CCLXXXI.—*Studies in Dielectric Polarisation. Part I. Benzene Solutions of Furan, Ethyl Mercaptan, and Ethyl Sulphide.*

By Eric Charles Edward Hunter and James Riddick Partington.

According to Debye, the polarisation of a dielectric in an electric field is the sum of two terms : (1) P_I, the polarisation due to the induced dipoles, proportional to the polarisability; and (2) P_O, the polarisation due to permanent dipoles, proportional to the square of the dipole moment μ, and inversely proportional to the absolute temperature :

$$P_O = 4\pi N\mu^2/9kT \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

N is Avogadro's number, and k is Boltzmann's constant.

Ebert (*Z. physikal. Chem.*, 1924, **113**, 1) treats the molecule as an elastic body capable of deformation in an electric field, the displacement of electrons giving rise to an average moment $\bar{\mu}_E$, and a similar displacement of the atoms to an average moment $\bar{\mu}_A$. Corresponding with these are the polarisations P_E and P_A. The total polarisation is then given by

$$P = P_O + P_E + P_A \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and by the Clausius–Mosotti equation

$$P = \frac{\varepsilon - 1}{\varepsilon + 2} \cdot \frac{M}{\rho} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where ε is the dielectric constant, ρ the density, and M the molecular weight. This equation holds strictly only for gases, where the interaction between molecules is negligible. It has, however, been applied to dilute solutions of polar compounds in non-polar solvents (*e.g.*, by Lange, *Z. Physik,* 1925, **33**, 169; Errera, *Physikal. Z.*, 1925, **27**, 764). The polarisation of the mixture is then given by

$$P_{12} = f_1P_1 + f_2P_2 \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where f_1 and f_2 are the molar fractions, and P_1 and P_2 are the polarisations of solvent and solute respectively, P_{12}, the mixture polarisation, being given by:

$$P_{12} = \frac{\varepsilon - 1}{\varepsilon + 2}\,\frac{M_1f_1 + M_2f_2}{\rho} \quad . \quad . \quad . \quad (5)$$

where ε and ρ apply now to the solution. P_{12} is plotted against f_2, and the curve extrapolated to $f_2 = 0$. A tangent to the curve at $f_2 = 0$, when produced to cut the axis $f_2 = 1$, then gives the polarisation at infinite dilution, P_{2_∞}. To calculate the electric moment, it is necessary to know P_O. This should be inversely proportional to T, hence the P–$1/T$ curve can be represented by $P = a + b/T$, where

$$b = 4\pi N\mu^2/9k \text{ and } a = P_E + P_A \quad . \quad . \quad . \quad (6)$$

This enables μ to be obtained without reference to $P_E + P_A$, but at the same time it enables these magnitudes to be ascertained. The variation of dielectric constant with temperature is small, so the method is liable to some error.

If the frequency of the field is sufficiently increased, the dipoles are unable to follow it, and the orientation polarisation disappears ($P_O = 0$). If the frequency is increased to optical frequencies, P_E alone forms the total polarisation. P_E can be found from the Lorenz–Lorentz equation for the pure polar compound, *viz.*,

$$P_E = \frac{n^2 - 1}{n^2 + 2}\cdot\frac{M}{\rho} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

in which n is the refractive index. It has been assumed that n should be extrapolated to infinite wave-length, but Debye ("Polar Molecules," p. 43, 1929) has criticised this on the ground that the dispersion in the infra-red is partly due to the permanent moment. He suggests that measurements of electron polarisation should be referred to the D sodium line. The contribution P_A is left undetermined by Debye and by Williams; it is probably small in most cases, but Williams (*J. Amer. Chem. Soc.*, 1928, **50**, 2350) found the moment of *s*-trinitrobenzene to be 0·8, although the molecule possesses a centre of symmetry. Other such cases are known, the moment being due to the neglect of the term P_A. In the present work P is determined from (3) and P_E from refractivity measurements.

Morgan and Lowry (*J. Physical Chem.*, 1930, **34**, 2385) suggest that if the polarisation were measured at a frequency just above that at which P_O disappears, it would give $P_E + P_A$, and P_O could be obtained by difference from the total polarisation. Such a frequency would be outside the range of radio-frequencies, but by using viscous compounds, the frequency might be brought into the range of experiment.

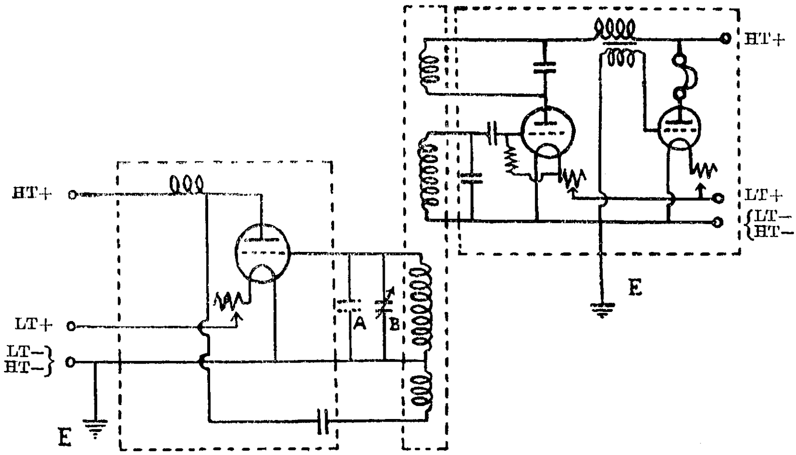
Ebert (*loc. cit.*) has used another method for determining P_O. He obtains P_E from refractivity data and assumes that $P_E + P_A$ is the same in the solid as in the liquid state. From the dielectric constant in the solid state, the polarisation is calculated by (3) and contains only the terms $P_E + P_A$. $P - (P_E + P_A)$ then gives P_O. The assumption that P_A is the same for the two states is not altogether justified in view of the experiments of Morgan and Lowry, who measured the dielectric constants of methyl bromide and iodide in the solid state, obtained P_{E+A} from the temperature effect, and calculated the corresponding dielectric constants for the solids. The two sets of values did not agree, although better agreement was found for methyl chloride, methylene chloride, and *p*-dichlorobenzene. Simons and Jessop (*J. Amer. Chem. Soc.*, 1931, **53**, 1265) found the dielectric constant and conductivity of crystalline phosphorus pentachloride to be greater than for the liquid, this substance being found to be a non-polar molecule (compare Partington, J., 1929, 2573). If in this case P_A is the same in the two states, $P - P_O$ must be negative. The cause of the abnormality, it is suggested, is the distortion of the molecule by the crystal forces, leading to an increased polarisation in the solid state, and such an effect may well exist in other cases.

EXPERIMENTAL.

In the present communication, the measurements of the dielectric constants of benzene solutions of furan, ethyl mercaptan and ethyl sulphide are described, together with determinations of the molecular refractions. The purpose of the investigation was principally to determine the effect of replacing oxygen by sulphur in simple compounds, and to see how far the chemical and physical properties can be explained on the basis of the calculated dipole moments.

Apparatus.—All measurements were made at 20°. The densities were determined with pyknometers (12 c.c.) fitted with ground caps. On account of the volatile nature of the substances, the densities are liable to an error of 2 units in the fourth place. The solutions were made up in 100-c.c. calibrated flasks, immersed in a thermostat at 20° ± 0·05°. Refractivities were determined with a Pulfrich refractometer at 20° ± 0·05° and are liable to an error of one unit in the fourth place. The dielectric constants were measured with an apparatus based on the heterodyne principle (*Physical Rev.*, 1920, **15**, 243; 1924, **23**, 345). The circuit (see Fig. 1) consisted of a valve oscillator maintained at a constant frequency, to which a stage of audio-frequency amplification was attached. Coupled to this circuit by the grid coils, was a valve oscillator the frequency of which could be varied by means of a Tinsley calibrated standard variable condenser of 300 μμfarads capacity, placed in parallel with the grid coil. The two oscillators were placed in separate earthed copper boxes, and the coupling coils were placed in an earthed copper screen. All external leads were of lead-covered cable, the outer covering of which was also earthed. Separate filament and plate batteries supplied the two circuits with current. Two glass cells, containing fixed multiplate chromium-plated condensers, held in position by ebonite stoppers, of capacities 70 and 42 μμfarads were used. The cell was filled to a definite mark with the solution and placed in a paraffin-bath contained in the thermostat. The capacity of the cell was determined by bringing the two oscillators into resonance by means of the variable condenser, and the reading of the latter was taken. The empty cell was placed in circuit, and the resonance point obtained. These two readings were translated into true capacities by means of a large-scale calibration chart, and the difference gave the capacity of the cell. This procedure was repeated with the cell filled to the mark with the solution, and the capacity obtained

FIG. 1.



A = *Dielectric cell.*
B = *Standard condenser.*

as before. The ratio of the two capacities gave the dielectric constant of the solution (air = 1). Readings of the resonance point were taken with the cell alternately in and out of circuit, ten such readings being taken for each capacity result. The accuracy of the dielectric constant is estimated at ± 0·5%. As an additional precaution, the standard condenser and the electrical apparatus were placed in an air thermostat at 20° ± 0·1°. Capacity effects of the operator were eliminated by using a remote control on the variable condenser, and the oil-bath was of copper and earthed.

Preparation of Materials.—Benzene. Kahlbaum's benzene "for analysis and molecular weight determinations" was tested for thiophen, which was absent, dried for a fortnight over phosphoric oxide, fractionated, dried with sodium, and refractionated, head and tail portions being rejected; $D_{4^\circ}^{20^\circ}$ 0·8791, $n_{\rm D}^{20^\circ}$ 1·5007, m. p. 5·45° on Anschütz thermometer standardised on ice (International Critical Tables give $D_{4^\circ}^{20^\circ}$ 0·87910).

Furan. The Kodak, Ltd., material was dried over anhydrous sodium sulphate for a week, and fractionated; b. p. 31·6°/757 mm., $D_{4^\circ}^{20^\circ}$ 0·9365, $n_{\rm D}^{20^\circ}$ 1·42136. Auwers (*Annalen*, 1915, **408**, 212) gives $D_{4^\circ}^{20^\circ}$ 0·9366; $n_{\rm D}^{20^\circ}$ 1·42157.

Ethyl mercaptan. This substance was obtained from the same source and subjected to the same treatment as furan; b. p. 35·3°/768 mm., $D_{4^\circ}^{20^\circ}$ 0·8398, $n_{\rm D}^{20^\circ}$ 1·43119. Nasini (*Ber.*, 1887, **20**, 3882) gives $D_{4^\circ}^{20^\circ}$ 0·83907; $n_{\rm D}^{20^\circ}$ 1·43055.

Ethyl mercaptan.

Weight in 100 c.c.	$D_{4^\circ}^{20^\circ}$.	ϵ.	f_1.	f_2.	P_{12}, c.c.
—	0·8791	2·261	1	—	26·28
0·7576	0·8789	2·288	0.9892	0·0108	26·61
1·8390	0·8783	2·331	0·9738	0·0262	27·16
3·7444	0·8769	2·412	0·9469	0·0531	28·18
5·7440	0·8758	2·480	0·9190	0·0810	28·93

$P_{2\infty}$ (extrap.) = 60·18; $P_{\rm E}$ = 19·07; μ = 1·39 × 10^{-18} E.S.U.

Ethyl sulphide.

—	0·8791	2·261	1	—	26·28
1·1720	0·8786	2·305	0·9882	0·0118	26·92
2·2482	0·8779	2·348	0·9775	0·0225	27·45
2·9302	0·8777	2·372	0·9710	0·0290	27·98
4·1238	0·8771	2·398	0·9591	0·0409	28·40
5·0026	0·8765	2·432	0·9502	0·0498	28·94

$P_{2\infty}$ (extrap.) = 80·68; $P_{\rm E}$ = 28·46; μ = 1·57 × 10^{-18} E.S.U.

Furan.

—	0·8791	2·261	1	—	26·28
4·5962	0·8819	2·275	0·9405	0·0595	26·20
6·9156	0·8832	2·295	0·9111	0·0889	26·30
9·5547	0·8849	2·322	0·8781	0·1219	26·55

$P_{2\infty}$ (extrap.) = 26·98; $P_{\rm E}$ = 18·43; μ = 0·63 × 10^{-18} E.S.U.

Ethyl sulphide. The product from the action of sodium ethyl sulphate on potassium hydrogen sulphide was extracted with sodium hydroxide to remove mercaptan, shaken with mercury, dried over anhydrous sodium sulphate, and fractionated twice; b. p. 91·5°/759 mm., $D_{4^\circ}^{20^\circ}$ 0·83679, $n_{\mathrm{D}}^{20^\circ}$ 1·44233. Nasini (*loc. cit.*) gives $D_{4^\circ}^{20^\circ}$ 0·83676; $n_{\mathrm{D}}^{20^\circ}$ 1·44233.

Results.—These are given in the subjoined table. The symbols are as defined on pp. 2062 and 2063. In each case μ was calculated from the formula $\mu = 0{\cdot}0127 \times 10^{-18}\sqrt{(P_{2_\infty} - P_{\mathrm{E}})T}$.

Discussion of Results.

Values of $\mu \times 10^{18}$ already recorded are given below, together with the references.

H_2S	1·10 [1]	H_2O	1·87 [4]	1·70 [5]	
Et·SH	1·39	EtOH	1·72 [6]	1·72 [7]	1·63 [8]
Et_2S	1·57	Et_2O	1·22 [9]	1·22 [10]	1·24 [11]
Ph_2S	1·47 [2]	Ph_2O	1·02 [12]	1·12 [13]	
Bz_2S	1·38 [2]	Bz_2O	—		
$Ph{\cdot}S{\cdot}CH_3$	1·27 [2]	$PhOCH_3$	1·16 [14]		
C_4H_4S	0·63 [3]	C_4H_4O	0·63		

[1] von Braunmühl, *Physikal. Z.*, 1927, **28**, 141.

[2] Bergmann, Engel, and Sandor, *Z. physikal. Chem.*, 1930, *B*, **10**, 397.

[3] Hassel and Naeshagen, *Tids. Kjemi*, 1930, **10**, 81.

[4] Jona, *Physikal. Z.*, 1919, **20**, 14.

[5] Williams, *ibid.*, 1928, **29**, 204.

[6, 7] Højendahl, Thesis, Copenhagen, 1928.

[8] Krchma and Williams, *J. Amer. Chem. Soc.*, 1927, **49**, 2408.

[9] Lange, *Z. Physik*, 1925, **33**, 169.

[10] Krchma and Williams, *J. Amer. Chem. Soc.*, 1927, **49**, 1676.

[11] See [8].

[12] Estermann, *Z. physikal. Chem.*, 1928, *B*, **1**, 134.

[13] Bretscher, *Helv. Phys. Acta*, 1929, **2**, 257.

[14] See [6].

The sulphides possess higher moments than the corresponding ethers. The increase in $\mu \times 10^{18}$ on substituting sulphur for oxygen is shown in the following table:

$$
\begin{aligned}
Et_2S &- Et_2O &&= 0{\cdot}35.\\
Ph_2S &- Ph_2O &&= 0{\cdot}35 \text{ or } 0{\cdot}45.\\
Ph{\cdot}SCH_3 &- Ph{\cdot}OCH_3 &&= 0{\cdot}11.\\
C_4H_4S &- C_4H_4O &&= 0
\end{aligned}
$$

The elements in a group in the periodic table show an increase in polarisability parallel with the increase in atomic volume, and this may be the reason for the larger moments of the sulphides. However, hydrogen sulphide and mercaptan have smaller moments than the oxygen compounds. The polarity of the alcohols is due to the hydroxyl group alone, since there is no alteration of moment with length of the hydrocarbon chain, and the moments are the same as for water. Ethyl mercaptan has a higher moment than hydrogen sulphide, and the increase may be due to induction along the hydrocarbon chain. Measurements are in progress on *n*-propyl and *n*-butyl mercaptans to test this possibility.

In view of the close similarity between the alcohols and the mercaptans, it is surprising to find that the latter are almost insoluble in water. Sunier (*J. Physical Chem.*, 1930, **34**, 2582) finds that the solubility of naphthalene in a series of alcohols increases regularly from methyl to *n*-butyl, as would be expected. The measured solubilities differ considerably from the ideal, and if the deviation is due only to association of the solvent, it is necessary to postulate aggregates of 5 molecules for butyl, and even more complex molecules for lower alcohols. It is unfortunate that there are at present no data on solubilities in mercaptans, but if the internal pressure runs parallel with the moment, naphthalene should show a higher solubility in mercaptans than in alcohols.

Bingham and Fornwald (*J. Rheology*, 1930, 372), by a comparison of the measured and calculated fluidities, find the degrees of association of 14 mercaptans to be given by the following empirical equation :

$$x = 1{\cdot}141 - 0{\cdot}0115\,N_1 - 0{\cdot}036(N_2\mathrm{SH}).$$

where N_1 is the number of carbon atoms, and N_2 is a correction for the *iso*-position.

The following table gives the chemical and physical properties of corresponding oxygen and sulphur compounds :

	B. p.	$\mu \times 10^{18}$.	Degree of asstn., x.
H_2O	100°	1·70	2·20
H_2S	–60	1·10	—
EtOH	78	1·70	1·74
EtSH	35	1·39	1·12
Et_2O	35	1·22	—
Et_2S	92	1·57	—

(The data for the oxygen compounds were taken from Turner, " Molecular Association," and were determined by the fluidity method.)

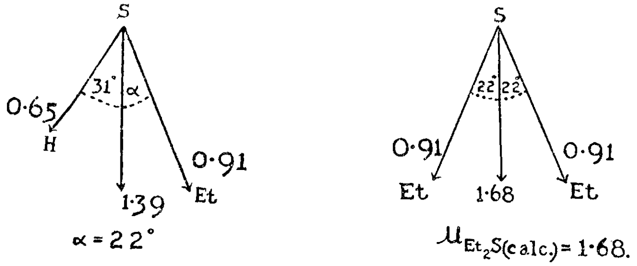
The order of association is roughly the same as for the moments. The SH group appears incapable of association either with itself or with the hydroxyl group, the latter circumstance affecting the ease of solubility.

The group moment in $\overleftarrow{\mathrm{HS}}$–C must be such that the sulphur atom is negative and the carbon atom positive, and it is in the same sense as in the hydroxyl group. The directive influence on substituents in the benzene ring should be ortho-para. No data are available for this.

The sulphides have higher moments than the ethers, and show greater tendency to form complexes, especially with metallic halides of the transition elements, mercury, and the platinum metals. They combine with alkyl halides to form ionised salts, which are converted by silver oxide into sulphonium hydroxides (von Ofele, *Annalen*, 1864, **132**, 82). The valency of sulphur can increase by co-ordination of oxygen to give sulphoxides and sulphones, whereas oxygen can only assume a valency above two by co-ordination of hydrion when there is some activating group in the molecule.

In view of the ease with which sulphur increases its valency, it would be of interest to determine if the sulphides show any anticatalytic effect in the esterification of carboxylic acids in the presence of hydrogen chloride as catalyst (Goldschmidt and Udby, *Z. physikal. Chem.*, 1907, **60**, 728; Lapworth and Partington, J., 1910, **97**, 19). The ethers show no such effect (Johnson and Partington, this vol., p. 86).

FIG. 2.



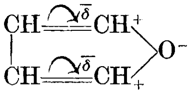
That the symmetrical compounds of sulphur discussed in this paper are polar, can be explained on the basis of a **V**-shaped molecule, in agreement with Hund (*Physikal. Z.*, 1925, **31**, 81), who concluded from spectroscopic data that hydrogen sulphide had this shape, and calculated the apex angle to be 62°. A similar calculation for water gave 66°. From the moment for hydrogen sulphide the group moment of $\overleftarrow{\mathrm{HS}}$ is calculated as $0·65 \times 10^{-18}$. This and the angle 31° can be combined with the moment of mercaptan to give the group moment of $\overleftarrow{\mathrm{EtS}}$ and the angle α (see Fig. 2).

These values can be combined to give the moment of ethyl sulphide as 1·68 (1·57 experimental). The agreement is fairly good, in view of the fact that no account has been taken of interaction between the groups. Bergmann, Engel, and Sandor (*loc. cit.*) calculate the angle between the thiophenyl groups in phenyl sulphide to be 142°.

If the angle between the groups in ethyl sulphide is calculated, it being assumed that (i) the radius of the sulphur ion is 1·69 Å.,

(ii) the distance between two carbon atoms is 1·5 Å., and (iii) the two groups just touch, an angle of 38° is obtained, and a similar calculation for phenyl sulphide gives 56°.

The moments of furan and thiophen are the same within the limits of experimental error. Furan (b. p. 32°) and thiophen (b. p. 84°) are a little more volatile than ethyl ether and ethyl sulphide respectively. The great difference in the moments, compared with the diethyl open-chain compounds, is probably due to the presence of double bonds, the high density of electrification associated with a double bond causing induction, and a decrease in moment.



Summary.

(1) The dielectric constants and densities of dilute benzene solutions of ethyl mercaptan, ethyl sulphide, and furan have been measured, and the molecular refractions of the pure compounds determined.

(2) The dipole moments have been calculated on the Debye theory, and compared with those of analogous oxygen and sulphur compounds. The sulphides have higher moments than the corresponding ethers, but the mercaptans have lower moments than the alcohols.

(3) The chemical and physical properties of water, hydrogen sulphide, ethyl alcohol, ethyl mercaptan, ethyl ether, and ethyl sulphide have been discussed. The degrees of association of the alcohols are higher than for the mercaptans, and this is the order of the moments.

(4) The group moments of HS and EtS, and the moment of ethyl sulphide have been calculated by the theory of vector moments. There is an increase in moment on substituting ethyl for hydrogen in the sulphur compounds which is not found in the oxygen series.

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EAST LONDON COLLEGE,
UNIVERSITY OF LONDON.

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