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An Application of Factor Analysis to the Electronic Spectra of Iodine in Mixed Solvents

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Synopsis. The electronic spectra of iodine diluted in three kinds of mixed solvents, ethanol-heptane, 1,4-dioxane-cyclohexane, and tetrahydrofuran-cyclohexane have been measured as a function of molar composition in mixed solvents and a factor analysis technique has been applied to interpret the results. The number of different iodine-solvent complexes in ethanol solutions is smaller than that in ether solutions.

It is well-known that iodine molecule can form charge-transfer complex with many organic molecules which act as an electron donor (e.g., benzene, alcohols, etc.) and its color becomes brown or red. In nonpolar solvents such as aliphatic hydrocarbons, however, the color of iodine remains purple just as in the vapor or solid phase. We may classify these solvents into complexing(C) and non-complexing(NC) solvents to iodine.

Now, what happen when we use mixed solvents? If we adopt a combination of C and NC solvents, there should be a preferential solvation of C solvent to iodine molecules because of stronger intermolecular interaction. The purpose of the present study is to investigate the behavior of iodine in some kinds of mixed solvents from the spectroscopic point of view.

When we adopt an associated liquid as the C solvent, we have again a preferential solvation because associated liquids are usually a strong C solvent and in addition, possible change in the state of the association of the solvent in mixed solvents may result anomalous behavior in some physical properties. We have already studied diffusion, solubility, and their temperature dependence of iodine in various kinds of mixed solvents.[1-3] In this paper, we will describe the results on the electronic spectra of iodine in the visible light region as a function of molar composition of some typical mixed solvents and an analysis of these spectra by a factor analysis technique developed by one of us.[4]

Spectral Measurements

Electronic spectra of iodine in three kinds of mixed solvents have been measured by using a Shimadzu multipurpose spectrophotometer. The mixed solvents used are ethanol-heptane, 1,4-dioxane–cyclohexane, and tetrahydrofuran–cyclohexane. Sample solutions were prepared by dissolving certain amounts of spectrograde iodine into mixed solvents which consist of two kinds of spectrograde reagents. The concentration of iodine which is near 1×10^{-3} M (1 M = 1 mol dm^{-3}) was determined by conventional iodometry and the molar composition of C solvent in mixed solvents is 0, 0.025, 0.05, 0.10, 0.15, 0.2, 0.4, 0.6, 0.8, or 1.0, respectively.

The wavelength range used is between 410 and 600 nm. Reproducibility of the spectra is ±0.003 for 100% absorbance and ±0.0005 for 0% absorbance and the effect of titration error on the absorbance is estimated to be ±0.0010. Total experimental error is thus as large as ±0.0025.

The spectra of iodine in the three mixed solvents obtained in the present study are shown in Fig. 1. Each absorbance value is corrected to that for a concentration of 1×10^{-3} M. Qualitative feature of the results is as follows: in the case of iodine in ethanol-heptane solutions, one can observe the presence of a rather clear isosbestic point, whereas there is no specific isosbestic point for 1,4-dioxane–cyclohexane and tetrahydrofuran–cyclohexane solutions. Note that the present measurement is different from that normally adopted when the charge-transfer complex between iodine and ethers is to be studied in dilute solution of inert solvents.[5] In this case, we would have a definite isosbestic point.

Factor Analysis

The Lambert-Beer law in the absorption spectra may be written as

$$A = \sum_{k=1}^{n_c} \varepsilon_k c_k \tag{1}$$

where A, ε, c, and n_c stand for the absorbance, molar extinction coefficient, the concentration of each component and the number of components, respectively. If we measure the absorbance in the wavelength between λ_1 and λ_r for some number(s) of solutions with different molar compositions, we obtain an absorbance matrix [A]

$$[A] = \begin{bmatrix} A_{11}\cdots\cdots A_{1s} \\ \vdots \qquad\quad \vdots \\ A_{r1}\cdots\cdots A_{rs} \end{bmatrix} \tag{2}$$

which has the elements A_{ij} given below.

$$A_{ij} = \sum_{k=1}^{n_c} \varepsilon_{ik} c_{kj} = \sum_{k=1}^{n_c} f_k \tag{3}$$

Here i and j refer to the number of wavelength used and of solutions with different molar composition, respectively.

The application of main component analysis in the factor analysis technique will permit us to determine the number of the factor n_c whenever the data matrix can be expressed by a linear summation of the factor f_k as in Eq. 3. This number n_c is equal to that of the component to be evaluated. Further details are referred to literature.[4]

We have prepared the data matrix which consist of the absorbance at each 10 nm for each finite molar composition

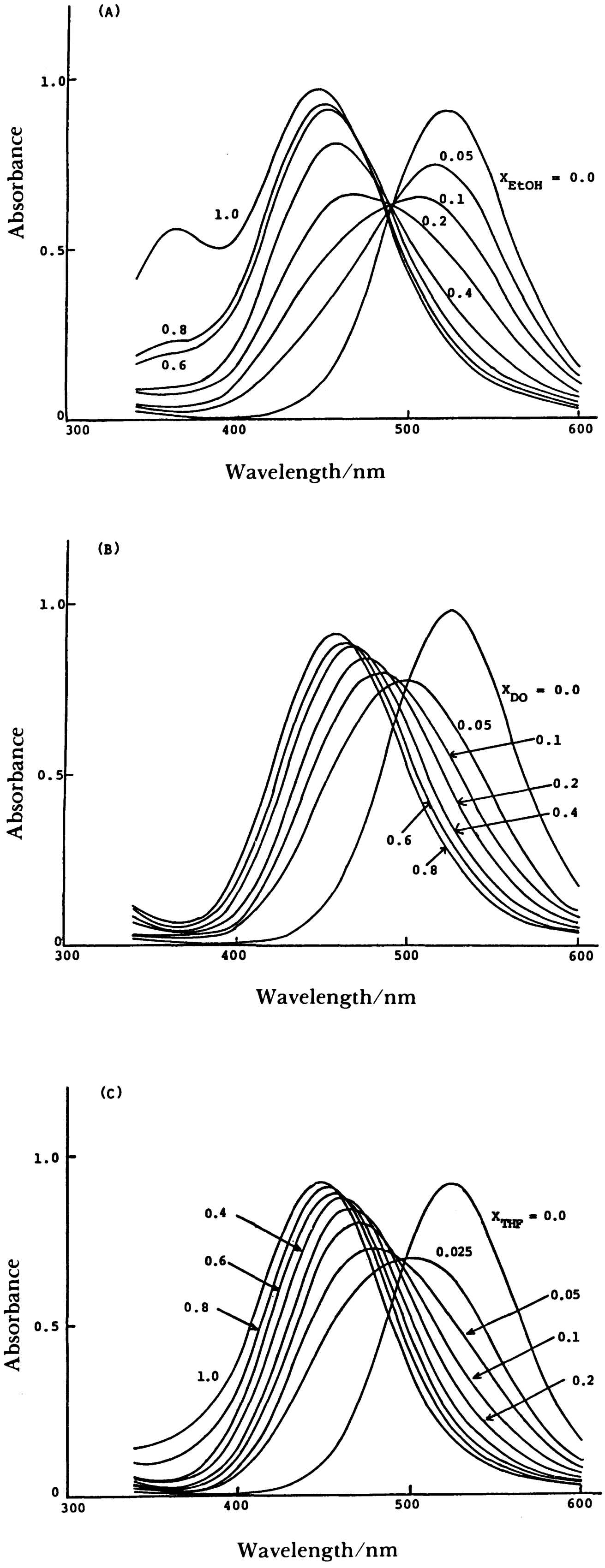

Fig. 1. Absorption spectra of iodine in mixed solvents at 293 K. (A): Ethanol-heptane, (B): 1,4-dioxane-cyclohexane, (C): tetrahydrofuran-cyclohexane.

Table 1. Factor Analysis of the Absorbances of Visible Spectra of Iodine in Mixed Solvents at 293 K

Factor	Eigenvalue	RMS Error	Error 1	Error 2
	1,4-Dioxane + Cyclohexane			
1	41.858549	0.16830	−0.5486	−0.5408
2	5.592714	0.03044	−0.1022	−0.0940
3	0.198604	0.00305	−0.0103	−0.0070
4	0.001504	0.00107	−0.0038	0.0035
5	0.000101	0.00078	−0.0027	0.0020
6	0.000055	0.00055	−0.0020	0.0017
7	0.000035	0.00036	0.0010	−0.0010
	Tetrahydrofuran + Cyclohexane			
1	39.410261	0.15932	−0.6422	−0.6147
2	5.210475	0.03421	−0.1292	−0.1214
3	0.254358	0.00243	0.0125	−0.0098
4	0.001134	0.00071	0.0022	−0.0020
5	0.000049	0.00050	0.0014	0.0014
6	0.000018	0.00038	−0.0012	0.0011
7	0.000016	0.00027	−0.0009	0.0009
	Ethanol + Heptane : case 1.[a]			
1	20.240611	0.11935	0.3328	0.3152
2	1.157937	0.00233	−0.0061	0.0056
3	0.000292	0.00115	−0.0031	0.0028
4	0.000083	0.00042	0.0019	−0.0017
	Ethanol + Heptane : case 2.[a]			
1	34.498014	0.17106	0.4951	0.4925
2	4.576991	0.00983	−0.0435	−0.0347
3	0.015547	0.00146	−0.0063	0.0043
4	0.000197	0.00088	−0.0026	0.0025
5	0.000049	0.00062	0.0023	−0.0021
6	0.000028	0.00043	0.0014	0.0013
7	0.000012	0.00030	−0.0011	0.0011

a) Case 1 : $x_{EtOH}<0.20$. Case 2 : $1>x_{EtOH}>0$.

c. By using these data matrix, we have made factor analysis explained above. Necessary computer program has been written by one of us(D.G.H.).

The results of the main component analysis are given in Table 1. The value for RMS error is based on the following equation.

$$\mathrm{RMS} = [\sum_{i=1}^{r}\sum_{j=1}^{s}(d_{ij}-d^*_{ij})^2/rs]^{1/2} \tag{4}$$

where r is the number of the wavelengths examined, s the number of solutions used, d^*_{ij} the raw data, and d_{ij} the reproduced data. Error 1 and Error 2 refer to the largest and second largest $(d_{ij}—d^*_{ij})$ values, respectively.

It is clear from the table that the RMS error becomes comparable with experimental uncertainty, ±0.0025, when the number of the factor is 3 for tetrahydrofuran-cyclohexane solution, 4 for 1,4-dioxane-cyclohexane solution, 2 or 3 for ethanol-heptane solution, respectively. More careful inspection of the table leads to the conclusion that the number of the factor for the first solution should be 4 rather than 3, because both Error 1 and Error 2 are as large as 0.01 for the factor number of 3.

We have made two analyses for ethanol-haptane solution with each different composition range. As shown in Table 1. the factor number is 3 for the whole composition range. This may be an effect of a small peak at 360 nm which is ascribed to the presence of I_3^- in the solution. If we confine the composition range to the heptane-rich region, the factor number becomes 2, namely the presence of the only one isosbestic point. This suggests that there should be only the 1:1 complex in ethanol solutions.

The above analysis clearly shows that ether solutions are more complex environment for iodine than ethanol solution and that the present results coincide with the tendency in the magnitude of molar enthalpy of complex formation between iodine and electron donors.[6] There is thus essentially no difference between 1,4-dioxane and tetrahydrofuran as electron donor or a partner in complex formation, suggesting that the mode of complex formation with iodine is independent of the number of ether oxygens in the molecule.

Finally, we point out that the present results should be taken into account in the interpretation of the diffusion behavior in mixed solvents.

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