

A general equation for the calculation of activity coefficients of sulfuric acid in glacial acetic acid solutions has been developed.

It has been shown that an equation of the type proposed by Hückel as a modification of the Debye-Hückel theory of strong electrolytes is applicable in a solvent of very low dielectric constant.

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

## THE DIPOLE MOMENT OF SEMI-POLAR BONDS

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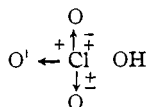
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The term semi-polar bond has been used to designate a shared electron bond in which both electrons are contributed by one atom. This term has been used in the absence of a more suitable designation without much idea as to its fitness since it has not been known with certainty whether any considerable degree of polarity is characteristic of this bond. Two common examples of this bond are ammonium chloride and perchloric acid.



In the case of the ammonium chloride the identity of the semi-polar bond is completely lost. In the perchloric acid the strength of the acid may be explained by assuming a considerable degree of polarity in the semi-polar bonds thus



Any other explanation of the strength of perchloric acid seems to be barred, since double bonds are out of the question.

It is impossible to determine the dipole moment of the semi-polar bonds in the above-mentioned molecules for obvious reasons. Recently, however, Professor Shriner<sup>1</sup> of this Laboratory has synthesized some organic sulfur compounds which contain semi-polar bonds. Professor Shriner has kindly furnished us with samples of these compounds for measurement of the electrostatic moment. The compounds were diphenyl sulfoxide, diphenyl sulfones and homologs. The electronic structures of the sulfoxide and sulfone are



<sup>1</sup> Shriner, Struck and Jorison, *THIS JOURNAL*, 52, 2060 (1930).

It is impossible to assign any other electronic structure which seems at all probable. In both compounds the electrons linking the oxygen to the sulfur are both furnished by the oxygen. These compounds are stable and sufficiently soluble in benzene for satisfactory determinations. For purposes of comparison measurements were made upon diphenyl sulfide.<sup>2</sup>

### Experimental

The method used to measure the dielectric constants of the liquids under consideration was essentially the same as that developed by Nernst<sup>3</sup> and his students. The apparatus consisted of a Type 216 capacity bridge manufactured by the General Radio Company in which capacities as well as resistance are balanced. The bridge consists of two resistance arms,  $R_1$  and  $R_2$ , of 5000 ohms each and two capacity arms. In one arm of the bridge was placed a balancing condenser, and in the other arm two standard variable air condensers made by the General Radio Company and having capacities of  $1500\mu\mu$  farads. Only one of these was accurately calibrated, the other being used so that there would be a larger capacitance in each arm of the bridge, this giving a sharper minimum point in the phones. Connected in parallel with these two condensers was the comparison condenser (modeled after that of Hartshorn and Oliver)<sup>4</sup> built of brass plates and mounted in a shielded Pyrex tube with a ground glass top. The capacity of this condenser was  $403.1\mu\mu$  farads. This was measured by submerging the plates in purified benzene, the dielectric constant of which has been accurately determined by Hartshorn and Oliver<sup>4</sup> as  $2.282 \pm 0.002$  at  $20^\circ$ . The capacity of this cell was frequently checked throughout the course of the work. All of the work was carried out at  $25^\circ$ .

The entire apparatus was placed on a metal topped table and carefully grounded. All possible precautions were taken to prevent stray capacities. The frequency used in measuring the dielectric constant was 1000 cycles, which was produced by a General Radio Audio oscillator. Power was brought from the oscillator to the bridge by a pair of twisted wires, heavily insulated.

### Experimental Procedure

The method of operation was to vary the capacity of the standard condenser and the balancing resistance of the bridge until a sharp minimum was received on the phones. This reading was noted and then the comparison cell containing the binary mixtures under investigation was connected in parallel and readings again were taken. The difference between the two readings represents the capacity of the cell plus the liquid. In filling the comparison condenser, care was taken to prevent the formation of bubbles between the plates by tilting the cell and allowing the liquid to flow slowly down the side of the tube.

It must be noted that the capacity of this cell is made up of two parts, the capacity due to the leads and insulation and the capacity between the plates. In the neighborhood of dilute solutions, when the dielectric con-

<sup>2</sup> Since this research was started, Bergmann, Engel and Sandor [*Z. physik. Chem.*, [B] 10, 397 (1930)] have published results for diphenyl sulfide and diphenyl sulfoxide. The agreement between their values and ours is satisfactory.

<sup>3</sup> Nernst, *ibid.*, 14, 622 (1894).

<sup>4</sup> Hartshorn and Oliver, *Proc. Royal Soc. (London)*, April, 1929.

stant is nearly the same as that of benzene, the error due to the leads capacity cancels out, as the capacity of the cell as obtained by us is really that of the cell plus the leads. In the neighborhood of the dilute solution where the highest accuracy is desired, this accuracy is also obtained.

To make certain, however, that this error due to the leads capacity might also be safely neglected in the range of the more concentrated solutions, where we measured dielectric constants in the neighborhood of four, it was decided to check the apparatus by measuring the moment of a compound already known. *p*-Nitrotoluene was selected, having an electric moment of  $4.50 \times 10^{-18}$  e. s. u. as reported by Williams.<sup>5</sup> The value as determined by our method is within the limits of the precision of any method to measure electric moments. The capacity of these leads as calculated from the law of infinite cylinders was  $1\mu\mu$  farad, a value small in comparison with the 1000–1500 $\mu\mu$  farads measured.

The method used to calculate the moment of a molecule was to make a saturated solution of the compound in benzene, the latter being a non-polar solvent. The dielectric constant was measured at each dilution five to seven readings being taken on each dilution and at various balanced capacities to check the readings. Variation here in capacity was as a maximum about  $1.5\mu\mu$  farads, although in the diluted solutions the readings checked within  $0.5\mu\mu$  farad. This represents an error of approximately 0.15% in the concentrated solutions. Densities were accurately determined by means of a specific gravity bottle, giving values accurate through the fourth decimal place.

The polarization of the solution was calculated by the method pointed out by Debye,<sup>6</sup> using the equation

$$P_{1,2} = P_1 f' + P_2 f_2 = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{f_1 M_1 + f_2 M_2}{\rho}$$

where  $P_{1,2}$  is molar polarization of the mixture;  $P_1$ , molar polarization of the solvent;  $P_2$ , molar polarization of the solute;  $f_1$ , mole fraction of the solvent;  $f_2$ , mole fraction of the solute;  $\rho$ , density of the solution;  $\epsilon$ , dielectric constant of the solution. The values of  $P_2$  were then obtained by plotting  $P_{1,2}$  values as abscissas and  $F_2$  values as ordinates. From this curve  $P_2$  values were calculated, which were then plotted against  $f_2$  and again extrapolated to infinite dilution, giving the value for the polarization of a single molecule between the plates of the condenser.

To obtain the values for the optical polarization (the polarization due to the deformation of the molecule) the individual atomic refractivities were added, proper allowances being made for the different types of linkages. This method was used as the refractive indices of the compounds under investigation have not as yet been determined. The difficulty we

<sup>5</sup> Williams, *Chem. Rev.*, 6, 589 (1929).

<sup>6</sup> Debye, "Polar Molecules," Chemical Catalog Co., Inc., New York, 1929.

encountered in calculating this  $P_0$  (optical polarization) is that no value is known for sulfur in the type of linkage we were interested in. The assumption was made that the values of sulfur from known compounds, *e. g.*, sulfides, disulfides, could be used, where the atomic refractivity has a value of eight. Debye justifies an assumption of this kind, considering the possible precision of the value obtainable for the optical polarization.

From the values of the molar polarization  $P_2$  of the polar molecule itself and the value  $P_0$  for the optical polarization, the electric moment  $\mu$  can be calculated as Debye shows by

$$\frac{4\pi}{3} N \frac{\mu^2}{3kT}$$

Substituting  $N = 6.06 \times 10^{23}$  and  $k = 1.372 \times 10^{-16}$ , the equation becomes

$$\mu = 0.0127 \times 10^{-18} \sqrt{(P_2 - P_0)T}$$

where  $T$  is the absolute temperature.

The values obtained are shown in Table I together with the values for some related compounds which have been determined by other investigations.

TABLE I  
DIPHENYL SULFIDE (Temp., 25°)

$f_2$	$\epsilon$	$\rho$	$P_{1,2}$ , cc.
0.23120	3.064	0.9658	43.49
.09605	2.641	.9195	34.00
.04626	2.458	.8973	29.91
.03670	2.418	.8940	29.45
.02814	2.389	.8904	28.82
.01790	2.354	.8870	28.04
.00890	2.323	.8814	27.44
.00620	2.310	.8791	27.22
.00270	2.292	.8774	26.84
Diphenyl Sulfoxide ( $T$ , 25°)			
0.051	3.807	0.908	44.92
.0481	3.679	.906	43.75
.04595	3.497	.904	42.08
.04265	3.46	.9022	41.62
.0396	3.307	.9002	40.08
.0367	3.214	.8987	39.03
.0339	3.132	.8970	38.1
.0312	3.037	.8952	37.04
.0283	2.968	.8935	36.16
.02465	2.8597	.8912	34.83
.02085	2.764	.8889	33.59
.01805	2.693	.8866	32.67
.01340	2.600	.8843	31.35
.0098	2.510	.882	30.09
.0062	2.426	.8799	28.87

TABLE I (Concluded)  
 Diphenyl Sulfone ( $T$ , 25°)

$f_2$	$\epsilon$	$\rho$	$P_{1,2}$ , cc.
0.0262	3.187	0.890	38.70
.0229	3.069	.888	37.33
.0201	2.958	.8865	36.01
.0173	2.872	.885	34.92
.0144	2.766	.8837	33.55
.0115	2.702	.882	32.67
.0088	2.606	.880	31.39

## POLARIZATION IN BENZENE

	$P_2$ , cc.	$P_0$ , cc.	$P_2 - P_0$	$\mu \times 10^{-18}$
Diphenyl sulfide	111	59	52	1.565
Diphenyl sulfoxide	423	60.5	362.5	4.17
Diphenyl sulfone	593.5	63.3	530.2	5.05

 TABLE II  
 VALUES FOR COMPOUNDS

	$\mu \times 10^{-18}$
Diphenyl ether.....	1.0
Sulfur dioxide.....	1.8
Benzophenone.....	2.5
Acetone.....	2.7

Attempts were also made to measure  $\mu$  for  $C_6H_5SO_2CH_2C_6H_5$ , and  $C_6H_5-CH_2SOC_6H_5$ , but their insolubility prevents an accurate determination of their electric moment by this method. All we can say is that they have a high moment, comparable to the simple sulfoxide and sulfone.

**Discussion.**—The results obtained indicate a surprisingly high value for the dipole moment of the semi-polar bond. This result seems to be established with certainty since the largest errors that may reasonably be assumed would not affect the results seriously. The value of 8.0 that was assumed for the atomic refraction of sulfur is a maximum; the correct value may be less. If this is the case the moments obtained are even larger.

It is to be expected of course that if the molecule has an approximately tetrahedral arrangement, the moment of the sulfone would not be much greater than that of the sulfoxide.

In Table II are given the accepted values for the electrostatic moments<sup>7</sup> of some compounds for comparison purposes. It will be noted that oxygen doubly bound to carbon has a moment much smaller than the semi-polar bond with sulfur.

One might be tempted to assume an even smaller moment for oxygen doubly bound to sulfur. If we assume a linear form for the sulfur dioxide molecule and that it contains one double bond and one semi-polar bond, then the moment of sulfur dioxide is about what would be expected. Great caution must be used, however, in drawing conclusions in this way.

<sup>7</sup> "Ergebnisse der exakten Naturwissenschaften," 1929, Vol. VIII, p. 288.

### Summary

The dipole moments have been determined in benzene solution for diphenyl sulfide, diphenyl sulfoxide and diphenyl sulfone. The sulfoxide and sulfone have a very large moment.

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[COMMUNICATION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

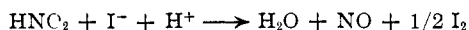
## THE REACTION BETWEEN NITRITE AND IODIDE AND ITS APPLICATION TO THE IODIMETRIC TITRATION OF THESE ANIONS

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The reaction between nitrous acid and iodide



occurs only in acid medium. In the presence of oxygen the nitric oxide is oxidized to nitrogen dioxide which partly reacts with water, forming nitrous and nitric acid. With regard to the application of the reaction between nitrite and iodide to the iodimetric determination of these components, it was desirable to know at which hydrogen-ion concentration the reaction between the two takes place with a measurable speed. Moreover, it was of importance to study the reaction between iodide, dissolved oxygen and nitric oxide at various  $P_{\text{H}}$  values.

To 10 ml. of Clark's buffer solutions, known amounts of potassium iodide and sodium nitrite were added and after definite times of standing the iodine was titrated with thiosulfate. Some results obtained at room temperature are given in Table I.

TABLE I  
REACTION BETWEEN NITRITE AND IODIDE AT VARIOUS  $P_{\text{H}}$

$P_{\text{H}}$ of buffer, 10 cc.	Concn. $\text{I}^-$ molarity	Concn. $\text{NO}_2^-$ molarity	Time of standing, in minutes	0.1 $N$ thiosulfate, cc.
3.4	0.2	0.2	5	2
4.0	.2	.2	5	1.5
4.0	.4	.2	5	2.5
5.0	.2	.2	5	0.4
5.0	.4	.2	5	.7
5.6	.2	.2	5	.05
5.6	.2	.2	30	.20
5.6	.4	.2	5	.10
5.6	.4	.2	30	.40
6.0	.4	.2	5	.04
6.0	.4	.2	240	.09
7.0	.4	.2	30	.00