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STUDIES ON THE DIELECTRIC PROPERTIES OF ORGANIC SOLVENTS III **

A NEW EQUATION ON THE VISCOSITY OF ORGANIC BINARY SOLVENT MIXTURE

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1) INTRODUCTION.

About five years ago, we took up the analysis of the weak interaction between the same or different kinds of molecules in a liquid state by comparing results of the measurement of dielectric constant with these of the measurements of refractive index and viscosity[1)2)]. The measurement of dielectric constant has often been used for the estimation of molecular structure, but its application to the estimation of mutual interaction has not practically been undertaken so far as this method is highly sensitive. Owing to the remarkable character of the method, it seems very useful for the estimation of very weak interaction between the molecules in mixed solvents. From these standpoints, we have examined the weak interaction between the dioxane and benzene molecules with reference to the viscosity analysis.

The dielectric constant vs. composition curves clearly showed the same inflextion points at the equi-molar composition and the same results were also obtained in the viscosity vs. composition curves for the mixture of dioxane and benzene. These results show that the dioxane molecule and the benzene molecule combine to form a weak intermediate complex in the above mixture of equi-molar composition.

This paper deals with the nature of the above mentioned molecular interaction from the viw-point of the internal friction of the solvent mixture in Newton flow and have intended to deduce a theoretical equation which describes the relation between the viscosity and the composition. The experimental certifications of the above equation were undertaken by the use of dioxane-benzene and dioxane-cyclohexane systems.

The basic idea on deducing the above equation was that the internal friction should be resulted from the force of molecular interaction which is effective only in a limited space around the center of the considering molecules. Naturally, the substance of this force may perphaps be started from the dipole-dipole or atom-dipole interaction as Debye mentioned. Accordingly, so far as taking these assumptions, the idea on the nature of viscosity must be essentially introduced from the problem of the probability of penetration of the considering molecules into such space as above mentioned, and it must be described only by the number of molecules when the temperature of the system and the other conditions were fixed.

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** These series of studies (1-a, 1-b and 11) were already published in the Mem. Fac. Educ., Shimane University, Vol. 1 (1968) and Vol. 2 (1969) respectively.

2) THEORETICAL.

Let the probabilities of the penetration concerning the molecules *i-i*, *j-j* and *i-j* be denoted respectively by P_{ii}, P_{jj} and P_{ij} according to the pairs of the confliction, then the frictional force F_{i+j} of the mixed solvent $i+j$ is represented by the sum of each frictional force F_{ii}, F_{jj} or F_{ij} as follows ;

$$F_{i+j}=P_{ii}F_{ii}+P_{jj}F_{jj}+P_{ij}F_{ij} \quad \cdots\cdots \quad 1)$$

where P_{ii}, P_{jj} and P_{ij} are respectively defined as ;

$$\left.\begin{aligned} P_{ii}&=k_{ii}n_i^2\\ P_{jj}&=k_{jj}n_j^2\\ P_{ij}&=k_{ij}n_in_j \end{aligned}\right| \quad \cdots\cdots \quad 2)$$

Thus we obtain ;

$$F_{i+j}=k_{ii}n_i^2F_{ii}+k_{jj}n_j^2F_{jj}+k_{ij}n_in_jF_{ij} \quad \cdots\cdots \quad 3)$$

where k_{ii}, k_{jj} and k_{ij} are the probability constants which are chiefly determined by the properties of molecules and the thermodynamic conditions of the system. n_i, n_j are the number of molecules in unit volume. From the definition of viscosity coefficient, we have ;

$$\left.\begin{aligned} F_{i+j}&=\eta_{i+j}\frac{\partial U_{i+j}}{\partial x}\\ F_{ii}&=\eta_{ii}\frac{\partial U_i}{\partial x}\\ F_{jj}&=\eta_{jj}\frac{\partial U_j}{\partial x}\\ F_{ij}&=\eta_{ij}\frac{\partial U_{ij}}{\partial x} \end{aligned}\right| \quad \cdots\cdots \quad 4)$$

where η_{ii}, η_{jj} and η_{ij} are the viscosity coefficients which will be given when the molecules of the pure components *i* and *j* act independently upon each other molecules in the mixture, η_{i+j} is the same coefficients of the mixed solvent. Similarly, U_i, U_j and U_{i+j} are the velocities of the respective molecules along the direction of flow.

Now, assuming $U_{i+j} = U_i = U_j = U_{ij} = U$, and putting Eq. 4) into Eq. 3) we have ;

$$\eta_{i+j}\frac{\partial U}{\partial x}=k_{ii}n_i^2\eta_{ii}\frac{\partial U}{\partial x}+k_{jj}n_j^2\eta_{jj}\frac{\partial U}{\partial x}+k_{ij}n_in_j\eta_{ij}\frac{\partial U}{\partial x} \quad \cdots\cdots \quad 5)$$

Dividing the both terms of this equation by $\partial U/\partial x$, we have ;

$$\eta_{i+j}=k_{ii}n_i^2\eta_{ii}+k_{jj}n_j^2\eta_{jj}+k_{ij}n_in_j\eta_{ij} \quad \cdots\cdots \quad 6)$$

In assuming η_{ij} is equal to the value of η_{i+j} when the mixed solvent is composed of the equi-molar solvents of i and j, and by denoting it with η^*, and Eq. 6) becomes ;

$$\eta_{i+j}=k_{ii}n_i^2\eta_{ii}+k_{jj}n_j^2\eta_{jj}+k_{ij}n_i n_j\eta^* \cdots\cdots\cdots 7)$$

On other hand, let the mass of respective pure solvents i and j in the unit volume of the mixture be m_i and m_j, then the number of molecul n_i, n_j and the product of them are respectively given by ;

$$\left.\begin{array}{l} n_i=\dfrac{m_i}{M_i}N \\ n_j=\dfrac{m_j}{M_j}N \\ n_i n_j=\dfrac{m_i m_j}{M_i M_j}N^2 \end{array}\right| \cdots\cdots\cdots 8)$$

where M_i and M_j are the molecular weights, N the Avogadoro's Number.

By the definition of weight fraction and that of density, m_i and m_j in Eq. 8) can be transformed into the following relations ;

$$\left.\begin{array}{l} m_i=w_i d_{i+j} \\ m_j=w_j d_{i+j} \end{array}\right| \cdots\cdots\cdots 9)$$

where w_i and w_j denote the weight fractions of the solvents i and j, and d_{i+j} the density of the mixed solvent. This value is calculated theoretically from the densities of the pure solvents and the weight fractions, if the volume change in mixing is omitted. The simple relation is as follows ; 3)4)

$$\frac{1}{d_{i+j}}=\frac{w_i}{d_i}+\frac{w_j}{d_j} \cdots\cdots\cdots 10)$$

From Eqs. 8) 9) and 10), we have ;

$$\left.\begin{array}{l} n_i=\dfrac{w_i}{M_i}\dfrac{d_i d_j N}{w_i d_j+w_j d_i} \\ n_j=\dfrac{w_j}{M_j}\dfrac{d_i d_j N}{w_i d_j+w_j d_i} \\ n_i n_j=\dfrac{w_i w_j}{M_i M_j}\left(\dfrac{d_i d_j}{w_i d_j+w_j d_i}\right)^2 N^2 \end{array}\right| \cdots\cdots\cdots 11)$$

By substituing these relations into Eq. 7) we have ;

$$\eta_{i+j}=k_{ii}\left(\frac{w_i}{M_i}\right)^2\frac{d_i^2 d_j^2 N^2}{(w_i d_j+w_j d_i)^2}\eta_{ii}+k_{jj}\left(\frac{w_j}{M_j}\right)^2\frac{d_i^2 d_j^2 N^2}{(w_i d_j+w_j d_i)^2}\eta_{jj}$$

$$+k_{ij}\left(\frac{w_i w_j}{M_i M_j}\right)N^2\frac{d_i^2 d_j^2}{(w_i d_j+w_j d_i)^2}\eta^* \cdots\cdots\cdots 12)$$

Eq. 12) holds with any value of w_i or w_j, we can determine the constants k_{ii}, k_{jj} and k_{ij} by introducing the critical values into this equation.

In determining the constants k_{ii} and k_{jj}, if we assume $w_j = 0$ in Eq. 12), then w_i becomes one and η_{i+j} becomes η_{ii}. By substituing these relations into Eq. 12), we have ;

$$\eta_{ii} = k_{ii}\left(\frac{1}{M_i}\right)^2 \frac{d_i^2 d_j^2}{d_j^2}\,\eta_{ii} N^2$$

$$k_{ii} = \frac{M_i^2}{d_i^2 N^2} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \quad 13)$$

With similar treatments as described above, and taking $w_i = 0$ in Eq. 12), then w_j becomes one and η_{i+j} becomes η_{jj}, and substituing these relations into Eq. 12), we obtain ;

$$k_{jj} = \frac{M_j^2}{d_j^2 N^2} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \quad 14)$$

By introducing the relations 13) and 14) into Eq. 12), provisionally Eq. 12) transformed into ;

$$\eta_{i+j} = \frac{w_i^2 d_j^2}{(w_i d_j + w_j d_i)^2}\,\eta_{ii} + \frac{w_j^2 d_i^2}{(w_i d_j + w_j d_i)^2}\,\eta_{jj}$$

$$+ k_{ij}\frac{w_i w_j}{M_i M_j}\,\frac{d_i^2 d_j^2 N^2}{(w_i d_j + w_j d_i)^2}\,\eta^* \quad \cdots\cdots\cdots\cdots\cdots \quad 15)$$

In this equation, the unknown constant k_{ij} can further be determined by using the equi-molar conditions of w_i and w_j. The weight fractions in equi-molar mixture of the solvent i and j are respectively given by

$$\left.\begin{aligned} w_i &= M_i/(M_i + M_j) = pM_i \\ w_j &= M_j/(M_i + M_j) = pM_j \end{aligned}\right| \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad 16)$$

And, under these conditions of w_i and w_j, η_{i+j} in Eq. 12) must be η^*. Accordingly, by inserting these relations into Eq. 15) we have ;

$$\eta^* = \frac{M_i^2 d_j^2}{(M_i d_j + M_j d_i)^2}\,\eta_{ii} + \frac{M_j^2 d_i^2}{(M_i d_j + M_j d_i)^2}\,\eta_{jj}$$

$$+ k_{ij}\frac{M_i M_j}{M_i M_j}\,\frac{d_i^2 d_j^2 N^2}{(M_i d_j + M_j d_i)^2}\,\eta^* \quad \cdots\cdots\cdots\cdots\cdots \quad 17)$$

By solving the above equation with k_{ij}, we have ;

$$k_{ij}=\frac{(M_i d_j+M_j d_i)^2}{d_i^2 d_j^2 N^2}-\frac{M_i^2 \eta_{ii}}{d_i^2 N^2 \eta^*}-\frac{M_j^2 \eta_{jj}}{d_j^2 N^2 \eta^*} \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad 18)$$

By putting these constants k_{ii}, k_{jj} and k_{ij} into Eq. 12), we have ;

$$\eta_{i+j}=\frac{w_i d_j^2 (w_i M_j - w_j M_i)}{M_j (w_i d_j + w_j d_i)^2}\,\eta_{ii}+\frac{w_j d_i^2 (w_j M_i - w_i M_j)}{M_i (w_i d_j + w_j d_i)^2}\,\eta_{jj}$$
$$+\frac{w_i w_j (M_i d_j + M_j d_i)^2}{M_i M_j (w_i d_j + w_j d_i)^2}\,\eta^* \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad 19)$$

or by transforming this equation into more simple form ;

$$\eta_{i+j}=\frac{d_i^2 d_j^2}{(w_i d_j + w_j d_i)^2}\left(\lambda w_i^2 \eta_{ii}+\mu w_j^2 \eta_{jj}+\nu w_i w_j \eta^*\right) \quad \cdots\cdots\cdots \quad 20)$$

where

$$\left.\begin{aligned} \lambda &= \frac{1}{d_i^2} \\ \mu &= \frac{1}{d_j^2} \\ \nu &= \frac{\eta^* (M_i d_j + M_j d_i)^2 - M_i^2 d_j^2 \eta_{ii} - M_j^2 d_i^2 \eta_{jj}}{d_i^2 d_j^2 M_i M_j \eta^*} \end{aligned}\right| \quad \cdots\cdots\cdots\cdots\cdots \quad 21)$$

3) APPLICATION AND DISCUSSION.

By the results of our measurements of Benzene (i)-Dioxane (j) mixture at 35°C, the following datas were obtained ; $d_i^{35} = 0.8630$, $d_j^{35} = 1.0132$, $\eta_{ii} = 0.5258$, $\eta_{jj} = 1.0030$ and $\eta^* = 0.7230$. This value of η^* at the same temperature was determined as the value of viscosity at the equimolar composition by the interpolation of the density-composition curve which was taken from the datas shown in Table 1. By using these values and the molecular weights $M_i = 78.11$ and $M_j = 88.11$, the constants λ, μ and ν in Eq. 21) were calculated respectively as $\lambda = 1.3427$, $\mu = 0.9743$ and $\nu = 2.1866$.

By applying these datas into Eq. 20), consequently we have ;

$$\eta_{i+j}=\frac{d_i^2 d_j^2}{(w_i d_j + w_j d_j)^2}\left(0.7059 w_i^2 + 0.9772 w_j^2 + 1.5809 w_i w_j\right) \quad \cdots\cdots \quad 22)$$

Table 1 shows the identity of the calculated value with the observed one for Benzene-Dioxane mixture at 35°C. These calculations were performed according to the Eq. 22). The measurements of the viscosity were undertaken by using Ostwards' viscosimeter under exact controlling the temperature (±0.005°C). The materials, benzene and dioxane, were used of extra pure reagents and of spectro-analysis use. The moisture absorption for dioxane was strictly avoided through these experiments as much as possible. As shown in Table 1, the difference between the calculated value and the observed one was very small.

The result obtained in Table 1 is one of the example for the ideal case that the molecules of the components i and j have very small dipole moments. The density relation which was represented in Eq. 10) holds good as shown in Table 2). Accordingly, in consideration of all conditions related, the application of this equation (11) will be admitted only for the case that the mixture is approximately ideal solution and the conformity of this equation would be considerably limited in the case of polar substance.

Table 1. The viscosity of Benzene(i)-Dioxane(j) mixture at 35°C.

$\lambda=1.3427$, $\mu=0.9743$, $\nu=2.1866$.

w_i	w_j	$\lambda w_i^2 \eta_{ii}$	$\mu w_j^2 \eta_{jj}$	$\nu w_i w_j \eta^*$	$\frac{d_i^2 d_j^2}{(w_i d_j+w_j d_i)^2}$	$(\eta_{i+j})_c$	$(\eta_{i+j})_o$	△
1.00000	0.00000	0.70599	0.00000	0.00000	0.74695	0.52733	0.52583	+0.00150
0.90374	0.09626	0.57660	0.00904	0.13751	0.76648	0.55428	0.55496	−0.00068
0.80163	0.19837	0.45367	0.03844	0.25139	0.79055	0.58777	0.58978	−0.00201
0.70418	0.29582	0.35006	0.08551	0.32615	0.81461	0.62050	0.62468	−0.00418
0.60365	0.39635	0.25724	0.15351	0.37821	0.84060	0.66319	0.66350	−0.00031
0.55344	0.44656	0.21622	0.19486	0.39070	0.85404	0.68475	0.68410	+0.00065
0.50415	0.49585	0.17942	0.24025	0.39518	0.86757	0.70693	0.70630	+0.00057
0.46963	0.53037	0.15569	0.27487	0.39374	0.87722	0.72309	0.72129	+0.00180
0.43043	0.56957	0.13079	0.31701	0.38757	0.88840	0.74214	0.73948	+0.00266
0.40232	0.59768	0.11426	0.34908	0.38014	0.89652	0.75619	0.75265	+0.00354
0.30509	0.69491	0.06569	0.47189	0.33516	0.92555	0.80776	0.80322	+0.00454
0.20069	0.79931	0.02842	0.62433	0.25358	0.95830	0.86853	0.86449	+0.00404
0.14838	0.85162	0.01549	0.70872	0.19974	0.97539	0.90121	0.89483	+0.00638
0.10210	0.89790	0.00734	0.78784	0.14490	0.99089	0.93151	0.93018	+0.00133
0.00000	1.00000	0.00000	0.97722	0.00000	1.02637	1.00299	1.00300	−0.00001

Table 2. The density of Benzene(i)-Dioxane(j) mixture at 25°C.

$d_i^{25}=0.87291$, $d_j^{25}=1.02776$.

w_i	w_j	$A=w_i/d_i$	$B=w_j/d_j$	$C=A+B$	$(d_{i+j})_c$	$(d_{i+j})_o$	△
1.00000	0.00000	1.14559	0.00000	1.14559	0.87291	0.87291	0.00000
0.76931	0.23069	0.88131	0.22445	1.10576	0.90435	0.90504	−0.00069
0.66358	0.33642	0.76020	0.32732	1.08752	0.91952	0.92053	−0.00101
0.56037	0.43963	0.64195	0.42775	1.06970	0.93484	0.93613	−0.00129
0.45962	0.54038	0.52653	0.52577	1.05230	0.95029	0.95144	−0.00115
0.36161	0.63839	0.41425	0.62114	1.03539	0.96581	0.96640	−0.00059
0.26861	0.73139	0.30771	0.71162	1.01933	0.98103	0.98172	−0.00069
0.17235	0.82765	0.19744	0.80528	1.00272	0.99728	0.99779	−0.00051
0.08582	0.91418	0.09831	0.88947	0.98778	1.01237	1.01267	−0.00030
0.00000	1.00000	0.00000	0.97298	0.97298	1.02776	1.02776	0.00000

Table 3*. The Viscosity of Dioxane(i)-Cyclohexane(j) Mixture at 30°C.

$\lambda=0.95317,\quad \mu=1.68401,\quad \nu=2.16946.$

$d_i^{30}=1.02427,\quad d_j^{30}=0.77060.$

w_i	w_j	$\lambda w_i^2 \eta_{ii}$	$\mu w_j^2 \eta_{jj}$	$\nu w_i w_j \eta^*$	$\frac{d_i^2 d_j^2}{(w_i d_j + w_j d_i)^2}$	$(\eta_{i+j})_c$	$(\eta_{i+j})_o$	△
0.00000	1.00000	0.00000	1.73001	0.00000	0.59381	1.02729	1.02732	−0.00003
0.13019	0.86981	0.02205	1.30885	0.24935	0.63404	1.00194	0.97954	+0.02240
0.24828	0.75172	0.08024	0.97759	0.41095	0.67418	0.99022	0.97343	+0.01679
0.36356	0.63644	0.17207	0.70074	0.50949	0.71716	0.99133	0.98065	+0.01068
0.47170	0.52830	0.28967	0.48284	0.54871	0.76130	1.00584	1.00446	+0.00138
0.52425	0.47575	0.35780	0.39155	0.54920	0.78425	1.01838	1.02065	−0.00227
0.57011	0.42989	0.42314	0.31970	0.53966	0.80513	1.03257	1.03272	−0.00015
0.62448	0.37552	0.50770	0.24394	0.51636	0.83098	1.05368	1.05809	−0.00441
0.66849	0.33151	0.58178	0.19011	0.48798	0.85284	1.07446	1.08143	−0.00697
0.71720	0.28280	0.66965	0.13834	0.44660	0.87804	1.10158	1.10779	−0.00621
0.75844	0.24156	0.74889	0.10094	0.40340	0.90026	1.12823	1.13400	−0.00577
0.84369	0.15631	0.92670	0.04226	0.29037	0.94897	1.19506	1.19817	−0.00311
0.92379	0.07621	1.11101	0.01003	0.15499	0.99841	1.27400	1.27306	−0.00094
1.00000	0.00000	1.30190	0.00000	0.00000	1.04910	1.36582	1.36587	−0.00005

Table 4*. The Density of Dioxane(i)-Cyclohexane(j) Mixture at 25°C.

$d_i^{25}=1.02828,\quad d_j^{25}=0.77365.$

w_i	w_i	$A=w_i/d_i$	$B=w_j/d_j$	$C=A+B$	$(d_{i+j})_c$	$(d_{i+j})_o$	△
0.00000	1.00000	0.00000	1.29257	1.29257	0.77365	0.77365	0.00000
0.08719	0.91281	0.08479	1.17987	1.26466	0.79072	0.78744	+0.00328
0.24861	0.75139	0.24177	0.97122	1.21299	0.82440	0.81761	+0.00679
0.43628	0.56372	0.42428	0.72864	1.15292	0.86736	0.85902	+0.00834
0.53779	0.46221	0.52299	0.59744	1.12043	0.89251	0.88338	+0.00913
0.60556	0.39444	0.58890	0.50984	1.09874	0.91013	0.90103	+0.00910
0.69726	0.30274	0.67808	0.39131	1.06939	0.93511	0.92725	+0.00786
0.84196	0.15804	0.81880	0.20427	1.02307	0.97745	0.97178	+0.00567
0.95029	0.04971	0.92415	0.06425	0.98840	1.01173	1.00941	+0.00232
1.00000	0.00000	0.97249	0.00000	0.97249	1.02828	1.02828	0.00000

* The materials used in these experiments were UV spectro-analysis use.

Tables 3) and 4) show the viscosity and the density of the dioxane (i)-cyclohexane (j) system as a function of weight fraction. The calculated values of density and viscosity were also obtained respectively from Eqs. 10) and 21). The necessary datas for calculations were estimated from our experiments as follows ; $d_i{}^{30} = 1.02427$, $d_j{}^{30} = 0.77060$, $\eta_{ii} = 1.36587$, $\eta_{jj} = 1.02732$ and $\eta^* = 1.0148$. From these datas, the values λ, μ and ν of Eq. 22) were calculated $\lambda = 0.95317$, $\mu = 1.68401$ and $\nu = 2.16946$ respectively. Accordingly, the viscosity equation which is applicable to the dioxane-cyclohexane mixed solvent system at 30°C is also given by the following equation ;

$$\eta_{i+j}=\frac{d_i^2 d_j^2}{(w_i d_j+w_j d_i)^2}\ (1.3019w_i^2+1.7300w_j^2+2.2020w_i w_j)\ \cdots\cdots\ 23)$$

As clearly shown in Tables 1), 2), 3) and 4), the difference between the calculated value and the observed value of the density or the viscosity is very small, and this fact show us that Eq. 10) or 20) is good applicable to the dioxane-benzene or dioxane-cyclohexane system with the accuracy of the same order. Figs. 1 and 2 respectively show the difference between the calculated value of viscosity and the observed one and the relation bwtween the viscosity and the weight fraction. The viscosity-weight fraction curve which was obtained from the dioxane-cyclohexane system is a typical parabolic one as expectad theoretically from Eq. 20) or 23).

The outline of these investigations was already presented at the conference of the Chemical Society of Japan[5] and the related associations, Nagoya, Sept, 1969. Support of these experimental works by H. Hayashi, R. Yoshida and H. Inada, the graduate course students of our laboratory, the faculty of education of the Shimane University, is gratefully acknowleged.

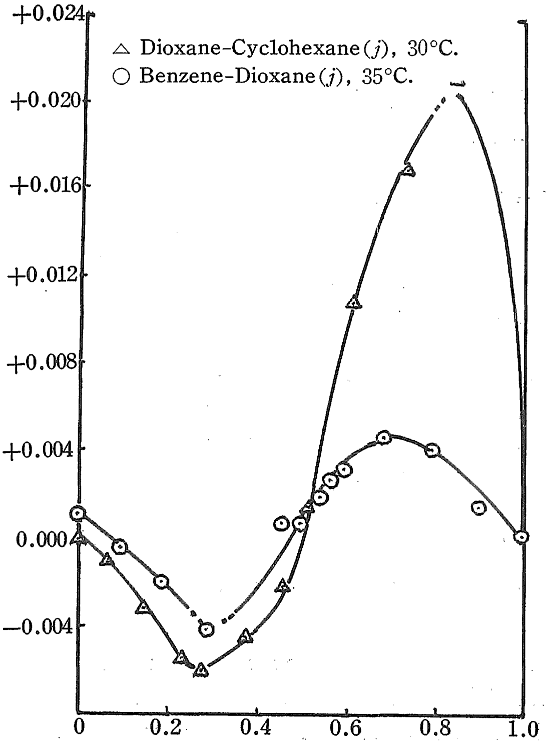

Fig. 1. The Differnce △-Curve of Viscosity.

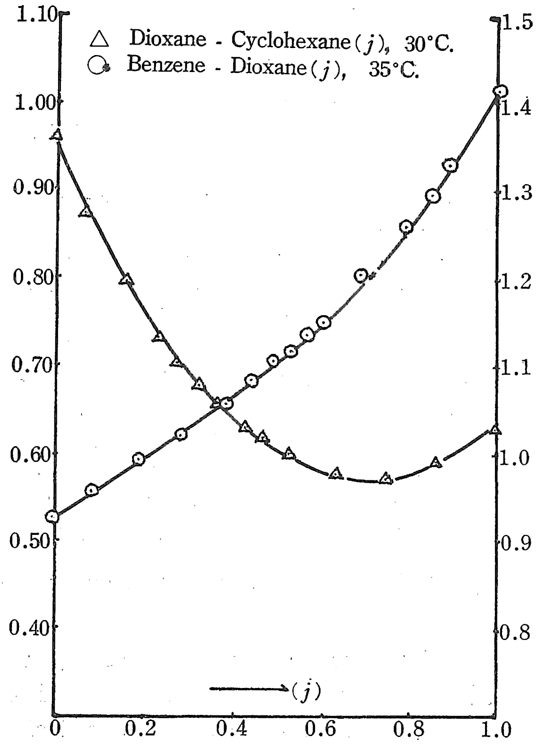

Fig. 2. The Relation between the Viscosity and the Weight Fraction.

References

1) Tetsuya Ishikawa ; Refractivity of a Binary Mixture and its Relation to the Molecular Size of the Components, *Chikashige Anniversary Volume*, Kyoto, **275** (**1930**).

2) Tetsuya Ishikawa ; Theories on the Viscosity of Organic Solvent Mixture (*Kongō-iki Nendo no Riron*), Marzen, Tokyo (1968).

3) Senseki Takano and Akira Yamamoto ; The Molecular Interactoin Observed in Specific Volume of Organic Binary Solvents. *Bull. Shimane Univ.*, No**16**, 98 (**1966**).

4) Senseki Takano ; Studies on the Dielectric Properties of Organic Solvents 1, Part 2), *Mem. Fac. Education, Shimane Univ.*, vol. **1**, 31, (**1967**).

5) Senseki Takano ; Preliminary Note, *Chem. Soc. of Japan*, page 13, (**1969**).