Mem. Fac. Educ., Shimane Univ. (Nat. Sci), Vol. 8, pp. 21–28, December 1974.

STUDIES ON THE DIELECTRIC PROPERTIES OF ORGANIC SOLVENTS VIII.

A CORESPONDENCE BETWEEN THE REFRACTIVE DISPERSION AND THE SHIFT OF INFRA-RED ABSORPTION SPECTRA.

By

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1. Introduction.

Weak molecular interactions between different molecules in a liquid state give rise to several breaking points on the curves of various physical properties vs composition at simple molar ratios. This fact has been examined in the previous papers for various kinds of physical properties such as dielectric constant, 1,2) viscosity, 4,5) optical refractivity 3,6,7) and refractive dispersion. 8,9) Through these investigations, it has been cleared out that the observation of the polarizability of a liquid mixture by the method of dielectric measurements is most effective for the detection of the weak molecular interactions and that of the refractive dispersion is more effective than that of simple refractivity measurements.

In the present paper, the method of infrared absorption was introduced and examined with related to the measurements of the refractive dispersion. However, especially in the case of weak interactions, the shifts of wave-number of the absorption spectra were very small, so it was very difficult to estimate qualitatively the shifts of these spectra excepting the pyridine-dioxane system.

The very interesting result obtained in the pyridine-dioxane system was that the curve of wave-number vs weight-fraction of dioxane showed a breaking point and this fact showed a remarkable difference from that of observed in the ordinal solvent effects as noted by Naofumi Oi in the case of benzene-phenol mixture. The curve expressed the relation between the composition which is ordinally expressed by the weight-fraction of j component (w_j) and the shift of wave-number of CH-extra-planer bending vibration of 700 to 750 cm^{-1} of pyridine molecule clearly showed a breaking point at a fixed molar ratio, and this composition of the mixture approximately coincides with that of obtained from refractive dispersion measurements.

2. Experimental Methods

Commercial reagents of special grade were used without further purification. But especially in pyridine, a special grade reagent was refluxed over potassium hydroxide for a few days and then distilled. The middle fraction was stored over barium oxide and redistilled before use. The measurements of refractive index and the refractive dispersion were both undertaken as same as reported in previous paper7). The theoretical values of refractive dispersion were calculated respectively according to the following formula8):

$$\frac{dn_{1\cdot2}}{d\lambda}=\frac{K_1n_2^3}{(K_1n_2^2+K_2n_1^2)^{3/2}}\frac{dn_1}{d\lambda}+\frac{K_2n_1^3}{(K_1n_2^2+K_2n_1^2)^{3/2}}\frac{dn_2}{d\lambda}\quad\cdots\cdots\cdots\cdots\cdots(1)$$

$$\left.\begin{aligned}K_1&=w_1d_2/(w_1d_2+w_2d_1)\\K_2&=w_2d_1/(w_1d_2+w_2d_1)\end{aligned}\right\}\cdots\cdots\cdots\cdots(2)$$

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The infra-red absorption spectra were observed by the use of Nihon Bunko IR-Spectrometer IRA-1. The identification of the spectra and the measurements of wave-number were respectively undertaken by the comparison of these lines with those obtained from standard polystyrene film.

3. Optical Properties.

1) Cyclohexylamine-Dioxane System.

Figs. 1, 2 and 3 respectively show the relationships between the weight-fraction of dioxane (w_j) and the several optical properties such as refractive index (n), refractive dispersion(Z) and Abbe's number (ν) at 25°C. Each of the curves was illustrated downward in equall distances for avoiding the overlapping. In Fig. 2 a graph illustrated in the most downwards shows the relation between the calculated values of Z according to the equation 1) and the weight-fraction w_j at 25°C. As shown in these curves, three breaking points are clearly recognized both in the refractive dispersion vs weight-fraction curves and Abbe's number vs weight-fraction curves.

The mean values of w_j coresponding to these three breaking points in Fig. 2 were estimated to 0.32 for the first point, 0.46 for the second point and 0.64 for the third point respectively, and these values obtained from Fig. 3 were almost identical to those of obtained above. The coresponding molar

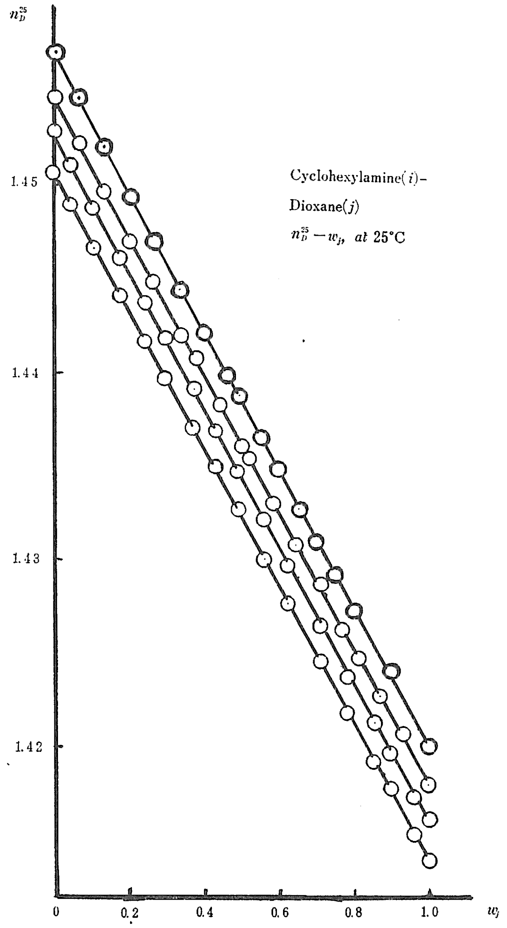

Fig. 1. The relationship between the refractive index and the weight-fraction of dioxane w_j, curves are illustrated downwards in regular order in situ.

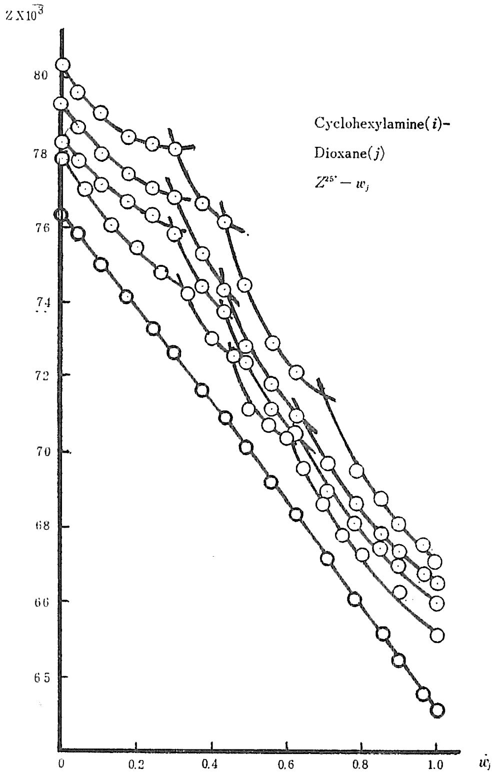

Fig. 2. The relationship between the refractive dispersion and the weight-fraction w_j of dioxane, curves are illustrated downwards in regular order in situ.

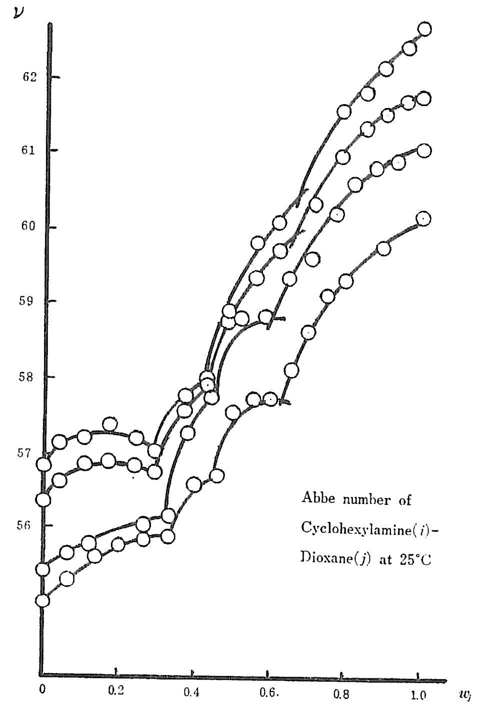

Fig. 3. Abbe's number plot in relation to the weightfraction of dioxane w_j, curves are illustrated downwards in regular order in situ.

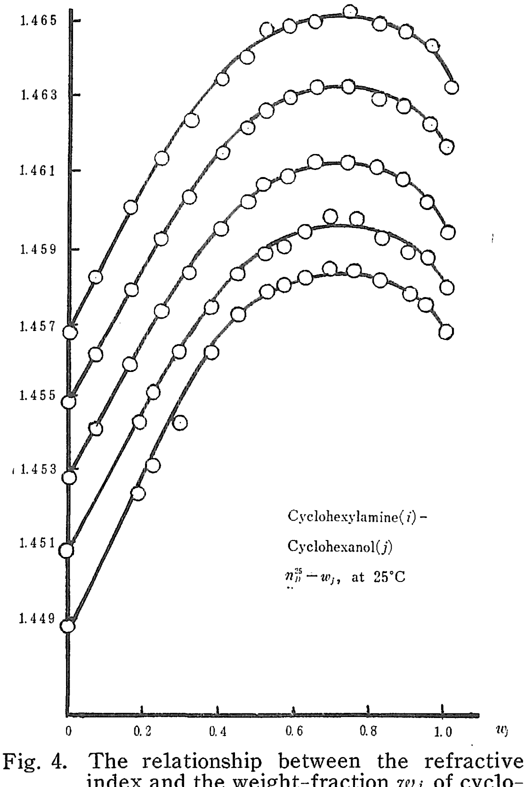

Fig. 4. The relationship between the refractive index and the weight-fraction w_j of cyclohexanol, curves are illustrated downwards in regular order in situ,

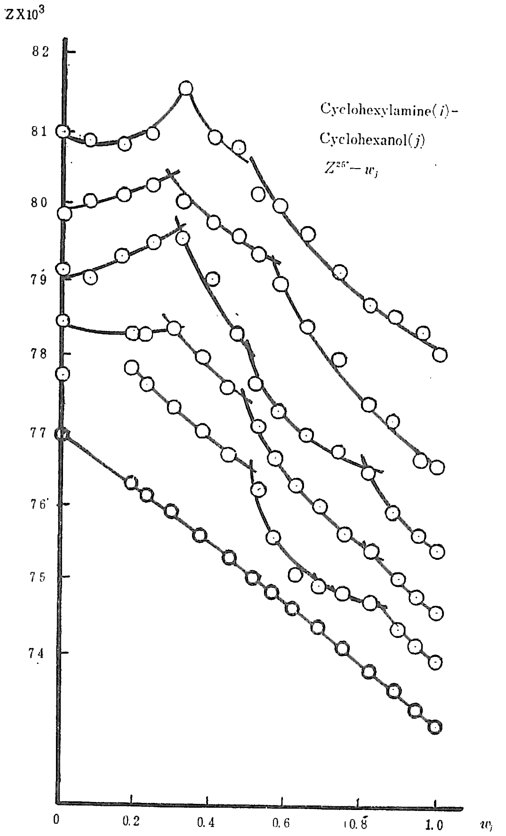

Fig. 5, The relationship between the refractive dispersion and the weight-fraction of cyclohexanol w_j, curves are illustrated downwards in regular order.

ratios were estimated to 2 : 1 for $w_j = 0.31$, 1 : 1 for 0.42 and 1 : 2 for 0.65 respectively.

2) Cyclohexylamine-cyclohexanol System.

Several examples of optical properties observed in this system were illustrated in Figs 4, 5 and 6. Fig. 4 shows the relationships between the refractive index (n) and the weight-fraction of cyclohexanol (w_j) at 25°C. Fig. 5 shows the relation between the refractive dispersion and the weightfraction of cyclohexanol (w_j) and Fig. 6 also shows the same relationship for Abbe's number at the same temperature.

Likely to the cyclohexylamine-dioxane system, three breaking points were also observed in this system and the appearance of the breaking points was more distinct than that of the former cases. The mean values of the coresponding three breaking points in Fig. 5 were respectively estimated for 0.30, 0.50 and 0.82, and these values estimated from Fig. 6 were also equall to those of obtained above.

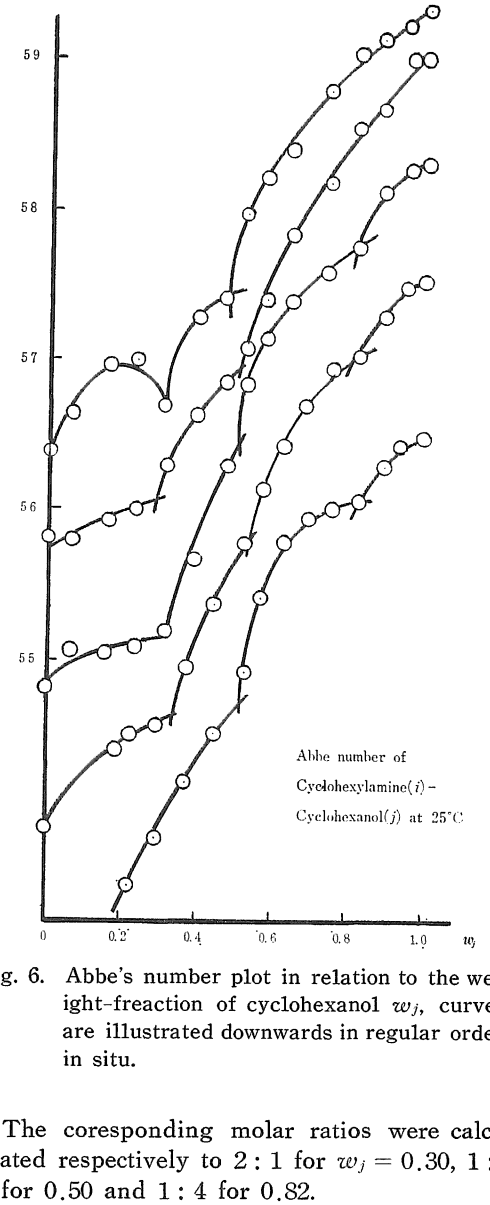

Fig. 6. Abbe's number plot in relation to the weight-freaction of cyclohexanol w_j, curves are illustrated downwards in regular order in situ.

The coresponding molar ratios were calculated respectively to 2 : 1 for $w_j = 0.30$, 1 : 1 for 0.50 and 1 : 4 for 0.82.

3) Pyridine-Dioxane System.

Some examples of optical properties of this system were summarized in Figs 7, 8 and 9. Fig. 7 shows the relation between the refrectivity (n) and the weight-fraction of Dioxane (w_j). at 30°C Fig. 8 shows the same relationship between the refractive dispersion (Z) and the weight-fraction w_j. Fig. 9 also shows that of Abbe's number (ν) and the weight-fraction. As clearly shown in Figs 8 and 9, the curves of refractive dispersion and Abbe's number vs weight-fraction of

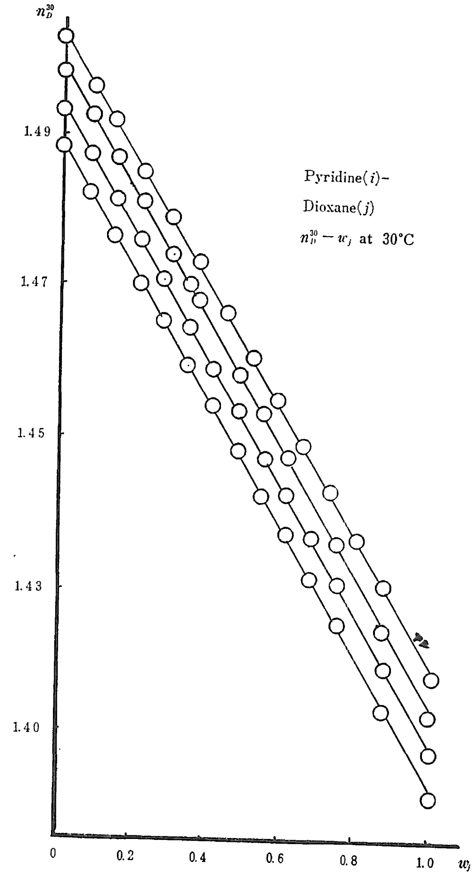

Fig. 7. The relationship between the refractive index and the weight-fraction of dioxane w_j, curves are illustrated downwards in regular order in situ.

dioxane respectively indicate us two clear breaking points at the compositions of $w_j = 0.35$ and $w_j = 0.70$. The coresponding molar ratios at these breaking points were estimated to 2 : 1 at $w_j = 0.35$ and 1 : 2 at $w_j = 0.70$ respectively. The details of these data were already reported in the previous paper7).

4. Infra-Red Absorption Spectra.

Figs 10, 11 and 12 respectively show the infra-red absorption spectra in the lower ranges of wave-number in cyclohexylamine-dioxane, cyclohexylamine-cyclohexanol and pyridine-dioxane systems with the comparison of the coresponding pure solvents. These data show us that a small amount of shift of

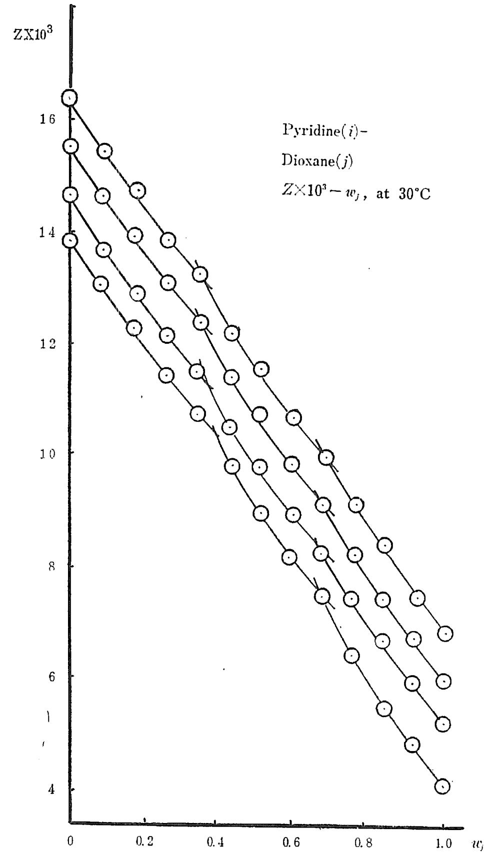

Fig. 8. The relationship between the refractive dispersion and the weight-fraction of dioxane w_j, curves are illustrated downwards in regular order in situ.

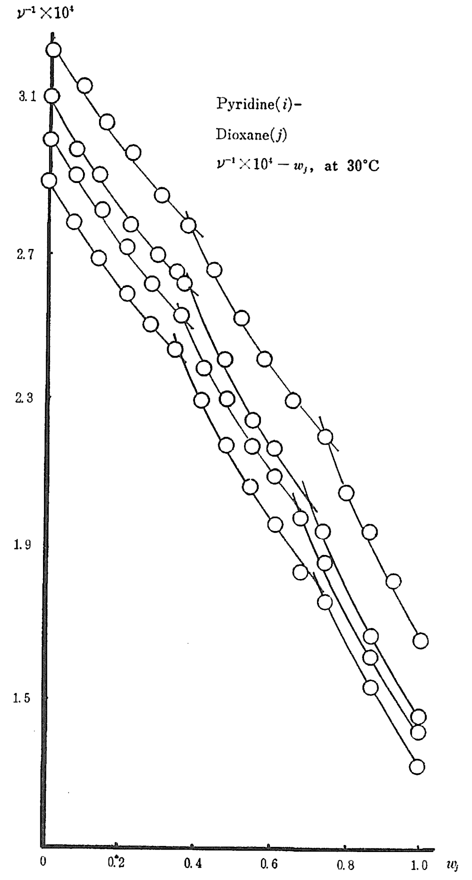

Fig. 9. The relationship between Abbe's number and the weight-fraction of dioxane, w_j, curves are illustrated downwards in regular order in situ.

characteristic absorption can be recognized in the range of 900 to 1200 cm^{-1} of the wave number which seems to be the absorption due to CH-extra-planer bending vibration of the respective molecules. Especially in pyridine-dioxane system, as illustrated in Figs. 12 and 13, a considerable amount of shift was observed in 700 and 749 cm^{-1} absorptions.

5. Discussion.

As already pointed out in the previous papers, the appearance of discontunity of the gradient of the dispersion curve, Z vs weight-fraction w_j, suggests us that the formation of some kinds of molecular cluster would be resulted in the liquid mixture. The above mentioned inference has been demonstrated by the fact that the observed values of the considering physical properties of the mixture are, in the range of the two breaking points or in the range of involving the points of pure solvents, completely coincided with those of the calculated from the equations which were theoretically introduced by assuming that the considering mixtures were completely ideal.

In another point of view, it would be presumably expected that if any structual changes of the liquid state may be resulted at the composition of the above mentioned discontunious points, it would be resulted to some changes in the mode of infra-red absorption spectrum at the coresponding discontinious points because the mode of vibration is exactly related to the mode of orientation of the nighbour molecules.

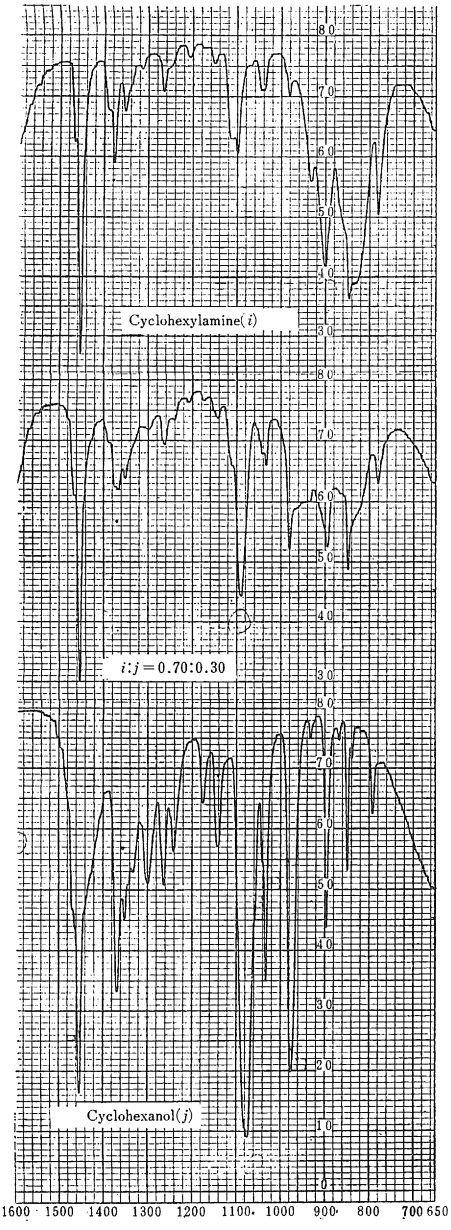

Fig. 10.

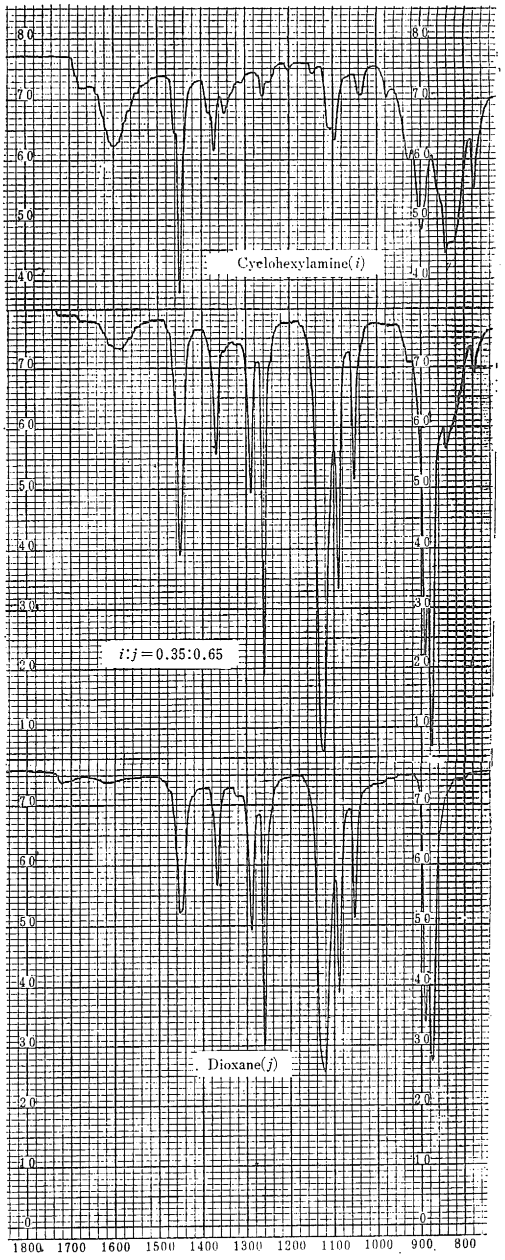

Fig. 11.

Fig. 13 shows one of the examples of the shifts of infra-red absorption spectra in pyridine-dioxane mixture. The absorptions of 700 and 750 cm^{-1} of pyridine molecules were clearly transfered to the higher wave-number side with the addition of dioxane molecules. Figs 14 and 15 respectively show the relation between the shifts of wave-number and the weight-fraction of added dioxane. As clearly shown in these figures, each of the curves has a breaking point nearly at the weight-fraction of $w_j = 0.70$, and this composition approximately coincides with that of observed from the curves of refractive dispersion vs weight-fraction. In these figures, likely to the infra-red absorption spectra which were obtained by Naofumi Oi in the benzene-phenol and benzene-anisole systems [10], the linear relation between the shift of wave-number and the weight-fraction may be attributed to

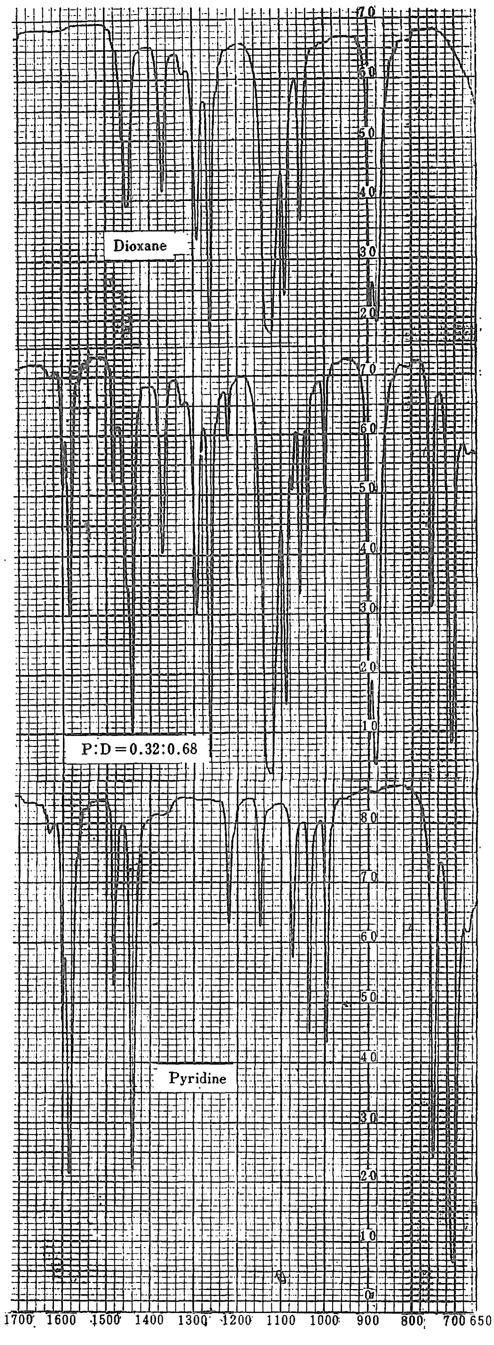

Fig. 12.

the ordinal solvent effect. Accordingly, the presence of a breaking point on the curve of infra-red absorption shift vs weight-fraction in pyridine-dioxane system suggest us that the two different clusters in its structure would be formed at the different sides of the breaking points.

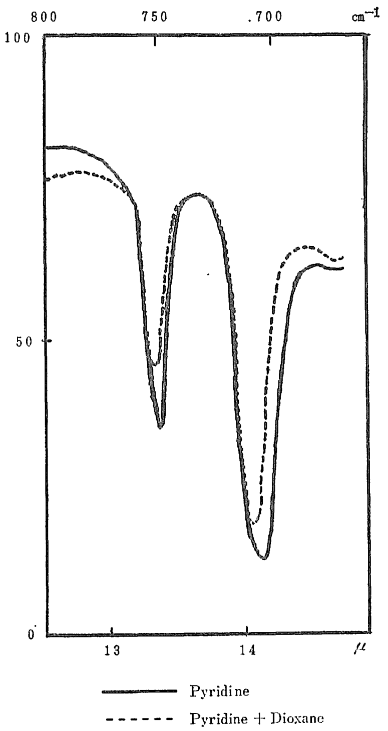

Fig. 13. Left-wards shift of CH-extraplaner bending vibration of pyridine molecule.

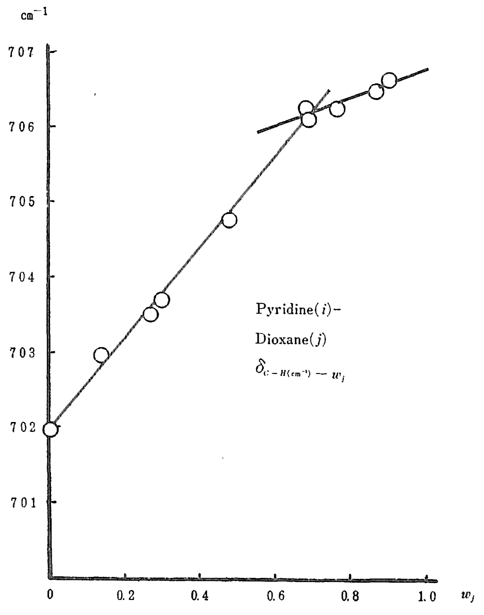

Fig. 14. Relationship between the shift of IR-absorption spectra in pyridine molecule and the weight-fraction of added dioxane.

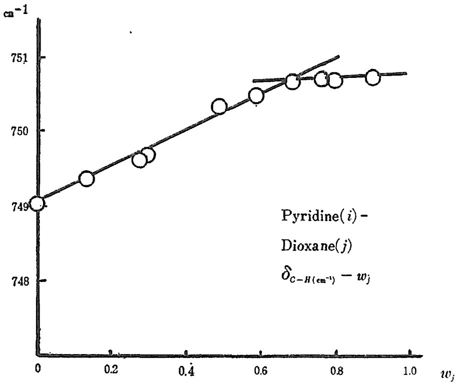

Fig. 15. Relationship between the shift of IR-absorption spectra in pyridine molecule and the weight-fraction of added dioxane.

Judging from these results of observations on the refractive dispersion as illustrated in Fig. 8 and 9, the stoichiometrical structure at these breaking points can be denoted as $[(Diox)_2 (Pyrid)_1]_n$, and that of the first breaking point can also be denoted as $[(Diox)_1 (Pryd)_2]_n$.

Acoordingly, the structural change in the considering cluster at the either side of the breaking point in Figs 14 and 15 may formally denoted as follows :

$$[(Diox)_1(Pryd)_2]_n + 3nDiox \longrightarrow 2[(Dlox)_2(Pryd)_1]_n$$

The authors wish to thank Hiroko Inoue, Mikio Hara and Yukio Takeuchi, the graduate course students of this laboratory, for the helpful assistance for this research.

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