The Formation Constants of 1 : 1 and 1 : 2 Complexes of Ethyl Acetate and Phenyl Acetate with Phenol

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The detection of complex formation is convincingly accomplished by the study of infrared spectra. A complete survey of the literature wherein infrared spectroscopy is used as an analytical tool for the detection of such complexes has been made by Pimentel and McClellan.[1] Several recent studies[2-4] of the hydrogen bonding of phenols to different proton-acceptor groups have indicated the existence of at least two different types complexes in most of the systems over a wide range of concentration. A large number of values of the equiliarium constants for the formation of 1 : 1 complexes is available for many systems, but no quantitative values are available for the 1 : 2 complexes. The main purpose of this work is to obtain the formation constants for such complexes, along with the formation constants for 1 : 1 complexes; these values will make possible the determination of the concentrations of different molecular species in the system under consideration.

The formation constants, K_{11} and K_{12}, of 1 : 1 and 1 : 2 complexes of ethyl acetate and phenyl acetate with phenol in carbon tetrachloride were determined by studying the infrared absorption in the hydroxyl and carbonyl regions. The measurements were made with a Hilger H 800 double-beam spectrophotometer equipped with sodium chloride optics; approximately 0.04 M solutions of phenyl acetate and ethyl acetate 0.25 mm. thick were placed in a variable-path-length micrometer cell supplied by the Hilger. The temperature of the cell was maintained at 22°C.

The modified method of Brown and Kubota[5] developed by Whetsel and Kagarise[4] was used for the calculation of the equilibrium constants for the formation of the complexes of the $A+B \rightleftarrows AB$ and $AB+B \rightleftarrows AB_2$ types, where A represents the ester and B, the monomeric phenol. This method, given in detail by those authors, involves the calculation of a set of K_{11} values for different assumed values of K_{12}. A plot of the values of K_{11} against the concentration of the phenol results in a series of lines with different slopes and intercepts (Fig. 1). The value of K_{12} which gave a line of zero slope was taken as the best value, and the intercept of this line was taken as K_{11}. The formation constants of 5.9 ± 1 l./mol. and 13.5 ± 2 l./mol. were obtained for the 1 : 1 and 1 : 2 phenyl acetate and phenol complexes respectively. For the ethyl acetate - phenol system, values of 8.6 ± 1 l./mol. and 25 ± 2 l./mol. were obtained for K_{11} and K_{12} respectively.

The formation constants for the 1 : 1 complexes were also obtained by the method suggested by Nash.[6] This method, derived by Nash, utilises the $Y=X(K-\alpha)-K$ relation, where Y is the reciprocal of the concentration of monomeric phenol at equilibrium and

$$X=\frac{1}{1-A/A_0}$$

where A_0 and A are the absorbances of the ester at a given frequency in the absence and in the presence of the donor respectively. The equilibrium concentrations of phenol required were determined from the hydroxyl absorption, and A and A_0 were taken in the carbonyl region near the characteristic frequency of the 1 : 1 complex. The intercept of the plot of Y against X is the negative value of the formation constant for the 1 : 1 complex.

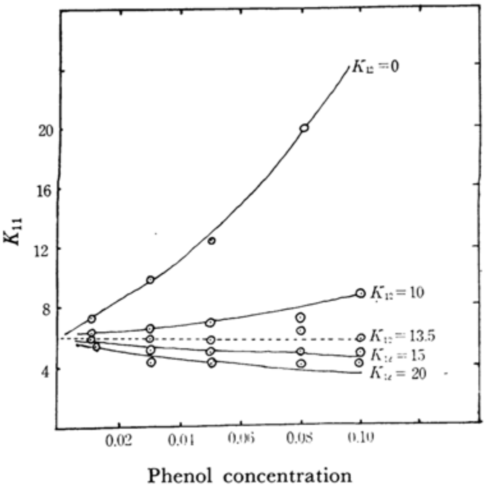

Fig. 1. Formation constants for 1:1 and 1:2 complexes of phenyl acetate and phenol in CCl_4 solution.

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[1] G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman & Co., London (1960), p. 67.

[2] E. Gray, *Ann. Chim.*, (12) **3**, 355 (1948).

[3] J. Lascombe, Thesis, University of Bordeaux (1960).

[4] R. E. Kagarise and K. B. Whetsel, *Spectrochim. Acta*, **18**, 315 (1962).

[5] T. L. Brown and M. Kubota, *J. Am. Chem. Soc.*, **83**, 331 (1961).

[6] C. P. Nash, *J. Phys. Chem.*, **64**, 950 (1960).

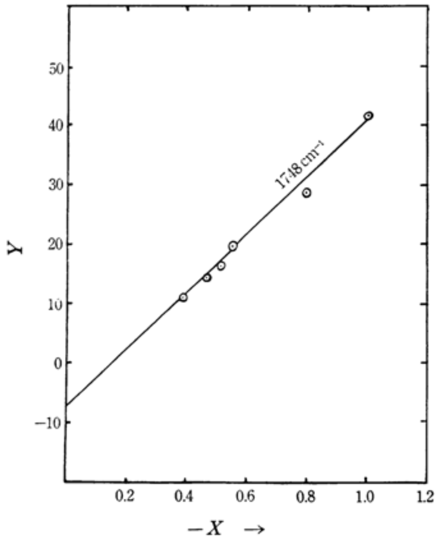

Fig. 2. Formation constant for 1:1 complex phenyl acetate with phenol determined by Nash method.

Figure 2 shows such a plot for the phenyl actate - phenol system. A value of 6.5 l./mol. was obtained for the formation constant K_{11} for the phenyl acetate - phenol system. In a similar manner, a value of 8 l./mol. was obtained for K_{11} for ethyl acetate - phenol system. The values of the formation constants of 1 : 1 complexes obtained by the two methods agree well.

The values of K_{11} obtained in the present investigation compare favourably with the value of 8.68 l./mol. at 27.85°C obtained by Powell and West[7] for the phenol - ethyl acetate system. Also, the value of 7.1 l./mol. at 30°C for the same system reported by Nagakura[8] from his ultraviolet studies agrees closely with the results of our present investigation.

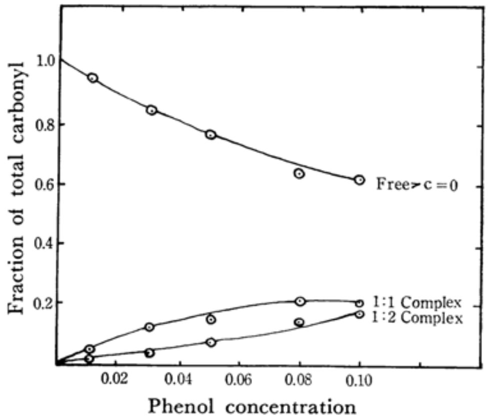

Fig. 3. Relative abundance of free and complexed phenyl acetate in mixtures of phenol and CCl_4.

It should be noted that the K_{11} and K_{12} values obtained in the present investigation for the phenyl acetate - phenol system are relatively lower than those for the ethyl acetate - phenol system. This may be due to the molecular complexity of phenyl acetate, which may hinder the possibility of the formation of specific complexes.

From the knowledge of the formation constants K_{11} and K_{12} the relative abundance of 1 : 1 and 1 : 2 complexes can be easily determined. Figure 3 shows that a high fraction of the complexed ester is present as 1 : 2 species and that at higher concentrations of phenol the 1 : 2 complex may predominate.

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7) D. L. Powell and R. West, *Spectrochim. Acta*, **20**, 983 (1964).
8) S. Nagakura, *J. Am. Chem. Soc.*, **76**, 3070 (1954).