STUDIES ON THE DIELECTRIC PROPERTIES
OF ORGANIC SOLVENTS VI.

MOLECULAR COMPLEX FORMATION IN WATER-PYRIDINE
AND PYRIDINE-DIOXANE MIXTURES

By

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1. Introduction

The complex formation between water and pyridine molecules has been studied by many researchers. A. N. Sidrov[1],H. Takahashi[2],K. Mamola and E. K. Plyler suggested the complex formation between these molecules from infra-red absorption data and J. Rouvier and J. Salvinien[3] also suggested from the Ramann spectrum data. They found that when the amount of pyridine is much smaller than that of water, the dominant species is supposed to be pyridine-H_2O and they estimated the formation constant for the above mentioned complex as 2.8l/mol. Recently, Y. Kasugai, Y. Arata and S. Fujiwara[4] of Tokyo University reported the presence of the above complex by using the method of NMR studies of protons and nitrogen-14 atoms. They pointed out the presence of anormalous concentration dependence of the viscosity and density in water-pyridine system. However, so long as our results are concerned, the concentration dependence of the various physical properties such as refractive index, dispersion, density and viscosity showed different curves from their results of investigations.

The NMR data they obtained showed a remarkable dependence on the concentration and especilily for the line width of the α-protons and N-14 atoms of pyridine molecules. From these results and also the facts that the N-14 spectrum of pyridine showed a single line in the whole range of concentration examined, they concluded that the complex formed in water-pyridine mixture may be considered as identical with what was given by J. Rouvier and J. Salvinien. The formation constant calculated by Y. Kasugai and their co-workers from the assumption of the relation between the line width and the fractional population of the hydrogen bonded pyridine molecules was almost identical to that of J. Rouvier and their coworkers.

In this paper, based on the theories on the refractive index and its dispersion in ideal mixture which were already derived by one of the writers, and in comparing the data of density and viscosity, the complex formation was discussed stoichiometralily for water-pyridine and pyridine-dioxane mixtures.

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2. Experimental and Results

1) Apparatus and Procedures.

Pyridine and dioxane used were both commercial extra-pure grade, with $d_4^{30} = 0.97251$ for pyridine, $d_4^{i5} = 1.02204$ for dioxane respectively. The distilled water was redistilled from the original pure water. A series of the mixed solvents was prepared in the whole range of concentration and the molar fraction was determined from the weight fraction. The measurements of density were undertaken with the use of Ostwald's pyknometer. The temperature of pyknometer and the samples were kept exactly at fixed
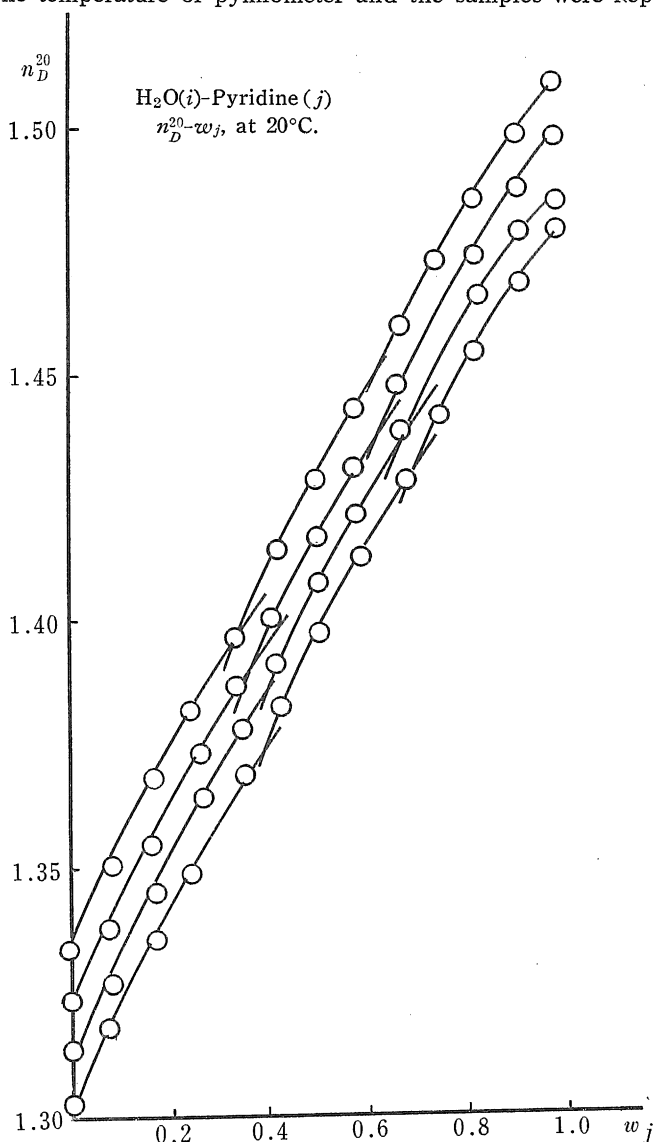

Fig. 1. The relationship betw. refractive index and weight fraction of pyridine(w_f). The curves 2, 3 and 4 are illustrated respectively 1, 2 and 3 cm downwards *in situ*.

temperatures by using a water thermostat. By the carefull treatments, the constancy of the density measurements was controlled to the order of 1×10^{-4} g/cm. The refractive index was measured by the use of abbe's New Type refractometer with the circulation of the water of fixed temperature by a small pump from the thermostat. The temperature variance in every measurement was controlled approximately into $\pm 0.05°$C. The dispersion of the refractive index and the Abbe number were respectively calculated from the table of dispersion and the readings of dispersion dial of the refractometer.

In parallel with these observations, the viscosity was also measured by using Ostwald's viscosimeter at the same order of temperature variance.
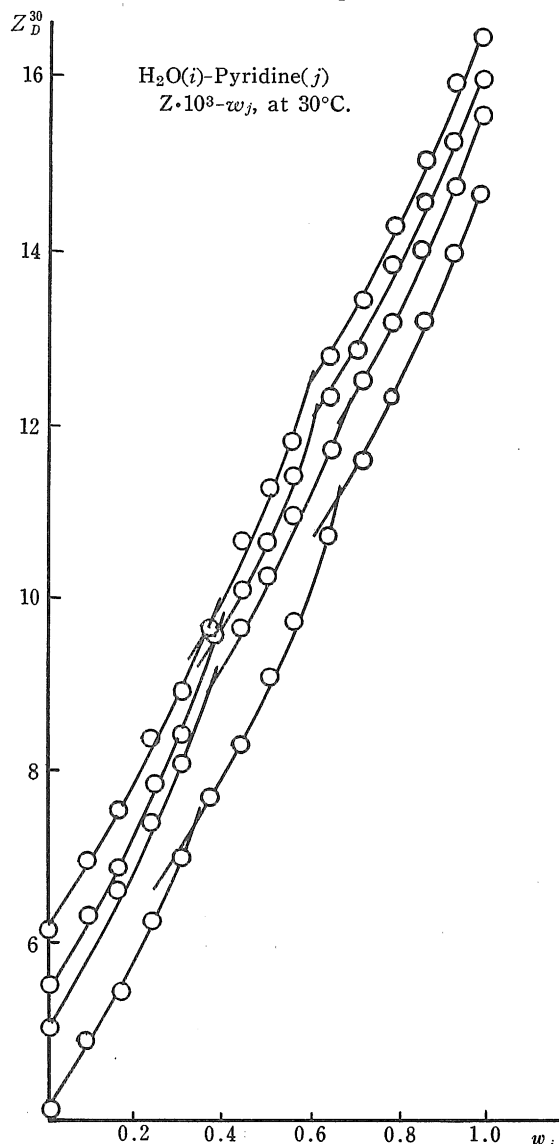

Fig. 2. The relationship betw. dispersion and weight fraction of pyridine(w_j). The curves 2, 3 and 4 are illustrated respectively 1, 2 and 3 cm downwards *in situ.*

2) Optical Analysis

Figures 1, 2 and 3 respectively show the results of experiments for water-pyridine system. Figure 1 shows the relation between the refractive index and the weight fraction of pyridine w_j. Figures 2 and 3 also show the curves of dispersion and Abbe's number. As shown in these curves, several break points were recognized at the points of fixed concentrations. In water-pyridine system, the first break point appears approximately on 2 : 1 in molar ratio and the second point on 8 : 1 respectively. These data are summarized in Table 1. The appearances of these break points show us the presence of some kinds of molecular complexes at the points of corresponding molar ratios.
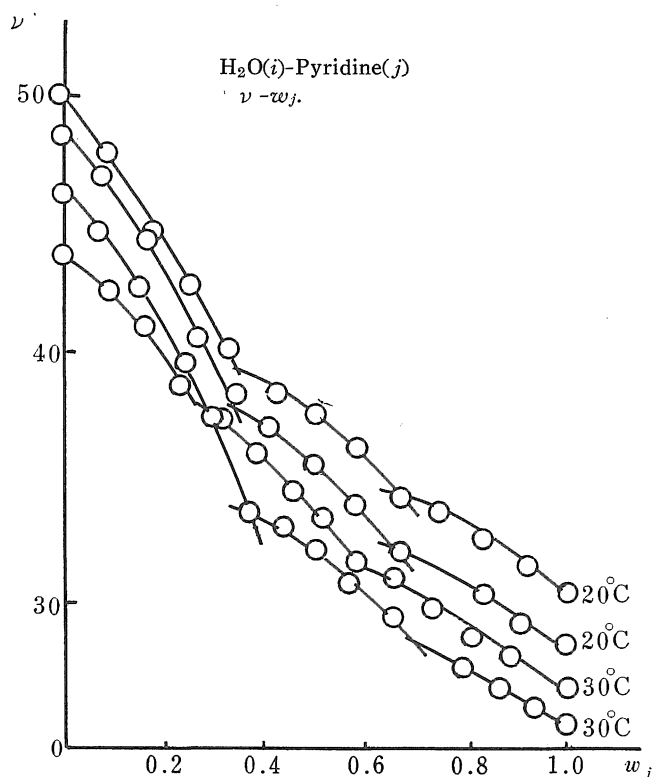

Fig. 3. The relationship betw. Abbes' number and weight fraction of pyridine(w_j). The curves 2, 3 and 4 are illustrated respectively 1, 2 and 3 cm downwards *in situ.*

Figures 4, 5 and 6 also show the results of pyridine-dioxane mixture. These results are almost identical with those of water-pyridine mixture excepting the corresponding molar ratios to these break points. The molar compositions of the observed break points are 2 : 1 and 1 : 2 respectively. These summarized data are given also in Table 1.
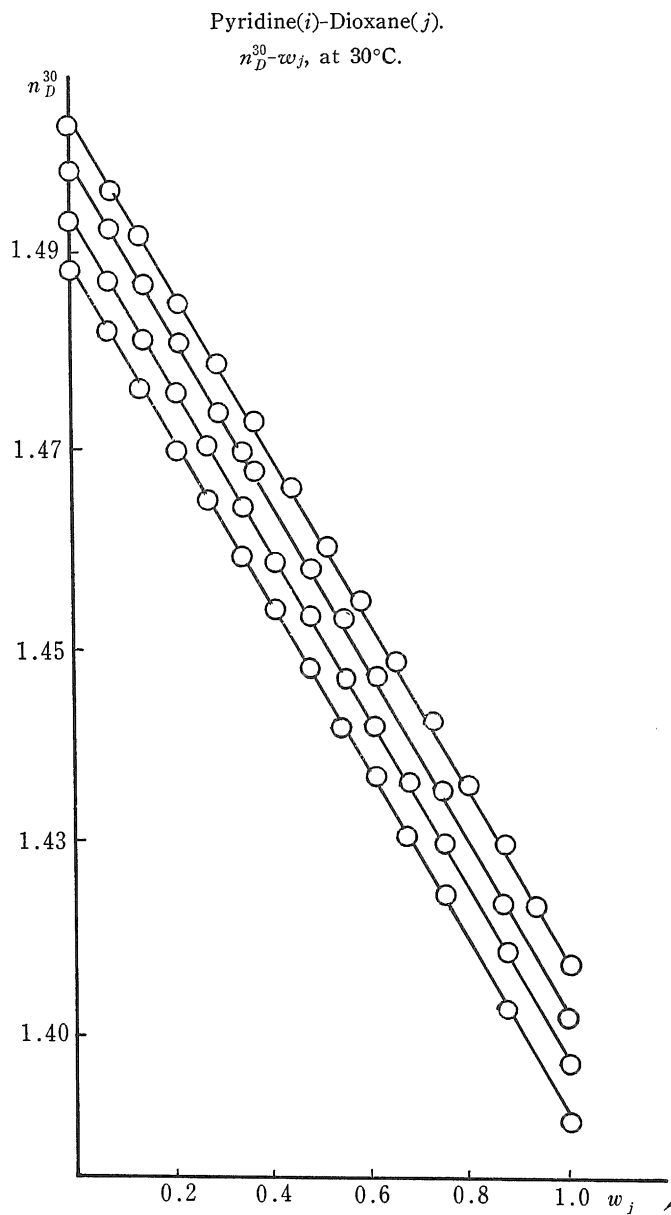
Pyridine(i)-Dioxane(j).

n_D^{30}-w_j, at 30°C.

Fig. 4. The relationship betw. refractive index and weight fraction
of dioxane (w_j). The curves 2, 3 and 4 are illustrated
respectively 1, 2 and 3 cm downwards *in situ.*

Pyridine(i)–Dioxane(j)
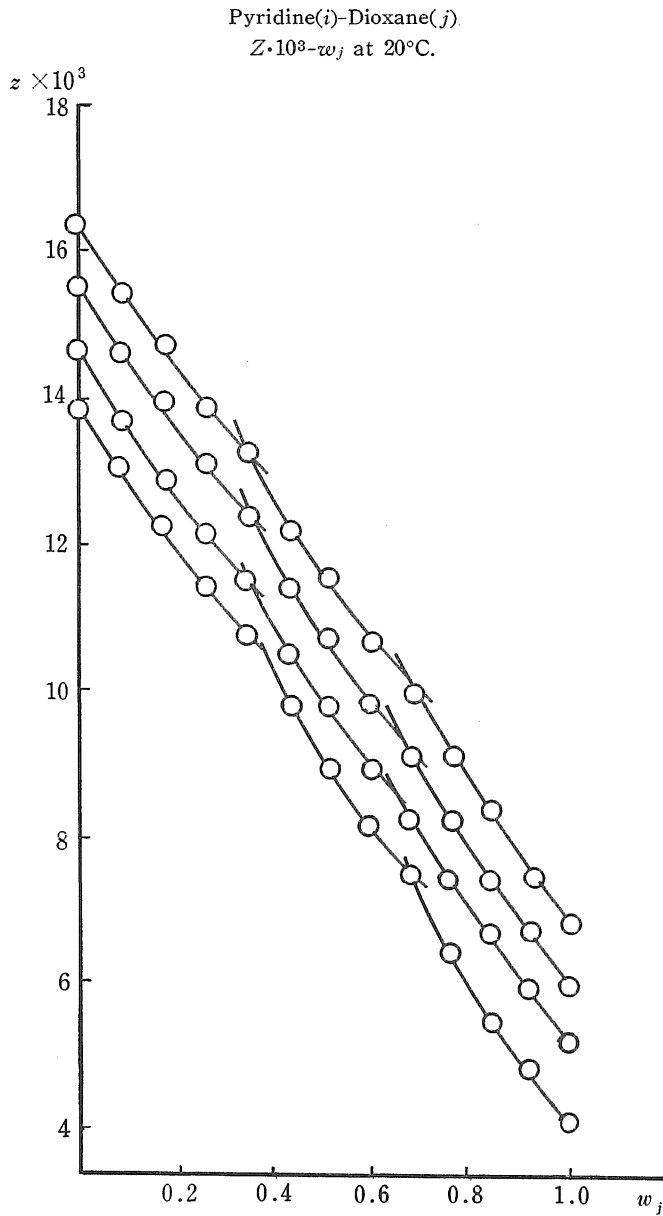
$Z \cdot 10^3$–w_j at 20°C.

$z \times 10^3$

Fig. 5.   The relationship betw. dispersion and weight fraction of dioxane (w_j).   The curves 2, 3 and 4 are illustrated respectively 1, 2 and 3 cm downwards *in situ*.

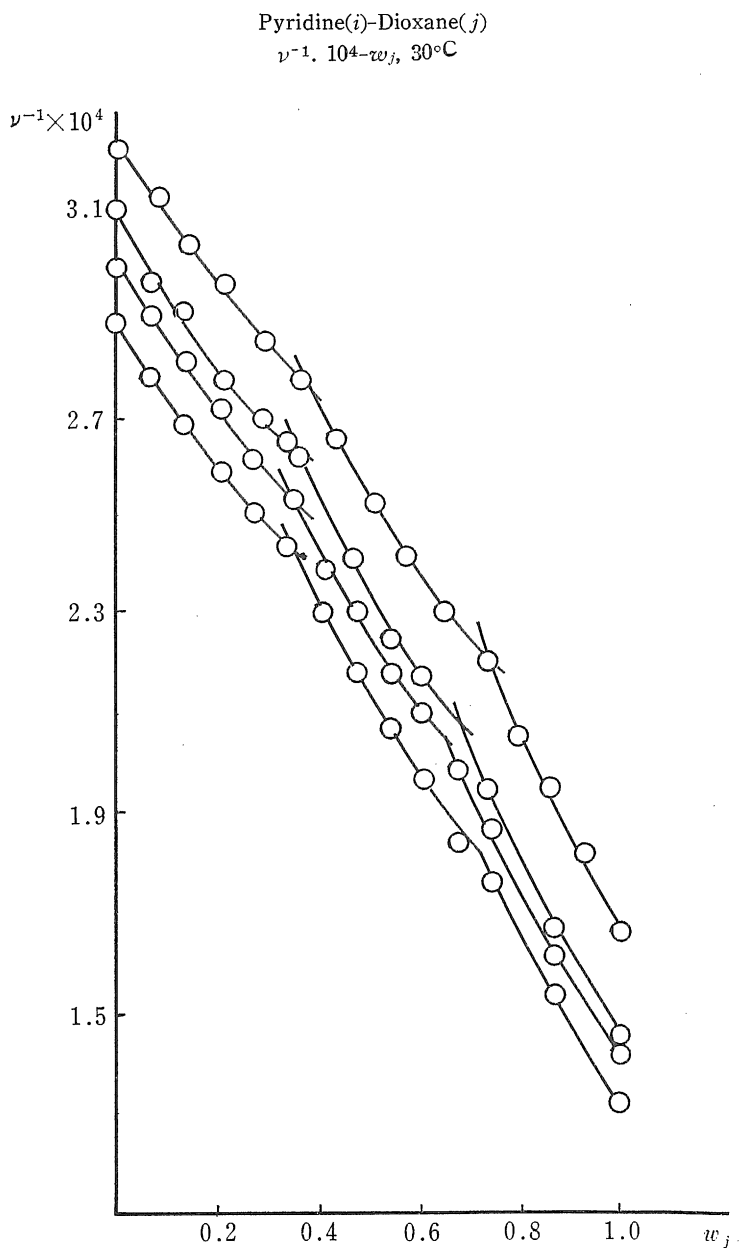Pyridine(i)-Dioxane(j)

ν^{-1}. 10^4-w_j, 30°C

Fig. 6. The relationship betw. reciprocal Abbe number and weight fraction of dioxane (w_j). The curves 2, 3 and 4 are illustrated respectively 1, 2 and 3 cm downwards *in situ*.

3) Density and Viscosity

Density and viscosity analysis was also undertaken in parallel with the optical measurements. Figures 7 and 8 respectively show some of the examples for water-pyridine system. The break points obtained through these experiments are almost identical with those obtained from optical analysis.
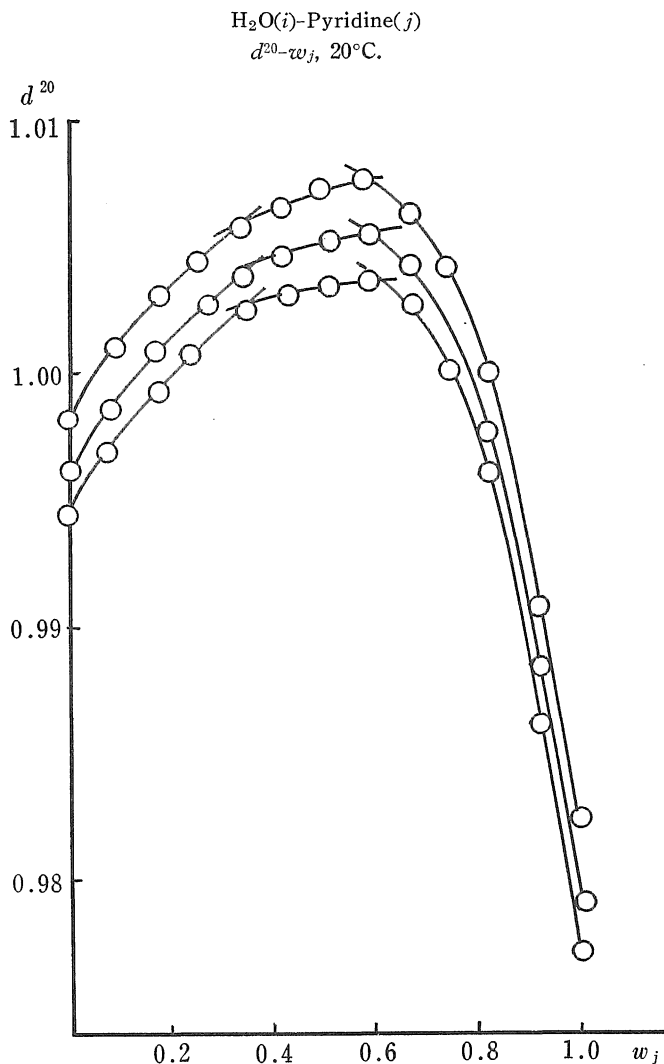

Fig. 7. The relationship betw. density and weight fraction of pyridine (w_j). The curves 2 and 3 are illustrated respectively 1 and 2 cm downwards *in situ*.
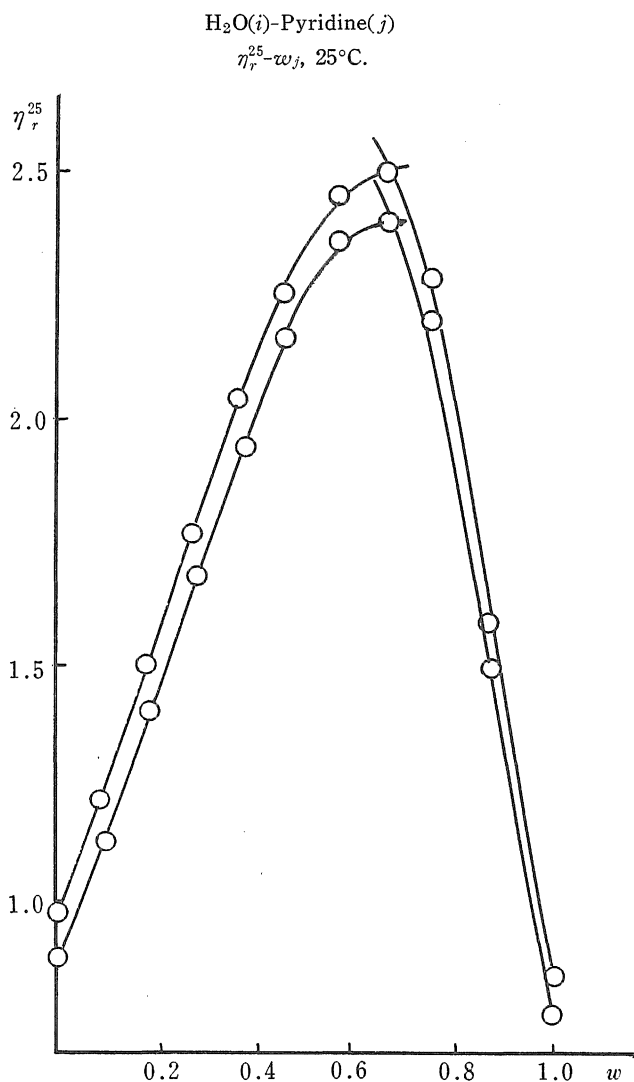
$H_2O(i)$-Pyridine(j)

η_r^{25}-w_j, 25°C.

Fig. 8. The relationship betw. viscosity and weight fraction w_j of pyridine. One of the curves is illustrated 1 cm downwards *in situ*.

3. Discussion and Conclusion

From the results of NMR investigations for water–pyridine system, which were already reported by Y. Kasugai, Y. Arata and S. Fujiwara, the siet of bonding between pyridine and water molecules is expected to be N and H atoms of these molecules. The hypothetical formula they obtained was pyridine-H_2 0 as already mentioned. However, the fact we obtained shows that the structual formulas respectively correspond to pyridine-$(H_2O)_2$ and pyridine-$(H_2O)_8$. These results also differ from those obtained by J. Rouvier, J. Salvinien and Y. Kasugai and their coworkers. It is a very interesting

fact that the molar ratios of these complexs are limited only to 2 : 1 and 8 : 1. The latter may perphaps be attributed to the association of water molecules in the corresponding temperature. The same structual formulas can be given for pyridine-dioxane mixture and the presumable formulas are given as follows ; a) (pyridine)$_2$−(dioxane) b) (pyridine)-(dioxane)$_2$, and perphaps these may be written ;
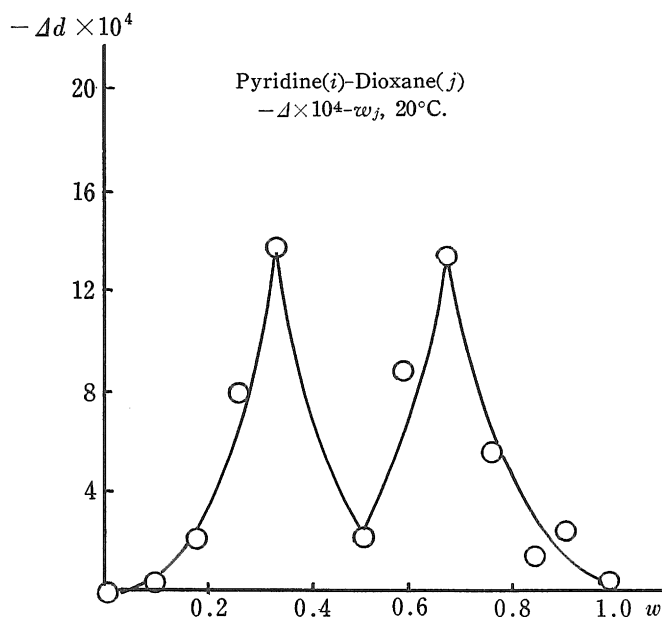

[a]

[b$_1$]

[b$_2$]

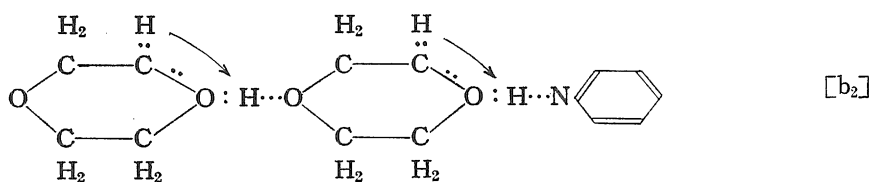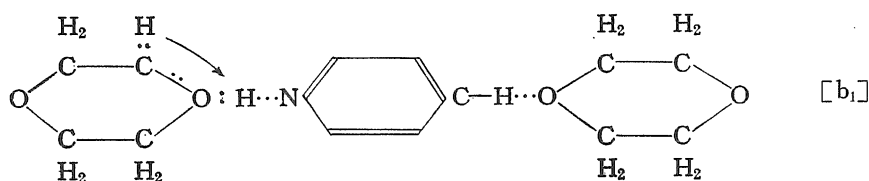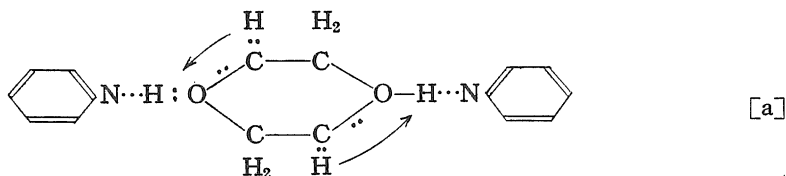
Fig. 9. The relationship betw. the deviation of density and weight fraction of dioxane (w_j).
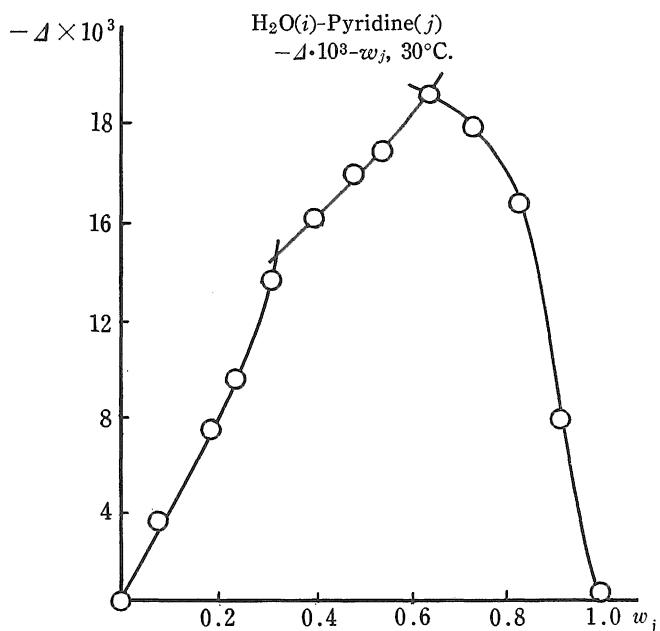
Fig. 10.   The relationship betw. the deviation of density
and weight fraction of pyridine w_j.

Table 1.   Break points estimated with various physical properties.

System	Temp.	Refractivity 1st	2nd	Dispersion 1st	2nd	Abbe Numb. 1st	2nd	Density 1st	2nd
Pyridine-Dioxane (i) (j)	20°C	not clear		0.34	0.68	0.35	0.67	0.29	0.63
				0.33	0.68	0.34	0.68	0.37	0.75
				0.34	0.68	0.34	0.68	0.34	0.68
				0.34	0.67	0.34	0.68	0.32	0.65
				0.28	0.64	0.28	0.66	0.33	0.69
				0.32	**0.67**	**0.33**	**0.67**	**0.33**	**0.68**
	30°C			0.34	0.72	0.37	0.72	0.32	0.69
				0.39	0.68	0.34	0.69	0.28	0.67
				0.34	0.64	0.34	0.69	0.33	0.67
				0.34	0.66	0.34	0.69	0.34	0.71
				0.34	0.72	0.34	0.68	0.32	0.65
				0.35	**0.68**	**0.34**	**0.69**	**0.32**	**0.68**
H₂O-Pyridine (i) (j)	20°C	0.37	0.63	0.38	0.61	0.35	0.64	0.35	0.63
		0.37	0.63	0.32	0.66	0.34	0.62	0.37	0.64
		0.40	0.68	0.34	0.67	0.30	0.65	0.35	0.64
		0.38	0.64	0.40	0.66	—	—	0.35	0.65
		0.38	0.64	0.36	0.65	—	—	0.35	0.64
		0.38	**0.64**	**0.36**	**0.65**	—	—	**0.35**	**0.64**
	30°C	0.38	0.67	0.36	0.68	0.35	0.63	0.34	0.69
		0.35	0.65	0.37	0.67	0.37	0.69	0.33	0.66
		0.33	0.61	0.36	0.62	0.33	0.64	0.32	0.73
		0.34	0.66	0.34	0.64	0.32	0.63	0.32	0.64
		0.30	0.60	0.35	0.65	0.32	0.62	0.34	0.69
		0.34	**0.63**	**0.35**	**0.65**	**0.33**	**0.64**	**0.33**	**0.68**

Analytically, another method of detecting such molecular formation in macroscopic method is to analyze the deviation of the observed value from the therotical one which is obtained from the theoretical formula for ideal solution.

These theoretical formulas were already given by one of the writers of this paper for such various physical properties of an ideal mixture as density[5], viscosity[6], dielectric constant[7]~[9], optical refractivity[10] and its dispersion[11]. For example, the observed deviation of density Δd_{i+j} is expressed by the following formula ;

$$\Delta d_{i+j} = \frac{d_i d_j}{d_j + (d_i - d_j) w_j} - (d_{i+j})_0 \cdots\cdots\cdots\cdots \quad 1)$$

where suffixs i and j respectively represent the pure components i and j, d the density, w the weight fraction and $(d_{i+j})_0$ shows the observed density of the mixture.

One of the examples of such analysis is given in Figures 9 and 10 for water-pyridine mixture at 30°C and pyridine-dioxane mixture at 20°C respectively.

The theoretical base of the above conception can be explained as follows ; the relation of the physical properties to weight fraction may theoreticalily be represented by a continuous curve as represented by the formula 1. However, if any molecular cluster or molecular complex will be formed in the mixed solvent system, the cluster or complex thus formed may be considered as a new component which would have a different physical properties from the original ones. Thus the new formed component k may act on the two components i and j as an independent one and this may result to devide the curve into two parts i-k and k-j respectively.

Literatures

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