Dipole Moments of Some Hydroxyl Compounds

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In this note the present author wishes to report some unpublished values of dipole moments of phenol derivatives and also discuss the influence of solvent upon the moments of hydroxyl compounds in general.

In Table 1 the electric moments of three isomers of cresol, chlorophenol and nitrophenol are recorded with those of phenol and chlorobenzene. The values of the table were obtained by the dilute solution method, toluene being chosen as solvent; and the following equation was used in the calculation of moments: $\mu = 0.127\sqrt{P_{2\infty} - MR_D}$, the symbols having the usual significance.

Table 1

Dipole Moments in Debye Unit

temp. (°C.)	ortho	meta	para
Cresols			
0	1.35	1.66	1.62
25	1.35	1.61	1.58
50	1.35	1.58	1.57
75	1.38	1.58	1.54
Chlorophenols			
0	1.23	2.06	2.26
25	1.24	2.08	2.24
50	1.24	2.10	2.25
75	1.24	2.12	2.23
Nitrophenols			
0	3.06	3.66	—
25	3.12	3.76	4.72
50	3.16	3.86	4.63
75	3.16	3.86	4.60

Phenol and Chlorobenzene

temp. (°C.)	Phenol	Chlorobenzene
0	1.52	1.54
25	1.49	1.56
50	1.44	1.57
75	1.43	1.57

As toluene is seldom used as the solvent for dipole moment work, a comparison is made with the values in benzene⁽¹⁾ for the substances measured (see Table 2). In spite of the difference in polarity between the two solvents, no appreciable deviation* is found between the values of the second and third columns of the table.

Table 2

Dipole Moments and Solvents

Solute	Solvent	
	Benzene	Toluene
o-Cresol	1.41	1.35
m- 〃	1.54	1.61
p- 〃	1.57	1.58
o-Chlorophenol	1.33	1.24
m- 〃	2.10	2.08
p- 〃	2.22	2.24
o-Nitrophenol	3.11	3.12
m- 〃	3.90	3.76
p- 〃	5.02	4.72
Phenol	1.56	1.49
Chlorobenzene	1.57	1.56

On inspection, it is seen in Table 1 that the moments of most of the ortho and meta disubstituted compounds increase with the increase in temperature. One might interpret this increase as the change of the equilibrium-ratio of the *cis-trans* isomers with temperature, or one might instead favor the hypothesis of inner-molecular rotation. Indeed, one could succeed in calculating the moments on any of these assumptions. However, such calculations are equally unreliable, since the moment of phenol itself is not independent of temperature. It is also to be noted that para derivatives of phenol show the same decrease with temperature in moment, which is certainly either due to association or to solute-solvent interaction.

Recently Nagakura and Baba⁽²⁾ pointed out that the electron migration plays an important role in moments of aromatic molecules. It is not unlikely that such an effect is also included in the moments recorded here, but admittedly the observed temperature-variation should not be regarded as arising solely from this cause.

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(1) "Table of Electric Dipole Moments" Massachusetts Institute of Technology, 1949.

* Exceptions to this rule occur in the cases of *m*- and *p*-nitrophenols.

(2) Nagakura, and Baba Shortly to be printed in J. Am. Chem. Soc., **74** (1952)

It is a well-known fact that hydroxyl compounds are apt to associate together into groups by the formation of hydrogen bonds. Further, it has often been pointed out that these molecules easily interact with hydrogen bonding solvents such as dioxane and ethers.(2) (3) The present author once examined the use of ethyl ether as a solvent for dipole moment studies and found that it reduces the degree of association of alcohol to a remarkable extent, that there should be no peak in P_2-x curve in ether solution(4) (Fig. 1). This remarkable phenomenon can be explained by the hypothesis that on account of the strong interaction between the solute and the solvent there are scarcely any associated solute molecules in the diluted part of the ether solution. This explanation is in good accord with the higher moment of alcohols in ether, *viz.*, 1.8-1.9D., while further support may be found in the recent work of Nagakura and Baba.(2) Moreover, the high dielectric constant of ether is certainly able to reduce the degree of association, but it cannot possibly be the dominant cause of this phenomenon.

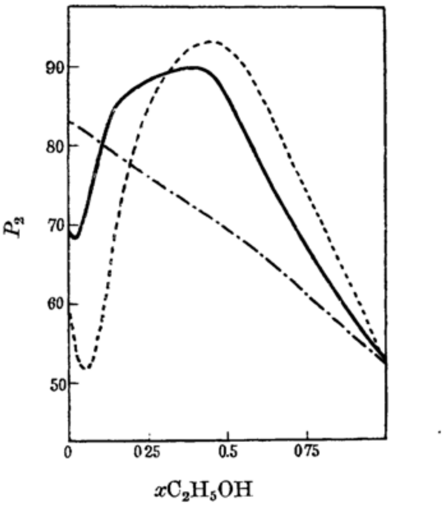

Fig. 1.—The molecular polarization of ethyl alcohol in various solvents. P_2 are plotted against the concentrations of alcohol: ——benzene; ····hexane; —·—· ethyl ether.

The formation of hydrogen bonds with benzene is not certain. But a very weak tendency to form such a solute-solvent interaction may be suspected, since benzene also gives a less pronounced maximum of polarization and a slightly higher moment for alcohols than any other normal solvents. Consequently, the result in toluene, which resembles benzene in many respects, may not be free from the possible errors arising from this sort of solute-solvent interaction.

Summary

Dipole moments of cresols, chlorophenols and nitrophenols were measured in toluene at 0°, 25°, 50° and 75°C. They are found to be in general agreement with the corresponding values measured in benzene. Further, factors which may affect the moment are considered in detail. As a connected topic it is shown that some anomalies of hydroxyl compound in ether are explainable by the hypothesis of hydrogen bond formation with the solvent.

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(3) Curran and Estok, *J. Am. Chem. Soc.*, **72**, 4575 (1950).

(4) Higasi, *Sc. Pap. I. P. C. R.* (Tokyo) **24**, 57 (1934).