A Convenient Method of Determining the Stability of a 1:1 Complex in Solution by the Refractometric Method

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Giles' method[1] of detecting complex formation in solution by the refractive index measurement is a well-established, simple and sensitive one, especially for detecting intermolecular hydrogen-bonding pairs, including the $X-H\cdots\pi$ electron type ($X=O$ and N).[2] In this communication the possibility of estimating the equilibrium constant, K, of a 1:1 complex formation ($X+Y\leftrightarrows XY$) by this method will be described.

In the Giles method, a physical property (the square of the refractive index) of the solution of X and Y is plotted against the solute molar ratio, while the total concentration (X+Y) is kept constant. The deviation from the "additivity" line PQ (see Fig. 1) is proportional to the concentration of the complex XY.[3] For an equimolar mixture of X and Y, where the deviation is the maximum value, RS[4], we can write:

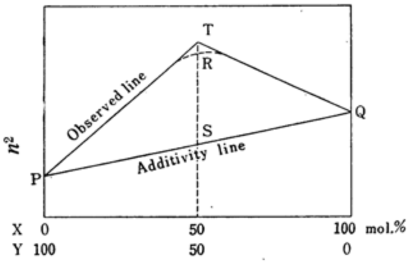

Fig. 1. Schematic representation of n^2 vs. molar ratio plot where 1:1 complex is formed between X and Y.

$$RS=\alpha Z \tag{1}$$

where Z is the maximum concentration of XY, and α is constant for the three substances X, Y and XY. When the total concentration, C, is changed to C' and the same procedure repeated, we can obtain the similar relation:

$$R'S'=\alpha Z' \tag{2}$$

From Eqs. 1 and 2 we obtain:

$$RS/R'S'=Z/Z'=k \tag{3}$$

The equilibrium constant, K, is given by:

$$K=Z/(C/2-Z)^2=Z'/(C'/2-Z')^2 \tag{4}$$

From Eqs. 3 and 4,

$$K=2\sqrt{k}\{\sqrt{k}(C+C')-(C+kC')\}/(C-kC')^2 \tag{5}$$

Thus K can be calculated from Eq. 5.

A preliminary test of the utility of this equation was carried out using an Abbe refractometer. The results are summarized in Table I.

Because of the limited accuracy of the Abbe refractometer (±0.0002), it was necessary to raise the concentration of the solute to 10^{-1} mol./l. in order to make the k term large enough to fit Eq. 5. At these large concentrations, howerver, the data obtained are less reliable because of the self-association of the solutes (over 30%). Nevertheless, the orders of K obtained are in agreement with the literature values: phenol-methyl acetate, K_{20° 13.4,[5] phenol-naphthalene K_{27° 4.6.[6] It will be possible to obtain reliable thermodynamic data on 1:1 association in solution by utilizing a differential refractometer of a higher precision.[7]

TABLE I. THE ESTIMATION OF THE K VALUE BY REFRACTIVE INDEX MEASUREMENT

X	Y	C, mol./l.	Temp., °C	K, l./mol.
Phenol	Methyl acetate	0.20—0.15	19	ca. 10
Phenol	Naphthalene	0.10—0.16	27	ca. 5
Ethanol	Naphthalene	0.30—0.40	28	ca. 5

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[1] C. H. Giles and R. B. Mckay, *J. Biol. Chem.*, **237**, 3388 (1962), and the preceding papers of this series.

[2] Z. Yoshida, E. Ōsawa and R. Oda, *J. Phys. Chem.*, **68**, 2895 (1964).

[3] F. M. Arshid, C. H. Giles, E. C. McLure, A. Ogilve, T. J. Rose and J. C. Eaton, *J. Chem. Soc.*, **1955**, 67.

[4] Practically RS is observed as TR, since the amount of TR is too small to be discerned.

[5] S. Nagakura, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **75**, 734 (1954).

[6] R. West, Intern. Symp. Mol. Struc. Spectroscopy, 1962, Tokyo, D117.

[7] A D.R. of a 7×10^{-7} accuracy has been manufactured; see *Chem. Eng. News*, **38**, [31] (1960), p. 55.