SURFACE FILMS OF ALKOXYCHLOROBENZENES

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(*Received* 11 *August* 1969 ; *revised* 14 *January* 1970)

Isotherms of surface films of methyl, ethyl and propyl ethers of 2-chlorophenol and 4-chlorophenol on water substrate have been determined in the range of 0-5 dynes/cm. with the help of a film balance. The films are in liquid expanded state. Their compressibilities range between 0·034 to 0·053 and the areas at zero compression, between 39·0 to 49·5A^2. Orientation of the molecules in the monolayer and a mechanism of permeation of aryl ethers in biological systems have been discussed.

Alkoxybenzenes, specially their chloro derivatives, are known to be good contact insecticides and bactericides. In order to function as such, a compound has to permeate through a barrier of cuticle and cell wall respectively, to pass into body fluid to interfere with some vital metabolic activity. Hence it should possess lipophilic as well as hydrophilic properties. These compounds are lipophilic in nature as is evident by constituent functional groups. As regards hydrophilic nature, the ether linkage is capable of functioning as a donor to form weak hydrogen bond but the strength of interactions of other centres in the compounds with water is expected to be of a very low order. The hydrophilic nature of the compounds can be established by the properties of surface films of the compounds on water substrate. A perusal of literature indicates that the surface films of such compounds have scarcely been studied. Therefore we have studied the film properties of methyl, ethyl and propyl ethers of 2-chlorophenol and 4-chlorophenol with the help of a modified Langmuir film balance in order to find out the state of the films and the molecular orientation. The isotherms have been determined in the film pressure range of 0·5 dynes/cm. as it sufficed for our purpose.

EXPERIMENTAL PROCEDURE

Chemicals

Methyl ethers of 2- and 4-chlorophenols: A mixture of chlorophenol (1 *M*), sodium hydroxide (1·1 *M*, 10 per cent) and dimethyl sulphate (0·8 *M*) was heated in a steam bath for 14 hours. Then dilute sodium hydroxide was added to the reaction mixture in order to decompose the unreacted dimethyl sulphate. After cooling, the mixture was extracted with diethyl ether, washed with water and dried over anhydrous potassium sulphate. The ether was removed by distillation and the aryl ether was obtained by distillation under reduced pressure. The ethers were further purified by second distillation, collecting the fraction at the exact boiling point.

Ethyl ethers of 2-and 4-chlorophenols: A mixture of chlorophenol (1 *M*) sodium hydroxide (1·1 *M*, 10 per cent) and diethyl sulphate (0·8 *M*) was heated on a steam bath for 16 hours and the aryl ether was obtained as usual. The ethers were further purified by second distillation, collecting the fraction at the exact boiling point.

Propyl ethers of 2-and 4-chlorophenols: Chlorophenol (1 *M*) and n-propyl bromide (1·1 *M*) were added to sodium ethoxide (1·5 *M*) in absolute alcohol and refluxed on a steam bath for three hours and the aryl ether was obtained as usual. The ethers were further purified by second distillation and collecting the fraction at exact boiling point.

Apparatus

Cenco hydrophil balance—The balance consists of a bronze tray 65 cm. long and 14 cm. wide. It is provided with levelling screws and a movable barrier. The inside of the tray is thoroughly coated with baked bakelite lacquer. A meter scale is attached along one edge of the tray for the measurement of the distances between the float and the barrier. A float of mica is attached to the two ends of the bridge by means of nylon threads fixed with wax such that the system of mica and the nylon threads cover the complete width of the tray. A torsional device consists of a suspension for a torsion wire, to one end of which a vernier pointer is attached for indicating the torsional force applied to the mica float on a circular graduated scale over which the vernier travels. The movable barrier is used to vary the area of the film.

Determination of Film Pressure

The balance was levelled to perfect horizontal position and the tray was filled with distilled water until the meniscus rose above the edge of the tray. The surface of the water on both sides of the float was swept free of contaminants by scraping the excess water away from the float by means of the straight edge of the movable barrier. The barrier was then kept at a considerable distance from the float.

Standard solution of an aryl ether was prepared by dissolving about 0·1 gm in 100 ml of A.R. benzene. The solution was taken in a syringe and a known weight (volume about 0·05 ml.) was added on the water surface between the float and the barrier. Benzene serves the dual purpose of diluting the aryl ether, so that its small quantity is dispersed over a large area and diminishing the viscosity of the ether so that the film is formed almost instantly. The experimental evidence indicates that under the experimental conditions, 30 minutes were more than sufficient for benzene to evaporate off completely from the water surface. Hence after this period the movable barrier was carefully moved towards the float until a point was reached at which the film begins to exert a pressure against the float. A number of readings of the film area, in terms of the position of the barrier, and

TABLE 1

SOME PROPERTIES OF ALKOXYCHLOROBENZENE MONOLAYERS

Name	Boiling point (°C)	Compressibility	Area at zero compression (A^2)	Film thickness (A)
1-methoxy-2-chlorobenzene	195-6	0·034	49·5	6·0
1-ethoxy-2-chlorobenzene	208	0·036	47·5	5·3
1-propoxy-2-chlorobenzene	119/26 mm.	0·048	43·0	6·6
1-methoxy-4-chlorobenzene	198	0·043	39·0	8·7
1-ethoxy-4-chlorobenzene	212	0·052	41·5	6·1
1-propoxy-4-chlorobenzene	224-5	0·053	44·0	6·7

the corresponding film pressure, in terms of the degrees of torsion necessary to bring the pointer back to zero pressure were taken. The experiments were performed in duplicate with all the ethers.

As the instrument was not equipped with a thermostat the observations were taken with water at room temperature which was different on different occasions. The temperatures of measurements were between 31 to 35°C.

RESULTS AND DISCUSSIONS

Film pressure π in terms of dynes/cm. and the corresponding area occupied by a molecule σ in terms of A^2 were calculated from the data obtained in the experiments. The isotherms giving correlation between π and σ for the compounds are given in Fig. 1 and Fig. 2. The isotherms were practically retraced in the duplicate experiments with all the ethers. Thickness of the films has also been calculated. All the above data have been reported in Table 1.

The compressibility K of the films has been calculated by the expression $K = \frac{-1}{\sigma}\left(\frac{d\sigma}{d\pi}\right) T$. The compressibilities range between 0·034 to 0·053. This order indicates[1,2] that the films are in the liquid expanded state L_1. In each homologous series the compressibility increases with increase in the number of carbon atoms in the alkyl chain.

The average area of a molecule at zero compression has been determined by extrapolating the isotherm to zero pressure. The areas range between 39.0 to 49·5 A^2. The order is in accordance with the fact that the liquid expanded films tend to an area about 48 A^2 at room temperature.

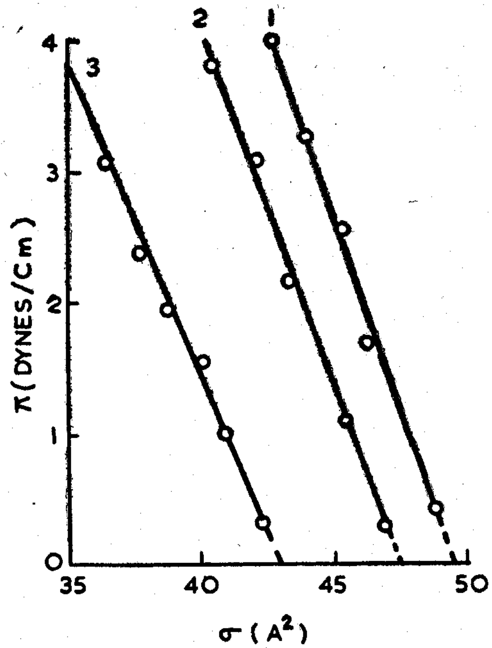

Fig. 1—Isotherms of 1-alkoxy-2-chlorobenzenes (1-methoxy, 2-ethoxy, 3-propoxy).

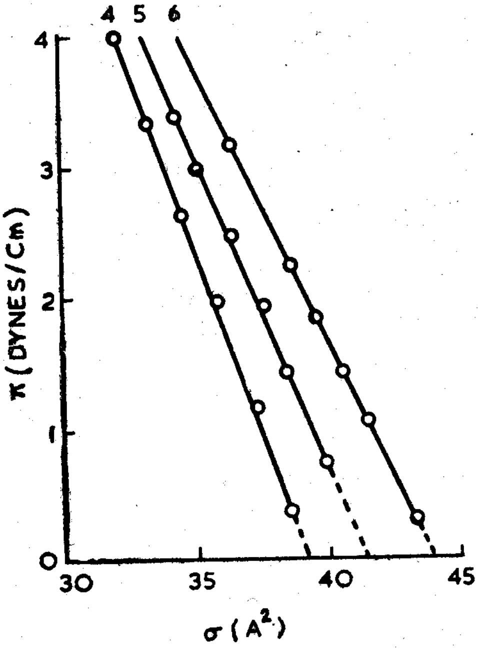

Fig. 2—Isotherms of 1-alkoxy-4-chlorobenzenes (4-methoxy, 5-ethoxy, 6-propoxy).

The thickness of the film has been calculated by the expression $\frac{M.d}{0.6\ \sigma_0}$ where M is the molecular weight, d, the density of the liquid and σ_0 the area of the molecule at zero compression. In the calculations the film density has been assumed to be equal to bulk density. The order of film thickness is a definite evidence regarding monomolecular nature of the film.

The alkoxychlorobenzenes possess three centres of interaction with water molecules through hydrogen bonding, oxygen[3], chlorine and π electrons of arene nucleus [4, 5]. The alkyl group is the centre of repulsion for water molecules. This action is more prominent with chain lengthening.

The presence of more than one centre of attraction for water molecules is an important cause for liquid expanded state of the monolayers. In order to compress the monolayers of such compounds, more pressure is required to overcome the attraction of second and third centres of attraction. Consequently the compressibility is less than that of gaseous films.

The orders of the film thickness and molecular area at zero compression furnish definite evidence regarding the monomolecular nature of the films. The area in these compounds range between 39·0 to 49·5 A^2, while in the case of phenols and other simple benzene derivatives[6-8], having para-substituted long alkyl groups, the area is 24 A^2. There fore the molecules of the compounds are not oriented in the erect form of p-alkyl phenols. In most of the cases, the film thickness is less than the erect length of the molecules. The density of π electron cloud round the benzene ring is high on both the sides which exert equal attraction for water molecules. Therefore the benzene ring should not lie flat over the water surface. This is confirmed by the order of the molecular area which should have been much higher in the case of such an orientation.

According to the views of Mittleman & Palmer[9] regarding the orientation of molecules in liquid expanded films, the orientation of alkoxychlorobenzene on water substrate is statistically distributed amongst various possible configurations. But the most predominant orientation of the compounds, depending on the relative strength of attraction and repulsion of various centres in a molecule, is given in Fig. 3.

Amongst the three interaction centres, oxygen has maximum affinity towards water. Therefore the molecules may not be exactly horizontal but slightly bent with the oxygen

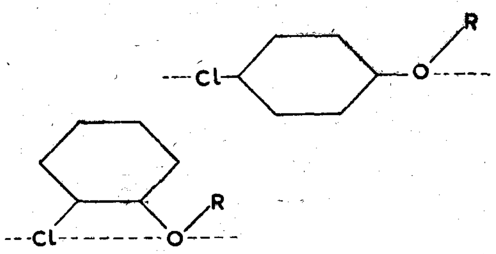

Fig. 3—Predominant orientation of alkoxychlorobenzenes on water substrate.

atom at the lowest point. The bending may be more pronounced in 1-alkoxy-4-chlorobenzenes. The repulsion of the alkyl group from water increases with lengthening of the chain. Therefore the bending of the molecules is expected to decrease with chain lengthening.

The strongest centre of attraction for water in alkoxychlorobenzenes is the ether group which forms only weak hydrogen bonding. Therefore the monolayers should not contain any appreciable amount of water between the molecules.

The formation of monolayers by the compounds on water substrate affirms the attraction of the ether group towards water. The group is also lipophilic in nature [10]. Therefore the compounds containing the ether group are capable of dissolving and diffusing in lipoid materials. The dual nature of the ether group may be facilitating the permeation of the aryl ethers into biological systems in order to interfere with some vital metabolic activities and thus to exert toxic influence. In their action as bactericides[11], three main types of resistances are encountered in the permeation to protoplasm : (a) water to cell membrane which is lipoid in nature; (b) diffusion through the membrane material; (c) passing out from membrane to protoplasm which is an aqueous suspension. In their action as contact insecticides[12], they have to permeate through cuticle. In this process again there are three types of main resistances : (a) passage to epicuticle which is lipoid in nature ; (b) diffusion through epicuticle; (c) passage to endocuticle which is constituted by chitin, protein and water. The toxic influence of a compound on insects can be exerted only if it can permeate to endocuticle. In both the actions, the first and second resistances are fairly counteracted because of the lipophilic nature of the ethers, and the third because of attraction towards water molecules. In the last phase of permeation the molecules concentrate at the lipoid-water interface from where they pass out to the aqueous phase to exert their toxic action. The concentration in the aqueous phase is also dependent on the partition coefficient of the compound between the two phases. In the case of halogenated phenyl ethers, having three centres of attraction for water, the rate limiting factor is the diffusion across the water-membrane interface in the direction of water to membrane[13].

ACKNOWLEDGEMENT

The authors are thankful to the Director, Defence Science Laboratory, Delhi for his kind interest in this work.

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