УДК 518.62 : 543.422.6

Ü. HALDNA, A. MURSHAK

ADAPTION OF FACTOR ANALYSIS FOR ESTIMATION OF DONOR—ACCEPTOR EQUILIBRIUM CONSTANT. A CASE OF IODINE—DIMETHYLFORMAMIDE INTERACTION

(Presented by O. Eisen)

The donor—acceptor interaction between iodine and dimethylformamide (DMF) has been recently studied by R. Makitra and I. Tsikantchuk [1]. This interaction was examined by measuring visible absorption of 0.001 M solutions of iodine in cyclohexane containing different amounts of DMF [1]. By the method of Drago [2], the respective constant

$$K = \frac{[DMF \cdot J_2]}{[DMF] \cdot [J_2]} \qquad (1)$$

has been calculated [1]. The K values obtained depend on the wavelength (λ) used [1]. In the $\lambda = 400$—460 nm range, K varies from 7.2 to 50 [1]. This result is not unexpected because of the absorption maximum of iodine shifts towards shorter wavelengths with increasing DMF concentration (Fig. 1). The aim of this paper is to show how the wavelength
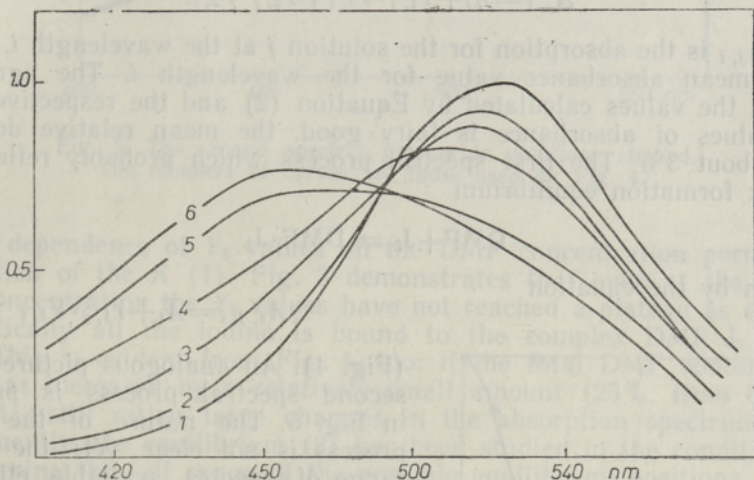

Fig. 1. Absorption spectra of 0.001 M iodine solutions in cyclohexane at different DMF concentrations: 1 — no DMF added, 2 — 0.010 M, 3 — 0.020 M, 4 — 0.040 M, 5 — 0.080 M, 6 — 0.100 M.

dependence of K values can be eliminated by using a less familiar approach, viz. the factor analysis (FA), for the treatment of spectral data. The method of FA has been described in detail [3], summarized by Simonds with reference to optical spectra [4] and used in a number of
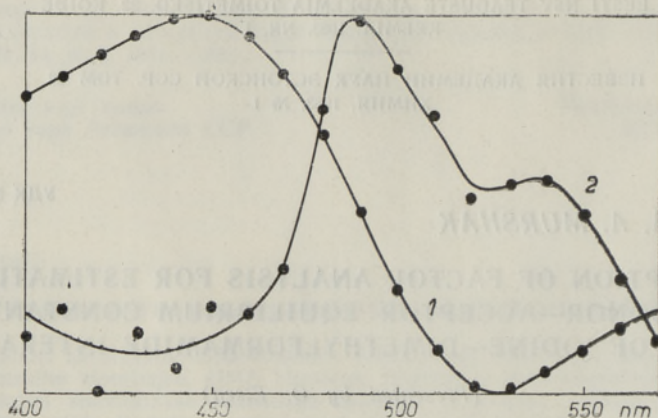
Fig. 2. Vectors obtained by factor analysis. *1* — first vector, *2* — second vector.

papers dealing with protonation problems [5—9]. No new experiments have been performed in this study. As initial data, the J_2 absorption spectra published by R. Makitra and I. Tsikantchuk [1] have been used (Fig. 1). These spectra have been treated by a computer program based on Simonds' FA algorithm [4]. It has been found that in the case studied two independent spectral processes occur. The first one accounts for 98.7% of the total variability in the spectra and the second is responsible for 0.9% only. The rest in the variability (0.4%) is due to the random error. The vectors (V_1 and V_2) and the corresponding coefficients (Y_1 and Y_2) obtained are presented in Figs 2 and 3, respectively. The absorption curves may be calculated from the equation

$$A_{j, i} = \bar{A}_i + Y_{1, j} \cdot V_{1, i} + Y_{2, j} \cdot V_{2, i}, \tag{2}$$

where $A_{j, i}$ is the absorption for the solution j at the wavelength i, and $\bar{A}_i$ is the mean absorbance value for the wavelength i. The agreement between the values calculated by Equation (2) and the respective measured values of absorbance is fairy good, the mean relative deviation being about 3%. The first spectral process which probably reflects the complex formation equilibrium

$$DMF + J_2 \rightleftarrows DMF \cdot J_2 \tag{3}$$
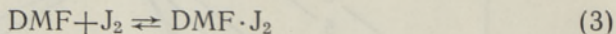
is given by the equation

$$A_{1, j, i} = \bar{A}_i + Y_{1, j} \cdot V_{1, i} \tag{4}$$
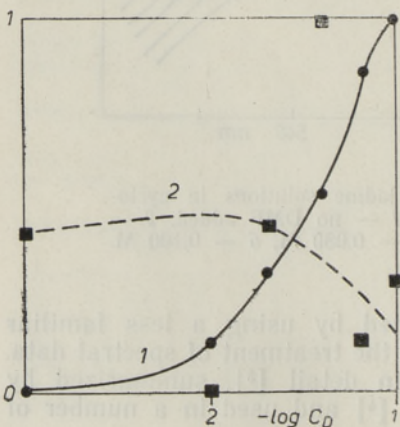
(Fig. 4). An analogous picture for the second spectral process is presented in Fig. 5. The nature of the second process is not clear yet; the limited range of spectra available eliminates the possibility of discussions on this subject.

Fig. 3. Coefficients obtained by factor analysis. C_D is stoichiometric DMF molar concentration: *1* — coefficient for the first vector, *2* — coefficient for the second vector.
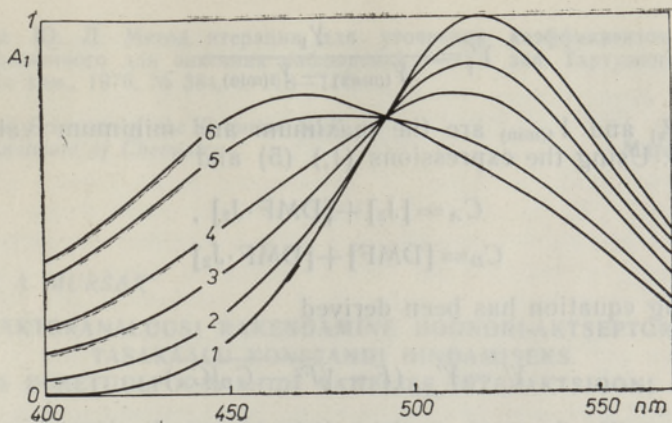
Fig. 4. The first spectral process at the following DMF concentrations: *1* — no DMF added, *2* — 0.010 M, *3* — 0.020 M, *4* — 0.040 M, *5* — 0.080 M, *6* — 0.100 M.
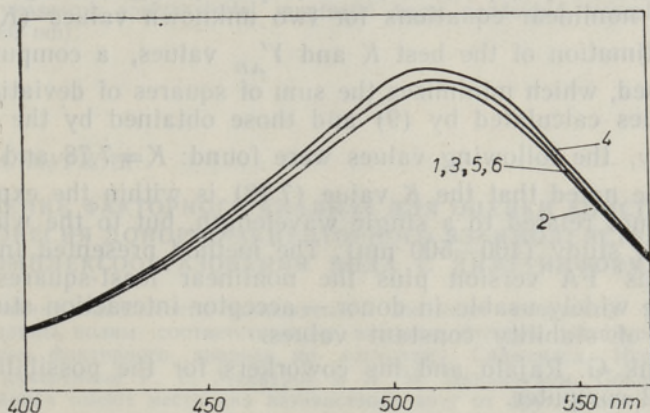

Fig. 5. The second spectral process in solutions studied. The numbers of curves are those used on Fig. 4.

The dependence of Y_1 values on the DMF concentration permits the calculation of the K (1). Fig. 3 demonstrates that even at the highest DMF concentration the Y_1 values have not reached a plateau as expected if practically all the iodine is bound to the complex $DMF \cdot J_2$ by the DMF. This is evident from Fig. 1, too: if the total DMF concentration (C_D) was increased by a relatively small amount (25%, from 0.080 to 0.100 M), still rather large changes in the absorption spectrum occur. Consequently, the equilibrium (3) has been studied in the conditions [1] not covering the full range of the possible equilibrium positions. In this case we have to estimate two parameters: the K (1) and the Y_{AD}. The latter is the Y_1 value corresponding to the case where practically all the iodine in the solution is included in $DMF \cdot J_2$. It is easy to show that

$$\frac{Y'_{AD} - Y'_1}{Y'_1} = \frac{[J_2]}{[DMF \cdot J_2]} \qquad (5)$$

where the prims (′) denote that the respective Y_1 values are given in a standardized scale from zero to one

$$Y''_1 = \frac{Y_1}{Y_{1(max)} - Y_{1(min)}} \qquad (6)$$

where $Y_{1(max)}$ and $Y_{1(min)}$ are the maximum and minimum values of Y_1, respectively. Using the expressions (1,) (5) and

$$C_A = [J_2] + [DMF \cdot J_2] , \qquad (7)$$

$$C_D = [DMF] + [DMF \cdot J_2] \qquad (8)$$

the following equation has been derived

$$Y'_1 = Y'_{AD}(F - \sqrt{F^2 - C_D/C_A}) \qquad (9)$$

where

$$F = \frac{C_A + C_D + K^{-1}}{2C_A}. \qquad (10)$$

The relationship (9) holds for each pair of C_A and C_D values. Thus we have 6 nonlinear equations for two unknown values (K and Y'_{AD}). For the estimation of the best K and Y'_{AD} values, a computer program [10] was used, which minimizes the sum of squares of deviations between the Y'_1 values calculated by (9) and those obtained by the FA method. In this way, the following values were found: $K = 7.78$ and $Y'_{AD} = 2.28$. It should be noted that the K value (7.78) is within the expected range [1] and is not related to a single wavelength, but to the whole spectral range under study (400—500 nm). The method presented in this paper, the Simonds' FA version plus the nonlinear least-squares treatment, seems to be widely usable in donor — acceptor interaction studies for the estimation of stability constant values.

We thank G. Rajalo and his coworkers for the possibility of using an EC-1022 computer.

REFERENCES

1. Makitra, R. G., Tsikantchuk, I. M. Solvent effects on the organic complexes. II. The UV-spectro-photometrical investigation of interaction between dimethylformamide and iodine. — Organic Reactivity, 1979, v. 16, N 4 (60), p. 505.
2. Гурьянова Е. Н., Гольдштейн А. П., Ромм И. П. Донорно-акцепторная связь. М., 1973, с. 45.
3. Harman, H. H. Modern Factor Analysis. Chicago, 1967.
4. Simonds, J. L. Application of characteristic vector analysis to photographic and optical response data. — J. Opt. Soc. Am., 1963, v. 53, p. 968—973.
5. Edward, J. T., Sin Cheong Wong. Ionization of carbonyl compounds in sulfuric acid. Correction for medium effects by characteristic vector analysis. — J. Am. Chem. Soc., 1977, v. 99, p. 4229—4233.
6. Zalewsky, R. I. Adaption of characteristic vector analysis and titration curve analysis for calculation of pK_{BH^+} from ultraviolet-visible spectral data. — J. Chem. Soc. Perkin Trans. II, 1979, p. 1637—1641.
7. Cox, R. A., Haldna, O. L., Idler, K. L., Yates, K. Resolution of Raman spectra of aqueous sulfuric acid mixtures using principal factor analysis. — Can. J. Chem., 1981, v. 59, p. 2591—2598.
8. Cox, R. A., Smith, C. R., Yates, K. The excess acidity method. The basicities of some acetophenones and acetone in moderately concentrated sulfuric acid. — Can. J. Chem., 1979, v. 57, p. 2952—2959.
9. Haldna, Y., Murshak, A., Kuus, H. The basicities of acetanilide and 4-cyanoacetanilide in aqueous solutions of sulfuric and perchloric acids. — Organic Reactivity, 1980, v. 17, N 3, p. 313—323.

10. Халдна Ю. Л. Метод итерации для уточнения коэффициентов уравнения, предложенного для описания наблюдений. — Уч. зап. Тартуского гос. ун-та. Тр. по хим., 1976, № 384, с. 118—120.

Ü. HALDNA, A. MURSAK

FAKTORANALÜÜSI RAKENDAMINE DOONORI-AKTSEPTORI TASAKAALU KONSTANDI HINDAMISEKS.
JOODI JA DIMETÜÜLFORMAMIIDI VAHELISE INTERAKTSIOONI JUHTUM

Eesmärgiga elimineerida doonori-aktseptori tasakaalu konstandi sõltuvus lainepikkusest tööldeli vastavaid aktseptori neeldumisspektreid faktoranalüüsimeetodil, rakendades Simondsi algoritmi (kasutatud joodi neeldumisspektrid on võetud R. G. Makitra ja I. M. Tsikantšuki tööst). Vaadeldavas süsteemis esineb kaks teineteisest sõltumatut tasakaalulist protsessi. Suuremaid spektraalseid muutusi põhjustav protsess on samastatud doonori-aktseptori tasakaaluga joodi ja dimetüülformamiidi vahel. Mittelineaarsete vähimruutude meetodil on arvutatud nimetatud tasakaalu konstandi väärtus ($K = 7{,}78$), mis baseerub spektraalsetel muutustel kogu vaadeldud lainepikkuste piirkonnas (400—460 nm).

Ю. ХАЛДНА, А. МУРШАК

ПРИМЕНЕНИЕ ФАКТОРНОГО АНАЛИЗА ДЛЯ ОЦЕНКИ КОНСТАНТЫ РАВНОВЕСИЯ ДОНОРНО-АКЦЕПТОРНОГО ВЗАИМОДЕЙСТВИЯ.
СЛУЧАИ КОМПЛЕКСООБРАЗОВАНИЯ ЙОДА С ДИМЕТИЛФОРМАМИДОМ

Для элиминирования зависимости вычисляемого значения константы устойчивости комплекса от длины волны соответствующие видимые спектры поглощения обрабатывались методом факторного анализа по алгоритму Саймондса. Использовались спектры йода, измеренные Р. Г. Макитрой и Я. М. Циканчуком. Показано, что в изученных растворах имеют место два независимых друг от друга спектральных процесса. Первый из них, описывающий основную часть изменений в измеренных спектрах, отражает реакцию донорно-акцепторного взаимодействия с образованием комплекса ДМФА·йод. Методом нелинейных наименьших квадратов вычислено значение константы устойчивости комплекса ($K = 7{,}78$), что базируется на спектральных изменениях во всем изученном диапазоне длин волн (400—460 *нм*).