Room-Temperature Ionic-Liquid-Incorporated Plasma-Deposited Thin Films for Discriminative Alcohol-Vapor Sensing

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We propose a room-temperature ionic-liquid-incorporated (RTIL) plasma-polymerized film (PPF) as a highly discriminative sensing layer for gas sensor array technology. PPF was prepared by radio frequency sputtering of D-phenylalanine (D-Phe). Incorporation of 1-ethyl-3-methyl imidazolium tetrafluoroborate (EMI-TFB) in the D-Phe film was performed by dropping the EMI-TFB onto the PPF, and it was confirmed by X-ray photoelectron spectroscopy and small-angle X-ray scattering spectroscopy. It was also found that EMI-TFB formed nanometer-scale patterns at the D-Phe film surface. A gas sensor array consisting of D-Phe films incorporating EMI-TFB to a concentration between 0 and 18 mmol L^{-1} was prepared, and discrimination of normal alcohol vapors (methanol, ethanol, *n*-propanol, and *n*-butanol) generated at concentrations ranging from 16 to 84 ppmv was demonstrated. The molecular selectivity of D-Phe films with and without EMI-TFB was evaluated using an approach based on linear solvation energy relationships.

Introduction

Electronic nose technology, which conceptually mimics the biological olfactory system,[1,2] has been applied in many fields, such as food and beverage manufacturing,[3,4] environmental assessment,[5] and personal healthcare,[6] as an alternative to costly time-consuming analytical methods. The solvation of gaseous molecules to sorptive polymers has been utilized as a molecular selection principle in gas sensor arrays and has the potential to widen selectivity and sensitivity for discriminating large numbers of mono- and mixed vapors.[7]

Array sensors comprising different chemically structured sorptive sensory films, such as synthetic polymers,[7−9] conducting polymers,[10] carbon black−polymer composites,[11,12] and vapoluminescent salts,[13] have been reported. These sensors can discriminate various organic vapors with different solubility parameters that are related to the chemical structure of the vapor molecule. We also have proposed a sensor array based on a sorptive polymer prepared by the sputtering of an organic solid.[14−18] The chemical structure of plasma-polymerized films (PPFs) prepared under an equivalent and low-temperature plasma is strongly related to the chemical structure of the starting material. PPFs are prepared from different starting materials, i.e., synthetic polymers (e.g., hydrocarbon and fluorocarbon) and biological material (e.g., amino acid, sugar, and nucleic acid), and therefore, PPFs have different affinities for gaseous molecules. Using a sensor array consisting of PPF-coated quartz crystal resonators (QCRs, with a fundamental resonance frequency of 9 MHz), we have shown that gases can be categorized by their representative functional groups, such as alcohol, ketone, and aldehyde,[17] through a statistical mathematical or chemometrics-based treatment of sensor signals.

However, the discrimination of different concentrated vapor samples is still difficult with a sensor array comprising PPFs prepared from the different target materials. This is because the different sensing layers (PPF prepared from different target materials) have different sensitivities to each kind of vapor, which can be expressed as [sensor response (in Hertz in our case)]/[concentration of vapor]. Therefore, even though the vapors with relatively similar sorptive characteristics are tested, large changes in the response pattern related to the concentration variations result in mistaking discrimination of the kind of vapor. To the best of our knowl-

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edge, other electronic noses based on an array comprising different chemically structured sorptive polymers can show the ability of discrimination of vapors with similar characteristics, such as normal alcohols.[19,20] However, very few studies have examined the response patterns to different concentration vapors, and those studies used transient sensor responses that required a rather complex data processing procedure for discrimination.[8,9]

Against this background, we considered modification of one kind of polymeric sorptive layer as a strategy for preparing a set of sensory films that could discriminate different concentration vapors from an array sensor's sorption curves. This strategy requires a method by which we can modify the polymeric phase without largely changing the sorptive characteristics of the films, but that still remains varied enough for discrimination of the kinds of vapors. As an additive to the sorptive polymer for modification, we are interested in room-temperature ionic liquid (RTIL), which is a group of ionic compounds that take liquid form around room temperature.[21−31] RTIL is nonvolatile[21,22] and can be used as a gelation agent with carbonous materials such as nanotubes,[23] which indicates that some RTILs have the ability to penetrate and remain in the polymer phase. In addition, RTIL can work as a solvent for gases, as it has already been used in chromatographic separations[24−26] or in sensors.[27,28] A thermodynamic theoretical investigation of gas solvation by RT-IL has been also reported.[28] RTIL is stable against volatile organic solvents, so it is expected that the RTIL concentration in carbonous material can be regulated by the addition of an RTIL solution diluted by volatile solvents and then dried.

This paper describes the first demonstration of our concept that modification of one kind of sorptive polymer by RTIL addition for preparation of the series of the sensory films for a sensor array can generate a discriminative response pattern that changes little with the sorption of different concentrated vapors. In this work, we used a PPF prepared from D-phenylalanine (D-Phe film) as a base polymer. Because of the deposition process under harsh plasma conditions, PPF is generally carbonous and stable to volatile organic solvents such as acetone and methylethyl ketone. In addition, the morphology of the sputtered D-Phe film (>200 nm in thickness) is rather coarse with many submicrometer cracks, which seems favorable for penetration of RITL solutions. Last, D-Phe films contain a benzene structure that is expected to interact with the imidazolium structure[23] found in many RTILs.

Among the many commercialized RTILs, we chose one composed of tetrafluoroborate (TFB) anion and imidazolium cation because it has a little stability against air and water[30] and because TFB-based RTIL has antielectrostatic characteristics that neutralize polar sites, such as silanols on silica.[29] TFB-based RTIL also has a low viscosity among RTILs (41 mPa s for EMI-TFB at 20 °C).[31] When RTIL is incorporated into the base polymer, the viscous effect on the quartz resonance is therefore expected to be small.[28]

We expected that the RTIL addition would neutralize the strong interactive functional group and fill some of the free volume for molecular sorption. A change in the free volume for molecular sorption would mean that the difference in RTIL concentration in the PPF would affect the molecular selectivity at sorption. In this paper, we describe the preparation of a PPF sensor array comprising D-Phe films containing RTIL concentrations between 0 and 18 mmol L^{-1}. Using X-ray photoelectron spectroscopy (XPS) and small-angle X-ray scattering spectroscopy (SAXS), we confirmed the incorporation of TFB-based RTIL in the D-Phe film under normal air.

Discriminative alcohol monitoring is important in fields such as medicine and brewing and is also utilized in judging the freshness/ripeness of foods.[32] Because alcohols have similar physicochemical characteristics, discriminative detection of alcohols is still difficult with gas sensor array technology.[33,34] So far, we have demonstrated the discriminative detection of normal alcohol vapors with the array of RTIL-added PPFs. We also performed an analysis of the RTIL-added PPFs using well-known Abraham's linear solvation energy relationships (LSER),[35−37] which have successfully explained the molecular selectivity of various materials such as synthetic polymer, biopolymer, silica, carbon, water, and organic solvent through the correlation of the chemical structures of both solvent and solute.

Experimental Section

Materials. D-Phe, *n*-propanol, and *n*-butanol were purchased from Tokyo Kasei Kogyo Co. Ltd., and methanol (>99.8%), ethanol (>99.5%), acetone (>99.5%), and 1-ethyl-3-methyl imidazolium (EMI)-TFB were purchased from Kanto Kagaku, Co. Ltd., Japan. All reagents were used without purification.

Preparation of Sensory Films. Powdery D-Phe was dissolved once in ethanol and then poured onto the bulk PE disk (13.5 mm in diameter, 10 mm in height), as we have described elsewhere.[18] After at least 8 h, ethanol on the PE disk was vaporized at room temperature, and the prepared target material was placed on a target holder situated over the lower electrode in a vacuum chamber. The QCR substrates (8 mmϕ, AT-cut, 9 MHz, Nihon Denpa Kogyo Co. Ltd., Japan) and a strip from a Si wafer were placed on a

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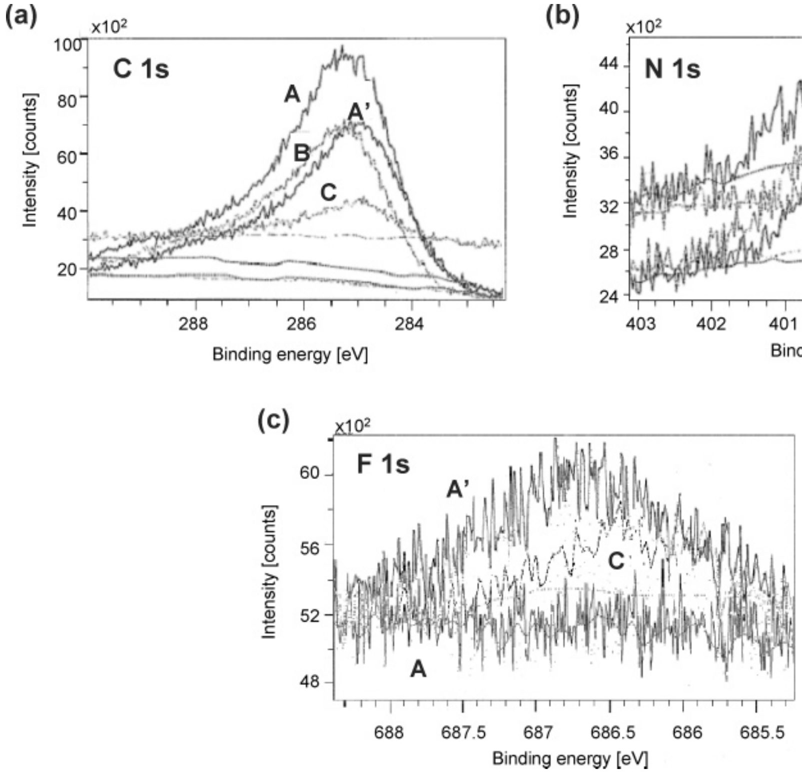

Figure 1. XPS spectra in the binding-energy region of (a) C 1s, (b) N 1s, and (c) F 1s of the D-Phe film (A), EMI-TFB-added D-Phe film (B), and EMI-TFB dropped on a Si wafer (C). The spectra labeled as A′ are those obtained after one etching process cycle.

substrate holder located just under the upper electrode. After evacuation of the chamber with a diffusion pump with a liquid nitrogen fore-line trap to a vacuum level of ca. 8×10^{-5} Pa, the evacuation system was changed to a mechanical booster pump. He gas was introduced to the chamber and radio frequency electric power (70 W) was applied to the lower electrode. The target and substrate holders were cooled with a circulating water flow during the sputtering process. The total thickness of the D-Phe films deposited on both sides of the QCR in the sensor array was 1188 ± 32 nm.

For preparation of the EMI-TFB-added D-Phe film for the QCR sensor, we first diluted EMI-TFB with acetone (ca. 0.23, 0.46, and 0.69 mmol L^{-1}) and stirred vigorously. Then, 500 nL of the EMI-TFB solution was dropped on the film deposited on a QCR. The EMI-TFB solution immediately spread and was dried under airflow for one night. The concentration of EMI-TFB in the D-Phe film was calculated assuming all acetone was evaporated by drying and that all EMI-TFB remained in the film. We labeled the sensors consisting of D-Phe films with EMI-TFB in calculated concentrations of 6, 12, and 18 mmol L^{-1} as sensors no. 2, no. 3, and no. 4, respectively. The nontreated D-Phe film was used as sensor no. 1. For surface analysis, we added 20 μL of EMI-TFB solution to the D-Phe film prepared on the Si strip. The calculated concentrations in the D-Phe film were ca. 1.7 and 2.6 mol L^{-1}.

XPS. Spectra were collected with an ESCA 3400 instrument (Shimadzu Co., Japan). A Cu Kα monochromatic X-ray source was employed, and samples were measured at an acceleration of less than 10 kV at 10 mA to prevent damage to the polymer surface. The polymer surface was etched during the collection of the spectra using an Ar ion gun with acceleration conditions of 0.5 kV and 10 mA. One etching process included two cycles of 15 s etching. All spectra were corrected on the basis of the core energy level of Ag 1s.

SAXS. Measurements were performed with a RIGAKU RINT2500 at room temperature. A monochrome Cu Kα X-ray was focused by a confocal mirror and radiated to the sample. The X-ray source was operated at 200 mA and 40 kV, and the $2\theta/\theta$ value was read with a resolution of 0.01°.

Gas Sorption Test. Sample vapors were prepared by a diffusion tube method using a gas generator (PD-1B, Gastec Co., Japan) with a stainless steel gas cell whose inner wall was cleaned by electropolishing. A glass diffusion tube was filled with vapor source reagent and mass-flow controlled air was introduced into the gas cell that held the diffusion tube. Stainless steel gas cells were immersed in a thermocontrolled water bath that was adjusted to between 30 and 40 °C according to the concentration of the desired sample vapors.

D-Phe-film-coated QCRs were placed in an acrylic flow cell that housed eight QCRs. The sensor cell was mounted on a circuit board that included the ASIC for QCR oscillation and frequency counting and a data transfer interface on the basis of IEEE-485. The resonance frequency change of each QCR was monitored at 5 s intervals.

The flow-controlled reference gas (synthetic air) was introduced to the sensor cell at least 2 h before the gas sorption test to obtain a stable initial state in the sensor. We changed the gas flow to the sensor cell by rotating a four-way valve from the reference air to the test vapor or vice versa. The sensor cell was placed in a thermostatically controlled bath that was regulated at 25 °C.

Results and Discussion

Chemical and Surface Analyses of EMI-TFB-Added D-Phe Films. We compared the reflective Fourier transform infrared spectra of D-Phe film on QCR with and without the addition of EMI-TFB, collected with a Spectrum2000 and a Multiscope (Perkin−Elmer), but no significant differences were observed (see the Supporting Information).

We then observed XPS spectra of the EMI-TFB-added D-Phe film (sample A), the nontreated D-Phe film (sample B), and the sample prepared by dropping EMI-TFB on a Si wafer and drying it under air (sample C), as shown in Figure 1. C1s and N1s peaks were first observed at the same

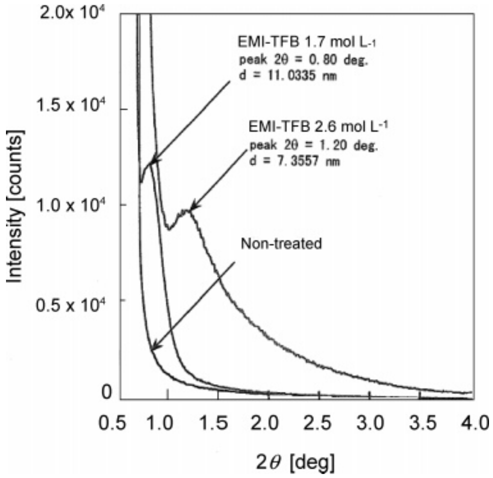

Figure 2. SAXS spectra of the EMI-TFB-added and nontreated D-Phe films prepared on Si wafers.

positions with samples A and B, 285.3 and 400.2 eV, respectively. After one cycle of etching, the C1s and N1s peaks of sample A (indicated as A′) both shifted lower than those of sample B. The peak of boron was not observed in either the wide or narrow scanned data of sample C; it was also not observable for other samples, which seemed to be because of the low concentration of boron in EMI-TFB. The F1s peak was clearly observed from the spectrum of sample C, but not in sample A in the first-cycle observation. After one cycle of etching, the F1s peak then appeared at 686.8 eV in the spectra of sample A. We therefore concluded that the EMI-TFB penetrated and remained in the vicinity of the D-Phe film surface even after the drying process.

Next, we recorded SAXS measurements, and Figure 2 shows that the EMI-TFB formed a nanometer-scale periodical pattern in the vicinity of the surface of the D-Phe film. There were apparent peaks at 0.80° ($d = 11.0335$ nm) and 1.20° ($d = 7.3557$ nm) when the EMI-TFB was added to D-Phe films. Without EMI-TFB, no peak was observed. Fluorine in the BF_4 anion has a large X-ray scattering efficiency, so it likely contributed to the peaks in Figure 2. Because the periodical space decreased as the concentration of EMI-TFB in the film increased, the creation of structured ion pairs or the isotropic dispersion of BF_4 anions can be considered as being the origin of the periodical pattern in the film. These X-ray analyses indicated the possibility that EMI-TFB molecules penetrated the D-Phe film and dispersed isotropically.

Responses to Alcohols with the EMI-TFB-Added D-Phe Film. We measured normal alcohol vapors with the sensor array consisting of the D-Phe films with different concentrations of EMI-TFB and the nontreated D-Phe film. The resonance frequency of QCR sensors coated with the EMI-TFB-added D-Phe films decreased and increased during sorption and desorption of vapors, like it did with nontreated D-Phe films, which was reported elsewhere.[5] So we used those sensors repeatedly. As shown in Figure 3, the response curves (the resonance frequency shifts (Δf) of the QCR sensors vs time) indicate that the gas sorption by the PPF began immediately after sample vapor was introduced to the sensor cell at time 0 and that the rate of increasing the frequency shifts is different with each sensor.

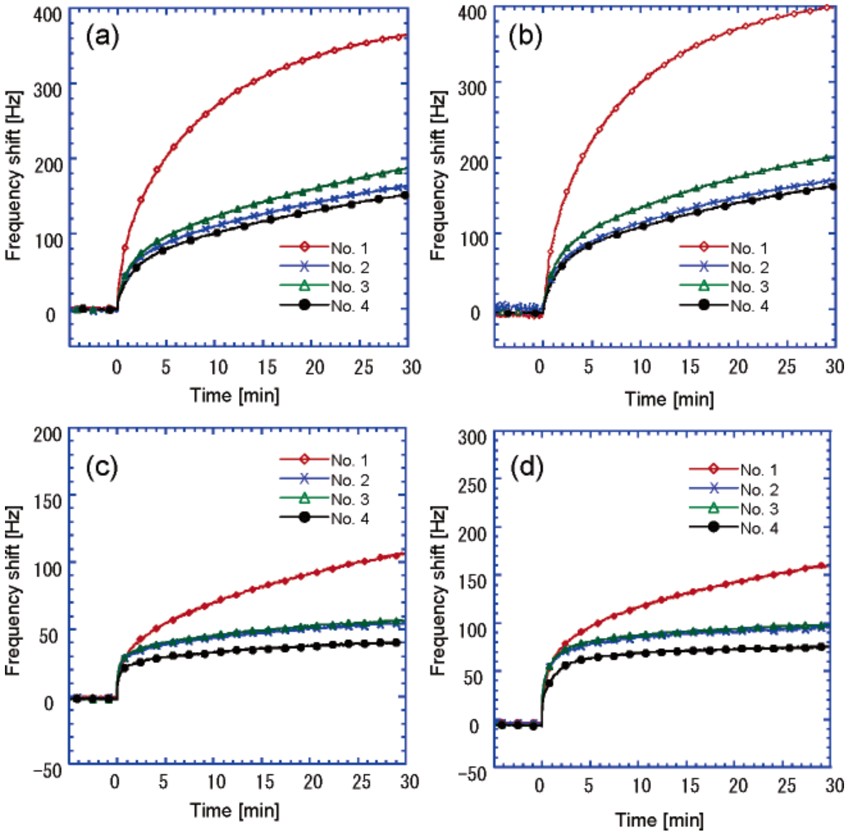

Figure 3. Frequency shift of the array consisting of four sensors at a vapor sorption of (a) 28.8 ppmv ethanol, (b) 55.5 ppmv ethanol, (c) 16.4 ppmv *n*-butanol, and (d) 37.3 ppmv *n*-butanol vapors. QCR sensor no. 1 consisted of a nontreated D-Phe film, and sensors no. 2, 3, and 4 consisted of D-Phe film with 6, 12, and 18 mmol L^{-1} EMI-TFB, respectively.

Table 1. Frequency Shifts to the Alcohol Vapors Obtained after the Sorption Test

		no. 1		no. 2		no. 3		no. 4		
analyte	*C* (ppm)	Δ*f* (Hz)	order	Δ*f* (Hz)	order	Δ*f* (Hz)	order	Δ*f* (Hz)	order	absorption time[a] (min)
methanol	44.7	308.7	1	270.2	4	303.6	2	293.8	3	40
	60.7	296.4	1	267.0	4	290.8	2	277.8	3	180
	81.4	351.5	1	311.9	4	338.5	2	326.1	3	180
ethanol	15.6	317.4	1	185.8	3	191.4	2	155.8	4	180
	28.8	452.3	1	299.5	3	345.0	2	299.1	4	180
	40.7	466.1	1	316.9	4	362.5	2	319.5	3	180
	55.5	489.3	1	298.3	3	348.3	2	298.0	4	180
n-propanol	16.4	159.6	1	52.4	3	53.8	2	40.8	4	180
	22.6	241.6	1	83.8	3	84.6	2	64.1	4	180
	27.2	205.2	1	77.5	3	81.3	2	63.3	4	180
	37.9	244.8	1	92.3	3	96.3	2	77.0	4	180
	51.3	292.4	1	113.8	3	120.8	2	97.8	4	180
n-butanol	16.4	219.2	1	80.4	3	85.3	2	58.2	4	180
	37.3	296.1	1	127.2	2	125.5	3	89.9	4	180
	53.3	266.6	1	120.3	3	127.6	2	99.3	4	180

[a] Absorption time indicates the period of the sorption test, which was normally 180 min. The exception, 40 min for absorption time, means that the frequency shifts reached a maximum after the 40 min sorption test and then began to decrease.

The gas sorption by EMI-TFB-added D-Phe films saturates after a certain sorption time, which is the same as that for nontreated PPF,[38] and those PPFs are considered to be saturated enough normally after a 180 min sorption test. The frequency shifts and the order of Δ*f* values among the four D-Phe film sensors for each kind of vapor sorption test are shown in Table 1. All the Δ*f* values of the EMI-TFB-added film sensors were smaller than that of the nontreated D-Phe film sensor. However, the addition of EMI-TFB did not merely decrease the sensitivity to alcohols. The Δ*f* of sensor no. 3 (12 mmol L^{-1} EMI-TFB) was larger than that of sensor no. 2 (6 mmol L^{-1} EMI-TFB) for sorption of methanol, ethanol, and *n*-propanol vapors. Therefore, the D-Phe film with more RTIL had a larger sorption capacity for those alcohols. Because RTILs themselves have solubility to alcohols,[28,39,40] it is expected that alcohols are dissolved in the EMI-TFB portion as well as in the scaffold D-Phe film.

The length of the hydrocarbon chain of vapor molecules seemed to affect the solubility to the D-Phe films. In the case of *n*-butanol, the difference in the Δ*f* values between sensors no. 2 and no. 3 became small. This suggests that the relatively longer hydrocarbon chain of *n*-butanol (compared with the length of methanol, ethanol, and *n*-propanol) became an obstacle to its ability to be sorbed by the films in these sensors. The order and magnitude of the Δ*f* values in Table 1 also indicate that the sensor array generated the characteristic response patterns to each kind of normal alcohol vapor. The order of the Δ*f* magnitudes was no. 1 > no. 3 > no. 2 > no. 4 for ethanol and *n*-propanol, but in the case of *n*-propanol, the ratio of the Δ*f* of sensor no. 1 to that of no. 2 was characteristically larger than that of ethanol. And for *n*-butanol, the order was no. 1 > no. 2 = no. 3 > no. 4. We believe that the addition of EMI-TFB covers the attractive sites for OH functional groups and, at the same time, fills some of the free volume, adsorbing vapor molecules in the D-Phe film.

The addition of EMI-TFB made the alcohol-vapor solubility of the D-Phe films different, which was effective for the discrimination of normal alcohol vapors, as shown in Figure 4. A principal component analysis (PCA) was performed using the maximum frequency shifts of each vapor sorption test as a parameter. PCA score plots representing each alcohol were located in separate areas. Therefore, the incorporation of RTIL into the plasma-deposited film was a useful film treatment for preparation of the series of sensory films for the discrimination of molecules with small chemical structural differences. Several researchers reported the discrimination of normal alcohols generated at different concentrations on the basis of polymeric sorptive layers with chemically different structures.[8,9] However, they used the transient state of sensor responses and extracted parameters that represent the characteristics of the kind of vapor through complex signal processing. In the case of the array comprising RTIL-added PPFs proposed in this paper, the response pattern delivered from raw sensor responses can be a discriminative response pattern, and we believe that is advantageous in applying the array sensor for the discrimination of larger numbers of vapor species or mixed vapors.

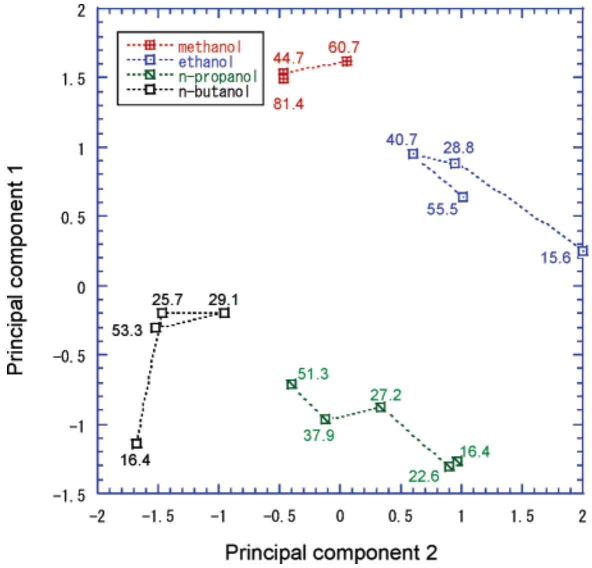

Figure 4. PCA score plots obtained with the sensor array responses to alcohol vapors. Numbers indicate the vapor concentration of each alcohol in ppmv unit.

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Table 2. Abraham's Solvation Descriptors of the Tested Vapor Molecules[35]

	R_2	π_2*	$\Sigma\alpha_2^H$	$\Sigma\beta_2^H$	log L^{16}
methanol	0.278	0.44	0.43	0.47	0.9700
ethanol	0.246	0.42	0.37	0.48	1.4850
n-propanol	0.236	0.42	0.37	0.48	2.0310
n-butanol	0.224	0.42	0.37	0.48	2.6010

Analysis of Discriminative Sorption Characteristics of the Films on the Basis of the LSER Approach. The difference in the sorption characteristics of the EMI-TFB-added and nontreated D-Phe films can be discussed in more-specific physicochemical terms by applying the LSER method to the sensor data. The LSER is a powerful analytical tool for correlating solubility with molecular descriptors of sorbent and solute, which have already been determined by Abraham and co-workers for thousands of chemicals.[35,36] The partition coefficient in the polymer-coated QCR sensor system, *k*, is determined from the resonance frequency shifts at the saturation condition of gas sorption by polymers as

$$k = (\Delta f_{\mathrm{vap}}\rho_{\mathrm{poly}})/(\Delta f_{\mathrm{poly}}M_{\mathrm{vap}}\cdot C_{\mathrm{vap}}) \qquad (1)$$

where Δf_{vap} (Hz) is the frequency shift (sensor response) measured upon exposure to a vapor of concentration C_{vap} (mol L^{-1}), Δf_{poly} (Hz) the frequency shift measured upon initial deposition of the polymer film, M_{vap} (kg mol^{-1}) the molar mass of the analyte vapor, and ρ_{poly} (kg L^{-1}) the polymer density. *k* is the sum of parameters that each is a multiple of solvent parameter and solute parameter with the corresponding physicochemical meanings as shown in eq 2

$$\log k = c + rR_2 + s\pi_2 + a\sum\alpha_2^{\mathrm{H}} + b\sum\beta_2^{\mathrm{H}} + l\log L^{16} \qquad (2)$$

where *k* is the partition coefficient (the ratio of gaseous analytes outside and inside the sorptive polymer film), *r* the ability of the adsorbent to interact with a solute's π- and *n*-electron pairs, *s* a measure of the adsorbent dipolarity/polarizability, *a* the complementary property to solute hydrogen-bond basicity, *b* the complementary property to solute hydrogen-bond acidity, and *l* a combination term of cavity/dispersion interactions. R_2, π_2, $\sum\alpha_2^{\mathrm{H}}$, $\sum\beta_2^{\mathrm{H}}$, and log L^{16} are the corresponding solute parameters. Therefore, R_2 is the excess molar refraction that reflects the ability of the solute to interact with a sorbent through π- and *n*-electron pairs; π_2 is the solute dipolarity/polarizability, $\sum\alpha_2^{\mathrm{H}}$ and $\sum\beta_2^{\mathrm{H}}$ are the overall solute hydrogen-bond basicity and acidity, respectively, and log L^{16} is the gas−hexadecane partition coefficient or the Ostwald solubility coefficient (the measure of the dispersion/cavity factor or lipophilicity of solute).

Abraham's solute parameters for normal alcohols (methanol, ethanol, *n*-propanol, and *n*-butanol) have similar values of dipolarity and hydrogen-bonding ability (acidity and basicity) (Table 2), which is due to their common OH functional group and similarity in other linear hydrocarbon structures. The parameters for the ability of the solute to interact with a sorbent through π- and *n*-electron pairs (R_2) and dispersion/cavity (or lipophilicity) (log L^{16}) differ depending on the kind of alcohol, which seems to be due to differences in the length of the hydrocarbon chain.

We performed linear multiregression to obtain the parameters for the EMI-TFB-added D-Phe films and the nontreated D-Phe film using the solute parameters in Table 2. For the calculation, we used commercial software (Statistica, Statsoft Japan, Japan) run on a personal computer with the Windows XP operation system. Calculated values in Table 3 explain the solubility characteristics of the EMI-TFB-added and nontreated D-Phe films. The value for hydrogen-bonding basicity (*a*) became more negative and the value for hydrogen-bond acidity (*b*) decreased with the addition of EMI-TFB. Such a loss of overall hydrogen-bonding acidity and basicity of the solvent phase by EMI-TFB addition is consistent with the expected way in which EMI-TFB is stabilized in the D-Phe film; i.e., by neutralizing the hydrogen-bonding sites as described in ref 29. The value for the ability of the adsorbent to interact with a solute's *n*- and π-electrons (*r*) increased as the π-electron density increased because of the increase in the EMI cation moiety by EMI-TFB addition at such a concentration level. The values for the adsorbent dipolarity/polarizability (*s*) decreased considerably when the EMI-TFB was added to the D-Phe film. This indicates that the interaction ability related to polarizability and dispersion of the EMI-TFB-added D-Phe films was smaller than the nontreated D-Phe film (sensor no.1).

The value of *l*, which is related to the sorbent film's cavity/dispersion factor, increased as the EMI-TFB concentration in the PPF increased. The difference in the lipophilic parameter of solute molecules was therefore effective for discrimination with the series of EMI-TFB-added D-Phe film when the hydrogen-bonding sites were already masked. Because the normal alcohols in Table 2 had the same values for π_2^{H}, $\sum\alpha_2^{\mathrm{H}}$, and $\sum\beta_2^{\mathrm{H}}$, it is considered that R_2 and log L^{16} parameters were more related to the discrimination of normal alcohols. The value of R_2 was smaller than log L^{16}, whereas the corresponding solvent's *r* parameter was much larger than *l*. Therefore, we considered that the balance of (rR_2) and ($l$log L^{16}) in eq 2 dominated the partitioning of alcohol vapors in the sensory film, which made our sensor array discriminative of normal alcohol vapors.

Table 3. Calculated Solvent Descriptors of the D-Phe and EMI-TFB-Added D-Phe Films

sensor no.	EMI-TFB in D-Phe film (mmol L^{-1})	*r*	*s*	*a*	*b*	*l*	*c*	R^2 [a]	SD[a]
1	0	10.7582	2.0232	−7.2030	8.7015	0.3959	−5.2517	0.9303	0.3713
2	6	11.6300	0.1929	−8.2861	4.3747	0.4327	−2.4636	0.9842	0.1457
3	12	17.4941	0.5392	−9.8259	5.8226	0.5831	−4.5389	0.9579	0.2550
4	18	18.6389	0.1087	−10.3113	4.6835	0.5815	−3.9805	0.9591	0.2576

[a] R^2 is the square of the correlation factor and SD is the standard deviation of the multiple-regression.

Conclusion

Plasma-polymerized film (PPF) prepared from D-phenylalanine (D-Phe) was a good scaffold for room-temperature ionic liquid (RTIL), and we showed that RTIL-incorporated D-Phe films offer a group of sensory films for the discriminative detection of gaseous normal alcohols with similar molecular structures and characteristics. We succeeded in the discrimination of alcohols with D-Phe films containing different concentrations of 1-ethyl-3-methyl imidazolium tetrafluoroborate (EMI-TFB). The response patterns of our sensor array were affected little by changes in analyte concentrations. From the sensor response data, we expected that the EMI-TFB worked to cover some of adsorption sites and also fill the free volume for molecular sorption. This prediction was confirmed by using the linear solvation energy relationships-based approach. The addition of RTIL to the PPF film caused a variation in both the solvent's cavity/dispersion factor (or lipophilicity) and the solvent's dipolarity/polarizability, which was effective for the discrimination of normal alcohol vapors with small molecular differences. Also, it was suggested that EMI-TFB suppressed the hydrogen-bonding ability of the solvent film. We confirmed that the effect of RTIL on the polymeric sensory film worked well for the precise discrimination of vapors with the same functional group and different concentrations. We consider that this result opens the way to the establishment of a kind of multistep data-processing strategy for the discrimination of large numbers of vapors. Rough discrimination on the basis of a vapor's functional group is performed with an array comprising different chemical structured polymers (or PPFs prepared from different target material). Precise discrimination among vapor candidates with the same functional group is then performed with an array comprising polymeric sensory films with RTIL at different concentrations. In this paper, we used PPF as a base polymer, but it is also expected that the concept of RTIL modification can be applied to other sorptive polymers that are already available for the gas sensor array. RTILs with various structures have been synthesized and used as reusable solvents for electrochemical reactions and organic syntheses. Therefore, there is the possibility of developing various RTIL-incorporated sorptive layers for specific group of vapors, which would be of much help in improving the selectivity of electronic nose technology.

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Supporting Information Available: IR absorption spectra obtained by applying the external reflection−absorption configuration. This material is available free of charge via the Internet at http://pubs.acs.org.

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