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# STUDIES ON THE DIELECTRIC PROPERTIES OF ORGANIC SOLVENTS V

## THE EXPERIMENTAL CERTIFICATION AND THE COMPARATIVE DISCUSSION ON THE FORMULAE OF THE REFRACTIVE INDEX FOR POLY-COMPONENT SOLVENT MIXTURE

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## I. INTRODUCTION

The refractivity of light and its dispersion is a very simple physical property of a matter, but it has recently been taken up in our laboratory as a new index of detecting an apparently short range force of molecular interaction. This problem on the relation between the refractive index and the molecular structure has widely been developed and the conformation of a molecule has also been theoretically analyzed by the use of the method of rotatory dispersion.

The classic theory of photo-refractivity which was first theoretically elucidated by Maxwell on the velocity of electro-magnetic wave in a substance have aboundantly exhibited the nature of a bonded electron with related to the magnetic properties of a matter and have given the knowlege of atomic polarization which gives a degree of shift of electron in an atomic orbital.

The basic aim of this investigation is to re-examine the hypothesis on the dielecrtic constant of a poly-component mixture which was given by us[1),2)] as a law of the reciprocal additivity of the dielectric constants of the pure solvents. By using the wave of ultra-low frequency or a high frequency of 3 Mc/s order, the experiments for the mixture of nonpolar or the slightly polar substances showed good identities and these experimental results were already reported in the series of this investigation.[3)] In the case of very short wave-length as light, far different from that of relaxation time of the molecule in the mixture, the more good identity will be expected if the hypothesis is really correct.

Thus, in this paper, the results of experiments in proving the theoretical formula on the refractive index of a poly-component solvent mixture which was formulized from the theory of dielectric constant of the same mixture were exhibited and comparatively discussed with related to the other several formulae.

The materials used for these certifications were respectively as follows ; i) the mixture of Dioxane, Cyclohexane, n-Hexane, n-Heptane and Toluene, ii) the mixture of Toluene, Pyridine, Benzene, Monochlorobenzene and Dioxane, iii) the mixture of Cyclohexane, n-Heptane, n-Pentane, p-Xylene and n-Hexane, iv) the mixture of Benzene and Dioxane.

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## II. THEORETICAL

Let the hypothetical dielectric constant of the mixture be denoted with $\varepsilon_{i+j}$, and those of the pure solvents be respectively denoted with $\varepsilon_i$ and $\varepsilon_j$, the volume fractions of the same solvents be denoted with $v_i$ and $v_j$, then the electro-static free energy stored in the unit volume of the mixture will be given by the follwing formula ;

$$\frac{D^2}{8\pi\varepsilon_{i+j}}=\frac{D^2v_i}{8\pi\varepsilon_i}+\frac{D^2v_j}{8\pi\varepsilon_j} \quad \cdots\cdots 1)$$

Expanding the above formula into the mixture of $n$-th component 1, 2, 3.....$n$, then we have ;

$$\frac{D^2}{8\pi\varepsilon_{1\cdot2\cdots n}}=\frac{D^2}{8\pi}\sum_{r=1}^{r=n}\frac{v_r}{\varepsilon_r} \quad \cdots\cdots 2)$$

In the case when the mixture and the pure solvents 1, 2, 3.....$n$ have very small permiabilities, the Maxwell relation $\varepsilon = n^2$ on the refractive index ($n$) and the dielectric constant ($\varepsilon$) may be applied for the formula 2), then we have ;

$$\frac{D^2}{8\pi n^2_{1\cdot2\cdots n}}=\frac{D^2}{8\pi}\sum_{r=1}^{r=n}\frac{v_r}{n_r^2} \quad \cdots\cdots 3)$$

By the definitions of the volume fraction and the weight fraction, the volume fraction of $r$-th component ($v_r$) can be transformed into the weight fraction ($w_r$) by the following formula ;

$$v_r=\frac{w_r(d_{r-i},\cdots d_{r-1},\ d_{r+1}\cdots d_{r+i})}{\sum_{r=1}^{r=n}w_r(d_{r-i},\cdots d_{r-i},\ d_{r+1},\cdots d_{r+i})} \quad \cdots\cdots 4)$$

where

$$\sum_{r=1}^{r=n}w_r=\sum_{r=1}^{r=n}v_r=1 \quad \cdots\cdots 5)$$

Applying the formula 5) into the formulae 2) and 3), we have ;

$$\frac{1}{\varepsilon_{1\cdot2\cdots n}}=\frac{\sum_{r=1}^{r=n}\frac{1}{\varepsilon_r}(d_{r-i}\cdots\cdots d_{r-1},\ d_{r+1},\cdots\cdots d_{r+i})}{\sum_{r=1}^{r=n}w_r(d_{r-i},\cdots\cdots d_{r-1},\ d_{r+1},\cdots\cdots d_{r+i})} \quad \cdots\cdots 6)$$

and

$$\frac{1}{n^2_{1\cdot 2\cdots n}} = \frac{\sum_{r=1}^{r=n} \frac{1}{n_r^2}(d_{r-i}, \cdots\cdots d_{r-1}, d_{r+1}, \cdots\cdots d_{r+i})}{\sum_{r=1}^{r=n} w_r(d_{r-i}, \cdots\cdots d_{r-1}, d_{r+1}, \cdots\cdots d_{r+i})} \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad 7)$$

## III. EXPERIMENTAL RESULTS and CALCULATIONS

The materials, Dioxane, Benzene, Cyclohexane, n-Heptane, n-Hexane, Toluene, Pyridine and Monochlorobenzene, were used of all guaranted grade chemicals from Kanto Chemical Company without further purification. A new Type Abbe's Refractometer from Atago Optical Instrument Co. was used for the measurements of refractive index. The water jacket of the instrumrnt was connected with a thermostat of large bulk and through which water of fixt temperature was circulated at a moderate speed to maintain the temperature of the sample exactly at 25°C ± 0.01 or 20°C ± 0.005 respectively. The temperature of the sample was measured exactly by a thermometer of special made which was fixed into the water jacket near the sample. The measurements of the refractive indices were carried out several times for the same samples and the mean value was taken into account, and, at the same time, the dispersion of the refractive index was also estimated.

The composition of the mixture was determined by weighing and calculated the volume fraction according to the formula 4). The determination of the density or the specific volume was undertaken with the use of pyknometer of Ostwald's Type. The pyknometer and the material which was stored in an Erlenmyer's flask of small type with a tight fitting glass stoper were both incubated in a large glass bottle in order to maintain the temperature constant. This large glass bottle was immersed in the above mentioned thermostat and the bottom of it the silica gell was filled as a moisture absorber. Through all the procedures of making samples, mixing and other treatments, the moisture absorption of the sample was strictly avoided.

The experimental results and the calculations were obtained at 25°C or 20°C for the following four mixed solvent systems ; i) Dioxane (1)-Cyclohexane (2)-n-Hexane (3)-n-Heptane (4)-Toluene (5), ii) Toluene (1)-Pyridine (2)-Benzene (3)-Monochlorobenzene (4)-Dioxane (5), iii) Cyclohexane (1)-n-Heptane (2)-n-Pentane (3)-p-Xylene (4)-n-Hexane (iv) and Benzene (1)-Dioxane (2) bi-component system. Calculations of refractive index were undertaken according to the formula 7) and the results were examined with the use of systems i), ii) and iii), and these were illustrated in the tables 1), 2) and 3). Calculations of the same index according to Lichtneckes's formula[4] were also undertaken for the systems i) and ii), and these results were given in the tables 4)and 5). The last system, Dioxane-Benzene, was used for the certification of Wallot's formla.[5] The detailes were also given in the table 6).

i) Experiment 1.

System.....Dioxane-Cyclohexane-n-Hexane-n-Heptane-Toluene.

Calculations.....According to Formula 7, (Takano).

Temperature.....25°C ± 0.01.
Data for Calculations ;

| Solvents | Density ($d_0^{25}$)* | Refractive Index ($n_D^{25}$)** |
|---|---|---|
| 1) Dioxane | 1.02687 | 1.42020 |
| 2) Cyclohexane | 0.80557 | 1.44436 |
| 3) n-Hexane | 0.65482 | 1.37912 |
| 4) n-Heptane | 0.67951 | 1.38552 |
| 5) Toluene | 0.86231 | 1.49400 |

*Weisberger, **Observed value.

Table 1. Dioxane-Cyclohexane-n-Hexane-n-Heptane-Toluene system, 25°C.

| $w_1$ | $w_2$ | $w_3$ | $w_4$ | $w_5$ | $n$(obs) | $n$(calc) | $\Delta$% |
|---|---|---|---|---|---|---|---|
| 0.11356 | 0.15086 | 0.14782 | 0.20888 | 0.37885 | 1.43409 | 1.43112 | 0.2070 |
| 0.49478 | 0.07042 | 0.11030 | 0.09127 | 0.23363 | 1.43010 | 1.42786 | 0.1566 |
| 0.26826 | 0.46048 | 0.05674 | 0.14944 | 0.14622 | 1.42910 | 1.43057 | 0.1028 |
| 0.17856 | 0.24273 | 0.30365 | 0.08932 | 0.18574 | 1.42007 | 1.41809 | 0.1394 |
| 0.20325 | 0.16310 | 0.18671 | 0.33317 | 0.11378 | 1.40817 | 1.40807 | 0.0085 |
| 0.45821 | 0.15018 | 0.12998 | 0.13032 | 0.13131 | 1.42053 | 1.41969 | 0.0591 |
| 0.19471 | 0.36621 | 0.12465 | 0.12386 | 0.19080 | 1.43004 | 1.42926 | 0.0545 |
| 0.19806 | 0.16040 | 0.32603 | 0.14734 | 0.16817 | 1.41324 | 1.41067 | 0.1818 |
| 0.21009 | 0.16081 | 0.12910 | 0.34515 | 0.15485 | 1.41303 | 1.41269 | 0.0240 |
| 0.19793 | 0.17056 | 0.11440 | 0.13258 | 0.38453 | 1.43954 | 1.43664 | 0.2014 |
| 0.25198 | 0.18212 | 0.15421 | 0.20166 | 0.21004 | 1.42312 | 1.42113 | 0.1398 |
| 0.18619 | 0.23892 | 0.25446 | 0.17943 | 0.14099 | 1.41505 | 1.41430 | 0.0530 |
| 0.27593 | 0.11802 | 0.21366 | 0.21443 | 0.17796 | 1.41486 | 1.41399 | 0.0614 |
| 0.24878 | 0.22945 | 0.11769 | 0.23584 | 0.16825 | 1.42022 | 1.42066 | 0.0309 |
| 0.15679 | 0.28423 | 0.25271 | 0.14328 | 0.16299 | 1.41917 | 1.41839 | 0.0549 |
| 0.16358 | 0.23028 | 0.12706 | 0.24940 | 0.22967 | 1.42390 | 1.42289 | 0.0709 |
| 0.32706 | 0.21462 | 0.10580 | 0.23154 | 0.12099 | 1.41727 | 1.41753 | 0.0183 |

ii) Experiment 2.
System...Toluene-Pyridine-Benzene-Monochlorobenzene-Dioxane.
Calculations.....According to Formula 7, (Takano).
Temperature.....20°C ±0.01.
Data for Calculations ;

| Solvents | Density ($d_0^{20}$)* | Refractive Index ($n_D^{20}$)* |
|---|---|---|
| 1) Toluene | 0.86854 | 1.49662 |
| 2) Pyridine | 0.98250 | 1.50955 |
| 3) Benzene | 0.87386 | 1.50082 |
| 4) Monochlorobenzene | 1.10667 | 1.52425 |
| 5) Dioxane | 1.03376 | 1.42232 |

*Observed value

Table 2. Toluene-Pyridine-Benzene-Monochlorobenzene-Dioxane system, 20°C.

| $w_1$ | $w_2$ | $w_3$ | $w_4$ | $w_5$ | $n$(obs) | $n$(calc) | $\Delta$% |
|---|---|---|---|---|---|---|---|
| 0.188049 | 0.174938 | 0.188049 | 0.229553 | 0.219409 | 1.49027 | 1.49134 | 0.0852 |
| 0.295889 | 0.239936 | 0.448124 | 0.171588 | 0.144461 | 1.49497 | 1.49259 | 0.1605 |
| 0.121876 | 0.302145 | 0.209499 | 0.226981 | 0.139497 | 1.49776 | 1.49726 | 0.1001 |
| 0.156325 | 0.156900 | 0.306173 | 0.169609 | 0.210990 | 1.49016 | 1.48832 | 0.1234 |
| 0.231381 | 0.171800 | 0.122936 | 0.184859 | 0.289022 | 1.48420 | 1.48213 | 0.1394 |
| 0.255905 | 0.243505 | 0.122273 | 0.204958 | 0.173356 | 1.49374 | 1.49204 | 0.1138 |
| 0.269415 | 0.198409 | 0.125524 | 0.224388 | 0.182261 | 1.49302 | 1.49132 | 0.1138 |
| 0.159164 | 0.345223 | 0.160627 | 0.144398 | 0.190617 | 1.49270 | 1.49069 | 0.1346 |
| 0.167137 | 0.162608 | 0.328224 | 0.152829 | 0.189199 | 1.49130 | 1.48974 | 0.1046 |
| 0.143801 | 0.146863 | 0.172614 | 0.392141 | 0.144578 | 1.49926 | 1.49769 | 0.1047 |
| 0.132417 | 0.133304 | 0.153534 | 0.210974 | 0.369769 | 1.47850 | 1.47621 | 0.1548 |
| 0.234121 | 0.272477 | 0.163917 | 0.150145 | 0.179337 | 1.49284 | 1.49087 | 0.1319 |
| 0.145085 | 0.270137 | 0.242687 | 0.171762 | 0.170326 | 1.49420 | 1.49237 | 0.1224 |
| 0.124920 | 0.188914 | 0.170448 | 0.310304 | 0.205412 | 1.49364 | 1.49161 | 0.1359 |
| 0.115536 | 0.152038 | 0.274403 | 0.296677 | 0.274403 | 1.48770 | 1.48558 | 0.1425 |

iii) Experiment 3.

System....Cyclohexane-n-Heptane-n-Pentane-p-Xylene-n-Hexane.
Calculations.....According to Formula 7, (Takano).
Temperature.....20°C ± 0.01.
Data for Calculations ;

| Solvents | Density ($d_0^{20}$)* | Refractive Index ($n_D^{20}$)* |
|---|---|---|
| 1) Cyclohexane | 0.77695 | 1.42610 |
| 2) n-Heptane | 0.68254 | 1.38762 |
| 3) n-Pentane | 0.62635 | 1.35790 |
| 4) p-Xylene | 0.86115 | 1.49562 |
| 5) n-Hexane | 0.67498 | 1.38130 |

*Observed value.

Table 3. Cyclohexane-n-Heptane-n-Pentane-p-Xylene-n-Hexane system, 20°C.

| $w_1$ | $w_2$ | $w_3$ | $w_4$ | $w_5$ | $n$(obs) | $n$(calc) | $\Delta$% |
|---|---|---|---|---|---|---|---|
| 0.184542 | 0.193507 | 0.152505 | 0.264807 | 0.204637 | 1.41242 | 1.40925 | 0.2244 |
| 0.357784 | 0.213709 | 0.101089 | 0.186032 | 0.141384 | 1.41306 | 1.41143 | 0.1153 |
| 0.130037 | 0.352666 | 0.166979 | 0.198158 | 0.152159 | 1.40390 | 1.40118 | 0.1937 |
| 0.137825 | 0.147225 | 0.276624 | 0.291634 | 0.146691 | 1.40958 | 1.40544 | 0.2937 |
| 0.130639 | 0.136229 | 0.089267 | 0.434016 | 0.209851 | 1.42930 | 1.42577 | 0.2469 |
| 0.200911 | 0.147384 | 0.098655 | 0.191630 | 0.361420 | 1.40650 | 1.40432 | 0.1549 |
| 0.385597 | 0.151808 | 0.111864 | 0.200085 | 0.150645 | 1.41520 | 1.41335 | 0.1307 |
| 0.167931 | 0.169311 | 0.317589 | 0.203335 | 0.141834 | 1.40120 | 1.39752 | 0.2626 |
| 0.182042 | 0.378072 | 0.103933 | 0.198292 | 0.137660 | 1.40766 | 1.40561 | 0.1456 |
| 0.126966 | 0.168178 | 0.334285 | 0.205885 | 0.164685 | 1.39965 | 1.39552 | 0.2950 |
| 0.125698 | 0.160763 | 0.111538 | 0.453213 | 0.148788 | 1.43070 | 1.43047 | 0.0160 |
| 0.130577 | 0.158077 | 0.123506 | 0.179198 | 0.408642 | 1.40200 | 1.39939 | 0.1861 |
| 0.190510 | 0.185717 | 0.240967 | 0.179764 | 0.203041 | 1.39869 | 1.40202 | 0.2380 |
| 0.277389 | 0.208212 | 0.162760 | 0.148627 | 0.203005 | 1.42315 | 1.42562 | 0.1735 |
| 0.213311 | 0.144129 | 0.149127 | 0.240004 | 0.253430 | 1.41092 | 1.40791 | 0.2133 |
| 0.199413 | 0.136687 | 0.254105 | 0.254105 | 0.192460 | 1.40976 | 1.40431 | 0.3866 |

iv) Experiment 4.

System ..... ditto Exp. i.
Calculations ..... According to Formula 17, (Lichtnecker).
Temperature..... 25°C ± 0.01.
Data for Calculations ..... ditto Exp. i

Table 4. Dioxane-Cyclohexane-n-Hexane-n-Heptane-Toluene system, 25°C.
(The volume fraction was calculated from the mass and density)

| $v_1$ | $v_2$ | $v_3$ | $v_4$ | $v_5$ | $n$(obs) | $n$(calc) | $\Delta$% |
|---|---|---|---|---|---|---|---|
| 0.087053 | 0.147418 | 0.177707 | 0.241979 | 0.345842 | 1.43409 | 1.43276 | 0.0927 |
| 0.421313 | 0.070509 | 0.147406 | 0.117670 | 0.237105 | 1.43010 | 1.39282 | 2.6068 |
| 0.269829 | 0.363093 | 0.066760 | 0.169571 | 0.130745 | 1.42910 | 1.42960 | 0.0349 |
| 0.135237 | 0.234348 | 0.360656 | 0.102235 | 0.167522 | 1.42007 | 1.42249 | 0.1704 |
| 0.152956 | 0.156455 | 0.220334 | 0.378888 | 0.091364 | 1.40819 | 1.40808 | 0.0078 |
| 0.379693 | 0.158637 | 0.168898 | 0.163196 | 0.129574 | 1.42053 | 1.42055 | 0.0014 |
| 0.153033 | 0.367306 | 0.153967 | 0.147115 | 0.178575 | 1.43004 | 1.43030 | 0.0182 |
| 0.148172 | 0.152963 | 0.382478 | 0.166566 | 0.149819 | 1.41324 | 1.41300 | 0.0169 |
| 0.158333 | 0.154950 | 0.153032 | 0.394286 | 0.139396 | 1.41303 | 1.41373 | 0.0495 |
| 0.157961 | 0.173517 | 0.143172 | 0.159893 | 0.365453 | 1.43954 | 1.43919 | 0.0243 |
| 0.200806 | 0.185002 | 0.192713 | 0.242861 | 0.178616 | 1.42312 | 1.42092 | 0.1546 |
| 0.140135 | 0.229225 | 0.300338 | 0.204088 | 0.126213 | 1.41505 | 1.41511 | 0.0042 |
| 0.212682 | 0.115953 | 0.258257 | 0.249761 | 0.163347 | 1.41486 | 1.41520 | 0.0240 |
| 0.187803 | 0.229987 | 0.144991 | 0.280008 | 0.157410 | 1.42022 | 1.42115 | 0.0655 |
| 0.118239 | 0.273234 | 0.298864 | 0.163287 | 0.146376 | 1.41917 | 1.42236 | 0.2247 |
| 0.125177 | 0.224631 | 0.152482 | 0.288415 | 0.209296 | 1.42390 | 1.42422 | 0.0224 |
| 0.259466 | 0.217033 | 0.131617 | 0.277584 | 0.114301 | 1.41717 | 1.41768 | 0.0289 |

v) Experiment 5.

System ..... ditto Exp. ii.
Calculations ..... According to Formula 17, (Lichtnecker).
Temperature ..... 20°C ± 0.01.
Data for Calculations ..... ditto Exp. ii.

Table 5. Toluene-Pyridine-Benzene-Monochlorobenzene-Dioxane system, 20°C.
(The volume fraction was calculated from the mass and density)

| $v_1$ | $v_2$ | $v_3$ | $v_4$ | $v_5$ | $n$(obs) | $n$(calc) | $\Delta$% |
|---|---|---|---|---|---|---|---|
| 0.210322 | 0.172964 | 0.209042 | 0.201497 | 0.206175 | 1.49027 | 1.48886 | 0.0946 |
| 0.324704 | 0.232762 | 0.161560 | 0.147781 | 0.133192 | 1.49497 | 1.49368 | 0.0862 |
| 0.157191 | 0.344590 | 0.268634 | 0.229822 | 0.151162 | 1.49776 | 1.59034 | 6.1812 |
| 0.171839 | 0.152467 | 0.334509 | 0.146323 | 0.194861 | 1.49016 | 1.53991 | 3.3387 |
| 0.259003 | 0.170003 | 0.136774 | 0.162401 | 0.271817 | 1.48420 | 1.48599 | 0.0930 |
| 0.284187 | 0.239051 | 0.134960 | 0.178633 | 0.163168 | 1.49374 | 1.49177 | 0.1318 |
| 0.299747 | 0.195142 | 0.138806 | 0.195931 | 0.170371 | 1.49302 | 1.49143 | 0.1064 |
| 0.177856 | 0.339816 | 0.177784 | 0.126199 | 0.178343 | 1.49270 | 1.49118 | 0.1018 |
| 0.182461 | 0.156926 | 0.356136 | 0.130940 | 0.173534 | 1.49130 | 1.49005 | 0.0838 |
| 0.164452 | 0.148472 | 0.196200 | 0.351958 | 0.138914 | 1.49926 | 1.49719 | 0.1380 |
| 0.150627 | 0.134047 | 0.173584 | 0.188347 | 0.353393 | 1.47850 | 1.47678 | 0.1163 |
| 0.258290 | 0.265739 | 0.179738 | 0.130001 | 0.166229 | 1.49284 | 1.49124 | 0.1071 |
| 0.160669 | 0.264454 | 0.267118 | 0.149282 | 0.158474 | 1.49420 | 1.49265 | 0.1037 |
| 0.142367 | 0.190327 | 0.193072 | 0.277547 | 0.196685 | 1.49364 | 1.49154 | 0.1405 |
| 0.132096 | 0.165333 | 0.172770 | 0.266210 | 0.263589 | 1.48770 | 1.48579 | 0.1283 |

vi) Experiment 6.

System ..... Benzene-Dioxane (system iv).

Calculations ..... According to Formula 19, (Wallot).

Temperature ..... 25°C ± 0.01.

Data for Calculations ; *

$N_{1.0} = n_{1.0} - 1$ ..... 0.49778

$N_{2.0} = n_{2.0} - 1$ ..... 0.42004

$d^{25}_{1.0}$ (Benzene) ..... 0.87368

$d^{25}_{2.0}$ (Dioxane) ..... 1.02687

$D_0^{-1} = v_{2.0}/v_{1.0}$ ..... 0.8508

*These data were obtained from the observed ones.

Table 6. Benzene-Dioxane system, 25°C.

| $z$ | 1-$z$ | $D^{-1}$ | $N$ | $n$(calc) | $n$(obs) | $\Delta$ | $\Delta$% |
|---|---|---|---|---|---|---|---|
| 0.00000 | 1.00000 | ..... | 0.49778 | 1.49778 | 1.49778 | 0.00000 | 0.00000 |
| 0.09912 | 0.90088 | 0.85998 | 0.49112 | 1.49112 | 1.49106 | 0.00006 | 0.00402 |
| 0.19922 | 0.80078 | 0.85379 | 0.48419 | 1.48419 | 1.48416 | 0.00003 | 0.00202 |
| 0.30235 | 0.69765 | 0.83904 | 0.47683 | 1.47683 | 1.47702 | 0.00019 | 0.01286 |
| 0.35091 | 0.64909 | 0.84713 | 0.47328 | 1.47328 | 1.47336 | 0.00008 | 0.00542 |
| 0.40165 | 0.59835 | 0.85273 | 0.46951 | 1.46951 | 1.46948 | 0.00003 | 0.00204 |
| 0.44980 | 0.55025 | 0.84768 | 0.46588 | 1.46588 | 1.46596 | 0.00008 | 0.00545 |
| 0.50066 | 0.49934 | 0.84782 | 0.46198 | 1.46198 | 1.46206 | 0.00008 | 0.00547 |
| 0.55168 | 0.44832 | 0.85159 | 0.45824 | 1.45824 | 1.45800 | 0.00024 | 0.01646 |
| 0.60091 | 0.39909 | 0.85261 | 0.45411 | 1.45411 | 1.45408 | 0.00003 | 0.00206 |
| 0.70089 | 0.29911 | 0.85415 | 0.44600 | 1.44600 | 1.44594 | 0.00006 | 0.00414 |
| 0.79960 | 0.20040 | 0.84888 | 0.43772 | 1.43772 | 1.43776 | 0.00004 | 0.00278 |
| 0.90108 | 0.09892 | 0.85128 | 0.42892 | 1.42892 | 1.42892 | 0.00000 | 0.00000 |
| 1.00000 | 0.00000 | ..... | ..... | ..... | 1.42004 | ..... | ..... |

$\hat{D}_0^{-1} = \overline{0.85055}$

$D_0^{-1} = v_{2.0}/v_{1.0} = 0.87368/1.02687 = \underline{0.85081}$

$A = 0.85055/0.85081 = 0.9996.$

## IV. DISCUSSION

Historicalily, many additive formulae of the refractive index of solvent mixture were introduced and discussed. In 1903, Wallot introduced the following additive formula on $N$ or $R$ ;

$$\frac{N_{2.0} - N(1+C_v)}{N(1+C_v) - N_{1.0}} = \frac{1-z}{z} D_0 \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \quad 8)$$

where $N$, $R$ and $D_0$ are respectively denote ;

$$\left.\begin{aligned} N &= n-1,\ \frac{n^2-1}{n^2+2} \text{ or } \frac{n^2-1}{n^2+x} \\ R &= \frac{n-1}{s} \quad \text{(Gladstone-Dale, Beer, Landolt)} \\ R &= \frac{n^2-1}{n^2+2}\frac{1}{s} \quad \text{(Lorentz-Lorentz)} \\ R &= \frac{n^2-1}{n^2+x}\frac{1}{s} \quad \text{(Kettelaar)} \\ D_0 &= s_{2\cdot0}/s_{1\cdot0} \end{aligned}\right\} \cdots\cdots 9)$$

In these above formulae, the symbols $n$, $s$ and $C_v$ respectivly denote the refractive index, density and the volume change on mixing per c. c., $z$ and $z_v$ respectively denote the weight fraction and volume fraction. In 1910, Schwers[8] and Holmes[7] (1915) modified Pruflich's additive formula, however, these formulae were not valid even for the limiting case when two different liquids are mixed and the volume change thereby is negligibly small, and the value of $\Delta N$, the difference between the calculated value of $N$ and the observed one, showed a remarkable value. In Wallot's formula, if we admit the case when the volume change $C_v$ of the mixture can be estimated nearly to zero, then the formula 8) can be written ;

$$\frac{N_{2\cdot0}-N}{N-N_{1\cdot0}}=\frac{1-z}{z}D_0 \cdots\cdots 10)$$

or according to Ishikawa it was written as follows ;

$$\left|\frac{(1-z)(N-N_{1\cdot0})}{z(N_{2\cdot0}-N)}\right|_{N=n-1} = A\left(\frac{v_{2\cdot0}}{v_{1\cdot0}}\right) \cdots\cdots 11)$$

In 1930, discussing Wallot's formula theoretically and experimentally, and by introducing a new constant A, Ishikawa[8] modified Wallot's formula by changing weight fraction $z$ into $z_v$, he denoted ;

$$N = N_{1\cdot0}+(N_{2\cdot0}-N_{1\cdot0})\frac{A\cdot z_v}{(1-z_v)+Az_v},\ N=n-1 \cdots\cdots 12)$$

and

$$A=\frac{1-\frac{\varphi_2}{v_{2\cdot0}}+\frac{C}{v_{2\cdot0}}}{1-\frac{\varphi_1}{v_{1\cdot0}}+\frac{C}{v_{1\cdot0}}} \cdots\cdots 13)$$

In the above formulae, the symboles $\varphi_1$ and $\varphi_2$ respectively denote the actual molar volumes of components 1 and 2, $C$ is the volume change in mixing per gr, and $v$ the specific volume. The noticiable point of his work was that he gave a new physical meanning on the constant $A$. He introduced into the constant $A$ a new conception in which the molecular size consistent within the pairs of the component molecules may be included. He expressed the conatant $A$ as the next formula ;

$$\text{Atheor.} = \frac{\dfrac{1-\frac{\pi}{6}\sigma_2^3 N_m}{M_2 v_{2\cdot 0}} + \dfrac{C}{v_{2\cdot 0}}}{\dfrac{1-\frac{\pi}{6}\sigma_1^3 \cdot N_m}{M_1 \cdot v_{1\cdot 0}} + \dfrac{C}{v_{1\cdot 0}}} \quad \cdots\cdots 14)$$

In the above formula, $M_1$ and $M_2$ are molecular weight, $N_m$ is the Avogadro's number, $\sigma_1$ and $\sigma_2$ are the molecular size in diameter. He calculated the molecular size of various kinds of organic substances from the refractivity measurements and compared them with that of calculated from the next Lorentz-Lorentz formula ;

$$\frac{n^2-1}{n^2+2} M_v = \frac{\pi}{6}\sigma^3 N_m \quad \cdots\cdots 15)$$

Thus, Ishikawa's conception on the refractivity of light in a mixture of liquids can be summarized as follows ; when the velocity of light decreases from $u_0$to $u$, the refractivity $n-1=(u_0-u)/u$ gives the rate of decrease of light velocity resulting from the reaction of the displacement electrons in the molecule. Accordingly, for a binary mixture of liquids, the less the electrons in a molecule of one kind are effected by the other kind of molecules, the more simple relation will be expected between their refractivities and the composition.

This idea assuredly leads the idea that the refractivity of a solvent mixture must be obeyed with a simple relation of law of additivity. Thus, the value $N$-$N_{1.0}$ or $N_{2.0}$-$N$ in Wallot's formula shows the decrement or the increment of the refractivity with related to the addition of the other molecules. Accordingly, the next formula will be expected ;

$$\left.\begin{aligned} &\frac{dN_{1\cdot 0}}{dz_{v1\cdot 0}} = A\frac{dN_{2\cdot 0}}{dz_{v2\cdot 0}} \\ \text{or}\quad &\\ &\frac{N-N_{1\cdot 0}}{z_v} = A\frac{N_{2\cdot 0}-N}{1-z_v} \end{aligned}\right\} \quad \cdots\cdots 16)$$

In 1925, quite apart from these ideas, Lichtnecker[9] introduced a new formula which is well known as a logarithmic formula ;

$$\log n_{1\cdot 2} = (1-z_v)\log n_{1\cdot 0} + z_v \log n_{2\cdot 0} \quad \cdots\cdots 17)$$

By expanding the above formula into the n-th componet mixture, we have ;

$$n_{1\cdot 2\cdots\cdots n} = \prod_{r=1}^{r=n} n_r^{w_r} \; ; \; \sum_{r=1}^{r=n} w_r = 1 \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \quad 18)$$

Formula 18) suggest us that the refractive index of a solvent mixture can be expressed by a multinomial probability of the refractivities of the component liquids.

In order to examine the validity of Wallot's formula with the experimental results, calculations were made and the results were given in the table 6. The 3rd column of the table 6 shows the calculated value of the constant $D_0^{-1}$ of Benzene-Dioxane mixtute at 25°C. The value of constant $D_0^{-1}$in the table 6 shows, even in taking the assumption $C_v = 0$, preferably good constancy. By using Ishikawa's formula (formula 14), and by taking the experimental value of 0.9996 as the constant $A$, and by taking the radius of Benzene molecule as $4.10\times10^{-8}$ cm into account, the radius of Dioxane molecule within the pairs of the two substances was estimated to $4.04\times10^{-8}$ cm.

Table 7. A Comparison of the Validity of Various Refractive Index Formulae.

| System | Mean Variation(%) | Formula |
|---|---|---|
| Dioxane-Cyclohexane-n-Hexane-n-Heptane-Toluene | 0.0920 | 7).* |
| Toluene-Pyridine-Benzene-Monochlorobenzene-Dioxane | 0.1254 | 7).* |
| Cyclohexane-n-Heptane-n-Pentane-p-Xylene-n-Hexane | 0.2047 | 7).* |
| Dioxane-Cyclohexane-n-Hexane-n-Heptane-Toluene | 0.2086 | 18).** |
| Toluene-Pyridine-Benzene-Monochlorobenzene-Dioxane | 0.7301 | 18).** |
| Benzene-Dioxane | 0.0048 | 20).*** |

*Takano, **Lichtnecker, ***Wallot

The last column of the table 6 shows the error in percent of the calculated refractive index of Dioxane-Benzene mixture according to Wallot's formula with the use of $D_0^{-1} = 0.8508$. The calculation was undertaken by the next formula in which the formula 11) was conveniently transformed into ;

$$N = \left| \frac{N_1 + N_2\left(\frac{z}{1-z}\,\frac{1}{D_0}\right)}{1+\left(\frac{z}{1-z}\cdot\frac{1}{D_0}\right)} \right|, \quad N = n-1 \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad 19)$$

Quite apart from the Wallot's way, the comparison of the calculated value and the observed value of the refractive index was given in the tables 4 and 5. These data were calculated according to Lichtnecker's formula for the systems of i) and ii).

These results show us that, not only Wallot's formula and Lichtnecker's formula, my formula also shows good validitiy to the experimental results. The degree of validity is slightly higher in my formula than Lichtnecker's as shown in table 7.

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