Transportation of Sulfur Mustard (HD) in Alkyd Coating

Rong-Zhang Hao, Zhen-Xing Cheng,* Hai-Yan Zhu, Guo-Min Zuo, and Chun-Ming Zhang

Department Number 3, Institute of Chemical Defence, P.O. Box 1048, Beijing 102205, China

Received: February 20, 2007; In Final Form: March 23, 2007

The kinetics of absorption, desorption, and degradation of sulfur mustard (HD) in alkyd coating was experimentally studied, and a one-dimension mass transfer model for the transportation of HD molecule in alkyd coating was established on the experimental data. The obtained results indicated that the persistence of HD molecule could be greatly increased due to the absorption of HD droplets by alkyd coating, and there still occurred the desorption of HD as vapor from coating for more than 3 days even after decontamination of HD droplets onto coating. It was also experimentally shown that the majority of HD both absorbed and desorbed was accomplished at an early stage, less than 10 h, and HD molecule was able to be degraded within the alkyd coating probably through the reactions of hydrolysis and elimination. The diffusion coefficient and degradation rate constant of HD in alkyd coating were determined to be practically around 10^{-9} cm^2/s and 2.4×10^{-5} min^{-1}, respectively.

1. Introduction

The decontamination of military equipment has been an important and complicated task in the defense against nuclear-biological-chemical (NBC) weapons,[1] and NBC terrorism attack as well. As is known, the persistence of chemical warfare agents (CWAs) would be greatly increased once they were absorbed by surface coating. Sulfur mustard (bis(2-chloroethyl)sulfide or HD), historically once called as “king” of the persistent CWAs, has a high vesicant toxicity. It would be easily absorbed due to its fat solubility by the coating at the state of droplets in contact with the surface. Although HD droplets can be completely washed away by decontaminant solution from the coating surface, the HD molecule absorbed inside the bulky coating cannot be easily decontaminated. Consequently, it will persistently desorb out of the contaminated coating to injure personnel even though there is only a trace amount of HD in air.[2−4] A method to reduce the amount of desorbed CWAs from the coating is to develop a tight-structured coating, such as polyurethane, which can heighten its resistance toward CWAs. Some progress has been made in this approach, while the price of such coatings is very high, and they cannot absolutely prevent the permeability of CWAs.[4−6] At present, the alkyd is the most widely used coating in military equipment.[7] Therefore, the absorption, desorption and degradation of CWAs in alkyd coating should still be the fundamental problems for the decontamination of military equipment.

Nowadays, polymer coating has been commonly used to cover metal or wood for anticorrosion or decoration.[7−8] Much work has been done to study the interaction of coating polymers with water or organic molecules.[9−11] The emission of volatile organic compounds (VOCs) in trace amount for a long time from polymer coating has become the problems of indoor air and health for people.[12] There are also many other cases dealing with the release of trace VOCs, especially some harmful and even toxic compounds for people, such as the utilization of polymer materials in daily life, the reuse of polymer container, drug delivery system using polymer, etc.[13] Therefore, establishing a model on the transportation process of HD in alkyd coating will also favor understanding these similar phenomena.

Up to now, there has been little literature concerning the transportation process of CWAs in the coating. In 1986, Schwope et al. studied the sorption and desorption of gaseous diethyl malonate, as a simulant for toxic chemicals, in polymer film in both experiment and model approach.[14] In 1990, Sturdivan et al. developed a “round-robin testing” method to measure the desorbed residual agent from chemical agent resistant coating paint, but they were not able to repeat the experimental results, and the gained data were statistically quite discrete.[4] This was possibly caused by the difference in experimental conditions of CWAs droplets contamination, rinsing process, temperatures, coating thickness, coating aging degree, etc. In 1992, Martens et al. reported an experimental study on test for desorption of HD and GD from the contaminated coating, and designed a solvent absorption method to evaluate CWAs desorbed from the coating.[2] In 2001, our group established a systematic method to investigate the absorbing and desorbing phenomena of CWAs in alkyd coating, and obtained an apparent desorption kinetic equation.[3] Herein, much more detailed experimental data, on absorption of HD droplets, desorption of HD vapor, and degradation of HD molecule in alkyd coating was reported, and a one-dimension mass transfer model for the transportation of HD molecule in alkyd coating was established. The diffusion coefficient and degradation rate constant of HD in alkyd coating were determined, and some of the products from degradation of HD were also detected and identified with GC/MS approach.

2. Experimental Section

Materials. HD has a purity >98%. The solvents such as ethanol and acetonitrile are of analytical grade. The alkyd coatings used in experiments were prepared and aged following the Chinese government specifications (GB1727-79 and GB/T 1865−1997). A steel panel (diameter 5.5 cm, surface 25 cm^2)

---

* Corresponding author. E-mail: chengzx04@tom.com. Tel: +86-10-69760164. Fax: +86-10-69760161.

10.1021/jp071453u CCC: $37.00

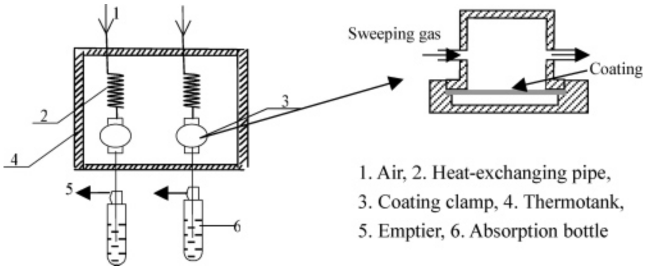

Figure 1. Schematic drawing of the experimental apparatus for HD desorption with the diagram of coating clamp on the top right corner.

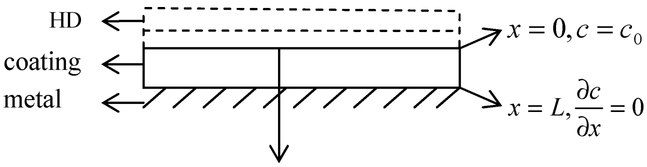

Figure 2. One-dimension mass transfer model of HD in coating.

was used to support an alkyd coating with a thickness of 60−140 μm. Aging coated panel was performed under well controlled conditions in an artificial chamber (Artificial Accelerating Aging Apparatus, SH60BII), where temperature, illumination, humidity and others were simulated in an accelerated way. (Caution: In view of its high toxicity, HD should only be handled by trained personnel using applicable safety procedures.)

Absorption, Desorption, and Degradation of HD. The experiments of contaminating panel sample by droplets of HD were carried out in a thermostatic chamber as follows. First, to preheat HD liquid, micro-injector and the coated panel in a thermostatic chamber (working between 10 and 60 °C with an accuracy ±1 °C) at a given temperature over 1 h, then to uniformly distribute 40 μL (47 mg, around 3.5 mg per droplet, 0.3 cm diameter totally 13 droplets) HD liquid onto the coating surface to achieve a distribution of density 20 g/m^2. Separation distance should be kept around 1 cm to avoid overlapping of the droplets with each other. Distributing the droplets should be accomplished within 2 min, and then the contaminated coating was immediately placed in the thermostatic chamber for a given time. Afterward, to erase the droplets of HD away off coating surface with cotton-ball, to immerse the contaminated coating panel into an aqueous calcium hypochlorite solution and to wash the coating surface for 0.5 h at 30 °C at a given stirring rate. Finally, to take the coating out of the decontamination solution and wash it with deionized water. Therefore, an augmentation weight around 10 mg could be determined as the amount of HD absorbed by the alkyd coating since the weight of non-contaminated coated panel was nearly constant upon being suffered the same treatment.

Desorption of HD vapor from the contaminated coating was accomplished with a self-designed apparatus located in the thermostatic chamber, where the coated panel was clamped with a specifically designed clamp, as schematically shown in Figure 1. The desorbed vapor of HD could be almost entirely swept into an absorption bottle containing 20 mL of cold ethanol and quantitatively analyzed with a colorimetric method.[15]

The experiments for kinetics of HD degraded in alkyd coating and its product detection were performed at 30 °C as follows. First, to make a series of coatings contaminated by HD droplets in a parallel way; second, to erase the droplets of HD away off coating surface with cotton-ball, to wash the panel in the decontaminant solution and then to seal and stew these panels in the thermostatic chamber for given periods; finally, to extract HD residual within the coatings, with ethanol for quantitative analysis, or with acetonitrile for the detection and identification of degradation products by GC/MS approaches.[16−17]

Determination of Diffusion Coefficient. The traditional method to determine diffusion coefficient D (cm^2/s) is to let solvent permeate through a paint film at a given thickness L (cm), and to get the time lag τ (s), i.e., the intercept on the time-axis of steady permeation linear,[14] and then the diffusion coefficient could be calculated according to $D = (L^2)/(6\tau)$. In order to determine the diffusion coefficient of HD molecule inside the alkyd coating, a series of alkyd paint films at given different thicknesses was prepared under the conditions like the coated panels but without artificial aging. These prepared films were contaminated by the droplets of HD in a similar manipulation to contaminating the coated panels, and the vapor of HD desorbed from the contaminated film was then swept off and quantitatively analyzed. On the other hand, it is also possible to calculate D with the transportation model established as follows.

3. Establishment of Transportation Model

In fact, the possible factors to influence the transportation of HD in alkyd coating are so complicated that it is hardly studied completely through experiment, but one is still able to establish a one-dimensional model of transportation of HD in alkyd coating on the basis of the Fick's Law, to get a mathematic solution under the experimental condition and to verify it with experimental measurement. This may not only reduce our experimental jobs, but can also be helpful to disclose the rules for the transportation of organic molecules, such as CWAs, VOCs, and others, in polymer materials including surface coating.

In our experiments, the diameter of HD droplet ($d \approx 0.3$ cm) is much larger than the thickness of coating ($L \approx 10^{-2}$ cm), the process can thus be regarded as one-dimensional diffusion model. In fact, the transportation of HD in alkyd coating proceeded together with a chemical reaction of degradation. To simplify this issue, one can consider the degradation of HD as a first-order reaction, and then the transportation of HD in the coating could be written into another modified Fick's second law:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - kc \tag{1}$$

where, D is the diffusion coefficient of HD in the coating and k is the rate constant for HD degradation. Equation 1 can give analytical solutions respectively for the two different processes, i.e., absorption of HD droplets and desorption of HD vapor, under certain postulated initial as well as boundary conditions, as shown in Figure 2. For the absorption of HD droplets by the coating, HD molecule does not present inside of the coating at the initial time in the process of absorption. Once HD droplet starts to contact with the coating surface, the concentration (c_A) of HD presented at surface layer will immediately reach an equilibrium limit (c_0) of solubility, which is always being kept at a constant value (c_0) along with the process of absorption. HD molecule can only diffuse down to the bottom of the coating but cannot pass through the metal panel. Therefore, the mass transfer during the process of absorption could be written into

$$\begin{cases} \dfrac{\partial c_A}{\partial t_A} = D\dfrac{\partial^2 c_A}{\partial x^2} - kc_A \\ c(x,0) = 0 \\ c(0,t_A) = c_0 \\ \left.\dfrac{\partial c_A}{\partial x}\right|_{x=L} = 0 \end{cases} \tag{2}$$

Where, t_A is the time for HD droplets in contact with the coating, i.e., absorption time. According to eq set 2, one can get a solution to the concentration of HD distributed inside the coating in one-dimension of coating thickness:

$$c_A(x,t_A) = \sum_{n=0}^{\infty}\left[\frac{-2c_0 D\beta_n \sin(\beta_n x)\mathrm{e}^{-(k+D\beta_n^2)tA}}{L(k+D\beta_n^2)}\right] + \frac{c_0\mathrm{e}^{-wx}(\mathrm{e}^{2wx}+\mathrm{e}^{2wL})}{1+\mathrm{e}^{2Lw}} \tag{3}$$

where

$$w = \sqrt{\frac{k}{D}} \tag{4}$$

$$\beta_n = \frac{n\pi + 0.5\pi}{L}, \qquad n = 0, 1, 2, 3, ... \tag{5}$$

Then the amount of HD absorbed into the coating is

$$q_A = \sum_{n=0}^{\infty}\frac{2c_0D^2\beta_n^{\,2}}{L(k+D\beta_n^{\,2})^2}f(t_A) + Dwc_0t_A\frac{1-\mathrm{e}^{2wL}}{1+\mathrm{e}^{2wL}} \tag{6}$$

where, the function $f(t)$ is defined as

$$f(t) = 1 - \mathrm{e}^{-(k+D\beta_n^2)t} \tag{7}$$

At the initial time for the desorption of residual HD inside the coating as vapor, the total amount of HD residual and its distribution, i.e., q_0 and $c_D(x,0)$, inside the coating certainly depended upon not only the contamination time (t_A), but also the process of washing the contaminated coating in decontamination solution for 0.5 h (t_W). Experimental results indicated that q_0 was mainly determined by t_A. The concentration of HD on the coating surface can be regarded as zero, because HD molecule diffuses in gaseous phase much more quickly than in coating bulky phase.

Thus, the mass transfer during the process of desorption could be

$$\begin{cases} \dfrac{\partial c_D}{\partial t_D} = D\dfrac{\partial^2 c_D}{\partial x^2} - kc_D \\ c_D(x,0) = c_A(x,t_A) \\ c_D(0,t_D) = 0 \\ \left.\dfrac{\partial c_D}{\partial x}\right|_{x=L} = 0 \end{cases} \tag{8}$$

where, t_D is the desorption time. Then the distribution of concentration, $c_D(x,t_D)$, during desorpton is

$$c_D(x,t_D) = \sum_{n=0}^{\infty}\left\{\frac{2\sin(\beta_n x)c_0D\beta_n}{L(k+D\beta_n^{\,2})}f(t_A)[1-f(t_D)]\right\} \tag{9}$$

Therefore, the cumulate amount of HD desorbed from unit area of the coating during the time t_D, q_D (g/m^2), is

$$q_D = \sum_{n=0}^{\infty}\left[\frac{-2c_0D^2\beta_n^{\,2}}{L(k+D\beta_n^{\,2})^2}f(t_A)f(t_D)\right] \tag{10}$$

4. Results and Discussion

Degradation of HD inside the Coating. The variation of the extraction ratio along with the time of degradation at 30 °C was given in Table 1. If the degradation of HD was assumed to be first-order, one would get a rate constant about 2.4×10^{-5} min^{-1}. This was much less than the rate constant for hydrolysis of HD in water reported in the literature,[18] 0.14 min^{-1} at 25 °C. It was probably because that the degradation of HD in alkyd coating was kinetically controlled by a very slow diffusion of HD molecule inside the coating. The products of HD degraded in alkyd coating over 60 days was identified by GC/MS, as shown in Figure 3 and given in Table 2. It can be seen that there were some hydrolysis and elimination products in the extracted components. However, the total extraction ratio of HD and its degradation products could only reach about 50% with ethanol and acetonitrile as extraction agent after a very long time of degradation. And chloroform as extractant could hardly increase the extraction ratio despite that the coating was severely swelling and damaged. This indicates that some sulfur compounds were not be extracted and possibly strongly bound on the coating.

If the degradation of HD inside the coating was neglected in the process of absorption to calculate the diffusion coefficient, eq 6 can thus become $q_A \approx (8c_0L)/(\pi^2)(1 - \mathrm{e}^{(-\pi^2Dt_A)/(4L^2)})$. If the contamination time is long enough ($t_A = \infty$), the amount of HD absorbed inside the coating would reach a maximum (q_0). One would get a linear curve of $\ln(1 - q_A/q_0)$ versus t_A with a slope m, and the diffusion coefficient for absorption could be given as $D = -(4mL^2)/(\pi^2)$. A similar result was expected in the case of desorption process. If the degradation of HD inside the coating was considered in the process of absorption and one assumed that $k = 2.4 \times 10^{-5}$ min^{-1}, the obtained value of D was very closed to that calculated on assumption of $k = 0$. This seemed to indicate that the degradation of HD inside the coating was too slow to influence the transportation of HD inside the alkyd coating in the processes of absorption and desorption. In fact, from the establish model, we can also simulate the absorption and desorption process with different degradation rate, as shown in Figure 4. It can be seen that both desorption and absorption process were somewhat influenced by the degradation rate of HD when $k < 2.4 \times 10^{-4}$min^{-1}.

TABLE 1: Relationship between the Extraction Ratio and the Degradation Time (L = 130 μm, T = 30 °C)

degradation time (days)	absorption amount (g/m^2)	extraction amount (g/m^2)	extraction ratio (%)
0	2.1	2.1	>99
2	1.8	1.7	94
5	1.5	1.3	87
9	2.3	1.7	74
18	2.3	1.3	56
26	2.2	0.9	41
40	1.2	0.3	25

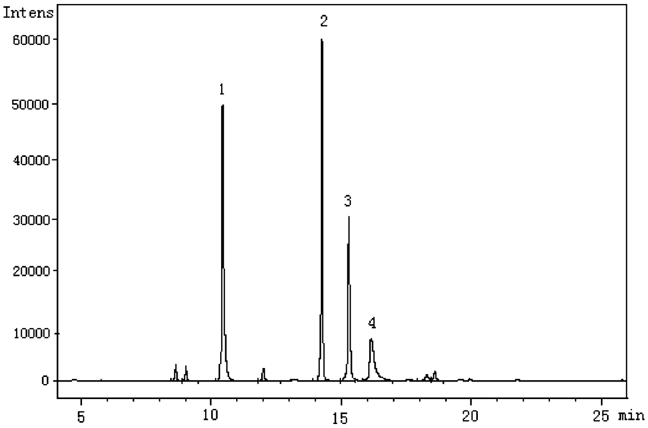

Figure 3. GC/MS total ion chromatogram for the extractant of HD degradation products in alkyd coating.

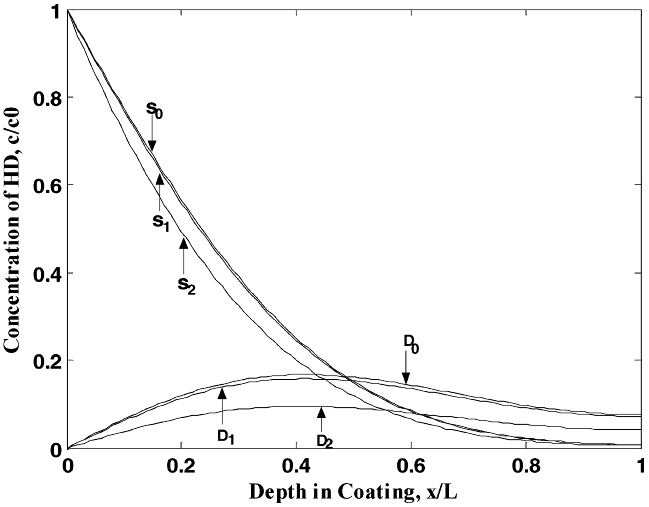

Figure 4. The influence of HD degradation on its transportation in the coating. S and D represent absorption and desorption process, respectively, and the degradation rate constants, which are distinguished by the subscript 0, 1, and 2, are 0, 2.4×10^{-4} min^{-1}, and 2.4×10^{-3} min^{-1} ($D = 9.5 \times 10^{-10}$cm^2/s, $L = 130$ μm, $t_A = 3$ h, $t_D = 3$ h).

Absorption of HD Droplets. Figure 5 presented the amount of HD absorbed by the coating of 130 μm at 30 °C for different contamination time from 0.5 to 24 h. It can be seen that the coating can achieve a maximum absorption amount of HD droplets with about 14 g/m^2. Thus, an equilibrium limit of solubility, i.e., the concentration of HD at out layer c_0, could be calculated as (14 g/m^2)/(130 μm) $\approx$ 0.3 g/cm^3. After 6 h, about half of the maximum absorbed amount was achieved. This would indicate that a very fast absorption of liquid HD by the coating occurred at the early stage. According to eq 6 and $k = 0$, the diffusion coefficient D was calculated as 8.1×10^{-10} cm^2/s.

The distribution of HD concentration in one-dimension inside the coating could be calculated with eq 3 on the conditions: $L = 130$ μm, $T = 30$ °C, c_0=0.3 g/cm^3, and $D = 8.1 \times 10^{-10}$ cm^2/s, as shown in Figure 6. It can be seen that the concentration of HD inside the coating decreases with increasing of the coating depth. Besides, the concentration distribution curves ascend as the contamination time increases. For instance, the concentration of HD (c_x/c_0) at the depth of $x/L = 0.5$ augments from 0.05 to 0.32 when the contamination time increases from 1 to 5 h. This indicated that the amount of HD diffusing into the coating augments along with the contamination time.

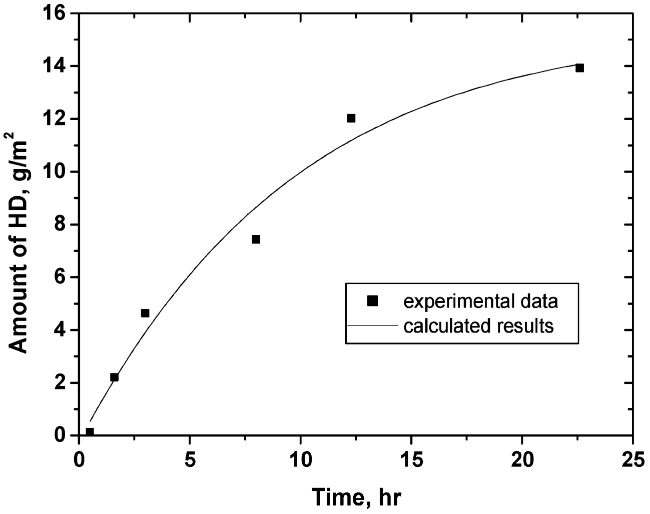

Figure 5. The absorption curve of HD in alkyd coating ($T = 30$ °C, $L = 130$ μm).

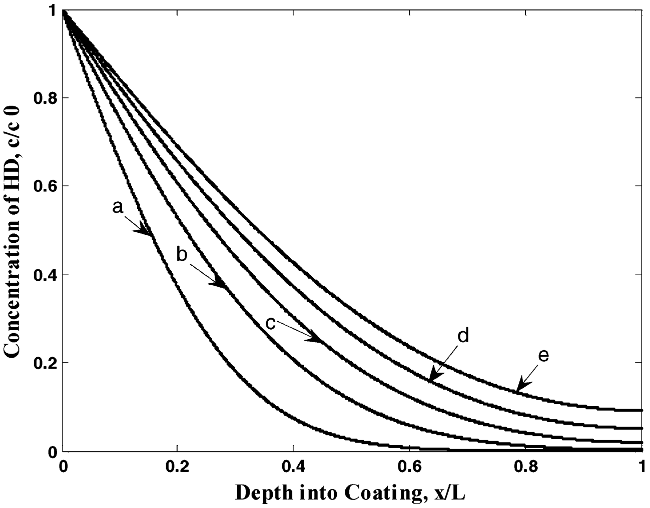

Figure 6. The concentration distribution of HD inside the coating during the absorption process. The contamination time is 1, 2, 3, 4, and 5 h from a to e, respectively ($D = 8.1 \times 10^{-10}$ cm^2/s, $L = 130$ μm, $k = 2.4 \times 10^{-5}$ min).

Desorption of HD as Vapor. Figure 7 presented the amount of HD desorbed from the alkyd coating, which was contaminated by HD droplets for 3 h and stewed over 72 h at 30 °C with an absorption amount of around 1.8 g/m^2. It was experimentally found that this desorption process could persist over one week, and there was seemingly a limit of maximum desorption around 2 g/m^2. At 10 h, over half amount of the maximum had been desorbed from the coating. This would indicate that a very fast desorption of HD from the contaminated coating occurred at

TABLE 2: Extraction Ratio and the Main Mass Fragments of HD and Its Degradation Products

no.	structural formula	extraction ratio	main mass fragments of the detected species
1	$ClCH_2CH_2SCH{=}CH_2$	3%	36, 45, 60, 73, 87, 96, 122, 133
2	$S(CH_2CH_2Cl)_2$	3%	34, 45, 63, 81, 96, 109, 123, 158
3	$ClCH_2CH_2SCH_2CH_2OH$	2%	36, 45, 63, 73, 91, 109, 123, 140, 158
4	$S(CH_2CH_2OH)_2$	41%	36, 45, 63, 73, 91, 109, 123, 140, 158

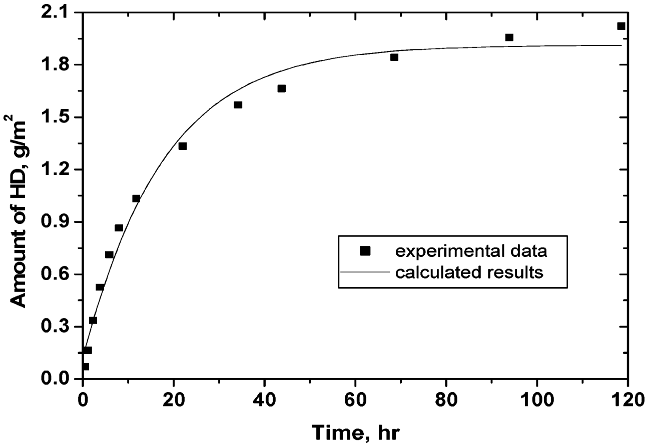

Figure 7. The desorption curve of HD from alkyd coating at 30 °C ($L = 130$ μm, $t_A = 3$ h).

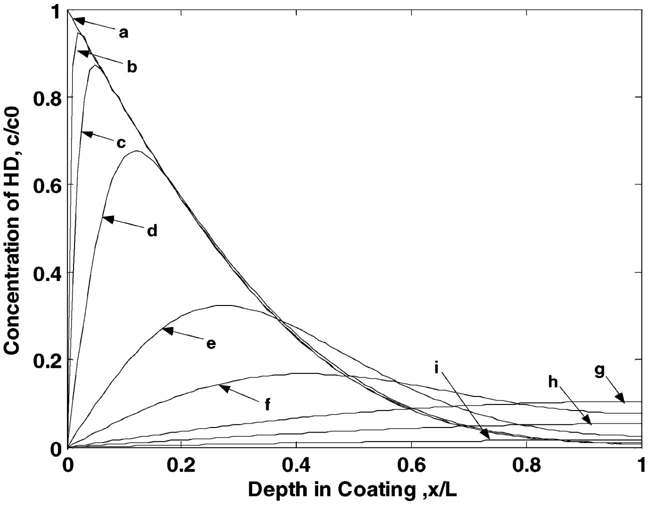

Figure 8. The concentration distribution of HD inside the coating during the desorption process. The desorption time is 0, 0.001, 0.01, 0.1, 1, 3, 10, 24, and 48 from a to i, respectively ($D = 9.5 \times 10^{-10}$cm^2/s, $L = 130$ μm, $k = 2.4 \times 10^{-5}$, $t_A = 3$ h).

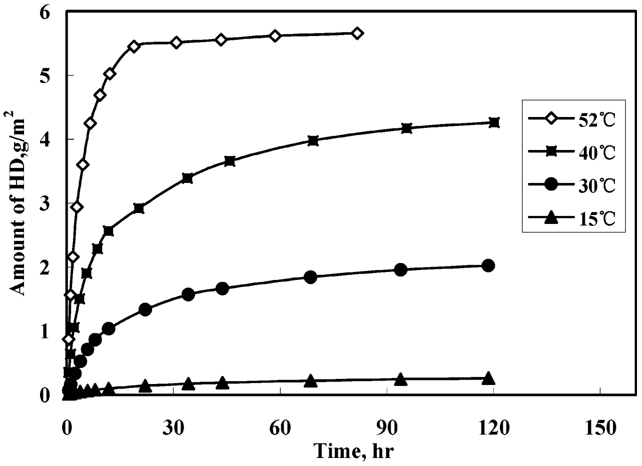

Figure 9. The influence of temperature on the desorption of HD from the coating ($L = 130$ μm).

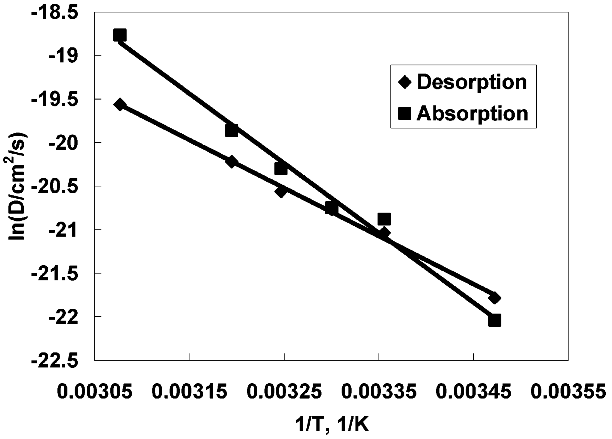

Figure 10. Relationship between the diffusion coefficient of HD in the coating and the temperature.

the early stage. According to eq 10 and $k = 0$, the diffusion coefficient D was calculated as 9.5×10^{-10} cm^2/s.

According to eq 9, in a similar way to absorption, the distribution of HD concentration inside the coating during desorption period could be calculated as illustrated in Figure 8. Equation 9 can be used to calculate the concentration of HD (c/c_0) in alkyd coating varying with desorption time and coating depth (x/L). The maximum concentration of HD inside the coating would decrease rapidly, and its position would shift from surface to bottom of the coating along with the desorption proceeded. The amount of HD residual inside the coating, i.e., the integrated area of the distribution of concentration (c_x/c_0) with the depth (x/L), decreased quickly at the early stage. This implied that the desorption rate was quite rapid at the early stage.

Effect of the Aging Degree, Temperature, and Thickness on Diffusion Coefficient. Table 3 listed the diffusion coefficients at different conditions calculated from the established model with the kinetic data of absorption and desorption. It is worthwhile noting that there was a somewhat difference between the diffusion coefficients determined by absorption and desorption.

The amount of HD absorbed by alkyd coating remarkably decreased with an increase of aging degree for the coating, as a consequence, the amount of HD desorbed from the coating was also diminished sharply. This was probably caused by the formation of a more crossed structure inside the coating. Undoubtedly, it would very much contribute to increasing the resistance of alkyd coating toward HD liquid. It can be seen that these D coefficients of HD molecule inside the coating were sensitive to the aging degree of the coating, which decreases along with the artificial aging days. The coatings disposed outdoors for 4 months and indoors for 5 years can achieve an approximately equal D coefficient.

The influence of the ambient temperature (15−52 °C) on the diffusion coefficient was studied, and the results were shown in Figure 9 and Table 3. It was found that the maximum desorption amount of HD augmented sharply as the temperature increased. This is probably because of an augmentation of equilibrium solubility in the coating for liquid HD along with an increase of temperature. It can be seen in Table 3 that the D coefficients calculated from the models studied augmented with the temperatures of both absorption and desorption. As shown in Figure 10, a good linear-ship, $\ln D - 1/T$, from Arrhenius equation $D = D_0 e^{-(E)/(RT)}$ can be achieved for both absorption ($E_A = 66$ kJ/mol) and desorption ($E_D = 46$ kJ/mol) process. It can also be seen from Table 3 that the D coefficient decreases along with lowering the thickness of the coating. Besides, the values of the diffusion coefficient determined in these two different methods, shown in Table 3, were approximate to each other, so it was feasible to determine the diffusion coefficient directly through the kinetic data of absorption or desorption.

In spite of aging degree, temperature and thickness having certain effects on diffusion coefficient, the determined results

TABLE 3: Diffusion Coefficients and Their Variations with Different Conditions

fixed conditions	alkyd coating; aged for 3 days and contaminated for 3 h; T =30 °C		
variable thickness (μm)	56	100	130
absorption D (10^{-10} cm^2/s)	1.0	6.1	8.1
desorption D (10^{-10} cm^2/s)	3.2	7.8	9.5

fixed conditions	alkyd coating of 130 μm thickness, aged for 3 days and contaminated for 3 h					
variable temp (°C)	15	25	30	35	40	52
absorption D (10^{-10} cm^2/s)	2.7	8.5	9.8	15	24	71
desorption D (10^{-10} cm^2/s)	3.5	7.3	9.5	12	17	32

fixed conditions	alkyd coating; 130 μm thickness; contaminated for 3 h; T = 30 °C					
variable artif aging (days)	0	1	3	5	*a*	*b*
absorption D (10^{-9} cm^2/s)	4.9	1.6	1.2	0.53	0.97	0.97
desorption D (10^{-9} cm^2/s)	2.0	1.8	1.2	0.92	0.27	0.88

[a] This sample had been disposed at outdoor for 4 months in spring and summer in Beijing. [b] This sample had been stored in laboratory for 5 years and was contaminated by HD droplets for 1 h.

listed in Table 3 could come to the conclusion that the diffusion coefficient for HD inside alkyd coating can be around 10^{-9} cm^2/s at normal temperature. The similar experimental results were obtained for a nerve agent sarin (GB). At 25 °C, the diffusion coefficient for the transportation of GB in alkyd coating was found to be around 10^{-9} cm^2/s, and its degradation rate constant is about 2.0×10^{-4}min^{-1}.

5. Conclusion

Once alkyd coating was contaminated by HD droplets or liquid, the persistence of HD could be greatly increased due to the absorption of HD droplets by alkyd coating. Desorption of HD as vapor from the coating may persist more than 3 days even after the decontamination of HD droplets onto the coating. The majority of HD either absorbed or desorbed was accomplished at an early stage less than 10 h. HD within the alkyd coating could be slowly degraded in a rate constant about 2.4×10^{-5}min^{-1}, probably through the reactions of hydrolysis and elimination.

The transportation of HD inside alkyd coating is a typical mass transfer process with chemical reaction. It is able to establish a one-dimensional model of HD mass transfer for the contamination of HD droplets onto alkyd coating and to experimentally determine a diffusion coefficient. Although several factors, such as aging degree, temperature and thickness, influenced on the diffusion coefficient to some extent, the diffusion coefficient determined at normal temperature was practically around 10^{-9} cm^2/s. Therefore, it would be possible to evaluate absorption, desorption and distribution of concentration for the coating or other polymer surface contaminated by HD, GB, and other CWAs or VOCs with the relevant parameters acquired.

Acknowledgment. This work is financially supported by the National Key Fundamental Research Program of China (Grant No. 2006CB300401).

References and Notes

(1) Yang, Y.-C.; Baker, J. A.; Ward, J. R. *Chem. Rev.* **1992**, *92*, 1929.

(2) Martens, H.; Göglus, K. *Proceedings of the 4th International Symposium on Protection against Chemical and Biological Warfare Agents*, Gothenburg, Sweden, June 1992; Swedish Defense Research Agency, NBC Defence: Sweden, 1992.

(3) Cheng, Z.-X.; Xu, M.; Wang, L.-Y.; Chang, Q.; Zhu, H.-Y. *Proceedings of the 7th International Symposium on Protection against Chemical and Biological Warfare Agents*, Gothenburg, Sweden, June 2001; Swedish Defense Research Agency, NBC Defence: Sweden, 2001.

(4) Sturdivan, L. M.; Thomas, J.; Bodt, B. A. *Test for Desorption of Agents HD and GD from Chemical Agent Resistant Coating (CARC)*; CRDEC-TR-190; Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, 1990.

(5) Escarsega, J. A.; Crawford, D. M.; Kaste, P. J. *Analysis and Performance Evaluations of Chemical Agent Resistant Coating Systems*; ARL-TR-2545; Army Research Laboratory, Aberdeen Proving Ground, MD, 2001.

(6) Crawford, D. M.; Escarsega, J. A. *Experimental Investigation of Polyurethane Camouflage Coating using Dynamic Mechanical Analysis*; ARL-TR-1929; Army Research Laboratory, Aberdeen Proving Ground, MD, 1999.

(7) Chang, J. C. S. *Capstone Report on the Development of a Standard Test Method for VOC Emissions from Interior Latex and Alkyd Paints*; EPA/600/ R-01/093; Environmental Protection Agency: Washington, DC 2001.

(8) Johnson, B. W.; Mcintyre, R. *Prog. Org. Coat.* **1996**, *27*, 95.

(9) Corfias, C.; Pebere, N.; Lacabanne, C. *Corros. Sci.* **1999**, *41*, 1539.

(10) González, S.; Mirza, R. I. C.; Souto. R. M. *Prog. Org. Coat.* **2001**, *43*, 282.

(11) Bin, L.; Ying, L.; Haichao, L.; Chu-nan, C. *Corros. Sci.* **2002**, *44*, 2657.

(12) Duncan, J. *Reduced VOC Chemical Agent Resistant Coating (CARC)*; ARL-MR-191; Army Research Laboratory, Fort Belvoir, VA, 1994.

(13) Comyn, J. *Polymer Permeability*; Elsevier: London, 1985.

(14) Schwope, A. D.; Klein, J.; Sidman, K. R.; Reib, R. C. *J. Hazard. Mater.* **1986**, *13*, 353.

(15) Franke S. *Lehrbuch der Militärchemie*, Band 2; Militärverlag der DDR: Berlin, 1977.

(16) Xavier, C.; Andre, T. *J. High Resol. Chromatogr.* **1998**, *21*, 457.

(17) Zuo, G.-M.; Cheng, Z.-X.; Li, G.-W.; Wang, L.-Y.; Miao, T. *Environ. Sci. Technol.* **2005**, *39*, 8742.

(18) Bartlett, P. D.; Swain, C. G. *J. Am. Chem. Soc.* **1949**, *71*, 1406.