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MONOMOLECULAR FILMS ON WATER: THE ORIENTED ADSORPTION OF DERIVATIVES OF BENZENE[1]

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Introduction. Films of Benzene Derivatives on Water

This investigation was made in order to secure experimental evidence concerning the orientation of the molecules of certain derivatives of benzene in films upon the surface of water. The simplest method would be to obtain insoluble, non-volatile substances and allow these to spread out into monomolecular films, and then to determine the force of compression of each film directly by the use of a balance. Benzene itself spreads on a water surface, but is too volatile to be used in this way, and all of its simple derivatives are too volatile, too soluble, or else they will not spread. For these reasons it was decided to use soluble substances and to determine the surface tensions of their solutions at different concentrations.

Experimental Methods and Purification of Materials

The surface tensions of all of the solutions were determined at 20° by the drop-weight method as outlined by Harkins and Brown, and their correction curve was used in the calculation of the results.[2]

Phenol.—The phenol used was of the best grade obtainable. This was frozen

TABLE I

SURFACE TENSION OF SOLUTIONS OF PHENOL AND THE ADSORPTION OF PHENOL

Moles per liter	Surface tension; dynes per cm.		Density of soln.	Molecules per sq. cm. $\times 10^{-14}$	Area Å.	$\sqrt{\text{Area}}$ Å.	Thickness of uniform film Å.
	Vapor	Dry					
0.0025	72.62		0.9982	0.062	1600	40	
.005	72.17		.9982	.16	600	25	
.01	71.69		.9982	.32	320	18	
.0125	71.26		.9982	.39	250	16	
.025	69.92		.9983	.85	120	11	
.05	66.50	66.17	.9988	1.50	67	8.2	
.075	64.93	63.54	.9989	2.01	50	7.0	
.10	61.12	60.93	.9990	2.73	36.6	6.0	4.0
.15	56.98	56.38	.9994	2.73	36.6	6.0	4.0
.20	53.97	53.31	.9999	2.73	36.6	6.0	4.0
.25	51.34	51.12	1.0004	2.73	36.6	6.0	4.0
.30	49.13	49.00	1.0010	2.73	36.6	6.0	4.0
.40	45.84	45.51	1.0019				
.50	44.02	43.79	1.0022				
.60	42.85	42.71	1.0036				

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[1] Presented in 1919 to the University of Chicago by E. H. Grafton in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Harkins and Brown, THIS JOURNAL, **41**, 499 (1919).

thrice, the crystals were melted and distilled twice at low pressures, and the final material was frozen from the second distillate, which was obtained at 61° at a pressure of 3 to 5 mm.

Pyrocatechol, Resorcinol, Hydroquinol and Pyrogallol.—These substances were used as prepared by Kahlbaum. To guard against oxidation, air-free conductivity water saturated with hydrogen was used to dissolve each substance, and hydrogen was also the gas kept in the drop-weight apparatus. A fresh solution was made immediately before carrying out the determination in which it was used.

Each surface tension given in the tables is the mean of six determinations made upon two solutions of the same concentration.

Discussion of Results and Evidence Concerning Orientation

The results obtained from the experimental work are summarized in Tables I and II, and Fig. 1. It may be noted that if the solutions of phenol are dropped into a weighing bottle which already contains some of the solution, so that the air is saturated with the vapor, the surface tensions are higher by as much as 1% than if the drops fall into a dry bottle.

TABLE II

SURFACE TENSION OF SOLUTIONS OF DIHYDROXY DERIVATIVES OF BENZENE AND THE ADSORPTION ON WATER

Moles per liter	Surface tension	Density of solution	Molecules per sq. cm. $\times 10^{-14}$	Area Å.	$\sqrt{\text{Area}}$ Å.	Thickness of uniform film Å.
HYDROQUINOL (PARA)						
0.05	72.27	0.9995	0.23	430	21	
.10	71.63	1.0007	.25	403	20	
.20	70.71	1.0025	.38	260	16	
.30	70.19	1.0050	.44	230	16	
.35	69.65	1.0061	.48	210	14.5	
.45	69.51	1.0080	.53	190	13.8	
.50	69.05	1.0093	.54	185	13.6	(0.7)
RESORCINOL (META)						
.03	72.12	0.9986	0.26	380	19.5	
.05	71.39	0.9995	.30	330	18.3	
.10	70.62	1.0007	.46	216	14.7	
.15	69.62	1.0016	.61	164	12.8	
.20	68.84	1.0025	.66	152	12.2	
.30	67.74	1.0050	.71	140	11.9	
.40	66.80	1.0068	.79	127	11.3	
.50	66.24	1.0093	1.04	96	9.8	1.4
.60	65.44	1.0116	1.04	96	9.8	1.4
.75	64.36	1.0146	1.04	96	9.8	1.4
1.0	63.41	1.0203	1.04	96	9.8	1.4
1.5	61.14	1.0317	1.04	96	9.8	1.4
2.0	60.46	1.0408	1.04	96	9.8	1.4
3.0	58.63	1.0648				
4.0	58.16	1.0872				
5.0	57.57	1.1101				
6.0	57.06	1.1316				

TABLE II (*Concluded*)

Moles per liter	Surface tension	Density of solution	Molecules per sq. cm. $\times 10^{-14}$	Area Å.	$\sqrt{\text{Area}}$ Å.	Thickness of uniform film Å.
		PYROCATECHOL (ORTHO)				
0.03	72.08	0.9986	0.11	880	30	
.05	71.66	0.9995	.41	250	16	
.10	69.72	1.0007	.89	113	11	
.20	66.83	1.0031	1.26	79	9	
.30	66.44	1.0053	1.64	61	7.8	
.40	62.42	1.0078	1.81	55	7.4	2.4
.50	60.78	1.0101	1.81	55	7.4	2.4
.60	59.67	1.0127	1.81	55	7.4	2.4
.75	57.75	1.0163	1.81	55	7.4	2.4
1.0	55.74	1.0222	1.81	55	7.4	2.4
2.0	51.56	1.0454				
		PYROGALLOL (1, 2, 3)				
0.1	71.71	1.0022	0.46	216	14.7	
.2	70.38	1.0058	0.76	132	11.5	
.3	68.24	1.0100	1.08	93	9.6	
.5	65.74	1.0177	1.65	61	7.8	
.6	64.87	1.0208	2.34	42.7	6.5	3.2
.75	62.37	1.0252	2.34	42.7	6.5	3.2
1.00	60.00	1.0359	2.34	42.7	6.5	3.2
1.50	56.10	1.0546	2.34	42.7	6.5	3.2
2.0	53.80	1.0733				

The most closely packed monomolecular film obtained contains the following numbers of molecules per sq. cm.: 2.73×10^{14} for phenol, 2.34×10^{14} for pyrogallol, 1.81×10^{14} for pyrocatechol, 1.04×10^{14} for resorcinol, while in the case of the *para* compound, hydroquinol, the solubility is not sufficiently great to give anything but a loosely packed film, and the largest number of molecules is 0.54×10^{14}. It may be seen that in every instance except with the *para* compound, the constancy of the adsorption over a considerable range of concentrations indicates that a monomolecular film of the "condensed" type is formed.

The last column in each table gives the thickness which the monomolecular film would have, provided the substance were spread in a uniform sheet of the same density as the substance in bulk. The surprising feature exhibited by these results is the extremely small average thickness of the organic part of the film obtained in this way; this for resorcinol is as low as 1.4×10^{-8} cm. (1.4 Å.), which is smaller than the diameter of a hydrogen molecule. Such values seem to indicate that the organic part of the film is not uniform in thickness.

Both Langmuir[3] and Harkins, Davies and Clark,[4] have considered the

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[3] Langmuir, *Chem. Met. Eng.*, **15**, 468 (1916).

[4] Harkins, Davies and Clark, THIS JOURNAL, **39**, 541 (1917).

probable orientation of derivatives of benzene in surfaces. Sugden[5] considers that the evidence presented for the orientation of such molecules, is entirely inconclusive.

If benzene is considered to have a structure somewhat analogous to its plane formula, that is, if it is a thin hexagonal disk, though probably not plane, the orientation of its derivatives which contain active groups such as the hydroxyl group, may be and has been worked out on the basis of the orientation theory. This theory indicates that active groups tend to bury themselves inside the surface. Thus with phenol, the hydroxyl group would bury itself in the water, and the phenyl group would lie toward the outer part of the surface. Here the area occupied per molecule in the monomolecular film is 36.6 Å. of area (10^{-16} sq. cm.), or about the same as for butyric, valeric, caprylic, or caproic acid.

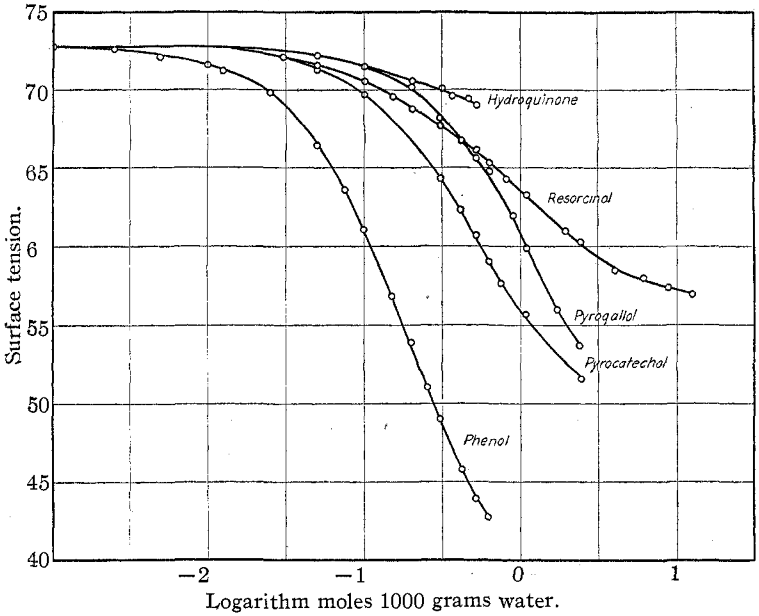

Fig. 1.

If the *ortho* groups in pyrocatechol are adjacent in space, the orientation of its molecules should be almost the same as for phenol. Here, the area per molecule is 55 Å., while for pyrogallol, with three presumably adjacent groups it is 42.4 Å. In the case of the *meta* compound the hydroxyl groups are not supposed to be adjacent, so the molecule would not be expected to be turned so much on edge, and the area occupied should be larger, as it is, 96 Å.; with two opposite, or *para* groups, it might be expected that the two groups would bury themselves equally, so that the

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[5] Sugden, *J. Chem. Soc.*, **125**, 1167 (1924).

benzene ring would be spread out on the surface, that is, the area should be the largest of all, as it is seen to be, though unfortunately the solubility of this substance is not sufficient to give a condensed monomolecular film.

Thus, the change in the area per molecule as a change is made from phenol to the *ortho*, *meta* and *para* disubstitution products in order, is just in the order predicted by the orientation theory, but the change is greater than is to be expected from the changed orientation of the molecules alone. This is evident also in the values which represent the mean thickness of the film, since when the compounds are taken in the same order, the films become thin more rapidly than would be expected.

This seems to indicate the probability that the thicker the film, that is, the more perfectly the molecules are set on edge by the orienting group, as with phenol, the larger are the areas of attachment between adjacent organic molecules in the film. As the film is thinned these attractions decrease, and the organic molecules are more free to move over the water surface, so that in the films of pyrocatechol and hydroquinol these molecules are to a considerable extent surrounded by molecules of water in the film itself, while with phenol the organic molecules predominate. That such a film is in a highly agitated, and not at all in a static condition, has been pointed out by one of the writers.[6]

When the molecules of these substances pass from the liquid into the surface region, the decrease of potential energy is greatest for phenol. Of the dihydroxy derivatives the decrease in potential energy is greatest for the *ortho*, intermediate for the *meta*, and least for the *para* compound, which is exactly according to the predictions of the orientation theory.

According to Bragg, the dimensions for a unit cell in a crystal of naphthalene are a = 8.34, b = 6.05, c = 8.69 Å. and for anthracene a = 8.7, b = 6.4 and c = 11.6, where the molecule is supposedly so placed that c is its length. From these data, and taking into consideration the fact that each unit cell contains two molecules, the dimensions of a molecule of benzene may be calculated as corresponding to a disk about 6 Å. in diameter, and 4.1 Å. thick. This corresponds almost exactly with the dimensions found for the space occupied by a phenol molecule on the surface of water. From data by Morgan, Langmuir[7] calculates that on water the area is 34 Å.^{2}, which corresponds to a thickness for a uniform film of 4.3 Å., so he concludes that the benzene ring lies flat on the surface. While this is the hypothesis suggested by the apparent coincidence of the numbers, the results obtained by us on the *ortho*, *meta* and *para* dihydroxy derivatives suggest rather that the molecule lies so tilted that the hydroxyl group is below, while the phenyl group is tilted on edge or on end. According to the figures derived from Bragg's work this would mean that

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[6] Harkins, "Colloidal Behavior," McGraw-Hill Book Co., **1924**, p. 149.

[7] Langmuir, THIS JOURNAL, **39**, 1895 (1917).

about 25 Å.^{2} of area are covered on the average by the phenol molecule, and the remaining 11.5 units of area are not so covered.

According to Morse the structure of benzene is on the whole octahedral, with a distance of 2.4 Å. between opposite carbon atoms, but the exact form and the distances of the hydrogen atoms and the hydroxyl groups depend upon the type of substitution. The most concentrated phenol film obtained by us is undoubtedly a *condensed film*, and probably obeys Hooke's law in its compression, but if the vertical orientation of the molecule is assumed, the film is not tightly packed if the dimensions used are those derived above from Bragg's data, but it may be closely packed if Morse's structure is assumed.

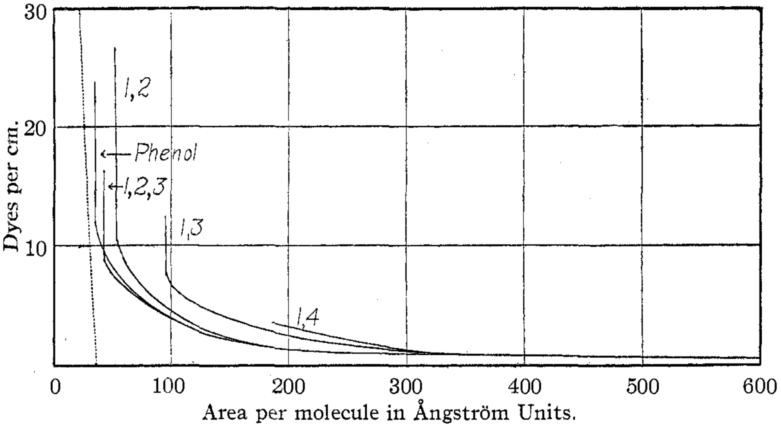

Fig. 2.—Force of compression for monomolecular films of phenol and its hydroxy derivatives on the surface of water. The force of compression is assumed to be equal to the surface tension of pure water minus the surface tension of the solution which is covered by the film. The dotted line represents direct measurements of the force of compression of a film of phenanthrol as made by Harkins and Morgan. The curved portion of the lines for phenol and its derivatives represent expanded or "gaseous" films, while the straight portions represent condensed films. Note that phenanthrol, though its molecules are very large, occupies the smallest area, while the *o*-dihydroxy phenol occupies the largest area.

If, however, the area given by the most tightly packed film of resorcinol (*meta*), 96 Å.^{2} is considered, it is seen that by no possible arrangement is it possible to account for such a large area on the basis of close packing, so it is necessary to conclude that the surface of the water is not entirely covered by the molecules of the organic substance, which is the conclusion reached in an earlier paragraph.

In Tables I and II the values inclosed in brackets refer to the most tightly packed film obtained in each case. A careful analysis of the data from which these values were obtained shows that the areas which are cited as constant in the table, for example, 36.6 Å.^{2} for phenol, actually increase slightly as the concentration increases, so that the general form for the compression is that indicated in Fig. 2. For comparison this figure gives the results obtained by the direct compression of phenanthrol in experiments by Harkins and Morgan.

The values for the adsorption obtained in Tables I and II were calculated by the use of Gibbs' equation $\mu = -\frac{1}{RT}\frac{d\gamma}{d\, ln\, c}$, in which γ is the surface tension and c is the concentration in moles per liter. Since the highest concentrations used in calculating the adsorption are 0.3 for phenol, 1.5 for pyrogallol, 1.0 for pyrocatechol, and 2 for resorcinol, it is apparent that the use of activities in place of concentrations would produce only a minor effect upon the results.

Summary

The areas occupied in films by the molecules of various hydroxyl derivatives of benzene have been obtained by determining the surface tensions of solutions of these substances. The probable orientation of the molecules of these substances on the surface of water is discussed, and the areas per molecule and the thickness calculated for uniform films are compared with the dimensions obtained for molecules of benzene, naphthalene and anthracene in their crystals. The conclusion is reached that while phenol, pyrocatechol, resorcinol and pyrogallol give condensed films, that is, films of extremely low compressibility, these films are nevertheless not "closely packed." All of the substances investigated give expanded or "gaseous" films at lower concentrations of the solutions. The solubility of hydroquinol is not sufficiently high to allow a condensed film to be formed by adsorption from the body of the liquid. It is concluded that the simplest interpretation of the results, together with those obtained on the orientation of derivatives of the fatty series, indicates that the hydroxyl group of phenol turns toward the water, while the phenyl group is on edge or on end above it. With hydroquinol (*ortho*), however, both hydroxyl groups bury themselves in the water, while the phenylene group remains on the surface. Since the derivatives investigated are soluble in water, and also somewhat volatile, there are constant interchanges of molecules between the surface region and the liquid and vapor regions, which undoubtedly affect the structure of the films.

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