The Interaction between Phenol and Some Compounds Containing CONH Group.*

Tokuzo Tonomura,** Juro Maruha** and Kenjiro Sumi**

In the present paper we report the results of a study of interaction between phenol and some compounds containing CONH group such as acetamide (I), benzamide (II), benzanilide (III) and acetanilide (IV).

Generally, the dielectric constant of a solution of single organic compound dissolved in a non-polar solvent changes in proportion to the concentration. In solutions of binary mixture of various composition, the dielectric constants change in proportion to the molecular ratio of solutes, only if no interaction occurs. If two components interact and form a complex, the solution will have a dielectric constant differing from the additive value. And the plot of dielectric constants against the molar composition of solutes should show a change of slope at a point corresponding to the composition of the complex formed.

C.H. Giles and coworker) measured previously the dielectric constants of a number of binary solutions of organic compounds, in order to study the hydrogen-bonding properties between two com-

---


** Faculty of science Kanazawa University, Sengoku-Cho, Kanazawa-City, Japan

ponents. They concluded that phenolic hydroxyl groups have a consistent tendency to bond with other similar groups, but not with a keto group.

In the present work the dielectric constant were measured by a ordinary heterodyne beat method at 5 Mc/sec. and at 20 ± 0.1°C. The solvent used was well refined dioxane. As Nagakura et al. pointed out that dioxane interacted with phenol in petroleum benzine, we examined in advance the change of the dielectric constant, and found that it changes practically linearly with concentration of phenol, up to 0.2 moles/l. In this work the total concentration of solutes was 0.2 or 0.1 moles/l. Consequently, if, in binary solutions, the curves of dielectric constant with composition change their slopes, it may be concluded that the two components interact with each other. Figs. 1, 2, 3, and 4 show the curve of the observed dielectric constant against molar ratio for each binary solution together with specific polarization, which is calculated from the relation \( p = (\varepsilon - 1)/(\varepsilon + 2)d \). The conclusions drawn from the whole series of results are summarised in Table 1 together with dipole moments.

Table 1 Dipole Moments of Solutes and Mole Ratio of Complex

<table>
<thead>
<tr>
<th>Solute</th>
<th>Dipole moment (D)</th>
<th>Mole ratio of complex</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetamide</td>
<td>3.6</td>
<td>1 : 1</td>
</tr>
<tr>
<td>Benzamide</td>
<td>3.87</td>
<td>1 : 1</td>
</tr>
<tr>
<td>Acetanilide</td>
<td>3.77</td>
<td>2 : 1</td>
</tr>
<tr>
<td>Benzanilide</td>
<td>3.83</td>
<td>1 : 2</td>
</tr>
</tbody>
</table>

Phenol has the consistent tendency to bond with amide molecules or anilide ones. However, phenol-amide systems exhibit a behavior different from phenol-anilide systems. The former system seems to be able to form 1 : 1 ratio complexes, and furthermore the curve of dielectric constant deviates upwards from the one expected from the additive rule. On the other hand, the latter interacts with 1 : 2 or 2 : 1 ratio and dielectric constants of the corresponding composition are lower than those expected from the additive value. As the four substances used here have nearly equal dipole moments, the electron distribution in molecule can be expected almost similar. Nevertheless the fact, that there are different behaviors between the two systems mentioned above, may be interpreted as steric effect in anilide molecules. It is the most reasonable interpretation to adopt the structure shown in Fig. 5 for the 1 : 1 ratio complex in phenol-amide systems. As for the anilide systems, such a configuration can not be realized, because anilide has such a large substituent as phenyl, and it takes a trans- position with respect to the other substituent. Giles considered that the complex formation of the ratio 2 : 1 in the phenol-acetanilide system was due to the enol form, C(OH) : N, which they considered as bifunctional, but their consideration is very doubtful. In the phenol-anilide system the interaction appears to be so weak that the curve is almost linear. This is interpreted by the fact that phenol can not approach to CONH group to form a bond with anilide molecule, and the case of benzanilide is especially so, for the molecule contains two phenyl groups.

(Received February 21, 1959)

Literature: