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STUDIES ON THE DIELECTRIC PROPERTIES OF ORGANIC SOLVENTS VII.

A THEORY ON THE DISPERSION OF THE REFRACTIVE INDEX OF POLY-COMPONENT SOLVENT SYSTEM

By

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1. Introduction

In this paper, a theoretical formula on the frequency dependence of the refractive index of a solvent mixture was introduced and the result of the certification of the theoretical formula was reported on several organic solvent mixtures. The difference between the theoretical value and the experimental one was also examined from the view-point of molecular interaction. In the case of cyclohexane-dioxane mixture, the above difference was scarecely observed, but in the case of benzene-cyclohexane mixture, it always showed a considerably large order of deviation and this fact gave us a speculation for the formation of a molecular complex.

2. Theoretical

As shown in the previous papers, the general formula of the refractive index $n_{1.2.3....}$ of n-th poly-component mixture of organic solvents 1, 2, 3, ..., n can be expressed by the following formula[5];

$$\frac{1}{n^2_{1,2,3...}}=\frac{\sum_{r=1}^{r=n}\frac{1}{n_r^2}(d_{r-i},\ldots d_{r-1},\ d_{r+1}\ldots d_{r+i})}{\sum_{r=1}^{r=n} w_r(d_{r-i}\ldots d_{r-1},\ d_{r+1}\ldots d_{r+i})} \qquad \cdots\cdots 1)$$

From this formula, we can easily introduce the most simple formula for two component mixture as follows;

$$\frac{1}{n^2_{1\cdot2}}=\frac{w_1d_2}{n_1^2(w_1d_2+w_2d_1)}+\frac{w_2d_1}{n_2^2(w_1d_2+w_2d_1)} \qquad \cdots\cdots 2)$$

where $n_{1.2}$ is the refractive index of the mixed solvent, n_1 and n_2 are the refractive indices of the pure solvents 1 and 2, w is the weight fraction, d denotes the density.

For simplification, we denote the terms of the weight fraction and density in the right hand of the formula 2) respectively as ;

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$$\left.\begin{aligned} K_1 &= w_1d_2/(w_1d_2+w_2d_1) \\ K_2 &= w_2d_1/(w_1d_2+w_2d_1) \end{aligned}\right\} \quad \cdots\cdots 3)$$

then the formula 2) can be transformed into ;

$$\frac{1}{n_{1\cdot 2}^2}=\frac{K_1}{n_1^2}+\frac{K_2}{n_2^2} \quad \cdots\cdots 4)$$

As shown in the formula 3), K_1 and K_2 although contain in it density d_1 and d_2, it is clear that these are indifferent to the wave-length, so we differenciate the both terms of the formula 4) with wave-lengh λ of the light, so we have ;

$$n_{1\cdot 2}^{-3}\cdot\frac{dn_{1\cdot 2}}{d\lambda}=K_1n_1^{-3}\frac{dn_1}{d\lambda}+K_2n_2^{-3}\frac{dn_2}{d\lambda} \quad \cdots\cdots 5)$$

In this formula 5), $dn_{1\cdot 2}/d\lambda$, $dn_1/d\lambda$ and $dn_2/d\lambda$ are respectively the dispersion of the refractivity of the mixture and the two pure solvents, now let us denote ;

$$\left.\begin{aligned} \frac{dn_{1\cdot 2}}{d\lambda} &\equiv z_{1\cdot 2} \\ \frac{dn_1}{d\lambda} &\equiv z_1 \\ \frac{dn_2}{d\lambda} &\equiv z_2 \end{aligned}\right\} \quad \cdots\cdots 6)$$

Now in the formula 5), the value $n_{1\cdot 2}$ in the left hand term can be obtained from the formula 2) as follows ;

$$n_{1\cdot 2}^{-3}=\left[\frac{K_1n_2^2+K_2n_1^2}{n_1^2\cdot n_2^2}\right]^{3/2}=\frac{(K_1n_2^2+K_2n_1^2)^{3/2}}{n_1^3\cdot n_2^3} \quad \cdots\cdots 7)$$

From the formulas 5), 6) and 7) easily we have ;

$$z_{1\cdot 2}=\frac{K_1z_1n_2^3+K_2z_2n_1^3}{(K_1n_2^2+K_2n_1^2)^{3/2}} \quad \cdots\cdots 8)$$

or

$$\frac{dn_{1\cdot 2}}{d\lambda}=\frac{K_1n_2^3}{(K_1n_2^2+K_2n_1^2)^{3/2}}\frac{dn_1}{d\lambda}+\frac{K_2n_1^3}{(K_1n_2^2+K_2n_1^2)^{3/2}}\frac{dn_2}{d\lambda} \quad \cdots\cdots 9)$$

Similarly the method of these transformations may be applied for the general formula for poly-component system which was given as the formula 1) although it is very complex. The formula 9) shows us that the refractive dispersion of the mixed solvent can be estimate only from the original quantities such as densities and the refractive dispersions of the original solvents, if the weight fraction of the mixture is given.

In the derivation of the formula 1), as we noted it in the previous papars[1),5)] we have started from the two assumptions that 1) the additivity law in the specific volumes and 2) the Maxwell law between dielectric constant and refractive index may be both admitted for the considering systems. Accordingly, it is natural that the formula 8) or 9) can be applied only for ideal mixture or approximatives. The first assumption may have a very important meaning for discussing the problem of molecular interaction as it will be discussed later.

3. Experimental

The refractive index and the refractive dispersion were measured by using Abbe's New Type refractometer. The temperature of the samples was kept within the range of 0.05°C by circulating the water of fixed temperature from the thermostat. The detailes of the method are as same as that of reported in the previous paper[3)]. The density of the pure solvents which is necessary in the calculation of the theoretical values of refractive index and refractive dispersion according to the formula 9) was precisely measured by using Ostwald's picknometer with the same order of the temperature variation as in the case of refractive index measurement. All the calculations were undertaken according to the following rule ;

$$\left.\begin{aligned} z_{1\cdot 2} &= B \backslash A^{3/2} \\ A &= K_1 n_2^2 + K_2 n_1^2 \\ B &= K_1 z_1 n_2^3 + K_2 z_2 n_1^3 \end{aligned}\right\} \cdots\cdots 10)$$

In these calculations, instead of $dn/d\lambda$ or z, we adopted dispersion Z and Abbe's

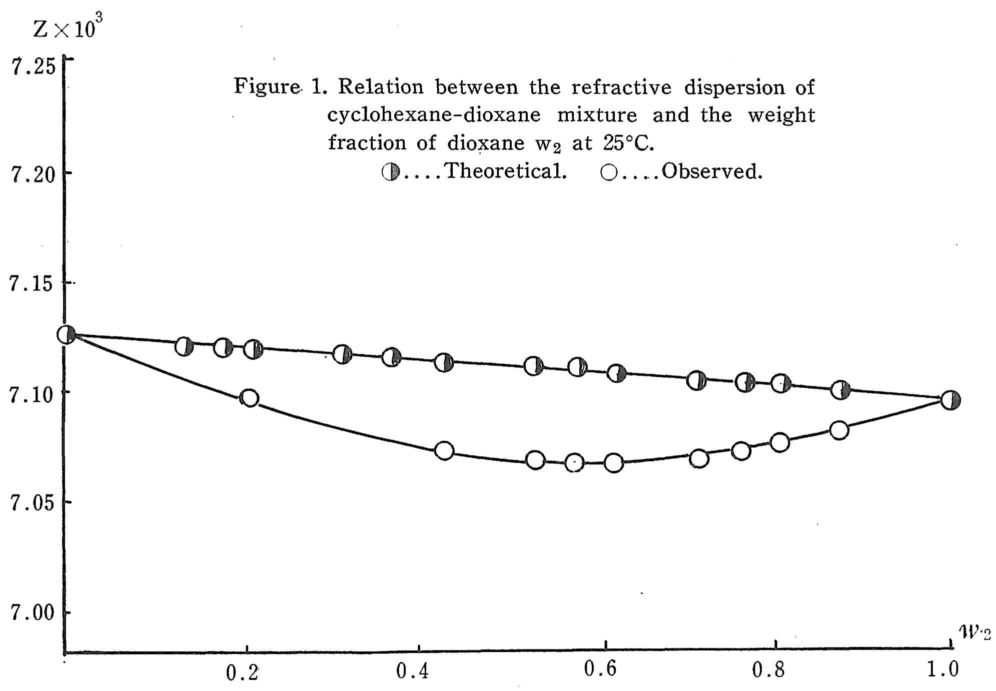

Figure. 1. Relation between the refractive dispersion of cyclohexane-dioxane mixture and the weight fraction of dioxane w_2 at 25°C.
◑.... Theoretical. ○.... Observed.

Number ν which are denoted usally by the following formula ;

$$Z = N_f - N_c,\ \nu = (N_D - 1)\backslash(N_f - N_c) \quad \cdots\cdots 11)$$

where N_f and N_c are the calculated value from the Table of Dispersion by using the observed data. N_D is the refractive index observed at the wave length corresponding to D-line of Natrium atom.

1) Cyclohexane-Dioxane System.

Data of calculations are as follows ;

Temperature..................25°C±0.05
Density of cyclohexane.........0.77385
Density of dioxane.............1.02830
Refractive index of cyclohexane....1.4240
Refractive index of dioxane........1.4198

The experimental datas are shown in Table 1.

Table 1. The dispersion of cyclohexane-dioxane system at 25°C.
Suffix ; 1...cyclohexane, 2...dioxane.

w_1	w_2	$n_{D\cdot 1\cdot 2}$	z*	ν	A	B	$(z_{1\cdot 2})_{calc.}$	$(z_{1\cdot 2})_{obs.}$	$\triangle\%$
1.00000	0.00000	1.4240	41.02	59.533	2.0158	0.028886	0.007122	0.007123	0.014
0.86394	0.13605	1.4216	41.02	59.461	2.0170	0.020393	0.007119	0.007091	0.394
0.82011	0.17988	1.4209	41.02	59.440	2.0174	0.020397	0.007118	0.007081	0.522
0.78548	0.21451	1.4203	41.00	59.222	2.0177	0.020399	0.007117	0.007097	0.281
0.68475	0.31524	1.4193	41.02	59.399	2.0188	0.020407	0.007114	0.007059	0.779
0.62662	0.37337	1.4189	41.00	59.183	2.0194	0.020411	0.007112	0.007078	0.480
0.57066	0.42933	1.4184	41.00	59.174	2.0200	0.020416	0.007111	0.007072	0.551
0.47012	0.52987	1.4180	41.00	59.156	2.0211	0.020424	0.007108	0.007066	0.594
0.41941	0.58058	1.4179	41.00	59.159	2.0217	0.020431	0.007107	0.007065	0.594
0.37613	0.62386	1.4179	41.00	59.162	2.0223	0.020432	0.007104	0.007165	0.552
0.28503	0.71496	1.4180	41.00	59.156	2.0235	0.020440	0.007101	0.007066	0.495
0.23680	0.76319	1.4182	41.00	59.159	2.0231	0.020445	0.007099	0.007069	0.424
0.19540	0.80459	1.4184	41.00	59.162	2.0247	0.020449	0.007098	0.007072	0.319
0.12384	0.87615	1.4189	41.00	59.186	2.0257	0.020457	0.007095	0.007078	0.240
0.00000	1.00000	1.4198	41.00	59.221	2.0277	0.020471	0.007090	0.007090	0.000

*The readings of dispersion dial.

2) Benzene-Cyclohexane System.

Datas of calculations are as follows ;

Temperature.......................25°C±0.05
Density of benzene................0.87310
Density of cyclohexane.............0.77386
Refractive index of benzene.........1.4979
Refractive index of cyclohexane......1.4237

The experimental datas are shown in Table 2.

Figure 2. Relation between the refractive dispersion of benzene-cyclohexane mixture and the weight fraction of cyclohexane w_2 at 25°C.
◑......Theoretical. ○.........Observed.

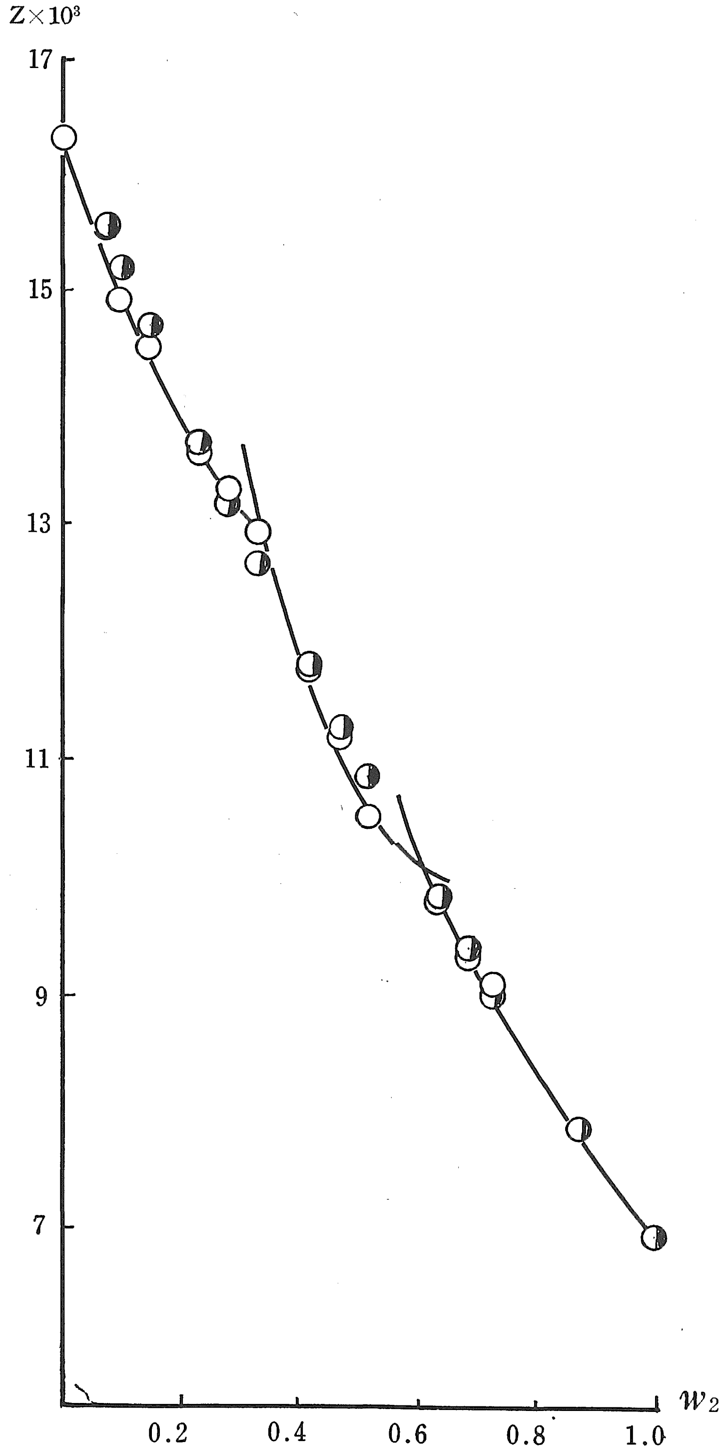

Table 2. The dispersion of benzene-cyclohexane system at 25°C
Suffix ; 1...benzene, 2...cyclohexane.

w_1	w_2	$n_{D\cdot 1\cdot 2}$	z*	ν	A	B	$(z_{1\cdot 2})_{calc.}$	$(z_{1\cdot 2})_{obs.}$	△ %
1.00000	0.00000	1.4979	35.04	30.60	2.024	0.04887	0.01627	0.01627	0.000
0.93521	0.06478	1.4914	35.58	31.78	2.039	0.04516	0.01551	0.01546	0.323
0.90599	0.09400	1.4888	35.98	32.78	2.045	0.04439	0.01548	0.01491	1.810
0.85426	0.14573	1.4839	36.22	33.37	2.056	0.04328	0.01468	0.01450	1.241
0.77279	0.22720	1.4768	36.82	35.11	2.077	0.04100	0.01369	0.01358	0.810
0.72356	0.27643	1.4728	37.04	35.62	2.088	0.03977	0.01318	0.01327	0.678
0.67515	0.32484	1.4684	37.23	36.25	2.099	0.03859	0.01269	0.01292	1.780
0.58363	0.41636	1.4611	38.00	39.27	2.120	0.03638	0.01178	0.01174	0.940
0.53143	0.46856	1.4569	38.37	40.79	2.131	0.03514	0.01129	0.01119	0.895
0.48498	0.51501	1.4535	38.82	43.14	2.141	0.03405	0.01087	0.01051	3.425
0.36899	0.63100	1.4452	39.28	45.47	2.166	0.03138	0.00984	0.00979	0.510
0.31993	0.68006	1.4421	39.61	47.58	2.176	0.03027	0.00943	0.00929	1.506
0.26834	0.73165	1.4388	39.79	48.70	2.187	0.02912	0.00900	0.00901	1.528
0.12178	0.87821	1.4299	40.52	54.41	2.218	0.02593	0.00786	0.00790	0.481
0.00000	1.00000	1.4237	41.04	60.78	2.241	0.02337	0.00697	0.00697	0.000

*The readings of dispersion dial.

4. Discussion

Judging from the data shown in Table 1 and 2, the deviations between the theoretical values and the observed values of the refractive dispersion are larger in the case of benzene-cyclohexane system than in the cyclohexane-dioxane system. The observed curve of refractive dispersion vis weight fraction is shown by a continuous curve of typical catenary type as shown in the figure 1. From this curve it may be concluded that perphaps no remarkable sign of formation of molecular cluster may be expected in this system.

On the contrary, benzene-cyclohexane system shows very clear break points on the curve of refractive dispersion vis weight fraction as shown in the figure 2. The detailed discussion on these problems will be given with related to the other results of observations[4] on cyclohexylamine-dioxane, cyclohexylamine-cyclohexanol and cyclo hexylamine-pyridine systems in near future.

Literatures

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