

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Hydrogen Bonding by S-H. VII.<sup>1</sup> Aryl Mercaptans

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It has been commonly held that hydrogen bonding is restricted to hydrogen atoms attached to fluorine, oxygen, or nitrogen. Recently, however, large masses of data involving diverse types of physical measurements (polarization measurements,<sup>2</sup> solubility,<sup>3,4</sup> heat of mixing,<sup>1,5</sup> infrared absorption,<sup>6,7</sup> and viscosity<sup>8</sup>) have shown definitely that a hydrogen attached to a highly negatively substituted carbon atom, for example,  $\text{CHCl}_3$ ,  $\text{CHCl}_2\text{F}$ ,  $\text{CH}_2\text{Cl}_2$ , or  $\text{C}_6\text{H}_5\text{C}\equiv\text{CH}$ , will bond to an unshared pair of electrons on an oxygen or a nitrogen atom in an organic molecule. Infrared absorption measurements by Buswell, Rodebush and Roy<sup>6</sup> and by others<sup>9</sup> have also shown that the ether-hydrogen chloride complex is another case of hydrogen bonding.

These results have suggested to the authors that hydrogen bonding is more common than hitherto believed, and that whenever a hydrogen is attached to another atom by a sufficiently ionic link, it will further bond to an unshared pair of electrons on a donor atom. To test this hypothesis, the heats of mixing of an alkyl mercaptan and of an aryl mercaptan with some donor solvents have been measured. The method followed in making the measurements has been described in a previous publication.<sup>5</sup> In Table I are tabulated the heat effects on mixing equimolar quantities of *n*-heptyl

or phenyl mercaptan with four organic solvents. For comparison, corresponding heats of mixing of chloroform and phenylacetylene<sup>1</sup> are included where available. Where the statement "No heat" is made, either a slight cooling or inappreciable heating was observed. In Fig. 1 the complete heat of mixing curves are shown for phenyl mercaptan with the three donor solvents, *N,N*-dimethylacetamide, ethyl ether, and acetone.

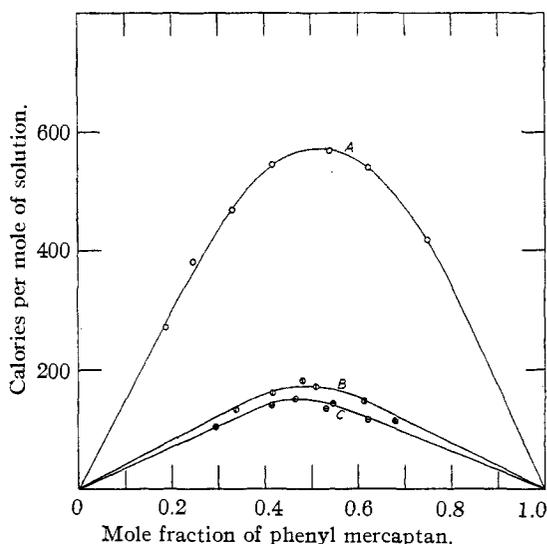


Fig. 1.—The heat evolved per mole of solution at 3° versus the mole fraction of phenyl mercaptan: A, *N,N*-dimethylacetamide, B, ethyl ether, and C, acetone.

TABLE I  
HEATS OF MIXING IN CALORIES PER MOLE OF SOLUTION  
AT 3° FOR EQUIMOLAR MIXTURES

	<i>n</i> -Heptyl mercaptan	Phenyl mercaptan	Phenyl- acetylene	Chloro- form
<i>N,N</i> -dimethyl- acetamide	No heat	572	644	920 <sup>a</sup>
Ethyl ether	No heat	173	272	700 <sup>b</sup>
Acetone	No heat	150	200	...
Benzene	No heat	No heat	No heat	No heat

<sup>a</sup> Unpublished data obtained in this Laboratory.

<sup>b</sup> McLeod and Wilson, *Trans. Faraday Soc.*, **31**, 596 (1935).

(1) For the sixth communication in this series see Copley and Holley, *THIS JOURNAL*, **61**, 1599 (1939).

(2) Glasstone, *Trans. Faraday Soc.*, **33**, 200 (1937).

(3) Zellhoefer, Copley and Marvel, *THIS JOURNAL*, **60**, 1337 (1938).

(4) Copley, Zellhoefer and Marvel, *ibid.*, **60**, 2666, 2714 (1938).

(5) Zellhoefer and Copley, *ibid.*, **60**, 1343 (1938).

(6) Buswell, Rodebush and Roy, *ibid.*, **60**, 2528 (1938).

(7) Gordy, *ibid.*, **60**, 605 (1938); *J. Chem. Phys.*, **7**, 163 (1939).

(8) Ewell, *ibid.*, **5**, 967 (1937).

(9) Gordy and Martin, *Phys. Rev.*, **52**, 1075 (1937); *J. Chem. Phys.*, **7**, 99 (1939).

The data show that whereas *n*-heptyl mercaptan gives no evidence of hydrogen bonding, the more acidic phenyl mercaptan bonds to the donor atoms, oxygen or nitrogen. The location of the maxima at 0.5 mole fraction suggests the formation of an equimolar complex in each case. From the magnitude of the heats of mixing alone, it appears that the S-H←O or N bonds are considerably weaker than the C-H←O or N bonds formed by chloroform, and slightly weaker than the C-H←O or N bonds formed by phenylacetylene; however, it must be remembered that if weak S-H←S bonds are present in phenyl mercaptan they would lead to lower heats of mixing.

In Table II the boiling points of methyl mercaptan, methyl sulfide, phenyl mercaptan, and phenylmethyl sulfide along with their oxygen analogs are listed. Methyl mercaptan has a lower

TABLE II

	B. p., °C.
Methyl mercaptan	7.2
Methyl sulfide	38
Phenyl mercaptan	169.5
Phenylmethyl sulfide	188
Methyl alcohol	64.5
Methyl ether	- 24.9
Phenol	182
Anisole	155.8

boiling point than methyl sulfide; similarly phenyl mercaptan has a lower boiling point than phenylmethyl sulfide; on the other hand, the reverse is true for the oxygen analogs. This indicates that phenyl mercaptan as well as alkyl mercaptans is unassociated or at most forms very weak S-H←S bonds. This is in agreement with previous work<sup>3</sup> which showed that a sulfur atom is an ex-

tremely poor donor atom for the bonding of a hydrogen on a carbon.

### Summary

The heats of mixing of *n*-heptyl and phenyl mercaptans with *N,N*-dimethylacetamide, ethyl ether, acetone, and benzene have been measured. The results afford evidence of hydrogen bonding to donor oxygen and nitrogen atoms by phenyl mercaptan, but not by *n*-heptyl mercaptan. The failure of aryl mercaptans to show association is a result of the weak donor ability of the sulfur atom for hydrogen bonding and not from any lack of acceptor ability on the part of the hydrogen of the S-H link. It is pointed out that whenever a hydrogen is attached to another atom by a sufficiently ionic link, hydrogen bonding is possible.

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## Electrical Characteristics of Molecular Films

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### 1. Introduction

It has been shown by Blodgett and Langmuir<sup>1,2</sup> that single layers of molecules on water surfaces can be transferred to polished metal slides by dipping the slide through the water surface. When one molecular layer goes on the slide as it is dipped downward, but none as the slide is withdrawn, this transferred layer is called an X film. When one layer is transferred on the down dip and one on the up dip, they are called Y films.

Porter and Wyman<sup>3,4</sup> found that X films of calcium and barium stearates, deposited from baths of pH above 9, possess a potential which increases with the number of molecular layers. The Y films of calcium and barium stearates, on the other hand, do not show this growth of potential with successive dips.

The experimental results of Porter and Wyman have been repeated and confirmed, using both the vibrating plate method and also a polonium-air electrode to measure surface potential. The interpretation of certain of our experiments indicates, according to the theory given by Langmuir,<sup>5</sup>

that the principal portion of the charge on calcium and barium stearate X films may be due, not to molecular orientation within the films, but to a surface electrification.

### 2. Apparatus

The vibrating plate method is that described by Zisman<sup>6</sup> and Porter.<sup>7</sup> A beat frequency oscillator (RCA type TMV 134-A) was used to produce the audio frequency which was amplified and fed to a loud speaker element in a sturdy support. This element vibrated an insulated polished nickel disk just above the film. When a potential exists between the disk and film, this vibration plate condenser feeds an alternating current into an audio-frequency amplifier. An opposing potentiometer and voltmeter was used to balance out the surface potential to a minimum of sound in earphones.

The polonium-air electrode affords an independent method of measuring surface potentials. The use of radioactive material for measuring contact potentials was described by Lord Kelvin shortly after the discovery of radioactivity. The polonium method has been used by Guyot, Frumkin, Rideal and others. Old radon tubes were crushed and soaked in 4 *N* hydrochloric acid. A buffed disk of nickel 0.5 cm. in diameter, 0.025 cm. (10 mils) thick was welded to a nickel wire. When this is rotated for a few minutes in hydrochloric acid extract from radon tubes, polonium is deposited on the nickel disk. The disk was then washed in distilled water and dried.

(1) Blodgett, *THIS JOURNAL*, **57**, 1007 (1935).

(2) Blodgett and Langmuir, *Phys. Rev.*, **51**, 964 (1937).

(3) Porter and Wyman, *THIS JOURNAL*, **59**, 2746 (1937).

(4) Porter and Wyman, *ibid.*, **60**, 1083 (1938).

(5) Langmuir, *ibid.*, **60**, 1190 (1938).

(6) Zisman, *Rev. Sci. Instruments*, **3**, 367 (1932).

(7) Porter, *THIS JOURNAL*, **59**, 1883 (1937).