

# Search for Simulants of Sulfur Mustard through Sorption Studies in Elastomers

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Received 10 March 2006; accepted 11 October 2006

DOI 10.1002/app.25830

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** With an aim to probe some of the safe and commercially available nonsulfur chemicals as simulants of sulfur mustard for testing of protective materials, the sorption of bis(2-chloroethyl) ether (2-CEE), 1,6-dichlorohexane, bis(4-chlorobutyl) ether, *n*-octane (OCT), dimethyl methylphosphonate, and ethylene glycol through butyl rubber (IIR) and polyisoprene (PI) rubber was studied at  $30 \pm 2^\circ\text{C}$  using gravimetric method. Among these compounds, sorption of OCT was maximum while bis(4-chlorobutyl) ether was sorbed least. The sorption of dimethyl methylphosphonate was intermediate between 2-CEE and 1,6-dichlorohexane. With the exception of OCT/IIR, OCT/PI, and 2-CEE/PI, all other simulant/elastomer systems showed non-Fickian behavior, implying the potential of OCT as a model compound. The diffusivity

of OCT was investigated in IIR and PI; the diffusion coefficient values for OCT/IIR and OCT/PI systems differed by one order of magnitude, being  $6.95 \times 10^{-15} \text{ m}^2/\text{s}$  and  $3.74 \times 10^{-14} \text{ m}^2/\text{s}$ , respectively, indicating the relative impermeability of IIR. The magnitude and dynamics of sorption in OCT/IIR as a function of its concentration and the amount of filler were further studied using the automated gravimetric analyzer. Incorporation of carbon black in IIR further reduced the extent of sorption, thereby implying an improvement in barrier performance. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 1801–1806, 2007

**Key words:** simulant; protective barrier; sorption; butyl rubber; polyisoprene rubber

## INTRODUCTION

Sulfur mustard (SM) is an infamous chemical warfare agent (CWA) that causes blistering of skin, eyes, and lungs<sup>1,2</sup> upon absorption or inhalation. Since it can penetrate almost any material and has no known commercial antidote till date, it is called the “King of CWA.” This dreaded chemical also poses a likely terrorist threat. Protection against SM is generally afforded by elastomeric barrier materials in the form of protective ensemble such as respirators, suits, gloves, and overboots. Performance evaluation of these devices involves testing of their breakthrough time against SM. Handling SM is extremely inconvenient and it can only be used at a limited number of restricted facilities employing stringent safety measures.

The use of simulant drastically reduces the risks with live agent testing. The desirable simulants are less hazardous molecular analogs of toxic chemicals, which mimic the diffusion properties of such agents. Realizing the importance of simulants, United States

established Agent Simulant Knowledge advisory office with the task to identify the past work with simulants.<sup>3</sup> Being less toxic and commercially available, simulants can also be used at manufacturers' site, thus reducing the product development time and cost and thereby expediting the supply of the product to the user. Another reason that invokes interest in the search for simulants is the ratification of Chemical Weapons Convention<sup>4</sup> by most nations, according to which the development, production, stockpiling, and use of CWAs such as SM is prohibited. With suitable simulants of CWAs, research efforts for the development of defense countermeasures and testing of protective devices can continue uninhibited without violation of the Convention. An additional advantage in using the simulant is that the liquid permeation can also be studied easily, unlike for toxic chemicals that pose practical difficulties because of the risk in handling.

In our previous study,<sup>5</sup> various thiocompounds were screened as potential SM simulants amenable to the standard colorimetric method viz. spot disc breakthrough time test<sup>5–8</sup> used for determining efficiency of a barrier. This rapid and reliable technique is based on the oxidation of thioethers with active halogen containing compound.<sup>6–9</sup> Nevertheless, certain constraints limit the wider applicability of this method. The technique is semiquantitative in nature,

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Contract grant sponsor: Defense Research and Development Establishment (DRDE), Gwalior, India.

i.e., it does not quantify the amount of permeant crossing the barrier upon breakthrough. Second, the observation of the color change on the detector paper is highly subjective. This technique also requires constant attendance of the observer to note the precise moment of breakthrough. Another limiting factor is that detector paper needs to be freshly prepared, the technology for which may not be available to local manufacturer. The need for use of the vesicant SM or its simulant thiocompound as the challenge chemical further limits the desirability of the method as most thiocompounds are obnoxious in odor.

An industry-friendly, safe, nontoxic, commercially available nonsulfur containing stimulant, which is also amenable to quantitative and automated methods for evaluation of protective barriers, is the demand of the day. Studies on nonsulfur simulants for testing of protective gear of military use are scarcely available in open literature. Pal et al.<sup>10</sup> used fluorescence quenching technique to evaluate permeation of dimethyl methylphosphonate (DMMP), a nerve agent simulant, through protective clothing material. National Institute for Occupational Safety and Health (NIOSH)<sup>3</sup> short-listed simulants for Sarin (a nerve agent) and SM include 1,6-dichlorohexane (DCH), bis(4-chlorobutyl) ether (4-CBE), 2,4-dichlorophenol, triethyl phosphate, etc. Rivin et al.<sup>11</sup> studied different simulants, namely, DCH, diethyl methylphosphonate, and diisopropyl methyl phosphonate. The diffusion and sorption of SM and its oxyanalogue viz bis(2-chloroethyl) ether (2-CEE) in elastomers such as polyisoprene (PI), nitrile rubber, polyisobutylene, butyl rubber (IIR), polybutadiene rubber, styrene-butadiene rubber, and ethylene-propylene-diene methylene rubber was extensively studied in an earlier work.<sup>7</sup> Sorption of SM and its oxyanalogue in black and nonblack filled IIR rubber membranes<sup>8</sup> was also reported. These studies recommended 2-CEE as a model compound for SM for evaluating barrier performance because 2-CEE diffuses faster than SM.

The aim of the present study was to probe some of the safe and commercially available nonsulfur chemicals as simulants of SM for testing of protective materials. Another objective of the present study was to search an alternative compound that could be employed safely in sophisticated and expensive microprocessor controlled instruments (such as the automated sorption analyzer) without the risk of corrosion. As SM is a highly toxic and corrosive chemical posing risk in sorption experiments, 2-CEE was used for the present study as a reference. The search for other alternatives with reference to 2-CEE was carried out based on their sorption studies through elastomeric barriers. IIR, the most preferred barrier material because of its impermeability, and

**TABLE I**  
**Characterization of Elastomer Membranes**

Property	IIR	PI
Thickness (mm)	0.24 ± 0.02	0.18 ± 0.02
Hardness <sup>o</sup> (Shore A) JIS	58 ± 1	55 ± 1
Density (g/cc)	0.9 ± 0.01	0.9 ± 0.01
% swelling in toluene	2.3 ± 0.2	3.9 ± 0.2
Mol wt between the cross-links	13,981	14,274
Number of cross-links	0.000081	0.000091

PI, the relatively permeable elastomer widely used in gloves for various chemical industries and semiconductor sectors, were chosen for the study. 2-CEE, 4-CBE, DCH, *n*-octane (OCT), DMMP, and ethylene glycol (EG) were evaluated as the candidate simulants.

## EXPERIMENTAL

### Materials

All the chemicals were used as received from Lancaster, UK. The details of IIR and chemicals used are as reported earlier.<sup>12,13</sup> Membranes of IIR were prepared by casting from 10% w/v solution of the rubber in toluene using the reported recipe.<sup>12,13</sup> PI samples were obtained from surgical glove manufacturer (Shree Umiya, Ahmedabad, India). IIR membranes with 10 and 20 phr carbon (GPF N660) filler were compounded using the reported procedure<sup>8</sup> and designated as C-10 and C-20, respectively. The membranes were characterized on the basis of properties mentioned in Table I adopting standard methods.<sup>12,13</sup> The membranes were dried in a vacuum oven for 24 h at 100°C to remove surface absorbed moisture prior to evaluation.

### Sorption and diffusivity of simulants

A gravimetric method<sup>7,8</sup> was used to determine the static vapor sorption of simulants. Membranes were exposed to the saturated vapors of the candidate simulant chemical in a closed chamber at 30 ± 2°C. The specimens were taken out periodically and weighed on an analytical balance (Shimadzu, Japan) with an accuracy of 0.1 mg. The mean of three readings was reported; the standard deviation ranged from 1.2 to 4.7. The mol % vapor sorption  $Q_t$  obtained from the gain in weight of the specimen was related to equilibrium sorption uptake  $Q_\infty$  through an empirical relation<sup>6-8,12-14</sup>

$$Q_t/Q_\infty = Kt^n \quad (1)$$

where  $K$  is a constant characteristic of the polymer-permeant interaction,  $t$  is the time of exposure, and

TABLE II  
Properties of SM and Its Simulants

Chemicals	Molecular formula	Molecular weight	Boiling point	Freezing point	Density	CAS registry number
SM	C <sub>4</sub> H <sub>8</sub> Cl <sub>2</sub> S	159	228	–	1.27	[505-60-2]
2-CEE	C <sub>4</sub> H <sub>8</sub> Cl <sub>2</sub> O	143	178	55	1.21	[111-44-4]
DCH	C <sub>4</sub> H <sub>12</sub> Cl <sub>2</sub>	155	86–88°/14 mm	73	1.067	[2163-00-0]
4-CBE	C <sub>8</sub> H <sub>16</sub> Cl <sub>2</sub> O	199	129–131°/10 mm	–	1.081	[6334-96-9]
OCT	C <sub>8</sub> H <sub>18</sub>	114	125–126°	15	0.703	[111-65-9]
DMMP	C <sub>3</sub> H <sub>9</sub> O <sub>3</sub> P	124	180–181°	–	1.160	[756-79-6]
EG	C <sub>2</sub> H <sub>6</sub> O <sub>2</sub>	62	196–198°	119	1.113	[107-21-1]

$n$  is the transport coefficient that describes the nature of sorption. For  $n \leq 0.5$ , diffusion is Fickian while for  $n > 0.5$ , it is non-Fickian.  $K$  and  $n$  were obtained from the intercept and slope, respectively, of the plot of  $\log Q_t/Q_\infty$  versus  $\log t$ . The diffusion coefficient for sorption  $D$  was calculated from the measurement of the initial slope ( $\theta$ ) of a plot of  $Q_t/Q_\infty$  versus  $\sqrt{t}$  from the equation<sup>7,8,12–14</sup>

$$D = \pi(h\theta/4Q_\infty)^2 \quad (2)$$

### Swelling index and solubility of simulants

Dry membranes of predetermined weights ( $W_d$ ) were immersed in simulants at  $30 \pm 1^\circ\text{C}$  for 72 h to allow them to attain equilibrium sorption. The specimens were removed from the mixture, quickly wiped between the folds of a filter paper to remove the adherent liquid, and weighed. The extent of sorption, also called the swelling index ( $Q$ ), was calculated using the formula<sup>14,15</sup>

$$Q = (W_s - W_d/W_d) \times 100 \quad (3)$$

where  $W_s$  is the weight of the membrane swelled in the simulant. The mean of three readings was reported; the standard deviation ranged from 4.3 to 8.7. The solubility coefficient ( $S$ ) was determined from the extent of sorption by computing the number of moles of the chemical sorbed per unit volume of the membrane at atmospheric pressure.

### Sorption isotherms

In accordance with reported procedure,<sup>16</sup> sorption isotherms were obtained using an intelligent gravimetric analyzer (Hiden Analytical Limited, UK), which is based on the principle of mass relaxation in the polymer upon uptake of the vapors of the candidate simulant. A 35- to 40-mg membrane specimen was placed in a stainless steel sample bucket of fine mesh and exposed to predetermined concentrations of simulant vapor. The partial pressure of the vapors was automatically computed by the system using Antoine's equations. The relative pressure ( $P/P_0$

$\approx$  activity or concentration) of the vapors was increased in 12–14 equal steps corresponding to a pressure change of 8–10 mbar at a constant temperature of  $30 \pm 0.01^\circ\text{C}$ . The temperature was maintained at  $30^\circ\text{C}$  using a Hubber Ministat (Hubber, Germany), with an accuracy of  $\pm 0.01^\circ\text{C}$ . The change in weight of the polymer with time was recorded and the isotherm was approximated from the kinetic data by autofitting into the appropriate sorption models.<sup>16</sup>

## RESULTS AND DISCUSSION

Physical properties of SM and its candidate simulants are reported in Table II. The molecular weights of the simulants ranged from 62 to 199 and their boiling points varied from 86 to  $88^\circ\text{C}/14$  mmHg to  $228^\circ\text{C}$ . The vapor sorption of candidate simulants as a function of time was studied at  $30 \pm 1^\circ\text{C}$  through similarly crosslinked ( $N \sim 10^{-5}$ ) IIR and PI membranes of thickness  $0.24 \pm 0.02$  mm and  $0.18 \pm 0.02$  mm, respectively, using the weight gain method. The sorption plots obtained from these data are shown in Figures 1–3. In general, the mol % sorption increases with time of exposure. Exceptionally high mol % sorption values of  $6.33 \times 10^{-5}$  and  $8.56 \times 10^{-5}$  for OCT were observed in IIR and PI, respectively (Fig. 3). In IIR, the mol % sorption of other simulants ranged from  $5.5 \times 10^{-3}$  to  $47 \times 10^{-3}$

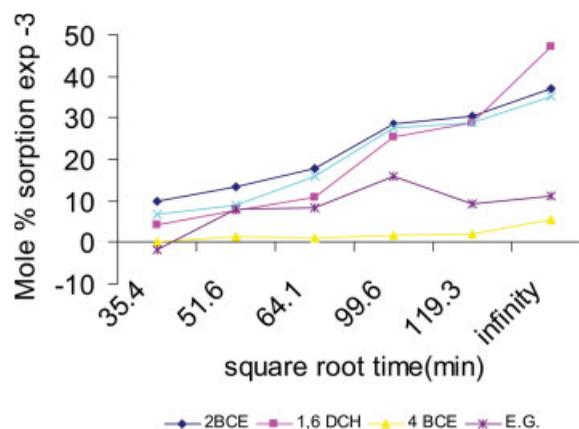
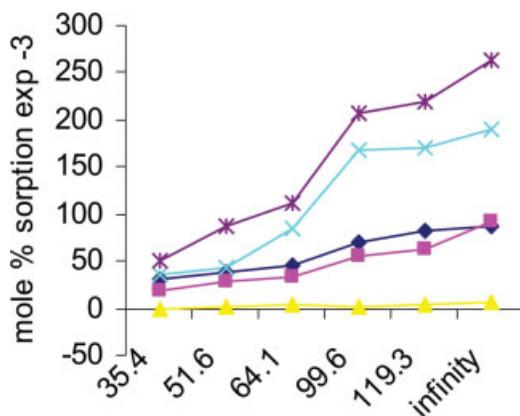


Figure 1 Sorption plots for simulant/IIR systems [ $\square$  2CEE,  $\blacksquare$  DCH,  $\triangle$  4-CBE,  $\times$  DMMP,  $*$  EG].



**Figure 2** Sorption plots for simulant/PI systems [ $\triangle$ - 2-CEE,  $\blacksquare$ - DCH,  $\triangle$ - 4-CBE,  $\times$ - DMMP,  $*$ - EG].

(Fig. 1); 4-CBE was sorbed least while DCH has a comparatively higher sorption. As observed from Figure 1 the sorption of DMMP was intermediate between 2-CEE and DCH. DMMP shows almost similar sorption profile as that of 2-CEE, while uptake of DCH increases sharply with the increase in the time of exposure. Unlike IIR, in PI the mol % sorption (Fig. 2) was much higher and ranged from  $6.7 \times 10^{-3}$  for 4-CBE to  $264.3 \times 10^{-3}$  for EG, implying that IIR is a better protective barrier than PI.

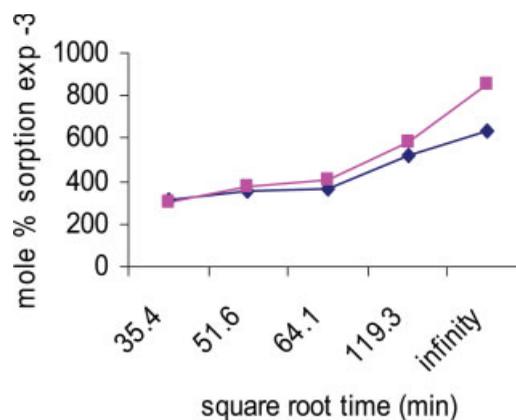
In our earlier studies<sup>6-8</sup> we recommended 2-CEE as a simulant for SM based on the observation that it is sorbed to a greater extent than SM in IIR. So, a barrier material providing resistance to 2-CEE would afford protection against SM as well. On the basis of these studies, NIOSH proposed that replacement of ethyl group of 2-CEE by butyl (viz. in compound 4-CBE) may approximate the transport parameters of the simulant to SM. However, the present study clearly indicates that 4-CBE shows a sluggish sorption; hence, if this compound is taken as a simulant, the protection potential values of barrier materials may be overestimated. On the basis of a similar logic, EG is not recommended as a simulant. OCT, DCH, and DMMP have a comparable sorption as that of 2-CEE and hence could be potential simulants.

The transport coefficient,  $n$ , polymer-permeant interaction parameter,  $K$ , and sorption coefficient,  $S$ , for the various systems, derived from the sorption plots in accordance with eqs. (1) and (3), are depicted in Table III. The molecular weight of sorbed molecules and their interaction with the polymer, together with extent of swelling and plasticization of the matrix, governs their uptake and sorption behavior. The extent to which molecules are sorbed and their mode of sorption in a polymer is dependent upon the relative strengths of the interactions between the permeant molecules and the polymer or between the polymer molecules themselves within the matrix. The sluggish sorption of 4-CBE is probably due to

its higher molecular weight than other simulants. For facilitating sorption it is also necessary to overcome the cohesive energy between the sorbed molecules. The lower sorption of EG in IIR is presumably due to its highly viscous nature and high cohesive energy attributed to the presence of hydrogen bonding. Despite prolonged duration of exposure the sorption of EG is not enhanced, implying that the EG/IIR interaction is insufficient to overcome the interaction between EG molecules.

A comparatively higher value of  $K$  for OCT and DCH in IIR and PI (Table III) indicates a relatively higher interaction of these elastomers with these compounds. Within the limits of experimental error, the sorption coefficient  $S$  also gives a fair idea of the polymer-penetrant interactions. The trend in  $S$  values as depicted in Table III indicates higher values for OCT and DCH as compared with other compounds, both in case of IIR and PI. These values are in agreement with % volume swell as well. A higher swelling of these elastomers by OCT and DCH leads to plasticization of the matrix with a subsequent increase in sorption.

From Table III it is also observed that with the exception of OCT/IIR, OCT/PI, and 2-CEE/PI,  $n > 0.5$ , thus implying a non-Fickian or anomalous mode of sorption in most cases. The  $D$  values in such cases calculated using eq. (2) are not representative and require suitable correction factors. Such an analysis was beyond the scope of the present study; hence, further investigation was limited to OCT which shows a Fickian mode of transport in both IIR and PI. Additionally, comparatively higher sorption of OCT among the studied simulants makes it attractive for further studies owing to the presumption that if protection against OCT is achieved by a barrier it would imply resistance against most of the other chemicals as well. Moreover, test time for specifying the protection criteria of a barrier can



**Figure 3** Sorption plots for OCT/IIR ( $\triangle$ ) and OCT/PI ( $\blacksquare$ ) systems.

TABLE III  
Transport Parameters for Simulants/Elastomer Systems at 298 K

Simulants	$n$		$K$ (g/g/min <sup>n</sup> )		Volume swell (%)		$S$ (mol m <sup>-3</sup> Pa <sup>-1</sup> )	
	IIR	PI	IIR	PI	IIR	PI	IIR	PI
2-CEE	0.5	0.4	0.22	0.30	9.0	43.3	0.005	0.026
DCH	1.0	0.6	0.06	0.17	56.3	324.2	0.032	0.184
4-CBE	0.5	0.9	0.07	0.23	18.3	220.5	0.008	0.097
OCT	0.3	0.3	0.40	0.32	230.9	192.1	0.1784	0.148
DMMP	1.0	0.8	0.10	0.15	0.7	62.2	0.0005	0.044
EG	1.0	0.8	0.67	0.16	1.2	9.7	0.001	0.0136

be minimized with OCT owing to adequate sorption even at shorter duration of exposure. Combined with nontoxicity and commercial availability, these features render OCT worth investigating as a potential simulant.

The  $D$  values for OCT/IIR and OCT/PI systems in accordance with eq. (2) differed by one order of magnitude, being  $6.95 \times 10^{-15}$  m<sup>2</sup>/s and  $3.74 \times 10^{-14}$  m<sup>2</sup>/s, respectively, indicating the relative impermeability of IIR. The highly saturated and closely packed isobutylene chains in IIR lead to a comparatively lower free volume<sup>6</sup> and hence a lower diffusivity. Since the pendant methyl groups are symmetrically substituted on the same carbon atom in the main chain, therefore during segmental mobility caused by bond rotation, the probability of an interchange of these methyl groups is significant, rather than the creation of free volume,<sup>6</sup> thereby rendering IIR relatively impermeable.

To further study the magnitude and dynamics of sorption in OCT/IIR as a function of its concentra-

tion and the amount of filler, sorption isotherms (Fig. 4) were obtained using the automated gravimetric analyzer. The hitherto used manual monitoring of weight gain upon sorption is time consuming; the detectable change in weight may take more than a week's time depending upon the thickness of the sample. Moreover, a precise control over environmental factors such as temperature and humidity is difficult. The automated system overcomes these limitations; the analysis is rapid (5–8 h, depending upon equilibration time).

As observed from Figure 4 for unfilled IIR, the mass uptake increased with the increase in relative pressure of OCT, reaching a value of 65% at unit concentration (saturated pressure). It was further observed that the isotherm for IIR lies toward the ordinate and for the filled IIR (C-10 and C-20) toward the abscissa, implying that interaction of OCT is higher in IIR and lowered upon incorporation of the filler. Consequently, the sorption of OCT is reduced by almost one third the value in unfilled

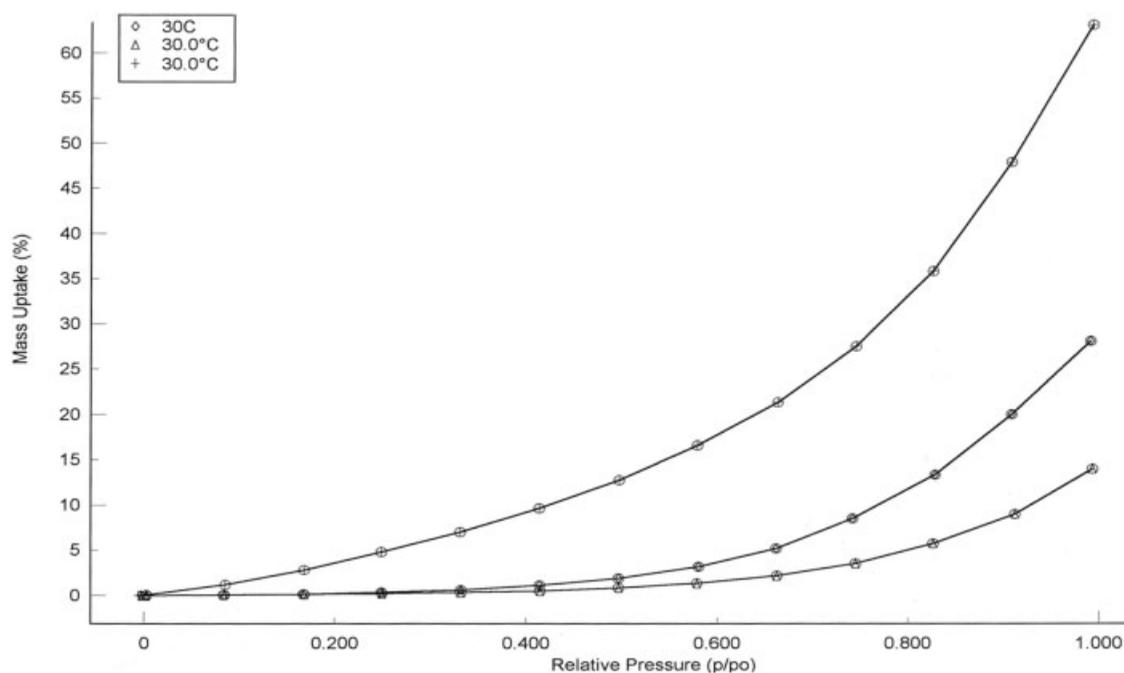


Figure 4 Sorption isotherms for (a) OCT/IIR, (b) OCT/C-10, and (c) OCT/C-20 systems.

IIR. Similar trend was reported<sup>8</sup> for SM vapor permeation in nonblack (C-0) and black (C-10, C-20) filled IIR membranes at 298 K monitored by gravimetric method. The sorption of SM decreased in the order C-0 > C-10 > C-20. Hence, protective potential of IIR may be enhanced by the incorporation of carbon black into the formulation. It seems likely that densely packed structures are formed when rubber is bound on the carbon surface, reducing the process of sorption through the matrix.<sup>8</sup>

### CONCLUSIONS

1. Among the simulants studied, 4-BCE shows the most sluggish sorption in IIR and PI while OCT, DCH, and DMMP have a comparable sorption as that of 2-CEE viz an earlier recommended simulant. However, with the exception of OCT/IIR, OCT/PI, and 2-CEE/PI, all other simulant/elastomer systems showed non-Fickian behavior.
2. OCT with a maximum extent of sorption is also amenable for studies using the automated gravimetric analyzer and is recommended as simulant of SM for testing of protective barriers.
3. IIR showed relatively lower sorption and diffusivity of OCT as compared with PI, indicating its higher protection potential. Incorporation of filler in IIR (Carbon black GPF N660) further reduced the extent of sorption, thereby implying an improvement in barrier performance.

The authors thank Er. K. Sekhar, Director, DRDE, for permitting Ms. Toral Parmar to work in DRDE as and when required and for keen interest in the study. The facilities extended by Dr. R. C. Malhotra, Joint Director, are gratefully acknowledged.

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