Surface Films of Phenolic Compounds.

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An investigation of the surface structure of di- and poly-phenols has been undertaken by the Langmuir trough technique, concentrated ammonium sulphate solutions being used to make the compounds form insoluble monolayers.

The diphenols form hair-pin structures when the hydrocarbon chain joining the phenolic group contains more than three methylene groups. There is an analogy between melting points of the compounds and their monolayer stability.

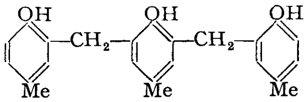
The polyphenols form gel films in which the structure of the molecule is such that one phenolic group is oriented underneath the array of the polyphenolic chain.

The adsorption of the diphenols from their aqueous solution on amine monolayers has been investigated.

CONCENTRATED ammonium sulphate solutions have recently been used to stabilise surface films of otherwise water-soluble copolymers (Allan and Alexander, *Trans. Faraday Soc.*, 1950, **46**, 316). Hence it seemed possible that polypolar compounds used for interaction with monolayers when injected into a dilute aqueous substrate might themselves give stable vaporous films on concentrated salt solutions. In the experiments described below the surface behaviour of a series of di- and poly-phenols was examined and compared with the interaction of the diphenols with amine monolayers.

EXPERIMENTAL

Materials.—The preparation of an increasing chain series of di- and poly-phenols has been described in detail by Pepper (Ph.D. Thesis, Cambridge, 1941) and we are indebted to him for the gift of samples. The polynuclear phenols were formed by repetition of the phenolic nucleus, the units being joined by a CH_2 link, thus :



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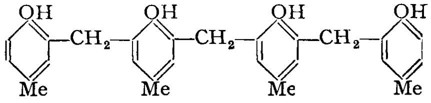


For convenience these are referred to as the " trimer " and " tetramer " and were prepared by Pepper, modifying the methods of Koebner (*Z. angew. Chem.*, 1933, **46**, 251) and Megson and Drummond (*J. Soc. Chem. Ind.*, 1930, **49**, 245). The diphenol series was formed by increasing the length of the hydrocarbon chain between two phenolic nuclei, *viz.*,

$$p\text{-HO}\cdot C_6H_4\cdot[CH_2]_n\cdot C_6H_4\cdot OH\text{-}p,$$

where n varies from 0 to 6. The first two members of the series are well known and were prepared by standard methods. The third member, *pp'*-dihydroxydibenzyl ($n = 2$) was prepared by reduction of anisil followed by demethylation with hydrobromic acid. The fourth member, 1 : 3-di-*p*-hydroxylphenylpropane ($n = 3$), was prepared *via* *pp'*-dimethoxychalkone, which was reduced to di-*p*-methoxyphenylpropane and the latter demethylated by aqueous acetic–hydrobromic acid.

The di-*p*-hydroxyphenylbutane was synthesised by using succinic anhydride and introducing the *p*-methoxyphenyl nuclei one at a time.

To prepare the sixth member, 1 : 5-di-*p*-hydroxyphenylpentane, Pepper first condensed anisaldehyde with acetone and obtained 1 : 5-di-*p*-methoxyphenylpentan-3-one by hydrogenation. This was reduced to 1 : 5-di-*p*-methoxyphenylpentane and the latter demethylated. The seventh member, 1 : 6-di-*p*-hydroxyphenylhexane was prepared by making dianisoylbutane from adipyl chloride and anisole and reducing it to 1 : 6-di-*p*-methoxyphenylhexane which was demethylated with aqueous acetic–hydrobromic acid.

The diphenols were soluble in aqueous ethanol and the polynuclear phenols dissolved in 10% alcohol–benzene. The solutions for spreading were *ca.* 0·5 mg./ml. and the substrates were solutions of " AnalaR " quality ammonium sulphate.

The interaction of the increasing chain series with octadecylamine hydrochloride films was examined. The amine films were spread from benzene–alcohol mixtures, and the phenolic compounds for injection were prepared in M/50-sodium hydroxide at concentrations of 0·5 mg./ml. In these experiments the substrates were M/50-sodium hydroxide and M/250-borate buffer.

Method.—The apparatus used was a Langmuir trough as modified by Alexander, Glazer, and Saggers (unpublished experiments) for automatic recording of surface pressure–area curves. The optical lever arrangement had a light spot indicating the surface pressures on a paper-covered drum. The drum rotated as the film was compressed, the steady rate of compression being controlled by an oil-immersed piston. It was found convenient to hold a pencil point on the light spot as the drum rotated. Calibration was carried out by marking the light spot for various small weights in the scale pan, with the drum stationary and a clean surface between the barriers and behind the float.

After the film had been spread the plunger was allowed to fall slowly in the oil cylinder, the speed of compression being regulated within wide limits. The rate of compression was usually about 3 cm. of trough length per min. but variation of the rate did not affect the results within reasonable limits. The films were spread from an all-glass micrometer syringe.

The phenolic substances were injected under the surface of the amine films by a pipette which was moved across the trough as the solution was expelled, directing the flow under the film from behind the barrier, thus avoiding contact with the film.

RESULTS and DISCUSSION

(i) *Diphenols on Concentrated Ammonium Sulphate Solution.*—The lowest members of the homologous series dissolved even in saturated ammonium sulphate and stable films could only be obtained with the three highest members ($n = 4$, 5, and 6). These were spread on 37·5% w/w ammonium sulphate solution and the highest member of series ($n = 6$) could be spread on 20% w/w solution. The Π–A curves shown in Fig. 1 are more expanded than the curves of ωω′-diresorcinyldecane obtained by Adam (*Proc. Roy. Soc.*, 1928, *A*, **119**, 639). The curves are seen to be similar, except in the values of the collapse pressures. These, together with the minimum areas at collapse are shown below.

No. of CH_2 groups, n	Minimum area at collapse pressure, Å^2/molecule.	Collapse pressure, dynes/cm.	M. p. of crystal
4	50	15·2	155°
5	48	27·0	101
6	53	13·3	142

If it is assumed that the area at collapse is the minimum area of close packing on the surface, it appears that both phenyl nuclei remain in the surface since the areas are approximately equal and equivalent to twice the area of a benzene ring at zero compression, *ca.* 24 Å^2. From molecular models it seems that there is little steric hindrance to compression of the molecule from a flat position to one where the phenyl rings are vertical to the surface and close packed with the methylene groups in the air phase. There is seen to be good agreement between collapse areas of the various stable compounds.

A further interesting point is shown in the above Table. The collapse pressure of the $n = 5$ compound is almost twice that of the other two. This is believed to be closely related to the alternate melting point phenomenon of homologous series in three dimensions. Several authors (see Smith, *Ann. Reports*, 1938, **35**, 255) have attributed this odd–even alternation in melting point to the ease of packing in the crystal form, and it is suggested that the collapse pressures of the diphenols are also functions of the ease of packing in the crystal form.

(ii) *Polyphenols on Concentrated Ammonium Sulphate Solutions.*—The two polynuclear phenols gave stable, fairly condensed, gel-like films on 37·5% w./w. ammonium sulphate solution, the Π–A curves being shown in Fig. 2. Although these films were not studied in detail, the areas at zero surface pressure and the minimum areas at collapse are noteworthy.

It would appear that each compound is initially fixed with all its phenolic nuclei in the surface. As these are packed more closely, there is a reorientation of the molecule so that one of the phenolic nuclei leaves the surface. At first sight this seems surprising, but consideration of steric effects with models shows that it is possible to pack the polar groups very closely together with one phenolic nucleus almost flat in the surface and one tilted so that the third is above the first and not contributing to the molecular area. This can be visualised as a box-like formation parallel to the surface, the fourth phenyl group being parallel to the second. Although this concept requires to be confirmed by surface-potential measurements it seems the only way to explain the reproducible and closely corresponding Π–*A* curves.

FIG. 1. Π–A *curves for diphenols on concentrated ammonium sulphate solutions.*

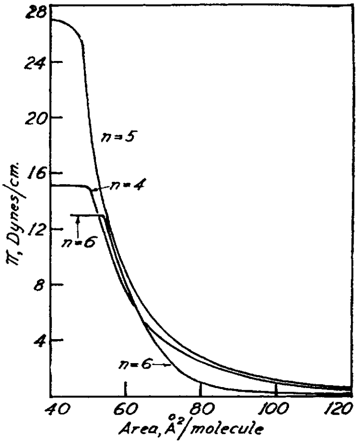
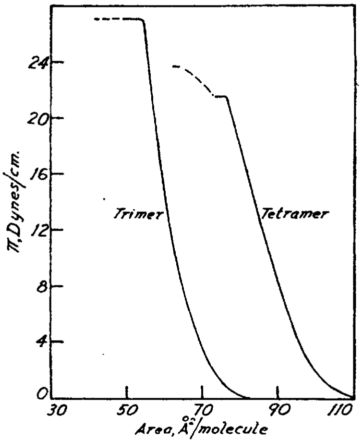


FIG. 2. Π–A *curves for polyphenols on* 37·5 w/w *ammonium sulphate solutions.*



(iii) *Interaction of Diphenols with Amine Monolayers.*—Films of octadecylamine hydrochloride on M/250-borate (pH 9) and M/250-sodium hydroxide (pH 12) were not affected by solutions of the *pp*′-dihydroxydiphenyl, although the 1 : 6-di-*p*-hydroxyphenylhexane showed a slow but stable interaction with both substrates. The Π–*A* curves are shown in Fig. 3. Pepper (*loc. cit.*) prepared both series of compounds for injection under amine monolayers to examine the effect on the films of the number and spacing of the polar groups and the size of the non-polar portion. Although he was unable to carry out detailed experiments he stated that there was considerable penetration of the amine film by all the compounds. Unfortunately, his experiments were complicated by injecting high concentrations of the diphenol (*ca.* 10 mg./l.) under the film so that thick polylayers of the diphenols were formed on each side of the barrier. In these experiments the concentration of the diphenol injected was reduced to a final value of 1 mg./l. in the substrate and a more dilute buffer was used. No film formation of the diphenol was observed on the surface of the substrate behind the barrier. The marked interaction of the 1 : 6-di-*p*-hydroxyphenylhexane is shown in Fig. 3, and has interesting characteristics. Although some two hours are required before the interaction is complete, thereafter the Π–*A* curve is reproducible on compression and re-expansion several times. A stable association seems to be formed between the amine and the diphenol, so that the latter is held by the amine in the surface and at the same time the octadecylamine-head groups are kept apart by the diphenol against their hydrocarbon chain cohesion. Cockbain and Schulman (*Trans. Faraday Soc.*, 1939, **35**, 716) studied the interaction of amines with organic acids and showed that the concentrations of organic acid in the substrate giving the same amount of change in the Π–*A* characteristics depend greatly on the nature of the non-polar residue. Thus, increasing the non-polar portion of the diphenol by 6 methylene groups results in marked interaction with the amine for the same concentration of diphenol in the substrate. This is analogous to the results of Cockbain and Schulman with azelaic acid and thapsic acid, $[CH_2]_n(CO_2H)_2$, $n = 7$ and 14, respectively.

The markedly expanded film in the experiments on M/250-borate buffer [curve (*a*), Fig. 3] shows a sharp kink at an area of 27 Å^2/molecule and a pressure of 24 dynes/cm. This area at the kink point is considered to confirm the belief that the diphenol can take up a hairpin-like structure on the surface. In this case it is thought that the diphenol is hooked under the amine film with the non-polar portion forced into the substrate. When the area of the amine film reaches 27 Å^2/molecule, the diphenol " sub-film " is close packed, *i.e.*, one diphenol molecule is attached beneath two amine groups. Below 27 Å^2/molecule the association of the amine and the diphenol is disrupted and the diphenol is squeezed partly into the substrate until the amine film itself is close packed (*c*).

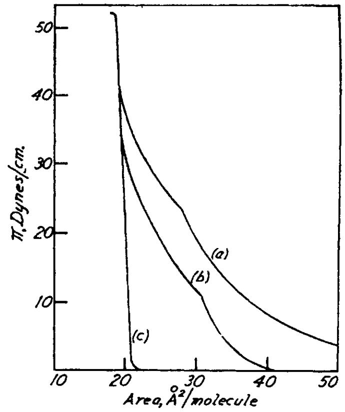


FIG. 3. Π–A *curves for octadecylamine hydrochloride with* 1 : 6-*di*-p-*hydroxyphenylhexane injected into substrate :* (a) M/250-*borate buffer,* pH 9; (b) M/50-*sodium hydroxide,* pH 12.

When M/50-sodium hydroxide is substituted for the M/250-borate buffer the kink point occurs at a slightly larger area, *ca.* 32 Å^2/molecule, and at a lower pressure, 9 dynes/cm. This may be due to salt formation of the phenolic group with the alkali at the increased pH of the substrate.

Surface-potential measurements are clearly necessary to confirm the orientations suggested by the surface pressure–area curves. All the same, there is strikingly close agreement between the members of the diphenol series and between the two polyphenols. The interaction between the amine monolayers and " sub-film " of 1 : 6-di-*p*-hydroxyphenylhexane supports the suggestion that the diphenol can take up a hairpin-like structure at an interface.

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