Quantitative Measures of Reliability and Sensitivity of Nanoparticle-Based Sensors in Detecting Volatile Organic Compounds

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ABSTRACT: We herein provide quantitative measures of sensors’ reliability and sensitivity as a function of the sensor’s capacity (maximum detection signal or saturation state) in addition to other adsorption–desorption parameters that define the detection signals toward volatile organic compounds (VOCs). The measures we have developed show differentiation between irregular dispersed points of sensors with low and high capacities. We show that the sharpest capacity that separates between the two types of distribution points, viz. the reliability limit (RL), is tightly linked with the desorption constant $k_d$. Less sharp RLs give interpretations of other reliability indicators. RL also provides information about the reliability of detecting signals of VOCs for a given sensor and sensors for a particular VOC. We show that sensors with high capacities are more reliable and sensitive to detecting signals of VOCs than sensors with lower capacities.

INTRODUCTION

Sensors based on monolayer-capped gold nanoparticles (GNPs) have the advantage of low detection limits for volatile organic compounds (VOCs), a wide dynamic range, ambient room operation, tolerance for varying humidity levels as in the case of exhaled breath, reasonable dimensions, and low cost.1–6 These advantages could be attributed to the fact that the chemical and physical properties of monolayer-capped GNP films can be accurately tailored to obtain the desired sensitivity and selectivity for a particular sensing application.1,6–16 On this account, these advantages grant control over the interparticle distance and make it possible to obtain nearly uniform composite films.

The most common configuration of monolayer-capped GNP sensors for breath analysis is based on a chemiresistor platform.6,10,17,18 Production of these sensors relies on the assembly of thin films of monolayer-capped GNP s between adjacent micro-electrodes. In the monolayer-capped GNP chemiresistive films, the sorption of VOCs is achieved by the organic film component, and the electric conductivity is achieved by GNPs.6,11,19–21 On exposure to gas samples, VOCs reach the sensing surface or diffuse into the sensing film and react with the capping ligands/functional groups, causing shrinkage/expansion in the volume of the nanomaterial film. Consequently, the steric position of the inorganic nanomaterial blocks shifts, producing an increase or decrease in film resistance. In other instances, exposure of the nanomaterial film to VOCs with high dielectric constants leads to a charge transfer due to changes in the dielectric constants of the medium surrounding the nanoparticles, leading to a decrease in the measured resistance of the monolayer-capped GNP film.9,22,23

A critical factor in the determination of the monolayer-capped GNP sensing characteristics relies on how VOCs interact with the GNP films, viz. on the adsorption–desorption (AD) kinetics. Several studies have reported on theoretical models based on first-order kinetics of VOCs with the immobilized ligands on the sensor’s surface.24–27 In one theoretical model, the equation of the rate reaction for a single analyte could successfully be extended to account for an $n$ VOCs mixture, assuming a single adsorbate molecule on one binding site.26 Another theoretical model for evaluation of the AD noise in the microfluidic structure with biosensors operating in an $n$ analytes environment could account for small fluctuations as a random process in the detection signal around the equilibrium.27 To improve the GNP sensors and to enable quantitative measures for their reliability and sensitivity, a better and more comprehensive understanding of AD parameters is required.

In this article, we have modified the desorption rate constant of the existing reaction model24–28 and applied it to derive AD parameters through its fit to the experimental data. Using this model, we demonstrate the impact of the AD parameters and input data on the function of the sensors and their practical implications. We achieve these findings from two datasets. One dataset was obtained from experiments carried out in this study, and the other one was based on an existing study. Our results show that the AD parameters give quantitative measures of sensors’ reliability and sensitivity and can be extended for an $n$ VOCs mixture, assuming a single VOC molecule per binding site.26

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**RESULTS**

Theoretical Considerations. The flux balance equation of AD of a single analyte on a sensor surface during the pulse time $t_p$ is\(^{34,30}\)

$$\frac{d\theta}{dt} = k^+_d C (1 - \theta) - k^-_{d,a} \theta$$

(1)

where $\theta$ is the fraction of bounded sites on a sensor’s surface, $t$ is the time, $k^+_d$ is the adsorption rate constant, $C$ is the analyte concentration adjacent to the sensor’s surface, and $k^-_{d,a}$ is the desorption rate constant during the adsorption stage within $0 < t < t_p$. For $t > t_p$, the desorption rate equation is derived from eq 1 for $C = 0$

$$\frac{d\theta}{dt} = -k^-_{d,a} \theta$$

(1a)

The desorption rate constant $k^-_{d,a}$ in eq 1a should be equal to or $> k^-_{d,a}$ in eq 1 because the desorption for $t > t_p$ is undisturbed by adsorption. Therefore, it is expected that, in general, $k^-_{d,a} \geq k^-_{d,a}$.

We consider the case of a step function of the inlet concentration $C_p$. In this case, the impulse within $0 \leq t \leq t_p$ yields constant bulk concentration. Thus, we may replace $k^+_d C$ in eq 1 with $k^+_d C_0$, in which $k^+_d = k^+_d C/C_0$ is an apparent adsorption rate constant. This replacement turns the bounded sites fraction $\theta$ at the adsorption stage in eq 1 into

$$\frac{d\theta}{dt} = k^+_d C_0 (1 - \theta) - k^-_{d,a} \theta, \quad 0 \leq t \leq t_p$$

(2)

Applying the initial condition $\theta = 0$ at $t = 0$ to eq 2 yields $\theta$ as in eq 3

$$\theta = \frac{\alpha}{\beta} (1 - e^{-\beta t}), \quad \alpha \equiv k^-_{d,a} C_0, \quad \beta \equiv \alpha + k^-_{d,a}, \quad 0 \leq t \leq t_p$$

(3)

For $t > t_p$ the adsorption process stops. Therefore, eqs 1, 2, and 3 vanish and eq 1a governs the free desorption, that is, desorption without disturbance by the adsorption. Using the initial condition $\theta_p = \theta (t_p)$ from eq 3, the solution of eq 1a yields

$$\theta = \theta_p e^{-k^-_{d,a}(t-t_p)}, \quad t \geq t_p$$

(4)

It is worth noting that in previous studies\(^{34,28}\), $k^-_{d,a}$ was assumed equal in both adsorption stage and free desorption. Desorption of VOCs during the adsorption stage should, in general, be slower than the free desorption after adsorption ends. Therefore, following the present fit of the model to 2 data sets and the fit therein,\(^{28}\) support the assumption of $k^-_{d,a} \leq k^-_{d,a}$ depends on sensors and data characteristics.

Sensor’s Capacity. Our typical raw data of each sensor described in the Experimental Section is shown in Figure 1. A sensor’s response, viz the change in the measured electrical resistance of the GNP-based chemiresistor upon exposure to analyte (or VOC), starts at the basic resistance of $R_b$ without analyte or $\theta = 0$. Adsorption endures from $t = 0$ to $t_p$ or from $\theta = 0$ to $\theta_p$ and the resistance changes from $R_b$ to $R_{sat}$ respectively. After several minutes of free desorption, the sensor was fed continuously with analytes until it reached its saturation level with $R_{sat}$ as a maximum resistance or $\theta = 1$.

Measuring the saturation level $\Delta R_{sat}$ of a sensor is necessary in determining the coverage fraction $\theta$ required for calculating the AD parameters through the fit of eqs 3 and 4 to experimental data. The $\Delta R_{sat}$ of a sensor also determines its capacity to contain analytes, and, as a result, its reliability (discussed below).

A typical fit of eqs 3 and 4 to the experimental data of nine out of twelve sensors described in the Experimental Section are represented in Figure 2. No detection signals were observed by sensors B3, B4, and T4; therefore, they have not been included in the analysis.

Figure 1. Typical detection signal followed by saturation measurements of sensors indicating analyte capacity. Definitions of main resistances of a sensor in response to its exposure to analytes: $R_s$ is the base resistance at $t = 0$, $R_p$ is the resistance at $t = t_p$, the pulse time, $R_{sat}$ is the resistance at maximum adsorption capacity of a sensor, and $\theta$ is the fractional coverage of a sensor reaction sites at time $t > 0$.

Figure 2. Typical fit of eqs 3 and 4 (solid lines) to experimental data (dots) described in the Experimental Section. The point $p$ on the pulse time define $t_p$ and the point $s$ defines $t_s$ viz the starting time of the slow desorption process.

The shape of the detection signal depicted in Figure 2 is governed by $k^-_{d,a}$ and $k^-_{d,a}$ in the adsorption stage and $k^-_{d,a}$ in the free desorption stage. The adsorption stage operates during the inlet concentration pulse $0 \leq t \leq t_p$. During the time span $t_p$, two simultaneous processes are active: analyte adsorption on the binding sites and desorption of a part of the bounded analyte. The net adsorbed molecules shape the adsorption part of the detection signal. The desorption stage during $t_p < t \leq t_s$ is characterized by fast free desorption (FFD). This stage is attributed to desorption of analytes from the outer layers of the ligands capping the nanoparticles. Analytes in deeper layers need first to diffuse out to the sensor’s surface before desorption. This stage occurs at $t > t_s$ as shown by the “tail” in Figure 2.\(^{31}\) Equation 4 may also be applied to the tail shape of the data (see Figure 2 for $t > t_s$) to simulate the slower desorption rate constants $k^-_{d,a}$.
Fit results of eqs 3 and 4 to the nine sensors data yield AD rate constants that determine the detection signal, as presented in Table 1. The maximum measured coverage range is between $\theta_{p} = 0.28$—0.75, with maximum sensor signal (capacity) ranging from 933 to 375 890 $\Omega$.

Table 1. Adsorption Parameters of the Sensors during $0 \leq t \leq t_{p}$

| $R_s$, $\Omega$ | $\Delta R_{max}$, $\Omega$ | $k_{c}C_{p}$, s$^{-1}$ | $k_{d}C_{p}$, s$^{-1}$ | $k_{d}/k_{c}$ | $\Delta R_{max}$ (m$\Omega$) |
|----------------|--------------------------|----------------------|----------------------|---------------|---------------------------|
| T6 0.000653    | 9.33 $\times$ 10$^{-9}$  | 0.389                | 0.311                | 1.1           | 0.283                     |
| T3 0.00239     | 0.000451                 | 0.527                | 0.173                | 0.7           | 0.247                     |
| B5 0.00762     | 0.000932                 | 0.0735               | 0.177                | 0.55          | 0.321                     |
| T1 0.00679     | 0.00441                  | 0.888                | 0.312                | 1.2           | 0.260                     |
| T5 0.0897      | 0.0165                   | 0.198                | 0.132                | 0.94          | 0.140                     |
| T2 0.235       | 0.0171                   | 0.319                | 0.241                | 0.9           | 0.268                     |
| B1 0.228       | 0.0739                   | 0.248                | 0.452                | 1             | 0.452                     |
| T6 1.84        | 0.160                    | 0.142                | 0.208                | 1.1           | 0.189                     |
| B2 2.74        | 0.376                    | 0.164                | 0.336                | 1.3           | 0.258                     |

“Desorption parameters are for $t > t_{p}$; T# and B# indicate top and bottom placement of the sensors respectively. Its associated numbers # indicate sensors’ position in the chamber along the flow direction. The data are arranged in the ascending order of the sensor capacity $\Delta R_{max}$ of octane-binding sites. The capacity, $\Delta R_{max} = R_{sat} - R_{b}$, where $R_{sat}$ is the saturation resistance at $\theta = 1$ and $R_{b}$ is the base resistance at $\theta = 0$, defined graphically in Figure 2.

Sensor capacity listed in Table 1 varies within 5 orders of magnitude. The impact of such a wide range of capacities on the sensor’s reliability will be discussed later. However, a much lower range of the adsorption rate constant $k_{c}C_{p}$ (ca order of magnitude) indicates the adsorbability range of the tested sensors. The desorption rate constant, $k_{d}$, shows the narrowest variation range of the nine sensors, indicating $k_{d}$ as practically invariable. This result is very significant in the reliability test to be discussed below. Measurement results of $R_s$ are listed in Table 1. The results show that the basic resistance, $R_{b}$, has a good correlation with the sensor capacity $\Delta R_{max}$ (Figure 3B). However, two pairs of sensors B5 & T1 and T2 & B1 exhibit an unexpected ascending order by changing places. As each pair of sensors are pretty close to each other we may attribute these shifts to measurements fluctuations such as shown in Figure 1.

Desorption. During $t > t_{p}$, desorption of the analytes is undisturbed by adsorption. Therefore, desorption of analytes at the adsorption stage $k_{d}$ for $t \leq t_{p}$ is lower by 14—45% than the free desorption rate constant $k_{d}$ ($t > t_{p}$). This result indicates that during the adsorption stage, analytes motion toward the binding sites on the sensor surface slows down the disconnection of already connected analytes from the binding sites. We denote points, $s$ and $p$, in Figure 2, as points of pulse time $t_{p}$ and start time $t_{s}$ of slow free desorption (SFD). During $t_{p} - t_{s}$, FFD occurs. The concept “free” means pure desorption without adsorption disturbances. The fast concept indicates disconnection of adsorbed molecules on the sensor surface and the slow step indicates molecules adsorbed in the inner layers of the sensors that need first to diffuse to the sensor surface before desorption.

FFD parameters of the nine sensors are summarized in Table 2. The last column of the table gives the desorption rates between 0.068 and 0.364 s$^{-1}$. The SFD starts at $t_{s}$ about 1.7 s after the pulse ends at $t_{p}$ as shown in column 5 of Table 2.

It is worth noting that in Table 2, the timespan of the FFD is practically $t_{p} - t_{s} = 1.7$ s for seven sensors and 1.2 s for the rest of the two sensors. These results indicate the impact of similar thickness of the active layers (1.7—2 $\mu$m). The thickness impact on desorption relates to several possible desorption mechanisms:32 surface reaction, inner particle diffusion, pore diffusion, film diffusion, and external diffusion. Desorption results shown in Figure 2 may be related to two main desorption mechanisms: (1) external diffusion or FFD of the analytes between $t_{p} - t_{s}$ (Figure 2) and (2) some combination of the diffusion mechanisms within the active layers resulting in rate-limiting mechanisms33 that slow down the rate desorption after $t_{p}$, which is the “tail” zone.

**Definition of the Reliability Limit.** Sensor capacity means the maximum detection signal that a sensor can produce for a given analyte. Alternatively, it is the maximum resistance change a sensor can have for a given analyte. In the case of our data in Figure 1, $\Delta R_{max}$ is a sensor capacity. Figure 3A shows that the desorption rate constant $k_{d}$ versus capacity $\Delta R_{max}$ graph is clearly distinct between regular and dispersed points. A distinction limit of $\Delta R_{max} = 0.016$ M$\Omega$ is obtained by the rate of desorption $-\Delta \theta_{ps}/\Delta t_{ps}$ between points $p$ and $s$ defined in Figure 2. It is less clear and sharp limit differentiates between ordered and dispersed points. For capacities <0.016 M$\Omega$, both rate and rate constant of desorption have dispersed and unclear dependency on the capacity. We define reliability limit (RL) (= 0.016 M$\Omega$ in this case) as the RL for detection signals of sensors between reliable ($\Delta R \geq RL$) and unreliable ($\Delta R < RL$) signals. The RLs are determined by reliability indicators such as $k_{d}$ and $-\Delta \theta_{ps}/\Delta t_{ps}$. Base resistance $R_{b}$ of the AD signal listed in Table 1 shows that $R_{b}$ is usually proportional to $\Delta R_{max}$. For this reason, it is interesting to check its ability to provide RL and its sharpness compared to that of the capacity, $\Delta R_{max}$. Figure 3B shows that it is possible to determine RL based on $k_{d} = R_{b}$ test. Its advantage is sparing...
In this section, we have used existing data in Figure 3 of ref 33 to evaluate the maximum capacity VOC, the capacities were then extrapolated to obtain an adsorption stage. Based on experimental data of adsorbed octane on nine sensors with one VOC listed in Table 1.

**Signal Analysis of the Ionogel (BmimNTf2) Sensor.** Thus far, we have described the analysis of detection signals based on experimental data of adsorbed octane on nine different sensors, as described in the Experimental Section. In this section, we have used existing data in Figure 3 of ref 33 to analyze detection signals of one sensor with 7 VOCs. The data in ref 33 contain 28 AD graphs of 7 VOCs. Adsorption capacity \( C \) at a concentration of \( p/p_0 = \epsilon \) is derived for each of the 4 concentrations \( p/p_0 = 0.2, 0.3, 0.4, 0.5 \) of the 7 VOCs. The capacity range of the ionogel sensor between the toluene and ethanol in Table 3 is ~1 order of magnitude. This is a very narrow range compared to the 5 orders of magnitudes of the capacity range of the nine sensors with one VOC listed in Table 1.

Comparison of the results in Figures 2 and 5 yields a much slower FFD of the ionogel sensor than that of the 9 sensors represented in Figure 2. The \( k_3 \) changes about 2-fold between the 2 datasets listed in Tables 2 and 5. Existence of sharp RLs

**Table 2. Parameters Determining the FFD during a Time Span \( t_s - t_p \) for the Nine Sensors**

| Sensor # | \( \Delta R_{\text{max}} \) [MΩ] | \( t_s \) [s] | \( t_p \) [s] | \( t_s - t_p \) [s] | \( \theta_s \) | \( \theta_p \) | \( -\Delta \theta_{\text{max}}/\Delta t_{sp} \) [1/s] |
|---|---|---|---|---|---|---|---|
| T6 | 9.3 \times 10^{-6} | 15.5 | 13.8 | 1.7 | 0.114 | 0.551 | 0.364 |
| T3 | 0.000451 | 15.5 | 13.8 | 1.7 | 0.236 | 0.747 | 0.301 |
| B5 | 0.000932 | 15.5 | 13.8 | 1.7 | 0.167 | 0.282 | 0.068 |
| T1 | 0.004407 | 15.5 | 13.8 | 1.7 | 0.141 | 0.385 | 0.144 |
| T5 | 0.016487 | 15 | 13.8 | 1.2 | 0.245 | 0.581 | 0.28 |
| T2 | 0.017128 | 15 | 13.8 | 1.2 | 0.247 | 0.564 | 0.144 |
| B1 | 0.073903 | 15.5 | 13.8 | 1.7 | 0.083 | 0.35 | 0.157 |
| B6 | 0.16031 | 15.5 | 13.8 | 1.7 | 0.141 | 0.385 | 0.144 |
| B2 | 0.37589 | 15.5 | 13.8 | 1.7 | 0.09 | 0.33 | 0.141 |

**Table 3. Maximum Capacity \( a_1 = (I_1 - I_0)/I_0 \) Evaluated for the Seven VOCs on the BmimNTf2 Surface**

| max. capacity | toluene | hexane | dichloro-methane | ethyl-acetate | trichloro-ethylene | methyl-ethyl-ketone | ethanol |
|---|---|---|---|---|---|---|---|
| \( a_1 \) | 2.55 | 3.59 | 10.9 | 19.9 | 28.6 | 34.5 | 47.8 |

\( \Delta R_{\text{max}} \) experiments. However, \( k_d - \Delta R_{\text{max}} \) test has two advantages over the \( k_d - R_b \) test: sharper RL and RL determined in a smaller capacity point, that is, more sensors become reliable. Results in Figure 4 show an example of indicator \( k_i \).

\[ \frac{C_0}{k_{da}} \] that yields further less clear RL than that of \( k_d \) which yields the sharpest limit of the three above indicators. More data are needed to support the consistency of these results.

Results in Figures 3 and 4 show that AD parameters are related to sensor’s capacity \( \Delta R_{\text{max}} \) and to the base resistance \( R_b \). Of the AD parameters, \( k_d \) shows the clearest relationship, namely, it clearly divides ordered and disordered points and enables determination of RL as well as the limit between the two groups of points.

The fraction of surface coverage defined as \( \theta = a/a_1 \) or \( (I - I_0)/(I_1 - I_0) \) was calculated for each of the seven VOCs and four concentrations using \( a_1 \) from Table 3. Then, AD parameters for each concentration of \( p/p_0 = 0.2-0.5 \), \( \theta \), \( k_{da} \), and \( k_{db} \) were derived from the fit of eqs 2 and 4 to the data of ref 33. Each value in Table 4 was averaged over the four concentrations, \( p/p_0 = 0.2-0.5 \). The capacity range of the ionogel sensor between the toluene and ethanol in Table 3 is ~1 order of magnitude. This is a very narrow range compared to the 5 orders of magnitudes of the capacity range of the nine sensors with one VOC listed in Table 1.

Comparison of the results in Figures 2 and 5 yields a much slower FFD of the ionogel sensor than that of the 9 sensors

**Figure 4. Impact of sensor capacity \( \Delta R_{\text{max}} \) on the adsorption rate constant \( k_{dp}/p_0 \) relative to desorption rate constant \( k_{da} \), during the adsorption stage.**

**Figure 5. Typical detection signal of AD, with specific VOC and \( p/p_0 \) of the BmimNTf2 sensor.**

**Table 4. AD Parameters of the Seven VOCs to and from the BmimNTf2**

| \( a_1 \) | \( k_d/C \) | \( k_{da}/k_{db} \) | \( k_d \) | \( k_{da}/k_{db} \) |
|---|---|---|---|---|
| 2.55 | 0.00823 | 0.00677 | 0.0425 | 0.159 |
| 3.59 | 0.00816 | 0.00834 | 0.0308 | 0.271 |
| 10.9 | 0.00250 | 0.00897 | 0.0155 | 0.579 |
| 19.9 | 0.00535 | 0.0154 | 0.04578 | 0.352 |
| 28.6 | 0.00606 | 0.00987 | 0.0331 | 0.298 |
| 34.5 | 0.00552 | 0.0106 | 0.0308 | 0.346 |
| 47.8 | 0.00133 | 0.0100 | 0.0293 | 0.343 |

**Table 5. Parameters Determining the FFD during a Time Span \( t_s - t_p \) for the Nine Sensors**

| Sensor # | \( \Delta R_{\text{max}} \) [MΩ] | \( t_s \) [s] | \( t_p \) [s] | \( t_s - t_p \) [s] | \( \theta_s \) | \( \theta_p \) | \( -\Delta \theta_{\text{max}}/\Delta t_{sp} \) [1/s] |
|---|---|---|---|---|---|---|---|
| T6 | 9.3 \times 10^{-6} | 15.5 | 13.8 | 1.7 | 0.114 | 0.551 | 0.364 |
| T3 | 0.000451 | 15.5 | 13.8 | 1.7 | 0.236 | 0.747 | 0.301 |
| B5 | 0.000932 | 15.5 | 13.8 | 1.7 | 0.167 | 0.282 | 0.068 |
| T1 | 0.004407 | 15.5 | 13.8 | 1.7 | 0.141 | 0.385 | 0.144 |
| T5 | 0.016487 | 15 | 13.8 | 1.2 | 0.245 | 0.581 | 0.28 |
| T2 | 0.017128 | 15 | 13.8 | 1.2 | 0.247 | 0.564 | 0.144 |
| B1 | 0.073903 | 15.5 | 13.8 | 1.7 | 0.083 | 0.35 | 0.157 |
| B6 | 0.16031 | 15.5 | 13.8 | 1.7 | 0.141 | 0.385 | 0.144 |
| B2 | 0.37589 | 15.5 | 13.8 | 1.7 | 0.09 | 0.33 | 0.141 |

**The last column is the average fast desorption rate during \( t_s - t_p \).**

**Values are averaged over four concentrations \( p/p_0 = 0.2-0.5 \).**
in both datasets shown in Figures 3 and 6 is because of the similar k_d range in both of them despite the differences in FFDs and capacity ranges. The ratio k_d,a/k_d changes within 0.16−0.58 in Table 4 and is greater than that of the nine sensors 0.14−0.45 in Table 1. This may be related to the differences between the 2 FFDs. High desorption speed yields higher disturbances to desorption by the adsorbed VOCs.

Impact of Adsorption Capacity a_1 of the BmimNTf2 Sensor on AD Parameters. The plot of k_d versus a_1 in Figure 6 shows that the lowest three capacities (blue dots) have different behavior than the higher capacities. It shows that a RL is within a_1 = 10.9−19.9. This result supports the existence of the RL found from analyzing our data, as shown in Figures 3 and 4. Further support for the existence of RL can be found in Figure 7, in which toluene and hexane—with the lowest capacities in the BmimNTf2 sensor—show irregular behavior compared with the other five VOCs. It is noteworthy that there is a disagreement in the RL values between the two reliability indicators k_d in Figure 6 and k_d,(p/p_0)/k_dh in Figure 7. However, because the k_d indicator shows the sharpest RL in Figures 4 and 5, it is more likely that the dichloromethane capacity is below the RL. More experiments are needed to determine the RL accompanied by a theoretical basis.

Relationships between Sensor Sensitivity and Capacity. Sensitivity, S, of a sensor is defined as a change in the sensor’s response to VOCs adsorption due to changes in the VOC concentration. Accordingly, the sensitivity of the BmimNTf2 sensor to the seven VOCs from ref 33 can be obtained from the slope of each curve in Figure 8. Plotting the resulting slopes versus sensor capacity gives a linear increase of the sensitivity with sensor capacity (Figure 9).

DISCUSSION

Quantitative Reliability Measure of a Sensor. Figure 3 shows a capacity limit of ΔR_{max} = 0.016 MΩ, above which k_d increases linearly with capacity. On the other hand, sensors with capacities <0.016 MΩ k_d dispersed irregularly with ΔR_{max}. We take the limit between the regular and irregular dependency of k_d on ΔR_{max} as a RL. The k_d in this case is the reliability indicator. The resulting conclusion from this reliability test is that sensors T1, T3, T6, and B5 are unreliable, whereas others listed in Table 2 are reliable.

**Table 5. Ligand Capping for Each Sensor by Its Position in the Chamber Shown in Figure 10A**

| sensor position | ligand chemistry                        |
|-----------------|-----------------------------------------|
| T1              | octadecanethiol                         |
| B1              | 2-ethylhexanethiol                      |
| T2              | tert-dodecanethiol                      |
| B2              | 3-ethoxythiophenol                     |
| T3              | dodecanethiol                           |
| B3              | 2-naphthalenethiol                      |
| T4              | 4-chlorobenzenehexethiol                |
| B4              | 2-nitro-4-(trifluoromethyl)benzenethiol |
| T5              | decanethiol                             |
| B5              | dibutyl disulfide                       |
| T6              | hexanethiol                             |
| B6              | 4-tert-butylbenzenethiol                |

"T = top; B = bottom; numbers 1 to 6 indicate sensor position along with the flow in ascending order.

**Figure 6.** Free desorption k_d averaged over the four VOCs concentrations p/p_0 = 0.2−0.5 vs BmimNTf2 sensor’s capacity a_1.

**Figure 7.** Effect of concentration p/p_0 and capacity a_1 on the ratio of adsorption over desorption (k_a · p/p_0)/k_da during the adsorption time.

**Figure 8.** Sensor detection signals (I-I_0)/I_0 vs concentration p/p_0 at t = 177 s, the longest adsorption time common to the 7 VOCs.

**Figure 9.** Sensitivity, S, averaged over p/p_0 = 0.2−0.5 (Figure 8) of the seven VOCs of ref 33 vs BmimNTf2 sensor capacity a_1.
experimental results show that basic resistance $R_b$ is proportional to the capacity $\Delta R_{\text{max}}$. Although it saves saturation experiments for measuring the $\Delta R_{\text{max}}$, the results show that RL based on $k_d-R_b$ test is less sharp and longer than the RL of $k_d-\Delta R_{\text{max}}$ test. Reliability test with the data of ref 33 reveals that the ionogel sensor is unreliable in detecting signals of toluene, hexane, and dichloromethane. Similar results are shown in Figure 3, with a rate decrease of the coverage fraction $\theta$ with the time between points $p$ and $s$ defined in Figure 2. This reliability indicator is less sharp than that of $k_d$. The ratio of adsorption over desorption rate constants for $t \leq t_p$ as another reliability indicator yields a further less sharp RL as shown in Figure 4. The reliability indicator $k_d$ when applied to the data of ref 33 yields an RL within $10.9 < a_i < 19.9$. More VOCs would further sharpen the RL, as shown in Figure 6. The AD ratio for $t \leq t_p$ in Figure 7 clearly differentiates toluene and hexane with lowest capacities $a_i$, but failed to differentiate the next lowest capacity of dichloromethane. These results imply that the reliability indicator $k_d$ gives the sharpest RL compared with other AD indicators. Further experiments dedicated to RL determination are needed as a basis for future theoretical evaluation of RL.

**Relationship between Sensor Capacity and Sensitivity.** Detection signals of the 7 VOCs of ref 33 against the concentration $p/p_0$ are plotted in Figure 8. The slopes in these graphs define sensitivity, $S$. Plotting the resulted $S$ against the capacity $a_i$ of the VOCs gives a linear relationship between $S$ and $a_i$, as shown in Figure 9, which means that the higher the sensor’s capacity, the higher is its sensitivity.

**SUMMARY AND CONCLUSIONS**

The purpose of this study was to relate sensor detection functions, such as reliability and sensitivity, to AD parameters of the detection signals derived from the fit of the equations of our analytical model to the experimental data. The results show that (1) sensors with high capacity are more reliable and sensitive to detecting signals of VOCs than sensors with lower capacities; (2) there is a sensor capacity limit, below which sensors are unreliable; (3) the most reliable indicator that provides the sharpest RL is the desorption rate constant $k_d$; and (4) sensitivity of sensors increases linearly with their capacities. Altogether, sensors with high capacities are more reliable and sensitive to detecting signals of VOCs than sensors with lower capacities. Results show that basic resistance $R_b$ is proportional to $\Delta R_{\text{max}}$. However, it yields less sharp and longer RL. Because it saves experiments of $\Delta R_{\text{max}}$, it may provide a rough estimation of RL.

**EXPERIMENTAL SECTION**

**Sensors Used to Produce Detection Signals.** The sensors tested in the experiment were made of monolayer-capped GPNs, as described in ref 9 and illustrated in Figure 10.

An array of 12 different GNP (ligand-capped)-based sensors was constructed. Different ligands capping the GPNs provide a different sensing capacity for the sensors, while maintaining a single drop of each capped GNP solution upon each sensor using the drop-casting method. The resulting layer thickness of all GNP layers are within 1.7–2 μm. Exposure to VOC samples induce a different response for each different sensor, resulting in a unique pattern relating to the exposed sample. Table S summarizes the capping ligands of the GPNs. The 12 sensors were arranged in the measurement system with six sensors on the top and 6 on the bottom facing each other, whereas the flow is moving in the gaps between them (Figure 10A).

The majority of the tested sensors listed in Table 5 are based on thiol derivatives. Other ligands that are based on thiol derivatives were used to test detection signals based on two thin-film-capped methods: layer-by-layer and drop-casting.29 These ligands show high sensitivity to VOCs such as hexane, ethyl benzene, and ethanol for the drop-casting method.

**Exposure System.** The system comprised a gas generator system (Umwelttechnik MCZ GmbH IC2000RL gas calibration system) connected to a syringe pump (Harvard Apparatus Pump 11 Pico Plus Elite) using a 250 μL Trajan SGE syringe. The gas generator system was connected to a measurement system (developed and manufactured by JLM Innovation GmbH, Tübingen, Germany) by a T-junction before a flowmeter and a solenoid valve. The same configuration was set up for the dry air inlet. Both flowmeters were set arbitrarily to 2.25 L/min, and the valves were controlled by LabVIEW software and an NI DAQ system. Figure 10B shows a diagram of the experimental setup used. The measurement system consists of an internal pump (flow 143 mL/min) and sensors’ chamber with 12 slots. The sampling rate of the sensors was 10 Hz with <0.1% error in the measurement of resistance.

**Measurement of Changes in Sensor Resistance Following Octane Adsorption.** The sensors were stored overnight in a vacuum. On the day of the experiment, the sensors were mounted in the testing chamber inside the measurement system open to room air. The internal pump of the measurement system remained active throughout the whole experiment. At the first stage, the baseline was obtained by exposing the sensors to dry air (i.e., the dry air valve open and gas generator system valve closed). After obtaining a steady signal from all sensors, a pulse of 8.1 ppm n-octane (>99%, Merck KGaA) was introduced (i.e., gas generator
system valve open and dry air valve is closed) for 10 s, followed by dry air. After returning to the baseline, the sensors were re-exposed to n-octane, but this time, it was left to reach saturation.

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**Notes**
The authors declare no competing financial interest.

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