 ppm),⁵⁸ we are comfortable stating caffeine is not contributing to our measured data. Knowing this, based on the differential absorbance spectra, fructose/glucose enters PMMA, EXP-4599, and CANVERA 1110 coatings and saturates in PMMA at a concentration about twice as for CANVERA 1110 and EXP-4599 (Figure 7e,f and SI Figure S5e,f).

CONCLUSIONS

Our results demonstrate that SEIRA is highly effective for characterizing the diffusion of molecules through polymer films at least as thin as 250 nm. Because SEIRA only interrogates a small volume and small thickness at the antenna-sample interface, it greatly simplifies analysis relative to methods which average the measurement through the thickness of the film, and perhaps even into the overlying analyte. Here we focus on diffusion and dissolution of L-ascorbic acid, ethanol, water, and sugars into polyolefin-based and PMMA-based films. We note, there is nothing about these analytes or polymers which makes them particularly attractive for SEIRA; many other polymer and analyte chemistries could have been studied. The key requirement is that the analyte has a distinct IR absorption. Because multiple IR absorptions can be concurrently followed, the transport of multiple compounds into polymer films can be investigated. As just one example of the kind of information that can be obtained via a SEIRA CNA-based study, we note the diffusion constant for water in thin CANVERA 1110 coatings $(1-2 x 10^{-10} cm^2 s^{-1})$ is 4-8 times smaller than previously observed in LDPE via ATR.47 The lower diffusion constant relative to LDPE is perhaps expected given CANVERA 1110 is semicrystalline.⁶¹ What is important is the finding that the polar dispersing agents present in

CANVERA 1110^{61} do not appear to provide fast diffusion pathways for water even when the film is thin and negate the barrier properties.

Vital to this approach is the over an order of magnitude signal enhancement provided by the plasmonic nanoantennas relative to that provided by ATR methods. By using crossed nanoantennas the system provides dual-band resonances, here covering the spectral region of 1000 cm⁻¹ to 1700 cm⁻¹, enabling simultaneous monitoring of two different penetrant species via their specific absorptions. We note that crossed nanoantennas are the best design for our system which uses unpolarized light. If polarized light had been used, a different approach, for example, parallel arrays of antenna of different lengths, may have been preferred. To determine analyte concentration, a rather tricky measurement in a thin polymer film, it was necessary to correlate the IR absorption to analyte concentration. Via a series of control and calibration experiments, we found a linear relationship between the integrated absorbance and analyte concentration, making quantitative determination of analyte concentration in the polymer film possible. As detailed in the Supporting Information, to illustrate the compatibility of this approach with complex mixtures, diffusion of molecules from beer and dog food into polymer coatings was also studied.

METHODS

Fabrication. Gold CNAs are patterned by electron beam lithography (Raith eLine) on IR transparent CaF2 substrates. A 250 nm thick PMMA e-beam resist layer is spin coated on the substrate and baked at 180 °C for 5 min. A 8 nm thick gold layer is sputtered on top of resist for grounding the substrate. After e-beam exposure with a dose of 400 μ C/cm² (using 20 kV voltage and a 10 μ m aperture), the resist is washed with gold etchant, developed in IPA:MIBK 3:1 for 45 s and dried under a stream of high-purity nitrogen. Using electron-beam evaporation, a 5 nm thick Cr adhesion layer followed by a 75 nm thick Au layer is deposited. Excess metal and resist is removed by soaking the sample in acetone for 45 min. The nanoantenna array fabrication is completed by a 2 min oxygen plasma exposure to remove resist residue. The width w and thickness h of the nanoantennas were fixed at 80 nm. The length of the x and y arms of the CNAs are 2.8 and 1.7 μ m, respectively. Choice of arm length depends on the IR resonance peaks of interest, which for the present study are centered around 1340 and 1770 cm⁻¹. The gap between the arms of adjacent CNAs was 200 nm. The cross-shape was chosen to take advantage of the randomly polarized light generated by the thermal light source (a globar).

Polymer Films. Three polymer coatings were investigated, CANVERA 1110 (Dow) (HDPE-based polyolefin), EXP-4599 (Dow) (polypropylene-based polyolefin), and poly(methyl methacrylate) (PMMA) (Sigma-Aldrich). All three polymers are spin coated onto CNA-coated substrates as 5 μ m thick coatings (SI Figure S6). The coated substrates are then mounted into flow cells enabling introduction of various analyte solutions. For PMMA coating, 3.0 wt % PMMA powder was dissolved in chloroform following by spin coating at 2500 rpm. Residual solvent was removed by baking at 180 °C for 7 min. For CANVERA 1110 and EXP-4599 coatings, the formulations are spin coated at 3000 and 2200 rpm, respectively. Then the samples are baked at 175 °C for 5.5 min and followed at 205 °C for 1.5 min. Depth of detection experiments (SI Figure S8) were performed specifically using high molecular weight PMMA (950 000) spin coated on a CaF₂ substrate containing CNAs.

Numerical Simulations. Far-field reflectance spectra are calculated using the FDTD software Lumerical FDTD-Solutions. The reflectance of nanoantennas arrays are obtained by numerically solving Maxwell's equations with under normal incidence plane wave source averaged with both polarizations parallel and perpendicular to the long antenna axis. A thin 5 nm thick Cr adhesion layer, present in

the fabricated samples, was omitted from the simulations. The gold cross nanoantenna arrays are placed on a CaF₂ substrates and situated at least one wavelength away from the edges of simulation box. CaF₂ was described by a refractive index of n = 1.3. The dielectric function of gold and CaF₂ are taken from Johnson and Christy⁶² and Li.⁶³ Periodic boundary conditions and perfect matched layers are applied in the x-y plane and z direction (along the light propagation direction).⁶⁴ To resolve the nanostructure, the antennas are discretized into $5 \times 5 \times 5$ nm³ meshes. Reflectances are calculated by integrating the power flux through a power monitor situated in air 1 μ m above the sample plane, then normalizing it with respect to the source power.

IR Spectroscopy. FTIR measurements were performed on a Bruker Vertex70 spectrometer using a liquid-nitrogen-cooled mercury cadmium telluride (MCT) detector. All data were taken under identical acquisition settings: a mirror velocity of 40 kHz, 512 scans coadded, and 8 cm⁻¹ resolution. All zero order reflectance spectra were collected by a Bruker Hyperion 3000 infrared microscope, which was coupled to the Fourier transform infrared (FTIR) spectrometer, using the globar internal source of the FTIR. The reflection data of the antenna arrays are normalized to the reflection spectrum from a layer of gold mirror, which provides a nearly 100% reflectivity in the wavelength range between 2000 and 1500 cm⁻¹. The incident light from the FTIR is coupled into the microscope and then focused onto the sample surface through a Cassegrain objective (Newport, 36 X, N.A. 0.4); the reflected light was collected by the same objective and then was guided by another optical path to an MCT detector inside the microscope. Inside the microscope, there is an aperture; its size was adjusted to match the size of the antenna array, eliminating reflection from areas outside the antenna array. The lateral diffraction limit of the system is about 12.5 μ m. As a comparison, with ATR, the crystal diameter is 4 mm (Thermo-Nicolet NEXUS 670). Light undergoes multiple internal reflections in the crystal. Strong attenuation of the IR signal is achieved with a long path length. But the lateral resolution is sacrificed (note, ATR can also be done in an imaging mode via single reflection in a FTIR microscope, to provide spatial resolution; however, we did not compare SEIRA with such a system).

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was performed using a Thermo-Nicolet NEXUS 670 FTIR system. The reflectance element was a θ = 45° ZnSe crystal with ten internal reflections. The ATR element was covered with sufficient volumes of each solution. All spectra were obtained using 8 cm⁻¹ spectral resolution with 512 scans. Spectra were corrected for wavelength dependent differences in penetration depth of the evanescent wave. We use the water spectrum as reference. Five measurements were made at each concentration. These measurements enable determination of the LOD for the ATR measurement.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsnano.1c02701.

Absorbance spectra on SEIRA substrate, bare substrate, and via ATR, SIERA investigations of diffusion into polymer coatings, calibration spectra, nanoantenna characterization, diffusion models (PDF), SEIRA investigations on ultrathin PMMA films, AFM of ultrathin PMMA films coated on an array of CNAs (PDF)

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Notes

The authors declare no competing financial interest.

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