

Study on the Surface Acoustic Wave Sensor with Self-Assembly Imprinted Film of Calixarene Derivatives to Detect Organophosphorus Compounds

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ABSTRACT

The molecularly imprinted technology and the self-assembly technique were used together on the calixarene surface acoustic wave (SAW) chemical sensors to detect organophosphorus compounds. 25-(thioalkyl-alkoxy)-*p*-tertbutylcalix[4]arene with self-assembled monolayer character was the sensitive coating of the sensors. The sensors had a special response to organophosphorus compounds and the response frequency shift of this sensor to organophosphorus compounds in 0.1 mg/m³ was 350 Hz. The response frequency increased linearly with the increase of the concentration of DMMP in the range from 0.1 to 0.6 mg/m³. The possible explanation of the interaction between the coatings and organophosphorus compounds was discussed.

Keywords: Calixarene; Self-Assembly; Molecular Imprinted; SAW Sensor; DMMP; Detection

1. Introduction

Nowadays, the SAW sensor technology to detect the poisonous and harmful gases is a focus in the sensor field. In 1992, Larry J. Kepley [1], for the first time, published a literature in which surface acoustic wave technique and self-assembly technique were put together to detect the compound Dimethyl Methylphosphonate (DMMP). The advantages of powerful selectivity, high sensitivity, short response time, simple membrane preparation and long usage time were reported. Because calixarenes had the inherent three dimensional structure and pre-organized cavities as recognition sites, studies on their self-assembly researches were more and more valuable [2]. The particular calixarene corpus molecules were assembled on the surface of a gum body, SiO₂, gold and other metals. Then monolayer or multilayer self-assembly system could be formed and used in molecular recognition, chemical sensors and phase transfer catalysis, enzyme mimics etc, so it exhibited an extensive application prospect [3,4]. Dermody [5] made use of the SAW sensor based on self-assembly polydiacetylene calixarene derivatives bilayer film to detect the chlorobenzene, toluene and other aromatic organics; the results indicated that the upper margin functional groups of calixarenes had important contributions to sensitivity and selectivity. By Schierbaum and Weiss [6,7], termination modified thio-ether resorcin

[4] arene derivatives, a self-assembly monomolecular membrane, were used to detect four chloroethylene, the sensitivity of those sensors could reach nanogram grade. In 1998, Dickert [8] published an article that the molecular imprinted polymer SAW sensor was used for checking *o*-dimethylbenzene, its detection had reached to 4.5 mg/m³ (The limit to the toxicity detection of *o*-dimethylbenzene was 450 mg/m³) which displayed excellent detection effects. Wang Cheng Heng [9] had prepared the molecular imprinted polymer SAW sensors based on calixarene membrane, which had higher sensitivity and selectivity to detect the sulphur and phosphorus compound.

There were few reports about calixarenes, the Third Generation Supramolecules, as sensitive film of the SAW sensor in the detection of poisonous and harmful gases. Furthermore no systematic study had been performed on its adsorption mechanism. In this article, Isopropyl hydrogen methylphosphonate 1) Was used as the template molecule, and 25-(thioalkyl-alkoxy)-*p*-tertbutylcalix[4]arene; 2) Self-assembly molecular imprinted film was used as the sensitive film in acoustic surface wave chemical sensor, to detect the organophosphorus compounds such as DMMP; 3) Diisopropyl Methyl-phosphonate (DIMP, 4) and other interference gases. The detection limit and the selectivity of the sensor were studied, and the influences of temperature and other factors were discussed. The structures of several compounds were shown in **Figure 1**.

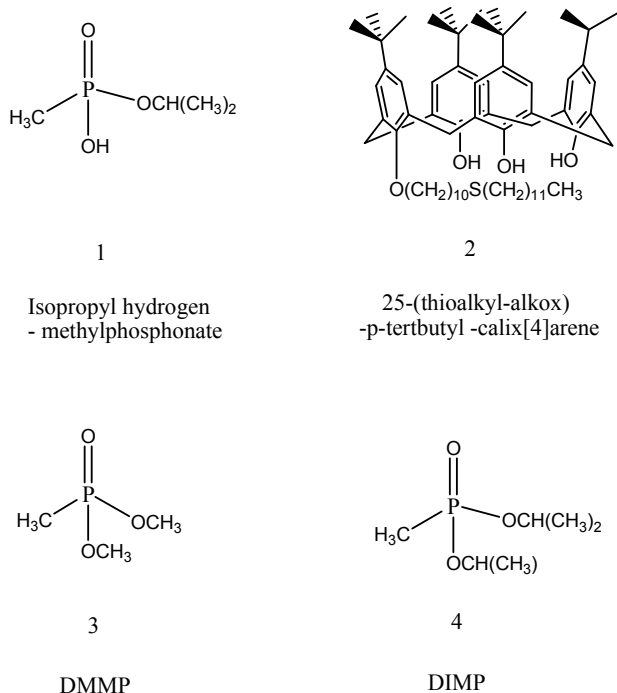


Figure 1. The structures of organophosphorus compounds and 25-(thioalkyl-alkoxy)-*p*-tertbutylcalix[4]arene.

2. Experimental

2.1. Reagents and Apparatus

25-(Thioalkyl-alkoxy)-*p*-tertbutylcalix[4]arene was synthesized by our laboratory and was liquid chromatography grade. Dimethyl Methylphosphonate (DMMP), Diisopropyl Methylphosphonate (DIMP), Isopropyl hydrogen methylphosphonate were reagent grade (Research Institute of Chemical Defence, China). The other chemicals were reagent grade (Beijing Chemical Reagent, Beijing, China).

For the instrumentations, a Surface Acoustic Wave dual delay line (the centre frequency 300 MHz, the area of delay line was 4 mm² gold films), a Model Proteck C3100 Frequency Meter, (Korean Proteck company) was used in this article.

2.2. Preparation of Self-Assembly Imprinted Film of SAW Sensors

100 mL of 0.1 mmol/L 25-(thioalkyl-alkoxy)-*p*-tertbutylcalix[4]arene self-assembly solution was prepared, 100 mL of 5 - 10 mol/L isopropyl hydrogen methylphosphonate was added into the above solution, deposited for 12 hs for using later.

The surface acoustic wave dual delay line was purged with *V* (sulphuric acid): *V* (hydrogen peroxide) = 3:1 Piranha solution to bright and clean, puffed with high purity N₂ to remove surface foreign substance, in the last its fundamental (f_0) frequency was measured.

The above-mentioned surface acoustic wave dual de-

lay line had been soaked in the self-assembly solution for 24 hs. After being taken out, the dual delay line was washed to eliminate isopropyl hydrogen methylphosphonate. Its fundamental frequency (f') and noise were measured at the end.

The thickness of self-assembly imprinted film was estimated by the fact that the fundamental frequency shift between coating and uncoating. Substrate conceptual diagram was shown in Figure 2.

2.3. Appreciation of Self-Assembly Imprinted Film of SAW Sensors

DMMP and DIMP were generated by gas dynamic generator at 28°C. Then the response signal, response time and recovery time to detect DMMP were obtained with the above-mentioned sensor.

At the same condition, to verify the influence of interference gases on the SAW sensor, interference gases, which concentrations were 100 - 1000 times more than that of DMMP and DIMP were detected with the above-mentioned sensor.

3. Results and Discussion

3.1. Evaluation of Film Thickness

Since the assembled film was prepared on SAW gold delay line, mass deposits would result in the frequency shift of baseline of the SAW-CA sensor, the relationship between frequency shift and film thickness abided by following Sauerbrey equation [10].

$$\Delta f = -1.26 \times 10^6 f_0^2 h \rho \quad (1)$$

In the Equation 1, Δf (Hz) was the frequency shift between coatings and uncoating, f_0 (Hz) was fundamental frequency of SAW sensor. h (cm) was film thickness of self-assembly imprinted film, ρ (g/cm³) was the density of film material. All data were calculated with the equation, the following Equation 2 was gotten.

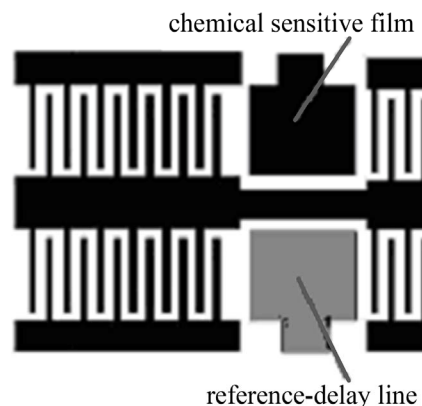


Figure 2. Dual-delay line of surface acoustic wave chemical sensor.

$$h = -\Delta f \times 0.657 \times 10^{-11} \tag{2}$$

The frequency shift between coating and uncoating was about 18 - 20 KHz, and the thickness of the film was about 2.5 - 3.5 nm grade approximately according to the Equation 2.

The noise frequency could be used to confirm the detection limit. In certain time, the noise frequency Δf_N of sensor was calculated with the following Equation 3:

$$\Delta f_N = \pm (f_{\max} - f_{\min}) / 2 \tag{3}$$

where f_{\max} was the biggest frequency and f_{\min} was the minimum frequency.

The experimental results indicated that the base frequency shift was 25 - 100 Hz, which was very small compared with fundamental frequency. The reason was that gold surface was coated with membrane and its surface structure was changed into loose porous shape, the flatness is smaller than that of smooth gold.

3.2. Detection of DMMP and DIMP at Different Concentrations with SAW-MIP Sensor

Under the same experimental conditions (28°C, RH = 70%), the different concentrations of DMMP were detected, the results such as the average response frequency shifts and the response time were listed in **Tables 1** and **2**.

Table 1. The detection results of SAW-MIP sensor to DMMP.

Dynamic concentration/ (mg/m ³)	Response frequency shift/KHz	Response time/min
0.10	0.352	6.80
0.20	0.680	6.02
0.40	1.392	5.61
0.60	2.144	5.22
1.00	2.995	5.03
1.50	3.772	4.81
2.00	4.025	4.72
2.50	4.255	4.64
3.00	4.352	4.53
5.00	4.402	4.52

Table 2. The detection results of SAW-MIP sensor to DIMP.

Dynamic concentration/ (mg/m ³)	Response frequency shift/KHz	Response time/min
0.10	0.489	6.00
0.20	1.026	5.40
0.40	1.960	5.22
0.60	2.852	5.03
1.00	3.820	4.81
1.50	4.710	4.72
2.00	5.771	4.64
2.50	4.352	4.53
3.00	5.865	4.52
5.00	6.041	4.48

From the **Table 1**, we found that with decrease of DMMP concentration, the response frequency shifts were reduced, the response time was lengthened gradually, and the recovery time was shortened. At high concentration, the molecules of DMMP combined with gold quickly, so that the time to reach balance was short and the recovery time was longer. On the contrary, at low concentration, since there were not so many adsorption molecules, the response frequency was relatively weak. Although the recovering speed was accelerated obviously, the equilibration needs longer time.

The SAW-MIP sensor had high sensitivity to low concentration DMMP and the results were shown in **Figure 3**. The response frequency shifts had a linear relationship with the concentrations of DMMP at 0.1 - 0.60 mg/m³. Even at 0.1 mg/m³, the SAW-MIP sensor still had almost 350 - 500 Hz response frequency shift, which was greater than the 100 Hz of detection limit.

Generally, there are four kinds of adsorption models between gas and film behavior: Henry laws, Langmuir model, Freundlich adsorb equation and BET multilayer adsorb model.

It had been shown in **Figure 3**, the detection curve assumed a linear relationship at the beginning stage (0.10 - 1.00 mg/m³) and the curve was cliffier. From the linear curve in **Figure 4**, the total correlation coefficient 0.98 had been obtained.

In the middle stage (1.00 - 3.00 mg/m³), the slope of the curve was gradually with concentration, but above 5.0 mg/m³, response frequency shift no longer increased conspicuously. We carried on a discussion to the above-mentioned results by Langmuir model:

$$\theta = \frac{V}{V_m} = \frac{aP}{1 + aP} \tag{4}$$

In the Formula 4, θ was surface fraction of coverage of

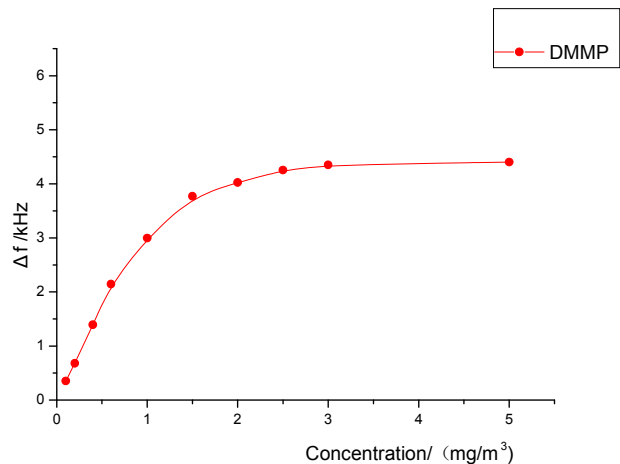
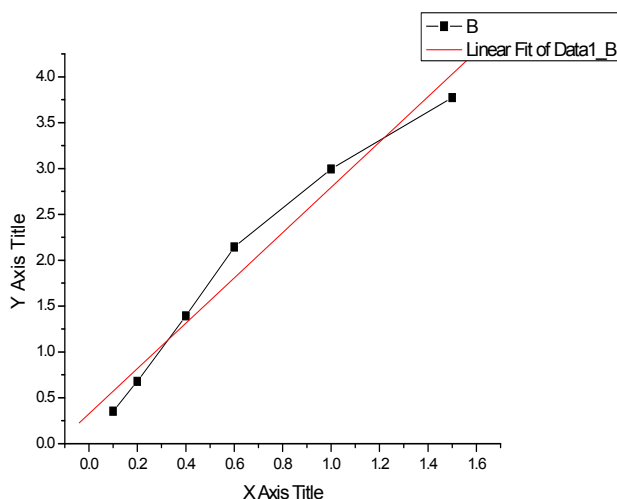


Figure 3. The detection curve of DMMP at different concentrations (28°C, RH = 70%).



R: 0.98335; SD: 0.27115; N: 6; P: 4.1359E-4.

Figure 4. The linear curve and the total correlation coefficient (0.10 - 1.00 mg/m³).

isothermal adsorption, a was equilibrium constant of adsorption, which represented the adsorb ability of solid surface, V_m was saturational adsorption quantity of DMMP, V was practical adsorption quantity of DMMP at fractional pressure P .

The variation amount (Δf) of response frequency and adsorption quantity (V) of imprinted sensitive film were measured to be a direct ratio relation. When all experimental data of the variety amount of response frequency and the concentration (C) of DMMP were introduced into the above-mentioned Formula 4, another Formula 5 would be obtained.

$$\frac{C}{\Delta F} = \frac{1}{\Delta F_m^a} + \frac{C}{\Delta F_m} \quad (5)$$

where ΔF_m was response frequency shift of saturational adsorption, at the given conditions it was a constant. From Formula 5, a straight line with the $C/\Delta F$ to C was gotten within range from 0.60 to 3.0 mg/m³ in **Figure 5** showed:

According to the slope and intercept of the line, the adsorption constant (a) of isothermal adsorption Langmuir model and the saturated frequency shift were calculated, $a = 2.083$, $\Delta F_m = 5.186$ KHz. In fact, when the molecular imprinted film reached adsorption balance at low concentration, the amounts of DMMP that had been attached on film would be very small. Therefore this adsorption behavior of Langmuir model on the film was inevitable. When concentration was enhanced, the adsorption behavior of film was changed, and it could not be described by the simple adsorption model. This result demonstrated that the adsorption behavior became comparatively complicated along with the increment of DMMP concentration. On the other hand, since the interactive com-

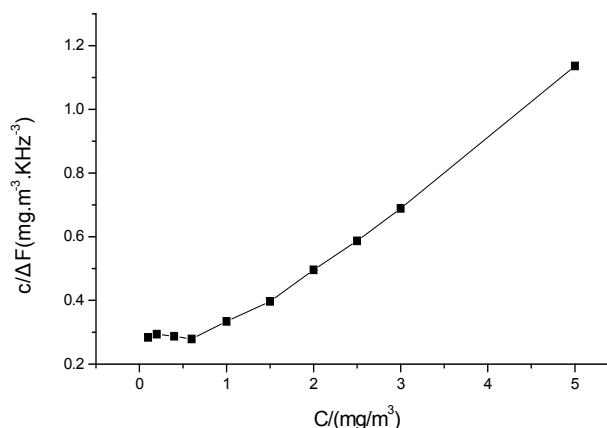


Figure 5. The calculation curve of parameter for langmuir isotherm adsorption (28°C, RH = 70%).

plexity between DMMP and the molecular imprinted film, a simple linear relationship might not exist between the response frequency shift and the concentration of DMMP.

The ideal molecular imprinted polymer has the imprinted hole with appearance matching molecular size of template, shape and functional group. Because imprinted films have unique space structure, including the capacity of discernment and 3D hole of displacement binding site, it could be used to detect gas and high response frequency shift was gotten in short time. It displays obvious molecular imprinted effect. In this article Isopropyl hydrogen methylphosphonate (1) was selected as the template, because its chemical structure was greatly similar to that of DMMP, as a result, a great frequency shift was obtained in this detection process.

3.3. Imprinted Effectiveness and Anti-interference Experiments of the SAW-MIP Sensors

In order to further confirming the imprinted effectiveness, many other gases were chosen to carry on comparative experiment. Spirits, hydrocarbon, aldehyde, ketene, aromatics, amines, organic acid, organophosphorus, herbosa smoke etc, about 30 kinds of interference gases whose concentrations were higher 100 - 1000 times than that of DMMP were detected. The experimental results were shown in **Table 3**:

It had been shown in **Table 3**, in general, common organic solvents and gases did not interference with the SAW-MIP sensors. Among them, because the structures of organophosphorus agrochemicals were similar to DMMP, their frequency shifted greatly, but to the imprinted effectiveness of DMMP, their responses were obviously lower than that of DMMP at the same concentration. Moreover, organic amines and high concentration organic acids would also produce some influence on the examination, this might be when the concentrations of these several compounds

Table 3. The response of the SAW-MIP sensor to interference gases.

Interference gas	Concentration/(mg/m ³)	Response frequency shift/KHz
Omethoate	1000	0.550
CH ₃ OH	10000	0.320
CH ₃ CH ₂ OH	10000	0.421
HCOOH	1000	0.330
CH ₃ COOH	1000	0.360
CH ₃ (CH ₂) ₄ COOH	1000	0.520
NH ₃	2000	0.521
C ₆ H ₅ NH ₂	2000	0.516
O-Anisidine	1000	0.212
C ₂ H ₅ OC ₂ H ₅	10000	0.220
Petroleumether	10000	0.510
THF	10000	0.510
n-C ₆ H ₁₄	10000	0.130
n-C ₈ H ₁₈	1000	0.310
CCl ₄	10000	0.290
HCHO	1000	0.125
CH ₃ COCH ₃	10000	0.120
CH ₃ COOC ₂ H ₅	10000	0.150
C ₆ H ₆	10000	0.140
C ₆ H ₅ CH ₃	1000	0.280
C ₆ H ₅ Cl	1000	0.113
H ₂ O	1000	0.160
CH ₃ CN	1000	0.190
Grass smog	High	0.130

were 100 times, even higher than that of DMMP, they had been to some extent linked or adsorbed on film surface. Besides, when 25-(thioalkyl-alkoxy)-*p*-tertbutylcalix[4]arene (2) non-imprinted film was used as SAW sensitive film to detected toxic agents, the results indicated that although it could be assembled into a film on Au surface and had cavity structure, this kind of film had no especially different 3D space structure, combining ability was small, and had no obviously response to DMMP, which further confirmed the imprinted effect.

4. Conclusion

In this paper, the SAW-MIP sensor to detect organophosphorus has been detailly studied with 25-(thioalkyl-alkoxy)-*p*-tertbutylcalix[4]arene self-assembly molecular imprinted film. Because this kind of SAW-MIP sensor has strong selectivity, high sensitivity, great response frequency shift and good recovery for DMMP, it was possible to be applied to detection of the low concentration organophosphorus gases or quickly early-warning and it could be widely applied in the future. Molecular imprinted tech-

nology with the self-assembly technique were used together in calixarene surface acoustic wave chemical sensor, must have important significance in studying on more gas sensitive films and sensors

REFERENCES

- [1] L. J. Kepley and R. M. Crook, "Selective Surface Acoustic Wave-Based Organophosphate Chemical Sensor Employing a Self-Assembled Composite Monolayer: A New Paradigm for Sensor Design," *Analytical Chemistry*, Vol. 64, No. 24, 1992, pp. 3191-3193. doi:10.1021/ac00048a018
- [2] X. Guo, F. Liu and G.-Y. Lv, "Recent Progress on Study of Calixarene Derivatives," *Chinese Journal of Organic Chemistry*, Vol. 25, No. 9, 2005, pp. 1021-1028.
- [3] D.-Q. Liu, Y.-Q. Feng and S.-X. Meng, "Progress of Calixarenes Used as Anion Receptor," *Chinese Journal of Organic Chemistry*, Vol. 26, No. 4, 2006, pp. 419-430.
- [4] H. Lv, B.-Q. Cao and Y. Pan, "The application of Calixarene Used in SAW Chemical Sensor," *Chemical Sensors*, Vol. 27, No. 2, 2007, pp. 7-11.
- [5] D. L. Dermody, R. M. Crooks and T. Kim, "Interactions between Organized, Surface-Confined Monolayers and Vapor-Phase Probe Molecules.11. Synthesis, Characterization, and Chemical Sensitivity of Self-Assembled Polydiacetylene/Calix[n]arene Bilayers," *Journal of American Chemistry Society*, Vol. 118, No. 47, 1996, pp. 11912-11917. doi:10.1021/ja961302x
- [6] K. D. Schierbaum, T. Weiss and E. U. Thoden van Velzen, "Molecular Recognition by Self-Assembled Monolayers of Cavitand Receptors," *Science*, Vol. 265, No. 5177, 1994, pp. 1413-1415. doi:10.1126/science.265.5177.1413
- [7] J. Rickert, T. Weiss and W. Gopel, "Detection of Oligonucleotide Sequences with Quartz Crystal Oscillators," *Sensors and Actuators B*, Vol. B31, No. 1-2, 1996, pp. 45-50. doi:10.1016/0925-4005(96)80015-3
- [8] F. L. Dickert, P. Forth and J. W. Grate, "Molecular Imprinting in Chemical Sensing—Detection of Aromatic," *Fresenius Journal of Analytical Chemistry*, Vol. 360, No. 7-8, 1998, pp. 759-762. doi:10.1007/s002160050801
- [9] C.-H. Wang, C.-Y. LI and X.-L. Xu, "Electrochemical Investigation of Parathion Imprinted Sensor and Its Application," *Chinese Journal of Applied Chemistry*, Vol. 23, No. 40, 2006, pp. 404-408.
- [10] J. W. Grate, S. L. Rose-Pehrsson and D. L. Venezky, "Smart Sensor System for Trace Organophosphorus and Organosulfur Vapor Detection Employing a Temperature-Controlled Array of Surface Acoustic Wave Sensors, Automated Sample Preconcentration, and Pattern Recognition," *Analytical Chemistry*, Vol. 65, No. 14, 1993, pp. 1868-1881. doi:10.1021/ac00062a011