THE HYDROGEN BOND AND THE VISCOSITY OF SOLUTIONS

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The formation of complexes due to hydrogen bonds between alcohol, phenol and acid molecules causes a sharp increase in the viscosity of liquids [1]. Inasmuch as the indicated complexes of molecules of dissolved substances survive in such solvents as benzene, an anomalously increased viscosity of benzene solutions of the substances under consideration is to be expected. Since the viscosity of liquids is determined not only by the coupling forces between molecules (including the hydrogen bond), but also by the mass of the molecules and the number of them in a unit volume, to detect the influence of the coupling forces it is reasonable to compare the values of the viscosity of solutions of identical-by-weight samples of the substances in a given volume of solution. In such solutions the increase in the mass of the molecules of the dissolved substance is accompanied by decrease in the number of molecules in a unit volume, and the difference in viscosity evoked by differences in the mass of the molecules is compensated for to a considerable extent by the differences in the number of molecules of the dissolved substance in a unit volume.

The results of viscosity measurements of the indicated type of solutions of 22 compounds (phenol, its derivatives and substituted phenols) in benzene at 50° are set forth in Table 1. As follows from the data obtained in the case of monosubstituted benzenes, the functional groups arrange themselves in a series according to the value of the viscosity of the corresponding solutions:

$$OH > NO_2 > COCH_3 > OCH_3 > CH_3,$$

i.e., form solutions with the greater viscosity, the greater their group moment. Only a solution of the hydroxyl-containing compound (phenol) has an anomalously high viscosity and the OH group occupies a position in the series which does not correspond with its group moment.

The viscosity of solutions of phenol, cresols, m- and p-nitrophenols is greater than the viscosity of solutions of the corresponding methoxy compounds by $7-28 \cdot 10^{-5}$ poise.

TABLE 1

Viscosity of Benzene Solutions (Samples of 0.9984 - 0.9990 g in Approximately 25 ml of Solution) at 50° ± 0.1

Compound	$\eta \cdot 10^5$ poise	Difference in the viscosity of solutions		
		$\eta_{m-} - \eta_{o-}$	$\eta_{p-} - \eta_{o-}$	$\eta_{OCH_3} - \eta_{OH}$
Nitrobenzene	443			
Nitrophenol: o-	443			
m-	455	+12		
p-	458		+15	
Nitroanisole: o-	454			+11
m-	448	−6		−7
p-	449		−5	−9
Acetophenone	442			
Hydroxyacetophenone: o-	453			
p-	482		+29	
Methoxyacetophenone: o-	456			+3
m-	454	−2		
p-	454		−2	−28
Toluene	436			
Cresol: o-	462			
m-	458	−4		
p-	464		+2	
Cresyl methyl ether: o-	447			−15
m-	444	−3		−14
p-	445		−2	−19
Phenol	449			—
Anisole	440			−9

Compounds with a hydrogen bond within the molecule (o-nitrophenol and o-hydroxyacetophenone) differ from the m- and p-isomers which are associated intermolecularly in solution. Thus, their methyl ethers yield solutions with a viscosity not lower but higher than that of solutions of the initial hydroxy compounds. While solutions of o-, m- and p-isomers ordinarily have almost the same viscosity, solutions of o-isomers with intramolecular hydrogen bonds within them have an appreciably smaller viscosity (of the order of $15\text{-}29 \cdot 10^{-5}$ poise) than their m- and p-isomers.

It is characteristic that all the relationships noted for benzene solutions are observed in the case of alcoholic solutions of the indicated substances.

In Table 2 are set forth the results of viscosity measurements of alcoholic solutions of 37 compounds of the indicated type (phenol, benzoic acid and their substituted and derived compounds). The functional groups (except OH and COOH) also arrange themselves by value of the viscosity of solutions of monosubstituted benzenes in alcohol in a series which basically agrees in order with that of their group moment:

$$COOH > OH \approx COCH_3 > NO_2 > CHO > COOC_2H_5 > OCH_3 > CH_3.$$

In alcohol phenol and particularly benzoic acid also yield solutions with an anomalously high viscosity related to the influence of intermolecular association. The viscosity of a solution of m- and p-hydroxyacetophenones is greater than the viscosity of a solution of the metameric m- and p-methoxybenzaldehydes by 3-5%. Alcoholic solutions of methoxy compounds, like benzene solutions, have an appreciably smaller viscosity than their initial hydroxy compounds. Solutions of esters of the acids (benzoic and hydroxybenzoic) also have a sharply reduced viscosity in comparison with that of solutions of the acids themselves.

TABLE 2

Viscosity of Alcoholic Solutions (Samples of 0.9984-0.9990 g in Approximately 25 ml of Solution) at 50° ± 0.1

Compound	$\eta \cdot 10^5$ poise	Difference in the viscosity of solutions			
		$\eta_{m-} - \eta_{o-}$	$\eta_{p-} - \eta_{o-}$	$\eta_{OCH_3} - \eta_{OH}$	$\eta_{COOC_2H_5} - \eta_{COOH}$
Nitrobenzene	721				
Nitrophenol: o-	698				
m-	724	+26			
p-	728		+30		
Nitroanisole: o-	717			+19	
m-	716	−1		− 8	
p-	722		+5	− 6	
Acetophenone	726				
Hydroxyacetophenone: o-	725				
m-	760	+35			
p-	775		+50		
Methoxyacetophenone: o-	726			+ 1	
m-	731	+ 5		−29	
p-	733		+ 7	−42	
Benzaldehyde	718				
Hydroxybenzaldehyde: o-	729				
m-	765	+36			
Methoxybenzaldehyde: o-	733			+ 4	
m-	737	+ 4		−28	
p-	737	+ 4			
Ethyl hydroxybenzoate: o-	708		+4		−28
m-	751	+43			−46
p-	751		+43		−63
Toluene	682				
Cresol: o-	738				
m-	741	+ 3			
p-	743		+ 5		
Cresyl methyl ethers: o-	704			−34	
m-	701	− 3		−40	
p-	702		− 1	−41	
Phenol	726				
Anisole	693			−33	
Benzoic acid	734				
Hydroxybenzoic acid: o-	736				
m-	797	+61			
p-	814		+78		
Ethyl benzoate	711				−23

Compounds with an intramolecular hydrogen bond, in contrast to their intermolecularly associated m- and p-isomers, yield solutions with a viscosity even lower than that of their methyl ethers and their non-associated metamers (o-hydroxyacetophenone and o-methoxybenzaldehyde) in spite of the presence of the hydroxyl group. In alcohol o-hydroxyacetophenone, o-nitrophenol, o-hydroxybenzoic acid, o-hydroxybenzaldehyde and ethyl o-hydroxybenzoate also tend to form an intramolecular hydrogen bond and to yield solutions which have an appreciably lower viscosity than that of their m- and p-isomers. All these correlations between the properties of the isomers are absent in the cresols, the o-isomer of which does not form an intramolecular hydrogen bond.

Thus, the same relations for the viscosities of alcohol solutions of non-associated and associated inter- and intramolecular compounds are found as for benzene solutions. Judging by certain data [2], such a relation also exists for the viscosity of 0.01 N solutions in amyl acetate; evidently in alcoholic solutions of the concentration under consideration the tendency of molecules of the dissolved substance, at least in part, toward the formation both of intramolecular hydrogen bonds and toward the formation of complexes between molecules due to the hydrogen bond is maintained. Data for the density of solutions [3] also leads to similar conclusions.

The correlations for the viscosity of solutions established above are identical with those detected for the viscosity of individual substances in the liquid state. This permits an estimate to be made from the data for the viscosity of solutions of corresponding compounds concerning the presence and character of association of a dissolved substance; this is particularly important for compounds which decompose on fusion.

EXPERIMENTAL

The synthesis and purification of the substances which were studied was carried out in accordance with the literature data. The purification of the solvents was described in the preceding article [3]. The relative viscosity was measured in an Ostwald viscosimeter. The viscosimeter was calibrated with the corresponding pure solvent. The measurement was carried out in a viscosimeter with the time of outflow for benzene equal to 279.9 seconds; for cresol solutions a viscosimeter was used with a time of outflow for benzene of 67.2 seconds. In the determination of the viscosity of alcoholic solutions the time of outflow of pure alcohol amounted to 120.0 and 129.2 seconds. In the calculations $\eta \cdot 10^5$ at 50° and the density were taken as 436 and 0.8464 for benzene, and as 702 and 0.7778 for alcohol. The value of the density of the solutions, necessary for the calculation of the value of η [3] was simultaneously determined. The data set forth in the tables for the viscosity of the solutions are the averages of several experiments which deviated from each other by not more than 0.4%.

SUMMARY

1. The values for the viscosity of solutions at 50° in benzene and in ethyl alcohol were determined for a number of phenols and acids and their esters.

2. It was established that the same relationships of the viscosities of non-associated and associated inter- and intramolecular compounds apply to benzene and alcohol solutions as to the individual substances in the liquid state.

3. The data for the viscosity of solutions of corresponding compounds can be utilized for the qualitative determination of the presence and character of association of a dissolved substance.

LITERATURE CITED

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Received March 23, 1953

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* See Consultants Bureau Translation, page 73.